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Study on Magnetic and Spectroscopic Properties of Lanthanide(III) Complexes Containing a Chelated Imino Nitroxide Radical

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2002

Contents

General Introduction..1

Chapter 1. Synthesis, Characterization and Spectroscopic Properties of Lanthanide(III) Complexes Containing Imino Nitroxide Radical
.... 6

Chapter 2. Magnetic Properties of Gadolinium(III) Complexes Containing Imino Nitroxide Radical
....29

Chapter 3. Magnetic Properties of Lanthanide(III) Complexes Containing Imino Nitorxide Radical
....44

Chapter 4. Synthesis, Structure and Magnetic Properties of Lanthanide(III) Complexes Containing Methyl-Substituted Pyridyl Imino Nitroxide Radicals
....66

Chapter 5. NMR Spectral Studies of Lanthanide(III) Complexes Containing Imino Nitroxide Radical
....85

Conclusion..104
References..105
Acknowledgement..110

Appendix..112

General Introduction

The chemistry of lanthanide(III) complexes is the chemistry concerned with the 4f-orbital electrons, whereas that of transition metal complexes possesses 3d-character(Figure I-1). In the last few years, there have been a number of investigations of lanthanide complexes. The significant characteristics of the lanthanide complexes are as follows. (i) From a synthetic point of view, the lanthanide chemistry is less developed than the transition metal chemistry. (ii) The high coordination of the lanthanide ion may lead to quite unusual molecular structures. (iii) The magnetic properties of the lanthanide complexes, even of the mononuclear species, are still poorly understood. Actually, the complexes potentially applicable to luminescent probes,[1,2] contrast agents in magnetic resonance imaging (MRI),[3] or building blocks in molecular-based magnetic materials.[4]

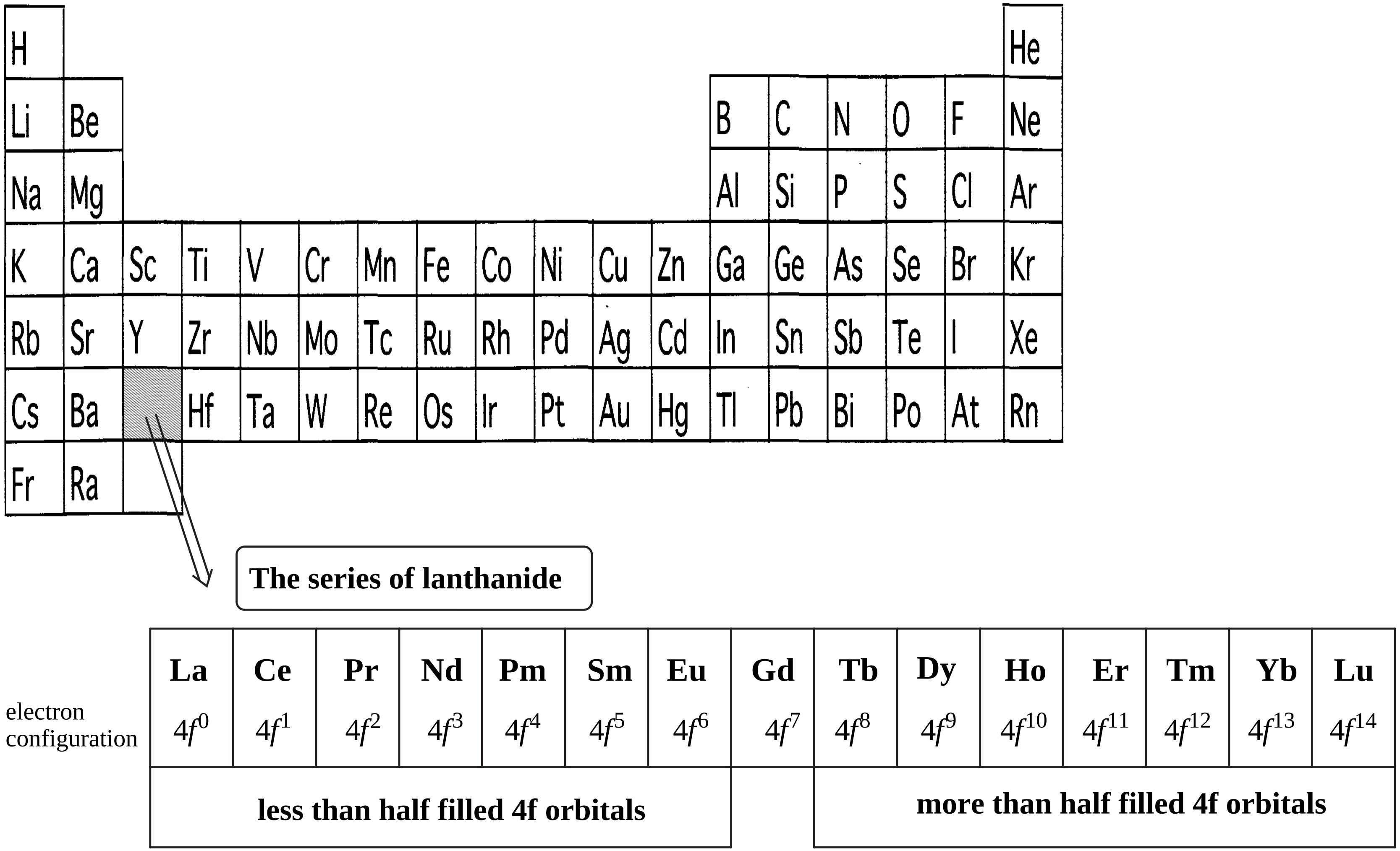
For example, the luminescence of lanthanide complexes coordinated β-diketonate[5] or Schiff-base[6], supramolecules,[7] and polymers[8] has been widely investigated because of the strong line emission important for luminescent and laser materials. As the contrast agents utilizing shortening bulk water proton relaxation in MRI, chelating complexes of gadolinium have been studied considerably.[9] In the field of magnetic resonance, the application to the shift reagent *e.g.* for chiral discrimination as well as biological probes[10] are expected from showing the paramagnetic shifts of most lanthanide(III) ions.

As models for novel magnetic materials in some relation with high-temperature superconducting ceramics, much attention has been paid to many heterometal 3d-4f complexes including metal ions such as Cu(II),[11] Ni(II),[12,13a] V(IV)O,[14] Co(III),[15] Zn(II),[16] Cr(III).[13b,17] Instead of paramagnetic metal ions, free nitroxide radical ligands[18] have been incorporated into lanthanide ions as well as transition metal complexes as building blocks which display a total spin higher than that of metal ions alone.[19] Among the recent studies of many transition metal nitronyl nitroxide radical complexes,[19a] T. Yoshida *et al.* have reported the preparation and magneto-optical properties of Cr(III) and Ni(II) NIT-2py complexes (NIT-2py=2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl).[20] The β-diketonato NIT-2py Ni(II) and Cr(III) complexes are found to exhibit a significant intensity enhancement of the formally spin-forbidden d-d bands and newly appeared MLCT components, of which the spectral behavior was discussed in connection with the observed magnetic coupling constants together with the NMR contact shifts of the β-diketonato methine proton, following two series of six-coordinate octahedral and four-coordinate tetrahedral divalent metal complexes with IM-2py or NIT-2py analogues.[21]

There have been also several lanthanide complexes with nitronyl nitroxide radicals. Some of them consist of polymeric chains formed by Ln(hfac)$_3$ moieties (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) bridged by a nitronyl nitroxide unit through the coodination of the oxygen atoms to the Ln atom.[22] The other complexes involve the chelation of a pyridine unit(NIT-2py) forming an six-membered N,O-chelate ring.[23] The intramolecular Gd-radical magnetic interactions in these complexes were found to be ferromagnetic.

For an imino nitroxide radical containing pyridyl unit (IM-2py=(2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl)) capable of forming a N,N-five-membered chelate ring (Scheme 1),[24] the intramolecular Ln-radical interaction may exhibit a different type of magnetic interaction between Ln ion and radical due to forming a more planar chelate ring as compared with NIT-2py.[25a] Transition metal complexes (*e.g.* Mn(II), Co(II), and Ni(II)) including IM-2py has already been reported[21a,,25b] in details to show the ferromagnetic interaction and the temperature dependent UV-vis-NIR spin-forbidden or spin allowed d-d transitions and the dσ or dπ to SOMO π* CT.[21a] A series of complexes of the IM-2py with lanthanide(III) ions could provide a clue to gain insight into the ground and lowest excited states in terms of electronic emission and absorption spectroscopy. However, there has been no lanthanide complex including IM-2py so far. This is why the new series of lanthanide-radical complexes containing IM-2py was noticed and studied in this study.

In chapter 1, the preparation and the crystal structures of a new series of lanthanide-radical complexes containing IM-2py are described and the absorption spectroscopy and solid state luminescence spectroscopy are compared with those of the corresponding NIT-2py complexes and the free ligands. In chapter 2–3, the magnetic properties are described about the Gd(III) complexes by compared to that of the nitronyl nitroxide radical complexes and about other lanthanide(III) complexes with qualitative treatment by the comparison to nonradical compounds. In chapter 4, lanthanide-radical complexes containing IM-nMe2py, of which the pyridine group is substituted by methyl group, are described in view of the function of the substituted group. In chapter 5, the unprecedented ^{1}H NMR behavior of the IM-2py in diamagnetic lanthanide(III) ions are described and the paramagnetic shifts of IM-2py are also referred as well as the common lanthanide complexes.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	▨	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																

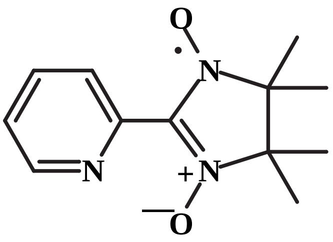
The series of lanthanide

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
electron configuration	$4f^0$	$4f^1$	$4f^2$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^8$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$
	less than half filled 4f orbitals								**more than half filled 4f orbitals**						

Table I-1. The series of lanthanide in periodic table.

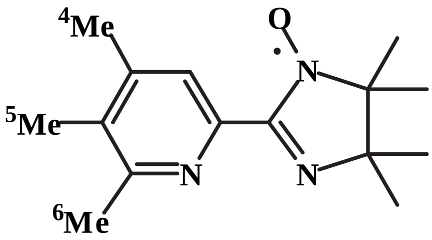
Abbrebiations

NIT-2py = 2-(2-pyridyl)-4,4,5,5-tetramethyl-1*H*-imidazolyl-3-oxide-1-oxyl

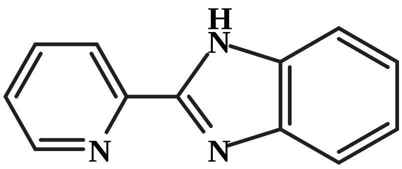


IM-2py = 2-(2-pyridyl)-4,4,5,5-tetramethyl-1*H*-imidazolyl-1-oxyl

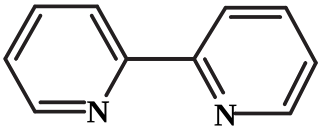
IM-nMe2py = 2-(n-methyl-2-pyridyl)-4,4,5,5-tetramethyl-1*H*-imidazolyl-1-oxyl (n = 4, 5, 6)



pybzim = 2-(2-pyridyl)-benzimidazole



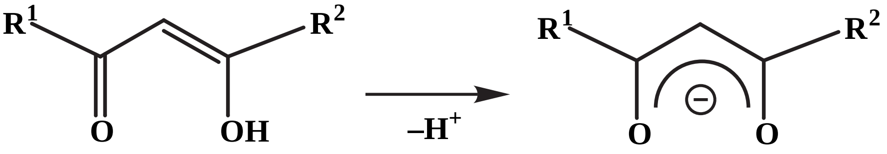
bpy = 2, 2'-bipyridine



Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (R^1=CF_3, R^2=CF_3)

Htfac = 1,1,1-trifluoro-2,4-pentanedione (R^1=CF_3, R^2=CH_3)

Hacac = 2,4-pentanedione (R^1=CH_3, R^2=CH_3)



Chapter 1. Synthesis, Characterization and Spectroscopic Properties of Lanthanide(III) Complexes Containing Imino Nitroxide Radical

1–1 Introduction

As described in General Introduction, the recent studies of many transition metal nitronyl nitroxide radical complexes have been reported, *e.g.* the preparation and magneto-optical properties of Cr(III) and Ni(II) NIT-2py complexes.[20] In addition, there have been also several lanthanide complexes with nitronyl nitroxide radicals. The complexes involve the intramolecular coordination of a pyridine unit of NIT-2py making an N,O-six-membered chelation.[23] In contrast to NIT-2py, an imino nitroxide radical containing pyridyl unit, IM-2py, is capable of five-membered N,N-chelation. Though the pair of donor atoms is different, the surrounding of the lanthanide ion is similar to each other. The intramolecular Ln-radical interaction may be a different type between Ln ion and radical due to forming a more planar chelate ring as compared with NIT-2py.

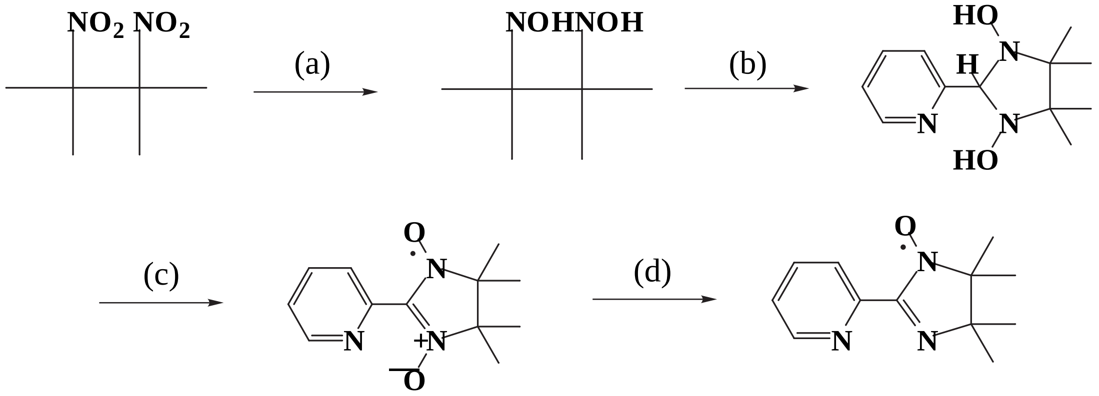
Transition metal complexes (*e.g.* Mn(II), Co(II), and Ni(II)) including IM-2py has already been reported in detail involving the temperature dependent UV-vis-NIR spin-forbidden or spin allowed d-d transitions and the dσ or dπ to SOMO π^* CT.[21a] On the other hand, in a series of complexes of the IM-2py with lanthanide(III) ions, the characteristics of f-f transition should be paid attention in terms of electronic emission and absorption spectroscopy. As mentioned above, the comparison between NIT-2py and IM-2py complexes is also available.

In this chapter, we describe the preparation and the crystal structures of a new series of lanthanide-radical complexes containing IM-2py. And the absorption spectroscopy and solid state luminescence spectroscopy are compared with those of the corresponding NIT-2py complexes and the free ligands.

1-2. Expecrimental Section

1-2-1. Synthesis of 2-(2’-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl

The NIT-2py and IM-2py ligand was prepared by the Ullman’s method (scheme 1-1 (a)–(c))[18] and Akita’s method (scheme 1-1 (d))[24], respectively.



Scheme 1-1. preparation scheme of nitroxide radical ligands

(a) 2,3-bis(hydroxyamino)-2,3-dimethylbutane

To the 50% aqueous ethanol (330 ml), 2,3-dimethyl-2,3-dinitrobutane (30 g) and ammonium chloride (17.1 g) was added, and then the mixture was stirred for 1 h. On cooling the mixture to 15 ℃, zinc powder (68.4 g) was added during 4 h and the mixture was stirred with keeping below 15 ℃ overnight. After filtration, the cake of zinc oxide was washed with four portions (50 ml) of water. The combined filtrate and washing were acidified to *ca.* pH2 with concentrated HCl and then evaporated under reduced pressure. The residue was neutralized and dried with anhydrous K_2CO_3. The solid was continuously extracted with ca. 600 ml $CHCl_3$ in a Soxhlet’s extractor for 15 h. On cooling the extract in a refrigerator, white and slightly volatile powder was obtained. Yield 11 g (44 %).

(b) 1,3-dihydroxy-2-(2’-pyridyl)-4,4,5,5-tetramethylimidazoline

A solution of 2.22 g of 2,3-bis(dimethylamino)-2,3-dihydroxybutane in 30 ml methanol was added dropwise to a solution of 1.71 g of 2-pyridinecalbaldehyde in 10 ml methanol over 5 min. The solution was stirred at room temperature for 18 h. The white precipitate was filtered and washed with methanol and ether. Yield 2.1 g (56 %).

(c) 2-(2’-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT-2py)

PbO_2 (24 g) was gradually added to a suspension of 2.7 g 1,3-dihydroxy-2-(2’-pyridyl)-4,4,5,5-tetramethylimidazoline in 80 ml dry benzene at room temperature with stirring. After stirring for *ca.* 1 h, The color of solution turned to blue violet. After filtration, the solution was evaporated to dryness under reduced pressure, and then the dark violet solid was obtained. Yield 2.2 g (82 %).

(d) 2-(2’-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (IM-2py)

2-(2’-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (2 g) was dissolved in 100 ml CH_2Cl_2. To the solution, $NaNO_2$ (4 g) and glacial acetic acid (6 ml) was added with stirring. After stirring for *ca.* 10 min., the color of solution turned from violet to red orange. The filtrate was added to a water solution of $NaHCO_3$ and neutralized with vigorously stirring. The organic layer was separated, washed with two portions of water (50 ml) and dried with Na_2SO_4. After evaporation of the filtrate, red orange oil product was obtained.

1-2-2. Synthesis of starting material complexes: tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)diaquagadolinium(III)

The product was prepared by the Richardson’s method.[26] The other lanathnide complexes were also prepared by replacement of gadolinium(III) to yttrium(III) or other lanthanide(III) ions.

$GdCl_3 \cdot 6H_2O$ (2.23 g, 6 mmol) was dissolved in 10 ml water and then the solution was placed in a separatory funnel. An ethereal solution of NH_4hfac was prepared by dissolving Hhfac (3.75 g, 18 mmol) in 50 ml ether and adding NH_3 aq. until the white smoke stoped being evolved. The aqueous $GdCl_3$ solution was then extracted twice with 50 ml of the ethereal NH_4hfac. The organic phase was washed with 10 ml water and dried over Na_2SO_4. The ether was evaporated in a rotary evaporator. To the resulting mixture of oil, 50 ml hot n-hexane was added. The solution was allowed to be cool and evaporated slowly. The resulting crystals were separated by filtration through a glass filter, air dried for a few hours.

1-2-3. Synthesis of [Ln(hfac)(IM-2py)]

The corresponding [Ln(hfac)$_3$(H$_2$O)$_2$] (1.0 mmol) was suspended in 10 ml CH$_2$Cl$_2$. IM-2py (1.37 mmol) in 10 ml CH$_2$Cl$_2$ (10 ml) was added to this suspension. After stirring for *ca.* 2 h, the red solution was obtained. The solution was poured into 20 ml of *n*-heptane, and stood to be evaporated slowly. Red orange crystals were obtained on standing for overnight.

The preparation method of [Nd(hfac)$_3$(IM-2py)] must be slightly altered since the use of the excess volume of ligand produces an oily product. CHCl$_3$ was used instead of CH$_2$Cl$_2$ for the other complexes and [Nd(hfac)$_3$(H$_2$O)$_2$] (1.0 mmol) was traeted with IM-2py (1.0 mmol) by the same method.

1-2-4. Spectral Measurement

Infrared spectra and UV/vis spectra were recorded on a Perkin-Elmer Lambda 19 and a Spectrum-GX FT-IR spectrophotometers, respectively. Luminescence spectra were recorded on a Perkin Elmer LS50B spectrophotometer at room temperature and 77 K, using an excitation slit width of 10 nm and an emission slit width of 2.5 nm with microcrystalline samples.

1-2-5. X-ray Crystallographic Analysis

Red orange crystals of [Ln(hfac)$_3$(IM-2py)] (Ln = Y, Sm, Gd, Dy, Er, Yb) suitable for X-ray crystal analyses were obtained by slowly evaporating the complex solution in a mixture of dichloromethane and *n*-heptane. Each crystal was mounted in a glass capillary. The X-ray intensities were measured at 23 ℃ with graphite-monochromated

MoKα radiation (λ = 0.71073Å) on a Rigaku AFC-5R or AFC-7R four-circle diffractometer using ω or ω-2θ scan technique was employed at scan rate. Final lattice constants were determined by least-squares refinements of the orientation angles of 25 centered reflections in the range $25° < 2\theta < 30°$. Three standard reflections were monitored every 150 reflections and showed no serious decomposition. ($|F_o|/(|F_o|)_{\text{initial}} >$ 97 %). The intensities collected for (-h, +k, ±l) octants at $2\theta \leqq 60°$, whereas in Sm complex at $2\theta \leqq 55°$, were corrected for Lorentz–polarization effects, and absorption corrections were made by the Gauss numerical integration method[27]. The structures of [Ln(hfac)$_3$(IM-2py)] could be solved reasonably by using direct method (SIR-92 programs[28]) and refined by a full matrix least squares procedures(SHELXL-97[29]). The positions of hydrogen atoms were fixed at calculated positions and only their isotropic displacement parameters were refined. All calculations were carried out on a Windows computer using Crystal Structure software.[30]

1–3. Results and discussion

1–3-1. Preparation and characterization of [Ln(hfac)$_3$(IM-2py)]

The treatment of [Ln(hfac)$_3$(H$_2$O)$_2$] and a small excess of IM-2py in dichloromethane gave readily a red solution of the corresponding [Ln(hfac)$_3$(IM-2py)] complexes. The recrystallization was performed from dichloromethane-*n*-heptane solution expect [Nd(hfac)$_3$(IM-2py)], which was recrystallized from chloroform-*n*-hexane. The La(III), Ce(III), and Pr(III) complexes, of which the ionic radii are larger than Nd(III), could not be prepared. The coordination number of the complexes containing these ion is expected to be more than eight, so the strange bridging complexes may be formed. In preparation of Nd complex, the use of an excess amount of IM-2py gives the same results. But this is avoided by using equimolar amount of IM-2py. The products are insoluble in water and dissolve in most organic solvents except aliphatic alkanes, but they readily decomposed in methanol, ethanol, and DMSO. As described later, this decomposition was confirmed with UV-vis spectra in solution of each solvent.

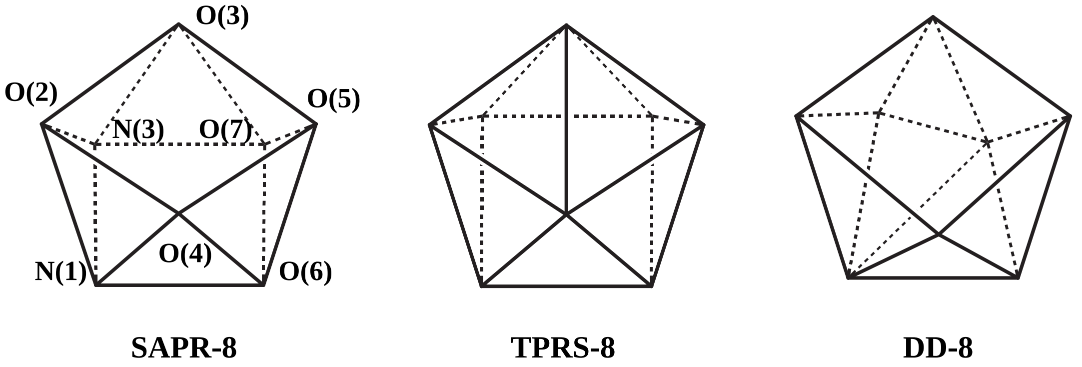
The elemental analyses data and characteristic IR bands for [Ln(hfac)$_3$(IM-2py)] complexes are summarized in Table 1-1. The elemental analyses show that the complexes have the chemical formula consisting of Ln(III), hfac and IM-2py with 1:3:1 ratio. All of the complexes give almost the identical IR spectra with two strong CO stretching bands due to lower symmetry of [Ln(hfac)$_3$(IM-2py)] than that of [Ln(hfac)$_3$(H$_2$O)$_2$]. In addition, these bands shift to higher wave number with increasing the atomic numbers of Ln, correlating with the lanthanide contraction as found for the oxalato complexes.[13b] Accordingly, it is plausible that the stretching band of the Y complex are similar to that of the Tm complex, since the ion radii of the Tm ion is close to the Y ion.

[Ln(hfac)$_3$(IM-2py)] (Ln = Y, Sm, Gd, Dy, Er, Yb) form red orange crystals with space group $P2_1/n$ by recrystallization from dichloromethane-*n*-heptane solution. The molecular structure of [Gd(hfac)$_3$(IM-2py)] is illustrated in Figure 1-1. The Gd atom of [Gd(hfac)$_3$(IM-2py)] is eight-coordinated with three didentate hfac ligands and one didentate IM-2py ligand. The structures of the other lanthanide complexes are similar to the Gd complex (Figure 1-2). Crystallographic data for each complex are listed in Table 1-2. Selected bond lengths and angles are also summarized in Table 1-3.

The bond length of N(2)-O(1) in the Gd complex is 1.282(7) Å, which is slightly longer than that of the other transition metal complexes containing IM-2py (1.265–1.271 Å)[21] but much shorter than that of average N–O single bond (1.41Å). This fact indicates the existence of a radical unpaired spin on complexation. The torsion angle of N(1)–C(1)–N(2)–O(1) is 2.7(7) ° suggesting that the plane (N(1), C(1), N(2), O(1)) is nearly planar. The torsion angle of N(1)–C(1)–C(2)–N(3) is 8.6(8)°, the plane (N(1), C(1), C(2), O(1)) being also nearly planar and SOMO(π^*) orbital expanding to ligated N(3) atom. The Gd-O(hfac) bond lengths can be classified into two groups. In the first group, the Gd-O bond lengths range from 2.328(4)Å to 2.354(4)Å (Gd-O(3), Gd-O(4), Gd-O(6) and Gd-O(7)). In the second group, they are 2.401(4)Å (Gd-O(2)) and 2.417(4)Å (Gd-O(5)), which are fairly longer than those in the first group. These lengths are similar to 2.34–2.42 Å for [Gd(hfac)$_3$Cu(salen)][31] (salen = N,N'-ethylenebis(salicylidene)diaminate). The bond length of the Gd-N(3) (pyridine-N) is 2.553(4)Å, which is compared with the Gd-N(py) bond length for the eight-coordinate complex [Gd(hfac)$_3$(NIT-2py)][23] (2.614(9)Å). The Gd-N(1) (imidazole-N) bond length is 2.540(5)Å, which is slightly larger than the Gd-N(3) length.

The other lanthanide atoms of [Ln(hfac)$_3$(IM-2py)] have a similar coordination geometry to each other. The Ln-O(hfac) bond lengths of all these complexes can also be classified into two groups. For example, in the Yb complex, the former ranges from 2.245(5)Å to 2.289(6)Å and the latter from 2.342(6)Å to 2.345(5)Å. Additionally, the Ln-N(1) and Ln-N(3) bond lengths are similar to each other. The Yb-N bond lengths are 2.480(6) (Yb-N(1)) and 2.480(5) (Yb-N(3)).

The N$_2$O$_6$ eight coordinate geometries are square antiprism (SAPR), dodecahedral (DD), and bicapped trigonal prism (TPRS) (Scheme 1-2). They were examined by using the semiquantitative method of polytopal analysis.[32] The δ and ϕ values are summarized in Table 4. In [Sm(hfac)$_3$(IM-2py)] complex, the δ_1 and δ_2 values showing planarity of the squares are 29.82° and 8.44° respectively. The δ_1 values are relatively large, but δ_2 are still small. The ϕ_1 and ϕ_2 values are 12.44° and 7.73°, respectively. These values are



SAPR-8 **TPRS-8** **DD-8**

Scheme 1-2. Coordination polyhedra of 8-coodination.

fairly close to the angle(14.1°) of the ideal TPRS polyhedron. Thus, the most reasonable geometry around the Sm atom is TPRS. All the complexes have almost a TPRS geometry. Two oxygen atoms in the longer Ln-O(hfac) bond lengths than the others are located in the square bicapped vertices. These values are examined in more details. The δ_2 value tends to increase from Sm to Yb, though the change is not always constant through the series. Both of the ϕ values decrease almost in this order. Therefore, it is suggested that the present complexes are slightly close to DD from TPRS with decreasing the ionic radii of the central Ln ion, in other words, these are on a geometric pathway to DD from TPRS.

1-3-2. Absorption spectra of [Ln(hfac)$_3$(IM-2py)]

(a) general spectral feature

Absorption spectra of [Sm(hfac)$_3$(IM-2py)] and [Yb(hfac)$_3$(IM-2py)] are shown together with IM-2py in Figure 1-3. The numerical data are summerized in Table 1-5. Since the absorption bands of IM-2py in the region from 19×10^3 cm^{-1} to 24×10^3 cm^{-1} are assigned to the intraligand n-π* transition, the absorption bands of [Ln(hfac)$_3$(IM-2py)] in the corresponding region are also assigned to the intraligand n-π* transition, which is shifted to the lower frequency. The lower energy shift of the n-π* transition in the lanthanide–radical complex have been also observed in [Gd(NITBzIMH)$_2$(NO$_3$)].[33] The vibrational structure of the present complex is observed more clearly than that of the free IM-2py ligand. The absorption coefficient of the complexes is much larger than that of free IM-2py ligand. The spectral behavior of the n-π* absorption bands are almost similar to those of all [Ln(hfac)$_3$(IM-2py)] complexes though a slight lower frequency shift is seen with decreasing the ion radii of the central Ln ion. Two causes of this behavior may be considered: (i) As a result of the chelation, the radical SOMO π* energy level are slightly stabilized due to increase in planarity between N=C-N=O moiety and pyridine ring leading to expansion of the conjugated system.; (ii) The electric state of the ligand is considerably affected by the formation of coordination bond with lanthanide(III) ion as found for Schiff base complexes.[34] The red shift of the n-π* absorption bands have been also observed for the diamagnetic Co(III) complexes[35] bearing NITnpy and IMnpy(3- or 4-pyridyl substituted NIT and IM) as unidentate ligands through pyridyl coordination.

Absorption spectrum of [Sm(hfac)$_3$(NIT-2py)] is shown together with NIT-2py in Figure 1-4. The absorption bands of [Sm(hfac)$_3$(IM-2py)] in the region from 14×10^3 cm^{-1} to 21×10^3 cm^{-1} are also assigned to the intraligand n-π* transition according to the assignment of the absorption bands of NIT-2py intraligand n-π* transition. But there is not significant band shifts of the n-π* transition though the band are slightly split. No enhancement of the absorption is observed as shown in IM-2py complex. In the case of NIT-2py complex, the planarity between N=C-N=O moiety and pyridine ring are broken. Enhancement and lower energy shift of n-π* transtition band in IM-2py complex caused the radical SOMO π* energy level stabilization due to increase in planarity between N=C-N=O moiety and pyridine ring leading to expansion of the conjugated system as a result of the chelation.

(b) The stability in solution shown by the spectra

The spectral change are shown in Figure 1-5 when the mixing ratio of [Y(hfac)$_3$(H$_2$O)] and IM-2py are changed. The complexation equilibrium are expected as the followed expression:

$$[\mathrm{Y(hfac)_3(H_2O)_2}] + \text{IM-2py} \rightleftarrows [\mathrm{Y(hfac)_3}(\text{IM-2py})] + 2\mathrm{H_2O}$$

With increasing the ratio of [IM-2py] / [Y(hfac)$_3$(H$_2$O)], the maximum absorptions of the n-π* band become larger until the ratio is equal to *ca*. 1. When the ratio is more than unity, the spectral change is negligible. On the contrary, little spectral change are observed when the mixing ratio of [Y(hfac)$_3$(IM-2py)] and H$_2$O are changed. Thus, the stabilization constant of this complexation is greatly large, and even if in solution, [Ln(hfac)$_3$(IM-2py)] are formed as major species.

The spectra of [Sm(hfac)$_3$(IM-2py)] in solution of various solvents are shown in Figure 1-6. In methanol or DMSO, the absorption intensity in the n-π* transition region is weaker and the position is shifted. The spectrum pattern is similar to that of free IM-2py ligand. It is suggested that [Sm(hfac)$_3$(IM-2py)] is dissociated in methanol or DMSO. On the baseis of the complexation equilibrium as mentioned above, with the presence of excess water, the dissociation proceeds to produce free IM-2py. Thus in methanol or DMSO, which can be coordinated to the lanthanide ion, the similar dissociation to proceed the formation of [Ln(hfac)$_3$(solvent)$_2$] occurs.

1-3-3. Emission spectra of [Ln(hfac)$_3$(IM-2py)]

It is generally found that characteristic sharp luminescences are observed for Eu(III) and Tb(III) complexes.[36] Actually, the microcrystalline samples of nonradical complexes [Eu(hfac)$_3$(bpy)] and [Tb(hfac)$_3$(bpy)] showed the sharp emission bands at room temperature, when they are irradiated with the 4f-4f transitions; 465 nm ($^7F_0 \rightarrow {}^5D_2$ for Eu(III)) or 488 nm ($^7F_6 \rightarrow {}^5D_4$ for Tb(III)), respectively(Figure 1-7). However, neither [Eu(hfac)$_3$(NIT-2py)] nor [Tb(hfac)$_3$(NIT-2py)] gives emission bands. That is, the efficient quenching occurs in luminescence resulting from the resonance between the Ln(III) excited levels and the broad absorption band of the NIT-2py, since the n-π* absorption band envelope for the NIT-2py ligand overlaps with the energy level of emission departure of Eu(III) and Tb(III) ($^5D_0$ for Eu(III) and $^5D_4$ for Tb(III)) as shown in Figure 1-8.

In the IM-2py complexes, [Tb(hfac)$_3$(IM-2py)] and [Eu(hfac)$_3$(IM-2py)] exhibit no emission bands due to the quenching insofar as the wavelength of irradiation is 465 nm as found for the NIT-2py complexes. No emission with excitation of 465 nm is due to no occurrence of energy transfer from IM-2py (n-π*) to Eu(III) ($^5D_0$) (Figure 1-7).

When the exciting wavelength is 222 nm, presumably corresponding to the CT due to the coordinated hfac ligand, the sharp emission bands are observed for the Eu(III) but not for the Tb(III) complex at room temperature (Figure 1-7). As compared with NIT-2py, the n-π* absorption band envelope for the IM-2py ligand does not overlap with the luminescent energy level of Eu(III) ($^5D_0$). Thus the energy radiation from $^5D_0$ level can be observed to some extent. But there is perfect overlap with that of the Tb(III)($^5D_4$). This overlap results in preventing from the effective quenching (Figure 1-8).

Table 1-1. Elemental analysis for the complexes (calculated values are given in parentheses)

Ln	C	H	N	ν (C=O) / cm^{-1}
[Y(hfac)$_3$(IM-2py)]	35.01 (34.93)	1.94 (2.06)	4.66 (4.53)	1651, 1668
[[Nd(hfac)$_3$(IM-2py)]	32.73 (32.97)	1.84 (1.95)	4.47 (4.27)	1648, 1664
[Sm(hfac)$_3$(IM-2py)]	32.95 (32.76)	1.90 (1.93)	4.66 (4.25)	1648, 1664
[Eu(hfac)$_3$(IM-2py)]	32.57 (32.71)	1.83 (1.93)	4.53 (4.24)	1648, 1665
[Gd(hfac)$_3$(IM-2py)]	32.89 (32.54)	1.86 (1.92)	4.45 (4.22)	1649, 1666
[Tb(hfac)$_3$(IM-2py)]	32.14 (32.48)	1.78 (1.92)	4.49 (4.21)	1649, 1667
[Dy(hfac)$_3$(IM-2py)]	32.74 (32.37)	1.85 (1.91)	4.43 (4.19)	1649, 1667
[Ho(hfac)$_3$(IM-2py)]	32.53 (32.29)	1.82 (1.91)	4.33 (4.18)	1649, 1667
[Er(hfac)$_3$(IM-2py)]	32.41 (32.21)	1.82 (1.90)	4.38 (4.17)	1650, 1668
[Tm(hfac)$_3$(IM-2py)]	32.23 (32.16)	1.96 (1.90)	4.65 (4.17)	1651, 1668
[Yb(hfac)$_3$(IM-2py)]	32.08 (32.03)	1.82 (1.89)	4.35 (4.15)	1652, 1669
[Lu(hfac)$_3$(IM-2py)]	32.12 (31.97)	1.81 (1.89)	4.27 (4.14)	1652, 1670

Table 1-2. Crystallographic data of [Ln(hfac)$_3$(IM-2py)]

	Ln = Sm	Gd	Dy	Er	Yb	Y
formula	$C_{27}H_{19}O_7N_3F_{18}Sm$	$C_{27}H_{19}O_7N_3F_{18}Gd$	$C_{27}H_{19}O_7N_3F_{18}Dy$	$C_{27}H_{19}O_7N_3F_{18}Er$	$C_{27}H_{19}O_7N_3F_{18}Yb$	$C_{27}H_{19}O_7N_3F_{18}Y$
formula weight	989.79	996.70	1001.93	1006.69	1012.47	928.34
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$/n(#14)	$P2_1$/n(#14)	$P2_1$/n(#14)	$P2_1$/n(#14)	$P2_1$/n(#14)	$P2_1$/n(#14)
Z value	4	4	4	4	4	4
a /Å	12.258 (5)	12.183 (1)	12.139 (3)	12.101 (1)	12.052 (4)	12.103(4)
b /Å	31.560 (6)	31.601 (3)	31.568 (7)	31.582 (4)	31.568 (6)	31.57(1)
c /Å	9.619 (5)	9.588 (2)	9.572 (3)	9.554 (1)	9.546 (5)	9.566(3)
β /°	98.72 (4)	98.56 (1)	98.54 (2)	98.48 (1)	98.37 (3)	98.53(3)
V /Å^3	3678.2 (2)	3650.2 (7)	3627.2 (1)	3611.4 (7)	3593.3 (2)	3614.8(2)
μ (Mo$K\alpha$)/mm^{-1}	1.736	1.954	2.198	2.463	2.742	1.752
$R1^a$	0.0435	0.0424	0.0479	0.0487	0.0583	0.0604
w$R2^b$	0.1158	0.1122	0.1330	0.1261	0.1498	0.1588
GOF	1.005	0.968	1.004	0.948	0.967	0.996

a : $R1=\Sigma\,|\,|F_o|-|F_c|\,|/\Sigma\,|F_o|$

b : $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

Table 1-3. Selected bond distances (Å), bond angles (°) and torsion angles (°) of [Gd(hfac)$_3$(IM-2py)].

Bond lengths			
Gd – O(2)	2.401 (4)	O(2) – C(14)	1.230 (7)
Gd – O(3)	2.346 (4)	O(3) – C(16)	1.268 (7)
Gd – O(4)	2.328 (4)	O(4) – C(19)	1.243 (7)
Gd – O(5)	2.417 (4)	O(5) – C(21)	1.222 (7)
Gd – O(6)	2.354 (4)	O(6) – C(24)	1.251 (8)
Gd – O(7)	2.349 (4)	O(7) – C(26)	1.237 (7)
Gd – N(1)	2.540 (5)	N(2) – O(1)	1.282 (7)
Gd – N(3)	2.553 (4)	N(1) – C(1)	1.287 (7)
Bond Angles			
O(2) – Gd – O(3)	72.00 (15)	O(2) – Gd – O(4)	74.78 (15)
O(2) – Gd – O(5)	128.64 (15)	O(2) – Gd – O(6)	136.87 (15)
O(2) – Gd – O(7)	142.03 (14)	O(2) – Gd – N(1)	70.06 (15)
O(2) – Gd – N(3)	72.89 (15)	O(3) – Gd – O(4)	93.78 (15)
O(3) – Gd – O(5)	72.35 (15)	O(3) – Gd – O(6)	146.68 (15)
O(3) – Gd – O(7)	90.83 (14)	O(3) – Gd – N(1)	136.63 (15)
O(3) – Gd – N(3)	84.98 (15)	O(4) – Gd – O(5)	72.00 (13)
O(4) – Gd – O(6)	82.39 (15)	O(4) – Gd – O(7)	141.57 (14)
O(4) – Gd – N(1)	95.86 (14)	O(4) – Gd – N(3)	146.36 (14)
O(5) – Gd – O(6)	75.03 (15)	O(5) – Gd – O(7)	73.21 (14)
O(5) – Gd – N(1)	150.35 (16)	O(5) – Gd – N(3)	137.83 (14)
O(6) – Gd – O(7)	73.31 (14)	O(6) – Gd – N(1)	76.62 (16)
O(6) – Gd – N(3)	115.98 (15)	O(7) – Gd – N(1)	106.58 (15)
O(7) – Gd – N(3)	72.05 (13)	N(1) – Gd – N(3)	64.43 (14)
Torsion Angles			
N(1) – C(1) – C(2) – N(3)	-9 (1)		
N(1) – C(1) – N(2) – O(1)	177.2 (9)		

Table 1-4. δ values and ϕ values of [Ln(hfac)$_3$(IM-2py)]

	TPRS-8	Ln = Sm	Gd	Dy	Er	Yb	DD-8
δ_1 : O(2) [O(3) O(4)] O(5)[a]	21.8	29.53	28.10	28.50	28.81	28.72	29.5
δ_2 : N(3) [N(1) O(7)] O(6)[a]	0.0	8.08	9.17	9.49	10.03	12.63	29.5
δ_3 : N(3) [O(3) O(7)] O(5)[a]	48.2	36.79	36.63	36.21	35.62	35.26	29.5
δ_4 : O(2) [N(1) O(4)] O(6)[a]	48.2	38.12	38.15	37.83	36.96	36.57	29.5
ϕ_1 : O(2) – N(3) – O(4) – O(7)[b]	14.1	12.43	12.44	11.97	10.53	9.94	0.0
ϕ_2 : O(5) – N(6) – O(3) – N(1)[b]	14.1	8.06	7.85	7.14	7.06	6.33	0.0

a : A [B C] D is dihedral angle between ABC plane and BCD plane.

b : A – B – C – D is dihedral angle between (AB)CD and AB(CD)plane, where (AB) is the center of A and B.

Table 1-5. λ_{max} (nm) of Absorption Spectra in $CHCl_3$ for IM-2py ligand and the Complexes.[a]

	IM-2py	[Sm(hfac)$_3$(IM-2py)]	[Yb(hfac)$_3$(IM-2py)]
n-π* transition	420 (299)	430 (384)	431 (389)
(intraligand)	444^{sh} (269)	455 (504)	456 (512)
	475^{sh} (188)	485 (541)	487 (566)
	510^{sh} (88)	523 (326)	524 (348)
f-f transition			978 (5)
			955 (2)
			931 (2)

[a] Absorption constants are given in parentheses

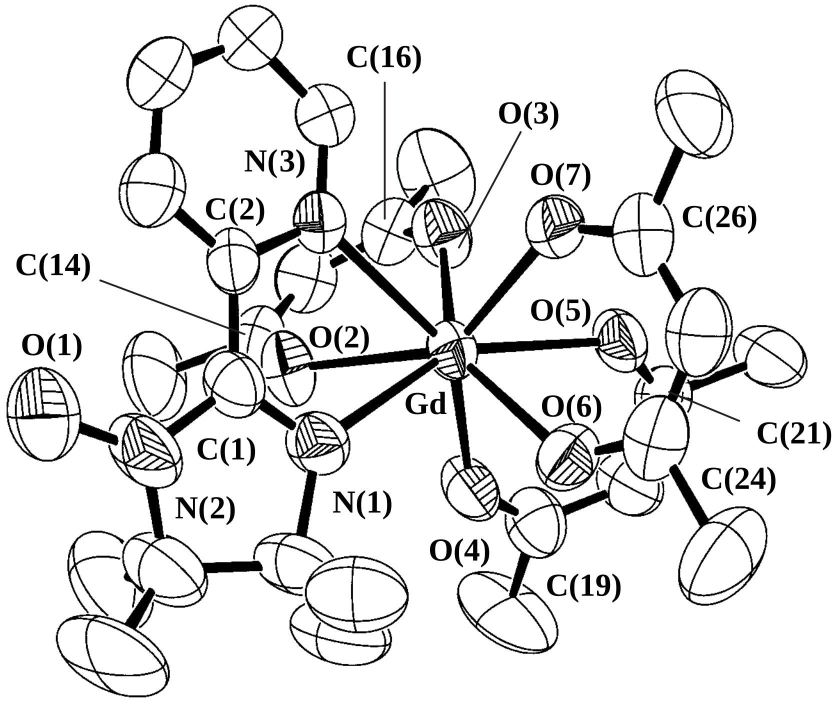


Figure 1-1. Molecular structure of [Gd(hfac)$_3$(IM-2py)] showing 50% probability ellipsoids(F atoms are omitted).

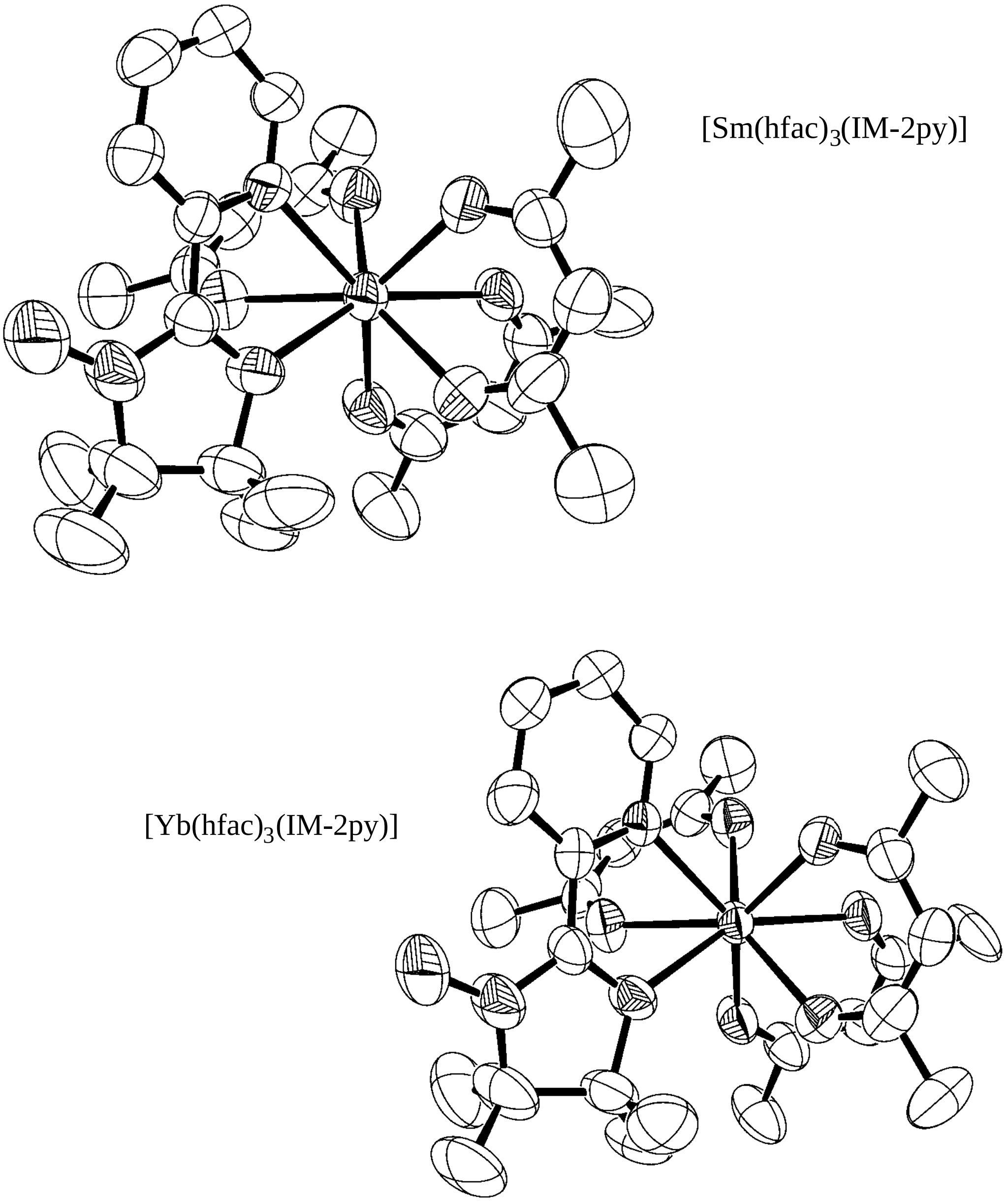


Figure 1-2. Molecular structures of [Sm(hfac)$_3$(IM-2py)] (upper) and [Yb(hfac)$_3$(IM-2py)] (lower) showing 50% probability ellipsoids(F atoms are omitted).

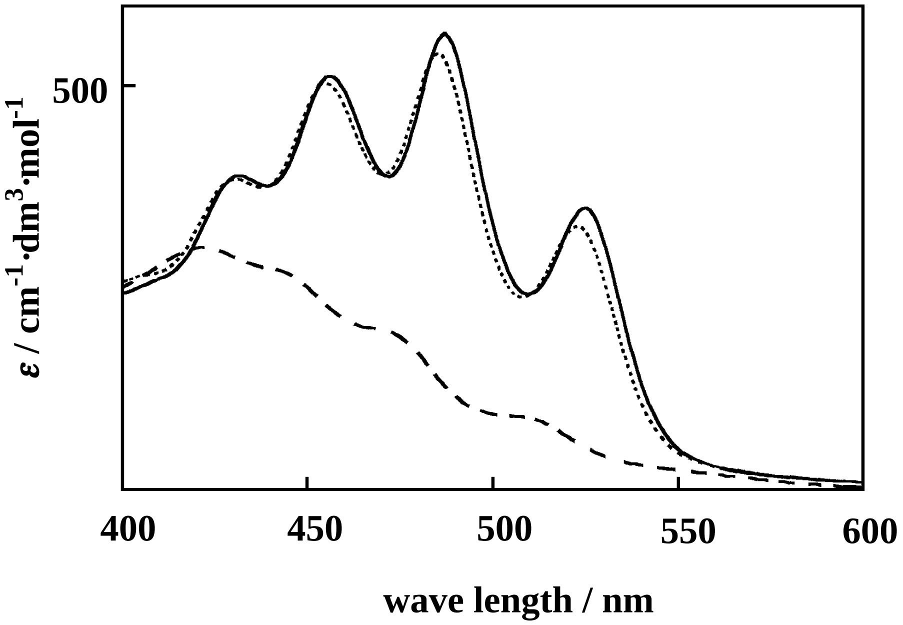


Figure 1-3. Absorption spectra of [Sm(hfac)$_3$(IM-2py)] (solid line), [Yb(hfac)$_3$(IM-2py)] (dotted line) and IM-2py (dashed line) in CHCl$_3$.

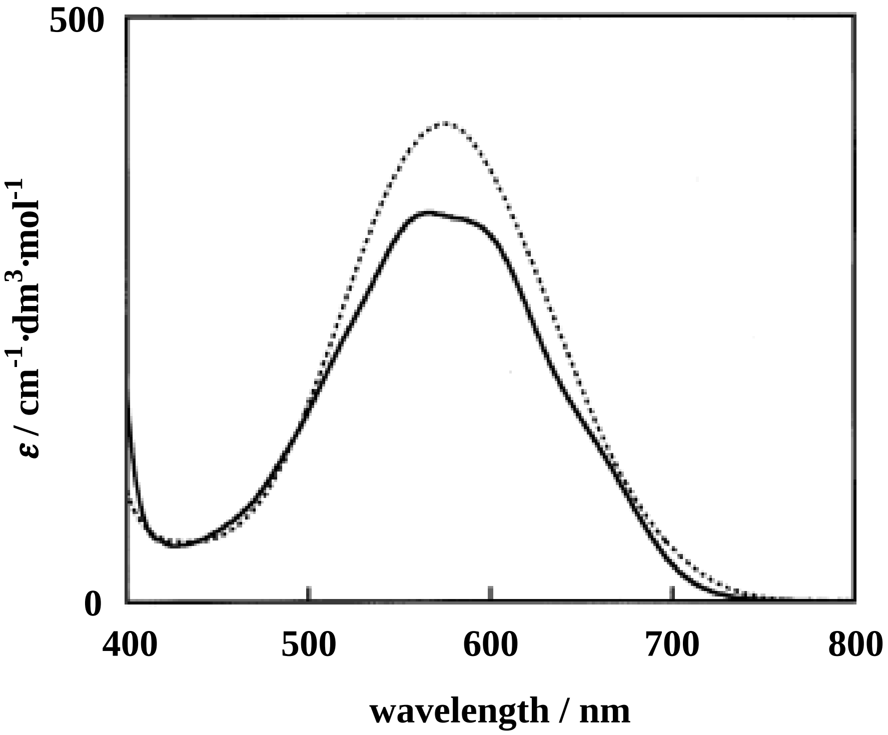


Figure 1-4. Absorption spectra of [Sm(hfac)$_3$(NIT-2py)] (solid line) and NIT-2py (dashed line).

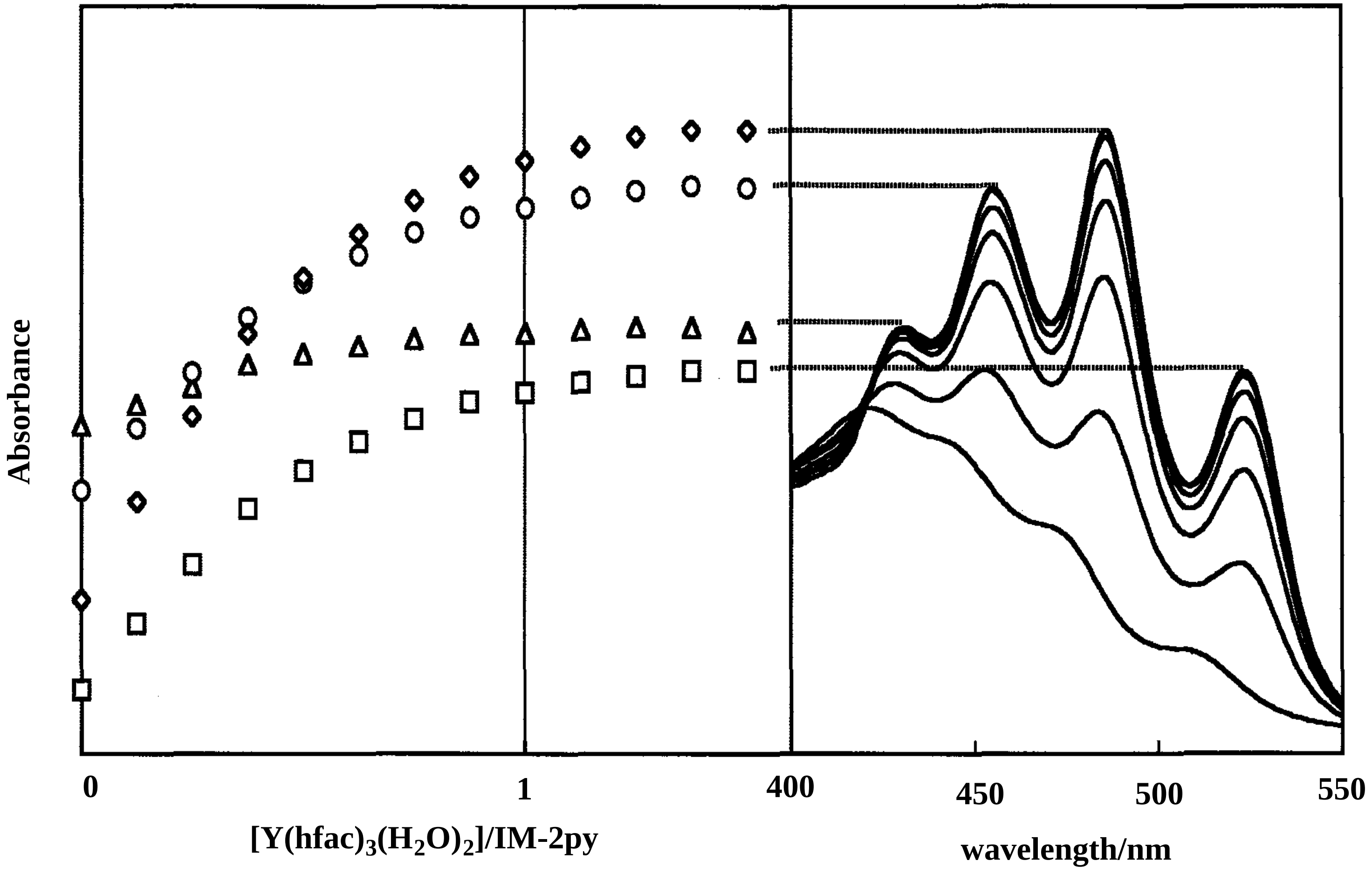


Figure 1-5. The change in UV-VIS absorption spectrum with the ratio $[Y(hfac)_3(H_2O)_2]$ / IM-2py increasing in acetonitrile. (, 524 nm;   , 486 nm;   , 451 nm;   432 nm)

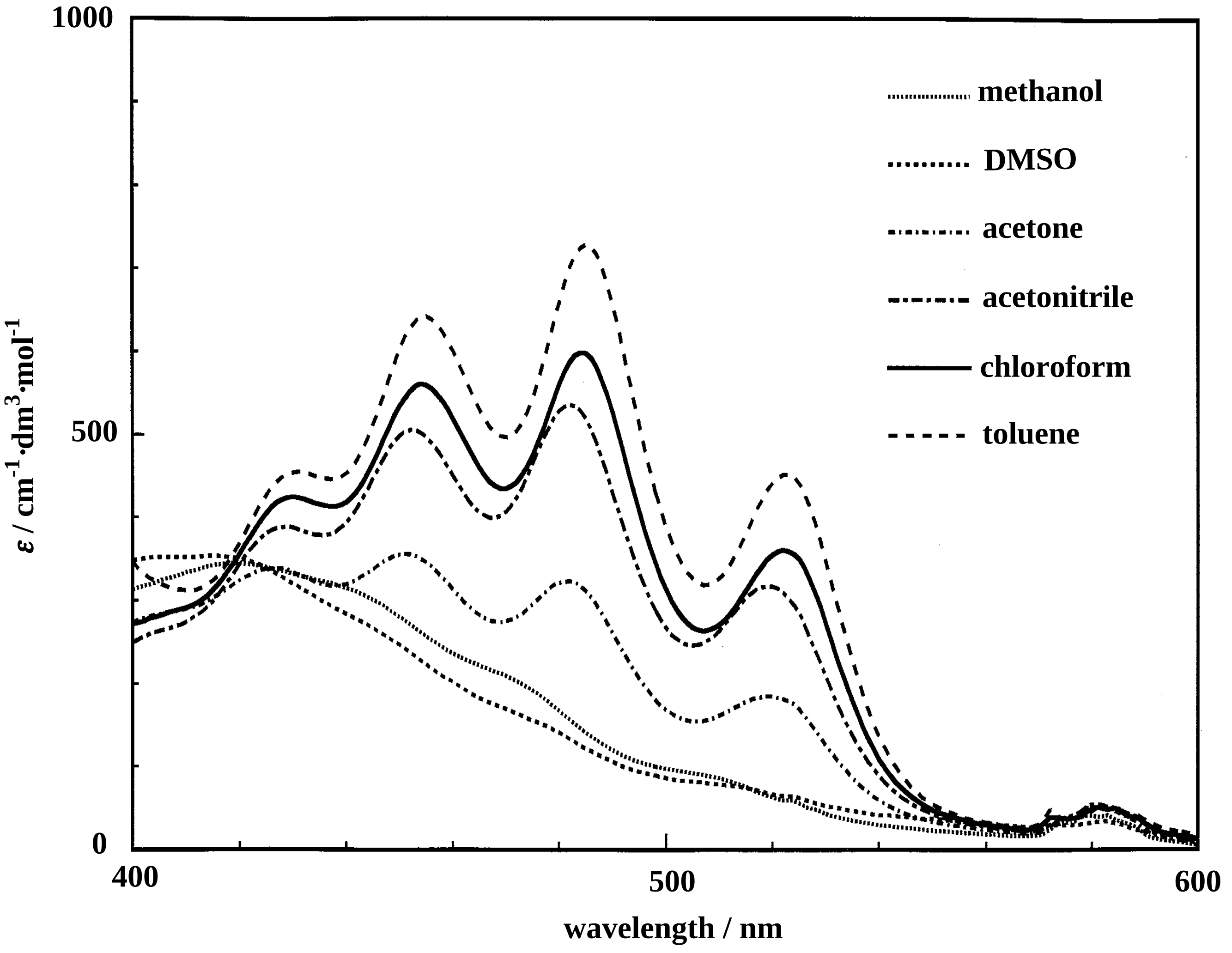


Figure 1-6. Absorption spectra of [Nd(hfac)$_3$(IM-2py)] in several solvent.

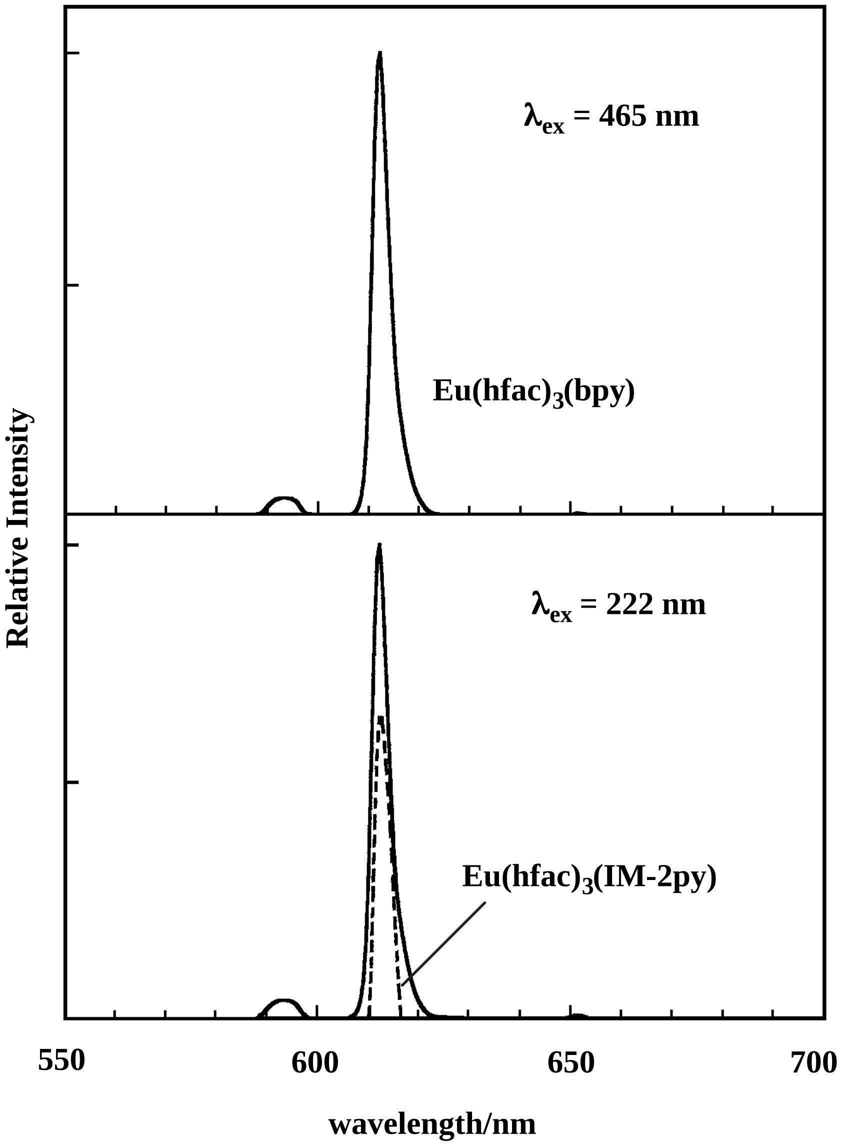


Figure 1-7. Emission spectra of [Eu(hfac)$_3$(bpy)] (solid line) and [Eu(hfac)$_3$(IM-2py)] (dashed line) complex in solid state.

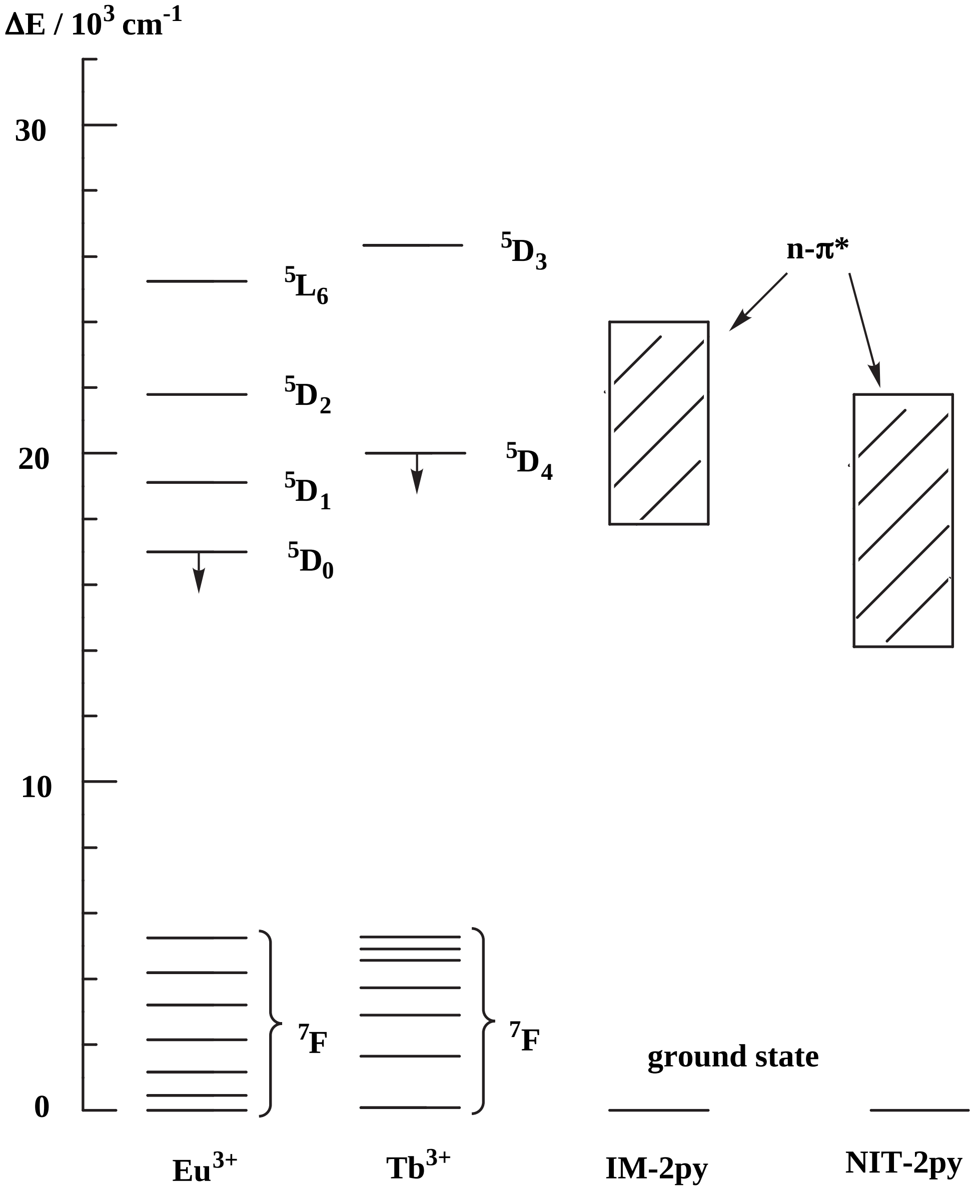


Figure 1-8. Energy level diagram showing 4f states of Ln(III) and ligand levels of NIT-2py and IM-2py. The arrows indicate emission levels of Eu(III) and Tb(III).

Chapter 2. Magnetic Properties of Gadolinium(III) Complexes Containing Imino Nitroxide Radical

2–1. Introduction

As mentioned in General Introduction, one of major attentions for lanthanide complexes is the magnetic property as building blocks in molecular-based magnetic materials. The transition metal or lanthanide complexes containing organic radical ligands can be referred as the smallest and the simplest unit of such materials, *e.g.* several lanthanide complexes with nitronyl nitroxide radicals. In such multi-spin system, the ferromagnetic or antiferromagnetic interaction between two unpaired spins is observed, depending on the alignment of the spins.[37] The interaction process can be related by the overlap between each magnetic orbital. In addition, the difference in the coexisted non-radical ligands also affects the magnetic properties and the magnitude.[20]

Needless to say, the lanthanide(III)–imino nitroxide complexes which were described in the previous chapter are constructed as the simplest multi-spin system and suitable on examining the interaction between 4f and π electrons. However, it can not be said that there is no problem. Since Ln(III) ions generally display relatively large spin-orbit coupling, which produces the rather large and anisotropic magnetic moments of most of the Ln(III) ions (See Chapter 3). But consequently, the Heisenberg-Dirac-Van Vleck phenomenological Hamiltonian is no longer appropriate in describing the spectrum of the low-lying states in such a case, thus the simple treatment for magnetic behavior is difficult.[22b] This is why most of the magnetic studies were limited to the case in which the Ln(III) is Gd(III). Since the isotropic Gd(III) ion has an $^8S_{7/2}$ single-ion ground state, the first-order orbital momentum does not have to be considered. In other words, the behavior can be treated with the same method as the first transition metal.

In this chapter, the magnetic property of Gd(III) complex containing IM-2py radical measured and analyzed as compared to that of the complexes containing other spin careers *e.g.* nitronyl nitroxide radical. In addition, when the coligand hfac are changed to tfac, the coligand effect of the magnetic property is described briefly.

2–2. Experimental Section

2–2-1. Synthesis of [Ln(tfac)$_3$(IM-2py)]

(a) tris(1,1,1-trifluoro-2,4-pentanedionato)diaquagadolinium(III) ([Gd(tfac)$_3$(H$_2$O)$_2$])

By the modified method for [Ln(hfac)$_3$(H$_2$O)$_2$] described in Chapter 1, [Gd(tfac)$_3$(H$_2$O)$_2$] was prepared. An ethereal solution of NH$_4$tfac was prepared by dissolving Htfac (2.77 g, 18 mmol) in 50 ml ether and adding NH$_3$ aq. until the white smoke was not evolved. After extraction and dry, the ether solution was evaporated. When 50 ml hot n-hexane was added to the resulting mixture of oil, a white precipitate was produced immediately. The white powder was obtained by filtration through glass filter and air dried for a few hours.

(b) [Gd(tfac)(IM-2py)]

The [Gd(hfac)$_3$(H$_2$O)$_2$] (1.0 mmol) was suspended in 10 ml CH$_2$Cl$_2$. IM-2py (1.37 mmol) in 10 ml CH$_2$Cl$_2$ (10 ml) was added to this suspension. After stirring for *ca.* 2 h, the red solution was obtained. The solution was poured into 20 ml of *n*-heptane, and stood to be evaporated slowly. Red orange crystals were obtained on standing for overnight.

2-2-2. X-ray Crystallographic Analysis

Red orange crystals of [Gd(tfac)$_3$(IM-2py)] suitable for X-ray crystal analyses were obtained by slowly evaporating the complex solution in a mixture of dichloromethane and *n*-heptane. The crystal was mounted in a glass capillary. The measurement was done in the almost similar condition to the complexes described in Chapter 1. The structure of [Gd(tfac)$_3$(IM-2py)] could be solved reasonably by using direct method (SHELXS-97 programs[38]) and refined by a full matrix least squares procedures(SHELXL-97[29]). The positions of hydrogen atoms were fixed at calculated positions and only their isotropic displacement parameters were refined. All calculations were carried out using Crystal Structure software.[30]

2–2-3. Magnetic Measurement

Temperature dependence of magnetic susceptibility at 2000 Oe between 2 and 300 K and magnetic field dependence at 2 K between 0 and 50 kOe were measured by using a SQUID susceptometer (MPMS-5S, Quantum Design). Pascal's constants were used to determine the continuent atom diamagnetism.

2-3. Results and Discussions

2–3-1. Preparation and characterization of [Ln(tfac)$_3$(IM-2py)]

In the similar method of [Gd(hfac)$_3$(IM-2py)], the treatment of [Ln(tfac)$_3$(H$_2$O)$_2$] and a small excess of IM-2py in dichloromethane also gave readily a red solution of the corresponding [Ln(tfac)$_3$(IM-2py)] complexes. But the crystals with space group *C*c were obtained by recrystallization from dichloromethane-*n*-heptane solution, while the space group in [Gd(hfac)$_3$(IM-2py)] is $P2_1$/n. The molecular structure of [Gd(tfac)$_3$(IM-2py)], which is illustrated in Figure 2-1, is similar to that of [Gd(hfac)$_3$(IM-2py)]. The Gd atom of [Gd(tfac)$_3$(IM-2py)] is eight-coordinated with three didentate tfac ligands and one didentate IM-2py ligand. Crystallographic data for each complex are listed in Table 2-1. Selected bond lengths and angles are also summarized in Table 2-2.

The bond length of N(2)-O(1) in the Gd complex is 1.255(14) Å, which is smaller than that in the other transition metal complexes containing IM-2py(1.265–1.271 Å). Thus the radical unpaired spin on complexation also exists. The planarity of the plane (N(1), C(1), N(2), O(1)) are also recognized from the torsion angle of N(1)–C(1)–N(2)–O(1) (0.3(13)°). The torsion angle of N(1)–C(1)–C(2)–N(3) (4(1)°) shows that the plane N(1)–C(1)–C(2)–N(3) is planar and SOMO(π^*) orbital expand to ligated N(3) atom of pyridine even in the complex.

The Gd-O(hfac) bond lengths also can be classified into two groups, though the classification pattern is different from the case of [Ln(hfac)$_3$(IM-2py)]. In the first group, the Gd-O bond lengths ranges from 2.327(10) Å to 2.330(8)Å (Gd-O(4), Gd-O(5), Gd-O(6) and Gd-O(7)). In the second group, they are 2.389(10) Å (Gd-O(2)) and 2.368(9)Å (Gd-O(3)), which are fairly longer than those in the first group. Considerable difference between the Gd–O length close to CF_3 group and CH_3 group is not observed. The bond length of the Gd-N(3) (pyridine-N) is 2.629(11)Å. The Gd-N(1) (imidazole-N) bond length is 2.645(9)Å, which is similar to the Gd-N(3) length. Both of them are considerably longer than those in [Gd(hfac)$_3$(IM-2py)].

The coordination polyhedron was also examined in terms of the semiquantitative method of polytopal analysis.[32] The δ_1 and δ_2 values showing planarity of the squares are 12.12° and 4.63° respectively. The δ_1 value are relatively large and δ_2 are still small, which is similar to that of [Ln(hfac)$_3$(IM-2py)]. But it is dangerous to conclude that of the most reasonable geometry is a TPRS only from these angles. The δ_3 and δ_4 values showing distortion between the squares are 49.30° and 53.12° respectively, which are relatively large. In addition, The ϕ_1 and ϕ_2 values are 27.28° and 20.89°. These values are close to 24.5°, of which the value is the angle of ideal SAPR rather than TPRS polyhedron. Thus, the most reasonable geometry around the Gd atom is a distorted SAPR.

2-3-2. Magnetic properties of [Gd(β-diketonato)$_3$(IM-2py)]

The variable temperature magnetic susceptibilities of [Gd(hfac)$_3$(IM-2py)] and [Gd(tfac)$_3$(IM-2py)] are shown in Figure 2-2. The observed $\chi_M T$ value at room temperature is 7.99 and 7.95 $cm^3 \cdot mol^{-1} \cdot K$, respectively. Both values are little smaller than the expected value for uncoupled Gd(III) and IM-2py (the calculated value is 8.12 $cm^3 \cdot mol^{-1} \cdot K$). The $\chi_M T$ values of these complexes slightly decrease as lowering the temperature, and then below 100 K, the drastic decrease appears. As the crystal packing showed that there are discrete molecules containing one gadolinium ion and one imino nitroxide without intermolecular interaction, the magnetic data was analyzed on the assumption of the interaction between these two spin centers. The usual van Vleck's equation for this type of dimer was derived by using the isotropic Hamiltonian $\boldsymbol{H} = -2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$.[23] The equation of the molar susceptibility is shown as follows;

$$\chi_{\mathrm{M}}T = \frac{Ng^2\beta^2}{kT} \cdot \frac{28\exp(-8J/kT) + 60}{7\exp(-8J/kT) + 9} \qquad (2\text{–}1)$$

A good fit to the experimental data of [Gd(hfac)$_3$(IM-2py)] is obtained for J =-3.00 cm^{-1} and g = 1.97 with the agreement factor $R = \Sigma[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{calc}}]^2/\Sigma(\chi_{\mathrm{M}})_{\mathrm{obs}}{}^2$ equal to 5.66×10^{-5}. The same treatment of [Gd(tfac)$_3$(IM-2py)] for *eq.* (2–1) gives the values, J=-2.93 and g = 1.98 with the agreement factor $R = 2.13 \times 10^{-4}$. When the coligand hfac are changed to tfac, the J and g values show only little change. In other words, the clear coligand effect of the magnetic property are not observed as the case of Ni(II) and Cr(III) complexes.[20]

In addition, the field dependence of the magnetization of [Gd(hfac)$_3$(IM-2py)] was measured at 2 K. The *M vs. H* curve is shown in Figure 2-3. In this figure, the experimental magnetization is compared to the theoretical magnetization given by the Brilloiun function for an J=3 total spin and to the sum of the isolated Gd(III) and nitroxide, which are represented as follows;[37]

$$M = N\beta[7\coth(\frac{7\beta H}{kT}) - \coth(\frac{\beta H}{kT})] \qquad (2\text{–}2)$$

for a J=3 state, and

$$M = N\beta[8\coth(\frac{8\beta H}{kT}) + 2\coth(\frac{2\beta H}{kT}) - 2\coth(\frac{\beta H}{kT})] \qquad (2\text{–}3)$$

for a J=7/2+1/2, respectively, where H is magnetic field. For any value of the field, the experimental magnetization is close to the value expected for a J=3 state. These results confirm that the interaction of [Gd(hfac)$_3$(IM-2py)] are substantially antiferromagnetic.

It is uncommon that the present complex exhibits the antiferromagnetic interaction of which only few examples were reported.[39,40] The interactions between Gd(III) and NIT type radical have been reported; the monodentate radical complex [Gd(hfac)$_3$(NIT-iPr)(H$_2$O)](J =0.33 cm^{-1})[22a], the didentate chelate type radical complex [Gd(hfac)$_3$(NIT-2py)] (J =1.51 cm^{-1})[23] and [Gd(NO$_3$)$_3$ (NITtrz)$_2$](J= 3.05 cm^{-1}).[39] Thus the magnetic interactions between Gd(III) ion and NIT-R type radical are generally found to be ferromagnetic. The interaction mechanism is discussed in detail in the next section.

2–3-3. Interpretation of the Magnetic properties of [Gd(β-diketonato)$_3$(IM-2py)]

As described above, the orbital contribution generally occurs for the most of the Ln(III) ions, each energy level displaying spin-orbit coupling. Thus the quantum number of the ground state should be represented as J(=L±S) not S. But since Gd(III) ion has an $^8S_{7/2}$ ground state, the orbital momentum does not be considered, *i.e*. J=S=7/2. (Note: to avoid confusion, the quantum number as far as Gd(III) is described "S=7/2" in the following) For the Gd(III) complexes containing an organic radical ligand, the interaction occurs between local octet and doublet states. If two spin centers interact upon coordination, then the local spins (S=7/2 and S=1/2) are not quantum numbers. The good quantum numbers are S=3 and S=4.

The mechanism to explain the magnetic nature of the Gd(III) and other unpaired spin(s) proposed as follows. The relative energies of the low-lying septet and nonet states depend on three contributions arising from different mechanisms; Two of them result from the interaction for the magnetic orbital of the ligand(π*) with the 4f orbitals, and the other results from the overlap of π* with the vacant 5d orbitals.

(i) The Heitler-London interaction[37] (Figure 2-4.) within the ground contribution

$(4f)^7(\pi^*)^1$ leads to a septet-nonet energy gap

$$J_a = 2k_{4f\text{-}\pi^*}+4\beta_{4f\text{-}\pi^*}\cdot S_{4f\text{-}\pi^*} \qquad (2\text{–}4)$$

where $k_{4f\text{-}\pi^*}$, $\beta_{4f\text{-}\pi^*}$ and $S_{4f\text{-}\pi^*}$ are the two electron exchange, transfer and overlap integrals, respectively, involving the overlap density. Only when the 4f and π* orbitals are orthogonal, the nonet state becomes the lowest. But in most cases, since the $4\beta_{4f\text{-}\pi^*}\cdot S_{4f\text{-}\pi^*}$ negative term dominates, the septet state is the lowest and J_a become negative value. So this interaction is referred as antiferromagnetic contribution in this case.

(ii) The interaction between the ground state configuration and the first excited charge-transfer configurations $(4f)^8$ or $(\pi^*)^2$ should be considered(Figure 2-4). This contribution gives a further stabilization of the septet state;

$$J_b = -2\beta_{4f\text{-}\pi^*}{}^2(1/U_A+1/U_B) \qquad (2\text{–}5)$$

where U_A and U_B are the energy costs associated with the 4f→π* and π*→4f electron transfers, respectively.

(iii) The ferromagnetic interaction between the lanthanide ion and paramagnetic radical ligands is proposed to involve the empty 5d orbitals of the metal, a fraction of the unpaired electrons of the organic ligands being transferred into these empty orbitals. (Figure 2-5.)[41,42] According to Hund's rule, the 4f electrons are expected to be aligned parallel to these 5d electrons, thus leading to ferromagnetism. Thus the ferromagnetism arises from the overlap between the singly occupied π* orbital of the nitroxide and the 5d orbitals of the metal. The interaction between the ground state configuration and the higher energy charge-transfer configuration $(4f)^7(5d)^1$, which stabilizes the nonet state of a J_c energy

$$J_c = 2\beta_{5d\text{-}\pi^*}{}^2\cdot k_{5d\text{-}\pi^*}/U'^2 \qquad (2\text{–}6)$$

where U' is the energy cost associated with this electron transfer and $k_{5d\text{-}\pi^*}$ is the one-site exchange integral. When 5d and π* orbitals are orthogonal, J_c vanished.

In the 4f-3d system *e.g.* Gd(III)-Cu(II) complex, the 4f orbitals are extremely weakly delocalized toward the donor atoms surrounding the lanthanide ion. As a consequence of this, the 4f-type magnetic orbitals do not interact with the 3d-type magnetic orbitals. Since all integrals involving a 4f-3d overlap density vanish, J_a and J_b values are also vanished and only J_c term can be detected. Since J_c always has positive values, it has been concluded that the interaction between Gd(III) and unpaired spin(s) is always ferromagnetic.

However, this mechanism cannot approproately explain the antiferromagnetic interaction in the Gd–IM-2py complexes. The radical ligands are directly coordinated to the central metal ion. Since the π orbitals are extended on the donor atoms, the unpaired spin density is also present on the donor atom. Though the delocalization of 4f orbitals is so weak, the non-zero overlap with the π orbital on the donor atom can be expected, which is different from the case of the transition metals. As a result, J_a and J_b term should not be neglected. Since J_a and J_b terms in the most cases have negative values, the septet state in the lowest ground state was stabilized. The stabilization leads to the antiferromagnetic interaction.

In addition, in imino-type radical complex containing Cu(II) ion, the coordination of imino nitroxide occurs in such a way that the copper(II) magnetic orbital and π^* orbital of IM-2py are orthogonal.[43] Accordingly, the overlap between the singly occupied π^* orbital and the 5d orbitals of the metal is also expected to be poor and the ferromagnetic interaction between the lanthanide ion and IM-2py radical is very small.

Since J_c in the general case is one order of magnitude smaller (in absolute value) than J_a and J_b, J_c value is neglected as compared with those two contribution. But as mentioned above, it is anticipated that the $\beta_{4f\text{-}\pi^*}$ involving 4f-type magnetic orbitals is not large enough to neglect the J_c term, although it is non-zero. Therefore, it is concluded that the overall magnetic interaction is decided by the delicate balance of these contributions; antiferromagnetic contribution(J_{AF}) which contains J_a and J_b, ferromagnetic one(J_F) which contains J_c.

Both NIT-type and IM-type radicals have ability for coordination to lanthanide centers. But since the donor character of nitrogen atom is superior to that of oxygen, the J_{AF} contribution for Gd–IM-2py is advantageous. Thus the total exchange constant is negative for the Gd–IM-2py complexes, whereas positive for the Gd-NIT radical complexes. Nevertheless, the absolute value of the total exchange constant for Gd-NIT radical complexes is relatively small compared with that for the Gd(III)-Cu(II) dinuclear complexes, in which 4f orbitals do not interact with the 3d orbital. It is also suggested that J_{af} contribution remains to some extent in the NIT radical complexes, whereas the J_{AF} term is almost zero in Gd–Cu complexes.

Table 2-1. Crystallographic data of [Gd(tfac)$_3$(IM-2py)]

formula	$C_{27}H_{28}N_3O_7F_9Gd$
Formula weight	834.77
crystal system	monoclinic
space group	*C*c (#9)
Z value	4
a / Å	12.206 (4)
b / Å	20.571(3)
c / Å	13.641 (2)
β / °	102.56 (2)
V / Å^3	3343 (1)
μ (Mo$K\alpha$)/mm^{-1}	20.84
$R1^a$	0.0484
w$R2^b$	0.1283
GOF	1.014

a : $R1=\Sigma \mid |F_o| - |F_c| \mid / \Sigma \mid F_o \mid$ b : w$R2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

Table 2-2. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) of [Gd(tfac)$_3$(IM-2py)].

Bond lengths

Gd – O(2)	2.389 (10)	O(2) – C(14)	1.235 (16)
Gd – O(3)	2.368 (9)	O(3) – C(16)	1.252 (15)
Gd – O(4)	2.330 (8)	O(4) – C(19)	1.237 (14)
Gd – O(5)	2.327 (10)	O(5) – C(21)	1.254 (17)
Gd – O(6)	2.329 (8)	O(6) – C(24)	1.249 (16)
Gd – O(7)	2.328 (8)	O(7) – C(26)	1.284 (17)
Gd – N(1)	2.645 (9)	N(2) – O(1)	1.255 (14)
Gd – N(3)	2.629 (11)	N(1) – C(1)	1.297 (19)

Bond Angels

O(2) – Gd – O(3)	71.2 (3)	O(2) – Gd – O(4)	79.5 (3)
O(2) – Gd – O(5)	124.2 (4)	O(2) – Gd – O(6)	141.6 (3)
O(2) – Gd – O(7)	135.7 (3)	O(2) – Gd – N(1)	73.3 (3)
O(2) – Gd – N(3)	72.8 (4)	O(3) – Gd – O(4)	111.5 (3)
O(3) – Gd – O(5)	75.2 (3)	O(3) – Gd – O(6)	147.1 (3)
O(3) – Gd – O(7)	81.8 (4)	O(3) – Gd – N(1)	137.6 (3)
O(3) – Gd – N(3)	85.5 (3)	O(4) – Gd – O(5)	73.1 (3)
O(4) – Gd – O(6)	80.3 (3)	O(4) – Gd – O(7)	144.3 (3)
O(4) – Gd – N(1)	83.5 (3)	O(4) – Gd – N(3)	140.6 (3)
O(5) – Gd – O(6)	79.6 (4)	O(5) – Gd – O(7)	79.2 (4)
O(5) – Gd – N(1)	146.0 (3)	O(5) – Gd – N(3)	146.1 (3)
O(6) – Gd – O(7)	72.9 (3)	O(6) – Gd – N(1)	72.3 (3)
O(6) – Gd – N(3)	104.9 (4)	O(7) – Gd – N(1)	109.4 (3)
O(7) – Gd – N(3)	70.6 (3)	N(1) – Gd – N(3)	62.2 (3)

Torsion Angles

N(1) – C(1) – C(2) – N(3)	4 (2)
N(1) – C(1) – N(2) – O(1)	0.3 (13)

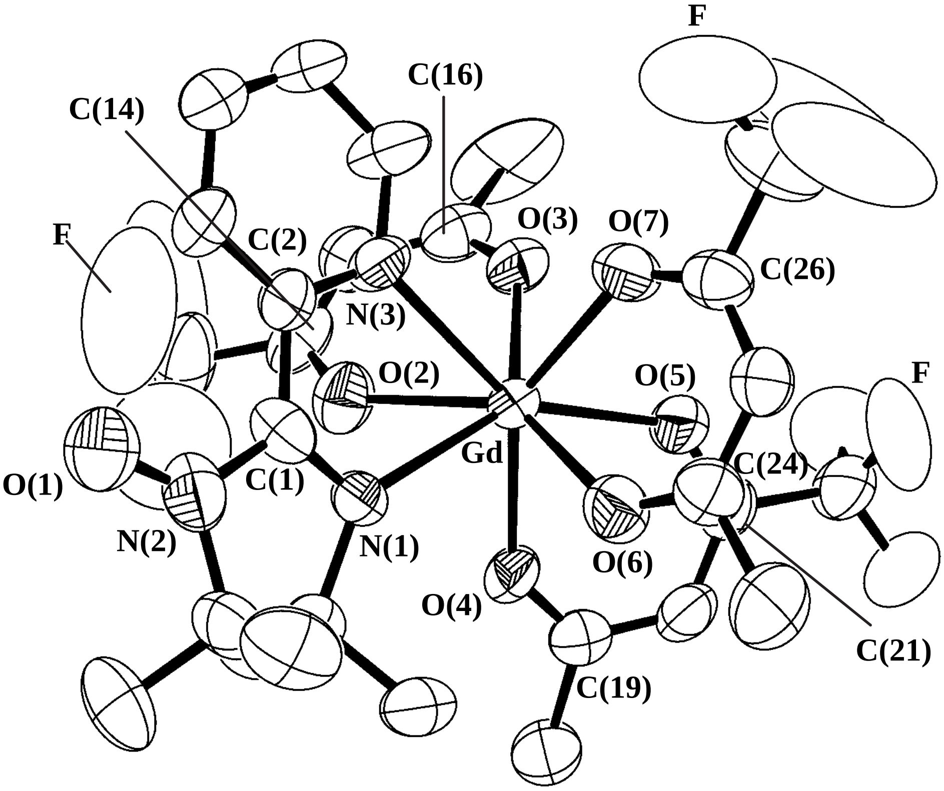


Figure 2-1. Molecular structure of [Gd(tfac)$_3$(IM-2py)] showing 50% probability ellipsoids.

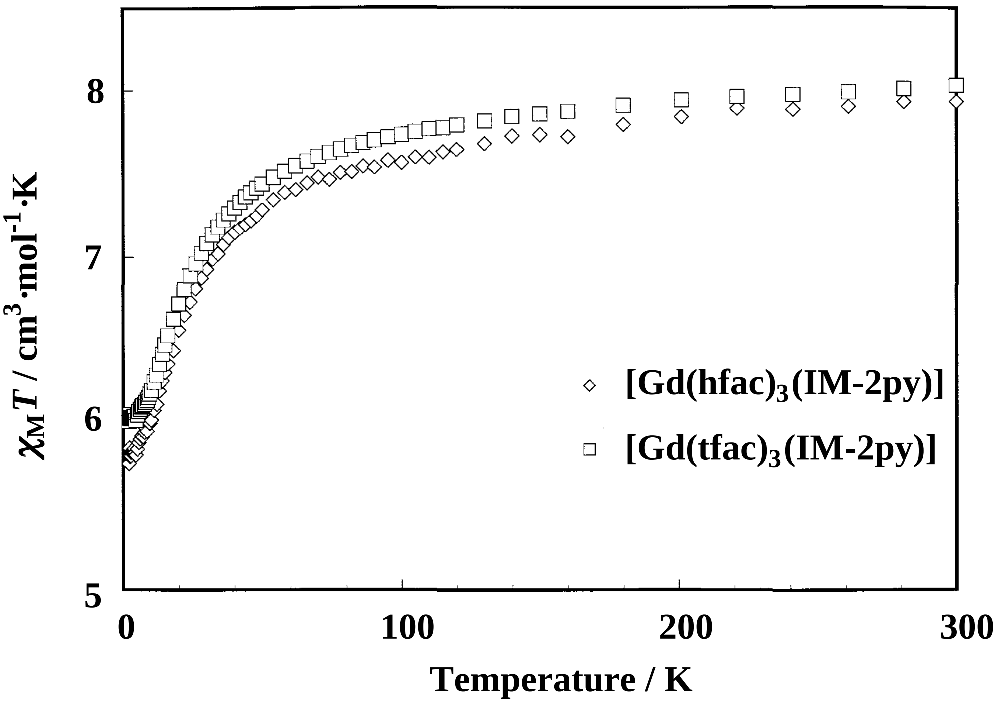


Figure 2-2. Temperature dependence of $\chi_M T$ values in the 4.2–300 K range for [Gd(β-diketonato)(IM-2py)].

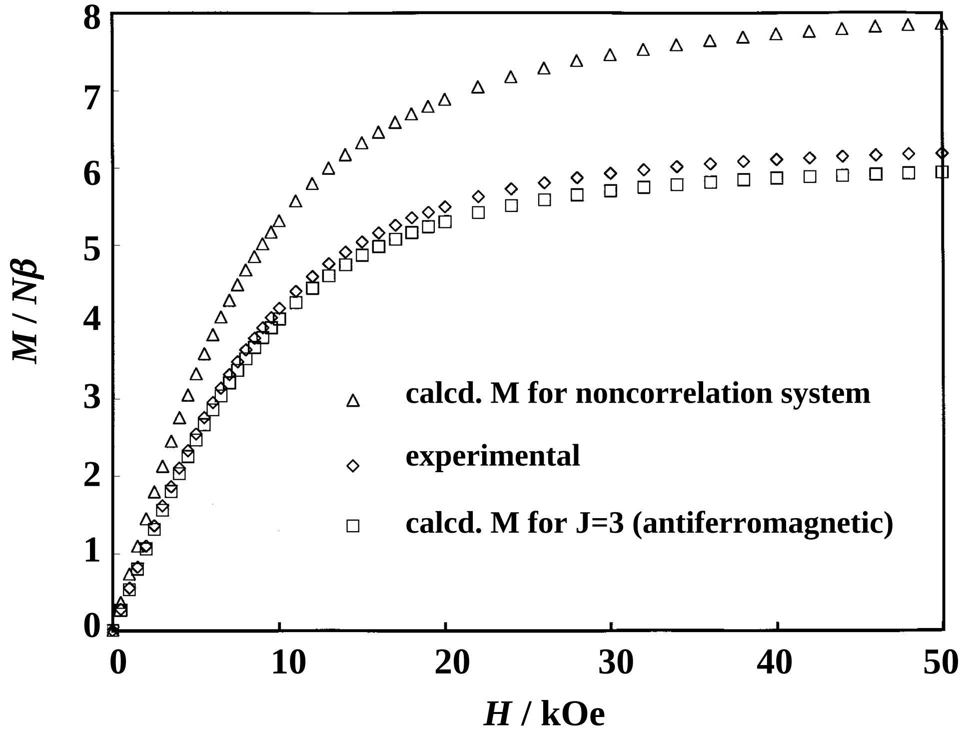
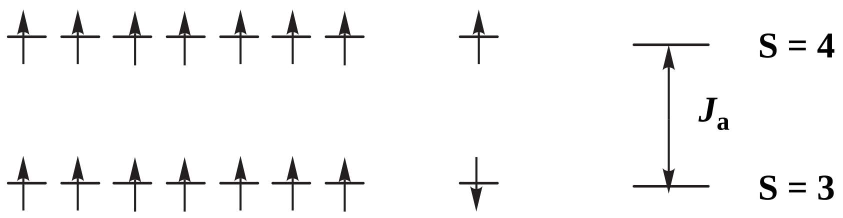


Figure 2-3. Field dependence of magnetization in the 0–50 kOe range for [Gd(hfac)$_3$(IM-2py)].

(a) Heitler-London Interaction



(b) GC–CTC(4f-π*) interaction

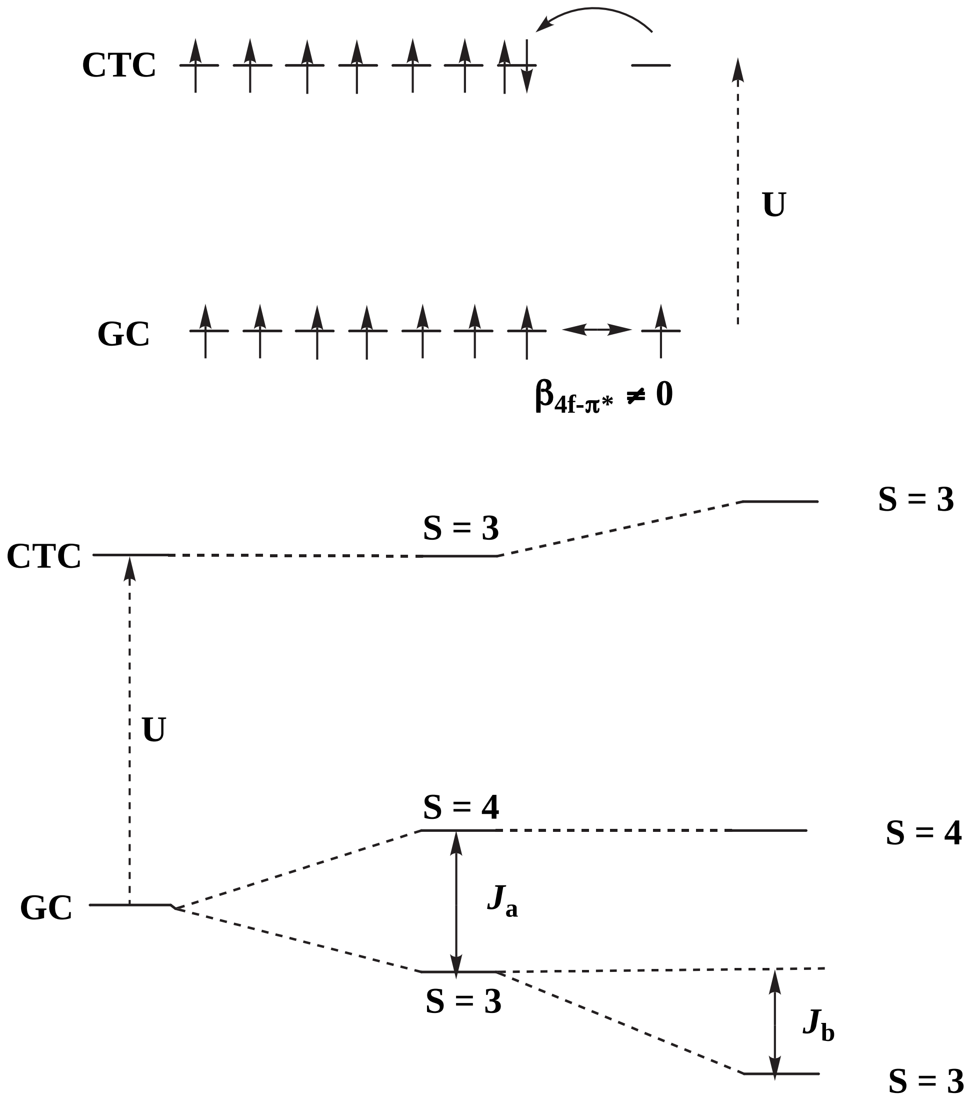


Figure 2-4. Schematic representation of the orbital mechanism explaining the Heitler –London and GC–CTC(4f-π*) interaction of the Gd(III)–radical complex.

(iii) GC-CTC(5d-π*) interaction

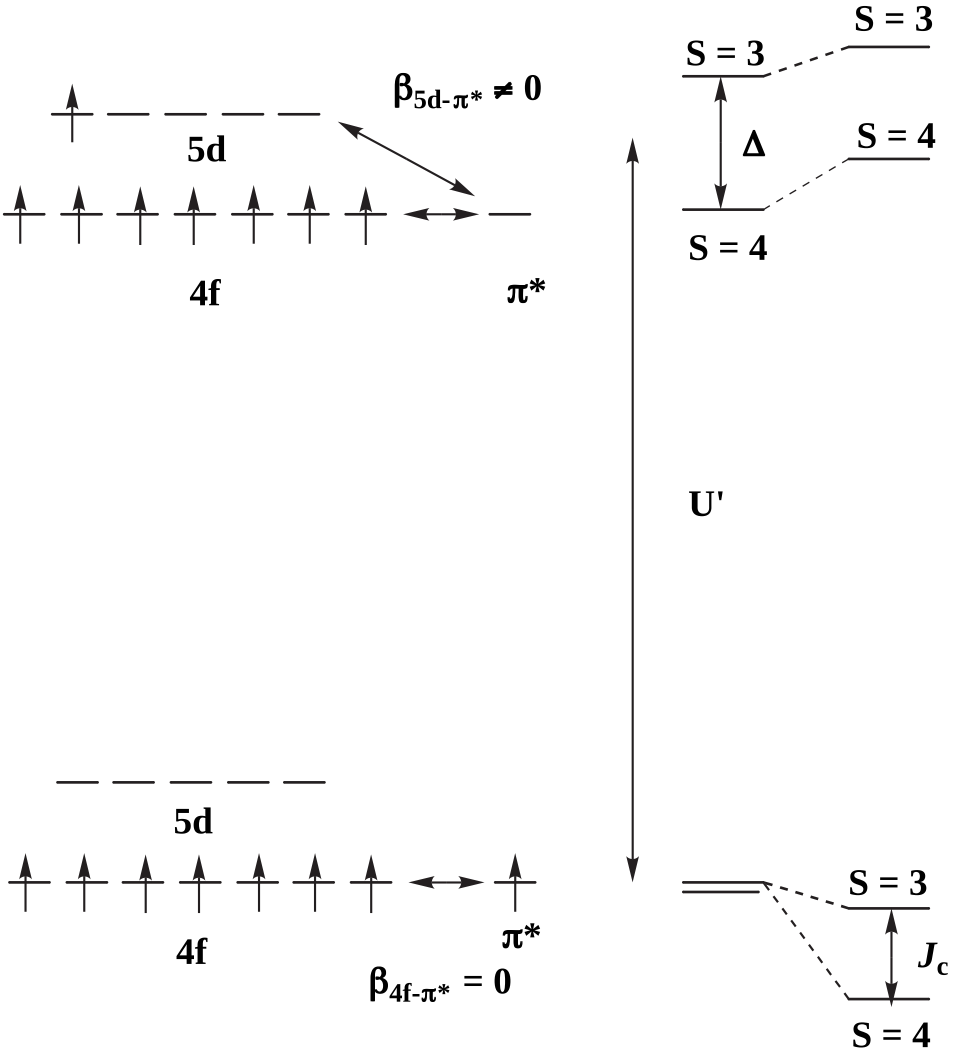


Figure 2-5. Schematic representation of the orbital mechanism explaining the GC–CTC(5d-π*) interaction of the Gd(III)–radical complex.

Chapter 3. Magnetic Properties of Lanthanide(III) Complexes Containing Imino Nitorxide Radical

3–1. Introduction

In Chapter 2, the magnetic property of Gd(III)-IM-2py complexes has been described, where there is found to be a significant antiferromagnetic interaction between Gd(III) ion and IM-2py. This is one of few exceptions, since the intramolecular Gd-radical magnetic interaction was found to be ferromagnetic in most cases.

There is very few information on the magnetic interactive nature in Ln-radical complexes except the isotropic Gd(III), partly owing to the orbital contribution arising from the ground state splitting(Figure 3-1).[37] For the $4f^n$ configuration of the Ln(III) ions, the $^{2S+1}L_J$ spectroscopic energy terms by interelectronic repulsion and spin-orbit coupling are split in Stark sublevels by the crystal field perturbation, of which the number for molecular complexes usually with C_1 symmetry is 2J+1 sublevels for even 4f electrons and J+1/2 for odd ones.[1] The violation of the Curie's law from the temperature dependence of $\chi_M T$ owing to a depopulation of the sublevels, which leads to decreases of a product of the $\chi_M T$ with decreasing the temperature. In this case, the variation of $\chi_M T$ nature between a Ln(III) ion with a first-order orbital momentum and the second unpaired spin(s) cannot be definitely elucidated only from the $\chi_M T$ *vs.* T curve, since the temperature dependence of $\chi_M T$ results from both the spin-orbit coupling of Ln(III) ion and the magnetic interaction between Ln(III) ion and radical ligands.

Kahn *et al.* have proposed the experimental approach to obtain more insight into magnetic interactive nature.[44,45] If the isostructuality of the complex has only to remain valid between Ln(III)-radical complexes and Ln(III) complexes containing analogous diamagnetic surroundings, it is possible to compare the magnetic behavior of these complexes together by an experimental approach, overcoming the difficulty with the spin-orbit coupling of the Ln(III) ions. In other words, a comparison of the magnetic characteristics of the Ln-radical with those of the corresponding complexes led to accurate information on the antiferro- or ferromagnetic nature of the Ln(III)-radical interaction. For Kahn's case, however, there remains one ambiguity concerning the intraligand magnetic interactions between the NIT radicals. On the other hand, the validity of this approach should be confirmed by the applicability to the opposite antiferromagnetic case. The desirable candidate could be our recent synthesized Ln–IM-2py complexes, since the interaction between Gd(III) and IM-2py radical shows significant antiferromagnetic interaction, which is different from nitronyl nitroxide type radical. We attempt to extend the magnetic study to the other lanthanide ions to gain more unambiguous information concerning the magnetic interaction between Ln(III) ion and paramagnetic radicals. In this chapter, the magnetic interactive nature in the Ln(III)-radical complexes from Nd to Yb, by comparison of the magnetic character of the Ln(III)-radical complex, [Ln(hfac)$_3$(IM-2py)], with corresponding Ln-nonradical complex, [Ln(hfac)$_3$(pybzim)].

3–2. Experimental Section

3-2-1. Synthesis of [Ln(hfac)$_3$(pybzim)]

The corresponding [Ln(hfac)$_3$(H$_2$O)$_2$] (1.0 mmol) was dissolved in 40 ml CH_2Cl_2. 2-(2'-pyridyl)-benzimidazole (pybzim) (1.37 mmol) in 10 ml CH_2Cl_2 (10 ml) was added to this solution. After stirring for *ca.* 2 h, the solution was evaporated to small volume(ca. 10 ml). The solution was poured into 10 ml of *n*-heptane, and stood to be evaporated slowly. Colorless needle crystals were obtained on standing for overnight.

3-2-2.Magnetic measurement

Temperature dependence of magnetic susceptibility was measured in the same condition described in Chapter 2.

In this chapter, $\chi_M T$ value of [Ln(hfac)$_3$(IM-2py)] and [Ln(hfac)$_3$(pybzim)] (Ln=Nd–Yb) are abbreviated as $\chi_M{}^{Ln}T$(IM) and $\chi_M{}^{Ln}T$(pybzim), respectively.

3-2-2. X-ray Crystallographic analysis

Colorless needle crystals of [Gd(hfac)$_3$(pybzim)] suitable for X-ray crystal analyses were obtained by slowly evaporating the complex solution in a mixture of dichloromethane and *n*-heptane. The crystal was mounted on a glass fiber. The measurement was done in the almost similar condition to the complexes described in Chapter 1. The structure of [Gd(hfac)$_3$(pybzim)] could be solved reasonably by using direct method (SHELXS-97[38] programs) and refined by a full matrix least squares procedures(SHELXL-97[29]). The positions of hydrogen atoms were fixed at calculated positions and only their isotropic displacement parameters were refined. All calculations were carried out using Crystal Structure software. [30]

3-3. Results and Discussions

3-3-1. Crystallographic studies of non-radical complex, [Gd(hfac)$_3$(pybzim)]

Colorless crystals of [Gd(hfac)$_3$(pybzim)] are formed with space group P2$_1$/n by recrystallization from diethylether-n-heptane solution. The molecular structure of [Gd(hfac)$_3$(pybzim)] is illustrated in Figure 3-2 and crystallographic data is shown in Table 3-1. The Gd atom of [Gd(hfac)$_3$(pybzim)] is eight-coordinated with three didentate hfac ligands and one didentate pybzim ligand. Selected bond lengths and angles of [Gd(hfac)$_3$(pybzim)] are shown in Table 3-2. The bond length of Gd–O ranges 2.335–2.430 Å, which is close to those of [Gd(hfac)$_3$(IM-2py)] (2.315–2.420 Å). The average bond length of Gd–N is 2.547 Å, which is similar to that of [Gd(hfac)$_3$(IM-2py)] (2.550 Å). The interplane distance between pybzim planes in adjacent molecules is *ca.* 3.60 Å, which is smaller than that of IM-2py complex. But the intermolecular interaction is negligibly small since the temperature dependence of $\chi_M{}^{Gd}T$(pybzim) is constant even at lower temperature; $\chi_M{}^{Gd}T$(pybzim) is 7.86 cm^3·mol^{-1}·K at 300 K and 7.81 cm^3·mol^{-1}·K at 2 K, respectively.

The examination for [Gd(hfac)$_3$(pybzim)] by using the semiquantitative method of polytopal analysis[32] gives the values as follows; the δ_1 and δ_2 values showing planarity of the squares are 31.04° and 13.86° and the δ_3 and δ_4 values showing distortion between the squares are 37.47° and 34.93°, respectively. In addition, The ϕ_1 and ϕ_2 values are 7.08° and 6.79°. It suggests that the most reasonable geometry around the Gd atom of the N_2O_6 eight coordinate [Gd(hfac)$_3$(pybzim)] is a distorted dodecahedron, whereas that of [Gd(hfac)$_3$(IM-2py)] is trigonal prism square bicapped. But since δ_2 value is relatively small and ϕ_1 and ϕ_2 are relatively large, it is also considered that the complex are on a geometric pathway to DD from TPRS. Therefore, in the view of their molecular structures, it can be considered that the ligand field effect in [Ln(hfac)$_3$(IM-2py)] and [Ln(hfac)$_3$(pybzim)] must be almost similar.

3-3-2. Magnetic Behavior of Eu(4f^6) compounds

What Eu(III) ion is distinct from the other lanthanide ion is that the ground state is nonmagnetic ($^7F_0$). Because of the nonmagnetic ground state of Eu(III), there is no Stark sublevel arising from the ground state. Consequently, the $\chi_M{}^{Eu}T$(IM) value of [Eu(hfac)$_3$(IM-2py)] is close to that of the isolated unpaired spin of IM-2py at low temperature as far as no other interactions, *e.g.* radical-radical interaction.

The magnetic behavior of Eu(III) complexes can be estimated by a theoretical model.[37,46] In the case of nonradical complex [Eu(hfac)$_3$(pybzim)], the behavior of $\chi_M{}^{Eu}T$(pybzim) shown in Figure 3-3, can be attributed to the contribution of the thermal population of the excited states of the Eu(III). The ^{7}F ground term is split by the spin-orbit coupling into seven states, ^7F_J, with J taking integer values from 0 to 6, and the energies of the states are

$$E(J) = \lambda J(J+1)/2 \qquad (3\text{–}1)$$

which the energy of the $^7F_0$ ground state is take as the origin. Since λ is small enough for the first excited states to be thermally populated, the magnetic susceptibility may be expressed as

$$\chi_{\mathrm{M}} = \frac{\sum_{\mathrm{J}=0}^{6}(2\mathrm{J}+1)\chi(\mathrm{J})\exp[-\lambda \mathrm{J}(\mathrm{J}+1)/2kT]}{\sum_{\mathrm{J}=0}^{6}(2\mathrm{J}+1)\exp[-\lambda \mathrm{J}(\mathrm{J}+1)/2kT]} \qquad (3\text{–}2)$$

In the free-ion approximation, the molar magnetic susceptibility for a mononuclear species is then given by[37,47]

$$\chi(\mathrm{J}) = \frac{Ng_{\mathrm{J}}^2\beta^2\mathrm{J}(\mathrm{J}+1)}{3kT} + \frac{2N\beta^2(g_{\mathrm{J}}-1)(g_{\mathrm{J}}-2)}{3\lambda} \qquad (3\text{–}3)$$

Where T is the temperature and g_{J} is the Zeeman factor

$$g_{\mathrm{J}} = 3/2 + [\mathrm{S}(\mathrm{S}+1)-\mathrm{L}(\mathrm{L}+1)]/2\mathrm{J}(\mathrm{J}+1) \qquad (3\text{–}4)$$

except g_0 which is equal to 2+L(=2+S)=5. Thus the temperature dependence of the magnetic behavior of [Eu(hfac)$_3$(pybzim)] is given as a function of the spin-orbit coupling parameter λ. Least-squares fitting of the theoretical expression of $\chi_{\mathrm{M}}^{\mathrm{Eu}}T$(*eq* (3–2)) gave a value of λ=329.7 cm^{-1}, which is compared well with that found by both luminescence and magnetic studies for the corresponding bpy complex. Owing to crystal field splitting, the experimental values are greatly deviated from calculated values using free-ion approximation at high temperature. But below 200 K, the effect from crystal field variation need not to be considered.

The temperature dependence of [Eu(hfac)$_3$(IM-2py)] is shown in Figure 3-4. It is found that the spin-orbit coupling and crystal field splitting are almost similar. If the noncorrelated spin system is shown in the case of [Eu(hfac)$_3$(IM-2py)] and the ligand field is similar to each other, $\chi_{\mathrm{M}}^{\mathrm{Eu}}T$(IM) value is expressed as

$$\chi_{\mathrm{M}}^{\mathrm{Eu}}T\,(\mathrm{IM}) = \chi_{\mathrm{M}}^{\mathrm{Eu}}T\,(\mathrm{pybzim}) + \chi_{\mathrm{M}}T\,(\mathrm{radical}) \qquad (5)$$

The temperature dependence of the sum of $\chi_{\mathrm{M}}^{\mathrm{Eu}}T$ (pybzim) and $\chi_{\mathrm{M}}T$ (radical) is shown in Figure 3-4. At low temperature, the $\chi_{\mathrm{M}}^{\mathrm{Eu}}T$(IM) values agree with this sum values, but at higher temperature the $\chi_M^{Eu}T$(IM) values become larger. It is suggested that the magnetic moment of excited states ^7F_J (J≥1) becomes larger than that of nonradical complex, probably arising from the existence of a ferromagnetic interaction between Eu(III) and IM-2py, whereas the ground state $^7F_0$ is nonmagnetic and does not affect the magnetic moment. At 2 K, the experimental $\chi_M^{Eu}T$(IM) value is similar the theoretical value of S=1/2 unpaired spin in IM-2py, confirming no intermolecular interaction as found for the Gd(III) complex(see Chapter 2). No intermolecular interaction in the IM-2py complex is more definite than the case of the NIT-type radical complex, where no intermolecular interaction is claimed only by considering the intraligand(NIT-NIT) antiferromagnetic ineteraction.[45]

3-3-3. Magnetic behavior of Nd($4f^3$) and Sm($4f^5$) compounds

In view of the isostructual coordination geometries of [Ln(hfac)$_3$(IM-2py)] through Nd to Yb, a series of the present Ln(III) complexes gives only the intramolecular magnetic interaction.

The temperature dependence of the magnetic susceptibility of [Nd(hfac)$_3$(IM-2py)] is shown as a $\chi_M^{Nd}T$(IM) *vs.* *T* plot in Figure 3-5. At 300 K, the $\chi_M^{Nd}T$(IM) is equal to 2.00 $cm^3 \cdot K \cdot mol^{-1}$, which is close to the calculated value for the uncorrelated magnetic moments of the Nd(III) ion and IM-2py. The gradual decrease of $\chi_M^{Nd}T$(IM) to 0.98 $cm^3 \cdot K \cdot mol^{-1}$ with lowering the temperature does not necessarily suggest the antiferromagnetic interaction between Nd(III) ion and IM-2py. The $\chi_M^{Nd}T$(pybzim) *vs.* *T* plots of [Nd(hfac)$_3$(pybzim)] does not follow the Curie's law (Figure 3-5). As shown for the IM-2py complex, the $\chi_M^{Nd}T$(pybzim) value decreases with lowering the temperature. Since the first excited state $^4I_{11/2}$ of free Nd(III) ion is located at *ca.* 2000 cm^{-1} above the ground state $^4I_{9/2}$, the excited state is expected to be completely depopulated at room temperature. The deviation of the magnetic behavior with respect to the Curie law results from the crystal field which splits the $^4I_{9/2}$ free-ion ground state into five Kramers doublets (Stark sublevels). The almost equally populated Kramers doublets at 300 K are progressively depopulated (the lowest Kramers doublet is populated) with lowering the temperature. Accordingly, the $\chi_M^{Nd}T$(pybzim) value decreases.

The temperature dependence of $\Delta\chi_M^{Nd}T = \chi_M^{Nd}T$ (IM) – $\chi_M^{Nd}T$ (pybzim) is also shown in Figure 3-5. At 300 K, the $\Delta\chi_M^{Nd}T$ value is 0.44 $cm^3{\cdot}K{\cdot}mol^{-1}$, close to the expected value for an uncorrelated S=1/2 spin. The gradual increase of the $\Delta\chi_M^{Nd}T$ values with lowering the temperature to 10 K suggests the ferromagnetic interaction within the IM-2py complex.

The similar behavior is found for the Sm(III) complexes. The temperature dependence of $\chi_M^{Sm}T$(IM), $\chi_M^{Sm}T$ (pybzim) and $\Delta\chi_M^{Sm}T$ are shown in Figure 3-6. Since the spin-orbit coupling parameter in Sm(III) ion is of the order 200 cm^{-1}, the first excited state $^6H_{7/2}$ can be populated at room temperature. Thus in the lower temperature range, the decrease of the $\chi_M^{Sm}T$ value results from both the multiplet splitting and Stark splitting. At 300K, the $\chi_M^{Sm}T$ (IM) and $\chi_M^{Sm}T$ (pybzim) values are 0.82 and 0.45 $cm^3{\cdot}K{\cdot}mol^{-1}$, respectively. Though both values are slightly larger than the theoretical value, the $\Delta\chi_M^{Sm}T$ value is 0.37 $cm^3{\cdot}K{\cdot}mol^{-1}$, which is close to the expected value for an uncorrelated S=1/2 spin. It is considered that the deviation from the expected value of $\chi_M^{Sm}T$) and $\chi_M^{Sm}T$ (pybzim) is given by the crystal field effect. The $\Delta\chi_M^{Sm}T$ value is almost constant above 100 K, but gradually increases below 100 K. This gradual increase may result from the depopulation of the first excited state $^6H_{7/2}$, leading to the interaction through only the Stark effect, as in the case of the Nd(III) complex. The lower temperature $\Delta\chi_M^{Sm}T$ behavior demonstrates that the magnetic interaction between the Sm(III) ion and IM-2py is ferromagnetic.

3-3-4. Magnetic behavior of Tb($4f^8$) to Yb($4f^{13}$) complexes

The temperature dependent plots of $\chi_M^{Ln}T$(IM) for the sequence of [Ln(hfac)$_3$(IM-2py)] (Ln=Tb–Yb) are shown in Figure 3-7. As temperature is lowered, $\chi_M^{Ln}T$(IM) decreases in all cases; *e.g.* $\chi_M^{Yb}T$(IM) at 300 K is equal to 2.71 $cm^3\cdot K\cdot mol^{-1}$, which is close to the expected value for an uncorrelated Yb(III) ion and IM-2py spin, and decreases as temperature is lowered to reach 2.50 $cm^3\cdot K\cdot mol^{-1}$ at 2 K. But this result does not necessarily show the antiferromagnetic interaction between metal ion and IM-2py ligand. The value of $\chi_M^{Yb}T$(pybzim) also decreases with lowering the temperature (Figure 3-8). Though the first excited state of Yb(III) ion ($^2F_{5/2}$) can be fully depopulated, the contribution arising from the thermal depopulation of the Stark sublevels is relatively large. But the decreasing slope of $\chi_M^{Yb}T$(pybzim) value is more gradual than that of [Yb(hfac)$_3$(IM-2py)], and below 170 K, $\chi_M^{Yb}T$(pybzim) value is larger than $\chi_M^{Yb}T$(IM) to reach 1.41 $cm^3\cdot K\cdot mol^{-1}$ at 2 K. The profile of $\Delta\chi_M^{Yb}T$ also shows the different behavior from the Nd(III) or Sm(III) complexes.(Figure 3-8.) with lowering the temperature, $\Delta\chi_M^{Yb}T$ gradually decreases. These facts suggest that the interaction between Yb(III) ion and IM-2py is antiferromagnetic.

The case of the Tb(III) is more remarkable. The $\chi_M^{Tb}T$(IM) *vs.* T and $\chi_M^{Tb}T$(pybzim) *vs.* T plot are shown in Figure 3-9. The value of $\chi_M^{Tb}T$(pybzim) is 11.6 $cm^3\cdot K\cdot mol^{-1}$ at 300 K, which is close to the theoretical value of Tb(III) free ion. At lower temperature, the values gradually increase to reach 11.8 $cm^3\cdot K\cdot mol^{-1}$ at *ca.* 50 K. As to the Eu(III) case, the magnetic behavior, $\chi_M^{Tb}T$, can be attributed to the contribution of the thermal population of the excited states of the Tb(III). But the ground state of Tb(III) are $^7F_6$, whereas that of Eu(III) is $^7F_0$; the former $\chi_M^{Tb}T$(ground state) is the largest value of ^7F states, the latter $\chi_M^{Eu}T$(ground state) is nonmagnetic. Thus the $\chi_M^{Tb}T$(pybzim) value becomes larger at lower temperature. On the other hand, the value of $\chi_M^{Tb}T$(IM) is 12.6 $cm^3\cdot K\cdot mol^{-1}$ at 300 K and then gradual decreases are observed as temperature is lowered. This behavior apparently show that the interaction between Tb(III) ion and IM-2py is antiferromagnetic. The $\Delta\chi_M^{Tb}T$ profile also shows the same tendency(Figure 3-9). Except Tb(III), it can not be clearly suggested that the decreasing of $\chi_M^{Ln}T$(IM) result from the interaction between Ln(III) ion and IM-2py. But the exceeding of $\chi_M^{Ln}T$(pybzim) over $\chi_M^{Ln}T$(IM) and the decreasing of $\Delta\chi_M^{Ln}T$(IM) at lower temperature are shown in the other lanthanide complexes(Figure 3-10, 11, 12 and 13). Thus it is suggested that the interaction is antiferromagnetic.

3-3-5. Summary of magnetic behavior for Ln–radical complexes

The experimental approach to get insight into the coupling between a Ln(III) ion displaying spin-orbit coupling and these paramagnetic species has been described. In this regard, the pybzim ligand is found to be ideal diamagnetic counterparts of the paramagnetic imino nitroxide substituted pyridyl derivative from X-ray structual study. If the ligand field in both series of compounds is the same, the energy spectrum of the Stark sublevels for the Ln(III) ion with either the pybzim or IM-2py ligand should be very close consequently. Intermolecular interactions to account for this behavior at low temperature can be excluded as they have been shown to be negligibly small in both of [Gd(hfac)$_3$(IM-2py)] and [Gd(hfac)$_3$(pybzim)]. In addition, the simpler spin interactive system of the mono(IM-2py) complexes like dinuclear species than that of the bis(NIT-radical)–Ln(III) complexes like trinuclear species provides more reliable elucidation of the magnetic interactive nature in a series of paramagnetic Ln(III) complexes with the radical ligand, because of not taking into consideration of the intraligand interaction in the former case.

Both the temperature dependent plots of $\Delta\chi_M^{Ln}T = \chi_M^{Ln}T$ (IM) – $\chi_M^{Ln}T$ (pybzim) give information concerning the antiferromagnetic or ferromagnetic interaction in the [Ln(hfac)$_3$(IM-2py)] compounds. The behavior of $\Delta\chi_M^{Ln}T$ *vs.* T reflects the variation of the magnetic moment of the molecular as a result of the coupling between the spin centers. For example, as observed in Figure 3-5 or Figure 3-8, the deviation of $\Delta\chi_M^{Ln}T$ at low temperature from the constant value 0.38 cm^3·K·mol^{-1}, which is the theoretical value of S=1/2 spin state, can only result from the variation of the magnetic moment of the complex as a consequence of the magnetic interactions between spin centers.

Consequently, it follows that the Ln-radical interaction is ferromagnetic when the whole magnetic moment in [Ln(hfac)$_3$(IM-2py)] is larger than the sum of the contribution of the uncorrelated spin centers. In the series of investigated [Ln(hfac)$_3$(IM-2py)] complexes, the temperature dependence of $\Delta\chi_M^{Ln}T$ clearly shows that the Ln–radical interaction is ferromagentic for Ln = Nd and Sm whereas it is antiferromagnetic for Ln=Tb–Yb.

The magnetic property between Eu(III) ion and IM-2py in [Eu(hfac)$_3$(IM-2py)] is uncertainly since the ground state of Eu(III) ion is nonmagnetic, $^7F_0$. But a comparison of $\chi_M^{Eu}T$(IM) with the sum of $\chi_M^{Eu}T$ (pybzim) and $\chi_M T$ (radical) gives us a trace to the magnetic interaction. The deviation from the sum value at *ca.* 100 K suggests that the interactions between Eu(III) and radical behaves as if ferromagnetic, thus the magnetic moment of excited states ^7F_J (J≥1) become larger. Thus the magnetic interaction between the spin centers can be considered as ferromagnetic.

Considering the numerous compounds for which a Gd(III) ion interacts with either nitroxide radicals[22,23] or Cu(II) ions,[48,49] it appears that neither the coordination number of the metal ion nor the topology of the compound affect the nature of the coupling, which was always found to be ferromagentic. On the other hand, the interaction between Gd(III) ion and IM-2py radical is antiferromagnetic in [Gd(hfac)$_3$(IM-2py)] as mentioned in Chapter 2. When the treatment as the complexes showing the ferromagnetic interaction applies for the other Ln(III) ions, the nature of the interactions found in this study for the [Ln(hfac)$_3$(IM-2py)] compounds could give the opposite results for related Gd(III)–Cu(II) or Gd(III)–NIT derivatives.

Indeed, the trend for the interactions between the Ln(III) and imino nitroxide seems to be the opposite to the previous report.[44,45] For the compounds involving Ln(III) ions in the lanthanide series with less than half-filled f-orbitals, the interaction was found to be ferromagnetic. Whereas the results reported for the Ln(III) – Cu(II) compounds are not consistent for the ions after Dy(III), it is apparent that the interaction in [Ln(hfac)$_3$(IM-2py)] with more than half-filled f-orbitals is antiferromagnetic.

It was assumed that this mechanism remained valid for the other magnetic Ln(III) ions, leading to an antiferromagnetic coupling between the Ln(III) and radical spins. When the number of 4f electrons is less than seven, the orbital and spin momenta of Ln(III) are antiparallel, and the antiferromagnetic spin coupling gives rise to an overall ferromagnetic interaction. When the number of 4f electrons is more than seven, the orbital and spin momenta of Ln(III) are parallel, and then antiferromagnetic spin coupling gives rise to an overall antiferromagentic interaction. This mechanism is schematized in Figure 3-14. This is an exactly reverse situation to that found for the NIT–Ln(III) complexes and confirms that Kahn’s approach is applicable to the present Ln–IM-2py complexes.

Table 3-1. Crystallographic Data for [Gd(hfac)$_3$(pybzim)]

formula	$C_{27}H_{12}O_6N_3F_{18}Gd$
formula weight	973.72
crystal system	monoclinic
space group	$P2_1/n$
Z value	4
a, Å	14.192 (3)
b, Å	13.220 (4)
c, Å	19.188 (4)
β, deg	108.93 (2)
V, Å^3	3405 (3)
μ(Mo$K\alpha$), mm^{-1}	1.754
$R1^a$	0.0638
w$R2^b$	0.1569
GOF	0.962

a : $R1=\Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$

b : $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

Table 3-2. Selected Bond Distances (Å), Bond Angles (deg) of [Gd(hfac)$_3$(pybzim)].

Bond lengths			
Gd – O(2)	2.430 (7)	Gd – O(3)	2.402 (7)
Gd – O(4)	2.382 (7)	Gd – O(5)	2.338 (7)
Gd – O(6)	2.346 (7)	Gd – O(7)	2.335 (7)
Gd – N(1)	2.474 (8)	Gd – N(3)	2.619 (9)
Bond Angels			
O(2) – Gd – O(3)	70.5 (3)	O(2) – Gd – O(4)	71.3 (2)
O(2) – Gd – O(5)	90.1 (2)	O(2) – Gd – O(6)	144.6 (2)
O(2) – Gd – O(7)	142.6 (2)	O(2) – Gd – N(1)	91.5 (2)
O(2) – Gd – N(3)	80.7 (2)	O(3) – Gd – O(4)	125.7 (3)
O(3) – Gd – O(5)	70.6 (3)	O(3) – Gd – O(6)	135.9 (3)
O(3) – Gd – O(7)	74.8 (3)	O(3) – Gd – N(1)	139.4 (3)
O(3) – Gd – N(3)	76.0 (3)	O(4) – Gd – O(5)	72.4 (2)
O(4) – Gd – O(6)	73.4 (3)	O(4) – Gd – O(7)	143.7 (3)
O(4) – Gd – N(1)	77.8 (3)	O(4) – Gd – N(3)	132.4 (3)
O(5) – Gd – O(6)	81.4 (3)	O(5) – Gd – O(7)	91.2 (2)
O(5) – Gd – N(1)	147.9 (3)	O(5) – Gd – N(3)	146.5 (3)
O(6) – Gd – O(7)	72.3 (2)	O(6) – Gd – N(1)	78.8 (3)
O(6) – Gd – N(3)	123.4 (3)	O(7) – Gd – N(1)	106.4 (3)
O(7) – Gd – N(3)	77.9 (3)	N(1) – Gd – N(3)	65.0 (3)
Torsion Angles			
N(1) – C(1) – C(2) – N(3)	1.6 (14)		

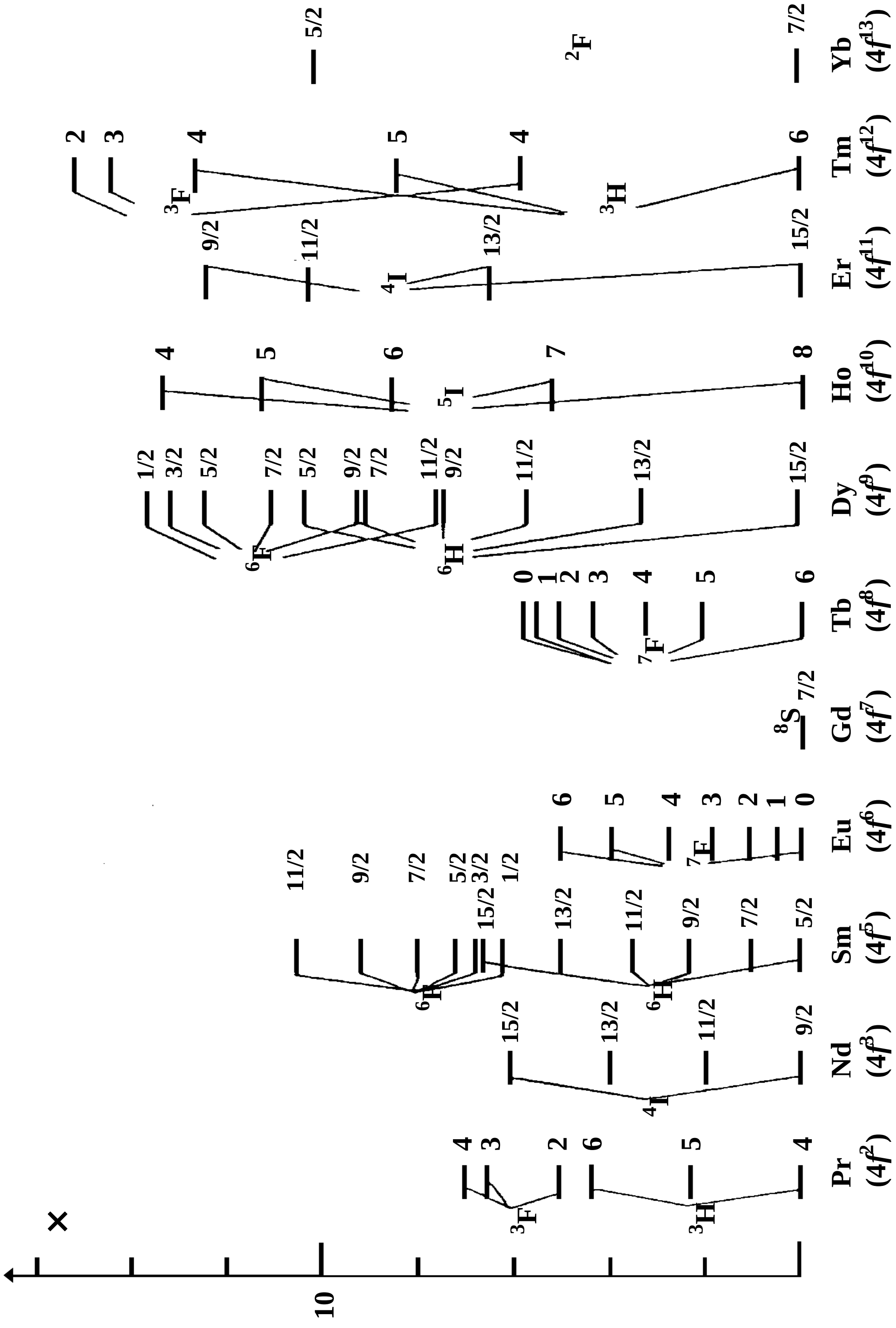


Figure 3-1. Energy levels of trivalent lanthanides in lower range (J indicated at right hand).

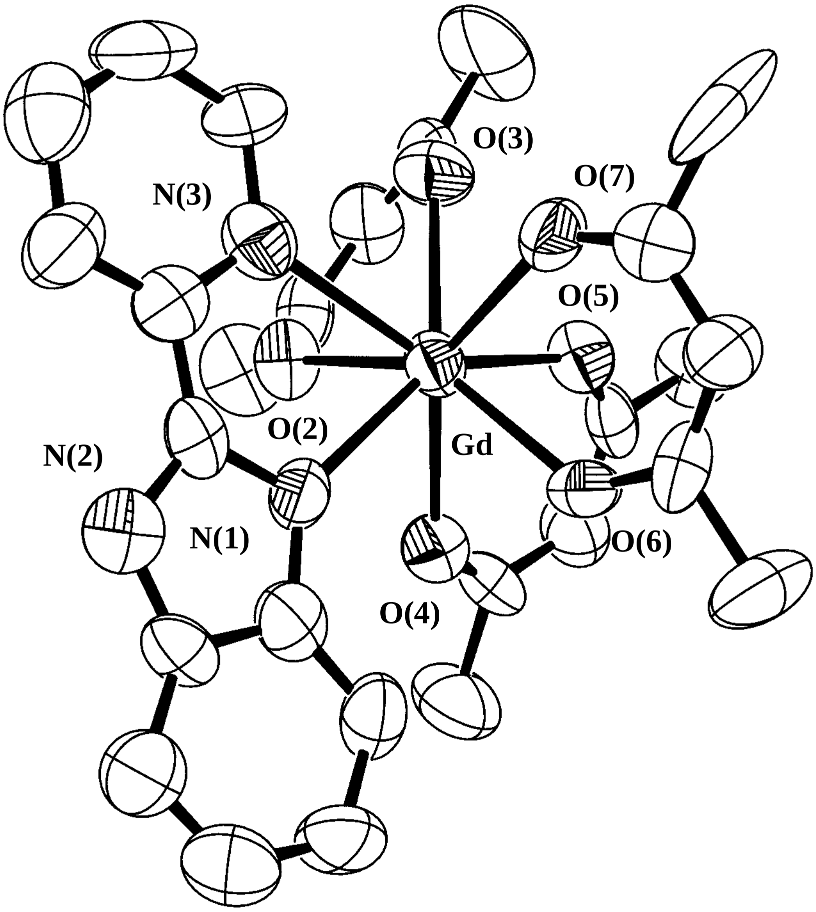


Figure 3-2. Molecular structure of [Gd(hfac)$_3$(IM-2py)] showing 50% probability ellipsoids(F atoms are omitted).

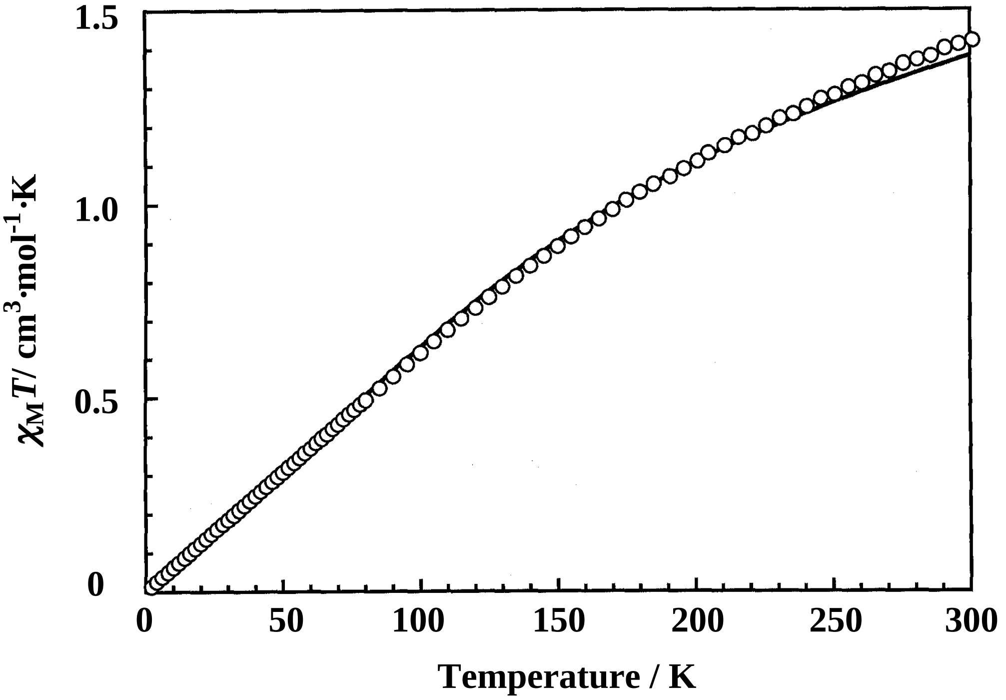


Figure 3-3. Temperature dependence of $\chi_M T$ of [Eu(hfac)$_3$(pybzim)]. The solid line represents the fit to the experimental data with the model described in the text.

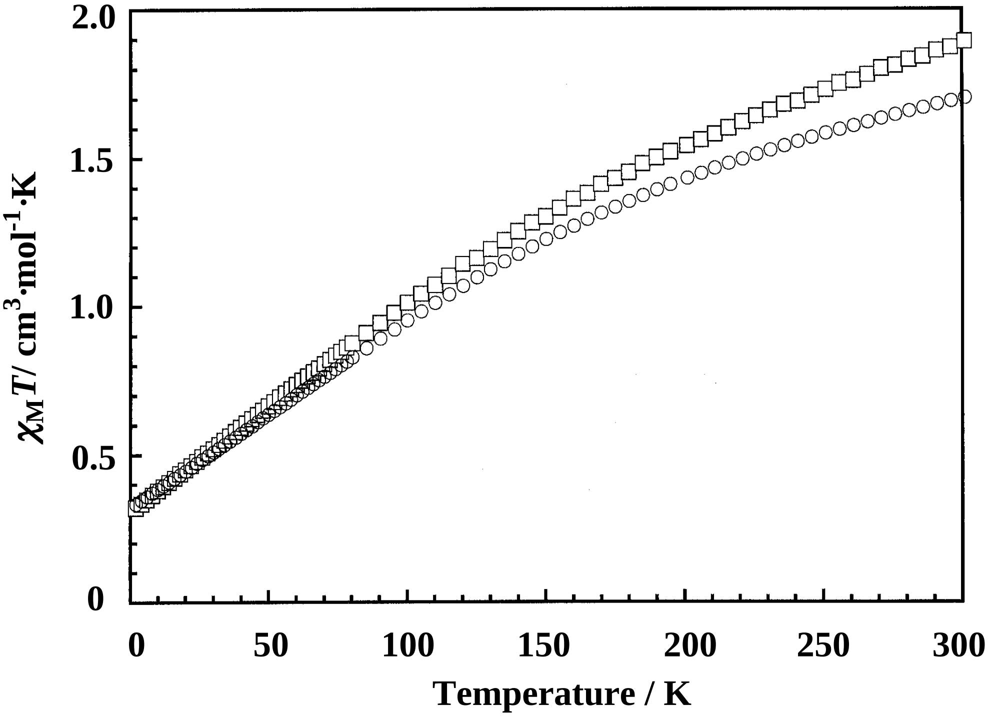


Figure 3-4. Temperature dependence of $\chi_M^{Eu}T$ (IM) (□) and the sum of $\chi_M^{Eu}T$(pybzim) and 0.32 cm^3·mol^{-1}·K (○), which is $\chi_M^{Eu}T$ (IM) at 2 K.

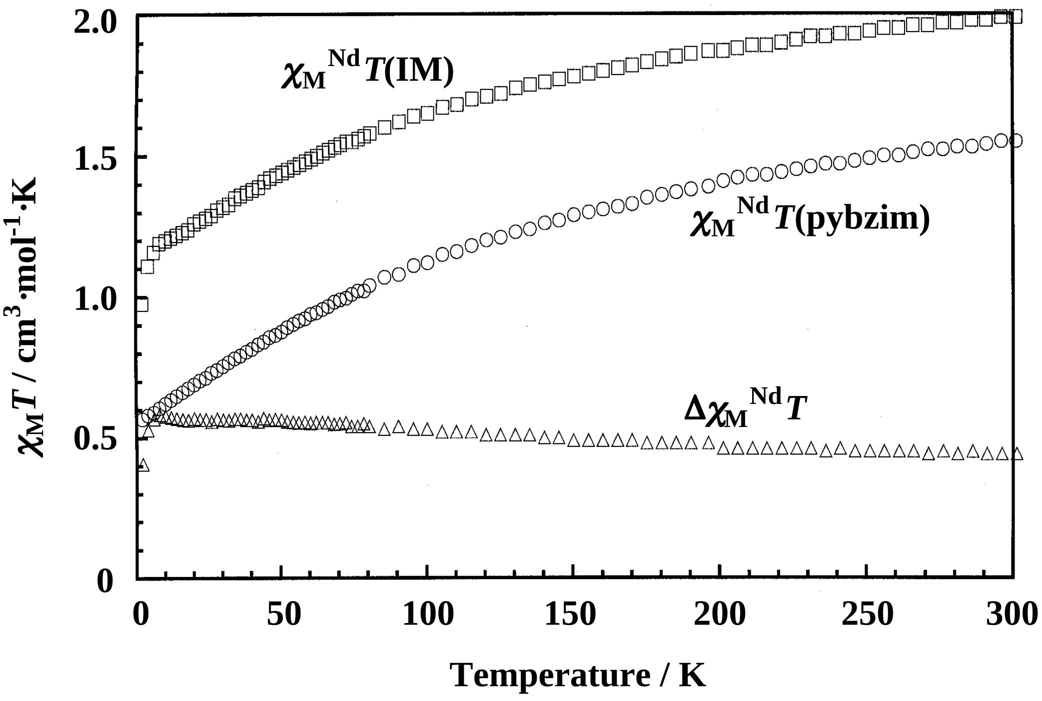


Figure 3-5. Temperature dependence of the $\chi_M{}^{Nd}T$(IM) (□), $\chi_M{}^{Nd}T$(pybzim) (○) and $\Delta\chi_M{}^{Nd}T$ （△） of Nd(III) complexes.

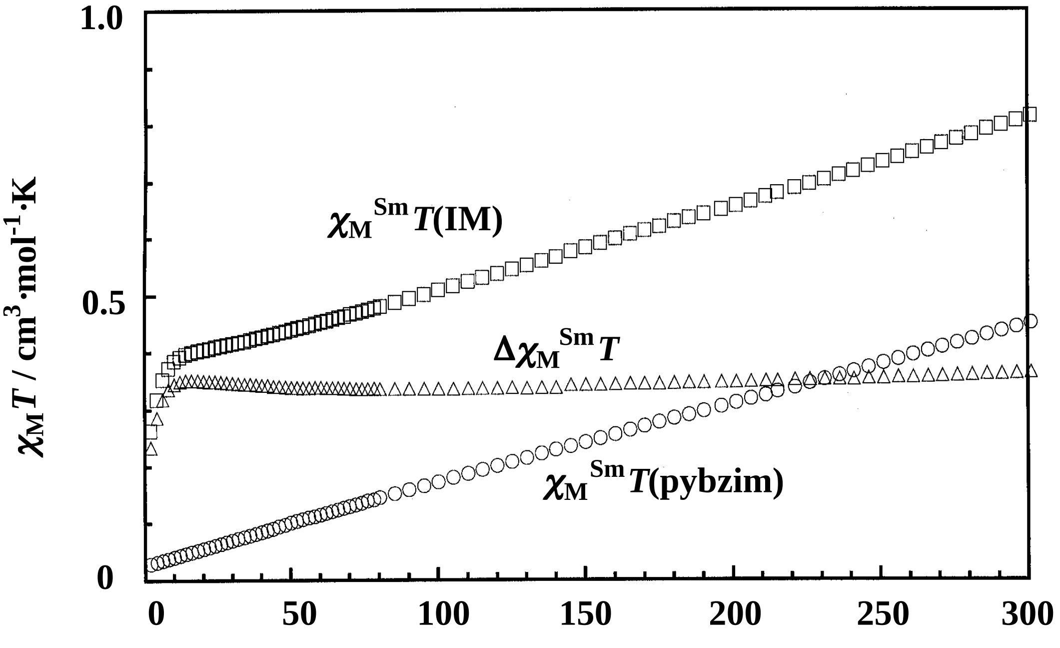


Figure 3-6. Temperature dependence of the $\chi_M{}^{Sm}T$(IM) (□), $\chi_M{}^{Sm}T$(pybzim) (○) and $\Delta\chi_M{}^{Sm}T$ （△） of Sm(III) complexes.

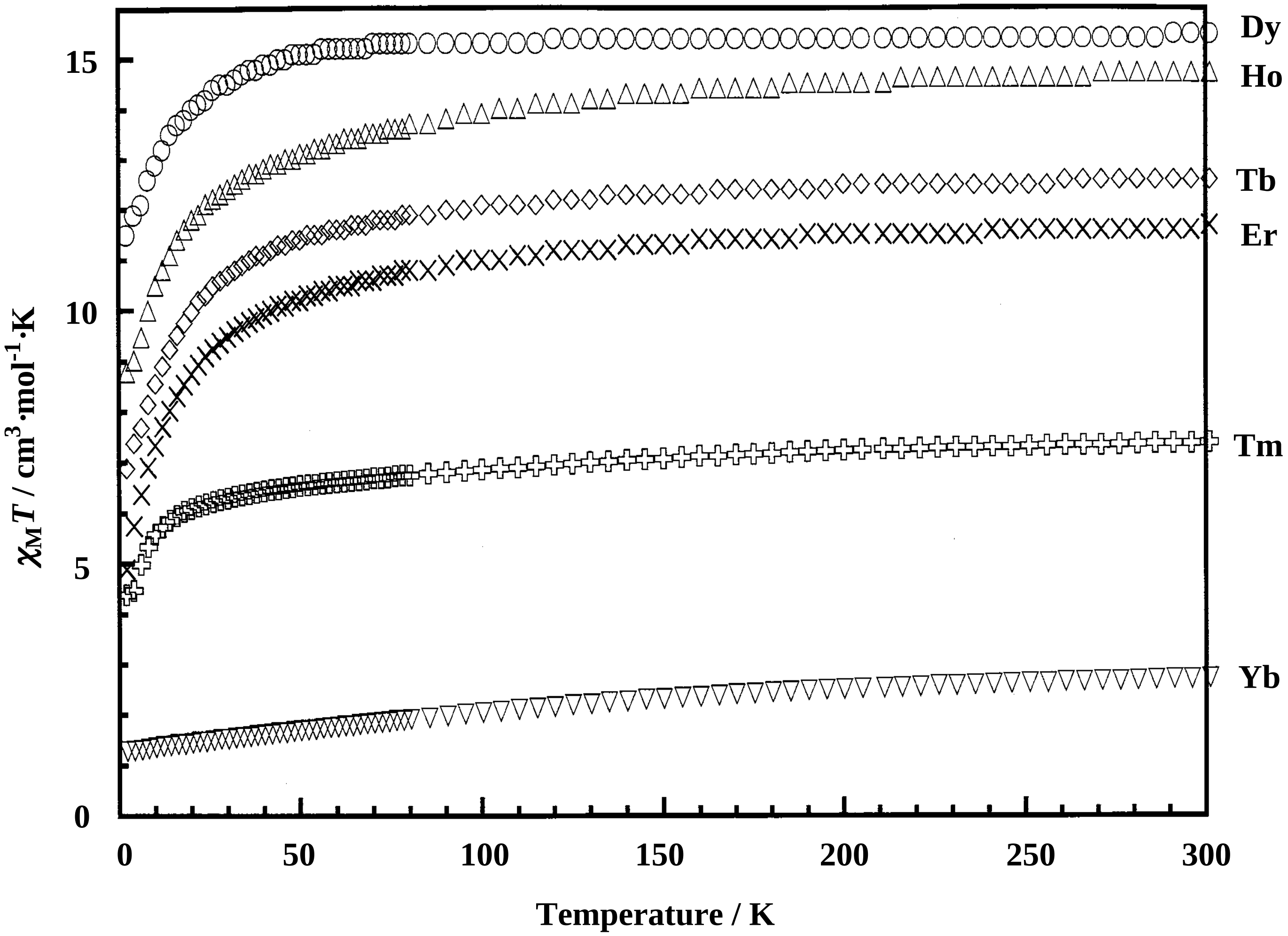


Figure 3-7. The temperature dependence of the experimental $\chi_M T$ values of [Ln(hfac)$_3$(IM-2py)] (Ln=Tb–Yb).

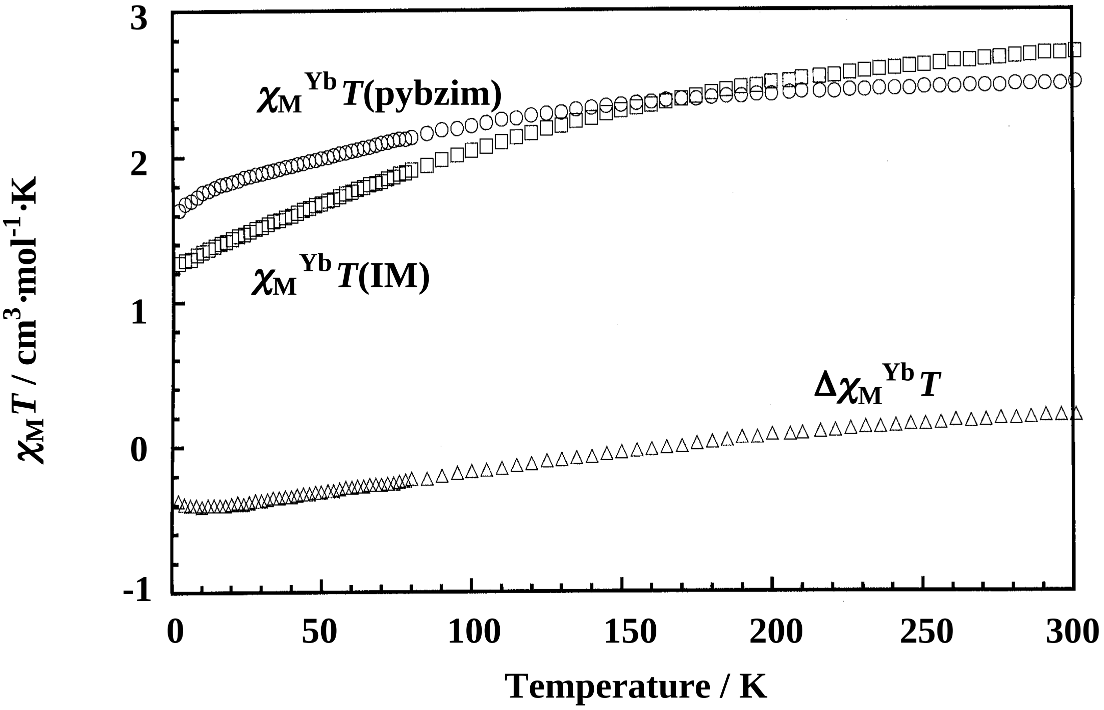


Figure 3-8. Temperature dependence of the $\chi_M^{Yb}T$(IM) (□), $\chi_M^{Yb}T$(pybzim) (○) and $\Delta\chi_M^{Yb}T$ （△） of Yb(III) complexes.

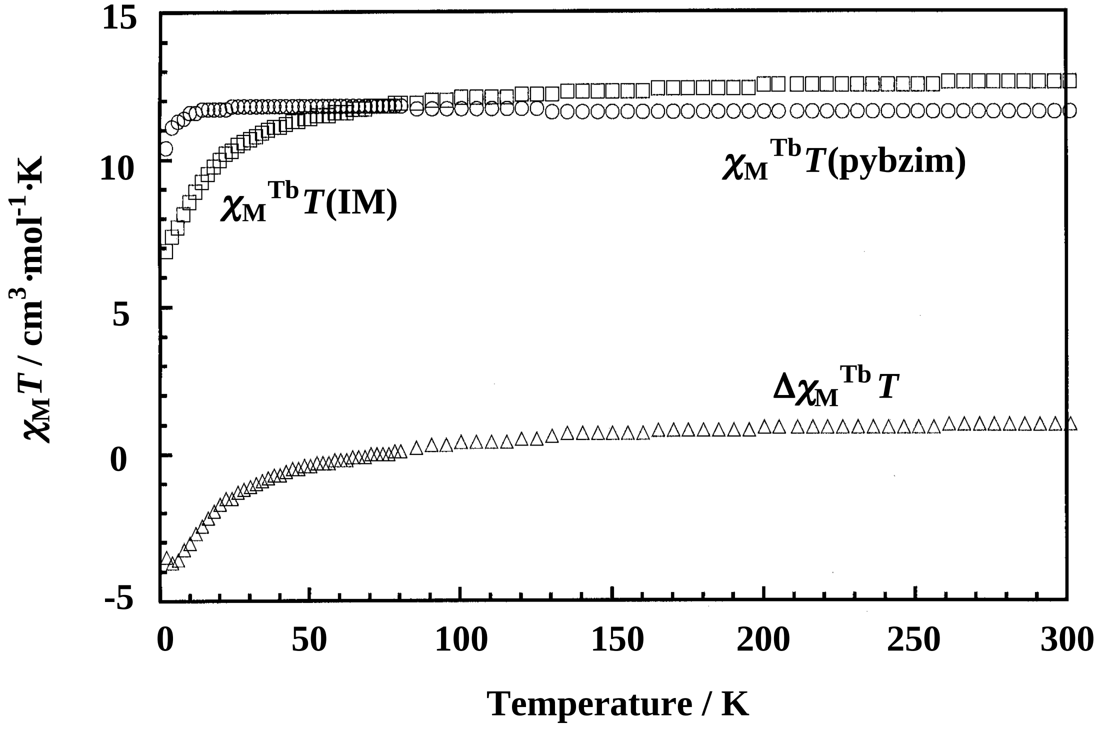


Figure 3-9. Temperature dependence of the $\chi_M^{Tb}T$(IM) (□), $\chi_M^{Tb}T$(pybzim) (○) and $\Delta\chi_M^{Tb}T$ （△） of Tb(III) complexes.

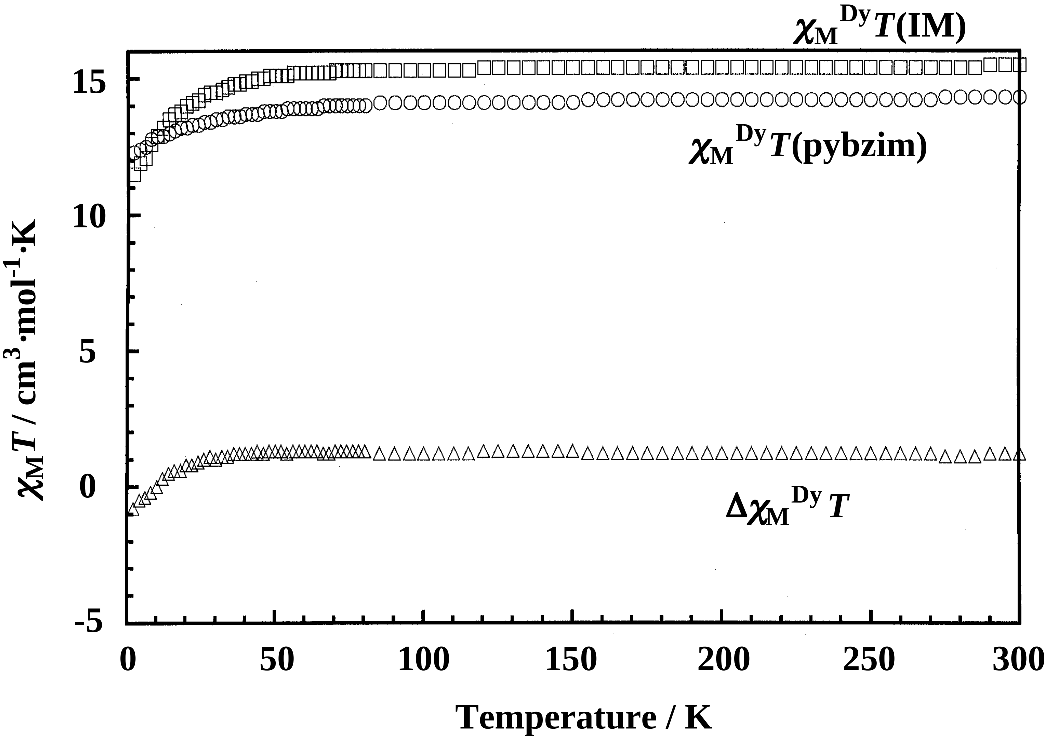


Figure 3-10. Temperature dependence of the $\chi_M^{Dy}T$(IM) (□), $\chi_M^{Dy}T$(pybzim) (○) and $\Delta\chi_M^{Dy}T$ （△） of Dy(III) complexes.

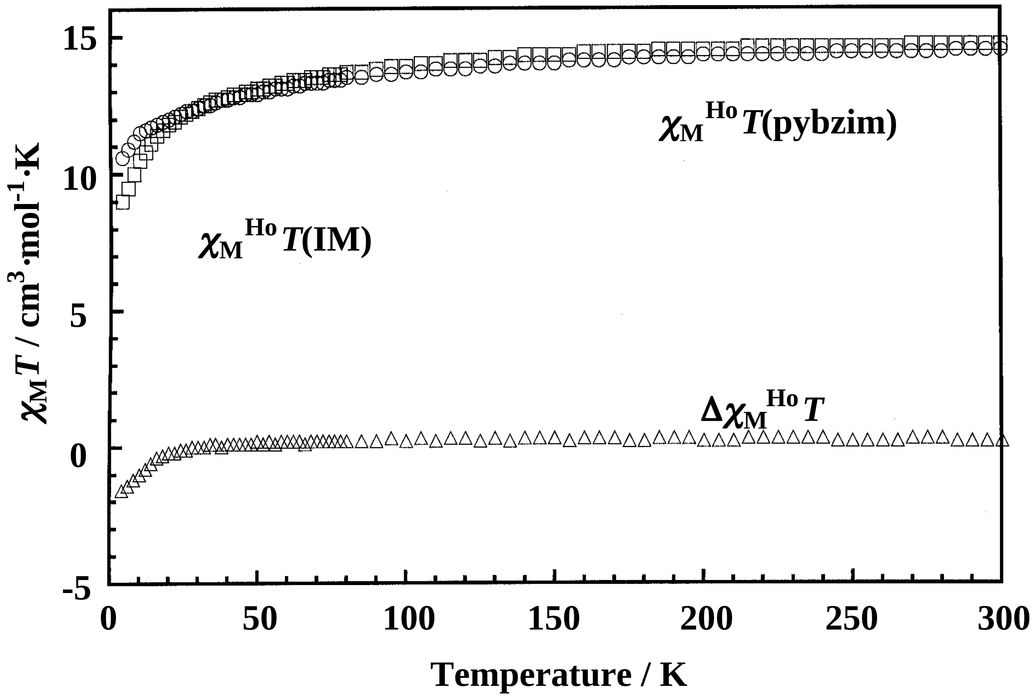


Figure 3-11. Temperature dependence of the $\chi_M^{Ho}T$(IM) (□), $\chi_M^{Ho}T$(pybzim) (○) and $\Delta\chi_M^{Ho}T$ （△） of Ho(III) complexes.

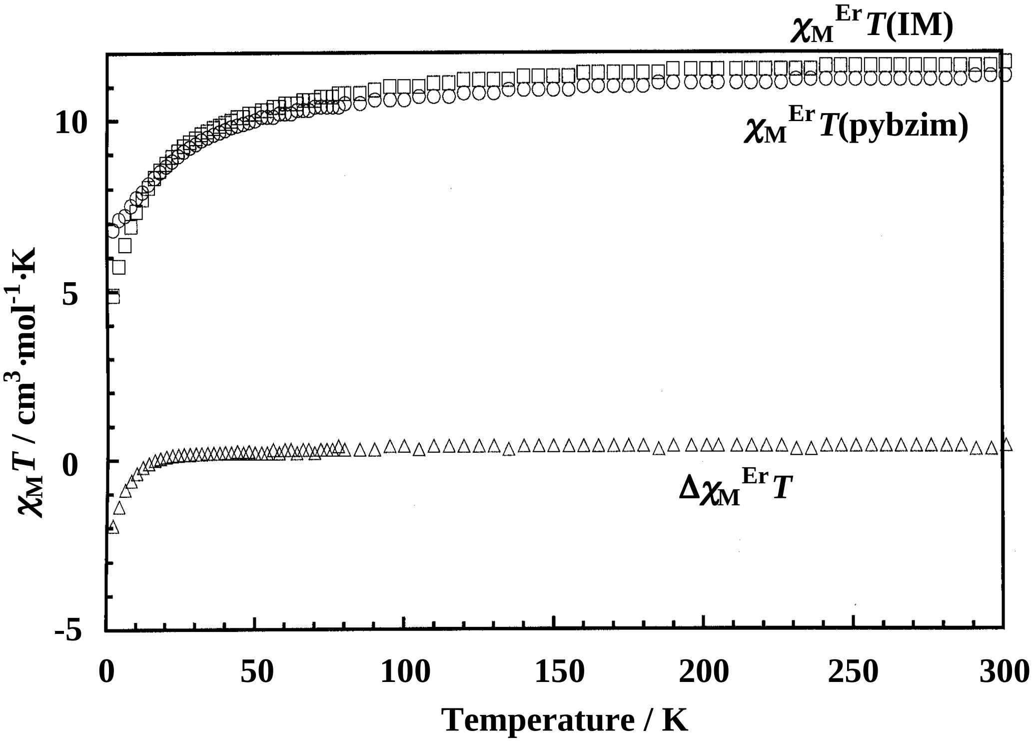


Figure 3-12. Temperature dependence of the $\chi_M{}^{Er}T$(IM) (□), $\chi_M{}^{Er}T$(pybzim) (○) and $\Delta\chi_M{}^{Er}T$（△） of Er(III) complexes.

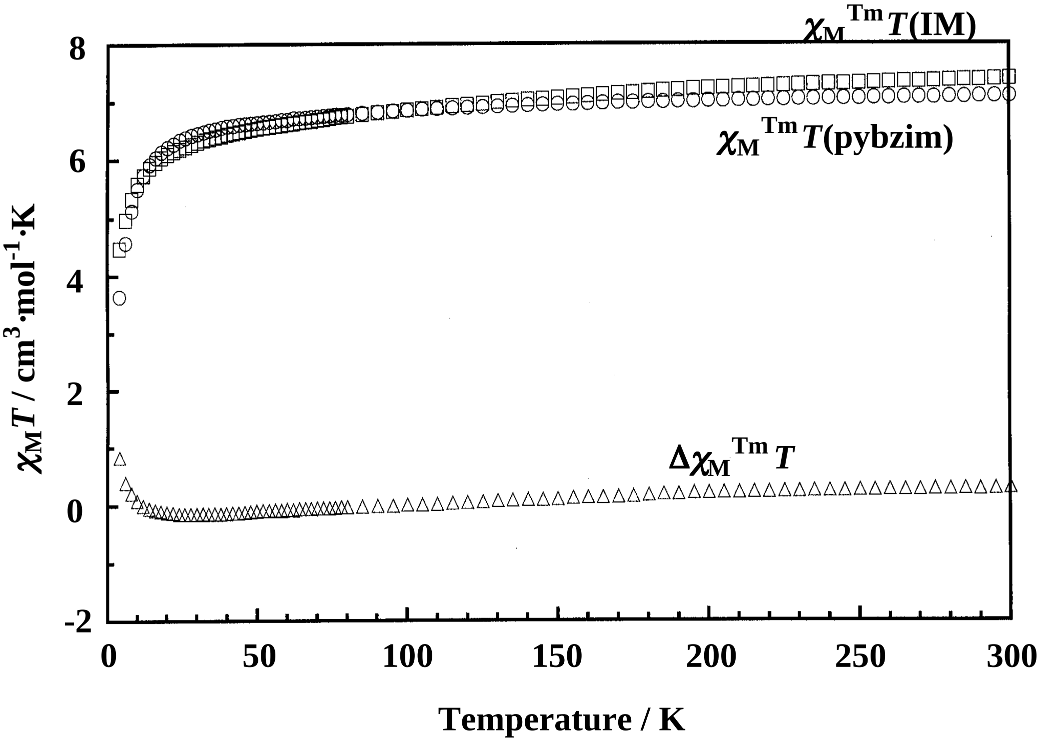


Figure 3-13. Temperature dependence of the $\chi_M{}^{Tm}T$(IM) (□), $\chi_M{}^{Tm}T$(pybzim) (○) and $\Delta\chi_M{}^{Tm}T$（△） of Tm(III) complexes.

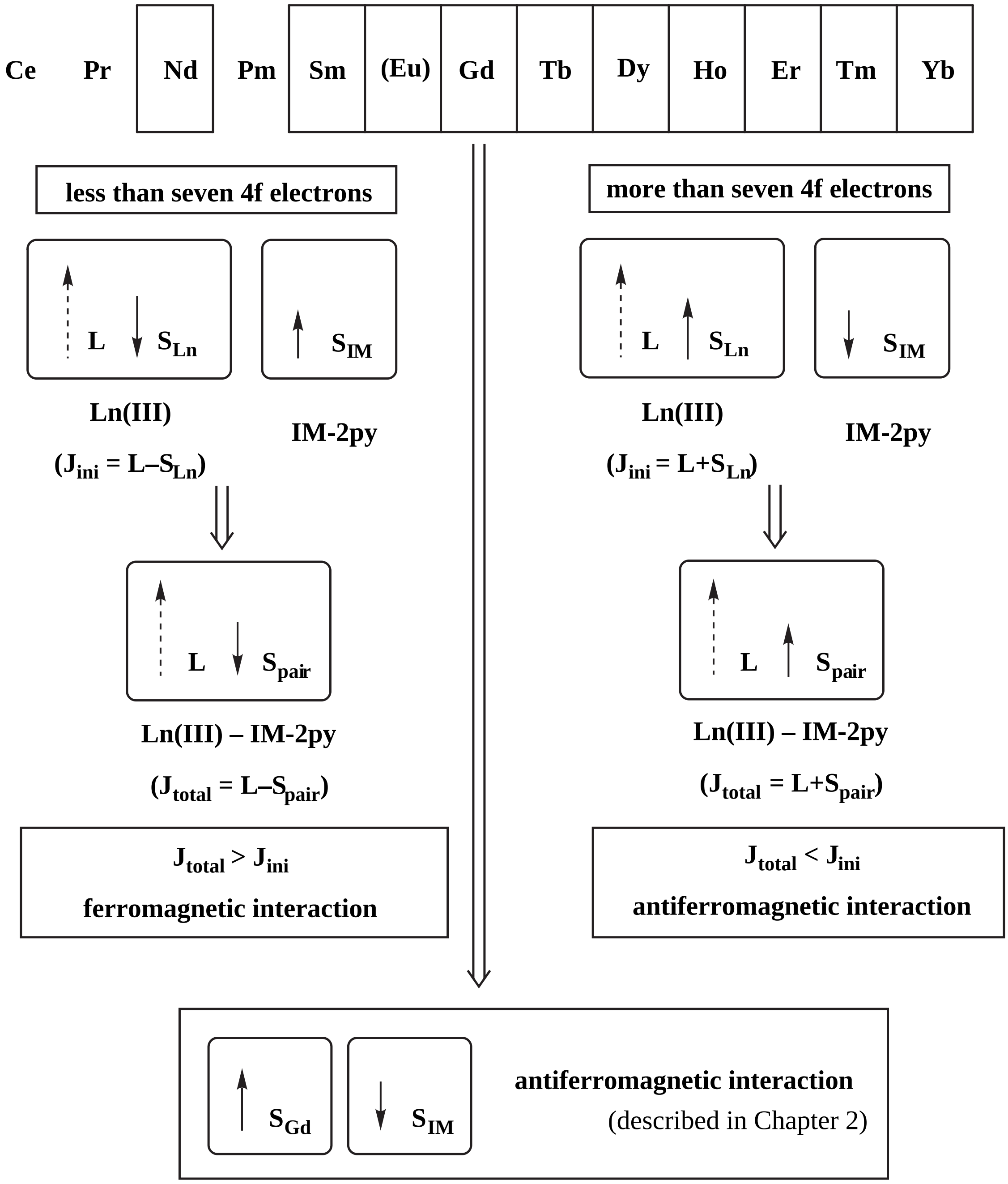


Figure 3-14. Schematic representation of the angular momentum in a Ln(III)–radical pair, where Ln(III) is a trivalent lanthanide ion carrying an orbital momentum.

Chapter 4. Synthesis, Structure and Magnetic Properties of Lanthanide(III) Complexes Containing Methyl-Substituted Pyridyl Imino Nitroxide Radicals

4–1. Introduction

In chapter 2 and 3, the magnetic interaction in the 4f-π* unpaired spin system of [Ln(hfac)$_3$(IM-2py)] has been described. Though the interaction is very weak antiferromagnetic, the extend of the interaction can be regarded as significant and evident. The discussion about the magnetic properties suggests that there must be a little interaction between 4f unpaired spin(s) and radical π* spin.

So far, the magnetic properties of the lanthanide–radical complexes in solid state have been mentioned mainly, except the descripition of the UV-vis spectra in solution in Chapter 1. The spectral change with varying mixing ratio shows that this type of complexes is also stable in solution, *i.e.*, that the spectral study in solution is reasonable. Next another attractive property of these complexes in solution, how the magnetic interaction affects NMR spectral pattern, *i.e.* paramagnetic shift and relaxation time, are going to be discussed.[1]

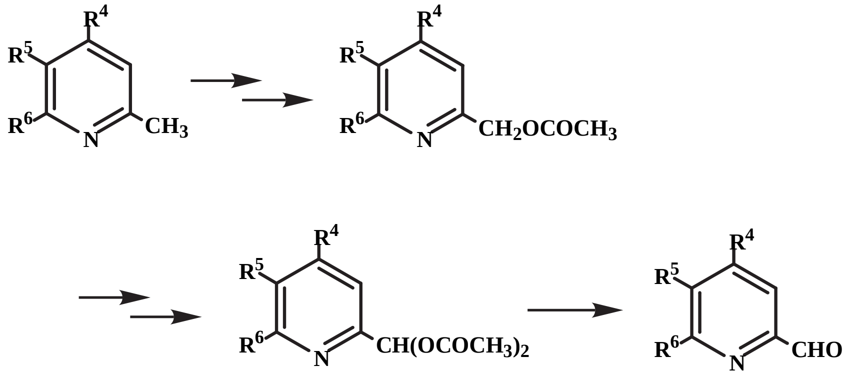
But before the discussion of NMR spectra, the synthesis of the lanthanide(III) complexes containing the *methyl-substituted-pyridyl* imino nitroxide radical is needed. The tendency for the paramagnetic shifts of the complexes containing paramagnetic species is difficult to be understandable, so the signals are not readily assigned.[1,50] In this regard, it should be useful that the complexes containing the substituted radical ligand are prepared and the spectral behavior of the substituted radical complexes compared with that of non-substituted radical complexes. Needless to say, of course, it is essential that the difference between structures of the complex is hardly observed and the physical properties are similar to each other.

In this chapter, the synthesis and properties of the complexes containing methyl-substituted-pyridyl imino nitroxide are described. Though it seems to make a detour, it will be understood in next chapter how the presence of the complexes is helpful to the assignment of the complex NMR spectra.

4–2. Experimental Section

4-2-1. Synthesis of n-methyl-2-pyridinecalbaldehyde(n=4, 5)

The aldehyde was prepared followed by the Wilson’s method (scheme 4-1).



Scheme 4-1. Synthesis of n-methylpyridinecalbaldehyde

(a) 4-methyl-2-acetoxymethylpyridine

To 2,4-lutidine (128.4 g, 1.2 mol) in glacial acetic acid (480 ml) was added 72 ml of H_2O_2 (30%) and the solution heated at 90 ℃ for *ca.* 3 h. Another portion of H_2O_2 (36 ml) was added and the solution was again heated for *ca.* 3 h. The solvents were distilled off under reduced pressure. Water (50 ml) was added to the residue and then the mixture was evaporated again. The residue was neutralized with K_2CO_3 and then extracted with two portions (50 ml) of $CHCl_3$. After drying the solution with K_2CO_3, the solvent was distilled off. The crude 2, 4-lutidine-N-oxide was obtained as yellow oil. The oxide was gradually added in acetic anhydride (300 ml) at 90 ℃ and heated for *ca.* 10 h. After the solvents were removed away under reduced pressure, the residue was fractionally distilled at 84–90 ℃ under reduced pressure (1 mmHg) and then the pale yellow oil was obtained.

(b) 4-methyl-2-pyridinecalbaldehyde

The acetoxymethylpyridine was dealt with the same method as (a), and then the 4-methyl-2-diacetoxymethylpyridine *via* the corresponding N-oxide was obtained. (b.p 160–166 ℃, 1 mmHg). The product was poured into the 10% HCl aq. (100 ml) and heated gently. After the hydrolysis, the solvent was excluded under reduced pressure. The residue was neutralized with K_2CO_3 and extracted with three portions (50 ml) of $CHCl_3$. The $CHCl_3$ solution was dried with Na_2SO_4, and then evaporated. The aldehyde was distilled at 48–55 ℃ under reduced pressure (1 mmHg). Yield 4.8 g (3.3%).

(c) 5-methyl-2-pyridinecalbaldehyde

The crude 5-methyl-2-pyridinecalbaldehyde was obtained with the same method as (a) and (b) from 2, 5-lutidine (25 g, 0.23 mol). The pure aldehyde was obtained by sublimation at 70 ℃ under reduced pressure (1 mmHg). Yield 2.0 g(8.1 %).

4-2-2. Synthesis of 2-(2’-(n-methylpyridyl))-4,4,5,5-tetramethylimidazoline-1-oxyl (n=4 (IM-4Me2py), 5 (IM-5Me2py), 6 (IM-6Me2py))

The products were prepared in replacement of 2-pyridinecalbaldehyde to the corresponding methyl-substituted pyridinecalbaldehyde in the method described in Chapter 1.

4-2-3. Synthesis of [Ln(hfac)$_3$(IM-nMe2py)]

The complexes was prepared by the treatment of the corresponding [Ln(hfac)$_3$(H_2O)$_2$] and IM-nMe2py as described in Chapter 1.

4-2-4. Crystallographic study

Red orange crystals of [Gd(hfac)$_3$(IM-6Me2py)] and [Dy(hfac)$_3$(IM-nMe2py)] (n=4, 5) suitable for X-ray crystal analyses were obtained by slowly evaporating the complex solution in a mixture of dichloromethane and *n*-heptane. Each crystal was mounted on a glass fiber. The measurement was done in the almost similar condition to the complexes described in Chapter 1. The structure could be solved reasonably by using direct method (SIR-92[28] or SHELXS-97[38] program) and refined by a full matrix least squares procedures (SHELXL-97[29]). The positions of hydrogen atoms were fixed at calculated positions and only their isotropic displacement parameters were refined. All calculations were carried out using Crystal Structure Software.[30]

4-2-5. Magnetic Measurement

Temperature dependence of magnetic susceptibility was measured in the same condition described in Chapter 2.

4–3. Results and Discussion

4-3-1. Preparation of [Ln(hfac)$_3$(IM-nMe2py)] (n=4, 5, 6)

In analogy with the IM-2py complexes, a red solution of the corresponding [Ln(hfac)$_3$(IM-nMe2py)] complexes were readily given by the treatment of [Ln(hfac)$_3$(H$_2$O)$_2$] and a small excess of IM-nMe2py in dichloromethane. The satisfactory elemental analyses show that the complexes have the chemical formula consisting of Ln^{3+}, hfac and IM-nMe2py with a 1:3:1 ratio. The coordination number of the complexes containing these ion is expected to be eight, which is similar to [Ln(hfac)$_3$(IM-2py)]. So the similarity of the surroundings makes it possible to compare the structual or magnetic properties. In a similar manner to [Ln(hfac)$_3$(IM-2py)], the products are insoluble in water and dissolve in most organic solvents except aliphatic alkanes, but they readily decomposed in methanol, ethanol, and DMSO.

4-3-2. Structual study of [Gd(hfac)$_3$(IM-6Me2py)]

X-ray suitable crystals of [Gd(hfac)$_3$(IM-6Me2py)] were easily obtained by recrystallization from dichloromethane-*n*-heptane solution. But the crystal system of the complex is triclinic with $P\bar{1}$ space group, in contrast to monoclinic with $P2_1/n$ space group in [Gd(hfac)$_3$(IM-2py)]. The molecular structure of [Gd(hfac)$_3$(IM-6Me2py)] is illustrated in Figure 4-1. Crystallographic data for each complex are listed in Table 4-1. Selected bond lengths and angles are also summarized in Table 4-2.

The bond length of N(2)-O(1) (1.260(7) Å) in the complex indicates the existence of a radical unpaired spin on complexation. The Gd atom of [Gd(hfac)$_3$(IM-6Me2py)] is also eight-coordinated with three didentate hfac ligands and one didentate IM-6Me2py ligand, which is similar to IM-2py complex. The torsion angle of N(1)–C(1)–N(2)–O(1) is 3.4 (7) ° suggesting that the plane (N(1), C(1), N(2), O(1)) is nearly planar. The torsion angle of N(1)–C(1)–C(2)–N(3) is 0.4(8)°, the plane (N(1), C(1), C(2), O(1)) being also nearly planar and SOMO(π^*) orbital expanding to ligated N(3) atom. The Gd-O(hfac) bond lengths can be classified into two groups. In the first group, the Gd-O bond lengths range from 2.324(4)Å to 2.349(4)Å (Gd-O(3), Gd-O(4) and Gd-O(7)). In the second group, they range from 2.377(4)Å to 2.418(4)Å (Gd-O(2), Gd-O(5) and Gd-O(6)), which are fairly longer than those in the first group. The bond lengths concerning Gd–IM radical are considerably different from IM-2py complex. The bond length of the Gd-N(3) (pyridine-N) is 2.622(5)Å, which is longer by 0.07 Å than the Gd-N(py) bond length for the [Gd(hfac)$_3$(IM-2py)]. It is suggested that the steric repulsion between the methyl group and the other surroundings is considerably large. The Gd-N(1) (imidazole-N) bond length is 2.512(4)Å, which becomes shorter than that of [Gd(hfac)$_3$(IM-2py)].

As described in Chapter 2, the N_2O_6 eight coordinate geometry[32] was examined by using the semiquantitative method of polytopal analysis. The δ and ϕ values are summarized in Table 4. In [Gd(hfac)$_3$(IM-6Me2py)] complex, the δ_1 and δ_2 values showing planarity of the squares are 36.81° and 28.64° respectively, both of which is relatively large. The δ_3 and δ_4 values showing distortion between the squares are 27.50° and 21.84° respectively, which are close to the δ_1 and δ_2 values. In addition, ϕ_1 and ϕ_2

values are 2.78° and 1.91°, respectively, which are close to 0°. Therefore, it is no doubt that the most reasonable geometry around the Gd atom of [Gd(hfac)$_3$(IM-6Me2py)] is dodecahedron (DD).

4-3-3. Structual study of [Dy(hfac)$_3$(IM-4Me2py)] and [Dy(hfac)$_3$(IM-5Me2py)]

Instead of the IM-4Me2py and IM-5Me2py Gd(III) complexes of which suitable crystals for X-ray analysis were not obtained so far, the X-ray structures of the corresponding Dy(III) complexes of which the structures are similar to the Gd(III) complex have been determined. This isostructuality was confirmed by powder X-ray diffraction (Figure 4-2). The crystal system of the both complexes is monoclinic with P2$_1$/n space group, which is similar to [Gd(hfac)$_3$(IM-2py)]. The molecular structure of [Dy(hfac)$_3$(IM-5Me2py)] and [Dy(hfac)$_3$(IM-4Me2py)] is illustrated in Figure 4-3 and 4-4, respectively. Crystallographic data for each complex are listed in Table 4-1. Selected bond lengths and angles are also summarized in Table 4-3 and Table 4-4.

The bond length of N(2)-O(1) (1.28 Å) in the complex indicates the existence of a radical unpaired spin on complexation. The Dy atom of [Dy(hfac)$_3$(IM-5Me2py)] and [Dy(hfac)$_3$(IM-5Me2py)] is also eight-coordinated with three didentate hfac ligands and one didentate imino nitroxide ligand. The torsion angle of N(1)–C(1)–N(2)–O(1) is 4.0 (6)° for [Dy(hfac)$_3$(IM-5Me2py)] and 3.0 (11)° for [Dy(hfac)$_3$(IM-4Me2py)], respectively. Both of the angles suggest that the plane (N(1), C(1), N(2), O(1)) is nearly planar. The torsion angle of N(1)–C(1)–C(2)–N(3) is *ca.* 3.0°, the plane (N(1), C(1), C(2), O(1)) being also nearly planar and SOMO(π*) orbital expanding to ligated N(3) atom. The bond lengths of the Dy-N(IM) (2.535(8) Å for the[Dy(hfac)$_3$(IM-4Me2py)] and 2.521(4) Å for [Dy(hfac)$_3$(IM-5Me2py)]) are close to those of the corresponding IM-2py complex (2.521(5) Å for [Dy(hfac)$_3$(IM-2py)]). The Gd-O(hfac) bond lengths also can be classified into two groups. For [Dy(hfac)$_3$(IM-4Me2py)], the Gd-O bond lengths range from 2.300(8)Å to 2.319(7)Å (Gd-O(2), Gd-O(6) and Gd-O(7)) in the first group, and from 2.341(8)Å to 2.366(8)Å (Gd-O(3), Gd-O(4) and Gd-O(5)) in the second group which are fairly longer than those in the first group. For [Dy(hfac)$_3$(IM-5Me2py)], the Gd-O bond lengths range from 2.312(4)Å to 2.320(4)Å (Gd-O(2), Gd-O(5) and Gd-O(6)) in the first group, and from 2.350(4)Å to 2.365(4)Å (Gd-O(3), Gd-O(4) and Gd-O(7)) in the second group which are fairly longer than those in the first group.

The δ and ϕ values obtained for using the semiquantitative method of polytopal analysis[32] are summarized in Table 4-5. Whereas the δ_1 values are 14.45° for [Dy(hfac)$_3$(IM-4Me2py)] and 10.57° for [Dy(hfac)$_3$(IM-5Me2py)], the δ_2 values are 0.67° for [Dy(hfac)$_3$(IM-4Me2py)] and 0.02° for [Dy(hfac)$_3$(IM-5Me2py)], both of which are almost 0°. Only these angles suggests that the reasonable geometry of these complexes is TPRS-8. But the ϕ_1 and ϕ_2 values of [Dy(hfac)$_3$(IM-4Me2py)] are 24.53° and 19.63°, respectively. The values of [Dy(hfac)$_3$(IM-5Me2py)] are 25.08° and 18.59°, respectively. Compared with the ϕ_1 and ϕ_2 values of theoretical TPRS-8 polyhedron, these experimental values are too large to claim that TPRS-8 is reasonable geometry of these complexes. It should rather be noted that the δ_1 values of these complexes are relatively smaller than the theoretical one, being considered the reasonable geometry is SAPR-8.

The methyl proton of the 4- or 5-methyl in the pyridyl group is close to the fluorine atom of the CF$_3$ in the neighboring molecule. Since the lengths of H····F (2.94 Å for [Dy(hfac)$_3$(IM-5Me2py) and 3.02 Å for [Dy(hfac)$_3$(IM-4Me2py)]) are longer than the sum of the van der Waals radii of hydrogen and fluorine(2.69 Å), there is no or little hydrogen bond between the molecules.[51] However, It is likely that the variation of the substituted pyridine makes it possible to form hydrogen bonded 1-D chain.

In summary, there is significant structural change from the IM-2py complex to [Gd(hfac)$_3$(IM-6Me2py)] probably due to the steric repulsion between the methyl group in IM-6Me2py and [Ln(hfac)$_3$] moiety, while the IM-2py, IM-4Me2py, IM-5Me2py complexes show a similar molecular structure with little difference in intermolecular interaction.

4-3-4. Magnetic Property of [Ln(hfac)$_3$(IM-nMe2py)] (n=4, 5, 6)

There is found to be some influence to the magnetic properties from the substituted group. The temperature dependence of the magnetic susceptibility in [Gd(hfac)$_3$(IM-6Me2py)], [Gd(hfac)$_3$(IM-5Me2py)] and [Gd(hfac)$_3$(IM-4Me2py)] are shown in Figure 4-5. As treated in Chapter 2, these are analyzed in terms of the Van Vleck equation based on the Heisenberg dimer model ($\boldsymbol{H}$=-2$J\boldsymbol{S}_1$·$\boldsymbol{S}_2$).[23,37] The results also indicate that the magnetic interaction between Gd(III) and IM-type radical in all of these complexes are antiferromagnetic. The estimated exchange coupling constants in the IM-nMe2py complex (J=-4.0 cm^{-1} for [Gd(hfac)$_3$(IM-6Me2py)], J=-3.8 cm^{-1} for [Gd(hfac)$_3$(IM-5Me2py)] and [Gd(hfac)$_3$(IM-4Me2py)]) are larger than that of the IM-2py complexes (J=-3.0 cm^{-1}), showing a small substitution effect on the magnetic interaction. It should be emphasized that the interaction between the Gd(III) and the imino nitroxide radical are antiferromagnetic in contrast to the ferromagnetic interaction between the Gd(III) and the other unpaired spin center *e.g.* nitronyl nitroxide.[23] In chapter 2, It have been claimed that the antiferromagnetic interaction are derived from the relatively large overlap between 4f and π* orbitals, *i.e.*, from relatively large donor character of radical ligand. Since the methyl group is generally electron-releasing, it is presumed that the antiferromagnetic interaction in the case of methyl-substituted ligand is larger than that of non-substituted ligand. But the increase of the donor character should involve the shortening of the bond length between metal and donor atom. Actually, the Gd–N(1) bond length of [Gd(hfac)$_3$(IM-6Me2py)] is shorter by *ca.* 0.04 Å than that of [Gd(hfac)$_3$(IM-2py)]. But the Dy–N(1) length of [Dy(hfac)$_3$(IM-5Me2py)] is similar to [Dy(hfac)$_3$(IM-2py)] and the length of [Dy(hfac)$_3$(IM-4Me2py)] is rather longer than that of the IM-2py. It is expected that the comparison of the bond lengths in Gd(III) complexes gave the same result. Therefore, it can not be assumed that the increase of antiferromagnetic interaction is caused by the donor character from only this behavior.

Table 4-1. Crystallographic data of [Ln(hfac)$_3$(IM-nMe2py)]

	Gd–IM-6Me2py	Dy–IM-5Me2py	Dy–IM-4Me2py
Formula	$C_{28}H_{21}N_3O_7F_{18}Gd$	$C_{28}H_{21}N_3O_7F_{18}Dy$	$C_{28}H_{21}N_3O_7F_{18}Dy$
M	1010.71	1015.96	1015.96
Crystal System	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$(#2)	$P2_1$/n (#14)	$P2_1$/n (#14)
Z value	2	4	4
a / Å	12.201 (3)	14.556 (3)	14.508 (2)
b / Å	16.482(3)	23.826 (5)	23.301 (4)
c / Å	11.960 (3)	11.003 (2)	11.588 (2)
α / °	93.67(2)		
β / °	118.93 (1)	96.38 (2)	93.37 (1)
γ / °	83.35 (2)		
V / Å^3	2090.8 (7)	3792 (1)	3907.8 (9)
μ (Mo$K\alpha$)/mm^{-1}	1.711	2.107	2.045
$R1$	0.0493	0.0465	0.0784
w$R2$	0.1750	0.1581	0.2926
GOF	1.077	1.008	0.970

Table 4-2. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) of [Gd(hfac)$_3$(IM-6Me2py)].

Bond lengths			
Gd – O(2)	2.418 (4)	O(2) – C(15)	1.233 (8)
Gd – O(3)	2.342 (4)	O(3) – C(17)	1.232 (7)
Gd – O(4)	2.324 (4)	O(4) – C(20)	1.259 (7)
Gd – O(5)	2.400 (4)	O(5) – C(22)	1.242 (7)
Gd – O(6)	2.377 (4)	O(6) – C(25)	1.243 (7)
Gd – O(7)	2.349 (4)	O(7) – C(27)	1.242 (7)
Gd – N(1)	2.512 (4)	N(2) – O(1)	1.260 (7)
Gd – N(3)	2.622 (5)	N(1) – C(1)	1.307 (7)
Bond Angels			
O(2) – Gd – O(3)	70.82 (15)	O(2) – Gd – O(4)	72.97 (16)
O(2) – Gd – O(5)	130.64 (15)	O(2) – Gd – O(6)	148.48 (15)
O(2) – Gd – O(7)	131.05 (16)	O(2) – Gd – N(1)	76.67 (15)
O(2) – Gd – N(3)	70.98 (15)	O(3) – Gd – O(4)	84.94 (16)
O(3) – Gd – O(5)	73.17 (16)	O(3) – Gd – O(6)	140.26 (15)
O(3) – Gd – O(7)	81.72 (15)	O(3) – Gd – N(1)	147.49 (16)
O(3) – Gd – N(3)	102.50 (2)	O(4) – Gd – O(5)	71.27 (15)
O(4) – Gd – O(6)	100.10 (17)	O(4) – Gd – O(7)	144.87 (15)
O(4) – Gd – N(1)	86.35 (15)	O(4) – Gd – N(3)	133.08 (14)
O(5) – Gd – O(6)	71.42 (16)	O(5) – Gd – O(7)	73.78 (15)
O(5) – Gd – N(1)	132.50 (16)	O(5) – Gd – N(3)	150.55 (15)
O(6) – Gd – O(7)	71.64 (15)	O(6) – Gd – N(1)	72.16 (15)
O(6) – Gd – N(3)	99.49 (15)	O(7) – Gd – N(1)	120.92 (15)
O(7) – Gd – N(3)	76.77 (15)	N(1) – Gd – N(3)	65.19 (15)
Torsion Angles			
N(1) – C(1) – C(2) – N(3)	0.4 (8)		
N(1) – C(1) – N(2) – O(1)	3.4 (7)		

Table 4-3. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) of [Dy(hfac)$_3$(IM-5Me2py)].

Bond lengths			
Dy – O(2)	2.315 (4)	O(2) – C(15)	1.256 (8)
Dy – O(3)	2.365 (4)	O(3) – C(17)	1.236 (7)
Dy – O(4)	2.350 (4)	O(4) – C(20)	1.255 (9)
Dy – O(5)	2.320 (4)	O(5) – C(22)	1.254 (8)
Dy – O(6)	2.312 (4)	O(6) – C(25)	1.254 (7)
Dy – O(7)	2.362 (4)	O(7) – C(27)	1.229 (6)
Dy – N(1)	2.521 (4)	N(2) – O(1)	1.284 (6)
Dy – N(3)	2.516 (4)	N(1) – C(1)	1.284 (6)
Bond Angels			
O(2) – Dy – O(3)	72.06 (15)	O(2) – Dy – O(4)	73.55 (18)
O(2) – Dy – O(5)	106.21 (16)	O(2) – Dy – O(6)	84.55 (15)
O(2) – Dy – O(7)	144.33 (15)	O(2) – Dy – N(1)	87.69 (16)
O(2) – Dy – N(3)	142.37 (16)	O(3) – Dy – O(4)	118.59 (16)
O(3) – Dy – O(5)	71.05 (15)	O(3) – Dy – O(6)	145.43 (14)
O(3) – Dy – O(7)	139.42 (13)	O(3) – Dy – N(1)	77.97 (14)
O(3) – Dy – N(3)	76.98 (14)	O(4) – Dy – O(5)	71.97 (16)
O(4) – Dy – O(6)	76.48 (15)	O(4) – Dy – O(7)	74.81 (16)
O(4) – Dy – N(1)	147.86 (15)	O(4) – Dy – N(3)	142.04 (17)
O(5) – Dy – O(6)	141.73 (14)	O(5) – Dy – O(7)	78.82 (14)
O(5) – Dy – N(1)	139.54 (14)	O(5) – Dy – N(3)	82.80 (15)
O(6) – Dy – O(7)	72.39 (13)	O(6) – Dy – N(1)	75.95 (13)
O(6) – Dy – N(3)	111.18 (14)	O(7) – Dy – N(1)	111.65 (14)
O(7) – Dy – N(3)	72.77 (14)	N(1) – Dy – N(3)	65.06 (14)
Torsion Angles			
N(1) – C(1) – C(2) – N(3)	2.9 (7)		
N(1) – C(1) – N(2) – O(1)	4.1 (6)		

Table 4-4. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) of [Dy(hfac)$_3$(IM-4Me2py)].

Bond lengths			
Dy – O(2)	2.314 (8)	O(2) – C(15)	1.53 (11)
Dy – O(3)	2.366 (8)	O(3) – C(17)	1.25 (5)
Dy – O(4)	2.356 (9)	O(4) – C(20)	1.14 (4)
Dy – O(5)	2.341 (8)	O(5) – C(22)	1.25 (4)
Dy – O(6)	2.300 (8)	O(6) – C(25)	1.261 (15)
Dy – O(7)	2.319 (7)	O(7) – C(27)	1.282 (14)
Dy – N(1)	2.535 (8)	N(2) – O(1)	1.283 (11)
Dy – N(3)	2.524 (8)	N(1) – C(1)	1.257 (11)
Bond Angels			
O(2) – Dy – O(3)	74.4 (3)	O(2) – Dy – O(4)	72.2 (4)
O(2) – Dy – O(5)	105.1 (4)	O(2) – Dy – O(6)	83.4 (3)
O(2) – Dy – O(7)	143.8 (4)	O(2) – Dy – N(1)	88.7 (4)
O(2) – Dy – N(3)	143.7 (4)	O(3) – Dy – O(4)	121.5 (3)
O(3) – Dy – O(5)	71.7 (3)	O(3) – Dy – O(6)	143.6 (3)
O(3) – Dy – O(7)	138.9 (3)	O(3) – Dy – N(1)	73.1 (3)
O(3) – Dy – N(3)	74.2 (3)	O(4) – Dy – O(5)	72.6 (3)
O(4) – Dy – O(6)	76.5 (4)	O(4) – Dy – O(7)	75.9 (3)
O(4) – Dy – N(1)	149.6 (3)	O(4) – Dy – N(3)	141.6 (4)
O(5) – Dy – O(6)	143.2 (3)	O(5) – Dy – O(7)	80.7 (3)
O(5) – Dy – N(1)	136.7 (3)	O(5) – Dy – N(3)	81.7 (3)
O(6) – Dy – O(7)	72.8 (3)	O(6) – Dy – N(1)	78.0 (3)
O(6) – Dy – N(3)	112.7 (3)	O(7) – Dy – N(1)	111.7 (3)
O(7) – Dy – N(3)	72.1 (3)	N(1) – Dy – N(3)	65.0 (3)
Torsion Angles			
N(1) – C(1) – C(2) – N(3)	3.1 (14)		
N(1) – C(1) – N(2) – O(1)	3.0 (11)		

Table 4-6. δ values and ϕ values of [Ln(hfac)$_3$(IM-nMe2py)]

	TPRS-8	SAPR-8	[Dy–IM-4Me2py]	[Dy–IM-5Me2py]	[Gd–IM-6Me2py)]	DD-8
δ_1	21.8	0.0	14.45	10.57	36.81	29.5
δ_2	0.0	0.0	0.67	0.02	28.64	29.5
δ_3	48.2	52.4	49.92	48.72	27.50	29.5
δ_4	48.2	52.4	50.11	52.87	21.84	29.5
ϕ_1	14.1	24.5	24.53	25.08	2.78	0.0
ϕ_2	14.1	24.5	19.63	18.59	1.91	0.0

The sets of the planes to calculate δ and ϕ values is as follows;

δ_1 : O(2) [O(3) O(4)] O(5)^a	δ_1 : O(4) [O(5) O(2)] O(3)^a
δ_2 : N(3) [N(1) O(7)] O(6)^a	δ_2 : O(7) [O(6) N(3)] N(1)^a
δ_3 : N(3) [O(3) O(7)] O(5)^a	δ_3 : O(7) [O(5) N(3)] O(3)^a
δ_4 : O(2) [N(1) O(4)] O(6)^a	δ_4 : O(4) [O(6) O(2)] N(1)^a
ϕ_1 : O(2) – N(3) – O(4) – O(7)^b	ϕ_1 : O(4) – O(7) – O(2) – N(3)^b
ϕ_2 : O(5) – N(6) – O(3) – N(1)^b	ϕ_2 : O(3) – N(1) – O(5) – O(6)^b

a : A [B C] D is dihedral angle between ABC plane and BCD plane.

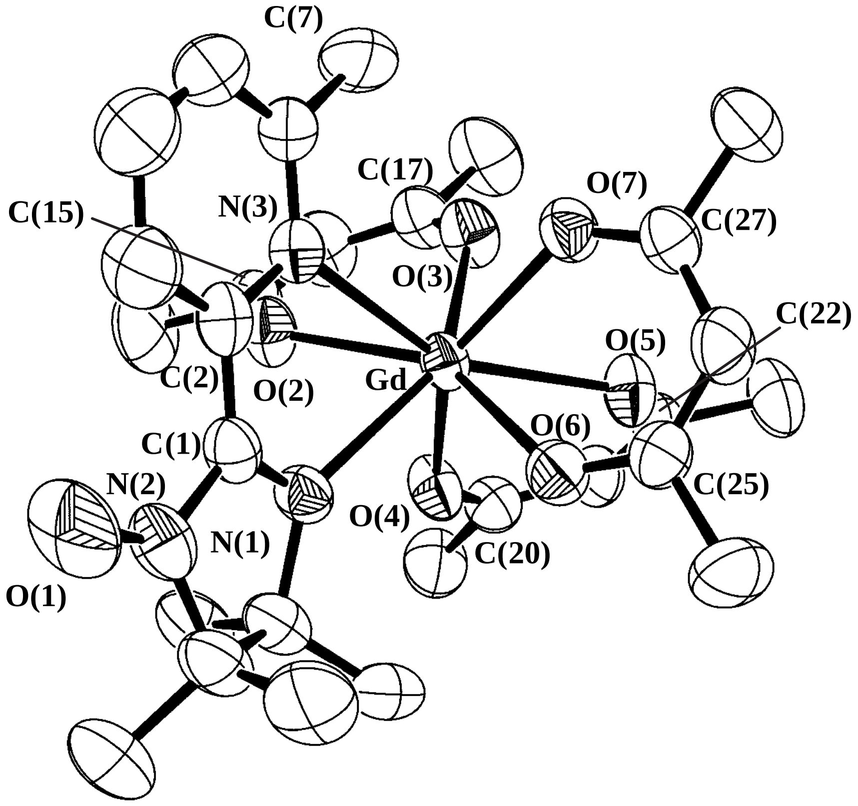
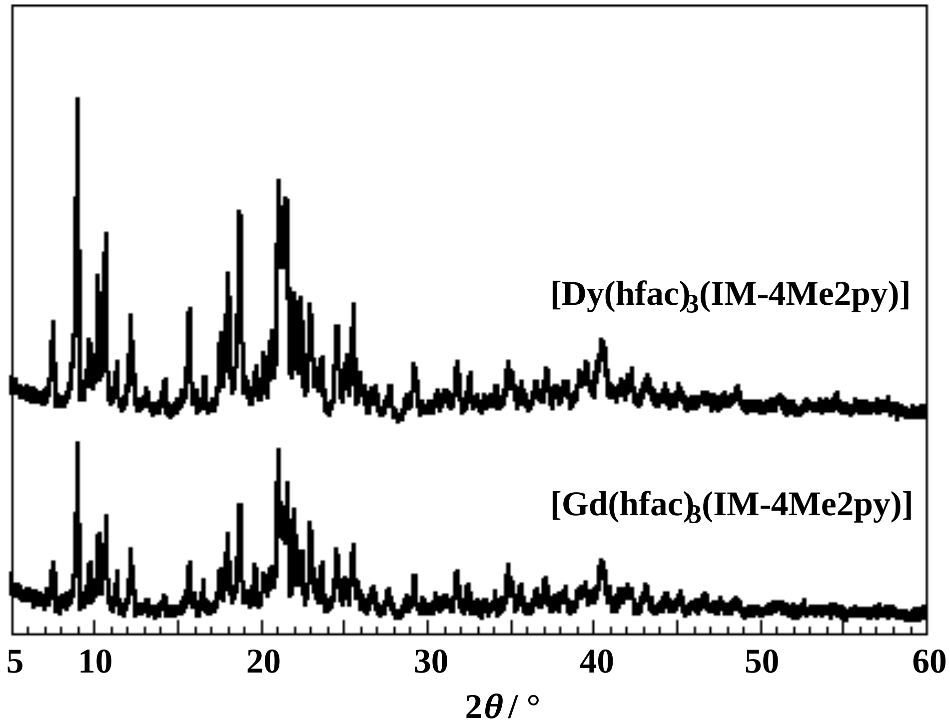


Figure 4-1. Molecular structure of [Gd(hfac)$_3$(IM-6Me2py)] showing 50% probability ellipsoids(F atoms are omitted).



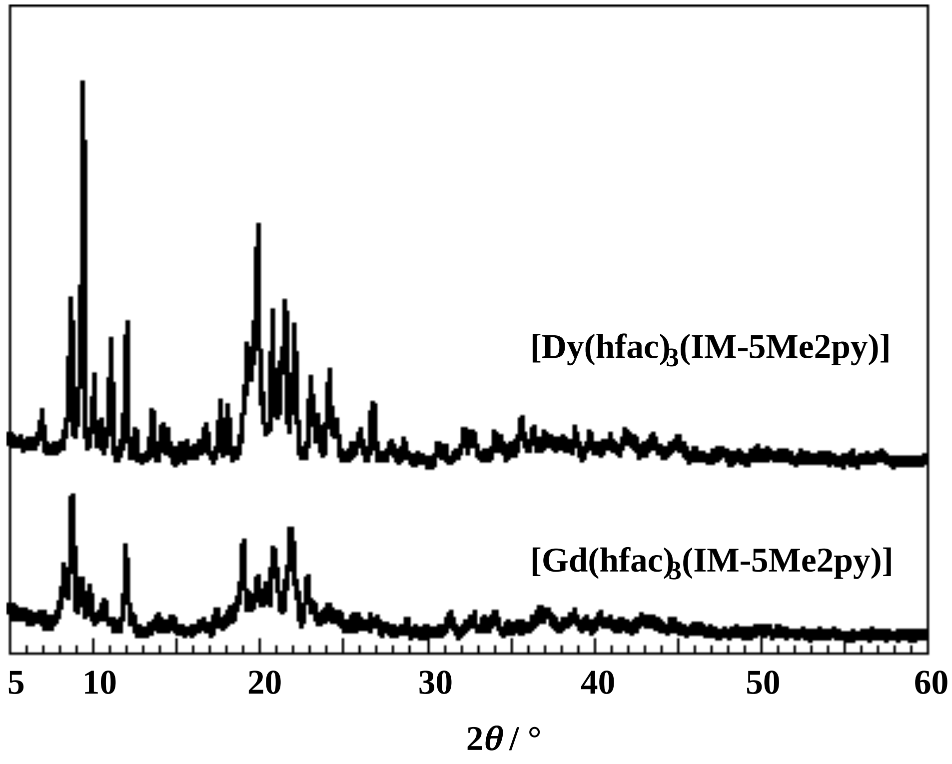


Figure 4-2. Powder X-ray diffraction spectra of Ln–IM4Me2py complexes (upper) and Ln–IM5Me2py complexes(lower).

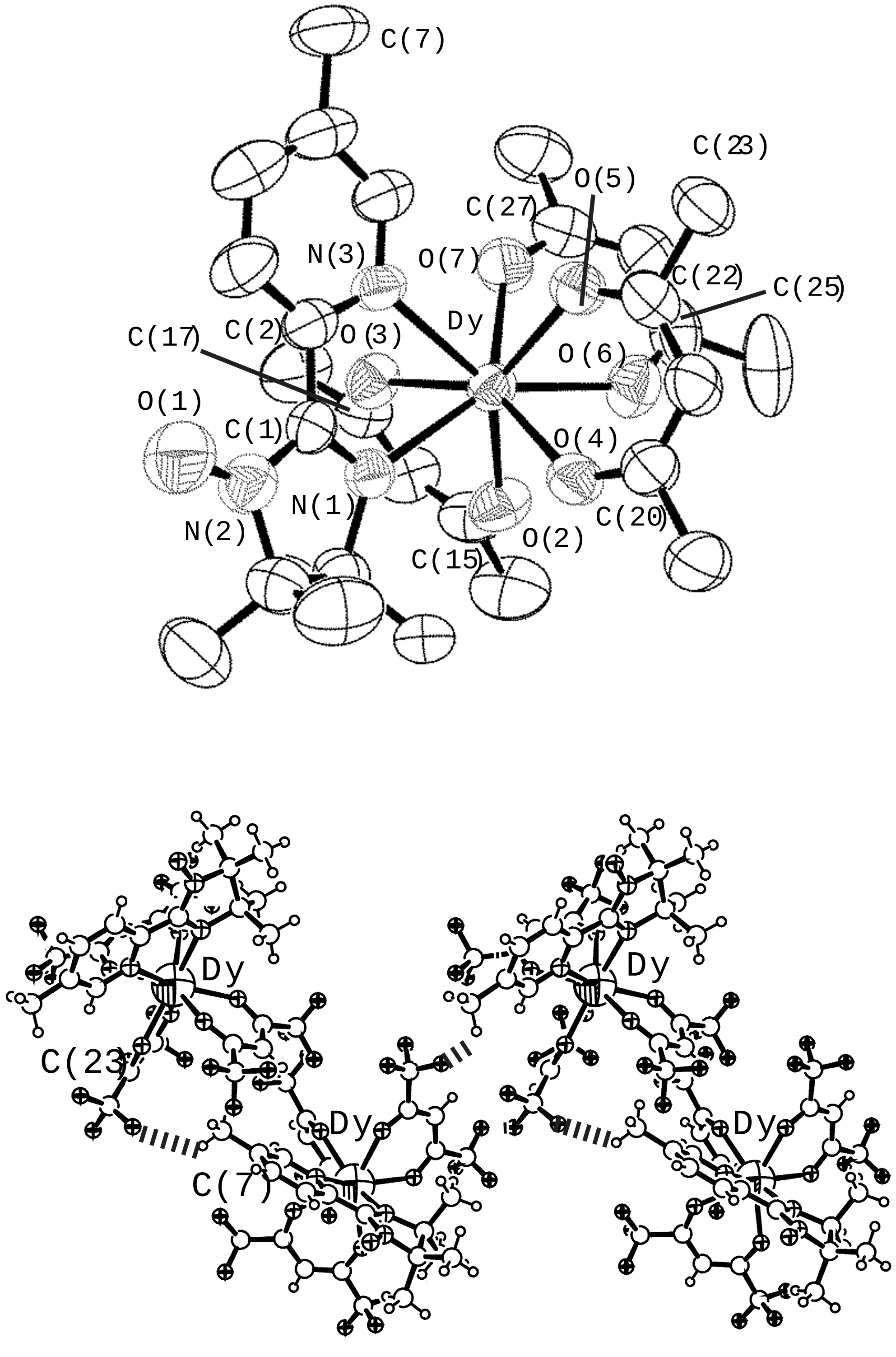


Figure 4-3. Molecular structure showing 50% probability ellipsoids (F atoms are omitted) and packing of [Dy(hfac)$_3$(IM-5Me2py)].

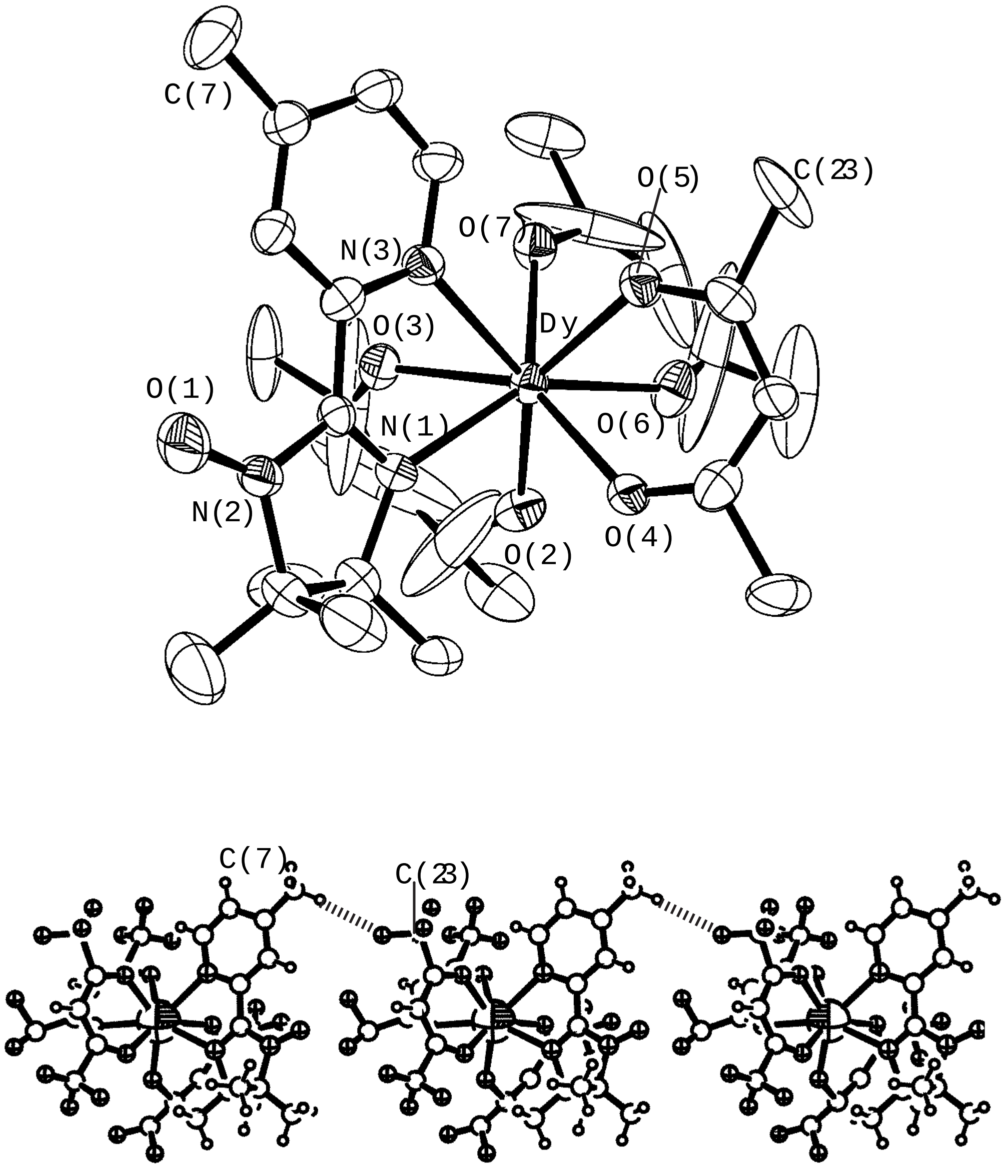
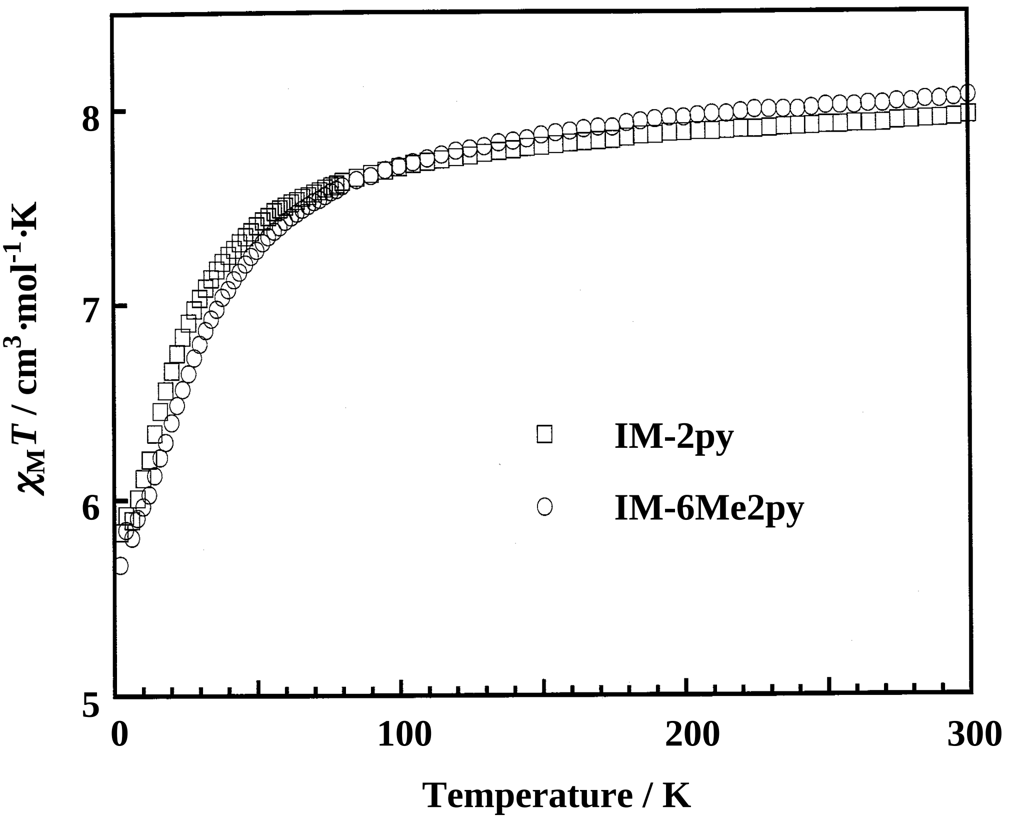


Figure 4-4. Molecular structure showing 30% probability ellipsoids (F atoms are omitted) and packing of [Gd(hfac)$_3$(IM-4Me2py)] .



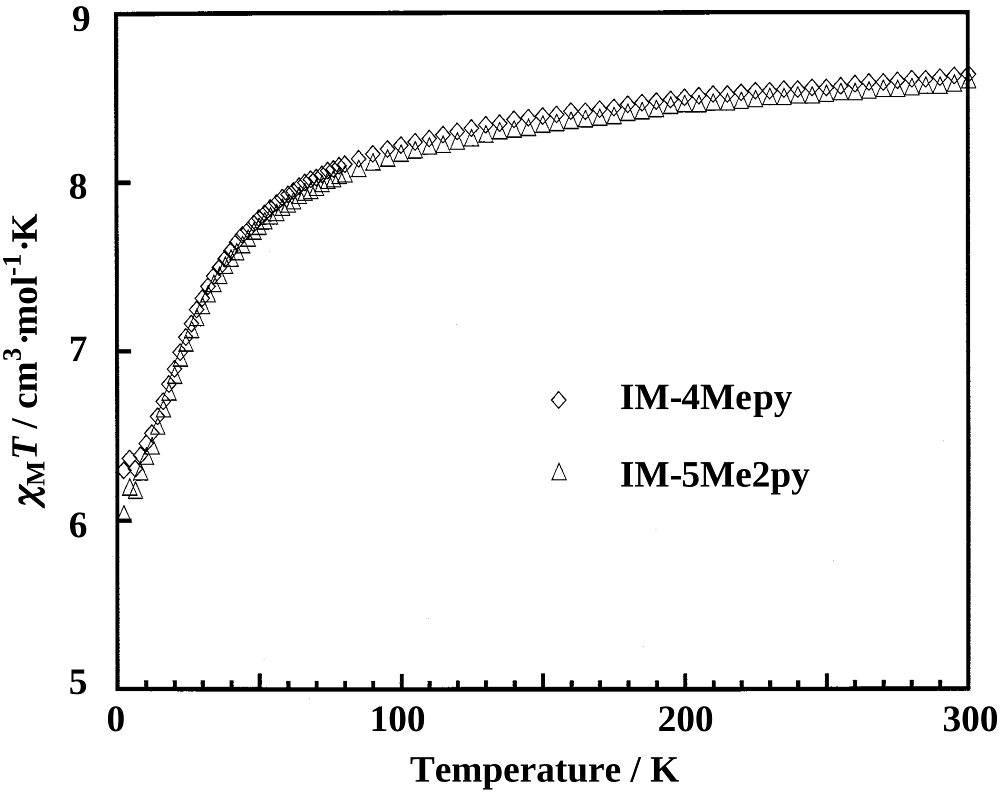


Figure 4-5. Teperature dependence of Gd(III) complexes containing IM-radical.

Chapter 5. NMR Spectral Studies of Lanthanide(III) Complexes Containing Imino Nitroxide Radical

5–1. Introduction

In previous chapters, the magnetic properties of the lanthanide–radical complexes in solid state have been mentioned mainly. Another attractive properties of these complexes in solution should be examined. Remember the UV-vis spectra in solution described in Chapter 1. Considering the spectral change with varying the mixing ratio, it should be emphasized that this type of complexes is so stable in solution that the spectral study in solution contrasted with in solid state is also reasonable.

There have been a number of NMR studies of lanthanide complexes as Lanthanide Shift Reagents (LSR) for advanced high resolution of complex NMR spectral patterns of the organic compounds, *e.g.* chiral discrimination as well as biological probes since the introduction by Hinkley in 1969.[52] Afterward, much attention has been paid to gadolinium(III) complexes as contrast agents for magnetic resonance imaging (MRI) due to the short relaxation time.[1,53]

However, there has been no report on NMR spectra of Ln(III) complexes containing the radical ligand(s). There are two reasons as follows; The NMR spectra would behave simply as an additive spectral pattern consisting of the unperturbed signals of the nonradical auxiliary ligands. The radical ligands in weak magnetically coupled Ln(III) complexes and the preservation of the considerable line broadening for radicals is predicted to make it difficult to assign signals and to examine the NMR spectra in detail. But when the measurements were put into practice, it is found that the behavior given by the spectra is not always predictable, especially in the case of diamagnetic metal ion complexes containing radical(s). Unexpectedly, the present ^{1}H NMR spectra in such a system will provide invaluable information on radical ligands in Ln(III) complexes.

In this chapter, unprecedented ^{1}H NMR behavior of the imino nitroxide radicals in diamagnetic yttrium(III) and lutetium(III) complexes as well as paramagnetic Ln(III) complexes chelated by a paramagnetic imino nitroxide radical IM-2py is described.

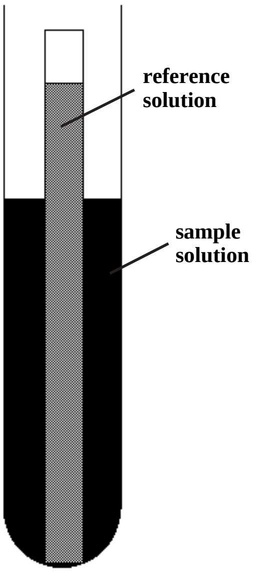
5-2. Experimental Section

5-2-1. Spectral measurement

ESR spectra were measured by a JES-RE1X ESR spectrometer at 296 K in CH_2Cl_2 and were analyzed with WinFonia software.[54] ^{1}H NMR spectra were measured by a JEOL EX-270 spectrometer in $CDCl_3$ except for a mixture of $[Y(hfac)_3(H_2O)_2]$ and IM-2py in $CDCl_3$–CD_3CN(4:1). The internal standard of tetramethylsilane(TMS) was assigned a chemical shift of 0 ppm.

5-2-2. Measurement of magnetic susceptibility with Evans method

The method proposed by Evans was modified and applied.[55] The reference solution was prepared by adding a drop of 1,4-dioxane in $CDCl_3$(0.05% v/v TMS). The sample solution was prepared by dissolving the sample complex in this reference solution. The sample solution was poured into 5 mm NMR tube, in which the glass capillary containing the reference solution was placed (Scheme 5-1). The observed difference in chemical shift of a signal from an inert reference material in the presence and absence of a paramagnetic solute with the following equation;



Scheme 5-1. Sample preparation for Evans' method

$$\chi_g = \frac{-3\Delta f}{4\pi f m} + \chi_0 + \frac{\chi_0(d_{solution} - d_{solvent})}{m} \qquad (5–1)$$

Where:

χ_g and χ_0: mass susceptibility of the solute and solvent($cm^3 \cdot g^{-1}$)

Δf: observed frequency shift of reference resonance (Hz)

f: spectrometer frequency (Hz)

m : mass of substance per cm^3 of solution

$d_{solution}$ and $d_{solvent}$: density of solution or solvent ($g \cdot cm^{-3}$)

As reference compound, TMS (internal standard), chloroform (solvent) and the inert 1,4-dioxane addition were applied. The Δf value is the average difference of the chemical shifts obtained with these references. In this experiment, the dilute solution (*ca.* 0.02 g / cm^3) was prepared and applied. Thus as the assumption that $d_{solution} = d_{solvent}$ approximately in this case, the third term was neglected.

5-3. Result and Discussion

5-3-1. Magnetic properties in solution

The UV-vis spectral change with various mixing ratio has proved the stability of the lanthanide–radical complexes. Furthermore, the measurements of the magnetic susceptibility and ESR spectra in [Y(hfac)$_3$(IM-2py)] make sure of the presence of the unpaired spin in the complexes.

The magnetic susceptibilities in the solid by the Gouy method and in the $CDCl_3$ solution by the Evans method with ^{1}H NMR spectra at 300 K of [Ln(hfac)$_3$(IM-2py)] (Ln = Y, Lu and Yb) are listed in Table 5-1. The values of Y and Lu complexes are close to the theoretical value of S=1/2 spin state (μ_{eff}= 1.73 μ_B), which result from IM-2py radical. The value of the Yb complex is also similar to the theoretical value of the noncorrelated spins (μ_{eff} = 4.86 μ_B)

In addition, the ESR spectrum in solution of [Y(hfac)$_3$(IM-2py)] displays hyperfine splittings to yttrium(III) ion and both nitrogens, N(1) for N(IM) and N(2) for N(N-O) of the IM moiety (Figure 5-1) where the unpaired electron resides with the increasing coupling of Y(III) and N(IM) owing to the coordination. These amounts of splitting were estimated by comparison with the simulated spectra. The nitrogen hyperfine splittings are 4.9 G(N(IM)) and 7.8 G(N(N-O)) for [Y(hfac)$_3$(IM-2py)], in contrast to 4.25 G(N(IM)) and 9.25 G(N(N-O)) for free IM-2py(Figure 5-1).[55] This effect is interpreted as due to electron delocalization from the ligand toward the metal. Due to ^{89}Y I=1/2 nuclear spin, the hyperfine splitting resulting from delocalization onto the metal is also expected. But the yttrium hyperfine splitting is only 0.4 G, which is considerably smaller than that of the corresponding ^{111,113}Cd or ^{199}Hg complexes (9.6 G for Cd, 46 G for Hg complex, respectively).

Considering these results, it is certain that [Y(hfac)$_3$(IM-2py)] remains paramagnetism in both the solid state and solution.

5-3-2. ^{1}H NMR spectra of the complexes containing diamagnetic center

As mentioned above, ^{1}H NMR spectra of [Y(hfac)$_3$(IM-2py)] and [Lu(hfac)$_3$(IM-2py)] in this situation are supposed to exhibit an additive pattern consisting of the signals of the diamagnetic hfac and the paramagnetic radical ligand IM-2py,[57] both of which are coordinated to the diamagnetic metal centers as if it were only a mixture of the Ln(hfac)$_3$ moieties and IM-2py. However, the NMR spectra in [Y(hfac)$_3$(IM-2py)] and [Lu(hfac)$_3$(IM-2py)] behave like those of diamagnetic products as shown in Figure 5-2. The ^{1}H NMR spectra of [Y(hfac)$_3$(IM-2py)] and [Lu(hfac)$_3$(IM-2py)] are observed in the diamagnetic range associated with line-broadening, in which no splitting by the spin-spin coupling is observed. There is no signal for the complexes in the paramagnetic range in which the signals of the IM-2py are observed. The broad signals from δ 7.5 to δ 8.5 are assigned the pyridyl protons on the basis of the ^{1}H–^{1}H COSY spectrum. This exhibits two kinds of cross peaks for the pyridyl protons(Figure. 5-3); discriminating two pairs of signals corresponding to each proton which are coupled with three (*ca.* δ 7.6 and δ 7.9) and two protons (*ca.* δ 7.5 and δ 8.7). Apparently, the former two are ascribed to the protons at the 4- and 5-position, the latter two to those at the 3- and 6-position of the pyridyl group. Since the signal at δ 7.5 is relatively broad, it can be assigned to the proton at 6-position which is closer to nitrogen atom. Therefore all the signals of pyridyl protons can be assigned as shown in Figure 5-3. A group of signals at δ 1.5 is assigned the methyl protons of the IM-2py. These assignments are in accordance with the chemical shifts of the diamagnetic analogous complex, *trans*-[Co(acac)$(NO_2)_2$(IMH-2py)] where IMH-2py is (2-(2’-pyridyl)-4,4,5,5-tetra-methyl-1-hydroxy-imidazoline) (Figure 5-4),[58] though the integrated intensities are found to be inconsistent with the ratios of the numbers of the protons in view of the line-broadening. The broad signal at δ 6.0 should be due to the methine proton of the hfac, since the position is close to that in the nonradical [Y$(hfac)_3$(bpy)] complex. The ^{1}H NMR line-widths in [Y$(hfac)_3$(IM-2py)] are similar to those of a mixture of [Y$(hfac)_3$(bpy)] and IM-2py, both of which are *ca.* five times as large as those of [Y$(hfac)_3$(bpy)]. Therefore, it is seen that the relaxation times of the methine proton of the hfac as well as the py and methyl protons of the IM-2py become shorter *via* the through-space or outer sphere dipolar interaction with the proximate molecules.

The ^{89}Y NMR spectrum of [Y$(hfac)_3$(IM-2py)] giving only a sharp singlet at δ 72.5 indicates that the Y(III) ion exists as only one species coordinated by IM-2py. Thus, the ^{1}H and ^{89}Y NMR behaviors originate from the radical complex itself, not from complexes containing the decomposed non-radical ligand. It is clear that the protons in the IM-2py give a diamagnetic ^{1}H NMR behavior in chemical shift, but not completely in line-width due to the outer-sphere interaction.

The diamagnetic behavior of ^{1}H NMR spectra is also observed for the low spin Co(III) complexes with the monodentate pyridyl substituted imino nitroxides (Figure 5-5).[35] The chemical shifts of [Co$(acac)_2(NO_2)$(IM-npy-κN(py))] (n=3, 4) with the coordinated pyridyl nitrogen ranges from δ 0 to δ 10. Thus, it is from the *coordination* in the complexes containing diamagnetic metal ions that the diamagnetic NMR behavior *arises*, but it does *not* necessarily depend on the *coordination mode*, the monodentate through the pyridyl nitrogen or the didentate through the IM and py nitrogens. The paramagnetic radical containing a diamagnetic lanthanide and/or transition metal ion may inhibit shifting of the NMR signals in the radical compounds and make it possible to analyze as if it were diamagnetic. This means the complete quenching of the unpaired electron around the protons in the IM radicals with respect to the NMR spectra.

5-3-3. ^{1}H NMR spectra of the complexes containing paramagnetic center

The ^{1}H NMR spectra of the paramagnetic lanthanide complex [Ln(hfac)$_3$(IM-2py)] is worth of remark in support of the diamagnetic NMR behavior of the IM-2py in complexes. The relatively sharp NMR signals are observed for the [Yb(hfac)$_3$(IM-2py)] with the chemical shifts ranging from δ 60 to δ –30 (Figure 5-6). If there were no or little magnetic interaction between Yb(III) and IM-2py, the ^{1}H NMR spectra would look like a sum of the paramagnetic shifted signals due to the Yb(III) ion and the free IM-2py as compared to those of the Ni(II) NIT-2py complexes.[20b] By taking into consideration of the diamagnetic NMR behavior of [Y(hfac)$_3$(IM-2py)] and [Lu(hfac)$_3$(IM-2py)], it is likely that one unpaired electron of IM-2py has no influence to the paramagnetic shift, or could be quenched with respect to the NMR spectra. In other words, the NMR signals of the IM-2py coordinated to Yb(III) behave as the *diamagnetic* ligand in the paramagnetic complex.

It is suggested that the NMR spectra can be analyzed in the same method as the common lanthanide complexes. The major problem is how the shifted signals are assigned. The hfac–H protons can be assigned readily by comparison with the spectra of non-radical complex *e.g.* [Ln(hfac)$_3$(bpy)]. As mentioned in Chapter 4, the lanthanide complexes containing the methyl substituted IM-2py are available according to the assignments of the ^{1}H NMR signals to the pyridyl protons. The ^{1}H NMR spectra of the Yb–IM-radical complexes are shown in Figure 5-6. Whereas the ^{1}H NMR spectra of [Yb(hfac)$_3$(IM-4Me2py)] and [Yb(hfac)$_3$(IM-5Me2py)] are similar to that of [Yb(hfac)$_3$(IM-2py)], the ^{1}H NMR spectrum of [Yb(hfac)$_3$(IM-6Me2py)] are different considerably. It has been described in Chapter 4 that there is significant structural change from the IM-2py complex to [Gd(hfac)$_3$(IM-6Me2py)] probably due to the steric repulsion between the methyl group in IM-6Me2py and [Ln(hfac)$_3$] moiety. The significant spectral behavior also results from this structual change. The signals at 4- and 5- position of [Ln(hfac)$_3$(IM-2py)] involving paramagnetic shift can be assigned by comparison with the ^{1}H NMR spectra of [Ln(hfac)$_3$(IM-nMe2py)] (n=4, 5). Therefore

By comparison with those of the methyl substituted IM-2py, the chemical shift for the pyridyl proton at the 4- and 5-positon in [Yb(hfac)$_3$(IM-2py)] is entirely different from that of the free IM-2py, whereas the methine proton of the hfac is mostly unshifted from that of the corresponding nonradical Yb(III) complex. There is a contradiction between these two facts; the former IM-2py and the latter hfac singals suggesting, respectively, the large and small magnetic interaction between the Yb(III) and IM-2py. From the examination of the variable temperature magnetic susceptibility(χ_M), however, the magnetic interaction is very weak at room temperature, showing almost a sum of the $\chi_M T$ values for the Yb(III) and IM-2py.

5-3-4. The analysis of lanthanide induced shift(LIS) of [Ln(hfac)$_3$(IM-2py)]

The fact that there is no influence from the IM-2py to NMR is substantiated by showing that these paramagnetic shifts result from only unpaired 4f-electrons in lanthanide ions. The further proof of the fact may be gained from a detailed analysis of the lanthanide induced shifts (LIS), δ_{ij}^{LIS}, which is represented as the difference between the resonances observed in a paramagnetic complexes (δ^{para}) and in a corresponding diamagnetic environment, *e.g.* the analogous Y and Lu compelxes (δ^{dia}). That is,

$$\delta_{ij}^{LIS} = \delta^{para} - \delta^{dia} \qquad (5\text{–}2)$$

As a result of through-space (dipolar) and through-bond (contact) interactions between the electronic spin on the Ln(III) and the proton nuclear spins of the ligand, the resonance of a given proton is remarkably shifted from the position observed in a corresponding diamagnetic environment.[1,59]

$$\delta_{ij}^{LIS} = \delta(dipolar)+\delta(contact) \qquad (5–3)$$

The dipolar interaction contains the information on the position in space of the ligand nuclei, since the contribution affects paramagnetic shifts for protons which are significantly remote from the paramagnetic center. Even in the case of lower symmetry complexes, the contribution is shown as the simplified form;

$$\delta_i(dipolar) = \frac{k_{CF}}{T^2}\left(\frac{3\cos^2\theta_i - 1}{r_i^3} + D\frac{\sin\theta_i \cos 2\phi_i}{r_i^3}\right)\cdot C_j = G_i \cdot C_j \qquad (5–4)$$

where k_{CF} and D are the crystal field parameters and r_i, θ_i, ϕ_i are the spherical coordinates of nuclei i with respect to the metal ion located at the origin. C_j is a lanthanide dependent term of which the theoretical values can be found in the literature. The parts depending on the spherical position can be taken as the geometrical factor G_i. The contact term provides information on the bonding, since the contribution results from though bond Fermi interactions with a metal center and thus depends on the unpaired spin density on the same nuclei. The contribution is given by;

$$\delta_i(contact) = \frac{A_i\langle S_z\rangle_j}{\hbar\gamma B_0 T} = F_i \cdot \langle S_z\rangle_j \qquad (5–5)$$

where A_i is the hyperfine coupling constant between the unpaired spins of the Ln(III) ion and the magnetic moment of the nucleus i, B_0 is the applied magnetic induction, $<S_z>_j$ is the spin expectation value of S_z. The parts depending on the environment of nucleus i can be described as contanct term F_i. The overall isotropic paramagnetic shift contains these two contributions and is given by:

$$\delta_{ij}^{LIS} = F_i<S_z>_j + G_i\cdot C_j \qquad (5–6)$$

Where *eq.* (5–6) is rearranged into the linear form given by:

$$\frac{\delta_{\mathrm{i}}^{\mathrm{LIS}}}{\langle S_{\mathrm{z}}\rangle_{\mathrm{j}}} = \frac{C_{\mathrm{j}}}{\langle S_{\mathrm{z}}\rangle_{\mathrm{j}}} \cdot G_{\mathrm{i}} + F_{\mathrm{i}} \qquad (5–7)$$

C_{j} and $<S_z>_{\mathrm{j}}$ values for each lanthanide(III) ion are listed in Table 5-2. Under the condition that the lanthanide complexes are isostructual, the linearity for a plot of $\delta_{ij}^{\mathrm{LIS}}/<S_z>$ against $F_i+G_i \cdot Cj/<S_z>$ should be obtained for a particular nucleus i of the ligand in the corresponding complexes across the entire series. In the case of multi-spin system such as [Ln(hfac)$_3$(IM-2py)], there is another requirement that the interaction between Ln and unparied spin(s) is similar to each other through the series. Taking into account the similarity of UV-vis spectra, it is supposed that this requirement is satisfied (the linearity of the plot suggests simultaneously that the requirement is satisfied) The treatment of [Ln(hfac)$_3$(IM-2py)] can be made in a similar manner for non-radical complexes.

The chemical shifts and $\delta^{\mathrm{LIS}}/<S_z>_{\mathrm{j}}$ values for [Ln(hfac)$_3$(IM-2py)] are listed in Table 5-3. The linearity is found for the methine proton of the hfac ligand and the pyridyl proton at the 4- and 5-positon of the IM-2py moiety through a series of Ln(III) complexes except Yb(III) (Figure 5-7). The deviation from linearity for Yb(III) complexes may result from the slight structual change in solution. The agreement factors are evaluated for each nucleus according to the following equation:

$$AF_{\mathrm{i}} = \sqrt{\frac{\sum_{\mathrm{j}} (\delta_{\mathrm{j}}^{\mathrm{exp}} - \delta_{\mathrm{j}}^{\mathrm{calc}})^2}{\sum_{\mathrm{j}} (\delta_{\mathrm{j}}^{\mathrm{exp}})^2}} \qquad (5–8)$$

The *AF* values for the protons are reliable ($0.003 < AF_{\mathrm{I}} < 0.076$). Least-squres values for each proton are listed in Table 5-4.

At first, the linearity of the plot suggests that the interaction between Ln and IM-2py are similar through the series as mentioned above. In addition, though the applied $<S_z>_{\mathrm{j}}$ and C_{j} values are evaluated only with 4f electrons contained in each free lanthanide(III) ion, the linearity are kept even under the presence of other unpaired spin involved in IM-2py. Accordingly, the paramagnetic shifts of the IM-2py ligand in the paramagnetic Ln(III) ion, *e.g.*, Yb(III) in [Yb(hfac)$_3$(IM-2py)] are induced only by unpaired 4f electrons in the Ln(III) ion. Surprisingly, the paramagnetic shifts in ^{1}H NMR are *hardly affected* by unpaired spin in IM-2py.

Table 5-1. The magnetic susceptibility (μ_B) of [Ln(hfac)$_3$(IM-2py)]

	Ln = Y	Lu	Yb
Theoretical value	1.73	1.73	4.86
Gouy method in the solid	1.81	1.90	5.07
Evans method in solution	2.20	2.17	4.80

Table 5-2. Theoretical Bleaney's factors (C_j) and spin expectation values of S_z ($<S_z>_j$) for spherical lanthanide(III) ions

Ln	C_j	$<S_z>_j$	$C_j/<S_z>_j$
Nd	-4.2	4.49	-0.9350
Sm	-0.7	-0.06	11.67
Eu	4	-10.68	-0.3745
Tb	-86	-31.82	2.703
Dy	-100	-28.55	3.503
Ho	-39	-22.63	1.723
Er	33	-15.37	-2.147
Tm	53	-8.21	-6.456
Yb	22	-2.59	-8.494

Table 5-3. Experimental ^{1}H NMR chemical shifts (ppm) and calculated δ^{LIS} values for [Ln(hfac)$_3$(IM-2py)].

Ln	hfac–H			py–H^4			py–H^5		
	δ	δ^{LIS}	$\delta^{LIS}/\langle S_z \rangle_j$	δ	δ^{LIS}	$\delta^{LIS}/\langle S_z \rangle_j$	δ	δ^{LIS}	$\delta^{LIS}/\langle S_z \rangle_j$
Y	6.20			7.6			7.9		
Eu	3.05	-3.15	0.29				21.15	13.25	-1.24
Tb	120.66	114.46	-3.60	-4.09	-11.69	0.37	-19.84	-27.74	0.87
Dy	137.87	131.67	-4.61	-40.72	-48.32	1.69	-1.76	-9.66	0.34
Ho	62.28	56.08	-2.48	-4.33	-11.93	0.53	2.86	-5.04	0.22
Er	-22.33	-28.53	1.86	32.32	24.72	-1.61	33.76	25.86	-1.68
Tm	-47.08	-53.28	6.49	14.52			41.99	34.09	-4.15
Yb	-11.01	-17.21	6.64	33.55	25.95	-10.02	26.99	19.09	-7.37

Table 5-4. Calculated G_i and F_i values and agreement factor (AF_i) for each proton in [Ln(hfac)$_3$(IM-2py)].

	hfac–CH	py-H^4	py-H^5
F_i	-1.112	0.525	0.492
G_i	-0.535	-0.514	-0.855
AF_i	0.0027	0.0755	0.0266

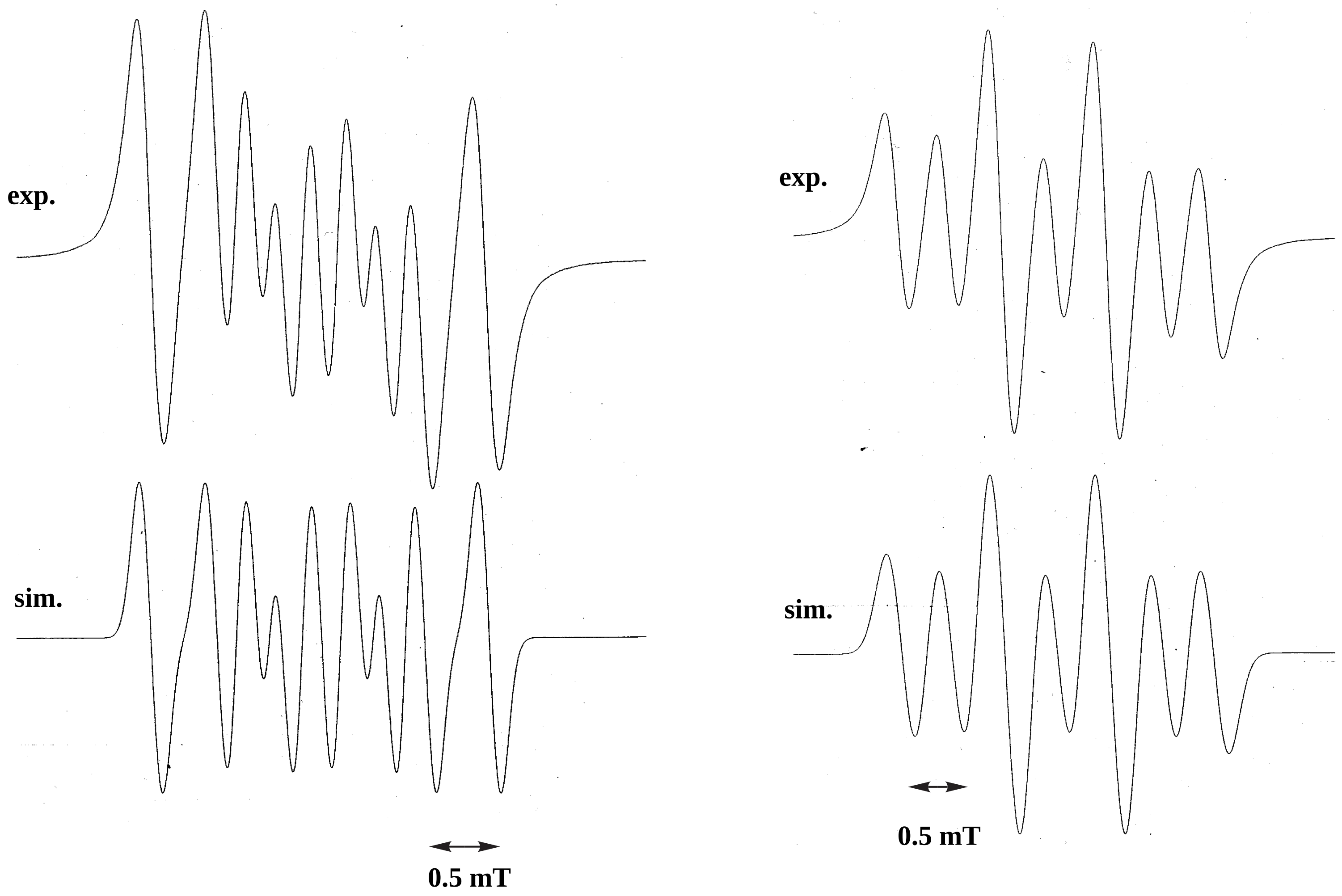


Figure 5-1. ESR spectra of [Y(hfac)$_3$(IM-2py)] (left) and IM-2py (right).

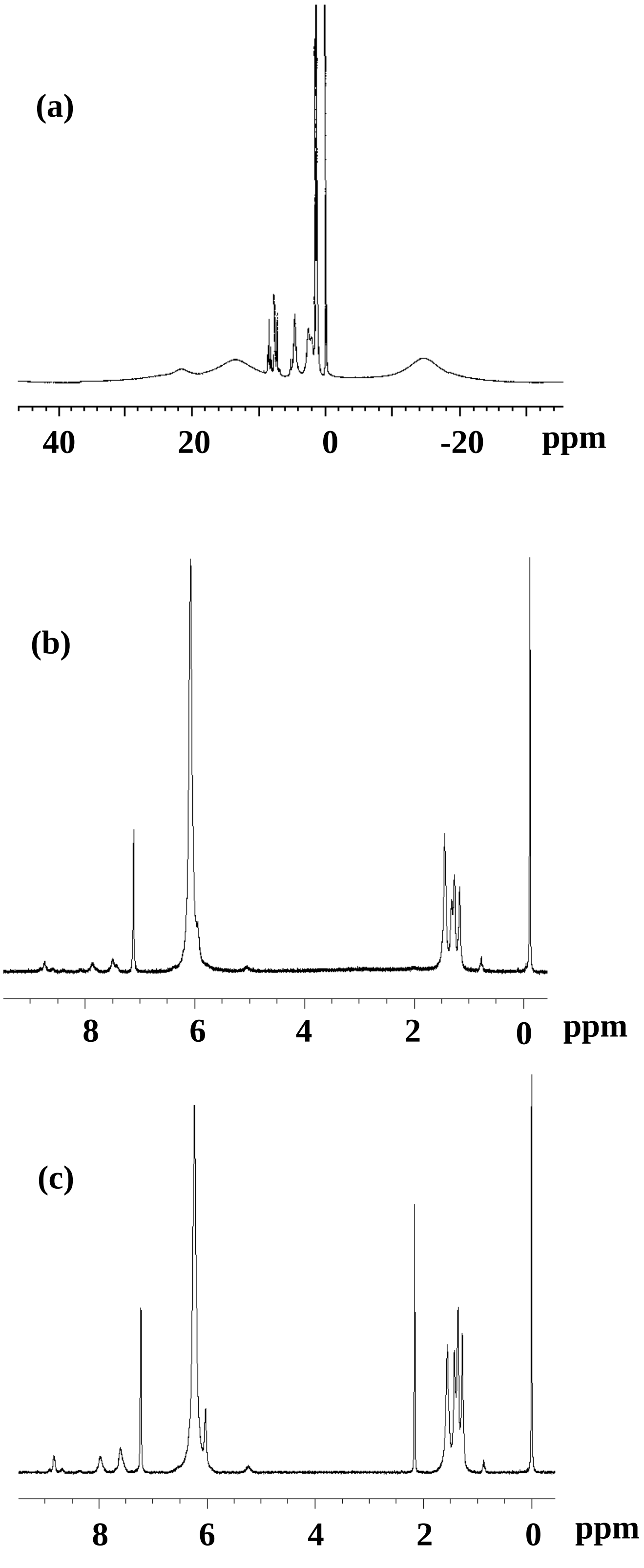


Figure 5-2. ^{1}H NMR spectra of free IM-2py (a), [Y(hfac)$_3$(IM-2py)] (b) and [Lu(hfac)$_3$(IM-2py) (c).

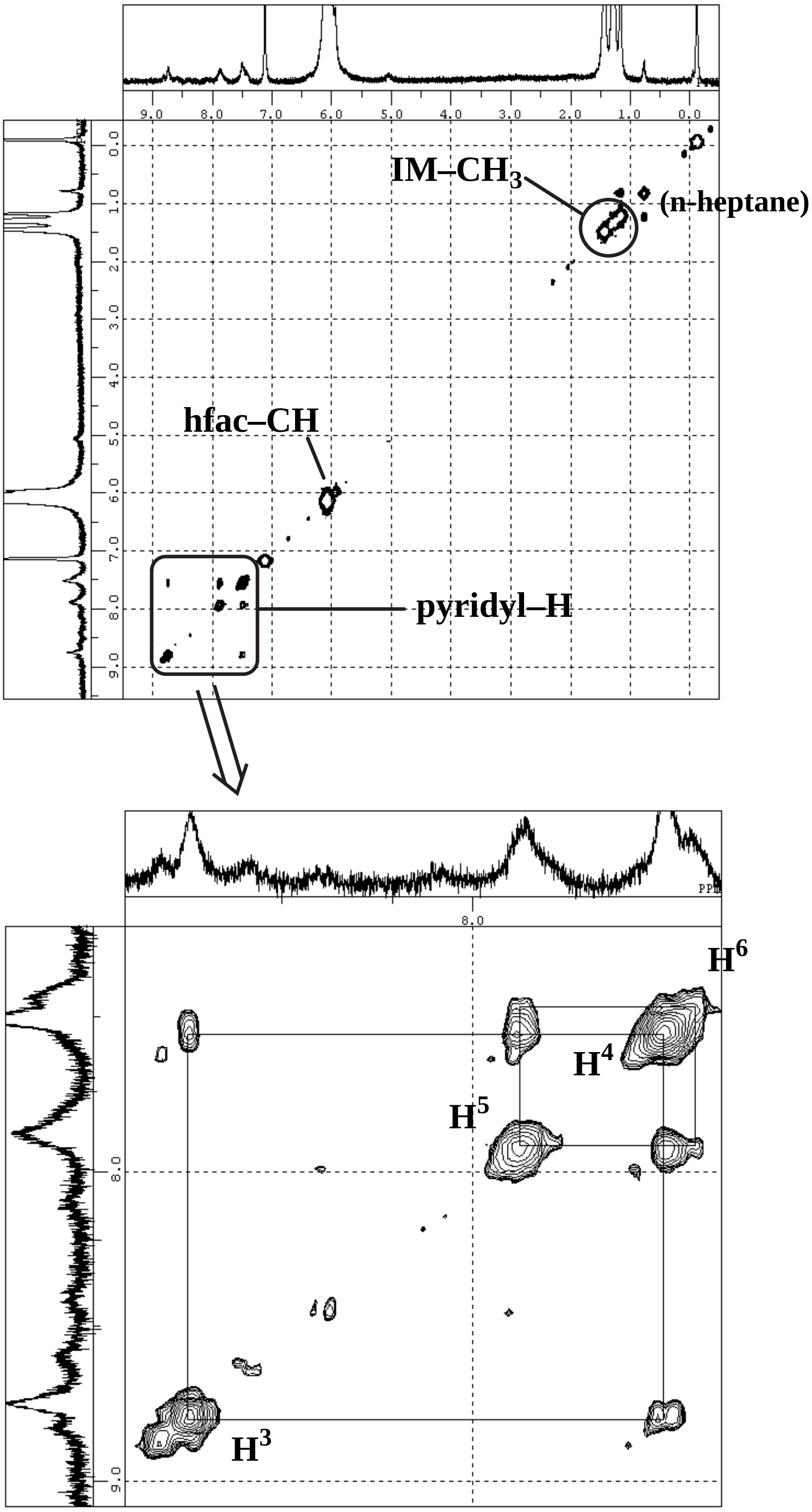
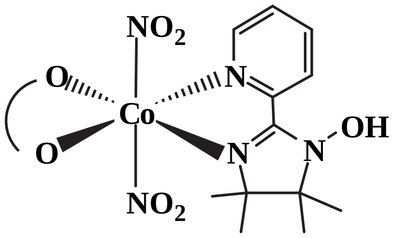


Figure 5-3. ^{1}H-^{1}H COSY spectrum of [Y(hfac)$_3$(IM-2py)]



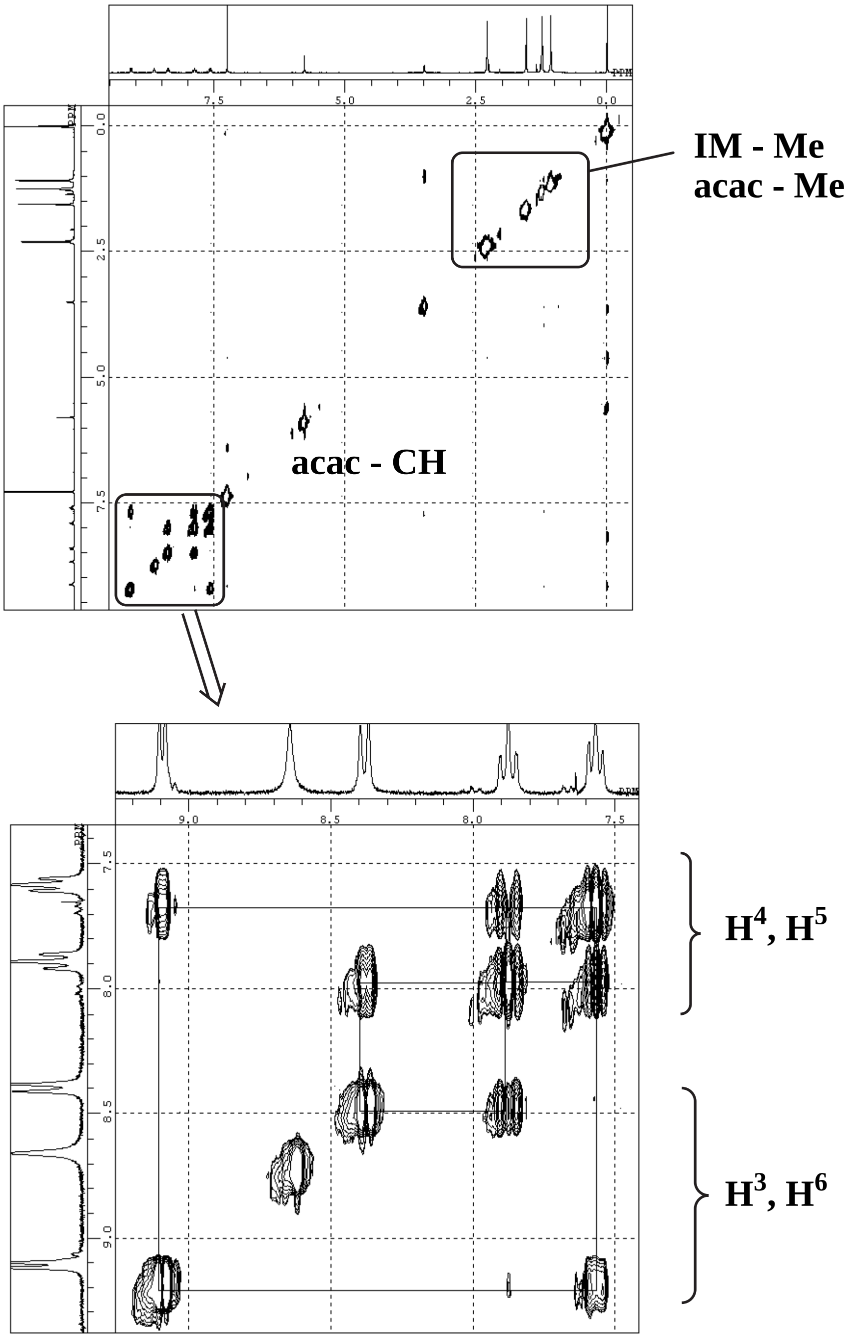


Figure 5-4. ^{1}H-^{1}H COSY spectrum of [Co(acac)((NO$_2$)$_2$(IMH-2py)]

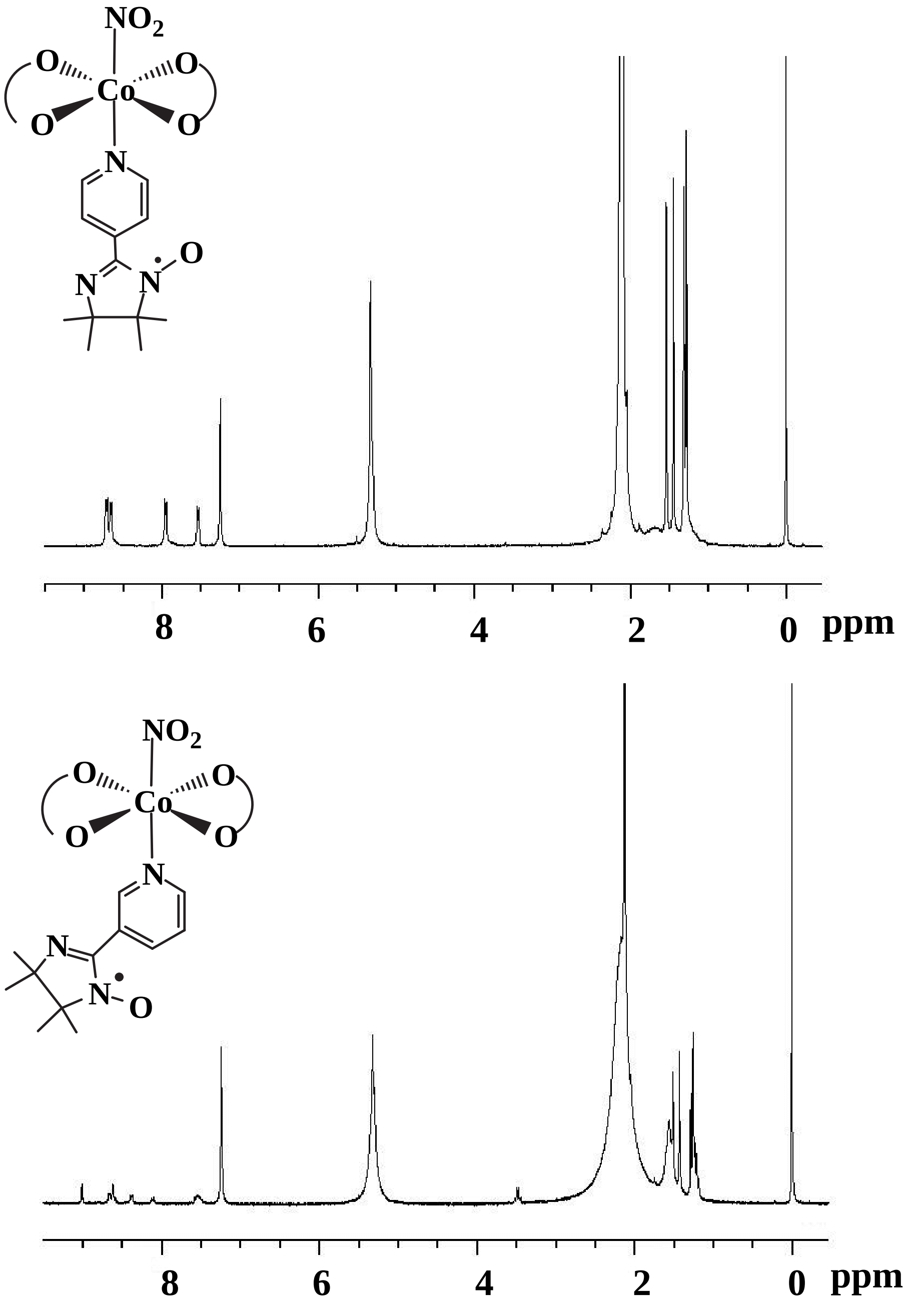


Figure 5-5. Diamagnetic ^{1}H NMR spectra of [Co(acac)$_2$(IM-4py)] (upper) and [Co(acac)$_2$(IM-3py)] (lower).

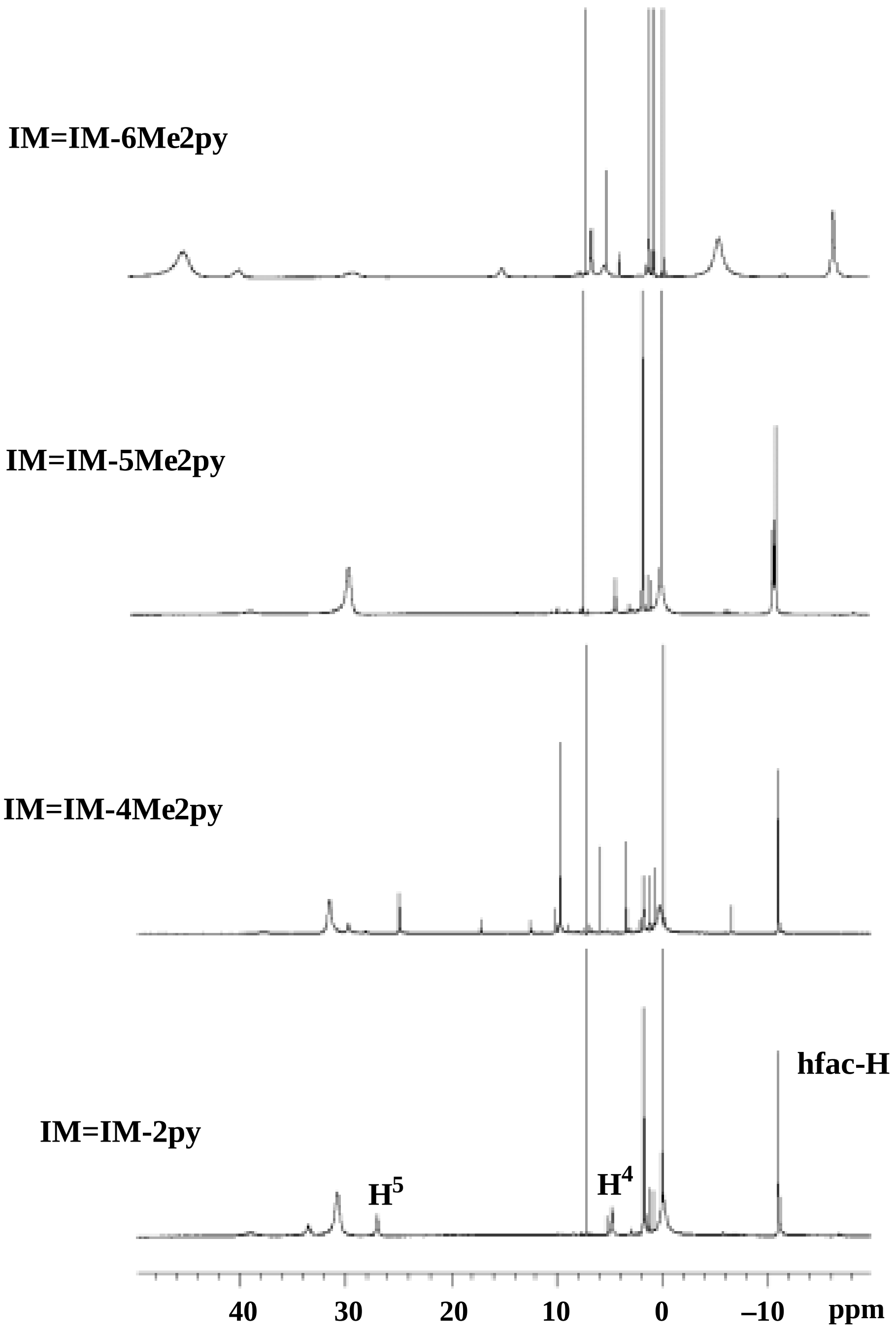


Figure 5-6. ^{1}H NMR spectra of [Yb(hfac)$_3$(IM)] (IM=IM-nMe2py; n=x, 4, 5, 6)

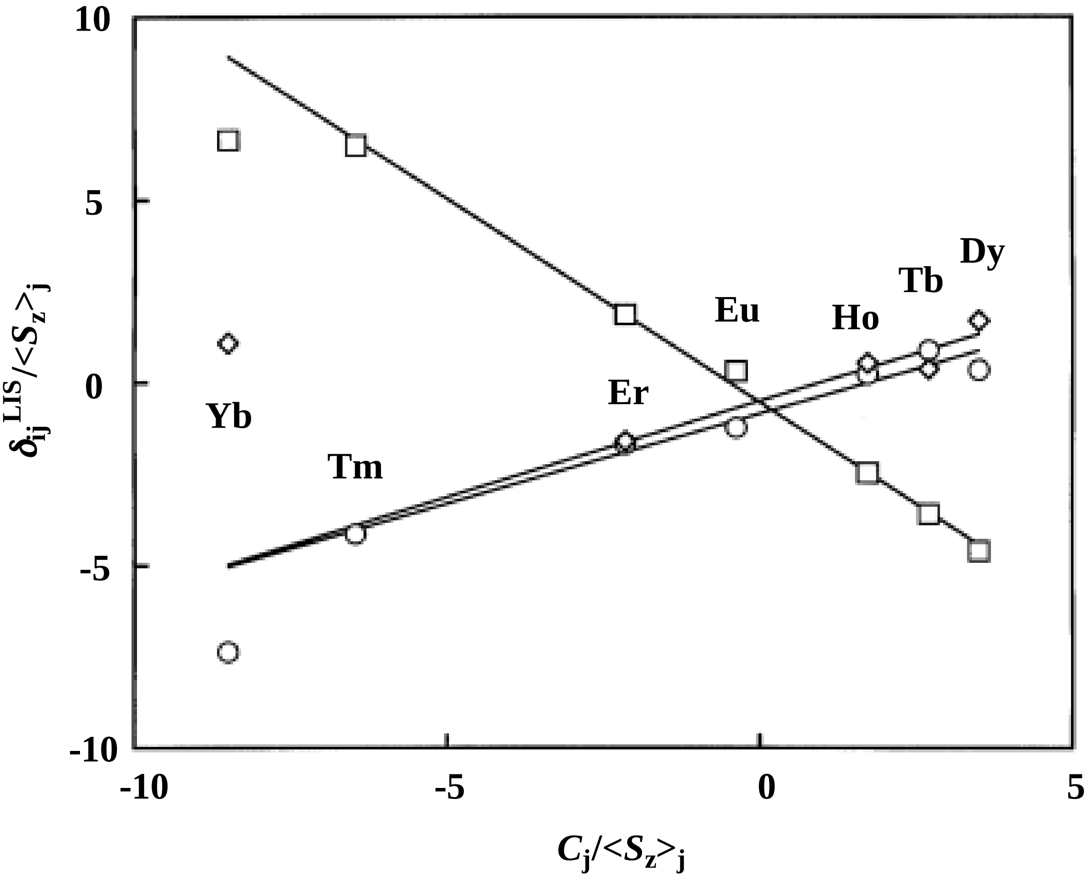


Figure 5-7. A plot of $\delta_{ij}^{LIS}/\langle S_z\rangle$ *vs.* $C_j/\langle S_z\rangle$ (□: hfac-CH, ◇: 4-position proton in IM-2py, ○:5-position proton in IM-2py, respectively)

Conclusion

A new series of the discrete Ln(III)-IM-2py complexes were readily prepared and stable in solution and solid. The interactions in the excited state are relatively strong in view of both the red shift and/or intensity enhancement with vibronic structure in the n-π^* intraligand transition of the IM-2py and the emission quenching behavior.

The magnetic interaction between Gd(III) and IM-2py are weakly antiferromagnetic in contrast to the ferromagnetic interaction between Gd(III) and nitronyl nitroxides. It suggests that the overlap between 4f and π^* orbital is relatively large. Valuable information concerning the properties of the interactions involving imino nitroxide radicals and Ln(III) ions displaying spin–orbit coupling is also provided. A systematic investigation of an isostructual series of the complexes allowed the evolution of these interactions to be compared as a function of the electronic configuration of the 4f orbitals. It is found that the Ln–radical for Ln(III) with $4f^3$ and $4f^5$ electronic configurations interaction is ferromagnetic, the interaction for Ln(III) $4f^8$ to $4f^{13}$ configurations is antiferromagnetic. Even for the other Ln(III) ion except Gd(III), we found that the unusual magnetic properties which are different from usual NIT type radical are shown.

The present ^{1}H NMR spectra of the coordinated IM radicals are the first example of the diamagnetic behavior to the best of our knowledge. The paramagnetic compounds containing diamagnetic lanthanide and/or transition metal ion may inhibit shifting and/or broadening of the NMR signals of radical compounds and make it possible to analyze as if it were diamagnetic. This means the complete quenching of the unpaired electron around the protons in the IM radicals. This anomalous ^{1}H NMR behavior may bring important electronic and/or stereochemical information for the IM-type radicals.

This new type of lanthanide–radical complexes shows several interesting properties. The complexes must give us the new direction for lanthanide chemistry.

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Appendix.

Bond lengths(Å), bond angles(°) and torsion angles(°) of the complexes described in this text.

•[Sm(hfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Sm(1)	O(2)	2.424(5)	Sm(1)	O(3)	2.370(4)
Sm(1)	O(4)	2.347(4)	Sm(1)	O(5)	2.422(4)
Sm(1)	O(6)	2.362(4)	Sm(1)	O(7)	2.365(4)
Sm(1)	N(1)	2.585(5)	Sm(1)	N(3)	2.574(5)
F(1)	C(13)	1.323(12)	F(2)	C(13)	1.290(12)
F(3)	C(13)	1.296(12)	F(4)	C(17)	1.321(13)
F(5)	C(17)	1.292(11)	F(6)	C(17)	1.301(11)
F(7)	C(18)	1.301(14)	F(8)	C(18)	1.277(11)
F(9)	C(18)	1.297(15)	F(10)	C(22)	1.304(18)
F(11)	C(22)	1.222(10)	F(12)	C(22)	1.166(19)
F(13)	C(23)	1.213(14)	F(14)	C(23)	1.151(16)
F(15)	C(23)	1.270(18)	F(16)	C(27)	1.302(13)
F(17)	C(27)	1.256(11)	F(18)	C(27)	1.197(12)
O(1)	N(2)	1.263(7)	O(2)	C(14)	1.226(8)
O(3)	C(16)	1.249(8)	O(4)	C(19)	1.234(8)
O(5)	C(21)	1.234(7)	O(6)	C(24)	1.248(9)
O(7)	C(26)	1.242(7)	N(1)	C(1)	1.282(7)
N(1)	C(7)	1.506(8)	N(2)	C(1)	1.403(7)
N(2)	C(8)	1.491(10)	N(3)	C(2)	1.354(7)
N(3)	C(6)	1.333(7)	C(1)	C(2)	1.469(8)
C(2)	C(3)	1.385(8)	C(3)	C(4)	1.369(9)
C(4)	C(5)	1.352(10)	C(5)	C(6)	1.379(9)
C(7)	C(8)	1.550(11)	C(7)	C(9)	1.549(11)
C(7)	C(10)	1.514(10)	C(8)	C(11)	1.504(11)
C(8)	C(12)	1.512(13)	C(13)	C(14)	1.530(11)
C(14)	C(15)	1.390(10)	C(15)	C(16)	1.367(10)
C(16)	C(17)	1.528(11)	C(18)	C(19)	1.521(11)
C(19)	C(20)	1.382(10)	C(20)	C(21)	1.383(9)
C(21)	C(22)	1.522(10)	C(23)	C(24)	1.526(12)
C(24)	C(25)	1.387(11)	C(25)	C(26)	1.398(10)
C(26)	C(27)	1.502(11)			

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Sm(1)	O(3)	71.01(16)	O(2)	Sm(1)	O(4)	75.30(16)
O(2)	Sm(1)	O(5)	128.64(16)	O(2)	Sm(1)	O(6)	137.31(17)
O(2)	Sm(1)	O(7)	142.27(15)	O(2)	Sm(1)	N(1)	70.22(17)
O(2)	Sm(1)	N(3)	72.95(15)	O(3)	Sm(1)	O(4)	92.67(16)
O(3)	Sm(1)	O(5)	72.88(16)	O(3)	Sm(1)	O(6)	147.09(16)
O(3)	Sm(1)	O(7)	91.86(16)	O(3)	Sm(1)	N(1)	135.88(16)
O(3)	Sm(1)	N(3)	85.66(16)	O(4)	Sm(1)	O(5)	71.18(15)
O(4)	Sm(1)	O(6)	82.63(17)	O(4)	Sm(1)	O(7)	140.63(14)
O(4)	Sm(1)	N(1)	97.15(15)	O(4)	Sm(1)	N(3)	146.94(15)
O(5)	Sm(1)	O(6)	74.79(17)	O(5)	Sm(1)	O(7)	72.94(15)
O(5)	Sm(1)	N(1)	150.57(17)	O(5)	Sm(1)	N(3)	138.23(14)
O(6)	Sm(1)	O(7)	72.78(16)	O(6)	Sm(1)	N(1)	76.99(17)
O(6)	Sm(1)	N(3)	115.46(16)	O(7)	Sm(1)	N(1)	106.36(16)
O(7)	Sm(1)	N(3)	72.42(14)	N(1)	Sm(1)	N(3)	63.46(15)
Sm(1)	O(2)	C(14)	134.7(5)	Sm(1)	O(3)	C(16)	133.6(5)
Sm(1)	O(4)	C(19)	137.2(4)	Sm(1)	O(5)	C(21)	134.2(4)
Sm(1)	O(6)	C(24)	132.8(5)	Sm(1)	O(7)	C(26)	134.2(4)
Sm(1)	N(1)	C(1)	117.3(4)	Sm(1)	N(1)	C(7)	133.0(4)
C(1)	N(1)	C(7)	108.6(5)	O(1)	N(2)	C(1)	125.6(6)
O(1)	N(2)	C(8)	124.5(6)	C(1)	N(2)	C(8)	108.8(5)
Sm(1)	N(3)	C(2)	121.1(4)	Sm(1)	N(3)	C(6)	121.0(4)
C(2)	N(3)	C(6)	117.8(5)	N(1)	C(1)	C(2)	123.2(5)
N(1)	C(1)	N(2)	112.5(5)	N(2)	C(1)	C(2)	124.3(5)
N(3)	C(2)	C(1)	113.1(5)	N(3)	C(2)	C(3)	121.1(6)
C(1)	C(2)	C(3)	125.8(5)	C(2)	C(3)	C(4)	119.2(6)
C(3)	C(4)	C(5)	120.1(6)	C(4)	C(5)	C(6)	118.2(7)
N(3)	C(6)	C(5)	123.4(6)	N(1)	C(7)	C(8)	103.4(6)
N(1)	C(7)	C(9)	105.3(6)	N(1)	C(7)	C(10)	109.6(6)
C(8)	C(7)	C(9)	113.9(7)	C(8)	C(7)	C(10)	113.7(7)
C(9)	C(7)	C(10)	110.4(8)	C(7)	C(8)	C(11)	117.0(10)
C(7)	C(8)	C(12)	114.5(8)	C(11)	C(8)	C(12)	109.5(10)
N(2)	C(8)	C(11)	109.9(7)	N(2)	C(8)	C(12)	105.9(9)
N(2)	C(8)	C(7)	98.9(6)	F(1)	C(13)	C(14)	112.9(9)
F(1)	C(13)	F(2)	106.1(9)	F(1)	C(13)	F(3)	107.5(10)
F(2)	C(13)	C(14)	111.5(8)	F(2)	C(13)	F(3)	107.7(10)
F(3)	C(13)	C(14)	110.9(8)	O(2)	C(14)	C(13)	113.6(8)
O(2)	C(14)	C(15)	127.1(7)	C(13)	C(14)	C(15)	119.3(8)
C(14)	C(15)	C(16)	121.6(7)	O(3)	C(16)	C(15)	128.4(7)

O(3)	C(16)	C(17)	113.2(7)	C(15)	C(16)	C(17)	118.4(7)
F(4)	C(17)	C(16)	110.7(9)	F(4)	C(17)	F(5)	103.5(10)
F(4)	C(17)	F(6)	105.9(10)	F(5)	C(17)	C(16)	111.6(8)
F(5)	C(17)	F(6)	110.6(10)	F(6)	C(17)	C(16)	113.8(9)
F(7)	C(18)	C(19)	111.4(11)	F(7)	C(18)	F(8)	109.6(12)
F(7)	C(18)	F(9)	103.3(9)	F(8)	C(18)	C(19)	115.5(8)
F(8)	C(18)	F(9)	104.9(13)	F(9)	C(18)	C(19)	111.3(10)
O(4)	C(19)	C(18)	114.7(7)	O(4)	C(19)	C(20)	127.8(6)
C(18)	C(19)	C(20)	117.5(7)	C(19)	C(20)	C(21)	121.1(6)
O(5)	C(21)	C(20)	128.4(6)	O(5)	C(21)	C(22)	116.1(7)
C(20)	C(21)	C(22)	115.5(7)	F(10)	C(22)	C(21)	107.7(13)
F(10)	C(22)	F(11)	104.6(16)	F(10)	C(22)	F(12)	93.7(11)
F(11)	C(22)	C(21)	119.7(8)	F(11)	C(22)	F(12)	112.1(14)
F(12)	C(22)	C(21)	114.9(14)	F(13)	C(23)	C(24)	117.9(12)
F(13)	C(23)	F(14)	108.1(19)	F(13)	C(23)	F(15)	100.5(14)
F(14)	C(23)	C(24)	116.4(12)	F(14)	C(23)	F(15)	103.1(15)
F(15)	C(23)	C(24)	108.6(15)	O(6)	C(24)	C(23)	115.8(9)
O(6)	C(24)	C(25)	128.3(7)	C(23)	C(24)	C(25)	115.9(9)
C(24)	C(25)	C(26)	121.6(7)	O(7)	C(26)	C(25)	127.3(7)
O(7)	C(26)	C(27)	115.9(7)	C(25)	C(26)	C(27)	116.8(7)
F(16)	C(27)	C(26)	109.7(9)	F(16)	C(27)	F(17)	97.3(11)
F(16)	C(27)	F(18)	103.4(12)	F(17)	C(27)	C(26)	117.3(10)
F(17)	C(27)	F(18)	111.4(11)	F(18)	C(27)	C(26)	115.1(10)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Sm(1)	O(2)	C(14)	-86.1(6)	O(6)	Sm(1)	O(2)	C(14)	-147.4(6)
O(7)	Sm(1)	O(2)	C(14)	79.2(7)	O(3)	Sm(1)	O(2)	C(14)	12.1(6)
O(5)	Sm(1)	O(2)	C(14)	-35.6(7)	N(3)	Sm(1)	O(2)	C(14)	103.3(6)
N(1)	Sm(1)	O(2)	C(14)	170.6(7)	O(4)	Sm(1)	O(3)	C(16)	52.9(6)
O(6)	Sm(1)	O(3)	C(16)	133.4(6)	O(7)	Sm(1)	O(3)	C(16)	-166.2(6)
O(5)	Sm(1)	O(3)	C(16)	122.3(6)	O(2)	Sm(1)	O(3)	C(16)	-20.6(6)
N(3)	Sm(1)	O(3)	C(16)	-94.0(6)	N(1)	Sm(1)	O(3)	C(16)	-50.2(7)
O(6)	Sm(1)	O(4)	C(19)	-70.7(7)	O(7)	Sm(1)	O(4)	C(19)	-19.6(9)
O(3)	Sm(1)	O(4)	C(19)	76.6(8)	O(5)	Sm(1)	O(4)	C(19)	5.7(7)
O(2)	Sm(1)	O(4)	C(19)	146.1(8)	N(3)	Sm(1)	O(4)	C(19)	162.7(7)
N(1)	Sm(1)	O(4)	C(19)	-146.5(7)	O(4)	Sm(1)	O(5)	C(21)	-4.1(7)
O(6)	Sm(1)	O(5)	C(21)	83.2(7)	O(7)	Sm(1)	O(5)	C(21)	159.5(7)
O(3)	Sm(1)	O(5)	C(21)	-103.1(7)	O(2)	Sm(1)	O(5)	C(21)	-56.1(7)
N(3)	Sm(1)	O(5)	C(21)	-165.4(6)	N(1)	Sm(1)	O(5)	C(21)	66.3(8)
O(4)	Sm(1)	O(6)	C(24)	130.6(7)	O(7)	Sm(1)	O(6)	C(24)	-18.3(6)

O(3)	Sm(1)	O(6)	C(24)	47.1(8)	O(5)	Sm(1)	O(6)	C(24)	58.1(7)
O(2)	Sm(1)	O(6)	C(24)	-170.6(6)	N(3)	Sm(1)	O(6)	C(24)	-78.5(7)
N(1)	Sm(1)	O(6)	C(24)	-130.3(7)	O(4)	Sm(1)	O(7)	C(26)	-38.5(7)
O(6)	Sm(1)	O(7)	C(26)	15.3(6)	O(3)	Sm(1)	O(7)	C(26)	-135.0(6)
O(5)	Sm(1)	O(7)	C(26)	-63.6(6)	O(2)	Sm(1)	O(7)	C(26)	164.3(5)
N(3)	Sm(1)	O(7)	C(26)	140.1(6)	N(1)	Sm(1)	O(7)	C(26)	85.7(6)
O(4)	Sm(1)	N(1)	C(1)	-140.6(5)	O(6)	Sm(1)	N(1)	C(1)	138.7(5)
O(7)	Sm(1)	N(1)	C(1)	71.3(5)	O(3)	Sm(1)	N(1)	C(1)	-39.2(6)
O(5)	Sm(1)	N(1)	C(1)	155.5(4)	O(2)	Sm(1)	N(1)	C(1)	-69.0(5)
N(3)	Sm(1)	N(1)	C(1)	11.2(4)	O(4)	Sm(1)	N(1)	C(7)	26.0(6)
O(6)	Sm(1)	N(1)	C(7)	-54.7(6)	O(7)	Sm(1)	N(1)	C(7)	-122.0(6)
O(3)	Sm(1)	N(1)	C(7)	127.4(6)	O(5)	Sm(1)	N(1)	C(7)	-37.9(8)
O(2)	Sm(1)	N(1)	C(7)	97.6(6)	N(3)	Sm(1)	N(1)	C(7)	177.9(7)
O(4)	Sm(1)	N(3)	C(6)	-124.8(5)	O(6)	Sm(1)	N(3)	C(6)	117.1(5)
O(7)	Sm(1)	N(3)	C(6)	56.8(5)	O(3)	Sm(1)	N(3)	C(6)	-36.6(5)
O(5)	Sm(1)	N(3)	C(6)	21.6(6)	O(2)	Sm(1)	N(3)	C(6)	-108.0(5)
N(1)	Sm(1)	N(3)	C(6)	176.0(5)	O(4)	Sm(1)	N(3)	C(2)	52.1(6)
O(6)	Sm(1)	N(3)	C(2)	-66.0(5)	O(7)	Sm(1)	N(3)	C(2)	-126.4(5)
O(3)	Sm(1)	N(3)	C(2)	140.3(4)	O(5)	Sm(1)	N(3)	C(2)	-161.6(4)
O(2)	Sm(1)	N(3)	C(2)	68.9(4)	N(1)	Sm(1)	N(3)	C(2)	-7.1(4)
C(7)	N(1)	C(1)	N(2)	-7.8(8)	Sm(1)	N(1)	C(1)	N(2)	161.9(4)
C(7)	N(1)	C(1)	C(2)	174.7(6)	Sm(1)	N(1)	C(1)	C(2)	-15.6(8)
O(1)	N(2)	C(1)	N(1)	-179.5(7)	C(8)	N(2)	C(1)	N(1)	-11.2(9)
O(1)	N(2)	C(1)	C(2)	-2.1(12)	C(8)	N(2)	C(1)	C(2)	166.2(7)
C(6)	N(3)	C(2)	C(3)	-0.6(9)	Sm(1)	N(3)	C(2)	C(3)	-177.5(5)
C(6)	N(3)	C(2)	C(1)	179.9(6)	Sm(1)	N(3)	C(2)	C(1)	3.0(7)
N(1)	C(1)	C(2)	N(3)	8.7(9)	N(2)	C(1)	C(2)	N(3)	-168.4(6)
N(1)	C(1)	C(2)	C(3)	-170.8(7)	N(2)	C(1)	C(2)	C(3)	12.1(10)
N(3)	C(2)	C(3)	C(4)	0.6(10)	C(1)	C(2)	C(3)	C(4)	180.0(7)
C(2)	C(3)	C(4)	C(5)	-0.4(12)	C(3)	C(4)	C(5)	C(6)	0.3(12)
C(2)	N(3)	C(6)	C(5)	0.5(10)	Sm(1)	N(3)	C(6)	C(5)	177.5(5)
C(4)	C(5)	C(6)	N(3)	-0.4(12)	C(1)	N(1)	C(7)	C(10)	144.2(7)
Sm(1)	N(1)	C(7)	C(10)	-23.3(10)	C(1)	N(1)	C(7)	C(9)	-97.1(7)
Sm(1)	N(1)	C(7)	C(9)	95.4(7)	C(1)	N(1)	C(7)	C(8)	22.7(8)
Sm(1)	N(1)	C(7)	C(8)	-144.8(5)	O(1)	N(2)	C(8)	C(11)	-44.9(14)
C(1)	N(2)	C(8)	C(11)	146.7(10)	O(1)	N(2)	C(8)	C(12)	73.2(10)
C(1)	N(2)	C(8)	C(12)	-95.2(9)	O(1)	N(2)	C(8)	C(7)	-168.0(8)
C(1)	N(2)	C(8)	C(7)	23.6(8)	N(1)	C(7)	C(8)	N(2)	-26.6(8)
C(10)	C(7)	C(8)	N(2)	-145.3(7)	C(9)	C(7)	C(8)	N(2)	87.1(8)
N(1)	C(7)	C(8)	C(11)	-144.4(8)	C(10)	C(7)	C(8)	C(11)	96.9(11)
C(9)	C(7)	C(8)	C(11)	-30.7(11)	N(1)	C(7)	C(8)	C(12)	85.4(9)

C(10)	C(7)	C(8)	C(12)	-33.2(11)	C(9)	C(7)	C(8)	C(12)	-160.8(8)
Sm(1)	O(2)	C(14)	C(15)	-2.4(11)	Sm(1)	O(2)	C(14)	C(13)	176.5(6)
F(2)	C(13)	C(14)	O(2)	-63.2(11)	F(3)	C(13)	C(14)	O(2)	56.9(11)
F(1)	C(13)	C(14)	O(2)	177.6(9)	F(2)	C(13)	C(14)	C(15)	115.9(10)
F(3)	C(13)	C(14)	C(15)	-124.0(10)	F(1)	C(13)	C(14)	C(15)	-3.4(13)
O(2)	C(14)	C(15)	C(16)	-8.4(12)	C(13)	C(14)	C(15)	C(16)	172.7(8)
Sm(1)	O(3)	C(16)	C(15)	20.7(11)	Sm(1)	O(3)	C(16)	C(17)	-159.5(6)
C(14)	C(15)	C(16)	O(3)	-0.7(13)	C(14)	C(15)	C(16)	C(17)	179.4(8)
O(3)	C(16)	C(17)	F(5)	49.4(13)	C(15)	C(16)	C(17)	F(5)	-130.7(10)
O(3)	C(16)	C(17)	F(6)	175.5(9)	C(15)	C(16)	C(17)	F(6)	-4.6(14)
O(3)	C(16)	C(17)	F(4)	-65.3(11)	C(15)	C(16)	C(17)	F(4)	114.6(10)
Sm(1)	O(4)	C(19)	C(20)	-4.9(14)	Sm(1)	O(4)	C(19)	C(18)	176.3(8)
F(8)	C(18)	C(19)	O(4)	176.7(12)	F(9)	C(18)	C(19)	O(4)	-63.8(14)
F(7)	C(18)	C(19)	O(4)	50.9(15)	F(8)	C(18)	C(19)	C(20)	-2.2(19)
F(9)	C(18)	C(19)	C(20)	117.2(10)	F(7)	C(18)	C(19)	C(20)	-128.1(10)
O(4)	C(19)	C(20)	C(21)	-0.7(15)	C(18)	C(19)	C(20)	C(21)	178.1(10)
Sm(1)	O(5)	C(21)	C(20)	1.7(13)	Sm(1)	O(5)	C(21)	C(22)	179.7(10)
C(19)	C(20)	C(21)	O(5)	2.1(15)	C(19)	C(20)	C(21)	C(22)	-175.8(12)
O(5)	C(21)	C(22)	F(12)	-60(2)	C(20)	C(21)	C(22)	F(12)	118.4(17)
O(5)	C(21)	C(22)	F(11)	162.2(15)	C(20)	C(21)	C(22)	F(11)	-20(2)
O(5)	C(21)	C(22)	F(10)	43(2)	C(20)	C(21)	C(22)	F(10)	-138.7(14)
Sm(1)	O(6)	C(24)	C(25)	16.2(13)	Sm(1)	O(6)	C(24)	C(23)	-166.4(10)
F(14)	C(23)	C(24)	O(6)	-46(3)	F(13)	C(23)	C(24)	O(6)	-177.1(16)
F(15)	C(23)	C(24)	O(6)	69.6(18)	F(14)	C(23)	C(24)	C(25)	132(2)
F(13)	C(23)	C(24)	C(25)	1(2)	F(15)	C(23)	C(24)	C(25)	-112.6(15)
O(6)	C(24)	C(25)	C(26)	-0.1(14)	C(23)	C(24)	C(25)	C(26)	-177.5(11)
Sm(1)	O(7)	C(26)	C(25)	-9.5(11)	Sm(1)	O(7)	C(26)	C(27)	169.6(7)
C(24)	C(25)	C(26)	O(7)	-3.4(13)	C(24)	C(25)	C(26)	C(27)	177.6(9)
O(7)	C(26)	C(27)	F(18)	-57.1(15)	C(25)	C(26)	C(27)	F(18)	122.0(12)
O(7)	C(26)	C(27)	F(17)	168.7(10)	C(25)	C(26)	C(27)	F(17)	-12.1(16)
O(7)	C(26)	C(27)	F(16)	59.0(13)	C(25)	C(26)	C(27)	F(16)	-121.9(11)

•[Gd(hfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Gd(1)	O(2)	2.401(4)	Gd(1)	O(3)	2.346(4)
Gd(1)	O(4)	2.328(4)	Gd(1)	O(5)	2.417(4)
Gd(1)	O(6)	2.354(4)	Gd(1)	O(7)	2.349(4)
Gd(1)	N(1)	2.540(5)	Gd(1)	N(3)	2.553(4)
F(1)	C(13)	1.310(11)	F(2)	C(13)	1.303(11)

F(3)	C(13)	1.287(12)	F(4)	C(17)	1.326(13)
F(5)	C(17)	1.296(11)	F(6)	C(17)	1.288(10)
F(7)	C(18)	1.279(10)	F(8)	C(18)	1.280(12)
F(9)	C(18)	1.306(13)	F(10)	C(22)	1.298(15)
F(11)	C(22)	1.219(9)	F(12)	C(22)	1.190(16)
F(13)	C(23)	1.258(13)	F(14)	C(23)	1.140(14)
F(15)	C(23)	1.252(15)	F(16)	C(27)	1.321(12)
F(17)	C(27)	1.260(10)	F(18)	C(27)	1.201(10)
O(1)	N(2)	1.282(7)	O(2)	C(14)	1.230(7)
O(3)	C(16)	1.268(7)	O(4)	C(19)	1.243(7)
O(5)	C(21)	1.222(7)	O(6)	C(24)	1.251(8)
O(7)	C(26)	1.237(7)	N(1)	C(1)	1.287(7)
N(1)	C(7)	1.507(7)	N(2)	C(1)	1.388(7)
N(2)	C(8)	1.487(9)	N(3)	C(2)	1.339(6)
N(3)	C(6)	1.323(7)	C(1)	C(2)	1.480(8)
C(2)	C(3)	1.388(8)	C(3)	C(4)	1.377(9)
C(4)	C(5)	1.354(9)	C(5)	C(6)	1.396(8)
C(7)	C(8)	1.570(11)	C(7)	C(9)	1.520(10)
C(7)	C(10)	1.498(9)	C(8)	C(11)	1.510(10)
C(8)	C(12)	1.478(12)	C(13)	C(14)	1.532(10)
C(14)	C(15)	1.394(9)	C(15)	C(16)	1.361(9)
C(16)	C(17)	1.518(11)	C(18)	C(19)	1.534(10)
C(19)	C(20)	1.375(9)	C(20)	C(21)	1.388(9)
C(21)	C(22)	1.511(9)	C(23)	C(24)	1.508(11)
C(24)	C(25)	1.373(10)	C(25)	C(26)	1.388(10)
C(26)	C(27)	1.502(10)			

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Gd(1)	O(3)	72.00(15)	O(2)	Gd(1)	O(4)	74.78(15)
O(2)	Gd(1)	O(5)	128.64(15)	O(2)	Gd(1)	O(6)	136.87(15)
O(2)	Gd(1)	O(7)	142.03(14)	O(2)	Gd(1)	N(1)	70.06(15)
O(2)	Gd(1)	N(3)	72.89(15)	O(3)	Gd(1)	O(5)	72.35(15)
O(3)	Gd(1)	O(6)	146.68(15)	O(3)	Gd(1)	O(7)	90.83(14)
O(3)	Gd(1)	N(1)	136.63(15)	O(3)	Gd(1)	N(3)	84.98(15)
O(4)	Gd(1)	O(3)	93.78(15)	O(4)	Gd(1)	O(5)	72.00(13)
O(4)	Gd(1)	O(6)	82.39(15)	O(4)	Gd(1)	O(7)	141.57(14)
O(4)	Gd(1)	N(1)	95.86(14)	O(4)	Gd(1)	N(3)	146.36(14)
O(5)	Gd(1)	O(6)	75.03(15)	O(5)	Gd(1)	O(7)	73.21(14)
O(5)	Gd(1)	N(1)	150.35(16)	O(5)	Gd(1)	N(3)	137.83(14)
O(6)	Gd(1)	O(7)	73.31(14)	O(6)	Gd(1)	N(1)	76.62(16)

O(6)	Gd(1)	N(3)	115.98(15)	O(7)	Gd(1)	N(1)	106.58(15)
O(7)	Gd(1)	N(3)	72.05(13)	N(1)	Gd(1)	N(3)	64.43(14)
Gd(1)	O(2)	C(14)	133.9(4)	Gd(1)	O(3)	C(16)	133.1(4)
Gd(1)	O(4)	C(19)	136.1(4)	Gd(1)	O(5)	C(21)	133.8(4)
Gd(1)	O(6)	C(24)	132.4(4)	Gd(1)	O(7)	C(26)	133.6(4)
Gd(1)	N(1)	C(1)	117.3(4)	Gd(1)	N(1)	C(7)	133.6(4)
C(1)	N(1)	C(7)	108.2(5)	O(1)	N(2)	C(1)	126.3(6)
O(1)	N(2)	C(8)	122.9(6)	C(1)	N(2)	C(8)	108.7(5)
Gd(1)	N(3)	C(2)	120.5(4)	Gd(1)	N(3)	C(6)	121.0(4)
C(2)	N(3)	C(6)	118.4(5)	N(1)	C(1)	C(2)	122.6(5)
N(1)	C(1)	N(2)	112.9(5)	N(2)	C(1)	C(2)	124.4(5)
C(1)	C(2)	C(3)	124.6(5)	N(3)	C(2)	C(1)	113.4(5)
N(3)	C(2)	C(3)	122.0(5)	C(2)	C(3)	C(4)	118.7(6)
C(3)	C(4)	C(5)	119.5(6)	C(4)	C(5)	C(6)	118.7(6)
N(3)	C(6)	C(5)	122.7(6)	C(10)	C(7)	N(1)	110.0(5)
C(8)	C(7)	C(10)	112.0(7)	C(8)	C(7)	C(9)	113.2(7)
C(9)	C(7)	C(10)	112.1(8)	N(1)	C(7)	C(8)	102.3(5)
N(1)	C(7)	C(9)	106.7(6)	C(11)	C(8)	C(12)	108.9(9)
C(7)	C(8)	C(11)	116.2(9)	C(7)	C(8)	C(12)	114.8(7)
N(2)	C(8)	C(11)	110.0(7)	N(2)	C(8)	C(12)	107.9(8)
N(2)	C(8)	C(7)	98.2(6)	F(1)	C(13)	C(14)	113.0(9)
F(1)	C(13)	F(2)	105.7(9)	F(1)	C(13)	F(3)	108.9(9)
F(2)	C(13)	C(14)	110.2(8)	F(2)	C(13)	F(3)	109.0(10)
F(3)	C(13)	C(14)	109.9(8)	C(13)	C(14)	C(15)	118.8(7)
O(2)	C(14)	C(13)	113.6(7)	O(2)	C(14)	C(15)	127.6(6)
C(14)	C(15)	C(16)	121.6(6)	C(15)	C(16)	C(17)	118.5(7)
O(3)	C(16)	C(15)	128.1(6)	O(3)	C(16)	C(17)	113.4(7)
F(4)	C(17)	C(16)	110.7(9)	F(4)	C(17)	F(5)	102.1(10)
F(4)	C(17)	F(6)	106.4(9)	F(5)	C(17)	C(16)	111.7(8)
F(5)	C(17)	F(6)	110.6(9)	F(6)	C(17)	C(16)	114.6(9)
F(7)	C(18)	C(19)	113.7(8)	F(7)	C(18)	F(8)	104.3(11)
F(7)	C(18)	F(9)	110.1(10)	F(8)	C(18)	C(19)	112.1(9)
F(8)	C(18)	F(9)	105.5(9)	F(9)	C(18)	C(19)	110.6(10)
C(18)	C(19)	C(20)	118.6(7)	O(4)	C(19)	C(18)	113.0(6)
O(4)	C(19)	C(20)	128.3(6)	C(19)	C(20)	C(21)	121.2(6)
C(20)	C(21)	C(22)	115.4(6)	O(5)	C(21)	C(20)	128.3(6)
O(5)	C(21)	C(22)	116.2(6)	F(10)	C(22)	C(21)	108.8(11)
F(10)	C(22)	F(11)	106.4(14)	F(10)	C(22)	F(12)	93.8(10)
F(11)	C(22)	C(21)	119.2(7)	F(11)	C(22)	F(12)	111.1(13)
F(12)	C(22)	C(21)	114.2(12)	F(13)	C(23)	C(24)	115.7(11)
F(13)	C(23)	F(14)	105.2(15)	F(13)	C(23)	F(15)	97.8(11)

F(14)	C(23)	C(24)	118.3(11)	F(14)	C(23)	F(15)	107.1(14)
F(15)	C(23)	C(24)	110.5(12)	C(23)	C(24)	C(25)	118.6(8)
O(6)	C(24)	C(23)	114.0(8)	O(6)	C(24)	C(25)	127.3(6)
C(24)	C(25)	C(26)	123.0(6)	C(25)	C(26)	C(27)	117.3(7)
O(7)	C(26)	C(25)	127.3(6)	O(7)	C(26)	C(27)	115.4(7)
F(16)	C(27)	C(26)	109.4(8)	F(16)	C(27)	F(17)	97.8(10)
F(16)	C(27)	F(18)	102.9(10)	F(17)	C(27)	C(26)	117.5(8)
F(17)	C(27)	F(18)	111.2(9)	F(18)	C(27)	C(26)	115.5(9)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Gd(1)	O(2)	C(14)	-86.7(6)	O(3)	Gd(1)	O(2)	C(14)	12.5(6)
O(7)	Gd(1)	O(2)	C(14)	79.4(6)	O(6)	Gd(1)	O(2)	C(14)	-147.3(5)
O(5)	Gd(1)	O(2)	C(14)	-35.6(7)	N(1)	Gd(1)	O(2)	C(14)	171.1(6)
N(3)	Gd(1)	O(2)	C(14)	102.7(6)	O(4)	Gd(1)	O(3)	C(16)	51.6(6)
O(7)	Gd(1)	O(3)	C(16)	-166.5(6)	O(6)	Gd(1)	O(3)	C(16)	133.5(5)
O(2)	Gd(1)	O(3)	C(16)	-21.0(5)	O(5)	Gd(1)	O(3)	C(16)	121.4(6)
N(1)	Gd(1)	O(3)	C(16)	-51.0(6)	N(3)	Gd(1)	O(3)	C(16)	-94.6(6)
O(3)	Gd(1)	O(4)	C(19)	76.1(7)	O(7)	Gd(1)	O(4)	C(19)	-20.1(8)
O(6)	Gd(1)	O(4)	C(19)	-70.7(7)	O(2)	Gd(1)	O(4)	C(19)	146.3(7)
O(5)	Gd(1)	O(4)	C(19)	6.0(6)	N(1)	Gd(1)	O(4)	C(19)	-146.3(7)
N(3)	Gd(1)	O(4)	C(19)	162.7(6)	O(4)	Gd(1)	O(5)	C(21)	-4.8(6)
O(3)	Gd(1)	O(5)	C(21)	-104.9(6)	O(7)	Gd(1)	O(5)	C(21)	158.6(6)
O(6)	Gd(1)	O(5)	C(21)	81.9(6)	O(2)	Gd(1)	O(5)	C(21)	-57.0(7)
N(1)	Gd(1)	O(5)	C(21)	64.5(7)	N(3)	Gd(1)	O(5)	C(21)	-165.7(6)
O(4)	Gd(1)	O(6)	C(24)	131.1(6)	O(3)	Gd(1)	O(6)	C(24)	45.8(7)
O(7)	Gd(1)	O(6)	C(24)	-18.8(6)	O(2)	Gd(1)	O(6)	C(24)	-171.0(5)
O(5)	Gd(1)	O(6)	C(24)	57.7(6)	N(1)	Gd(1)	O(6)	C(24)	-131.0(6)
N(3)	Gd(1)	O(6)	C(24)	-78.6(6)	O(4)	Gd(1)	O(7)	C(26)	-38.3(6)
O(3)	Gd(1)	O(7)	C(26)	-135.4(6)	O(6)	Gd(1)	O(7)	C(26)	14.8(5)
O(2)	Gd(1)	O(7)	C(26)	163.5(5)	O(5)	Gd(1)	O(7)	C(26)	-64.2(5)
N(1)	Gd(1)	O(7)	C(26)	84.9(6)	N(3)	Gd(1)	O(7)	C(26)	140.1(6)
O(4)	Gd(1)	N(1)	C(1)	-140.3(4)	O(3)	Gd(1)	N(1)	C(1)	-38.4(5)
O(7)	Gd(1)	N(1)	C(1)	71.3(4)	O(6)	Gd(1)	N(1)	C(1)	139.0(5)
O(2)	Gd(1)	N(1)	C(1)	-68.8(4)	O(5)	Gd(1)	N(1)	C(1)	156.3(4)
N(3)	Gd(1)	N(1)	C(1)	11.2(4)	O(4)	Gd(1)	N(1)	C(7)	27.7(6)
O(3)	Gd(1)	N(1)	C(7)	129.6(5)	O(7)	Gd(1)	N(1)	C(7)	-120.7(6)
O(6)	Gd(1)	N(1)	C(7)	-53.0(6)	O(2)	Gd(1)	N(1)	C(7)	99.2(6)
O(5)	Gd(1)	N(1)	C(7)	-35.7(7)	N(3)	Gd(1)	N(1)	C(7)	179.2(6)
O(4)	Gd(1)	N(3)	C(6)	-125.0(5)	O(3)	Gd(1)	N(3)	C(6)	-35.7(5)
O(7)	Gd(1)	N(3)	C(6)	56.8(5)	O(6)	Gd(1)	N(3)	C(6)	117.2(5)

O(2)	Gd(1)	N(3)	C(6)	-108.4(5)	O(5)	Gd(1)	N(3)	C(6)	20.9(6)
N(1)	Gd(1)	N(3)	C(6)	176.0(5)	O(4)	Gd(1)	N(3)	C(2)	52.0(5)
O(3)	Gd(1)	N(3)	C(2)	141.3(4)	O(7)	Gd(1)	N(3)	C(2)	-126.2(4)
O(6)	Gd(1)	N(3)	C(2)	-65.8(4)	O(2)	Gd(1)	N(3)	C(2)	68.6(4)
O(5)	Gd(1)	N(3)	C(2)	-162.1(4)	N(1)	Gd(1)	N(3)	C(2)	-7.0(4)
C(7)	N(1)	C(1)	N(2)	-7.6(8)	Gd(1)	N(1)	C(1)	N(2)	163.3(4)
C(7)	N(1)	C(1)	C(2)	173.7(5)	Gd(1)	N(1)	C(1)	C(2)	-15.4(7)
O(1)	N(2)	C(1)	N(1)	-177.3(7)	C(8)	N(2)	C(1)	N(1)	-13.7(9)
O(1)	N(2)	C(1)	C(2)	1.4(11)	C(8)	N(2)	C(1)	C(2)	165.0(6)
C(6)	N(3)	C(2)	C(3)	-2.2(9)	Gd(1)	N(3)	C(2)	C(3)	-179.2(4)
C(6)	N(3)	C(2)	C(1)	179.9(5)	Gd(1)	N(3)	C(2)	C(1)	2.8(6)
N(1)	C(1)	C(2)	N(3)	8.6(8)	N(2)	C(1)	C(2)	N(3)	-169.9(6)
N(1)	C(1)	C(2)	C(3)	-169.3(6)	N(2)	C(1)	C(2)	C(3)	12.2(10)
N(3)	C(2)	C(3)	C(4)	3.3(10)	C(1)	C(2)	C(3)	C(4)	-179.0(6)
C(2)	C(3)	C(4)	C(5)	-2.8(11)	C(3)	C(4)	C(5)	C(6)	1.4(11)
C(2)	N(3)	C(6)	C(5)	0.7(10)	Gd(1)	N(3)	C(6)	C(5)	177.8(5)
C(4)	C(5)	C(6)	N(3)	-0.4(11)	C(1)	N(1)	C(7)	C(10)	143.3(7)
Gd(1)	N(1)	C(7)	C(10)	-25.5(9)	C(1)	N(1)	C(7)	C(9)	-94.9(7)
Gd(1)	N(1)	C(7)	C(9)	96.3(7)	C(1)	N(1)	C(7)	C(8)	24.2(7)
Gd(1)	N(1)	C(7)	C(8)	-144.6(5)	O(1)	N(2)	C(8)	C(11)	-47.1(13)
C(1)	N(2)	C(8)	C(11)	148.6(9)	O(1)	N(2)	C(8)	C(12)	71.5(10)
C(1)	N(2)	C(8)	C(12)	-92.7(8)	O(1)	N(2)	C(8)	C(7)	-169.0(7)
C(1)	N(2)	C(8)	C(7)	26.8(8)	C(10)	C(7)	C(8)	N(2)	-147.0(7)
N(1)	C(7)	C(8)	N(2)	-29.3(7)	C(9)	C(7)	C(8)	N(2)	85.1(7)
C(10)	C(7)	C(8)	C(11)	95.8(10)	N(1)	C(7)	C(8)	C(11)	-146.5(8)
C(9)	C(7)	C(8)	C(11)	-32.1(10)	C(10)	C(7)	C(8)	C(12)	-32.8(10)
N(1)	C(7)	C(8)	C(12)	84.9(8)	C(9)	C(7)	C(8)	C(12)	-160.8(8)
Gd(1)	O(2)	C(14)	C(15)	-2.4(10)	Gd(1)	O(2)	C(14)	C(13)	176.4(6)
F(3)	C(13)	C(14)	O(2)	56.8(11)	F(2)	C(13)	C(14)	O(2)	-63.3(11)
F(1)	C(13)	C(14)	O(2)	178.7(8)	F(3)	C(13)	C(14)	C(15)	-124.3(9)
F(2)	C(13)	C(14)	C(15)	115.6(10)	F(1)	C(13)	C(14)	C(15)	-2.5(13)
O(2)	C(14)	C(15)	C(16)	-8.9(11)	C(13)	C(14)	C(15)	C(16)	172.4(7)
Gd(1)	O(3)	C(16)	C(15)	20.7(11)	Gd(1)	O(3)	C(16)	C(17)	-158.8(6)
C(14)	C(15)	C(16)	O(3)	-0.3(12)	C(14)	C(15)	C(16)	C(17)	179.2(8)
O(3)	C(16)	C(17)	F(6)	175.8(9)	C(15)	C(16)	C(17)	F(6)	-3.7(14)
O(3)	C(16)	C(17)	F(5)	49.1(12)	C(15)	C(16)	C(17)	F(5)	-130.4(9)
O(3)	C(16)	C(17)	F(4)	-63.9(10)	C(15)	C(16)	C(17)	F(4)	116.6(9)
Gd(1)	O(4)	C(19)	C(20)	-5.4(13)	Gd(1)	O(4)	C(19)	C(18)	176.2(7)
F(7)	C(18)	C(19)	O(4)	176.9(10)	F(8)	C(18)	C(19)	O(4)	-65.1(12)
F(9)	C(18)	C(19)	O(4)	52.3(12)	F(7)	C(18)	C(19)	C(20)	-1.7(16)
F(8)	C(18)	C(19)	C(20)	116.3(10)	F(9)	C(18)	C(19)	C(20)	-126.2(9)

O(4)	C(19)	C(20)	C(21)	0.0(14)	C(18)	C(19)	C(20)	C(21)	178.3(9)
Gd(1)	O(5)	C(21)	C(20)	3.0(12)	Gd(1)	O(5)	C(21)	C(22)	180.0(8)
C(19)	C(20)	C(21)	O(5)	1.0(13)	C(19)	C(20)	C(21)	C(22)	-176.0(10)
O(5)	C(21)	C(22)	F(12)	-62.6(19)	C(20)	C(21)	C(22)	F(12)	114.8(14)
O(5)	C(21)	C(22)	F(11)	162.7(13)	C(20)	C(21)	C(22)	F(11)	-20(2)
O(5)	C(21)	C(22)	F(10)	40.6(18)	C(20)	C(21)	C(22)	F(10)	-142.0(13)
Gd(1)	O(6)	C(24)	C(25)	18.2(12)	Gd(1)	O(6)	C(24)	C(23)	-166.3(8)
F(14)	C(23)	C(24)	O(6)	-52(2)	F(15)	C(23)	C(24)	O(6)	71.9(15)
F(13)	C(23)	C(24)	O(6)	-178.2(13)	F(14)	C(23)	C(24)	C(25)	123.9(17)
F(15)	C(23)	C(24)	C(25)	-112.2(14)	F(13)	C(23)	C(24)	C(25)	-2.3(19)
O(6)	C(24)	C(25)	C(26)	-2.9(13)	C(23)	C(24)	C(25)	C(26)	-178.2(9)
Gd(1)	O(7)	C(26)	C(25)	-9.6(10)	Gd(1)	O(7)	C(26)	C(27)	170.1(6)
C(24)	C(25)	C(26)	O(7)	-1.6(12)	C(24)	C(25)	C(26)	C(27)	178.7(8)
O(7)	C(26)	C(27)	F(18)	-57.9(13)	C(25)	C(26)	C(27)	F(18)	121.8(11)
O(7)	C(26)	C(27)	F(17)	167.8(9)	C(25)	C(26)	C(27)	F(17)	-12.5(14)
O(7)	C(26)	C(27)	F(16)	57.6(12)	C(25)	C(26)	C(27)	F(16)	-122.7(10)

•[Dy(hfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Dy(1)	O(2)	2.387(4)	Dy(1)	O(3)	2.316(4)
Dy(1)	O(4)	2.295(4)	Dy(1)	O(5)	2.384(3)
Dy(1)	O(6)	2.336(4)	Dy(1)	O(7)	2.321(4)
Dy(1)	N(1)	2.519(4)	Dy(1)	N(3)	2.526(4)
F(1)	C(13)	1.305(11)	F(2)	C(13)	1.301(11)
F(3)	C(13)	1.286(11)	F(4)	C(17)	1.338(12)
F(5)	C(17)	1.305(10)	F(6)	C(17)	1.297(10)
F(7)	C(18)	1.265(9)	F(8)	C(18)	1.293(11)
F(9)	C(18)	1.322(12)	F(10)	C(22)	1.251(14)
F(11)	C(22)	1.215(8)	F(12)	C(22)	1.258(16)
F(13)	C(23)	1.202(14)	F(14)	C(23)	1.187(15)
F(15)	C(23)	1.214(13)	F(16)	C(27)	1.343(12)
F(17)	C(27)	1.264(10)	F(18)	C(27)	1.170(10)
O(1)	N(2)	1.295(7)	O(2)	C(14)	1.231(7)
O(3)	C(16)	1.254(7)	O(4)	C(19)	1.245(7)
O(5)	C(21)	1.236(6)	O(6)	C(24)	1.258(7)
O(7)	C(26)	1.246(6)	N(1)	C(1)	1.295(7)
N(1)	C(7)	1.503(7)	N(2)	C(1)	1.382(7)
N(2)	C(8)	1.471(9)	N(3)	C(2)	1.347(6)
N(3)	C(6)	1.331(6)	C(1)	C(2)	1.484(7)

C(2)	C(3)	1.372(7)	C(3)	C(4)	1.395(9)
C(4)	C(5)	1.367(9)	C(5)	C(6)	1.386(8)
C(7)	C(10)	1.514(11)	C(7)	C(8)	1.562(10)
C(7)	C(9)	1.523(9)	C(8)	C(11)	1.511(10)
C(8)	C(12)	1.522(13)	C(13)	C(14)	1.545(9)
C(14)	C(15)	1.386(9)	C(15)	C(16)	1.393(9)
C(16)	C(17)	1.499(10)	C(18)	C(19)	1.532(9)
C(19)	C(20)	1.368(8)	C(20)	C(21)	1.373(8)
C(21)	C(22)	1.523(8)	C(23)	C(24)	1.486(10)
C(24)	C(25)	1.364(10)	C(25)	C(26)	1.394(9)
C(26)	C(27)	1.519(9)			

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Dy(1)	O(3)	72.68(14)	O(2)	Dy(1)	O(4)	74.39(15)
O(2)	Dy(1)	O(5)	129.40(14)	O(2)	Dy(1)	O(6)	135.73(15)
O(2)	Dy(1)	O(7)	141.82(13)	O(2)	Dy(1)	N(1)	69.85(15)
O(2)	Dy(1)	N(3)	72.60(14)	O(3)	Dy(1)	O(4)	93.86(14)
O(3)	Dy(1)	O(5)	72.48(14)	O(3)	Dy(1)	O(6)	146.79(14)
O(3)	Dy(1)	O(7)	90.84(14)	O(3)	Dy(1)	N(1)	136.99(15)
O(3)	Dy(1)	N(3)	84.20(14)	O(4)	Dy(1)	O(5)	72.60(13)
O(4)	Dy(1)	O(6)	81.82(15)	O(4)	Dy(1)	O(7)	142.42(13)
O(4)	Dy(1)	N(1)	95.71(14)	O(4)	Dy(1)	N(3)	145.95(13)
O(5)	Dy(1)	O(6)	74.84(15)	O(5)	Dy(1)	O(7)	73.41(13)
O(5)	Dy(1)	N(1)	149.97(15)	O(5)	Dy(1)	N(3)	137.27(12)
O(6)	Dy(1)	O(7)	74.24(14)	O(6)	Dy(1)	N(1)	76.17(16)
O(6)	Dy(1)	N(3)	117.22(14)	O(7)	Dy(1)	N(1)	105.90(15)
O(7)	Dy(1)	N(3)	71.62(12)	N(1)	Dy(1)	N(3)	65.14(13)
Dy(1)	O(2)	C(14)	133.0(4)	Dy(1)	O(3)	C(16)	134.0(4)
Dy(1)	O(4)	C(19)	135.8(4)	Dy(1)	O(5)	C(21)	133.8(3)
Dy(1)	O(6)	C(24)	132.0(4)	Dy(1)	O(7)	C(26)	132.9(4)
Dy(1)	N(1)	C(1)	117.0(4)	Dy(1)	N(1)	C(7)	134.1(3)
Dy(1)	N(3)	C(2)	120.8(3)	Dy(1)	N(3)	C(6)	121.8(3)
O(1)	N(2)	C(1)	125.0(6)	O(1)	N(2)	C(8)	123.1(5)
C(1)	N(1)	C(7)	108.1(4)	C(1)	N(2)	C(8)	110.4(5)
C(2)	N(3)	C(6)	117.4(4)	N(1)	C(1)	C(2)	122.6(5)
N(1)	C(1)	N(2)	112.0(5)	N(2)	C(1)	C(2)	125.4(5)
C(3)	C(2)	C(1)	123.8(5)	N(3)	C(2)	C(1)	112.8(4)
N(3)	C(2)	C(3)	123.3(5)	C(2)	C(3)	C(4)	117.9(5)
C(3)	C(4)	C(5)	119.7(5)	C(4)	C(5)	C(6)	118.3(6)
N(3)	C(6)	C(5)	123.3(5)	C(8)	C(7)	C(10)	113.5(6)

C(8)	C(7)	C(9)	113.0(6)	C(9)	C(7)	C(10)	110.9(7)
N(1)	C(7)	C(10)	106.6(6)	N(1)	C(7)	C(8)	103.2(5)
N(1)	C(7)	C(9)	109.1(5)	C(11)	C(8)	C(12)	110.6(9)
C(7)	C(8)	C(11)	115.7(8)	C(7)	C(8)	C(12)	113.6(7)
N(2)	C(8)	C(11)	110.7(7)	N(2)	C(8)	C(12)	107.4(8)
N(2)	C(8)	C(7)	98.0(5)	F(1)	C(13)	C(14)	112.9(8)
F(1)	C(13)	F(2)	107.6(8)	F(1)	C(13)	F(3)	108.9(8)
F(2)	C(13)	C(14)	110.7(7)	F(2)	C(13)	F(3)	107.2(9)
F(3)	C(13)	C(14)	109.4(7)	C(13)	C(14)	C(15)	118.3(6)
O(2)	C(14)	C(13)	113.4(7)	O(2)	C(14)	C(15)	128.3(6)
C(14)	C(15)	C(16)	121.1(6)	C(15)	C(16)	C(17)	118.4(6)
O(3)	C(16)	C(15)	127.0(6)	O(3)	C(16)	C(17)	114.6(6)
F(4)	C(17)	C(16)	110.5(8)	F(4)	C(17)	F(5)	101.4(9)
F(4)	C(17)	F(6)	105.2(8)	F(5)	C(17)	C(16)	113.3(7)
F(5)	C(17)	F(6)	109.9(8)	F(6)	C(17)	C(16)	115.3(8)
F(7)	C(18)	C(19)	115.5(7)	F(7)	C(18)	F(8)	105.1(10)
F(7)	C(18)	F(9)	110.3(9)	F(8)	C(18)	C(19)	111.6(8)
F(8)	C(18)	F(9)	102.4(8)	F(9)	C(18)	C(19)	111.0(8)
C(18)	C(19)	C(20)	118.1(6)	O(4)	C(19)	C(18)	113.6(5)
O(4)	C(19)	C(20)	128.2(5)	C(19)	C(20)	C(21)	121.7(5)
C(20)	C(21)	C(22)	117.2(5)	O(5)	C(21)	C(20)	127.5(5)
O(5)	C(21)	C(22)	115.3(6)	F(10)	C(22)	C(21)	112.4(9)
F(10)	C(22)	F(11)	112.9(12)	F(10)	C(22)	F(12)	94.1(10)
F(11)	C(22)	C(21)	119.1(7)	F(11)	C(22)	F(12)	104.9(11)
F(12)	C(22)	C(21)	110.1(10)	F(13)	C(23)	C(24)	113.4(10)
F(13)	C(23)	F(14)	101.4(13)	F(13)	C(23)	F(15)	101.1(14)
F(14)	C(23)	C(24)	115.8(11)	F(14)	C(23)	F(15)	104.2(12)
F(15)	C(23)	C(24)	118.6(10)	C(23)	C(24)	C(25)	117.1(7)
O(6)	C(24)	C(23)	115.0(8)	O(6)	C(24)	C(25)	127.9(6)
C(24)	C(25)	C(26)	122.4(6)	C(25)	C(26)	C(27)	118.1(6)
O(7)	C(26)	C(25)	127.8(6)	O(7)	C(26)	C(27)	114.1(6)
F(16)	C(27)	C(26)	109.2(7)	F(16)	C(27)	F(17)	96.4(9)
F(16)	C(27)	F(18)	103.3(10)	F(17)	C(27)	C(26)	116.1(8)
F(17)	C(27)	F(18)	112.4(9)	F(18)	C(27)	C(26)	116.5(8)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Dy(1)	O(2)	C(14)	-87.4(5)	O(3)	Dy(1)	O(2)	C(14)	11.8(5)
O(7)	Dy(1)	O(2)	C(14)	80.0(6)	O(6)	Dy(1)	O(2)	C(14)	-147.6(5)

O(5)	Dy(1)	O(2)	C(14)	-36.6(6)	N(1)	Dy(1)	O(2)	C(14)	170.3(6)
N(3)	Dy(1)	O(2)	C(14)	101.0(6)	O(4)	Dy(1)	O(3)	C(16)	50.7(5)
O(7)	Dy(1)	O(3)	C(16)	-166.6(5)	O(6)	Dy(1)	O(3)	C(16)	131.7(5)
O(5)	Dy(1)	O(3)	C(16)	121.1(5)	O(2)	Dy(1)	O(3)	C(16)	-21.6(5)
N(1)	Dy(1)	O(3)	C(16)	-51.9(6)	N(3)	Dy(1)	O(3)	C(16)	-95.2(5)
O(3)	Dy(1)	O(4)	C(19)	75.7(6)	O(7)	Dy(1)	O(4)	C(19)	-20.7(7)
O(6)	Dy(1)	O(4)	C(19)	-71.1(6)	O(5)	Dy(1)	O(4)	C(19)	5.5(6)
O(2)	Dy(1)	O(4)	C(19)	146.5(6)	N(1)	Dy(1)	O(4)	C(19)	-146.2(6)
N(3)	Dy(1)	O(4)	C(19)	161.1(5)	O(4)	Dy(1)	O(5)	C(21)	-5.1(6)
O(3)	Dy(1)	O(5)	C(21)	-105.1(6)	O(7)	Dy(1)	O(5)	C(21)	158.6(6)
O(6)	Dy(1)	O(5)	C(21)	80.9(6)	O(2)	Dy(1)	O(5)	C(21)	-56.7(6)
N(1)	Dy(1)	O(5)	C(21)	65.4(7)	N(3)	Dy(1)	O(5)	C(21)	-165.2(5)
O(4)	Dy(1)	O(6)	C(24)	133.4(6)	O(3)	Dy(1)	O(6)	C(24)	48.9(7)
O(7)	Dy(1)	O(6)	C(24)	-17.4(5)	O(5)	Dy(1)	O(6)	C(24)	59.3(6)
O(2)	Dy(1)	O(6)	C(24)	-169.1(5)	N(1)	Dy(1)	O(6)	C(24)	-128.6(6)
N(3)	Dy(1)	O(6)	C(24)	-76.5(6)	O(4)	Dy(1)	O(7)	C(26)	-37.6(6)
O(3)	Dy(1)	O(7)	C(26)	-135.0(5)	O(6)	Dy(1)	O(7)	C(26)	14.9(5)
O(5)	Dy(1)	O(7)	C(26)	-63.6(5)	O(2)	Dy(1)	O(7)	C(26)	162.6(5)
N(1)	Dy(1)	O(7)	C(26)	85.1(5)	N(3)	Dy(1)	O(7)	C(26)	141.4(6)
O(4)	Dy(1)	N(1)	C(1)	-139.8(4)	O(3)	Dy(1)	N(1)	C(1)	-37.9(5)
O(7)	Dy(1)	N(1)	C(1)	71.3(4)	O(6)	Dy(1)	N(1)	C(1)	140.1(4)
O(5)	Dy(1)	N(1)	C(1)	155.5(3)	O(2)	Dy(1)	N(1)	C(1)	-68.7(4)
N(3)	Dy(1)	N(1)	C(1)	10.8(4)	O(4)	Dy(1)	N(1)	C(7)	27.7(6)
O(3)	Dy(1)	N(1)	C(7)	129.6(5)	O(7)	Dy(1)	N(1)	C(7)	-121.3(5)
O(6)	Dy(1)	N(1)	C(7)	-52.5(6)	O(5)	Dy(1)	N(1)	C(7)	-37.0(7)
O(2)	Dy(1)	N(1)	C(7)	98.7(6)	N(3)	Dy(1)	N(1)	C(7)	178.3(6)
O(4)	Dy(1)	N(3)	C(6)	-123.3(4)	O(3)	Dy(1)	N(3)	C(6)	-35.0(4)
O(7)	Dy(1)	N(3)	C(6)	57.8(4)	O(6)	Dy(1)	N(3)	C(6)	118.3(4)
O(5)	Dy(1)	N(3)	C(6)	21.2(5)	O(2)	Dy(1)	N(3)	C(6)	-108.7(4)
N(1)	Dy(1)	N(3)	C(6)	176.0(4)	O(4)	Dy(1)	N(3)	C(2)	54.2(5)
O(3)	Dy(1)	N(3)	C(2)	142.5(4)	O(7)	Dy(1)	N(3)	C(2)	-124.7(4)
O(6)	Dy(1)	N(3)	C(2)	-64.2(4)	O(5)	Dy(1)	N(3)	C(2)	-161.2(3)
O(2)	Dy(1)	N(3)	C(2)	68.9(4)	N(1)	Dy(1)	N(3)	C(2)	-6.5(4)
C(7)	N(1)	C(1)	N(2)	-7.7(7)	Dy(1)	N(1)	C(1)	N(2)	162.8(4)
C(7)	N(1)	C(1)	C(2)	174.2(5)	Dy(1)	N(1)	C(1)	C(2)	-15.3(7)
O(1)	N(2)	C(1)	N(1)	-178.9(7)	C(8)	N(2)	C(1)	N(1)	-12.3(8)
O(1)	N(2)	C(1)	C(2)	-0.8(11)	C(8)	N(2)	C(1)	C(2)	165.7(6)
C(6)	N(3)	C(2)	C(3)	-1.2(8)	Dy(1)	N(3)	C(2)	C(3)	-178.8(4)
C(6)	N(3)	C(2)	C(1)	179.7(5)	Dy(1)	N(3)	C(2)	C(1)	2.0(6)
N(1)	C(1)	C(2)	N(3)	9.0(7)	N(2)	C(1)	C(2)	N(3)	-168.8(6)
N(1)	C(1)	C(2)	C(3)	-170.1(6)	N(2)	C(1)	C(2)	C(3)	12.1(9)

N(3)	C(2)	C(3)	C(4)	0.8(9)	C(1)	C(2)	C(3)	C(4)	179.9(6)
C(2)	C(3)	C(4)	C(5)	-0.5(10)	C(3)	C(4)	C(5)	C(6)	0.6(10)
C(2)	N(3)	C(6)	C(5)	1.2(8)	Dy(1)	N(3)	C(6)	C(5)	178.9(5)
C(4)	C(5)	C(6)	N(3)	-1.0(10)	C(1)	N(1)	C(7)	C(10)	-96.8(6)
Dy(1)	N(1)	C(7)	C(10)	95.0(6)	C(1)	N(1)	C(7)	C(9)	143.4(6)
Dy(1)	N(1)	C(7)	C(9)	-24.8(9)	C(1)	N(1)	C(7)	C(8)	23.0(7)
Dy(1)	N(1)	C(7)	C(8)	-145.2(5)	O(1)	N(2)	C(8)	C(11)	-47.0(12)
C(1)	N(2)	C(8)	C(11)	146.2(8)	O(1)	N(2)	C(8)	C(12)	73.8(9)
C(1)	N(2)	C(8)	C(12)	-93.0(8)	O(1)	N(2)	C(8)	C(7)	-168.3(7)
C(1)	N(2)	C(8)	C(7)	24.8(8)	N(1)	C(7)	C(8)	N(2)	-27.4(7)
C(10)	C(7)	C(8)	N(2)	87.6(7)	C(9)	C(7)	C(8)	N(2)	-145.1(6)
N(1)	C(7)	C(8)	C(11)	-145.0(7)	C(10)	C(7)	C(8)	C(11)	-30.0(9)
C(9)	C(7)	C(8)	C(11)	97.3(9)	N(1)	C(7)	C(8)	C(12)	85.6(8)
C(10)	C(7)	C(8)	C(12)	-159.4(7)	C(9)	C(7)	C(8)	C(12)	-32.1(9)
Dy(1)	O(2)	C(14)	C(15)	-0.8(10)	Dy(1)	O(2)	C(14)	C(13)	176.3(5)
F(3)	C(13)	C(14)	O(2)	56.5(10)	F(2)	C(13)	C(14)	O(2)	-61.4(10)
F(1)	C(13)	C(14)	O(2)	177.9(8)	F(3)	C(13)	C(14)	C(15)	-126.1(9)
F(2)	C(13)	C(14)	C(15)	116.0(8)	F(1)	C(13)	C(14)	C(15)	-4.6(11)
O(2)	C(14)	C(15)	C(16)	-10.3(11)	C(13)	C(14)	C(15)	C(16)	172.7(7)
Dy(1)	O(3)	C(16)	C(15)	21.0(9)	Dy(1)	O(3)	C(16)	C(17)	-157.5(6)
C(14)	C(15)	C(16)	O(3)	0.4(10)	C(14)	C(15)	C(16)	C(17)	178.8(7)
O(3)	C(16)	C(17)	F(6)	176.3(8)	C(15)	C(16)	C(17)	F(6)	-2.3(12)
O(3)	C(16)	C(17)	F(5)	48.5(11)	C(15)	C(16)	C(17)	F(5)	-130.2(8)
O(3)	C(16)	C(17)	F(4)	-64.6(9)	C(15)	C(16)	C(17)	F(4)	116.8(8)
Dy(1)	O(4)	C(19)	C(20)	-3.3(12)	Dy(1)	O(4)	C(19)	C(18)	176.1(6)
F(7)	C(18)	C(19)	O(4)	176.4(10)	F(8)	C(18)	C(19)	O(4)	-63.7(10)
F(9)	C(18)	C(19)	O(4)	49.8(11)	F(7)	C(18)	C(19)	C(20)	-4.2(15)
F(8)	C(18)	C(19)	C(20)	115.7(9)	F(9)	C(18)	C(19)	C(20)	-130.7(9)
O(4)	C(19)	C(20)	C(21)	-2.7(13)	C(18)	C(19)	C(20)	C(21)	178.0(8)
Dy(1)	O(5)	C(21)	C(20)	2.7(11)	Dy(1)	O(5)	C(21)	C(22)	-177.3(7)
C(19)	C(20)	C(21)	O(5)	2.8(13)	C(19)	C(20)	C(21)	C(22)	-177.3(9)
O(5)	C(21)	C(22)	F(11)	167.3(12)	C(20)	C(21)	C(22)	F(11)	-12.6(18)
O(5)	C(21)	C(22)	F(10)	31.9(17)	C(20)	C(21)	C(22)	F(10)	-148.0(13)
O(5)	C(21)	C(22)	F(12)	-71.5(14)	C(20)	C(21)	C(22)	F(12)	108.5(11)
Dy(1)	O(6)	C(24)	C(25)	15.5(11)	Dy(1)	O(6)	C(24)	C(23)	-164.0(7)
F(14)	C(23)	C(24)	O(6)	56.7(16)	F(13)	C(23)	C(24)	O(6)	-59.9(18)
F(15)	C(23)	C(24)	O(6)	-178.4(13)	F(14)	C(23)	C(24)	C(25)	-122.9(14)
F(13)	C(23)	C(24)	C(25)	120.5(15)	F(15)	C(23)	C(24)	C(25)	2.0(19)
O(6)	C(24)	C(25)	C(26)	-1.1(12)	C(23)	C(24)	C(25)	C(26)	178.4(9)
Dy(1)	O(7)	C(26)	C(25)	-10.1(10)	Dy(1)	O(7)	C(26)	C(27)	170.2(5)
C(24)	C(25)	C(26)	O(7)	-1.8(12)	C(24)	C(25)	C(26)	C(27)	177.9(8)

O(7)	C(26)	C(27)	F(18)	-55.0(13)	C(25)	C(26)	C(27)	F(18)	125.3(11)
O(7)	C(26)	C(27)	F(17)	169.2(9)	C(25)	C(26)	C(27)	F(17)	-10.5(13)
O(7)	C(26)	C(27)	F(16)	61.6(11)	C(25)	C(26)	C(27)	F(16)	-118.1(9)

•[Er(hfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Er(1)	O(2)	2.373(5)	Er(1)	O(3)	2.298(5)
Er(1)	O(4)	2.269(4)	Er(1)	O(5)	2.368(4)
Er(1)	O(6)	2.320(4)	Er(1)	O(7)	2.298(5)
Er(1)	N(1)	2.496(5)	Er(1)	N(3)	2.501(5)
F(1)	C(13)	1.327(13)	F(2)	C(13)	1.301(12)
F(3)	C(13)	1.290(14)	F(4)	C(17)	1.324(13)
F(5)	C(17)	1.311(12)	F(6)	C(17)	1.311(11)
F(7)	C(18)	1.255(11)	F(8)	C(18)	1.286(13)
F(9)	C(18)	1.327(14)	F(10)	C(22)	1.286(15)
F(11)	C(22)	1.221(10)	F(12)	C(22)	1.218(16)
F(13)	C(23)	1.196(14)	F(14)	C(23)	1.188(15)
F(15)	C(23)	1.216(16)	F(16)	C(27)	1.338(13)
F(17)	C(27)	1.280(12)	F(18)	C(27)	1.188(11)
O(1)	N(2)	1.285(8)	O(2)	C(14)	1.227(9)
O(3)	C(16)	1.247(8)	O(4)	C(19)	1.256(8)
O(5)	C(21)	1.236(8)	O(6)	C(24)	1.246(9)
O(7)	C(26)	1.246(8)	N(1)	C(1)	1.298(8)
N(1)	C(7)	1.512(8)	N(2)	C(1)	1.387(8)
N(2)	C(8)	1.466(10)	N(3)	C(2)	1.353(7)
N(3)	C(6)	1.317(8)	C(1)	C(2)	1.483(9)
C(2)	C(3)	1.375(9)	C(3)	C(4)	1.395(10)
C(4)	C(5)	1.379(10)	C(5)	C(6)	1.368(9)
C(7)	C(10)	1.494(11)	C(7)	C(8)	1.551(12)
C(7)	C(9)	1.504(12)	C(8)	C(11)	1.517(12)
C(8)	C(12)	1.508(15)	C(13)	C(14)	1.545(12)
C(14)	C(15)	1.387(11)	C(15)	C(16)	1.374(11)
C(16)	C(17)	1.510(12)	C(18)	C(19)	1.526(11)
C(19)	C(20)	1.373(10)	C(20)	C(21)	1.372(10)
C(21)	C(22)	1.498(10)	C(23)	C(24)	1.481(12)
C(24)	C(25)	1.380(12)	C(25)	C(26)	1.374(11)
C(26)	C(27)	1.498(11)			

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Er(1)	O(3)	73.27(17)	O(2)	Er(1)	O(4)	74.17(18)
O(2)	Er(1)	O(5)	129.77(17)	O(2)	Er(1)	O(6)	135.34(18)
O(2)	Er(1)	O(7)	141.75(17)	O(2)	Er(1)	N(1)	69.74(19)
O(2)	Er(1)	N(3)	72.44(18)	O(3)	Er(1)	O(4)	94.13(17)
O(3)	Er(1)	O(5)	72.21(17)	O(3)	Er(1)	O(6)	146.41(17)
O(3)	Er(1)	O(7)	90.48(17)	O(3)	Er(1)	N(1)	137.52(18)
O(3)	Er(1)	N(3)	83.57(17)	O(4)	Er(1)	O(5)	73.14(16)
O(4)	Er(1)	O(6)	81.44(18)	O(4)	Er(1)	O(7)	142.80(16)
O(4)	Er(1)	N(1)	95.22(17)	O(4)	Er(1)	N(3)	145.74(17)
O(5)	Er(1)	O(6)	74.66(18)	O(5)	Er(1)	O(7)	73.26(16)
O(5)	Er(1)	N(1)	149.74(19)	O(5)	Er(1)	N(3)	136.60(16)
O(6)	Er(1)	O(7)	74.69(17)	O(6)	Er(1)	N(1)	76.04(19)
O(6)	Er(1)	N(3)	118.20(17)	O(7)	Er(1)	N(1)	105.95(18)
O(7)	Er(1)	N(3)	71.47(15)	N(1)	Er(1)	N(3)	66.07(17)
Er(1)	O(2)	C(14)	131.9(5)	Er(1)	O(3)	C(16)	133.4(5)
Er(1)	O(4)	C(19)	136.1(4)	Er(1)	O(5)	C(21)	133.6(4)
Er(1)	O(6)	C(24)	131.5(5)	Er(1)	O(7)	C(26)	132.9(5)
Er(1)	N(1)	C(1)	116.8(4)	Er(1)	N(1)	C(7)	134.3(4)
Er(1)	N(3)	C(2)	120.0(4)	Er(1)	N(3)	C(6)	122.3(4)
O(1)	N(2)	C(1)	125.4(7)	O(1)	N(2)	C(8)	124.0(6)
C(1)	N(1)	C(7)	108.1(5)	C(1)	N(2)	C(8)	109.5(6)
C(2)	N(3)	C(6)	117.7(5)	N(1)	C(1)	C(2)	122.4(6)
N(1)	C(1)	N(2)	112.3(6)	N(2)	C(1)	C(2)	125.2(6)
C(1)	C(2)	C(3)	123.7(6)	N(3)	C(2)	C(1)	113.4(5)
N(3)	C(2)	C(3)	122.9(6)	C(2)	C(3)	C(4)	118.4(6)
C(3)	C(4)	C(5)	118.1(7)	C(4)	C(5)	C(6)	119.6(7)
N(3)	C(6)	C(5)	123.4(7)	C(10)	C(7)	N(1)	110.1(6)
C(8)	C(7)	C(10)	113.9(8)	C(8)	C(7)	C(9)	113.7(8)
C(9)	C(7)	C(10)	110.5(9)	C(9)	C(7)	N(1)	105.5(7)
N(1)	C(7)	C(8)	102.5(6)	C(11)	C(8)	C(12)	107.8(10)
C(7)	C(8)	C(11)	115.7(10)	C(7)	C(8)	C(12)	115.7(9)
N(2)	C(8)	C(11)	110.1(8)	N(2)	C(8)	C(12)	107.2(10)
N(2)	C(8)	C(7)	99.7(6)	F(1)	C(13)	C(14)	112.2(10)
F(1)	C(13)	F(2)	105.6(10)	F(1)	C(13)	F(3)	108.2(10)
F(2)	C(13)	C(14)	111.3(8)	F(2)	C(13)	F(3)	108.8(11)
F(3)	C(13)	C(14)	110.6(9)	C(13)	C(14)	C(15)	118.9(8)
O(2)	C(14)	C(13)	111.9(8)	O(2)	C(14)	C(15)	129.2(7)
C(14)	C(15)	C(16)	120.4(7)	C(15)	C(16)	C(17)	118.6(7)
O(3)	C(16)	C(15)	128.1(7)	O(3)	C(16)	C(17)	113.2(7)
F(4)	C(17)	C(16)	111.9(9)	F(4)	C(17)	F(5)	103.4(10)

F(4)	C(17)	F(6)	105.5(9)	F(5)	C(17)	C(16)	112.3(8)
F(5)	C(17)	F(6)	108.3(10)	F(6)	C(17)	C(16)	114.7(9)
F(7)	C(18)	C(19)	114.6(8)	F(7)	C(18)	F(8)	107.4(12)
F(7)	C(18)	F(9)	108.8(11)	F(8)	C(18)	C(19)	111.5(9)
F(8)	C(18)	F(9)	103.4(9)	F(9)	C(18)	C(19)	110.5(10)
C(18)	C(19)	C(20)	118.8(7)	O(4)	C(19)	C(18)	113.5(6)
O(4)	C(19)	C(20)	127.6(7)	C(19)	C(20)	C(21)	121.6(7)
C(20)	C(21)	C(22)	116.6(7)	O(5)	C(21)	C(20)	127.8(6)
O(5)	C(21)	C(22)	115.6(7)	F(10)	C(22)	C(21)	111.3(11)
F(10)	C(22)	F(11)	107.5(13)	F(10)	C(22)	F(12)	94.5(11)
F(11)	C(22)	C(21)	119.9(8)	F(11)	C(22)	F(12)	107.4(13)
F(12)	C(22)	C(21)	113.1(11)	F(13)	C(23)	C(24)	120.7(13)
F(13)	C(23)	F(14)	101.9(15)	F(13)	C(23)	F(15)	102.2(13)
F(14)	C(23)	C(24)	116.2(12)	F(14)	C(23)	F(15)	99.3(15)
F(15)	C(23)	C(24)	113.5(13)	C(23)	C(24)	C(25)	116.3(9)
O(6)	C(24)	C(23)	115.5(9)	O(6)	C(24)	C(25)	128.1(7)
C(24)	C(25)	C(26)	121.7(8)	C(25)	C(26)	C(27)	117.8(8)
O(7)	C(26)	C(25)	128.4(7)	O(7)	C(26)	C(27)	113.8(8)
F(16)	C(27)	C(26)	110.0(9)	F(16)	C(27)	F(17)	95.9(10)
F(16)	C(27)	F(18)	103.0(11)	F(17)	C(27)	C(26)	116.2(9)
F(17)	C(27)	F(18)	110.9(11)	F(18)	C(27)	C(26)	117.7(9)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Er(1)	O(2)	C(14)	-88.1(7)	O(3)	Er(1)	O(2)	C(14)	11.3(6)
O(7)	Er(1)	O(2)	C(14)	79.8(7)	O(6)	Er(1)	O(2)	C(14)	-147.6(6)
O(5)	Er(1)	O(2)	C(14)	-37.0(7)	N(1)	Er(1)	O(2)	C(14)	170.1(7)
N(3)	Er(1)	O(2)	C(14)	99.8(7)	O(4)	Er(1)	O(3)	C(16)	51.2(6)
O(7)	Er(1)	O(3)	C(16)	-165.7(6)	O(6)	Er(1)	O(3)	C(16)	131.9(6)
O(5)	Er(1)	O(3)	C(16)	122.0(7)	O(2)	Er(1)	O(3)	C(16)	-20.9(6)
N(1)	Er(1)	O(3)	C(16)	-51.1(7)	N(3)	Er(1)	O(3)	C(16)	-94.4(6)
O(3)	Er(1)	O(4)	C(19)	76.0(7)	O(7)	Er(1)	O(4)	C(19)	-20.3(9)
O(6)	Er(1)	O(4)	C(19)	-70.5(7)	O(5)	Er(1)	O(4)	C(19)	5.9(7)
O(2)	Er(1)	O(4)	C(19)	147.3(8)	N(1)	Er(1)	O(4)	C(19)	-145.5(7)
N(3)	Er(1)	O(4)	C(19)	160.6(7)	O(4)	Er(1)	O(5)	C(21)	-3.9(7)
O(3)	Er(1)	O(5)	C(21)	-104.0(7)	O(7)	Er(1)	O(5)	C(21)	159.9(7)
O(6)	Er(1)	O(5)	C(21)	81.6(7)	O(2)	Er(1)	O(5)	C(21)	-55.4(8)
N(1)	Er(1)	O(5)	C(21)	66.8(8)	N(3)	Er(1)	O(5)	C(21)	-163.3(6)
O(4)	Er(1)	O(6)	C(24)	133.3(7)	O(3)	Er(1)	O(6)	C(24)	48.8(8)
O(7)	Er(1)	O(6)	C(24)	-17.9(6)	O(5)	Er(1)	O(6)	C(24)	58.6(7)
O(2)	Er(1)	O(6)	C(24)	-169.7(6)	N(1)	Er(1)	O(6)	C(24)	-129.1(7)

N(3)	Er(1)	O(6)	C(24)	-76.5(7)	O(4)	Er(1)	O(7)	C(26)	-38.4(8)
O(3)	Er(1)	O(7)	C(26)	-135.9(6)	O(6)	Er(1)	O(7)	C(26)	13.6(6)
O(5)	Er(1)	O(7)	C(26)	-64.6(6)	O(2)	Er(1)	O(7)	C(26)	161.2(6)
N(1)	Er(1)	O(7)	C(26)	83.8(6)	N(3)	Er(1)	O(7)	C(26)	141.1(7)
O(4)	Er(1)	N(1)	C(1)	-140.1(5)	O(3)	Er(1)	N(1)	C(1)	-38.2(6)
O(7)	Er(1)	N(1)	C(1)	70.8(5)	O(6)	Er(1)	N(1)	C(1)	140.1(5)
O(5)	Er(1)	N(1)	C(1)	154.8(4)	O(2)	Er(1)	N(1)	C(1)	-69.1(5)
N(3)	Er(1)	N(1)	C(1)	10.0(5)	O(4)	Er(1)	N(1)	C(7)	27.5(7)
O(3)	Er(1)	N(1)	C(7)	129.5(7)	O(7)	Er(1)	N(1)	C(7)	-121.5(7)
O(6)	Er(1)	N(1)	C(7)	-52.3(7)	O(5)	Er(1)	N(1)	C(7)	-37.6(9)
O(2)	Er(1)	N(1)	C(7)	98.5(7)	N(3)	Er(1)	N(1)	C(7)	177.7(8)
O(4)	Er(1)	N(3)	C(6)	-123.2(5)	O(3)	Er(1)	N(3)	C(6)	-35.3(5)
O(7)	Er(1)	N(3)	C(6)	57.4(5)	O(6)	Er(1)	N(3)	C(6)	117.6(5)
O(5)	Er(1)	N(3)	C(6)	20.2(7)	O(2)	Er(1)	N(3)	C(6)	-109.8(6)
N(1)	Er(1)	N(3)	C(6)	175.1(6)	O(4)	Er(1)	N(3)	C(2)	55.9(6)
O(3)	Er(1)	N(3)	C(2)	143.8(5)	O(7)	Er(1)	N(3)	C(2)	-123.6(5)
O(6)	Er(1)	N(3)	C(2)	-63.3(5)	O(5)	Er(1)	N(3)	C(2)	-160.8(4)
O(2)	Er(1)	N(3)	C(2)	69.3(5)	N(1)	Er(1)	N(3)	C(2)	-5.8(5)
C(7)	N(1)	C(1)	N(2)	-8.7(9)	Er(1)	N(1)	C(1)	N(2)	162.0(5)
C(7)	N(1)	C(1)	C(2)	175.1(7)	Er(1)	N(1)	C(1)	C(2)	-14.2(9)
O(1)	N(2)	C(1)	N(1)	-179.2(8)	C(8)	N(2)	C(1)	N(1)	-10.5(10)
O(1)	N(2)	C(1)	C(2)	-3.2(14)	C(8)	N(2)	C(1)	C(2)	165.6(8)
C(6)	N(3)	C(2)	C(3)	-0.4(10)	Er(1)	N(3)	C(2)	C(3)	-179.5(6)
C(6)	N(3)	C(2)	C(1)	-179.3(6)	Er(1)	N(3)	C(2)	C(1)	1.6(7)
N(1)	C(1)	C(2)	N(3)	8.6(10)	N(2)	C(1)	C(2)	N(3)	-167.0(7)
N(1)	C(1)	C(2)	C(3)	-170.3(7)	N(2)	C(1)	C(2)	C(3)	14.0(12)
N(3)	C(2)	C(3)	C(4)	1.3(12)	C(1)	C(2)	C(3)	C(4)	-179.8(7)
C(2)	C(3)	C(4)	C(5)	-1.2(12)	C(3)	C(4)	C(5)	C(6)	0.3(12)
C(2)	N(3)	C(6)	C(5)	-0.7(11)	Er(1)	N(3)	C(6)	C(5)	178.4(6)
C(4)	C(5)	C(6)	N(3)	0.7(12)	C(1)	N(1)	C(7)	C(10)	144.5(8)
Er(1)	N(1)	C(7)	C(10)	-23.9(11)	C(1)	N(1)	C(7)	C(9)	-96.3(8)
Er(1)	N(1)	C(7)	C(9)	95.3(8)	C(1)	N(1)	C(7)	C(8)	23.0(9)
Er(1)	N(1)	C(7)	C(8)	-145.5(6)	O(1)	N(2)	C(8)	C(12)	71.5(12)
C(1)	N(2)	C(8)	C(12)	-97.4(9)	O(1)	N(2)	C(8)	C(11)	-45.4(15)
C(1)	N(2)	C(8)	C(11)	145.7(10)	O(1)	N(2)	C(8)	C(7)	-167.5(9)
C(1)	N(2)	C(8)	C(7)	23.5(10)	C(10)	C(7)	C(8)	N(2)	-145.6(8)
C(9)	C(7)	C(8)	N(2)	86.6(9)	N(1)	C(7)	C(8)	N(2)	-26.8(9)
C(10)	C(7)	C(8)	C(12)	-31.1(12)	C(9)	C(7)	C(8)	C(12)	-158.9(9)
N(1)	C(7)	C(8)	C(12)	87.8(10)	C(10)	C(7)	C(8)	C(11)	96.4(11)
C(9)	C(7)	C(8)	C(11)	-31.5(11)	N(1)	C(7)	C(8)	C(11)	-144.8(8)
Er(1)	O(2)	C(14)	C(15)	-0.9(12)	Er(1)	O(2)	C(14)	C(13)	177.0(6)

F(3)	C(13)	C(14)	O(2)	58.0(12)	F(2)	C(13)	C(14)	O(2)	-62.9(12)
F(1)	C(13)	C(14)	O(2)	179.0(9)	F(3)	C(13)	C(14)	C(15)	-123.8(11)
F(2)	C(13)	C(14)	C(15)	115.2(10)	F(1)	C(13)	C(14)	C(15)	-2.9(14)
O(2)	C(14)	C(15)	C(16)	-9.3(13)	C(13)	C(14)	C(15)	C(16)	172.8(8)
Er(1)	O(3)	C(16)	C(15)	20.8(12)	Er(1)	O(3)	C(16)	C(17)	-158.9(7)
C(14)	C(15)	C(16)	O(3)	-0.5(13)	C(14)	C(15)	C(16)	C(17)	179.1(8)
O(3)	C(16)	C(17)	F(5)	51.0(13)	C(15)	C(16)	C(17)	F(5)	-128.7(10)
O(3)	C(16)	C(17)	F(6)	175.2(9)	C(15)	C(16)	C(17)	F(6)	-4.5(15)
O(3)	C(16)	C(17)	F(4)	-64.7(11)	C(15)	C(16)	C(17)	F(4)	115.6(9)
Er(1)	O(4)	C(19)	C(20)	-5.6(14)	Er(1)	O(4)	C(19)	C(18)	175.9(7)
F(7)	C(18)	C(19)	O(4)	172.5(12)	F(8)	C(18)	C(19)	O(4)	-65.4(12)
F(9)	C(18)	C(19)	O(4)	49.0(13)	F(7)	C(18)	C(19)	C(20)	-6.2(18)
F(8)	C(18)	C(19)	C(20)	116.0(10)	F(9)	C(18)	C(19)	C(20)	-129.6(10)
O(4)	C(19)	C(20)	C(21)	-0.1(16)	C(18)	C(19)	C(20)	C(21)	178.4(10)
Er(1)	O(5)	C(21)	C(20)	1.4(14)	Er(1)	O(5)	C(21)	C(22)	-178.5(8)
C(19)	C(20)	C(21)	O(5)	2.0(16)	C(19)	C(20)	C(21)	C(22)	-178.1(10)
O(5)	C(21)	C(22)	F(12)	-67.9(18)	C(20)	C(21)	C(22)	F(12)	112.2(14)
O(5)	C(21)	C(22)	F(11)	163.6(13)	C(20)	C(21)	C(22)	F(11)	-16(2)
O(5)	C(21)	C(22)	F(10)	37.0(18)	C(20)	C(21)	C(22)	F(10)	-142.9(14)
Er(1)	O(6)	C(24)	C(25)	18.1(13)	Er(1)	O(6)	C(24)	C(23)	-166.3(8)
F(14)	C(23)	C(24)	O(6)	-56(2)	F(13)	C(23)	C(24)	O(6)	179.9(16)
F(15)	C(23)	C(24)	O(6)	58.1(19)	F(14)	C(23)	C(24)	C(25)	120.0(19)
F(13)	C(23)	C(24)	C(25)	-4(2)	F(15)	C(23)	C(24)	C(25)	-125.8(17)
O(6)	C(24)	C(25)	C(26)	-4.4(15)	C(23)	C(24)	C(25)	C(26)	-179.9(10)
Er(1)	O(7)	C(26)	C(25)	-8.9(12)	Er(1)	O(7)	C(26)	C(27)	170.4(6)
C(24)	C(25)	C(26)	O(7)	-0.6(14)	C(24)	C(25)	C(26)	C(27)	-179.9(9)
O(7)	C(26)	C(27)	F(18)	-54.7(15)	C(25)	C(26)	C(27)	F(18)	124.7(13)
O(7)	C(26)	C(27)	F(17)	170.4(11)	C(25)	C(26)	C(27)	F(17)	-10.3(15)
O(7)	C(26)	C(27)	F(16)	62.9(12)	C(25)	C(26)	C(27)	F(16)	-117.8(11)

•[Yb(hfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Yb(1)	O(2)	2.342(6)	Yb(1)	O(3)	2.273(5)
Yb(1)	O(4)	2.245(5)	Yb(1)	O(5)	2.345(5)

Yb(1)	O(6)	2.289(6)	Yb(1)	O(7)	2.275(5)
Yb(1)	N(1)	2.480(6)	Yb(1)	N(3)	2.480(5)
F(1)	C(13)	1.331(14)	F(2)	C(13)	1.301(16)
F(3)	C(13)	1.267(16)	F(4)	C(17)	1.356(15)
F(5)	C(17)	1.330(14)	F(6)	C(17)	1.290(12)
F(7)	C(18)	1.342(16)	F(8)	C(18)	1.239(12)
F(9)	C(18)	1.275(14)	F(10)	C(22)	1.282(18)
F(11)	C(22)	1.228(13)	F(12)	C(22)	1.21(2)
F(13)	C(23)	1.229(18)	F(14)	C(23)	1.183(18)
F(15)	C(23)	1.186(18)	F(16)	C(27)	1.307(15)
F(17)	C(27)	1.259(13)	F(18)	C(27)	1.194(13)
O(1)	N(2)	1.283(10)	O(2)	C(14)	1.232(10)
O(3)	C(16)	1.249(9)	O(4)	C(19)	1.247(9)
O(5)	C(21)	1.229(9)	O(6)	C(24)	1.258(10)
O(7)	C(26)	1.249(9)	N(1)	C(1)	1.287(10)
N(1)	C(7)	1.508(10)	N(2)	C(1)	1.382(9)
N(2)	C(8)	1.483(13)	N(3)	C(2)	1.354(8)
N(3)	C(6)	1.316(9)	C(1)	C(2)	1.479(10)
C(2)	C(3)	1.388(10)	C(3)	C(4)	1.379(12)
C(4)	C(5)	1.376(12)	C(5)	C(6)	1.386(11)
C(7)	C(8)	1.556(15)	C(7)	C(9)	1.529(15)
C(7)	C(10)	1.522(13)	C(8)	C(11)	1.512(14)
C(8)	C(12)	1.495(18)	C(13)	C(14)	1.545(14)
C(14)	C(15)	1.407(13)	C(15)	C(16)	1.390(12)
C(16)	C(17)	1.491(13)	C(18)	C(19)	1.539(12)
C(19)	C(20)	1.382(11)	C(20)	C(21)	1.387(12)
C(21)	C(22)	1.534(11)	C(23)	C(24)	1.481(14)
C(24)	C(25)	1.374(14)	C(25)	C(26)	1.407(13)
C(26)	C(27)	1.515(13)			

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Yb(1)	O(3)	73.65(19)	O(2)	Yb(1)	O(4)	73.6(2)
O(2)	Yb(1)	O(5)	129.6(2)	O(2)	Yb(1)	O(6)	135.2(2)
O(2)	Yb(1)	O(7)	141.47(19)	O(2)	Yb(1)	N(1)	70.1(2)
O(2)	Yb(1)	N(3)	72.11(19)	O(3)	Yb(1)	O(4)	93.8(2)
O(3)	Yb(1)	O(5)	71.4(2)	O(3)	Yb(1)	O(6)	146.2(2)
O(3)	Yb(1)	O(7)	90.59(19)	O(3)	Yb(1)	N(1)	138.2(2)
O(3)	Yb(1)	N(3)	83.52(19)	O(4)	Yb(1)	O(5)	73.74(18)
O(4)	Yb(1)	O(6)	81.9(2)	O(4)	Yb(1)	O(7)	143.76(18)
O(4)	Yb(1)	N(1)	95.3(2)	O(4)	Yb(1)	N(3)	144.94(18)

O(5)	Yb(1)	O(6)	75.2(2)	O(5)	Yb(1)	O(7)	73.70(19)
O(5)	Yb(1)	N(1)	149.9(2)	O(5)	Yb(1)	N(3)	136.28(19)
O(6)	Yb(1)	O(7)	74.8(2)	O(6)	Yb(1)	N(1)	75.6(2)
O(6)	Yb(1)	N(3)	118.52(19)	O(7)	Yb(1)	N(1)	105.1(2)
O(7)	Yb(1)	N(3)	71.30(17)	N(1)	Yb(1)	N(3)	66.24(19)
Yb(1)	O(2)	C(14)	132.9(6)	Yb(1)	O(3)	C(16)	134.2(5)
Yb(1)	O(4)	C(19)	136.4(5)	Yb(1)	O(5)	C(21)	132.9(5)
Yb(1)	O(6)	C(24)	133.2(6)	Yb(1)	O(7)	C(26)	133.4(5)
Yb(1)	N(1)	C(1)	116.7(5)	Yb(1)	N(1)	C(7)	134.6(5)
Yb(1)	N(3)	C(2)	120.0(5)	Yb(1)	N(3)	C(6)	122.2(5)
O(1)	N(2)	C(1)	125.5(8)	O(1)	N(2)	C(8)	123.0(8)
C(1)	N(1)	C(7)	107.5(6)	C(1)	N(2)	C(8)	109.8(7)
C(2)	N(3)	C(6)	117.8(6)	N(1)	C(1)	C(2)	122.4(6)
N(1)	C(1)	N(2)	112.9(7)	N(2)	C(1)	C(2)	124.7(7)
C(1)	C(2)	C(3)	124.6(6)	N(3)	C(2)	C(1)	113.0(6)
N(3)	C(2)	C(3)	122.4(7)	C(2)	C(3)	C(4)	118.5(7)
C(3)	C(4)	C(5)	119.3(7)	C(4)	C(5)	C(6)	118.5(8)
N(3)	C(6)	C(5)	123.6(7)	C(8)	C(7)	C(10)	113.8(10)
C(8)	C(7)	C(9)	113.0(9)	C(9)	C(7)	C(10)	110.5(10)
N(1)	C(7)	C(10)	109.2(7)	N(1)	C(7)	C(8)	103.9(8)
N(1)	C(7)	C(9)	105.7(8)	C(11)	C(8)	C(12)	109.9(12)
C(7)	C(8)	C(11)	116.4(12)	C(7)	C(8)	C(12)	113.6(10)
N(2)	C(8)	C(11)	111.1(9)	N(2)	C(8)	C(12)	107.1(11)
N(2)	C(8)	C(7)	97.7(8)	F(1)	C(13)	C(14)	111.7(11)
F(1)	C(13)	F(2)	105.7(11)	F(1)	C(13)	F(3)	107.4(12)
F(2)	C(13)	C(14)	110.7(10)	F(2)	C(13)	F(3)	109.0(13)
F(3)	C(13)	C(14)	112.2(10)	C(13)	C(14)	C(15)	119.2(9)
O(2)	C(14)	C(13)	112.5(9)	O(2)	C(14)	C(15)	128.3(8)
C(14)	C(15)	C(16)	119.9(8)	C(15)	C(16)	C(17)	117.2(8)
O(3)	C(16)	C(15)	127.5(8)	O(3)	C(16)	C(17)	115.3(8)
F(4)	C(17)	C(16)	109.9(10)	F(4)	C(17)	F(5)	101.4(11)
F(4)	C(17)	F(6)	105.4(10)	F(5)	C(17)	C(16)	112.1(9)
F(5)	C(17)	F(6)	110.0(11)	F(6)	C(17)	C(16)	116.7(11)
F(7)	C(18)	C(19)	108.5(11)	F(7)	C(18)	F(8)	106.7(12)
F(7)	C(18)	F(9)	101.6(10)	F(8)	C(18)	C(19)	116.6(9)
F(8)	C(18)	F(9)	110.2(14)	F(9)	C(18)	C(19)	112.2(10)
C(18)	C(19)	C(20)	116.7(8)	O(4)	C(19)	C(18)	115.6(7)
O(4)	C(19)	C(20)	127.7(8)	C(19)	C(20)	C(21)	120.1(7)
C(20)	C(21)	C(22)	115.8(8)	O(5)	C(21)	C(20)	128.7(7)
O(5)	C(21)	C(22)	115.5(8)	F(10)	C(22)	C(21)	110.5(12)
F(10)	C(22)	F(11)	107.6(16)	F(10)	C(22)	F(12)	96.8(14)

F(11)	C(22)	C(21)	118.2(9)	F(11)	C(22)	F(12)	109.3(15)
F(12)	C(22)	C(21)	112.2(14)	F(13)	C(23)	C(24)	117.4(15)
F(13)	C(23)	F(14)	101.8(18)	F(13)	C(23)	F(15)	102.9(16)
F(14)	C(23)	C(24)	114.6(13)	F(14)	C(23)	F(15)	103.0(19)
F(15)	C(23)	C(24)	115.2(15)	C(23)	C(24)	C(25)	117.3(10)
O(6)	C(24)	C(23)	115.8(11)	O(6)	C(24)	C(25)	126.8(8)
C(24)	C(25)	C(26)	121.5(8)	C(25)	C(26)	C(27)	117.5(8)
O(7)	C(26)	C(25)	127.5(8)	O(7)	C(26)	C(27)	115.0(8)
F(16)	C(27)	C(26)	109.7(10)	F(16)	C(27)	F(17)	97.3(12)
F(16)	C(27)	F(18)	104.3(14)	F(17)	C(27)	C(26)	116.6(11)
F(17)	C(27)	F(18)	112.0(12)	F(18)	C(27)	C(26)	114.7(10)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Yb(1)	O(2)	C(14)	-87.1(8)	O(3)	Yb(1)	O(2)	C(14)	12.0(8)
O(7)	Yb(1)	O(2)	C(14)	81.4(8)	O(6)	Yb(1)	O(2)	C(14)	-146.9(7)
O(5)	Yb(1)	O(2)	C(14)	-35.6(9)	N(3)	Yb(1)	O(2)	C(14)	100.3(8)
N(1)	Yb(1)	O(2)	C(14)	170.8(8)	O(4)	Yb(1)	O(3)	C(16)	50.6(7)
O(7)	Yb(1)	O(3)	C(16)	-165.4(7)	O(6)	Yb(1)	O(3)	C(16)	131.8(7)
O(2)	Yb(1)	O(3)	C(16)	-21.1(7)	O(5)	Yb(1)	O(3)	C(16)	122.1(7)
N(3)	Yb(1)	O(3)	C(16)	-94.3(7)	N(1)	Yb(1)	O(3)	C(16)	-51.7(8)
O(3)	Yb(1)	O(4)	C(19)	75.9(9)	O(7)	Yb(1)	O(4)	C(19)	-20.3(11)
O(6)	Yb(1)	O(4)	C(19)	-70.3(9)	O(2)	Yb(1)	O(4)	C(19)	147.7(9)
O(5)	Yb(1)	O(4)	C(19)	6.5(9)	N(3)	Yb(1)	O(4)	C(19)	160.0(8)
N(1)	Yb(1)	O(4)	C(19)	-144.9(9)	O(4)	Yb(1)	O(5)	C(21)	-5.2(8)
O(3)	Yb(1)	O(5)	C(21)	-105.0(8)	O(7)	Yb(1)	O(5)	C(21)	158.7(9)
O(6)	Yb(1)	O(5)	C(21)	80.6(8)	O(2)	Yb(1)	O(5)	C(21)	-56.6(9)
N(3)	Yb(1)	O(5)	C(21)	-163.4(8)	N(1)	Yb(1)	O(5)	C(21)	66.7(10)
O(4)	Yb(1)	O(6)	C(24)	133.6(8)	O(3)	Yb(1)	O(6)	C(24)	48.9(9)
O(7)	Yb(1)	O(6)	C(24)	-18.3(8)	O(2)	Yb(1)	O(6)	C(24)	-169.5(7)
O(5)	Yb(1)	O(6)	C(24)	58.4(8)	N(3)	Yb(1)	O(6)	C(24)	-76.6(8)
N(1)	Yb(1)	O(6)	C(24)	-128.7(8)	O(4)	Yb(1)	O(7)	C(26)	-37.3(9)
O(3)	Yb(1)	O(7)	C(26)	-134.6(7)	O(6)	Yb(1)	O(7)	C(26)	14.6(7)
O(2)	Yb(1)	O(7)	C(26)	161.5(7)	O(5)	Yb(1)	O(7)	C(26)	-64.1(7)
N(3)	Yb(1)	O(7)	C(26)	142.5(7)	N(1)	Yb(1)	O(7)	C(26)	84.6(7)
O(4)	Yb(1)	N(1)	C(1)	-138.4(6)	O(3)	Yb(1)	N(1)	C(1)	-36.7(7)
O(7)	Yb(1)	N(1)	C(1)	71.8(6)	O(6)	Yb(1)	N(1)	C(1)	141.3(6)
O(2)	Yb(1)	N(1)	C(1)	-68.0(6)	O(5)	Yb(1)	N(1)	C(1)	155.2(5)
N(3)	Yb(1)	N(1)	C(1)	10.6(5)	O(4)	Yb(1)	N(1)	C(7)	27.3(9)
O(3)	Yb(1)	N(1)	C(7)	129.0(8)	O(7)	Yb(1)	N(1)	C(7)	-122.4(8)
O(6)	Yb(1)	N(1)	C(7)	-53.0(8)	O(2)	Yb(1)	N(1)	C(7)	97.7(9)

O(5)	Yb(1)	N(1)	C(7)	-39.0(10)	N(3)	Yb(1)	N(1)	C(7)	176.3(9)
O(4)	Yb(1)	N(3)	C(6)	-123.4(6)	O(3)	Yb(1)	N(3)	C(6)	-36.0(6)
O(7)	Yb(1)	N(3)	C(6)	56.8(6)	O(6)	Yb(1)	N(3)	C(6)	116.8(6)
O(2)	Yb(1)	N(3)	C(6)	-110.9(6)	O(5)	Yb(1)	N(3)	C(6)	18.3(7)
N(1)	Yb(1)	N(3)	C(6)	173.5(6)	O(4)	Yb(1)	N(3)	C(2)	57.9(6)
O(3)	Yb(1)	N(3)	C(2)	145.3(5)	O(7)	Yb(1)	N(3)	C(2)	-121.9(5)
O(6)	Yb(1)	N(3)	C(2)	-61.8(5)	O(2)	Yb(1)	N(3)	C(2)	70.4(5)
O(5)	Yb(1)	N(3)	C(2)	-160.4(4)	N(1)	Yb(1)	N(3)	C(2)	-5.2(5)
C(7)	N(1)	C(1)	N(2)	-6.0(10)	Yb(1)	N(1)	C(1)	N(2)	163.4(6)
C(7)	N(1)	C(1)	C(2)	174.8(8)	Yb(1)	N(1)	C(1)	C(2)	-15.8(9)
O(1)	N(2)	C(1)	N(1)	-179.1(10)	C(8)	N(2)	C(1)	N(1)	-13.5(12)
O(1)	N(2)	C(1)	C(2)	0.1(15)	C(8)	N(2)	C(1)	C(2)	165.7(9)
C(6)	N(3)	C(2)	C(3)	1.6(11)	Yb(1)	N(3)	C(2)	C(3)	-179.6(6)
C(6)	N(3)	C(2)	C(1)	-178.7(7)	Yb(1)	N(3)	C(2)	C(1)	0.0(7)
N(1)	C(1)	C(2)	N(3)	10.8(10)	N(2)	C(1)	C(2)	N(3)	-168.4(8)
N(1)	C(1)	C(2)	C(3)	-169.6(8)	N(2)	C(1)	C(2)	C(3)	11.3(13)
N(3)	C(2)	C(3)	C(4)	-0.6(12)	C(1)	C(2)	C(3)	C(4)	179.7(8)
C(2)	C(3)	C(4)	C(5)	0.0(14)	C(3)	C(4)	C(5)	C(6)	-0.5(14)
C(2)	N(3)	C(6)	C(5)	-2.1(11)	Yb(1)	N(3)	C(6)	C(5)	179.2(6)
C(4)	C(5)	C(6)	N(3)	1.5(13)	C(1)	N(1)	C(7)	C(10)	143.6(9)
Yb(1)	N(1)	C(7)	C(10)	-23.0(14)	C(1)	N(1)	C(7)	C(9)	-97.4(9)
Yb(1)	N(1)	C(7)	C(9)	95.9(9)	C(1)	N(1)	C(7)	C(8)	21.8(11)
Yb(1)	N(1)	C(7)	C(8)	-144.8(7)	O(1)	N(2)	C(8)	C(12)	73.3(13)
C(1)	N(2)	C(8)	C(12)	-92.7(11)	O(1)	N(2)	C(8)	C(11)	-46.8(18)
C(1)	N(2)	C(8)	C(11)	147.3(12)	O(1)	N(2)	C(8)	C(7)	-169.0(10)
C(1)	N(2)	C(8)	C(7)	25.0(11)	N(1)	C(7)	C(8)	N(2)	-26.9(10)
C(10)	C(7)	C(8)	N(2)	-145.6(9)	C(9)	C(7)	C(8)	N(2)	87.2(10)
N(1)	C(7)	C(8)	C(12)	85.6(12)	C(10)	C(7)	C(8)	C(12)	-33.1(14)
C(9)	C(7)	C(8)	C(12)	-160.2(11)	N(1)	C(7)	C(8)	C(11)	-145.2(10)
C(10)	C(7)	C(8)	C(11)	96.1(13)	C(9)	C(7)	C(8)	C(11)	-31.1(14)
Yb(1)	O(2)	C(14)	C(15)	-2.9(14)	Yb(1)	O(2)	C(14)	C(13)	177.8(7)
F(3)	C(13)	C(14)	O(2)	56.5(15)	F(2)	C(13)	C(14)	O(2)	-65.5(14)
F(1)	C(13)	C(14)	O(2)	177.1(11)	F(3)	C(13)	C(14)	C(15)	-122.9(12)
F(2)	C(13)	C(14)	C(15)	115.2(12)	F(1)	C(13)	C(14)	C(15)	-2.2(16)
O(2)	C(14)	C(15)	C(16)	-6.9(15)	C(13)	C(14)	C(15)	C(16)	172.4(10)
Yb(1)	O(3)	C(16)	C(15)	21.4(13)	Yb(1)	O(3)	C(16)	C(17)	-158.0(8)
C(14)	C(15)	C(16)	O(3)	-2.1(15)	C(14)	C(15)	C(16)	C(17)	177.2(9)
O(3)	C(16)	C(17)	F(6)	175.7(11)	C(15)	C(16)	C(17)	F(6)	-3.7(17)
O(3)	C(16)	C(17)	F(5)	47.6(14)	C(15)	C(16)	C(17)	F(5)	-131.8(11)
O(3)	C(16)	C(17)	F(4)	-64.4(12)	C(15)	C(16)	C(17)	F(4)	116.2(11)
Yb(1)	O(4)	C(19)	C(20)	-4.9(17)	Yb(1)	O(4)	C(19)	C(18)	174.3(8)

F(8)	C(18)	C(19)	O(4)	169.1(14)	F(9)	C(18)	C(19)	O(4)	-62.6(15)
F(7)	C(18)	C(19)	O(4)	48.8(14)	F(8)	C(18)	C(19)	C(20)	-12(2)
F(9)	C(18)	C(19)	C(20)	116.7(12)	F(7)	C(18)	C(19)	C(20)	-131.9(11)
O(4)	C(19)	C(20)	C(21)	-1.8(18)	C(18)	C(19)	C(20)	C(21)	179.0(11)
Yb(1)	O(5)	C(21)	C(20)	2.3(16)	Yb(1)	O(5)	C(21)	C(22)	-178.6(9)
C(19)	C(20)	C(21)	O(5)	2.8(18)	C(19)	C(20)	C(21)	C(22)	-176.3(12)
O(5)	C(21)	C(22)	F(12)	-70(2)	C(20)	C(21)	C(22)	F(12)	109.3(17)
O(5)	C(21)	C(22)	F(11)	161.4(15)	C(20)	C(21)	C(22)	F(11)	-19(2)
O(5)	C(21)	C(22)	F(10)	37(2)	C(20)	C(21)	C(22)	F(10)	-143.9(16)
Yb(1)	O(6)	C(24)	C(25)	16.7(15)	Yb(1)	O(6)	C(24)	C(23)	-164.2(9)
F(15)	C(23)	C(24)	O(6)	56(2)	F(14)	C(23)	C(24)	O(6)	-63(2)
F(13)	C(23)	C(24)	O(6)	177.5(16)	F(15)	C(23)	C(24)	C(25)	-125(2)
F(14)	C(23)	C(24)	C(25)	116(2)	F(13)	C(23)	C(24)	C(25)	-3(2)
O(6)	C(24)	C(25)	C(26)	-1.6(16)	C(23)	C(24)	C(25)	C(26)	179.4(11)
Yb(1)	O(7)	C(26)	C(25)	-9.1(13)	Yb(1)	O(7)	C(26)	C(27)	170.9(7)
C(24)	C(25)	C(26)	O(7)	-2.3(15)	C(24)	C(25)	C(26)	C(27)	177.7(10)
O(7)	C(26)	C(27)	F(18)	-56.8(16)	C(25)	C(26)	C(27)	F(18)	123.2(14)
O(7)	C(26)	C(27)	F(17)	169.5(12)	C(25)	C(26)	C(27)	F(17)	-10.5(17)
O(7)	C(26)	C(27)	F(16)	60.3(14)	C(25)	C(26)	C(27)	F(16)	-119.7(12)

•[Y(hfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Y(1)	O(2)	2.378(4)	Y(1)	O(3)	2.301(4)
Y(1)	O(4)	2.281(4)	Y(1)	O(5)	2.369(4)
Y(1)	O(6)	2.315(4)	Y(1)	O(7)	2.306(4)
Y(1)	N(1)	2.518(5)	Y(1)	N(3)	2.518(5)
F(1)	C(13)	1.324(11)	F(2)	C(13)	1.320(12)
F(3)	C(13)	1.266(11)	F(4)	C(17)	1.307(11)
F(5)	C(17)	1.306(10)	F(6)	C(17)	1.293(10)
F(7)	C(18)	1.307(12)	F(8)	C(18)	1.260(10)
F(9)	C(18)	1.303(12)	F(10)	C(22)	1.253(18)
F(11)	C(22)	1.242(14)	F(12)	C(22)	1.212(10)
F(13)	C(23)	1.239(14)	F(14)	C(23)	1.218(12)
F(15)	C(23)	1.153(13)	F(16)	C(27)	1.310(12)
F(17)	C(27)	1.252(10)	F(18)	C(27)	1.196(11)
O(1)	N(2)	1.280(7)	O(2)	C(14)	1.220(7)
O(3)	C(16)	1.256(7)	O(4)	C(19)	1.240(7)
O(5)	C(21)	1.206(7)	O(6)	C(24)	1.239(8)
O(7)	C(26)	1.250(7)	N(1)	C(1)	1.284(7)

N(1)	C(8)	1.518(8)	N(2)	C(1)	1.387(8)
N(2)	C(7)	1.464(10)	N(3)	C(6)	1.309(8)
N(3)	C(2)	1.358(7)	C(1)	C(2)	1.473(9)
C(2)	C(3)	1.372(8)	C(3)	C(4)	1.387(10)
C(4)	C(5)	1.378(9)	C(5)	C(6)	1.369(9)
C(7)	C(8)	1.565(11)	C(7)	C(9)	1.542(12)
C(7)	C(10)	1.482(11)	C(8)	C(11)	1.532(11)
C(8)	C(12)	1.488(10)	C(13)	C(14)	1.517(11)
C(14)	C(15)	1.406(10)	C(15)	C(16)	1.366(9)
C(16)	C(17)	1.525(11)	C(18)	C(19)	1.525(11)
C(19)	C(20)	1.379(9)	C(20)	C(21)	1.400(9)
C(21)	C(22)	1.521(9)	C(23)	C(24)	1.509(11)
C(24)	C(25)	1.375(10)	C(25)	C(26)	1.385(10)
C(26)	C(27)	1.497(11)			

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Y(1)	O(3)	72.62(15)	O(2)	Y(1)	O(4)	73.94(16)
O(2)	Y(1)	O(5)	128.97(16)	O(2)	Y(1)	O(6)	136.10(16)
O(2)	Y(1)	O(7)	141.89(15)	O(2)	Y(1)	N(1)	70.46(16)
O(2)	Y(1)	N(3)	72.70(15)	O(3)	Y(1)	O(4)	93.69(16)
O(3)	Y(1)	O(5)	72.27(16)	O(3)	Y(1)	O(6)	146.39(16)
O(3)	Y(1)	O(7)	90.56(15)	O(3)	Y(1)	N(1)	137.34(16)
O(3)	Y(1)	N(3)	83.92(15)	O(4)	Y(1)	O(5)	72.65(15)
O(4)	Y(1)	O(6)	82.15(17)	O(4)	Y(1)	O(7)	142.64(14)
O(4)	Y(1)	N(1)	95.97(16)	O(4)	Y(1)	N(3)	145.69(15)
O(5)	Y(1)	O(6)	74.69(16)	O(5)	Y(1)	O(7)	73.44(15)
O(5)	Y(1)	N(1)	149.90(17)	O(5)	Y(1)	N(3)	137.14(15)
O(6)	Y(1)	O(7)	74.21(16)	O(6)	Y(1)	N(1)	76.21(16)
O(6)	Y(1)	N(3)	117.63(16)	O(7)	Y(1)	N(1)	105.70(16)
O(7)	Y(1)	N(3)	71.67(14)	N(1)	Y(1)	N(3)	65.34(15)
Y(1)	O(2)	C(14)	134.1(4)	Y(1)	O(3)	C(16)	133.5(4)
Y(1)	O(4)	C(19)	136.5(4)	Y(1)	O(5)	C(21)	133.9(4)
Y(1)	O(6)	C(24)	133.0(5)	Y(1)	O(7)	C(26)	133.6(4)
Y(1)	N(1)	C(1)	116.9(4)	Y(1)	N(1)	C(8)	132.9(4)
Y(1)	N(3)	C(2)	119.9(4)	Y(1)	N(3)	C(6)	122.4(4)
O(1)	N(2)	C(1)	124.9(6)	O(1)	N(2)	C(7)	123.6(6)
C(1)	N(2)	C(7)	110.5(5)	C(2)	N(3)	C(6)	117.6(5)
C(1)	N(1)	C(8)	108.9(5)	N(1)	C(1)	C(2)	122.9(5)
N(1)	C(1)	N(2)	112.2(6)	N(2)	C(1)	C(2)	124.9(6)
C(1)	C(2)	C(3)	125.1(6)	N(3)	C(2)	C(1)	113.3(5)

N(3)	C(2)	C(3)	121.6(6)	C(2)	C(3)	C(4)	119.6(7)
C(3)	C(4)	C(5)	118.3(7)	C(4)	C(5)	C(6)	118.2(7)
N(3)	C(6)	C(5)	124.7(6)	C(8)	C(7)	C(10)	116.5(9)
C(8)	C(7)	C(9)	111.6(7)	C(9)	C(7)	C(10)	109.2(10)
N(2)	C(7)	C(10)	113.4(7)	N(2)	C(7)	C(8)	99.4(6)
N(2)	C(7)	C(9)	106.1(8)	C(11)	C(8)	C(12)	109.6(8)
C(12)	C(8)	N(1)	111.1(6)	C(7)	C(8)	C(11)	111.8(7)
C(7)	C(8)	C(12)	116.1(8)	N(1)	C(8)	C(11)	105.0(6)
N(1)	C(8)	C(7)	102.5(5)	F(1)	C(13)	C(14)	112.9(9)
F(1)	C(13)	F(2)	104.8(9)	F(1)	C(13)	F(3)	108.5(9)
F(2)	C(13)	C(14)	110.0(8)	F(2)	C(13)	F(3)	108.6(10)
F(3)	C(13)	C(14)	111.7(8)	C(13)	C(14)	C(15)	119.2(7)
O(2)	C(14)	C(13)	113.6(7)	O(2)	C(14)	C(15)	127.2(6)
C(14)	C(15)	C(16)	120.7(7)	C(15)	C(16)	C(17)	118.3(7)
O(3)	C(16)	C(15)	128.4(7)	O(3)	C(16)	C(17)	113.4(7)
F(4)	C(17)	C(16)	111.5(8)	F(4)	C(17)	F(5)	103.8(9)
F(4)	C(17)	F(6)	106.6(9)	F(5)	C(17)	C(16)	111.1(8)
F(5)	C(17)	F(6)	109.1(9)	F(6)	C(17)	C(16)	114.1(8)
F(7)	C(18)	C(19)	110.8(10)	F(7)	C(18)	F(8)	110.0(10)
F(7)	C(18)	F(9)	102.8(8)	F(8)	C(18)	C(19)	115.8(7)
F(8)	C(18)	F(9)	106.5(11)	F(9)	C(18)	C(19)	109.9(9)
C(18)	C(19)	C(20)	117.2(7)	O(4)	C(19)	C(18)	114.7(6)
O(4)	C(19)	C(20)	128.0(6)	C(19)	C(20)	C(21)	119.7(6)
C(20)	C(21)	C(22)	114.9(7)	O(5)	C(21)	C(20)	128.9(6)
O(5)	C(21)	C(22)	116.3(7)	F(10)	C(22)	C(21)	110.5(13)
F(10)	C(22)	F(11)	94.3(10)	F(10)	C(22)	F(12)	105.8(13)
F(11)	C(22)	C(21)	111.9(11)	F(11)	C(22)	F(12)	110.4(14)
F(12)	C(22)	C(21)	120.6(8)	F(13)	C(23)	C(24)	109.6(11)
F(13)	C(23)	F(14)	101.2(12)	F(13)	C(23)	F(15)	103.6(13)
F(14)	C(23)	C(24)	118.3(10)	F(14)	C(23)	F(15)	105.1(13)
F(15)	C(23)	C(24)	117.0(11)	C(23)	C(24)	C(25)	116.7(8)
O(6)	C(24)	C(23)	116.3(8)	O(6)	C(24)	C(25)	126.8(7)
C(24)	C(25)	C(26)	123.1(7)	C(25)	C(26)	C(27)	118.3(7)
O(7)	C(26)	C(25)	126.6(7)	O(7)	C(26)	C(27)	115.1(7)
F(16)	C(27)	C(26)	109.4(8)	F(16)	C(27)	F(17)	98.3(10)
F(16)	C(27)	F(18)	102.2(11)	F(17)	C(27)	C(26)	116.5(9)
F(17)	C(27)	F(18)	112.0(10)	F(18)	C(27)	C(26)	115.8(9)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Y(1)	O(2)	C(14)	-88.6(6)	O(3)	Y(1)	O(2)	C(14)	10.6(6)

O(7)	Y(1)	O(2)	C(14)	78.1(6)	O(6)	Y(1)	O(2)	C(14)	-148.3(6)
O(5)	Y(1)	O(2)	C(14)	-37.8(7)	N(1)	Y(1)	O(2)	C(14)	168.8(6)
N(3)	Y(1)	O(2)	C(14)	99.5(6)	O(4)	Y(1)	O(3)	C(16)	51.2(6)
O(7)	Y(1)	O(3)	C(16)	-165.9(6)	O(6)	Y(1)	O(3)	C(16)	132.6(6)
O(5)	Y(1)	O(3)	C(16)	121.7(6)	O(2)	Y(1)	O(3)	C(16)	-20.7(6)
N(1)	Y(1)	O(3)	C(16)	-51.7(7)	N(3)	Y(1)	O(3)	C(16)	-94.4(6)
O(3)	Y(1)	O(4)	C(19)	77.6(7)	O(7)	Y(1)	O(4)	C(19)	-18.2(8)
O(6)	Y(1)	O(4)	C(19)	-68.9(7)	O(5)	Y(1)	O(4)	C(19)	7.4(7)
O(2)	Y(1)	O(4)	C(19)	148.3(7)	N(1)	Y(1)	O(4)	C(19)	-144.1(7)
N(3)	Y(1)	O(4)	C(19)	162.2(6)	O(4)	Y(1)	O(5)	C(21)	-4.9(7)
O(3)	Y(1)	O(5)	C(21)	-104.8(7)	O(7)	Y(1)	O(5)	C(21)	159.2(7)
O(6)	Y(1)	O(5)	C(21)	81.5(7)	O(2)	Y(1)	O(5)	C(21)	-56.2(7)
N(1)	Y(1)	O(5)	C(21)	66.3(8)	N(3)	Y(1)	O(5)	C(21)	-164.2(6)
O(4)	Y(1)	O(6)	C(24)	133.0(6)	O(3)	Y(1)	O(6)	C(24)	48.2(7)
O(7)	Y(1)	O(6)	C(24)	-17.8(6)	O(5)	Y(1)	O(6)	C(24)	59.0(6)
O(2)	Y(1)	O(6)	C(24)	-170.1(6)	N(1)	Y(1)	O(6)	C(24)	-128.8(6)
N(3)	Y(1)	O(6)	C(24)	-76.6(6)	O(4)	Y(1)	O(7)	C(26)	-40.1(7)
O(3)	Y(1)	O(7)	C(26)	-136.9(6)	O(6)	Y(1)	O(7)	C(26)	12.7(5)
O(5)	Y(1)	O(7)	C(26)	-65.6(6)	O(2)	Y(1)	O(7)	C(26)	161.2(5)
N(1)	Y(1)	O(7)	C(26)	83.0(6)	N(3)	Y(1)	O(7)	C(26)	139.7(6)
O(4)	Y(1)	N(1)	C(1)	-139.1(5)	O(3)	Y(1)	N(1)	C(1)	-37.0(6)
O(7)	Y(1)	N(1)	C(1)	71.6(5)	O(6)	Y(1)	N(1)	C(1)	140.5(5)
O(5)	Y(1)	N(1)	C(1)	155.6(4)	O(2)	Y(1)	N(1)	C(1)	-68.5(5)
N(3)	Y(1)	N(1)	C(1)	10.9(4)	O(4)	Y(1)	N(1)	C(8)	26.7(6)
O(3)	Y(1)	N(1)	C(8)	128.7(6)	O(7)	Y(1)	N(1)	C(8)	-122.6(6)
O(6)	Y(1)	N(1)	C(8)	-53.7(6)	O(5)	Y(1)	N(1)	C(8)	-38.7(8)
O(2)	Y(1)	N(1)	C(8)	97.3(6)	N(3)	Y(1)	N(1)	C(8)	176.6(7)
O(4)	Y(1)	N(3)	C(6)	-123.3(5)	O(3)	Y(1)	N(3)	C(6)	-35.7(5)
O(7)	Y(1)	N(3)	C(6)	57.0(5)	O(6)	Y(1)	N(3)	C(6)	117.2(5)
O(5)	Y(1)	N(3)	C(6)	19.9(6)	O(2)	Y(1)	N(3)	C(6)	-109.3(5)
N(1)	Y(1)	N(3)	C(6)	174.7(5)	O(4)	Y(1)	N(3)	C(2)	55.4(5)
O(3)	Y(1)	N(3)	C(2)	143.0(4)	O(7)	Y(1)	N(3)	C(2)	-124.4(4)
O(6)	Y(1)	N(3)	C(2)	-64.1(4)	O(5)	Y(1)	N(3)	C(2)	-161.4(4)
O(2)	Y(1)	N(3)	C(2)	69.4(4)	N(1)	Y(1)	N(3)	C(2)	-6.6(4)
C(8)	N(1)	C(1)	N(2)	-6.8(8)	Y(1)	N(1)	C(1)	N(2)	162.3(4)
C(8)	N(1)	C(1)	C(2)	175.8(6)	Y(1)	N(1)	C(1)	C(2)	-15.1(8)
O(1)	N(2)	C(1)	N(1)	-179.7(7)	C(7)	N(2)	C(1)	N(1)	-10.9(9)
O(1)	N(2)	C(1)	C(2)	-2.4(12)	C(7)	N(2)	C(1)	C(2)	166.4(7)
C(6)	N(3)	C(2)	C(3)	-0.9(9)	Y(1)	N(3)	C(2)	C(3)	-179.6(5)
C(6)	N(3)	C(2)	C(1)	-178.9(6)	Y(1)	N(3)	C(2)	C(1)	2.3(7)
N(1)	C(1)	C(2)	N(3)	8.8(9)	N(2)	C(1)	C(2)	N(3)	-168.3(6)

N(1)	C(1)	C(2)	C(3)	-169.2(7)	N(2)	C(1)	C(2)	C(3)	13.7(11)
N(3)	C(2)	C(3)	C(4)	0.8(11)	C(1)	C(2)	C(3)	C(4)	178.7(7)
C(2)	C(3)	C(4)	C(5)	-0.6(11)	C(3)	C(4)	C(5)	C(6)	0.3(11)
C(2)	N(3)	C(6)	C(5)	0.7(10)	Y(1)	N(3)	C(6)	C(5)	179.4(5)
C(4)	C(5)	C(6)	N(3)	-0.4(11)	O(1)	N(2)	C(7)	C(10)	-44.6(14)
C(1)	N(2)	C(7)	C(10)	146.4(10)	O(1)	N(2)	C(7)	C(9)	75.2(10)
C(1)	N(2)	C(7)	C(9)	-93.8(8)	O(1)	N(2)	C(7)	C(8)	-169.0(7)
C(1)	N(2)	C(7)	C(8)	22.0(9)	C(1)	N(1)	C(8)	C(12)	144.7(8)
Y(1)	N(1)	C(8)	C(12)	-21.9(11)	C(1)	N(1)	C(8)	C(11)	-96.8(7)
Y(1)	N(1)	C(8)	C(11)	96.6(7)	C(1)	N(1)	C(8)	C(7)	20.1(8)
Y(1)	N(1)	C(8)	C(7)	-146.5(5)	N(2)	C(7)	C(8)	C(12)	-145.2(7)
C(10)	C(7)	C(8)	C(12)	92.5(11)	C(9)	C(7)	C(8)	C(12)	-33.7(11)
N(2)	C(7)	C(8)	N(1)	-24.0(8)	C(10)	C(7)	C(8)	N(1)	-146.2(9)
C(9)	C(7)	C(8)	N(1)	87.6(8)	N(2)	C(7)	C(8)	C(11)	88.0(8)
C(10)	C(7)	C(8)	C(11)	-34.2(11)	C(9)	C(7)	C(8)	C(11)	-160.5(8)
Y(1)	O(2)	C(14)	C(15)	-0.5(11)	Y(1)	O(2)	C(14)	C(13)	178.7(6)
F(3)	C(13)	C(14)	O(2)	56.7(11)	F(2)	C(13)	C(14)	O(2)	-63.9(11)
F(1)	C(13)	C(14)	O(2)	179.4(8)	F(3)	C(13)	C(14)	C(15)	-123.9(10)
F(2)	C(13)	C(14)	C(15)	115.4(9)	F(1)	C(13)	C(14)	C(15)	-1.3(13)
O(2)	C(14)	C(15)	C(16)	-8.4(12)	C(13)	C(14)	C(15)	C(16)	172.4(8)
Y(1)	O(3)	C(16)	C(15)	21.9(11)	Y(1)	O(3)	C(16)	C(17)	-159.6(6)
C(14)	C(15)	C(16)	O(3)	-2.2(12)	C(14)	C(15)	C(16)	C(17)	179.4(8)
O(3)	C(16)	C(17)	F(6)	175.0(8)	C(15)	C(16)	C(17)	F(6)	-6.4(13)
O(3)	C(16)	C(17)	F(5)	51.1(11)	C(15)	C(16)	C(17)	F(5)	-130.2(9)
O(3)	C(16)	C(17)	F(4)	-64.2(10)	C(15)	C(16)	C(17)	F(4)	114.4(9)
Y(1)	O(4)	C(19)	C(20)	-7.8(13)	Y(1)	O(4)	C(19)	C(18)	175.8(7)
F(8)	C(18)	C(19)	O(4)	173.3(11)	F(9)	C(18)	C(19)	O(4)	-65.8(12)
F(7)	C(18)	C(19)	O(4)	47.0(12)	F(8)	C(18)	C(19)	C(20)	-3.6(17)
F(9)	C(18)	C(19)	C(20)	117.3(9)	F(7)	C(18)	C(19)	C(20)	-129.8(9)
O(4)	C(19)	C(20)	C(21)	1.6(14)	C(18)	C(19)	C(20)	C(21)	177.9(9)
Y(1)	O(5)	C(21)	C(20)	2.8(13)	Y(1)	O(5)	C(21)	C(22)	-177.1(9)
C(19)	C(20)	C(21)	O(5)	0.7(14)	C(19)	C(20)	C(21)	C(22)	-179.4(11)
O(5)	C(21)	C(22)	F(12)	166.3(14)	C(20)	C(21)	C(22)	F(12)	-14(2)
O(5)	C(21)	C(22)	F(11)	34(2)	C(20)	C(21)	C(22)	F(11)	-146.1(15)
O(5)	C(21)	C(22)	F(10)	-69.9(18)	C(20)	C(21)	C(22)	F(10)	110.2(13)
Y(1)	O(6)	C(24)	C(25)	17.7(12)	Y(1)	O(6)	C(24)	C(23)	-167.0(7)
F(15)	C(23)	C(24)	O(6)	-54(2)	F(14)	C(23)	C(24)	O(6)	179.2(13)
F(13)	C(23)	C(24)	O(6)	63.9(16)	F(15)	C(23)	C(24)	C(25)	122.2(17)
F(14)	C(23)	C(24)	C(25)	-5.0(18)	F(13)	C(23)	C(24)	C(25)	-120.4(14)
O(6)	C(24)	C(25)	C(26)	-3.2(13)	C(23)	C(24)	C(25)	C(26)	-178.5(9)
Y(1)	O(7)	C(26)	C(25)	-7.4(10)	Y(1)	O(7)	C(26)	C(27)	170.8(6)

C(24)	C(25)	C(26)	O(7)	-2.1(12)	C(24)	C(25)	C(26)	C(27)	179.9(8)
O(7)	C(26)	C(27)	F(18)	-53.5(14)	C(25)	C(26)	C(27)	F(18)	124.8(11)
O(7)	C(26)	C(27)	F(17)	171.7(10)	C(25)	C(26)	C(27)	F(17)	-10.0(15)
O(7)	C(26)	C(27)	F(16)	61.3(12)	C(25)	C(26)	C(27)	F(16)	-120.4(10)

•[Gd(tfac)$_3$(IM-2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Gd(1)	O(2)	2.389(10)	Gd(1)	O(3)	2.368(9)
Gd(1)	O(4)	2.330(8)	Gd(1)	O(5)	2.327(10)
Gd(1)	O(6)	2.329(8)	Gd(1)	O(7)	2.328(8)
Gd(1)	N(1)	2.645(9)	Gd(1)	N(3)	2.629(11)
F(1)	C(13)	1.31(4)	F(2)	C(13)	1.14(3)
F(3)	C(13)	1.10(4)	F(4)	C(22)	1.25(2)
F(5)	C(22)	1.299(18)	F(6)	C(22)	1.33(2)
F(7)	C(27)	1.26(2)	F(8)	C(27)	1.19(2)
F(9)	C(27)	1.24(3)	O(1)	N(2)	1.255(14)
O(2)	C(14)	1.235(16)	O(3)	C(16)	1.252(15)
O(4)	C(19)	1.237(14)	O(5)	C(21)	1.254(17)
O(6)	C(24)	1.249(16)	O(7)	C(26)	1.284(17)
N(1)	C(1)	1.297(19)	N(1)	C(7)	1.511(13)
N(2)	C(1)	1.359(19)	N(2)	C(8)	1.51(2)
N(3)	C(2)	1.335(17)	N(3)	C(6)	1.357(18)
C(1)	C(2)	1.48(2)	C(2)	C(3)	1.370(19)
C(3)	C(4)	1.39(2)	C(4)	C(5)	1.38(2)
C(5)	C(6)	1.41(2)	C(7)	C(10)	1.51(2)
C(7)	C(8)	1.51(2)	C(7)	C(9)	1.55(2)
C(8)	C(11)	1.476(19)	C(8)	C(12)	1.54(2)
C(13)	C(14)	1.49(3)	C(14)	C(15)	1.41(2)
C(15)	C(16)	1.39(2)	C(16)	C(17)	1.55(2)
C(18)	C(19)	1.543(18)	C(19)	C(20)	1.38(2)
C(20)	C(21)	1.41(2)	C(21)	C(22)	1.52(2)
C(23)	C(24)	1.52(2)	C(24)	C(25)	1.382(18)
C(25)	C(26)	1.369(18)	C(26)	C(27)	1.50(2)

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Gd(1)	O(3)	71.2(3)	O(2)	Gd(1)	O(4)	79.5(3)
O(2)	Gd(1)	O(5)	124.2(4)	O(2)	Gd(1)	O(6)	141.6(3)
O(2)	Gd(1)	O(7)	135.7(3)	O(2)	Gd(1)	N(1)	73.3(3)

O(2)	Gd(1)	N(3)	72.8(4)	O(3)	Gd(1)	O(4)	111.5(3)
O(3)	Gd(1)	O(5)	75.2(3)	O(3)	Gd(1)	O(6)	147.1(3)
O(3)	Gd(1)	O(7)	81.8(4)	O(3)	Gd(1)	N(1)	137.6(3)
O(3)	Gd(1)	N(3)	85.5(3)	O(4)	Gd(1)	O(5)	73.1(3)
O(4)	Gd(1)	O(6)	80.3(3)	O(4)	Gd(1)	O(7)	144.3(3)
O(4)	Gd(1)	N(1)	83.5(3)	O(4)	Gd(1)	N(3)	140.6(3)
O(5)	Gd(1)	O(6)	79.6(4)	O(5)	Gd(1)	O(7)	79.2(4)
O(5)	Gd(1)	N(1)	146.0(3)	O(5)	Gd(1)	N(3)	146.1(3)
O(6)	Gd(1)	O(7)	72.9(3)	O(6)	Gd(1)	N(1)	72.3(3)
O(6)	Gd(1)	N(3)	104.9(4)	O(7)	Gd(1)	N(1)	109.4(3)
O(7)	Gd(1)	N(3)	70.6(3)	N(1)	Gd(1)	N(3)	62.2(3)
Gd(1)	O(2)	C(14)	138.0(11)	Gd(1)	O(3)	C(16)	136.1(10)
Gd(1)	O(4)	C(19)	135.7(8)	Gd(1)	O(5)	C(21)	129.9(10)
Gd(1)	O(6)	C(24)	134.9(8)	Gd(1)	O(7)	C(26)	133.7(8)
Gd(1)	N(1)	C(1)	118.5(9)	Gd(1)	N(1)	C(7)	132.9(7)
C(1)	N(1)	C(7)	107.2(11)	O(1)	N(2)	C(1)	127.6(14)
O(1)	N(2)	C(8)	122.6(11)	C(1)	N(2)	C(8)	109.0(13)
Gd(1)	N(3)	C(2)	122.5(9)	Gd(1)	N(3)	C(6)	117.6(10)
C(2)	N(3)	C(6)	119.1(13)	N(1)	C(1)	C(2)	122.7(13)
N(1)	C(1)	N(2)	113.4(15)	N(2)	C(1)	C(2)	123.8(14)
C(1)	C(2)	C(3)	123.8(13)	N(3)	C(2)	C(1)	113.6(12)
N(3)	C(2)	C(3)	122.6(13)	C(2)	C(3)	C(4)	120.0(16)
C(3)	C(4)	C(5)	117.7(15)	C(4)	C(5)	C(6)	120.2(15)
N(3)	C(6)	C(5)	120.2(16)	C(8)	C(7)	C(10)	116.0(14)
C(8)	C(7)	C(9)	111.6(12)	C(9)	C(7)	C(10)	108.6(14)
N(1)	C(7)	C(10)	109.7(10)	N(1)	C(7)	C(8)	104.4(10)
N(1)	C(7)	C(9)	106.0(11)	C(11)	C(8)	C(12)	108.1(14)
C(11)	C(8)	N(2)	110.7(15)	C(7)	C(8)	C(11)	119.1(14)
C(7)	C(8)	C(12)	114.1(15)	N(2)	C(8)	C(12)	104.6(13)
N(2)	C(8)	C(7)	99.0(10)	F(1)	C(13)	C(14)	106(3)
F(1)	C(13)	F(2)	97(4)	F(1)	C(13)	F(3)	109(4)
F(2)	C(13)	C(14)	108(3)	F(2)	C(13)	F(3)	123(5)
F(3)	C(13)	C(14)	111(3)	C(13)	C(14)	C(15)	121.3(15)
O(2)	C(14)	C(13)	115.3(17)	O(2)	C(14)	C(15)	123.4(15)
C(14)	C(15)	C(16)	123.5(14)	C(15)	C(16)	C(17)	119.8(15)
O(3)	C(16)	C(15)	126.5(15)	O(3)	C(16)	C(17)	113.7(15)
C(18)	C(19)	C(20)	117.1(14)	O(4)	C(19)	C(18)	119.1(13)
O(4)	C(19)	C(20)	123.8(14)	C(19)	C(20)	C(21)	122.9(16)
C(20)	C(21)	C(22)	118.8(14)	O(5)	C(21)	C(20)	128.0(14)
O(5)	C(21)	C(22)	113.1(14)	F(4)	C(22)	C(21)	113.6(15)
F(4)	C(22)	F(5)	106.4(18)	F(4)	C(22)	F(6)	107.1(18)

F(5)	C(22)	C(21)	117.1(15)	F(5)	C(22)	F(6)	103.0(16)
F(6)	C(22)	C(21)	108.7(17)	C(23)	C(24)	C(25)	118.7(14)
O(6)	C(24)	C(23)	115.2(14)	O(6)	C(24)	C(25)	126.1(12)
C(24)	C(25)	C(26)	123.0(13)	C(25)	C(26)	C(27)	119.8(15)
O(7)	C(26)	C(25)	126.7(12)	O(7)	C(26)	C(27)	113.3(13)
F(7)	C(27)	C(26)	116.2(18)	F(7)	C(27)	F(8)	102(2)
F(7)	C(27)	F(9)	99(2)	F(8)	C(27)	C(26)	115.6(16)
F(8)	C(27)	F(9)	105(2)	F(9)	C(27)	C(26)	116.2(19)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(5)	Gd(1)	O(2)	C(14)	-67.2(16)	O(6)	Gd(1)	O(2)	C(14)	172.4(14)
O(7)	Gd(1)	O(2)	C(14)	44.5(17)	O(4)	Gd(1)	O(2)	C(14)	-128.3(15)
O(3)	Gd(1)	O(2)	C(14)	-11.1(15)	N(3)	Gd(1)	O(2)	C(14)	80.0(15)
N(1)	Gd(1)	O(2)	C(14)	145.3(16)	O(5)	Gd(1)	O(3)	C(16)	134.5(13)
O(6)	Gd(1)	O(3)	C(16)	175.8(12)	O(7)	Gd(1)	O(3)	C(16)	-144.6(13)
O(4)	Gd(1)	O(3)	C(16)	69.8(13)	O(2)	Gd(1)	O(3)	C(16)	-0.2(13)
N(3)	Gd(1)	O(3)	C(16)	-73.5(13)	N(1)	Gd(1)	O(3)	C(16)	-34.8(15)
O(5)	Gd(1)	O(4)	C(19)	23.9(12)	O(6)	Gd(1)	O(4)	C(19)	-58.1(12)
O(7)	Gd(1)	O(4)	C(19)	-16.7(15)	O(3)	Gd(1)	O(4)	C(19)	90.0(12)
O(2)	Gd(1)	O(4)	C(19)	154.7(12)	N(3)	Gd(1)	O(4)	C(19)	-159.8(11)
N(1)	Gd(1)	O(4)	C(19)	-131.1(12)	O(6)	Gd(1)	O(5)	C(21)	57.3(14)
O(7)	Gd(1)	O(5)	C(21)	131.7(14)	O(4)	Gd(1)	O(5)	C(21)	-25.6(13)
O(3)	Gd(1)	O(5)	C(21)	-144.0(14)	O(2)	Gd(1)	O(5)	C(21)	-89.6(14)
N(3)	Gd(1)	O(5)	C(21)	158.6(13)	N(1)	Gd(1)	O(5)	C(21)	23.1(17)
O(5)	Gd(1)	O(6)	C(24)	64.6(13)	O(7)	Gd(1)	O(6)	C(24)	-17.1(13)
O(4)	Gd(1)	O(6)	C(24)	139.1(13)	O(3)	Gd(1)	O(6)	C(24)	24.2(17)
O(2)	Gd(1)	O(6)	C(24)	-161.9(12)	N(3)	Gd(1)	O(6)	C(24)	-81.0(13)
N(1)	Gd(1)	O(6)	C(24)	-134.7(14)	O(5)	Gd(1)	O(7)	C(26)	-67.5(11)
O(6)	Gd(1)	O(7)	C(26)	14.8(11)	O(4)	Gd(1)	O(7)	C(26)	-28.2(14)
O(3)	Gd(1)	O(7)	C(26)	-144.0(11)	O(2)	Gd(1)	O(7)	C(26)	164.0(10)
N(3)	Gd(1)	O(7)	C(26)	128.0(12)	N(1)	Gd(1)	O(7)	C(26)	78.4(11)
O(5)	Gd(1)	N(1)	C(1)	157.4(10)	O(6)	Gd(1)	N(1)	C(1)	121.9(10)
O(7)	Gd(1)	N(1)	C(1)	58.0(10)	O(4)	Gd(1)	N(1)	C(1)	-156.3(10)
O(3)	Gd(1)	N(1)	C(1)	-41.2(12)	O(2)	Gd(1)	N(1)	C(1)	-75.4(10)
N(3)	Gd(1)	N(1)	C(1)	3.6(10)	O(5)	Gd(1)	N(1)	C(7)	-37.8(13)
O(6)	Gd(1)	N(1)	C(7)	-73.3(10)	O(7)	Gd(1)	N(1)	C(7)	-137.3(10)
O(4)	Gd(1)	N(1)	C(7)	8.5(10)	O(3)	Gd(1)	N(1)	C(7)	123.5(10)
O(2)	Gd(1)	N(1)	C(7)	89.4(11)	N(3)	Gd(1)	N(1)	C(7)	168.3(11)
O(5)	Gd(1)	N(3)	C(2)	-159.9(11)	O(6)	Gd(1)	N(3)	C(2)	-66.4(12)
O(7)	Gd(1)	N(3)	C(2)	-131.8(12)	O(4)	Gd(1)	N(3)	C(2)	26.4(14)

O(3)	Gd(1)	N(3)	C(2)	145.3(12)	O(2)	Gd(1)	N(3)	C(2)	73.6(12)
N(1)	Gd(1)	N(3)	C(2)	-6.2(11)	O(5)	Gd(1)	N(3)	C(6)	30.0(13)
O(6)	Gd(1)	N(3)	C(6)	123.5(11)	O(7)	Gd(1)	N(3)	C(6)	58.1(11)
O(4)	Gd(1)	N(3)	C(6)	-143.7(10)	O(3)	Gd(1)	N(3)	C(6)	-24.8(11)
O(2)	Gd(1)	N(3)	C(6)	-96.5(11)	N(1)	Gd(1)	N(3)	C(6)	-176.3(12)
C(7)	N(1)	C(1)	N(2)	7.3(17)	Gd(1)	N(1)	C(1)	N(2)	175.6(9)
C(7)	N(1)	C(1)	C(2)	-169.8(14)	Gd(1)	N(1)	C(1)	C(2)	-1.5(19)
O(1)	N(2)	C(1)	N(1)	-179.7(13)	C(8)	N(2)	C(1)	N(1)	10.5(18)
O(1)	N(2)	C(1)	C(2)	-3(2)	C(8)	N(2)	C(1)	C(2)	-172.4(15)
C(6)	N(3)	C(2)	C(3)	-5(2)	Gd(1)	N(3)	C(2)	C(3)	-175.2(13)
C(6)	N(3)	C(2)	C(1)	177.7(14)	Gd(1)	N(3)	C(2)	C(1)	7.7(18)
N(1)	C(1)	C(2)	N(3)	-4(2)	N(2)	C(1)	C(2)	N(3)	179.2(14)
N(1)	C(1)	C(2)	C(3)	178.9(16)	N(2)	C(1)	C(2)	C(3)	2(3)
N(3)	C(2)	C(3)	C(4)	5(3)	C(1)	C(2)	C(3)	C(4)	-178.7(17)
C(2)	C(3)	C(4)	C(5)	-2(3)	C(3)	C(4)	C(5)	C(6)	1(3)
C(2)	N(3)	C(6)	C(5)	4(2)	Gd(1)	N(3)	C(6)	C(5)	174.3(12)
C(4)	C(5)	C(6)	N(3)	-2(3)	C(1)	N(1)	C(7)	C(10)	-146.7(15)
Gd(1)	N(1)	C(7)	C(10)	47.3(17)	C(1)	N(1)	C(7)	C(8)	-21.8(15)
Gd(1)	N(1)	C(7)	C(8)	172.2(10)	C(1)	N(1)	C(7)	C(9)	96.2(14)
Gd(1)	N(1)	C(7)	C(9)	-69.8(14)	O(1)	N(2)	C(8)	C(11)	41(2)
C(1)	N(2)	C(8)	C(11)	-148.5(14)	O(1)	N(2)	C(8)	C(7)	167.0(13)
C(1)	N(2)	C(8)	C(7)	-22.6(15)	O(1)	N(2)	C(8)	C(12)	-75.1(17)
C(1)	N(2)	C(8)	C(12)	95.3(14)	N(1)	C(7)	C(8)	C(11)	145.3(15)
C(10)	C(7)	C(8)	C(11)	-94(2)	C(9)	C(7)	C(8)	C(11)	31(2)
N(1)	C(7)	C(8)	N(2)	25.4(13)	C(10)	C(7)	C(8)	N(2)	146.2(13)
C(9)	C(7)	C(8)	N(2)	-88.6(13)	N(1)	C(7)	C(8)	C(12)	-85.0(14)
C(10)	C(7)	C(8)	C(12)	35.8(18)	C(9)	C(7)	C(8)	C(12)	160.9(13)
Gd(1)	O(2)	C(14)	C(15)	14(3)	Gd(1)	O(2)	C(14)	C(13)	-165.7(17)
F(3)	C(13)	C(14)	O(2)	-35(5)	F(2)	C(13)	C(14)	O(2)	-173(4)
F(1)	C(13)	C(14)	O(2)	84(3)	F(3)	C(13)	C(14)	C(15)	146(4)
F(2)	C(13)	C(14)	C(15)	8(5)	F(1)	C(13)	C(14)	C(15)	-95(3)
O(2)	C(14)	C(15)	C(16)	-2(3)	C(13)	C(14)	C(15)	C(16)	177(2)
Gd(1)	O(3)	C(16)	C(15)	8(2)	Gd(1)	O(3)	C(16)	C(17)	-169.6(12)
C(14)	C(15)	C(16)	O(3)	-8(3)	C(14)	C(15)	C(16)	C(17)	169.0(18)
Gd(1)	O(4)	C(19)	C(20)	-15(2)	Gd(1)	O(4)	C(19)	C(18)	163.2(11)
O(4)	C(19)	C(20)	C(21)	-5(3)	C(18)	C(19)	C(20)	C(21)	176.7(16)
Gd(1)	O(5)	C(21)	C(20)	22(3)	Gd(1)	O(5)	C(21)	C(22)	-161.0(12)
C(19)	C(20)	C(21)	O(5)	1(3)	C(19)	C(20)	C(21)	C(22)	-176.2(17)
O(5)	C(21)	C(22)	F(4)	50(2)	C(20)	C(21)	C(22)	F(4)	-133.1(19)
O(5)	C(21)	C(22)	F(5)	174.3(18)	C(20)	C(21)	C(22)	F(5)	-8(3)
O(5)	C(21)	C(22)	F(6)	-70(2)	C(20)	C(21)	C(22)	F(6)	107.8(19)

Gd(1)	O(6)	C(24)	C(25)	15(2)	Gd(1)	O(6)	C(24)	C(23)	-163.5(12)
O(6)	C(24)	C(25)	C(26)	-2(3)	C(23)	C(24)	C(25)	C(26)	177.1(15)
Gd(1)	O(7)	C(26)	C(25)	-11(2)	Gd(1)	O(7)	C(26)	C(27)	173.2(10)
C(24)	C(25)	C(26)	O(7)	0(2)	C(24)	C(25)	C(26)	C(27)	175.2(15)
O(7)	C(26)	C(27)	F(8)	-75(3)	C(25)	C(26)	C(27)	F(8)	110(3)
O(7)	C(26)	C(27)	F(9)	49(3)	C(25)	C(26)	C(27)	F(9)	-126(3)
O(7)	C(26)	C(27)	F(7)	165(2)	C(25)	C(26)	C(27)	F(7)	-10(3)

•[Gd(tfac)$_3$(pybzim)]

Bond lengths

atom	atom	distance	atom	atom	distance
Gd(1)	O(2)	2.430(7)	Gd(1)	O(3)	2.402(7)
Gd(1)	O(4)	2.382(7)	Gd(1)	O(5)	2.338(7)
Gd(1)	O(6)	2.346(7)	Gd(1)	O(7)	2.335(7)
Gd(1)	N(1)	2.474(8)	Gd(1)	N(3)	2.619(9)
F(1)	C(13)	1.310(17)	F(2)	C(13)	1.213(15)
F(3)	C(13)	1.310(17)	F(4)	C(17)	1.33(2)
F(5)	C(17)	1.29(3)	F(6)	C(17)	1.21(2)
F(7)	C(18)	1.303(15)	F(8)	C(18)	1.245(19)
F(9)	C(18)	1.290(19)	F(10)	C(22)	1.290(15)
F(11)	C(22)	1.271(15)	F(12)	C(22)	1.296(14)
F(13)	C(23)	1.270(18)	F(14)	C(23)	1.260(17)
F(15)	C(23)	1.237(16)	F(16)	C(27)	1.41(3)
F(16)	F(18)	1.717(18)	F(17)	C(27)	1.118(15)
F(18)	C(27)	1.133(15)	O(2)	C(14)	1.294(12)
O(3)	C(16)	1.237(14)	O(4)	C(19)	1.256(11)
O(5)	C(21)	1.252(12)	O(6)	C(24)	1.278(12)
O(7)	C(26)	1.236(12)	N(1)	C(1)	1.346(11)
N(1)	C(7)	1.374(12)	N(2)	C(1)	1.372(12)
N(2)	C(8)	1.368(12)	N(3)	C(2)	1.332(12)
N(3)	C(6)	1.363(13)	C(1)	C(2)	1.434(14)
C(2)	C(3)	1.362(14)	C(3)	C(4)	1.379(15)
C(4)	C(5)	1.385(15)	C(5)	C(6)	1.366(15)
C(7)	C(12)	1.375(14)	C(7)	C(8)	1.403(14)
C(8)	C(9)	1.351(14)	C(9)	C(10)	1.352(16)
C(10)	C(11)	1.372(15)	C(11)	C(12)	1.381(13)
C(13)	C(14)	1.514(18)	C(14)	C(15)	1.334(15)
C(15)	C(16)	1.404(17)	C(16)	C(17)	1.476(19)
C(18)	C(19)	1.513(15)	C(19)	C(20)	1.369(13)
C(20)	C(21)	1.398(14)	C(21)	C(22)	1.521(14)

C(23)	C(24)	1.529(16)	C(24)	C(25)	1.381(14)
C(25)	C(26)	1.374(14)	C(26)	C(27)	1.59(3)

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Gd(1)	O(3)	70.5(3)	O(2)	Gd(1)	O(4)	71.3(2)
O(2)	Gd(1)	O(5)	90.1(2)	O(2)	Gd(1)	O(6)	144.6(2)
O(2)	Gd(1)	O(7)	142.6(2)	O(2)	Gd(1)	N(1)	91.5(2)
O(2)	Gd(1)	N(3)	80.7(2)	O(3)	Gd(1)	O(4)	125.7(3)
O(3)	Gd(1)	O(5)	70.6(3)	O(3)	Gd(1)	O(6)	135.9(3)
O(3)	Gd(1)	O(7)	74.8(3)	O(3)	Gd(1)	N(1)	139.4(3)
O(3)	Gd(1)	N(3)	76.0(3)	O(4)	Gd(1)	O(5)	72.4(2)
O(4)	Gd(1)	O(6)	73.4(3)	O(4)	Gd(1)	O(7)	143.7(3)
O(4)	Gd(1)	N(1)	77.8(3)	O(4)	Gd(1)	N(3)	132.4(3)
O(5)	Gd(1)	O(6)	81.4(3)	O(5)	Gd(1)	O(7)	91.2(2)
O(5)	Gd(1)	N(1)	147.9(3)	O(5)	Gd(1)	N(3)	146.5(3)
O(6)	Gd(1)	O(7)	72.3(2)	O(6)	Gd(1)	N(1)	78.8(3)
O(6)	Gd(1)	N(3)	123.4(3)	O(7)	Gd(1)	N(1)	106.4(3)
O(7)	Gd(1)	N(3)	77.9(3)	N(1)	Gd(1)	N(3)	65.0(3)
Gd(1)	O(2)	C(14)	124.0(7)	Gd(1)	O(3)	C(16)	128.5(9)
Gd(1)	O(4)	C(19)	133.6(6)	Gd(1)	O(5)	C(21)	136.4(7)
Gd(1)	O(6)	C(24)	133.4(7)	Gd(1)	O(7)	C(26)	136.5(8)
Gd(1)	N(1)	C(1)	116.8(7)	Gd(1)	N(1)	C(7)	136.1(7)
C(1)	N(1)	C(7)	107.0(9)	C(1)	N(2)	C(8)	111.7(11)
Gd(1)	N(3)	C(2)	119.0(8)	Gd(1)	N(3)	C(6)	123.5(9)
C(2)	N(3)	C(6)	117.3(11)	N(1)	C(1)	C(2)	125.8(11)
N(1)	C(1)	N(2)	107.7(10)	N(2)	C(1)	C(2)	126.3(11)
C(1)	C(2)	C(3)	123.8(13)	N(3)	C(2)	C(1)	112.8(11)
N(3)	C(2)	C(3)	123.4(12)	C(2)	C(3)	C(4)	120.2(15)
C(3)	C(4)	C(5)	116.7(15)	C(4)	C(5)	C(6)	120.9(13)
N(3)	C(6)	C(5)	121.5(14)	C(8)	C(7)	C(12)	119.4(11)
N(1)	C(7)	C(12)	129.7(11)	N(1)	C(7)	C(8)	110.8(11)
C(7)	C(8)	C(9)	124.4(13)	C(9)	C(8)	N(2)	132.8(13)
N(2)	C(8)	C(7)	102.7(10)	C(8)	C(9)	C(10)	114.0(15)
C(9)	C(10)	C(11)	124.8(14)	C(10)	C(11)	C(12)	120.4(13)
C(7)	C(12)	C(11)	116.8(12)	F(1)	C(13)	C(14)	112.3(14)
F(1)	C(13)	F(2)	108.4(16)	F(1)	C(13)	F(3)	99.7(15)
F(2)	C(13)	C(14)	119.8(15)	F(2)	C(13)	F(3)	104.8(17)
F(3)	C(13)	C(14)	109.7(15)	C(13)	C(14)	C(15)	118.7(13)
O(2)	C(14)	C(13)	113.1(12)	O(2)	C(14)	C(15)	128.2(12)
C(14)	C(15)	C(16)	123.7(13)	C(15)	C(16)	C(17)	120.3(17)

O(3)	C(16)	C(15)	125.0(13)	O(3)	C(16)	C(17)	114.7(18)
F(4)	C(17)	C(16)	113.7(18)	F(4)	C(17)	F(5)	99.2(19)
F(4)	C(17)	F(6)	105(2)	F(5)	C(17)	C(16)	114(3)
F(5)	C(17)	F(6)	108(2)	F(6)	C(17)	C(16)	115(2)
F(7)	C(18)	C(19)	114.9(12)	F(7)	C(18)	F(8)	106.0(16)
F(7)	C(18)	F(9)	106.6(17)	F(8)	C(18)	C(19)	114.7(16)
F(8)	C(18)	F(9)	103.4(14)	F(9)	C(18)	C(19)	110.3(15)
C(18)	C(19)	C(20)	118.1(12)	O(4)	C(19)	C(18)	112.8(10)
O(4)	C(19)	C(20)	129.1(10)	C(19)	C(20)	C(21)	121.2(12)
C(20)	C(21)	C(22)	117.5(12)	O(5)	C(21)	C(20)	126.9(11)
O(5)	C(21)	C(22)	115.5(11)	F(10)	C(22)	C(21)	109.7(12)
F(10)	C(22)	F(11)	104.1(13)	F(10)	C(22)	F(12)	102.9(13)
F(11)	C(22)	C(21)	115.2(12)	F(11)	C(22)	F(12)	109.0(14)
F(12)	C(22)	C(21)	114.8(12)	F(13)	C(23)	C(24)	114.0(15)
F(13)	C(23)	F(14)	103.4(15)	F(13)	C(23)	F(15)	108.0(15)
F(14)	C(23)	C(24)	112.4(14)	F(14)	C(23)	F(15)	102.2(17)
F(15)	C(23)	C(24)	115.5(14)	C(23)	C(24)	C(25)	119.3(12)
O(6)	C(24)	C(23)	111.4(12)	O(6)	C(24)	C(25)	129.2(11)
C(24)	C(25)	C(26)	119.9(12)	C(25)	C(26)	C(27)	118.1(12)
O(7)	C(26)	C(25)	127.9(11)	O(7)	C(26)	C(27)	112.9(12)
F(16)	C(27)	C(26)	94(2)	F(16)	C(27)	F(17)	88(2)
F(16)	C(27)	F(18)	84(2)	F(17)	C(27)	C(26)	116.1(18)
F(17)	C(27)	F(18)	130(2)	F(18)	C(27)	C(26)	113.8(17)
C(27)	F(16)	F(18)	41.0(8)	C(27)	F(18)	F(16)	54.9(19)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(5)	Gd(1)	O(2)	C(14)	-28.1(9)	O(7)	Gd(1)	O(2)	C(14)	64.1(10)
O(6)	Gd(1)	O(2)	C(14)	-103.4(9)	O(4)	Gd(1)	O(2)	C(14)	-99.4(9)
O(3)	Gd(1)	O(2)	C(14)	41.2(8)	N(1)	Gd(1)	O(2)	C(14)	-176.0(9)
N(3)	Gd(1)	O(2)	C(14)	119.6(9)	O(5)	Gd(1)	O(3)	C(16)	54.3(10)
O(7)	Gd(1)	O(3)	C(16)	151.1(11)	O(6)	Gd(1)	O(3)	C(16)	108.1(10)
O(4)	Gd(1)	O(3)	C(16)	4.6(11)	O(2)	Gd(1)	O(3)	C(16)	-43.0(10)
N(1)	Gd(1)	O(3)	C(16)	-111.2(10)	N(3)	Gd(1)	O(3)	C(16)	-127.9(11)
O(5)	Gd(1)	O(4)	C(19)	-2.4(11)	O(7)	Gd(1)	O(4)	C(19)	-69.2(12)
O(6)	Gd(1)	O(4)	C(19)	-88.5(12)	O(3)	Gd(1)	O(4)	C(19)	46.5(12)
O(2)	Gd(1)	O(4)	C(19)	93.9(12)	N(1)	Gd(1)	O(4)	C(19)	-170.3(12)
N(3)	Gd(1)	O(4)	C(19)	151.2(11)	O(7)	Gd(1)	O(5)	C(21)	152.4(10)
O(6)	Gd(1)	O(5)	C(21)	80.5(10)	O(4)	Gd(1)	O(5)	C(21)	5.3(10)
O(3)	Gd(1)	O(5)	C(21)	-134.2(10)	O(2)	Gd(1)	O(5)	C(21)	-65.0(10)
N(1)	Gd(1)	O(5)	C(21)	28.0(12)	N(3)	Gd(1)	O(5)	C(21)	-138.1(9)

O(5)	Gd(1)	O(6)	C(24)	86.9(10)	O(7)	Gd(1)	O(6)	C(24)	-7.1(10)
O(4)	Gd(1)	O(6)	C(24)	161.0(11)	O(3)	Gd(1)	O(6)	C(24)	36.6(12)
O(2)	Gd(1)	O(6)	C(24)	164.9(9)	N(1)	Gd(1)	O(6)	C(24)	-118.5(10)
N(3)	Gd(1)	O(6)	C(24)	-68.8(11)	O(5)	Gd(1)	O(7)	C(26)	-71.0(11)
O(6)	Gd(1)	O(7)	C(26)	9.6(11)	O(4)	Gd(1)	O(7)	C(26)	-9.8(13)
O(3)	Gd(1)	O(7)	C(26)	-140.5(11)	O(2)	Gd(1)	O(7)	C(26)	-162.8(10)
N(1)	Gd(1)	O(7)	C(26)	81.8(11)	N(3)	Gd(1)	O(7)	C(26)	140.9(11)
O(5)	Gd(1)	N(1)	C(1)	-165.4(6)	O(7)	Gd(1)	N(1)	C(1)	74.0(7)
O(6)	Gd(1)	N(1)	C(1)	141.5(7)	O(4)	Gd(1)	N(1)	C(1)	-143.3(7)
O(3)	Gd(1)	N(1)	C(1)	-11.7(9)	O(2)	Gd(1)	N(1)	C(1)	-72.8(7)
N(3)	Gd(1)	N(1)	C(1)	6.2(6)	O(5)	Gd(1)	N(1)	C(7)	9.0(12)
O(7)	Gd(1)	N(1)	C(7)	-111.6(10)	O(6)	Gd(1)	N(1)	C(7)	-44.0(10)
O(4)	Gd(1)	N(1)	C(7)	31.1(10)	O(3)	Gd(1)	N(1)	C(7)	162.7(9)
O(2)	Gd(1)	N(1)	C(7)	101.6(10)	N(3)	Gd(1)	N(1)	C(7)	-179.3(10)
O(5)	Gd(1)	N(3)	C(2)	165.9(6)	O(7)	Gd(1)	N(3)	C(2)	-120.7(8)
O(6)	Gd(1)	N(3)	C(2)	-61.7(8)	O(4)	Gd(1)	N(3)	C(2)	36.2(9)
O(3)	Gd(1)	N(3)	C(2)	162.1(8)	O(2)	Gd(1)	N(3)	C(2)	90.1(7)
N(1)	Gd(1)	N(3)	C(2)	-6.0(7)	O(5)	Gd(1)	N(3)	C(6)	-9.8(11)
O(7)	Gd(1)	N(3)	C(6)	63.5(8)	O(6)	Gd(1)	N(3)	C(6)	122.6(8)
O(4)	Gd(1)	N(3)	C(6)	-139.6(8)	O(3)	Gd(1)	N(3)	C(6)	-13.6(8)
O(2)	Gd(1)	N(3)	C(6)	-85.7(8)	N(1)	Gd(1)	N(3)	C(6)	178.3(9)
C(7)	N(1)	C(1)	N(2)	0.8(11)	Gd(1)	N(1)	C(1)	N(2)	176.8(5)
C(7)	N(1)	C(1)	C(2)	176.7(9)	Gd(1)	N(1)	C(1)	C(2)	-7.3(12)
C(8)	N(2)	C(1)	N(1)	-0.2(11)	C(8)	N(2)	C(1)	C(2)	-176.1(9)
C(6)	N(3)	C(2)	C(3)	-0.5(16)	Gd(1)	N(3)	C(2)	C(3)	-176.5(8)
C(6)	N(3)	C(2)	C(1)	-179.3(9)	Gd(1)	N(3)	C(2)	C(1)	4.7(11)
N(1)	C(1)	C(2)	N(3)	1.6(14)	N(2)	C(1)	C(2)	N(3)	176.8(9)
N(1)	C(1)	C(2)	C(3)	-177.1(10)	N(2)	C(1)	C(2)	C(3)	-1.9(16)
N(3)	C(2)	C(3)	C(4)	-0.5(18)	C(1)	C(2)	C(3)	C(4)	178.1(10)
C(2)	C(3)	C(4)	C(5)	0.9(19)	C(3)	C(4)	C(5)	C(6)	0(2)
C(2)	N(3)	C(6)	C(5)	1.2(17)	Gd(1)	N(3)	C(6)	C(5)	177.0(9)
C(4)	C(5)	C(6)	N(3)	-1(2)	C(1)	N(1)	C(7)	C(12)	-177.3(11)
Gd(1)	N(1)	C(7)	C(12)	7.9(18)	C(1)	N(1)	C(7)	C(8)	-1.1(12)
Gd(1)	N(1)	C(7)	C(8)	-175.9(6)	C(1)	N(2)	C(8)	C(9)	-178.7(11)
C(1)	N(2)	C(8)	C(7)	-0.4(11)	N(1)	C(7)	C(8)	C(9)	179.4(10)
C(12)	C(7)	C(8)	C(9)	-4.0(17)	N(1)	C(7)	C(8)	N(2)	0.9(12)
C(12)	C(7)	C(8)	N(2)	177.6(10)	N(2)	C(8)	C(9)	C(10)	-178.5(12)
C(7)	C(8)	C(9)	C(10)	3.6(18)	C(8)	C(9)	C(10)	C(11)	-3(2)
C(9)	C(10)	C(11)	C(12)	4(2)	N(1)	C(7)	C(12)	C(11)	179.6(11)
C(8)	C(7)	C(12)	C(11)	3.7(16)	C(10)	C(11)	C(12)	C(7)	-3.6(18)
Gd(1)	O(2)	C(14)	C(15)	-32.9(17)	Gd(1)	O(2)	C(14)	C(13)	149.5(10)

F(2)	C(13)	C(14)	O(2)	-172.4(16)	F(1)	C(13)	C(14)	O(2)	58.7(19)
F(3)	C(13)	C(14)	O(2)	-51.2(19)	F(2)	C(13)	C(14)	C(15)	10(2)
F(1)	C(13)	C(14)	C(15)	-119.2(16)	F(3)	C(13)	C(14)	C(15)	130.9(16)
O(2)	C(14)	C(15)	C(16)	-1(2)	C(13)	C(14)	C(15)	C(16)	176.1(14)
Gd(1)	O(3)	C(16)	C(15)	32.3(18)	Gd(1)	O(3)	C(16)	C(17)	-148.7(15)
C(14)	C(15)	C(16)	O(3)	3(2)	C(14)	C(15)	C(16)	C(17)	-175.9(18)
O(3)	C(16)	C(17)	F(6)	81(3)	C(15)	C(16)	C(17)	F(6)	-100(3)
O(3)	C(16)	C(17)	F(5)	-45(3)	C(15)	C(16)	C(17)	F(5)	134(2)
O(3)	C(16)	C(17)	F(4)	-158(2)	C(15)	C(16)	C(17)	F(4)	21(3)
Gd(1)	O(4)	C(19)	C(20)	1(2)	Gd(1)	O(4)	C(19)	C(18)	-178.5(11)
F(8)	C(18)	C(19)	O(4)	-64(2)	F(9)	C(18)	C(19)	O(4)	52(2)
F(7)	C(18)	C(19)	O(4)	172.4(16)	F(8)	C(18)	C(19)	C(20)	115.7(17)
F(9)	C(18)	C(19)	C(20)	-127.9(16)	F(7)	C(18)	C(19)	C(20)	-7(3)
O(4)	C(19)	C(20)	C(21)	0(2)	C(18)	C(19)	C(20)	C(21)	179.3(13)
Gd(1)	O(5)	C(21)	C(20)	-6.9(18)	Gd(1)	O(5)	C(21)	C(22)	171.2(8)
C(19)	C(20)	C(21)	O(5)	3.2(18)	C(19)	C(20)	C(21)	C(22)	-174.8(12)
O(5)	C(21)	C(22)	F(11)	27.5(19)	C(20)	C(21)	C(22)	F(11)	-154.2(13)
O(5)	C(21)	C(22)	F(10)	-89.5(14)	C(20)	C(21)	C(22)	F(10)	88.8(15)
O(5)	C(21)	C(22)	F(12)	155.3(13)	C(20)	C(21)	C(22)	F(12)	-26.4(19)
Gd(1)	O(6)	C(24)	C(25)	7(2)	Gd(1)	O(6)	C(24)	C(23)	-175.4(10)
F(15)	C(23)	C(24)	O(6)	173.5(16)	F(14)	C(23)	C(24)	O(6)	57(2)
F(13)	C(23)	C(24)	O(6)	-61(2)	F(15)	C(23)	C(24)	C(25)	-8(3)
F(14)	C(23)	C(24)	C(25)	-125.0(16)	F(13)	C(23)	C(24)	C(25)	117.7(16)
O(6)	C(24)	C(25)	C(26)	-3(2)	C(23)	C(24)	C(25)	C(26)	179.2(13)
Gd(1)	O(7)	C(26)	C(25)	-11(2)	Gd(1)	O(7)	C(26)	C(27)	156.4(14)
C(24)	C(25)	C(26)	O(7)	5(2)	C(24)	C(25)	C(26)	C(27)	-162.0(17)
F(16)	F(18)	C(27)	F(17)	-82(4)	F(16)	F(18)	C(27)	C(26)	92(3)
F(18)	F(16)	C(27)	F(17)	130(3)	F(18)	F(16)	C(27)	C(26)	-113.5(16)
O(7)	C(26)	C(27)	F(17)	-167(3)	C(25)	C(26)	C(27)	F(17)	2(4)
O(7)	C(26)	C(27)	F(18)	18(4)	C(25)	C(26)	C(27)	F(18)	-173(3)
O(7)	C(26)	C(27)	F(16)	103.7(18)	C(25)	C(26)	C(27)	F(16)	-87.5(19)

•[Gd(hfac)$_3$(IM-6Me2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Gd(1)	O(2)	2.418(4)	Gd(1)	O(3)	2.342(4)
Gd(1)	O(4)	2.324(4)	Gd(1)	O(5)	2.400(4)
Gd(1)	O(6)	2.377(4)	Gd(1)	O(7)	2.349(4)
Gd(1)	N(1)	2.512(4)	Gd(1)	N(3)	2.622(5)
F(1)	C(14)	1.219(13)	F(2)	C(14)	1.205(14)

F(3)	C(14)	1.179(16)	F(4)	C(18)	1.240(12)
F(5)	C(18)	1.194(16)	F(6)	C(18)	1.204(13)
F(7)	C(19)	1.305(10)	F(8)	C(19)	1.300(9)
F(9)	C(19)	1.344(11)	F(10)	C(23)	1.258(11)
F(11)	C(23)	1.290(10)	F(12)	C(23)	1.235(11)
F(13)	C(24)	1.319(13)	F(14)	C(24)	1.234(11)
F(15)	C(24)	1.233(10)	F(16)	C(28)	1.301(10)
F(17)	C(28)	1.300(10)	F(18)	C(28)	1.283(10)
O(1)	N(2)	1.260(7)	O(2)	C(15)	1.233(8)
O(3)	C(17)	1.232(7)	O(4)	C(20)	1.259(7)
O(5)	C(22)	1.242(7)	O(6)	C(25)	1.243(7)
O(7)	C(27)	1.242(7)	N(1)	C(1)	1.307(7)
N(1)	C(8)	1.508(8)	N(2)	C(1)	1.384(7)
N(2)	C(9)	1.482(10)	N(3)	C(2)	1.350(7)
N(3)	C(6)	1.355(8)	C(1)	C(2)	1.457(9)
C(2)	C(3)	1.380(9)	C(3)	C(4)	1.420(13)
C(4)	C(5)	1.291(14)	C(5)	C(6)	1.385(10)
C(6)	C(7)	1.492(10)	C(8)	C(9)	1.544(9)
C(8)	C(10)	1.510(10)	C(8)	C(11)	1.533(10)
C(9)	C(13)	1.538(10)	C(9)	C(12)	1.548(11)
C(14)	C(15)	1.526(10)	C(15)	C(16)	1.385(10)
C(16)	C(17)	1.373(10)	C(17)	C(18)	1.527(10)
C(19)	C(20)	1.533(9)	C(20)	C(21)	1.371(8)
C(21)	C(22)	1.385(9)	C(22)	C(23)	1.532(9)
C(24)	C(25)	1.546(10)	C(25)	C(26)	1.379(10)
C(26)	C(27)	1.391(9)	C(27)	C(28)	1.524(9)

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Gd(1)	O(3)	70.82(15)	O(2)	Gd(1)	O(4)	72.97(16)
O(2)	Gd(1)	O(5)	130.64(15)	O(2)	Gd(1)	O(6)	148.48(15)
O(2)	Gd(1)	O(7)	131.05(16)	O(2)	Gd(1)	N(1)	76.67(15)
O(2)	Gd(1)	N(3)	70.98(15)	O(3)	Gd(1)	O(4)	84.94(16)
O(3)	Gd(1)	O(5)	73.17(16)	O(3)	Gd(1)	O(6)	140.26(15)
O(3)	Gd(1)	O(7)	81.72(15)	O(3)	Gd(1)	N(1)	147.49(16)
O(3)	Gd(1)	N(3)	102.50(16)	O(4)	Gd(1)	O(5)	71.27(15)
O(4)	Gd(1)	O(6)	100.10(17)	O(4)	Gd(1)	O(7)	144.87(15)
O(4)	Gd(1)	N(1)	86.35(15)	O(4)	Gd(1)	N(3)	138.08(14)
O(5)	Gd(1)	O(6)	71.42(16)	O(5)	Gd(1)	O(7)	73.78(15)
O(5)	Gd(1)	N(1)	132.50(16)	O(5)	Gd(1)	N(3)	150.55(15)

O(6)	Gd(1)	O(7)	71.64(15)	O(6)	Gd(1)	N(1)	72.16(15)
O(6)	Gd(1)	N(3)	99.49(15)	O(7)	Gd(1)	N(1)	120.92(15)
O(7)	Gd(1)	N(3)	76.77(15)	N(1)	Gd(1)	N(3)	65.19(15)
Gd(1)	O(2)	C(15)	131.5(4)	Gd(1)	O(3)	C(17)	134.0(4)
Gd(1)	O(4)	C(20)	134.1(4)	Gd(1)	O(5)	C(22)	132.6(4)
Gd(1)	O(6)	C(25)	131.5(4)	Gd(1)	O(7)	C(27)	133.1(4)
Gd(1)	N(1)	C(1)	117.9(4)	Gd(1)	N(1)	C(8)	133.0(4)
C(1)	N(1)	C(8)	109.1(5)	O(1)	N(2)	C(1)	126.5(6)
O(1)	N(2)	C(9)	123.2(6)	C(1)	N(2)	C(9)	109.5(5)
Gd(1)	N(3)	C(2)	116.6(4)	Gd(1)	N(3)	C(6)	124.1(4)
C(2)	N(3)	C(6)	119.1(5)	N(1)	C(1)	N(2)	111.2(5)
N(1)	C(1)	C(2)	123.5(5)	N(2)	C(1)	C(2)	125.3(5)
N(3)	C(2)	C(3)	121.6(6)	N(3)	C(2)	C(1)	115.7(5)
C(1)	C(2)	C(3)	122.7(6)	C(2)	C(3)	C(4)	117.2(8)
C(3)	C(4)	C(5)	120.4(8)	C(4)	C(5)	C(6)	121.5(8)
N(3)	C(6)	C(5)	120.0(6)	N(3)	C(6)	C(7)	119.2(6)
C(5)	C(6)	C(7)	120.8(7)	N(1)	C(8)	C(10)	111.8(5)
N(1)	C(8)	C(11)	104.6(5)	C(10)	C(8)	C(11)	109.0(7)
N(1)	C(8)	C(9)	102.3(5)	C(9)	C(8)	C(10)	114.8(6)
C(9)	C(8)	C(11)	113.7(6)	N(2)	C(9)	C(13)	109.6(7)
N(2)	C(9)	C(8)	99.5(5)	C(8)	C(9)	C(13)	116.2(7)
N(2)	C(9)	C(12)	106.5(7)	C(12)	C(9)	C(13)	110.8(7)
C(8)	C(9)	C(12)	113.2(7)	F(2)	C(14)	F(3)	102.6(15)
F(1)	C(14)	F(3)	97.2(13)	F(1)	C(14)	F(2)	109.1(14)
F(3)	C(14)	C(15)	113.2(12)	F(2)	C(14)	C(15)	115.8(8)
F(1)	C(14)	C(15)	116.5(11)	O(2)	C(15)	C(16)	128.3(6)
O(2)	C(15)	C(14)	114.5(7)	C(14)	C(15)	C(16)	117.2(7)
C(15)	C(16)	C(17)	120.0(6)	O(3)	C(17)	C(16)	129.0(6)
O(3)	C(17)	C(18)	113.8(7)	C(16)	C(17)	C(18)	117.2(6)
F(5)	C(18)	F(6)	100.7(14)	F(4)	C(18)	F(5)	104.1(13)
F(4)	C(18)	F(6)	105.8(13)	F(5)	C(18)	C(17)	113.0(10)
F(6)	C(18)	C(17)	114.8(8)	F(4)	C(18)	C(17)	116.7(9)
F(7)	C(19)	F(8)	110.7(8)	F(8)	C(19)	F(9)	104.6(7)
F(7)	C(19)	F(9)	105.4(8)	F(8)	C(19)	C(20)	114.4(7)
F(7)	C(19)	C(20)	110.7(7)	F(9)	C(19)	C(20)	110.5(7)
O(4)	C(20)	C(21)	128.4(6)	O(4)	C(20)	C(19)	112.9(6)
C(19)	C(20)	C(21)	118.7(6)	C(20)	C(21)	C(22)	120.2(5)
O(5)	C(22)	C(21)	128.1(5)	O(5)	C(22)	C(23)	114.1(6)
C(21)	C(22)	C(23)	117.9(6)	F(10)	C(23)	F(12)	105.9(10)
F(11)	C(23)	F(12)	105.5(9)	F(10)	C(23)	F(11)	105.1(9)
F(12)	C(23)	C(22)	113.2(7)	F(10)	C(23)	C(22)	111.8(7)

F(11)	C(23)	C(22)	114.6(7)	F(14)	C(24)	F(15)	109.2(11)
F(13)	C(24)	F(15)	103.8(10)	F(13)	C(24)	F(14)	102.0(10)
F(15)	C(24)	C(25)	117.1(8)	F(14)	C(24)	C(25)	113.2(8)
F(13)	C(24)	C(25)	110.0(8)	O(6)	C(25)	C(26)	128.2(6)
O(6)	C(25)	C(24)	114.9(6)	C(24)	C(25)	C(26)	116.8(6)
C(25)	C(26)	C(27)	121.4(6)	O(7)	C(27)	C(26)	126.7(6)
O(7)	C(27)	C(28)	114.8(6)	C(26)	C(27)	C(28)	118.5(6)
F(18)	C(28)	F(17)	104.1(8)	F(18)	C(28)	F(16)	114.3(9)
F(17)	C(28)	F(16)	100.0(8)	F(18)	C(28)	C(27)	114.1(7)
F(17)	C(28)	C(27)	112.3(7)	F(16)	C(28)	C(27)	110.9(7)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	Gd(1)	O(2)	C(15)	-65.3(6)	O(3)	Gd(1)	O(2)	C(15)	25.2(6)
O(7)	Gd(1)	O(2)	C(15)	84.8(6)	O(6)	Gd(1)	O(2)	C(15)	-146.8(6)
O(5)	Gd(1)	O(2)	C(15)	-20.2(7)	N(1)	Gd(1)	O(2)	C(15)	-155.6(7)
N(3)	Gd(1)	O(2)	C(15)	136.4(6)	O(4)	Gd(1)	O(3)	C(17)	49.7(7)
O(7)	Gd(1)	O(3)	C(17)	-162.9(7)	O(6)	Gd(1)	O(3)	C(17)	149.4(6)
O(5)	Gd(1)	O(3)	C(17)	121.6(7)	O(2)	Gd(1)	O(3)	C(17)	-24.1(6)
N(1)	Gd(1)	O(3)	C(17)	-25.4(8)	N(3)	Gd(1)	O(3)	C(17)	-88.5(7)
O(3)	Gd(1)	O(4)	C(20)	50.4(6)	O(7)	Gd(1)	O(4)	C(20)	-17.4(7)
O(6)	Gd(1)	O(4)	C(20)	-89.8(6)	O(5)	Gd(1)	O(4)	C(20)	-23.5(6)
O(2)	Gd(1)	O(4)	C(20)	121.9(6)	N(1)	Gd(1)	O(4)	C(20)	-160.9(6)
N(3)	Gd(1)	O(4)	C(20)	153.5(5)	O(4)	Gd(1)	O(5)	C(22)	21.9(6)
O(3)	Gd(1)	O(5)	C(22)	-68.4(6)	O(7)	Gd(1)	O(5)	C(22)	-154.5(6)
O(6)	Gd(1)	O(5)	C(22)	129.9(6)	O(2)	Gd(1)	O(5)	C(22)	-23.8(7)
N(1)	Gd(1)	O(5)	C(22)	88.2(6)	N(3)	Gd(1)	O(5)	C(22)	-154.1(5)
O(4)	Gd(1)	O(6)	C(25)	118.7(6)	O(3)	Gd(1)	O(6)	C(25)	24.4(7)
O(7)	Gd(1)	O(6)	C(25)	-26.0(6)	O(5)	Gd(1)	O(6)	C(25)	52.5(6)
O(2)	Gd(1)	O(6)	C(25)	-167.5(5)	N(1)	Gd(1)	O(6)	C(25)	-158.5(6)
N(3)	Gd(1)	O(6)	C(25)	-98.5(6)	O(4)	Gd(1)	O(7)	C(27)	-53.5(7)
O(3)	Gd(1)	O(7)	C(27)	-122.3(6)	O(6)	Gd(1)	O(7)	C(27)	27.8(5)
O(5)	Gd(1)	O(7)	C(27)	-47.5(5)	O(2)	Gd(1)	O(7)	C(27)	-177.8(5)
N(1)	Gd(1)	O(7)	C(27)	82.7(6)	N(3)	Gd(1)	O(7)	C(27)	132.7(6)
O(4)	Gd(1)	N(1)	C(1)	-156.5(4)	O(3)	Gd(1)	N(1)	C(1)	-81.8(5)
O(7)	Gd(1)	N(1)	C(1)	47.0(5)	O(6)	Gd(1)	N(1)	C(1)	101.7(4)
O(5)	Gd(1)	N(1)	C(1)	143.2(4)	O(2)	Gd(1)	N(1)	C(1)	-83.2(4)
N(3)	Gd(1)	N(1)	C(1)	-8.2(4)	O(4)	Gd(1)	N(1)	C(8)	24.5(5)
O(3)	Gd(1)	N(1)	C(8)	99.1(6)	O(7)	Gd(1)	N(1)	C(8)	-132.0(5)
O(6)	Gd(1)	N(1)	C(8)	-77.4(5)	O(5)	Gd(1)	N(1)	C(8)	-35.9(6)
O(2)	Gd(1)	N(1)	C(8)	97.8(5)	N(3)	Gd(1)	N(1)	C(8)	172.8(5)

O(4)	Gd(1)	N(3)	C(2)	60.2(5)	O(3)	Gd(1)	N(3)	C(2)	156.6(4)
O(7)	Gd(1)	N(3)	C(2)	-125.1(4)	O(6)	Gd(1)	N(3)	C(2)	-56.7(4)
O(5)	Gd(1)	N(3)	C(2)	-125.5(4)	O(2)	Gd(1)	N(3)	C(2)	92.3(4)
N(1)	Gd(1)	N(3)	C(2)	8.5(4)	O(4)	Gd(1)	N(3)	C(6)	-123.2(4)
O(3)	Gd(1)	N(3)	C(6)	-26.7(5)	O(7)	Gd(1)	N(3)	C(6)	51.5(4)
O(6)	Gd(1)	N(3)	C(6)	120.0(4)	O(5)	Gd(1)	N(3)	C(6)	51.1(6)
O(2)	Gd(1)	N(3)	C(6)	-91.1(4)	N(1)	Gd(1)	N(3)	C(6)	-174.8(5)
C(8)	N(1)	C(1)	N(2)	6.3(7)	Gd(1)	N(1)	C(1)	N(2)	-172.9(4)
C(8)	N(1)	C(1)	C(2)	-172.8(5)	Gd(1)	N(1)	C(1)	C(2)	8.0(7)
O(1)	N(2)	C(1)	N(1)	-176.6(7)	C(9)	N(2)	C(1)	N(1)	13.3(7)
O(1)	N(2)	C(1)	C(2)	2.4(11)	C(9)	N(2)	C(1)	C(2)	-167.6(6)
C(6)	N(3)	C(2)	C(3)	-3.4(9)	Gd(1)	N(3)	C(2)	C(3)	173.4(6)
C(6)	N(3)	C(2)	C(1)	175.0(5)	Gd(1)	N(3)	C(2)	C(1)	-8.2(6)
N(1)	C(1)	C(2)	N(3)	0.4(8)	N(2)	C(1)	C(2)	N(3)	-178.5(6)
N(1)	C(1)	C(2)	C(3)	178.8(7)	N(2)	C(1)	C(2)	C(3)	-0.1(10)
N(3)	C(2)	C(3)	C(4)	1.7(12)	C(1)	C(2)	C(3)	C(4)	-176.6(8)
C(2)	C(3)	C(4)	C(5)	-1.1(16)	C(3)	C(4)	C(5)	C(6)	2.1(17)
C(2)	N(3)	C(6)	C(5)	4.3(9)	Gd(1)	N(3)	C(6)	C(5)	-172.3(5)
C(2)	N(3)	C(6)	C(7)	-175.7(7)	Gd(1)	N(3)	C(6)	C(7)	7.7(9)
C(4)	C(5)	C(6)	N(3)	-3.7(13)	C(4)	C(5)	C(6)	C(7)	176.3(10)
C(1)	N(1)	C(8)	C(10)	-145.5(6)	Gd(1)	N(1)	C(8)	C(10)	33.6(8)
C(1)	N(1)	C(8)	C(11)	96.7(6)	Gd(1)	N(1)	C(8)	C(11)	-84.2(7)
C(1)	N(1)	C(8)	C(9)	-22.1(7)	Gd(1)	N(1)	C(8)	C(9)	157.0(4)
O(1)	N(2)	C(9)	C(13)	41.7(10)	C(1)	N(2)	C(9)	C(13)	-147.9(6)
O(1)	N(2)	C(9)	C(8)	164.0(7)	C(1)	N(2)	C(9)	C(8)	-25.6(7)
O(1)	N(2)	C(9)	C(12)	-78.2(9)	C(1)	N(2)	C(9)	C(12)	92.2(7)
N(1)	C(8)	C(9)	N(2)	27.2(6)	C(10)	C(8)	C(9)	N(2)	148.6(6)
C(11)	C(8)	C(9)	N(2)	-85.0(7)	N(1)	C(8)	C(9)	C(13)	144.7(7)
C(10)	C(8)	C(9)	C(13)	-94.0(9)	C(11)	C(8)	C(9)	C(13)	32.5(10)
N(1)	C(8)	C(9)	C(12)	-85.4(7)	C(10)	C(8)	C(9)	C(12)	35.9(9)
C(11)	C(8)	C(9)	C(12)	162.4(7)	Gd(1)	O(2)	C(15)	C(16)	-20.1(12)
Gd(1)	O(2)	C(15)	C(14)	160.8(7)	F(3)	C(14)	C(15)	O(2)	81.3(17)
F(2)	C(14)	C(15)	O(2)	-36.8(18)	F(1)	C(14)	C(15)	O(2)	-167.2(16)
F(3)	C(14)	C(15)	C(16)	-97.9(17)	F(2)	C(14)	C(15)	C(16)	144.0(14)
F(1)	C(14)	C(15)	C(16)	14(2)	O(2)	C(15)	C(16)	C(17)	-1.8(14)
C(14)	C(15)	C(16)	C(17)	177.3(9)	Gd(1)	O(3)	C(17)	C(16)	17.1(13)
Gd(1)	O(3)	C(17)	C(18)	-162.2(6)	C(15)	C(16)	C(17)	O(3)	4.1(14)
C(15)	C(16)	C(17)	C(18)	-176.7(8)	O(3)	C(17)	C(18)	F(5)	-84.3(16)
C(16)	C(17)	C(18)	F(5)	96.3(16)	O(3)	C(17)	C(18)	F(6)	30.5(18)
C(16)	C(17)	C(18)	F(6)	-148.9(15)	O(3)	C(17)	C(18)	F(4)	155.1(12)
C(16)	C(17)	C(18)	F(4)	-24.3(16)	Gd(1)	O(4)	C(20)	C(21)	18.5(11)

Gd(1)	O(4)	C(20)	C(19)	-161.4(5)	F(8)	C(19)	C(20)	O(4)	-164.5(8)
F(7)	C(19)	C(20)	O(4)	69.6(10)	F(9)	C(19)	C(20)	O(4)	-46.8(9)
F(8)	C(19)	C(20)	C(21)	15.6(11)	F(7)	C(19)	C(20)	C(21)	-110.3(9)
F(9)	C(19)	C(20)	C(21)	133.2(7)	O(4)	C(20)	C(21)	C(22)	2.6(11)
C(19)	C(20)	C(21)	C(22)	-177.4(7)	Gd(1)	O(5)	C(22)	C(21)	-15.3(10)
Gd(1)	O(5)	C(22)	C(23)	163.5(5)	C(20)	C(21)	C(22)	O(5)	-3.7(11)
C(20)	C(21)	C(22)	C(23)	177.6(7)	O(5)	C(22)	C(23)	F(12)	-77.5(11)
C(21)	C(22)	C(23)	F(12)	101.4(10)	O(5)	C(22)	C(23)	F(10)	42.0(11)
C(21)	C(22)	C(23)	F(10)	-139.1(9)	O(5)	C(22)	C(23)	F(11)	161.5(8)
C(21)	C(22)	C(23)	F(11)	-19.6(12)	Gd(1)	O(6)	C(25)	C(26)	20.4(11)
Gd(1)	O(6)	C(25)	C(24)	-156.8(6)	F(15)	C(24)	C(25)	O(6)	-166.8(11)
F(14)	C(24)	C(25)	O(6)	64.8(13)	F(13)	C(24)	C(25)	O(6)	-48.6(11)
F(15)	C(24)	C(25)	C(26)	15.6(15)	F(14)	C(24)	C(25)	C(26)	-112.8(11)
F(13)	C(24)	C(25)	C(26)	133.8(9)	O(6)	C(25)	C(26)	C(27)	0.3(13)
C(24)	C(25)	C(26)	C(27)	177.5(8)	Gd(1)	O(7)	C(27)	C(26)	-23.3(10)
Gd(1)	O(7)	C(27)	C(28)	153.9(5)	C(25)	C(26)	C(27)	O(7)	0.7(12)
C(25)	C(26)	C(27)	C(28)	-176.4(7)	O(7)	C(27)	C(28)	F(18)	156.1(9)
C(26)	C(27)	C(28)	F(18)	-26.5(12)	O(7)	C(27)	C(28)	F(17)	37.9(9)
C(26)	C(27)	C(28)	F(17)	-144.6(8)	O(7)	C(27)	C(28)	F(16)	-73.1(9)
C(26)	C(27)	C(28)	F(16)	104.3(9)					

•[Dy(hfac)$_3$(IM-5Me2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Dy(1)	O(2)	2.315(4)	Dy(1)	O(3)	2.365(4)
Dy(1)	O(4)	2.350(4)	Dy(1)	O(5)	2.320(4)
Dy(1)	O(6)	2.312(4)	Dy(1)	O(7)	2.362(4)
Dy(1)	N(1)	2.521(4)	Dy(1)	N(3)	2.516(4)
F(1)	C(14)	1.247(15)	F(2)	C(14)	1.187(12)
F(3)	C(14)	1.252(11)	F(4)	C(18)	1.181(11)
F(5)	C(18)	1.196(11)	F(6)	C(18)	1.238(12)
F(7)	C(19)	1.188(12)	F(8)	C(19)	1.148(14)
F(9)	C(19)	1.337(16)	F(10)	C(23)	1.281(12)
F(11)	C(23)	1.302(12)	F(12)	C(23)	1.271(12)
F(13)	C(24)	1.313(11)	F(14)	C(24)	1.252(11)
F(15)	C(24)	1.283(8)	F(16)	C(28)	1.293(8)
F(17)	C(28)	1.303(9)	F(18)	C(28)	1.236(9)
O(1)	N(2)	1.284(6)	O(2)	C(15)	1.256(8)
O(3)	C(17)	1.236(7)	O(4)	C(20)	1.255(9)
O(5)	C(22)	1.254(8)	O(6)	C(25)	1.254(7)

O(7)	C(27)	1.229(6)	N(1)	C(1)	1.284(6)
N(1)	C(8)	1.504(7)	N(2)	C(1)	1.375(7)
N(2)	C(9)	1.492(8)	N(3)	C(6)	1.338(7)
N(3)	C(2)	1.352(7)	C(1)	C(2)	1.468(7)
C(2)	C(3)	1.378(8)	C(3)	C(4)	1.367(10)
C(4)	C(5)	1.388(11)	C(5)	C(6)	1.376(9)
C(5)	C(7)	1.503(9)	C(8)	C(11)	1.532(8)
C(8)	C(10)	1.536(8)	C(8)	C(9)	1.557(8)
C(9)	C(12)	1.502(9)	C(9)	C(13)	1.538(9)
C(14)	C(15)	1.487(10)	C(15)	C(16)	1.390(10)
C(16)	C(17)	1.374(9)	C(17)	C(18)	1.523(9)
C(19)	C(20)	1.537(13)	C(20)	C(21)	1.404(11)
C(21)	C(22)	1.359(10)	C(22)	C(23)	1.517(11)
C(24)	C(25)	1.531(9)	C(25)	C(26)	1.365(9)
C(26)	C(27)	1.397(8)	C(27)	C(28)	1.549(8)

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Dy(1)	O(3)	72.06(15)	O(2)	Dy(1)	O(4)	73.55(18)
O(2)	Dy(1)	O(5)	106.21(16)	O(2)	Dy(1)	O(6)	84.55(15)
O(2)	Dy(1)	O(7)	144.33(15)	O(3)	Dy(1)	O(4)	118.59(16)
O(3)	Dy(1)	O(5)	71.05(15)	O(3)	Dy(1)	O(6)	145.43(14)
O(3)	Dy(1)	O(7)	139.42(13)	O(4)	Dy(1)	O(5)	71.97(16)
O(4)	Dy(1)	O(6)	76.48(15)	O(4)	Dy(1)	O(7)	74.81(16)
O(5)	Dy(1)	O(6)	141.73(14)	O(5)	Dy(1)	O(7)	78.82(14)
O(6)	Dy(1)	O(7)	72.39(13)	N(3)	Dy(1)	N(1)	65.06(14)
O(2)	Dy(1)	N(1)	87.69(16)	O(2)	Dy(1)	N(3)	142.37(16)
O(3)	Dy(1)	N(1)	77.97(14)	O(3)	Dy(1)	N(3)	76.98(14)
O(4)	Dy(1)	N(1)	147.86(15)	O(4)	Dy(1)	N(3)	142.04(17)
O(5)	Dy(1)	N(1)	139.54(14)	O(5)	Dy(1)	N(3)	82.80(15)
O(6)	Dy(1)	N(1)	75.95(13)	O(6)	Dy(1)	N(3)	111.18(14)
O(7)	Dy(1)	N(1)	111.65(14)	O(7)	Dy(1)	N(3)	72.77(14)
N(1)	C(1)	C(2)	123.2(5)	N(1)	C(1)	N(2)	113.1(5)
N(2)	C(1)	C(2)	123.7(5)	F(1)	C(14)	C(15)	114.0(10)
F(1)	C(14)	F(2)	103.5(13)	F(1)	C(14)	F(3)	93.6(12)
F(2)	C(14)	C(15)	117.7(9)	F(2)	C(14)	F(3)	111.3(11)
F(3)	C(14)	C(15)	113.8(10)	C(14)	C(15)	C(16)	119.1(8)
O(2)	C(15)	C(14)	113.9(8)	O(2)	C(15)	C(16)	126.9(6)
C(15)	C(16)	C(17)	120.8(6)	C(16)	C(17)	C(18)	117.5(6)
O(3)	C(17)	C(16)	128.5(6)	O(3)	C(17)	C(18)	114.0(6)
F(4)	C(18)	C(17)	118.1(8)	F(4)	C(18)	F(5)	106.3(11)

F(4)	C(18)	F(6)	103.2(13)	F(5)	C(18)	C(17)	113.2(10)
F(5)	C(18)	F(6)	101.4(10)	F(6)	C(18)	C(17)	112.9(8)
F(7)	C(19)	C(20)	115.4(9)	F(7)	C(19)	F(8)	112.7(18)
F(7)	C(19)	F(9)	96.5(12)	F(8)	C(19)	C(20)	117.2(10)
F(8)	C(19)	F(9)	104.6(12)	F(9)	C(19)	C(20)	107.3(13)
C(1)	C(2)	C(3)	125.6(6)	N(3)	C(2)	C(1)	113.1(4)
N(3)	C(2)	C(3)	121.2(5)	C(19)	C(20)	C(21)	121.9(8)
O(4)	C(20)	C(19)	111.2(9)	O(4)	C(20)	C(21)	126.9(7)
C(20)	C(21)	C(22)	120.2(7)	C(21)	C(22)	C(23)	119.4(7)
O(5)	C(22)	C(21)	128.7(7)	O(5)	C(22)	C(23)	111.9(7)
F(10)	C(23)	C(22)	114.0(8)	F(10)	C(23)	F(11)	104.8(10)
F(10)	C(23)	F(12)	105.6(11)	F(11)	C(23)	C(22)	112.4(10)
F(11)	C(23)	F(12)	105.8(10)	F(12)	C(23)	C(22)	113.5(8)
F(13)	C(24)	C(25)	108.9(8)	F(13)	C(24)	F(14)	103.9(8)
F(13)	C(24)	F(15)	109.5(8)	F(14)	C(24)	C(25)	111.5(7)
F(14)	C(24)	F(15)	106.8(8)	F(15)	C(24)	C(25)	115.6(7)
C(26)	C(25)	C(24)	117.6(6)	O(6)	C(25)	C(24)	114.0(6)
O(6)	C(25)	C(26)	128.4(6)	C(25)	C(26)	C(27)	120.0(5)
C(26)	C(27)	C(28)	116.3(5)	O(7)	C(27)	C(26)	128.6(5)
O(7)	C(27)	C(28)	115.1(5)	F(16)	C(28)	C(27)	114.0(6)
F(16)	C(28)	F(17)	101.5(7)	F(16)	C(28)	F(18)	108.4(7)
F(17)	C(28)	C(27)	111.8(6)	F(17)	C(28)	F(18)	107.9(8)
F(18)	C(28)	C(27)	112.6(7)	C(2)	C(3)	C(4)	119.4(7)
C(3)	C(4)	C(5)	120.3(7)	C(4)	C(5)	C(6)	117.0(6)
C(4)	C(5)	C(7)	122.2(7)	C(6)	C(5)	C(7)	120.8(8)
N(3)	C(6)	C(5)	123.7(7)	C(10)	C(8)	C(11)	109.0(5)
C(9)	C(8)	C(10)	111.3(5)	C(9)	C(8)	C(11)	114.6(5)
N(1)	C(8)	C(10)	105.7(4)	N(1)	C(8)	C(11)	112.4(5)
N(1)	C(8)	C(9)	103.4(4)	C(12)	C(9)	C(13)	110.8(7)
C(8)	C(9)	C(12)	115.8(6)	C(8)	C(9)	C(12)	112.5(6)
N(2)	C(9)	C(12)	111.9(6)	N(2)	C(9)	C(13)	106.2(5)
N(2)	C(9)	C(8)	98.6(4)	C(1)	N(1)	C(8)	108.3(4)
Dy(1)	N(1)	C(1)	117.5(3)	Dy(1)	N(1)	C(8)	134.1(3)
C(1)	N(2)	C(9)	109.7(4)	O(1)	N(2)	C(1)	127.7(5)
O(1)	N(2)	C(9)	121.3(5)	C(2)	N(3)	C(6)	118.4(5)
Dy(1)	N(3)	C(2)	120.7(3)	Dy(1)	N(3)	C(6)	120.9(4)
Dy(1)	O(2)	C(15)	134.1(4)	Dy(1)	O(3)	C(17)	132.3(4)
Dy(1)	O(4)	C(20)	135.3(5)	Dy(1)	O(5)	C(22)	135.9(4)
Dy(1)	O(6)	C(25)	133.5(4)	Dy(1)	O(7)	C(27)	132.3(4)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(6)	Dy(1)	O(2)	C(15)	177.5(6)	O(5)	Dy(1)	O(2)	C(15)	-40.0(7)
O(4)	Dy(1)	O(2)	C(15)	-105.0(6)	O(7)	Dy(1)	O(2)	C(15)	-133.4(6)
O(3)	Dy(1)	O(2)	C(15)	23.3(6)	N(3)	Dy(1)	O(2)	C(15)	59.4(7)
N(1)	Dy(1)	O(2)	C(15)	101.4(6)	O(6)	Dy(1)	O(3)	C(17)	-72.1(6)
O(2)	Dy(1)	O(3)	C(17)	-22.3(5)	O(5)	Dy(1)	O(3)	C(17)	92.7(5)
O(4)	Dy(1)	O(3)	C(17)	36.7(6)	O(7)	Dy(1)	O(3)	C(17)	136.9(5)
N(3)	Dy(1)	O(3)	C(17)	179.4(6)	N(1)	Dy(1)	O(3)	C(17)	-113.7(5)
O(6)	Dy(1)	O(4)	C(20)	-147.6(7)	O(2)	Dy(1)	O(4)	C(20)	124.2(7)
O(5)	Dy(1)	O(4)	C(20)	10.4(6)	O(7)	Dy(1)	O(4)	C(20)	-72.5(6)
O(3)	Dy(1)	O(4)	C(20)	65.9(7)	N(3)	Dy(1)	O(4)	C(20)	-40.4(8)
N(1)	Dy(1)	O(4)	C(20)	-179.2(5)	O(6)	Dy(1)	O(5)	C(22)	27.9(7)
O(2)	Dy(1)	O(5)	C(22)	-74.1(6)	O(4)	Dy(1)	O(5)	C(22)	-8.0(6)
O(7)	Dy(1)	O(5)	C(22)	69.5(6)	O(3)	Dy(1)	O(5)	C(22)	-138.1(6)
N(3)	Dy(1)	O(5)	C(22)	143.2(6)	N(1)	Dy(1)	O(5)	C(22)	179.8(5)
O(2)	Dy(1)	O(6)	C(25)	130.2(6)	O(5)	Dy(1)	O(6)	C(25)	20.8(7)
O(4)	Dy(1)	O(6)	C(25)	55.8(6)	O(7)	Dy(1)	O(6)	C(25)	-22.3(6)
O(3)	Dy(1)	O(6)	C(25)	177.1(5)	N(3)	Dy(1)	O(6)	C(25)	-85.1(6)
N(1)	Dy(1)	O(6)	C(25)	-140.8(6)	O(6)	Dy(1)	O(7)	C(27)	20.5(5)
O(2)	Dy(1)	O(7)	C(27)	-31.7(6)	O(5)	Dy(1)	O(7)	C(27)	-134.0(5)
O(4)	Dy(1)	O(7)	C(27)	-59.9(5)	O(3)	Dy(1)	O(7)	C(27)	-176.3(5)
N(3)	Dy(1)	O(7)	C(27)	140.2(5)	N(1)	Dy(1)	O(7)	C(27)	86.9(5)
O(6)	Dy(1)	N(1)	C(1)	116.6(4)	O(2)	Dy(1)	N(1)	C(1)	-158.4(4)
O(5)	Dy(1)	N(1)	C(1)	-45.9(4)	O(4)	Dy(1)	N(1)	C(1)	148.2(4)
O(7)	Dy(1)	N(1)	C(1)	52.4(4)	O(3)	Dy(1)	N(1)	C(1)	-86.3(4)
N(3)	Dy(1)	N(1)	C(1)	-5.2(3)	O(6)	Dy(1)	N(1)	C(8)	-66.7(4)
O(2)	Dy(1)	N(1)	C(8)	18.2(4)	O(5)	Dy(1)	N(1)	C(8)	130.8(4)
O(4)	Dy(1)	N(1)	C(8)	-35.1(6)	O(7)	Dy(1)	N(1)	C(8)	-131.0(4)
O(3)	Dy(1)	N(1)	C(8)	90.4(4)	N(3)	Dy(1)	N(1)	C(8)	171.5(5)
O(6)	Dy(1)	N(3)	C(6)	120.7(4)	O(2)	Dy(1)	N(3)	C(6)	-129.7(4)
O(5)	Dy(1)	N(3)	C(6)	-22.4(4)	O(4)	Dy(1)	N(3)	C(6)	25.6(5)
O(7)	Dy(1)	N(3)	C(6)	58.1(4)	O(3)	Dy(1)	N(3)	C(6)	-94.5(4)
N(1)	Dy(1)	N(3)	C(6)	-177.1(5)	O(6)	Dy(1)	N(3)	C(2)	-58.2(4)
O(2)	Dy(1)	N(3)	C(2)	51.4(5)	O(5)	Dy(1)	N(3)	C(2)	158.7(4)
O(4)	Dy(1)	N(3)	C(2)	-153.3(4)	O(7)	Dy(1)	N(3)	C(2)	-120.9(4)
O(3)	Dy(1)	N(3)	C(2)	86.5(4)	N(1)	Dy(1)	N(3)	C(2)	3.9(4)
C(8)	N(1)	C(1)	N(2)	8.8(6)	Dy(1)	N(1)	C(1)	N(2)	-173.7(3)
C(8)	N(1)	C(1)	C(2)	-170.9(4)	Dy(1)	N(1)	C(1)	C(2)	6.6(6)
O(1)	N(2)	C(1)	N(1)	175.9(6)	C(9)	N(2)	C(1)	N(1)	9.2(6)
O(1)	N(2)	C(1)	C(2)	-4.4(9)	C(9)	N(2)	C(1)	C(2)	-171.1(5)
C(6)	N(3)	C(2)	C(3)	-1.9(8)	Dy(1)	N(3)	C(2)	C(3)	177.1(4)

C(6)	N(3)	C(2)	C(1)	178.6(5)	Dy(1)	N(3)	C(2)	C(1)	-2.4(6)
N(1)	C(1)	C(2)	N(3)	-2.9(7)	N(2)	C(1)	C(2)	N(3)	177.4(5)
N(1)	C(1)	C(2)	C(3)	177.6(6)	N(2)	C(1)	C(2)	C(3)	-2.1(9)
N(3)	C(2)	C(3)	C(4)	2.4(10)	C(1)	C(2)	C(3)	C(4)	-178.2(6)
C(2)	C(3)	C(4)	C(5)	-1.2(12)	C(3)	C(4)	C(5)	C(6)	-0.4(12)
C(3)	C(4)	C(5)	C(7)	179.5(8)	C(2)	N(3)	C(6)	C(5)	0.2(9)
Dy(1)	N(3)	C(6)	C(5)	-178.8(5)	C(4)	C(5)	C(6)	N(3)	0.9(10)
C(7)	C(5)	C(6)	N(3)	-179.0(7)	C(1)	N(1)	C(8)	C(11)	-146.2(5)
Dy(1)	N(1)	C(8)	C(11)	36.9(7)	C(1)	N(1)	C(8)	C(10)	95.0(6)
Dy(1)	N(1)	C(8)	C(10)	-81.9(6)	C(1)	N(1)	C(8)	C(9)	-22.1(5)
Dy(1)	N(1)	C(8)	C(9)	161.0(4)	O(1)	N(2)	C(9)	C(12)	48.5(9)
C(1)	N(2)	C(9)	C(12)	-143.8(7)	O(1)	N(2)	C(9)	C(13)	-72.6(8)
C(1)	N(2)	C(9)	C(13)	95.1(6)	O(1)	N(2)	C(9)	C(8)	170.8(6)
C(1)	N(2)	C(9)	C(8)	-21.4(6)	N(1)	C(8)	C(9)	N(2)	24.8(5)
C(11)	C(8)	C(9)	N(2)	147.5(5)	C(10)	C(8)	C(9)	N(2)	-88.3(6)
N(1)	C(8)	C(9)	C(12)	144.3(6)	C(11)	C(8)	C(9)	C(12)	-93.0(8)
C(10)	C(8)	C(9)	C(12)	31.2(8)	N(1)	C(8)	C(9)	C(13)	-86.8(6)
C(11)	C(8)	C(9)	C(13)	35.9(7)	C(10)	C(8)	C(9)	C(13)	160.1(6)
Dy(1)	O(2)	C(15)	C(16)	-18.4(11)	Dy(1)	O(2)	C(15)	C(14)	165.6(6)
F(2)	C(14)	C(15)	O(2)	67.0(16)	F(1)	C(14)	C(15)	O(2)	-54.4(15)
F(3)	C(14)	C(15)	O(2)	-160.1(14)	F(2)	C(14)	C(15)	C(16)	-109.2(13)
F(1)	C(14)	C(15)	C(16)	129.3(14)	F(3)	C(14)	C(15)	C(16)	23.6(18)
O(2)	C(15)	C(16)	C(17)	-1.4(12)	C(14)	C(15)	C(16)	C(17)	174.3(8)
Dy(1)	O(3)	C(17)	C(16)	16.8(10)	Dy(1)	O(3)	C(17)	C(18)	-162.3(6)
C(15)	C(16)	C(17)	O(3)	1.8(12)	C(15)	C(16)	C(17)	C(18)	-179.1(7)
O(3)	C(17)	C(18)	F(4)	-5.7(16)	C(16)	C(17)	C(18)	F(4)	175.1(13)
O(3)	C(17)	C(18)	F(5)	119.3(11)	C(16)	C(17)	C(18)	F(5)	-59.9(13)
O(3)	C(17)	C(18)	F(6)	-126.3(12)	C(16)	C(17)	C(18)	F(6)	54.6(14)
Dy(1)	O(4)	C(20)	C(21)	-7.9(11)	Dy(1)	O(4)	C(20)	C(19)	172.6(7)
F(8)	C(19)	C(20)	O(4)	90.3(17)	F(7)	C(19)	C(20)	O(4)	-46.2(18)
F(9)	C(19)	C(20)	O(4)	-152.4(11)	F(8)	C(19)	C(20)	C(21)	-89.2(19)
F(7)	C(19)	C(20)	C(21)	134.3(16)	F(9)	C(19)	C(20)	C(21)	28.0(15)
O(4)	C(20)	C(21)	C(22)	-3.0(12)	C(19)	C(20)	C(21)	C(22)	176.4(8)
Dy(1)	O(5)	C(22)	C(21)	2.8(11)	Dy(1)	O(5)	C(22)	C(23)	-178.0(6)
C(20)	C(21)	C(22)	O(5)	5.6(12)	C(20)	C(21)	C(22)	C(23)	-173.6(8)
O(5)	C(22)	C(23)	F(12)	-65.9(12)	C(21)	C(22)	C(23)	F(12)	113.4(11)
O(5)	C(22)	C(23)	F(10)	55.0(12)	C(21)	C(22)	C(23)	F(10)	-125.7(10)
O(5)	C(22)	C(23)	F(11)	174.1(10)	C(21)	C(22)	C(23)	F(11)	-6.6(14)
Dy(1)	O(6)	C(25)	C(26)	17.6(11)	Dy(1)	O(6)	C(25)	C(24)	-164.1(5)
F(14)	C(24)	C(25)	O(6)	51.0(11)	F(15)	C(24)	C(25)	O(6)	173.2(8)
F(13)	C(24)	C(25)	O(6)	-63.1(10)	F(14)	C(24)	C(25)	C(26)	-130.5(9)

F(15)	C(24)	C(25)	C(26)	-8.3(13)	F(13)	C(24)	C(25)	C(26)	115.4(9)
O(6)	C(25)	C(26)	C(27)	2.1(12)	C(24)	C(25)	C(26)	C(27)	-176.1(7)
Dy(1)	O(7)	C(27)	C(26)	-14.1(10)	Dy(1)	O(7)	C(27)	C(28)	164.8(4)
C(25)	C(26)	C(27)	O(7)	-3.6(11)	C(25)	C(26)	C(27)	C(28)	177.5(6)
O(7)	C(27)	C(28)	F(18)	-108.8(9)	C(26)	C(27)	C(28)	F(18)	70.3(10)
O(7)	C(27)	C(28)	F(16)	15.3(9)	C(26)	C(27)	C(28)	F(16)	-165.7(7)
O(7)	C(27)	C(28)	F(17)	129.6(7)	C(26)	C(27)	C(28)	F(17)	-51.3(9)

•[Dy(hfac)$_3$(IM-4Me2py)]

Bond lengths

atom	atom	distance	atom	atom	distance
Dy(1)	O(2)	2.314(11)	Dy(1)	O(3)	2.366(8)
Dy(1)	O(4)	2.356(9)	Dy(1)	O(5)	2.341(8)
Dy(1)	O(6)	2.300(8)	Dy(1)	O(7)	2.319(7)
Dy(1)	N(1)	2.535(8)	Dy(1)	N(3)	2.524(8)
F(1)	C(14)	1.11(3)	F(2)	C(14)	1.17(3)
F(3)	C(14)	1.23(3)	F(4)	C(18)	1.23(4)
F(5)	C(18)	1.25(3)	F(6)	C(18)	1.23(3)
F(7)	C(19)	1.33(4)	F(8)	C(19)	1.36(7)
F(9)	C(19)	1.03(7)	F(10)	C(23)	1.30(4)
F(11)	C(23)	1.19(2)	F(12)	C(23)	1.10(3)
F(13)	C(24)	1.201(19)	F(14)	C(24)	1.27(3)
F(15)	C(24)	1.15(3)	F(16)	C(28)	1.29(3)
F(17)	C(28)	1.14(2)	F(18)	C(28)	1.26(2)
O(1)	N(2)	1.283(11)	O(2)	C(15)	1.53(11)
O(3)	C(17)	1.25(5)	O(4)	C(20)	1.14(4)
O(5)	C(22)	1.25(4)	O(6)	C(25)	1.261(15)
O(7)	C(27)	1.282(14)	N(1)	C(1)	1.257(11)
N(1)	C(8)	1.491(15)	N(2)	C(1)	1.389(12)
N(2)	C(9)	1.519(15)	N(3)	C(2)	1.334(13)
N(3)	C(6)	1.344(14)	C(1)	C(2)	1.484(14)
C(2)	C(3)	1.378(14)	C(3)	C(4)	1.366(16)
C(4)	C(5)	1.425(18)	C(4)	C(7)	1.507(18)
C(5)	C(6)	1.340(17)	C(8)	C(11)	1.457(18)
C(8)	C(9)	1.477(18)	C(8)	C(10)	1.61(2)
C(9)	C(12)	1.47(2)	C(9)	C(13)	1.60(2)
C(14)	C(15)	1.35(6)	C(15)	C(16)	1.40(10)
C(16)	C(17)	1.41(8)	C(17)	C(18)	1.53(5)
C(19)	C(20)	1.45(4)	C(20)	C(21)	1.40(10)
C(21)	C(22)	1.40(7)	C(22)	C(23)	1.60(5)

C(24)	C(25)	1.60(2)	C(25)	C(26)	1.373(19)
C(26)	C(27)	1.395(18)	C(27)	C(28)	1.57(2)

Bond angles

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Dy(1)	O(3)	74.4(3)	O(2)	Dy(1)	O(4)	72.2(4)
O(2)	Dy(1)	O(5)	105.1(4)	O(2)	Dy(1)	O(6)	83.4(3)
O(2)	Dy(1)	O(7)	143.8(4)	O(2)	Dy(1)	N(1)	88.7(4)
O(2)	Dy(1)	N(3)	143.7(4)	O(3)	Dy(1)	O(4)	121.5(3)
O(3)	Dy(1)	O(5)	71.7(3)	O(3)	Dy(1)	O(6)	143.6(3)
O(3)	Dy(1)	O(7)	138.9(3)	O(3)	Dy(1)	N(1)	73.1(3)
O(3)	Dy(1)	N(3)	74.2(3)	O(4)	Dy(1)	O(5)	72.6(3)
O(4)	Dy(1)	O(6)	76.5(4)	O(4)	Dy(1)	O(7)	75.9(3)
O(4)	Dy(1)	N(1)	149.6(3)	O(4)	Dy(1)	N(3)	141.6(4)
O(5)	Dy(1)	O(6)	143.2(3)	O(5)	Dy(1)	O(7)	80.7(3)
O(5)	Dy(1)	N(1)	136.7(3)	O(5)	Dy(1)	N(3)	81.7(3)
O(6)	Dy(1)	O(7)	72.8(3)	O(6)	Dy(1)	N(1)	78.0(3)
O(6)	Dy(1)	N(3)	112.7(3)	O(7)	Dy(1)	N(1)	111.7(3)
O(7)	Dy(1)	N(3)	72.1(3)	N(1)	Dy(1)	N(3)	65.0(3)
Dy(1)	O(2)	C(15)	137.2(18)	Dy(1)	O(3)	C(17)	133(2)
Dy(1)	O(4)	C(20)	143(2)	Dy(1)	O(5)	C(22)	131(2)
Dy(1)	O(6)	C(25)	131.9(8)	Dy(1)	O(7)	C(27)	134.6(8)
Dy(1)	N(1)	C(1)	116.6(6)	Dy(1)	N(1)	C(8)	133.3(7)
C(1)	N(1)	C(8)	109.5(9)	O(1)	N(2)	C(1)	127.8(9)
O(1)	N(2)	C(9)	122.2(10)	C(1)	N(2)	C(9)	109.3(8)
Dy(1)	N(3)	C(2)	121.1(7)	Dy(1)	N(3)	C(6)	121.0(7)
C(2)	N(3)	C(6)	117.8(9)	N(1)	C(1)	N(2)	111.4(8)
N(1)	C(1)	C(2)	125.1(8)	N(2)	C(1)	C(2)	123.5(8)
N(3)	C(2)	C(3)	122.8(10)	N(3)	C(2)	C(1)	112.1(8)
C(3)	C(2)	C(1)	125.1(10)	C(4)	C(3)	C(2)	120.2(11)
C(3)	C(4)	C(5)	116.1(11)	C(3)	C(4)	C(7)	123.8(13)
C(5)	C(4)	C(7)	120.1(13)	C(6)	C(5)	C(4)	120.5(13)
C(5)	C(6)	N(3)	122.6(12)	C(11)	C(8)	C(9)	120.8(13)
C(11)	C(8)	N(1)	113.8(10)	C(9)	C(8)	N(1)	105.9(11)
C(11)	C(8)	C(10)	102.9(16)	C(9)	C(8)	C(10)	105.7(16)
N(1)	C(8)	C(10)	106.8(12)	C(12)	C(9)	C(8)	130.0(16)
C(12)	C(9)	N(2)	114.5(14)	C(8)	C(9)	N(2)	98.7(10)
C(12)	C(9)	C(13)	98(2)	C(8)	C(9)	C(13)	111.2(14)
N(2)	C(9)	C(13)	101.1(12)	F(1)	C(14)	F(2)	87(3)
F(1)	C(14)	F(3)	124(2)	F(2)	C(14)	F(3)	83(5)
F(1)	C(14)	C(15)	125(5)	F(2)	C(14)	C(15)	137(6)

F(3)	C(14)	C(15)	97(3)	C(14)	C(15)	C(16)	123(6)
C(14)	C(15)	O(2)	107(4)	C(16)	C(15)	O(2)	113(6)
C(15)	C(16)	C(17)	125(6)	O(3)	C(17)	C(16)	130(4)
O(3)	C(17)	C(18)	109(5)	C(16)	C(17)	C(18)	120(5)
F(6)	C(18)	F(4)	97.2(19)	F(6)	C(18)	F(5)	102(3)
F(4)	C(18)	F(5)	105(3)	F(6)	C(18)	C(17)	135(3)
F(4)	C(18)	C(17)	100(5)	F(5)	C(18)	C(17)	112.4(16)
F(9)	C(19)	F(7)	109(4)	F(9)	C(19)	F(8)	88(4)
F(7)	C(19)	F(8)	106(5)	F(9)	C(19)	C(20)	141(6)
F(7)	C(19)	C(20)	105(4)	F(8)	C(19)	C(20)	100(7)
O(4)	C(20)	C(21)	116(4)	O(4)	C(20)	C(19)	125(5)
C(21)	C(20)	C(19)	119(4)	C(20)	C(21)	C(22)	129(4)
O(5)	C(22)	C(21)	126(4)	O(5)	C(22)	C(23)	103(4)
C(21)	C(22)	C(23)	131(4)	F(12)	C(23)	F(11)	114(3)
F(12)	C(23)	F(10)	94(3)	F(11)	C(23)	F(10)	105(4)
F(12)	C(23)	C(22)	107(4)	F(11)	C(23)	C(22)	115(2)
F(10)	C(23)	C(22)	120(4)	F(15)	C(24)	F(13)	112(3)
F(15)	C(24)	F(14)	98(2)	F(13)	C(24)	F(14)	108(3)
F(15)	C(24)	C(25)	114(2)	F(13)	C(24)	C(25)	116.5(16)
F(14)	C(24)	C(25)	106(3)	O(6)	C(25)	C(26)	131.2(13)
O(6)	C(25)	C(24)	114.1(13)	C(26)	C(25)	C(24)	114.6(13)
C(25)	C(26)	C(27)	118.8(12)	O(7)	C(27)	C(26)	126.2(11)
O(7)	C(27)	C(28)	110.5(13)	C(26)	C(27)	C(28)	123.1(14)
F(17)	C(28)	F(18)	114(3)	F(17)	C(28)	F(16)	112.6(19)
F(18)	C(28)	F(16)	95.0(19)	F(17)	C(28)	C(27)	119.5(14)
F(18)	C(28)	C(27)	108.1(14)	F(16)	C(28)	C(27)	104(2)

Torsion angles

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(6)	Dy(1)	O(2)	C(15)	150(3)	O(7)	Dy(1)	O(2)	C(15)	-161(3)
O(5)	Dy(1)	O(2)	C(15)	-66(3)	O(4)	Dy(1)	O(2)	C(15)	-132(3)
O(3)	Dy(1)	O(2)	C(15)	-1(3)	N(3)	Dy(1)	O(2)	C(15)	30(3)
N(1)	Dy(1)	O(2)	C(15)	72(3)	O(6)	Dy(1)	O(3)	C(17)	-65(4)
O(2)	Dy(1)	O(3)	C(17)	-11(4)	O(7)	Dy(1)	O(3)	C(17)	152(4)
O(5)	Dy(1)	O(3)	C(17)	101(4)	O(4)	Dy(1)	O(3)	C(17)	46(4)
N(3)	Dy(1)	O(3)	C(17)	-172(4)	N(1)	Dy(1)	O(3)	C(17)	-104(4)
O(6)	Dy(1)	O(4)	C(20)	-176(9)	O(2)	Dy(1)	O(4)	C(20)	96(9)
O(7)	Dy(1)	O(4)	C(20)	-101(9)	O(5)	Dy(1)	O(4)	C(20)	-17(9)
O(3)	Dy(1)	O(4)	C(20)	38(9)	N(3)	Dy(1)	O(4)	C(20)	-67(9)
N(1)	Dy(1)	O(4)	C(20)	150(9)	O(6)	Dy(1)	O(5)	C(22)	43(2)
O(2)	Dy(1)	O(5)	C(22)	-56(2)	O(7)	Dy(1)	O(5)	C(22)	87(2)

O(4)	Dy(1)	O(5)	C(22)	9(2)	O(3)	Dy(1)	O(5)	C(22)	-124(2)
N(3)	Dy(1)	O(5)	C(22)	160(2)	N(1)	Dy(1)	O(5)	C(22)	-161(2)
O(2)	Dy(1)	O(6)	C(25)	131.1(12)	O(7)	Dy(1)	O(6)	C(25)	-21.3(11)
O(5)	Dy(1)	O(6)	C(25)	24.6(14)	O(4)	Dy(1)	O(6)	C(25)	57.9(12)
O(3)	Dy(1)	O(6)	C(25)	-176.7(10)	N(3)	Dy(1)	O(6)	C(25)	-82.7(12)
N(1)	Dy(1)	O(6)	C(25)	-138.8(12)	O(6)	Dy(1)	O(7)	C(27)	20.5(10)
O(2)	Dy(1)	O(7)	C(27)	-30.7(13)	O(5)	Dy(1)	O(7)	C(27)	-133.7(10)
O(4)	Dy(1)	O(7)	C(27)	-59.5(10)	O(3)	Dy(1)	O(7)	C(27)	178.4(9)
N(3)	Dy(1)	O(7)	C(27)	142.1(11)	N(1)	Dy(1)	O(7)	C(27)	89.5(10)
O(6)	Dy(1)	N(1)	C(1)	124.5(8)	O(2)	Dy(1)	N(1)	C(1)	-152.0(8)
O(7)	Dy(1)	N(1)	C(1)	58.7(8)	O(5)	Dy(1)	N(1)	C(1)	-41.0(9)
O(4)	Dy(1)	N(1)	C(1)	158.0(8)	O(3)	Dy(1)	N(1)	C(1)	-77.9(7)
N(3)	Dy(1)	N(1)	C(1)	2.2(7)	O(6)	Dy(1)	N(1)	C(8)	-66.0(10)
O(2)	Dy(1)	N(1)	C(8)	17.5(10)	O(7)	Dy(1)	N(1)	C(8)	-131.8(10)
O(5)	Dy(1)	N(1)	C(8)	128.4(10)	O(4)	Dy(1)	N(1)	C(8)	-32.5(13)
O(3)	Dy(1)	N(1)	C(8)	91.6(10)	N(3)	Dy(1)	N(1)	C(8)	171.7(11)
O(6)	Dy(1)	N(3)	C(2)	-67.8(8)	O(2)	Dy(1)	N(3)	C(2)	43.2(11)
O(7)	Dy(1)	N(3)	C(2)	-129.6(8)	O(5)	Dy(1)	N(3)	C(2)	147.5(8)
O(4)	Dy(1)	N(3)	C(2)	-164.6(7)	O(3)	Dy(1)	N(3)	C(2)	74.3(8)
N(1)	Dy(1)	N(3)	C(2)	-4.1(7)	O(6)	Dy(1)	N(3)	C(6)	116.9(10)
O(2)	Dy(1)	N(3)	C(6)	-132.1(10)	O(7)	Dy(1)	N(3)	C(6)	55.1(10)
O(5)	Dy(1)	N(3)	C(6)	-27.8(10)	O(4)	Dy(1)	N(3)	C(6)	20.0(12)
O(3)	Dy(1)	N(3)	C(6)	-101.1(10)	N(1)	Dy(1)	N(3)	C(6)	-179.5(10)
C(8)	N(1)	C(1)	N(2)	8.3(12)	Dy(1)	N(1)	C(1)	N(2)	-179.8(6)
C(8)	N(1)	C(1)	C(2)	-172.4(10)	Dy(1)	N(1)	C(1)	C(2)	-0.5(12)
O(1)	N(2)	C(1)	N(1)	177.0(11)	C(9)	N(2)	C(1)	N(1)	6.8(12)
O(1)	N(2)	C(1)	C(2)	-2.3(17)	C(9)	N(2)	C(1)	C(2)	-172.4(9)
C(6)	N(3)	C(2)	C(3)	-0.9(16)	Dy(1)	N(3)	C(2)	C(3)	-176.4(8)
C(6)	N(3)	C(2)	C(1)	-179.3(10)	Dy(1)	N(3)	C(2)	C(1)	5.2(11)
N(1)	C(1)	C(2)	N(3)	-3.1(14)	N(2)	C(1)	C(2)	N(3)	176.1(9)
N(1)	C(1)	C(2)	C(3)	178.5(10)	N(2)	C(1)	C(2)	C(3)	-2.3(16)
N(3)	C(2)	C(3)	C(4)	1.3(17)	C(1)	C(2)	C(3)	C(4)	179.5(10)
C(2)	C(3)	C(4)	C(5)	-1.6(17)	C(2)	C(3)	C(4)	C(7)	-179.3(13)
C(3)	C(4)	C(5)	C(6)	1.6(19)	C(7)	C(4)	C(5)	C(6)	179.4(14)
C(4)	C(5)	C(6)	N(3)	-1(2)	C(2)	N(3)	C(6)	C(5)	1(2)
Dy(1)	N(3)	C(6)	C(5)	176.4(11)	C(1)	N(1)	C(8)	C(11)	-155.6(13)
Dy(1)	N(1)	C(8)	C(11)	34.4(18)	C(1)	N(1)	C(8)	C(9)	-20.6(14)
Dy(1)	N(1)	C(8)	C(9)	169.4(8)	C(1)	N(1)	C(8)	C(10)	91.7(17)
Dy(1)	N(1)	C(8)	C(10)	-78.4(17)	C(11)	C(8)	C(9)	C(12)	-75(3)
N(1)	C(8)	C(9)	C(12)	154(2)	C(10)	C(8)	C(9)	C(12)	41(3)
C(11)	C(8)	C(9)	N(2)	153.0(13)	N(1)	C(8)	C(9)	N(2)	21.9(12)

C(10)	C(8)	C(9)	N(2)	-91.2(12)	C(11)	C(8)	C(9)	C(13)	47.4(18)
N(1)	C(8)	C(9)	C(13)	-83.7(14)	C(10)	C(8)	C(9)	C(13)	163.3(13)
O(1)	N(2)	C(9)	C(12)	29(3)	C(1)	N(2)	C(9)	C(12)	-160(2)
O(1)	N(2)	C(9)	C(8)	171.0(12)	C(1)	N(2)	C(9)	C(8)	-18.3(12)
O(1)	N(2)	C(9)	C(13)	-75.3(15)	C(1)	N(2)	C(9)	C(13)	95.4(13)
F(2)	F(1)	C(14)	F(3)	-80(5)	F(2)	F(1)	C(14)	C(15)	149(7)
F(3)	F(2)	C(14)	F(1)	-125(2)	F(1)	F(2)	C(14)	F(3)	125(2)
F(1)	F(2)	C(14)	C(15)	-142(8)	F(3)	F(2)	C(14)	C(15)	94(7)
F(2)	F(3)	C(14)	F(1)	82(4)	F(2)	F(3)	C(14)	C(15)	-137(6)
F(1)	C(14)	C(15)	C(16)	4(11)	F(2)	C(14)	C(15)	C(16)	135(9)
F(3)	C(14)	C(15)	C(16)	-137(8)	F(1)	C(14)	C(15)	O(2)	-129(4)
F(2)	C(14)	C(15)	O(2)	2(9)	F(3)	C(14)	C(15)	O(2)	90(4)
Dy(1)	O(2)	C(15)	C(14)	158(2)	Dy(1)	O(2)	C(15)	C(16)	19(5)
C(14)	C(15)	C(16)	C(17)	-164(6)	O(2)	C(15)	C(16)	C(17)	-33(7)
Dy(1)	O(3)	C(17)	C(16)	2(8)	Dy(1)	O(3)	C(17)	C(18)	-167.4(12)
C(15)	C(16)	C(17)	O(3)	26(9)	C(15)	C(16)	C(17)	C(18)	-166(6)
O(3)	C(17)	C(18)	F(6)	85(5)	C(16)	C(17)	C(18)	F(6)	-85(8)
O(3)	C(17)	C(18)	F(4)	-163(4)	C(16)	C(17)	C(18)	F(4)	26(5)
O(3)	C(17)	C(18)	F(5)	-52(6)	C(16)	C(17)	C(18)	F(5)	137(4)
F(8)	F(9)	C(19)	F(7)	106(5)	F(8)	F(9)	C(19)	C(20)	-103(13)
F(9)	F(8)	C(19)	F(7)	-109(3)	F(9)	F(8)	C(19)	C(20)	142(5)
Dy(1)	O(4)	C(20)	C(21)	13(14)	Dy(1)	O(4)	C(20)	C(19)	-172(3)
F(9)	C(19)	C(20)	O(4)	-8(20)	F(7)	C(19)	C(20)	O(4)	143(8)
F(8)	C(19)	C(20)	O(4)	-107(10)	F(9)	C(19)	C(20)	C(21)	167(11)
F(7)	C(19)	C(20)	C(21)	-42(10)	F(8)	C(19)	C(20)	C(21)	68(8)
O(4)	C(20)	C(21)	C(22)	3(12)	C(19)	C(20)	C(21)	C(22)	-172(5)
Dy(1)	O(5)	C(22)	C(21)	-3(5)	Dy(1)	O(5)	C(22)	C(23)	174.8(11)
C(20)	C(21)	C(22)	O(5)	-7(8)	C(20)	C(21)	C(22)	C(23)	176(6)
F(10)	F(12)	C(23)	F(11)	-109(5)	F(10)	F(12)	C(23)	C(22)	123(4)
F(12)	F(10)	C(23)	F(11)	116(3)	F(12)	F(10)	C(23)	C(22)	-112(4)
O(5)	C(22)	C(23)	F(12)	-164(4)	C(21)	C(22)	C(23)	F(12)	13(5)
O(5)	C(22)	C(23)	F(11)	68(4)	C(21)	C(22)	C(23)	F(11)	-115(4)
O(5)	C(22)	C(23)	F(10)	-60(4)	C(21)	C(22)	C(23)	F(10)	118(5)
Dy(1)	O(6)	C(25)	C(26)	17(2)	Dy(1)	O(6)	C(25)	C(24)	-159.4(17)
F(15)	C(24)	C(25)	O(6)	46(4)	F(13)	C(24)	C(25)	O(6)	179(3)
F(14)	C(24)	C(25)	O(6)	-60(3)	F(15)	C(24)	C(25)	C(26)	-131(3)
F(13)	C(24)	C(25)	C(26)	2(4)	F(14)	C(24)	C(25)	C(26)	122(2)
O(6)	C(25)	C(26)	C(27)	2(3)	C(24)	C(25)	C(26)	C(27)	178.3(19)
Dy(1)	O(7)	C(27)	C(26)	-13.8(19)	Dy(1)	O(7)	C(27)	C(28)	170.4(12)
C(25)	C(26)	C(27)	O(7)	-4(2)	C(25)	C(26)	C(27)	C(28)	171.6(17)
O(7)	C(27)	C(28)	F(17)	-11(3)	C(26)	C(27)	C(28)	F(17)	174(3)

O(7)	C(27)	C(28)	F(18)	122(2)	C(26)	C(27)	C(28)	F(18)	-54(3)
O(7)	C(27)	C(28)	F(16)	-138(2)	C(26)	C(27)	C(28)	F(16)	47(3)