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論 文 内 容 の 要 旨

1) Novel configurational chirality and remarkable chiroptical properties of Cr(ox)Ln and Ln-Ln complexes

The syntheses and characterizations of 3d-4f heterodinuclear complexes, $[(\text{acac})_2\text{Cr}(\text{ox})\text{Ln}(\text{HBpz}_3)_2]$ have been made with particular attentions on the configurational chirality around metal ions of Cr(ox)Ln complexes. Configurational chirality around Yb(III) ion in the Cr(ox)Yb complex induced by optically resolved complex ligand $\Lambda\text{-}[\text{Cr}(\text{acac})_2(\text{ox})]^-$ was revealed by comparing with to the $\Lambda, \Delta\text{-}[\text{Yb}(\text{S-pba})(\text{HBpz}_3)_2]$ complex. In this course, I attempted preparation of the series of both mononuclear *S* or *RS*-pba complexes depending on the lanthanide ionic radii and steric control of ancillary HBPz₃⁻ and bulky pba ligands to compare with the Cr(ox)Ln.

In view of the solution NIR CD spectra of $(\Lambda\text{-}\Delta)\text{-Cr}(\text{ox})\text{Yb}$, it is seen that a pair of $\Lambda\text{-}[\text{Cr}(\text{ox})(\text{acac})_2]^-$ and $\Delta\text{-}[\text{Yb}(\text{HBpz}_3)_2]^+$ found by the X-ray structure results from stereospecific assembling due to chiral discrimination around the Yb ion induced by the absolute configuration of the Cr(III) entity, but not from accidental pickup from a racemic mixture of $\Lambda\text{-Cr}(\text{ox})\text{-}\Delta\text{-Yb}$ and $\Lambda\text{-Cr}(\text{ox})\text{-}\Lambda\text{-Yb}$ diastereomers. To the best of my knowledge, this is the first example of the stereospecific $(\Lambda\text{-}\Delta)\text{-Cr}(\text{ox})\text{Ln}$ assembly with configurational chirality of the lanthanide complexes in solution without asymmetric carbon atoms. It is noted that this kind of stereospecific assembling occurs in spite of the facts that the long Yb-Cr distance (5.631 Å (the racemic)-5.672 Å (the chiral)). The CD in the 4f-4f transitions of these structurally well characterized complexes enable us to propose a criterion to determine the absolute configuration; a positive sign for the Δ absolute configuration in support of the NIR absorption and MCD which confirm the positions and the relative intensities of the 4f-4f transitions.

Synthesis of two series of both mononuclear $[\text{Ln}(\text{S or RS-pba})_2(\text{HBpz}_3)]$ and dinuclear $[\text{Ln}_2\{\mu\text{-}(\text{S or RS-pba})\}_4(\text{HBpz}_3)_2]$ complexes are also described, of which the formations depend on the lanthanide ionic radii and steric controls of the pba and HBPz₃. The X-ray structural analysis of some of the complexes demonstrate the stereospecific formation of the *R-R-S-S* assembly in the bridging moiety of the $\mu\text{-}(\text{R, S-pba})_4$ complexes.

The difference in g values between the Yb(III) complex and the other Ln(III) complexes (Ho, Dy, and Nd) may result in the difference in chirality between the local dissymmetry from the asymmetric carbon in *S*-pba and the configurations due to the bent $B \cdots Ln \cdots Ln \cdots B$ arrangement in *Chiral*-Ln-Ln. The smaller g value of the chiral Yb-Yb complex than that of the Cr-Yb complex substantiate the configurational chirality in the latter complex. For the *meso*-pba Ln-Ln complexes, 7-coordinated structure may retain in terms of weak $CH \cdots \pi$ interactions between the methyl proton in the ethyl group of the pba and the phenyl ring of the adjacent pba. Whereas in case of chiral complexes there are no such $CH \cdots \pi$ interactions.

2) Simultaneous observation of 3d-3d and 4f-4f emissions and Characteristics of 2E emission in Cr-Ln complexes

On warming from 10 K to 300 K, in the Cr(ox)Ln complexes, there is a rapid quenching of the $^2E \rightarrow ^4A_2$ emission associated with the observation of the 4f-4f emissions in the overlapping spectral region (Ho, Er and Tm), which may substantiate the nonradiative energy transfer from 2E (Cr) to the excited levels of the Ln(III) ions. Such emission behaviors are the first examples of the low temperature simultaneous $^2E \rightarrow ^4A_2$ (Cr^{III}) and 4f-4f (Ln^{III}) emissions. It is revealed that the simultaneous observation of the $^2E \rightarrow ^4A_2$ and 4f-4f emissions in Cr-Ln dinuclear complexes depend on the bridging ligand which result in differentiating the Cr-Ln distance and the energy gap between the 2E and 4f excited states in Cr(ox)Ln and Cr(bpyz)Ln complexes, respectively. That is, the Cr-Ln distance and the energy gap between 2E and excited 4f (Ln) levels for the Cr(bpyz)Ln complexes are shorter and smaller, respectively than those of the complexes Cr(ox)Ln.

論文審査の結果の要旨

M. A. Subhan 君は、本来、置換活性であるため、合成・単離が困難とされていた立体配置が光学活性なランタニド(III)錯体を、光学活性クロム(III)錯体[Cr(acac)₂(ox)]⁻を用いることで、シュウ酸架橋二核錯体 $\Lambda \cdot \Delta$ -[(acac)Cr(μ -ox)Ln(HBpz₃)₂]として容易に得られることを明らかにした。また、一連の光学活性ランタニド錯体の合成と X 線構造解析およびそれらの近赤外領域の円二色性 (CD) と磁気円二色性 (MCD) の測定を行い、4f-4f 遷移の旋光強度の選択則に基づく考察から、これらが溶液中でも安定で、立体特異的に生成していることや錯体の絶対配置と CD 符号の経験則を初めて見いだした。さらに、phenylbutylate (ラセミ *RS*-pba と光学活性 *S*-pba) が架橋した[(HBpz₃)Lu(μ -pba)₄Lu(HBpz₃)]を合成し、それらの X 線構造解析によって、*RS*-pba 錯体は(*R*-pba)₂(*S*-pba)₂ のメソ構造で、 $B \cdots Ln \cdots Ln \cdots B$ が直線状であるが、*S*-pba 錯体は $B \cdots Ln \cdots Ln \cdots B$ が折曲った光学活性配置をとる立体特異的な構造であることを明らかにした。CD から溶液中でも、この構造を保っていることを見いだした。このような光学活性配置は初めての例である。さらに、これらの一連の Cr-Ln の発光スペクトルや励起スペクトル、発光寿命を測定し、Cr から Ln へのエネルギー移動が起こるとともに、クロム(III)の $^2E \rightarrow ^4A_2$ の発光が架橋配位子の違いやランタニドのイオン半径に依存していることを明らかにし、発光特性のチューニングの可能性を示した。

以上の研究成果は、ランタニド(III)錯体とクロム(III)錯体に関して、新しい光学活性配置、円二色性・磁気円二色性や発光特性についての重要な知見であって、博士(理学)の学位論文として十分価値あるものと認められる。