Studies on Structures and Electronic States of Copper(II) Complexes with Imidate Ligands

Takashiro Akitsu

Department of Chemistry
Graduate School of Science
Osaka University

2000

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Dissertation Presented by
Takashiro Akitsu
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy (Science)

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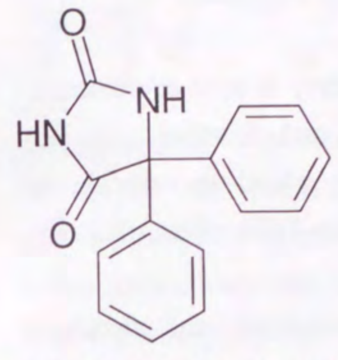
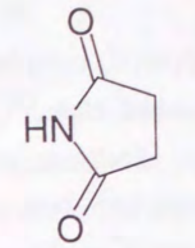
2000

Contents.

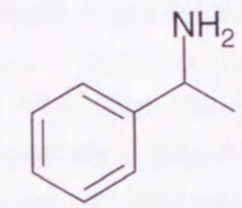
List of Ligands with Their Abbreviations.



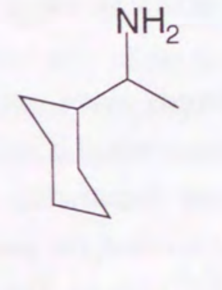
5,5-diphenylhydantoin
(phent)



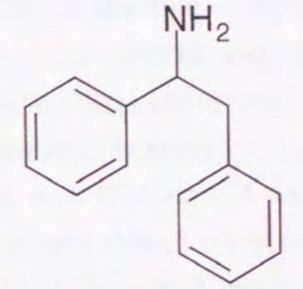
succinimide
(succim)



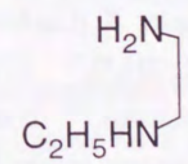
1-phenylethylamine
(phenea)



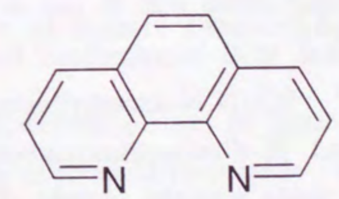
1-cyclohexylethylamine
(chea)



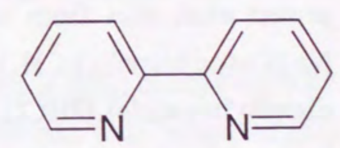
1,2-diphenylethylamine
(1,2-diphenea)



N-ethylethylenediamine
(N-Eten)



1,10-phenanthoroline
(phen)



2,2'-bipyridine
(bpy)

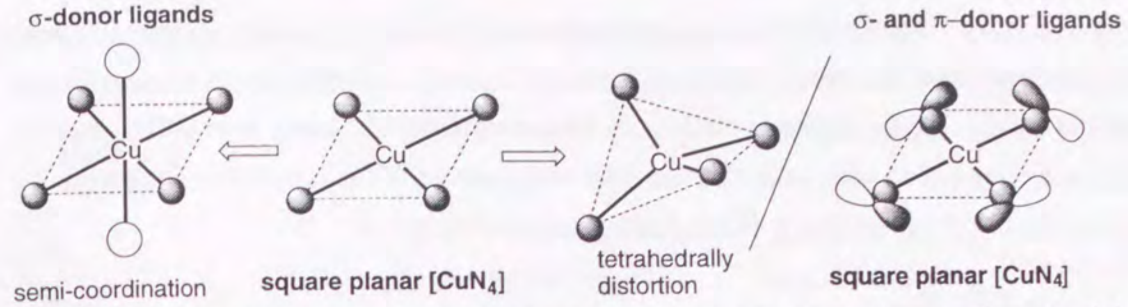
Chapter 1. General Introduction.

1.1 Structures of Copper(II) Complexes and Imidate Ligands.

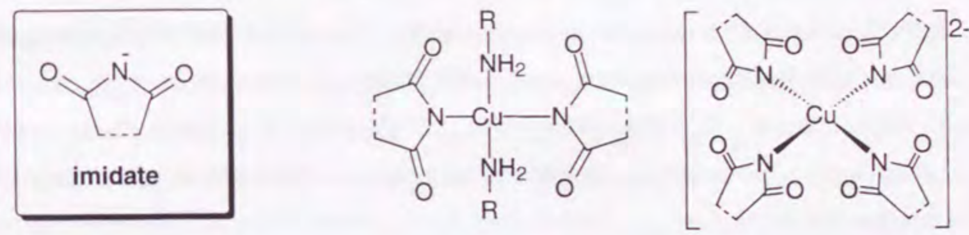
Generally, copper(II) complexes exhibit a remarkable variety in their coordination geometries,[1] and gradual changes between the regular ones and distorted ones are observed commonly. Electronic properties of copper(II) ions related to variation of coordination geometries have been pointed out, for example, Jahn-Teller effect, plasticity effect (bending, distortion, or elongation of coordination bonds).[2]

Being focused on the four-coordinated copper(II) complexes, the electronic properties of copper(II) ion makes the complexes afford a tetrahedral coordination for reducing the steric repulsion between the ligands. In general, this tendency is remarkable for weak field ligands. In contrast, strong field ligands prefers a square planar coordination.[3] Therefore, the determining factors of coordination geometrires four-coordinated copper(II) complexes would be concerned with both steric and electronic factors of the ligands.

The ligands coordinating nitrogen atoms can be classified into a moderate field ligand. The survey of structurally characterized [CuN_4] complexes having monodentate or bidentate ligands with less structural requirement tell us that structural or electronic features of the ligands contribute to maintain the planarity of the [CuN_4] chromophores. For example, four monodentate amine nitrogen ligands of pure σ-donor character give a compressed tetrahedral [CuN_4] coordination geometry such as [Cu(1-cyclohexylamine)$_4$](NO_3)$_2$.[4] In contrast, [Cu(en)$_2$]$^{2+}$ complexes (en = ethylenediamine) having bidentate chelate ligands are susceptible to long-distance axial coordination (so called 'semi-coordination')[5] to give rise to five- or six-coordinated complexes. Nevertheless, coordination nitrogen atoms with σ- and π-donor character contributes to protect axial sites from additional axial coordination. For example, K_2[Cu(biuret)$_2$],[6] Na_2[Cu(pr(biuret))$_2$](CH_3)$_2$SO,[7] [Cu(N,N-dimethylbiganide)$_2$]Cl_2·2H_2O,[8] [Cu(N,N-dimethylbiganide)$_2$]2HCO_3,[9] and [Cu(bis(methoxycarboimido)aminato)$_2$][10] complexes having bidentate deprotonated amide nitrogen ligands afford a square planar [CuN_4] coordination geometry regardless of sufficient space for additional axial coordination. For these complexes not only σ- and π-donor character of the ligands but also bidentate chelate ligands are effective to retain their planarity of [CuN_4] chromophores.



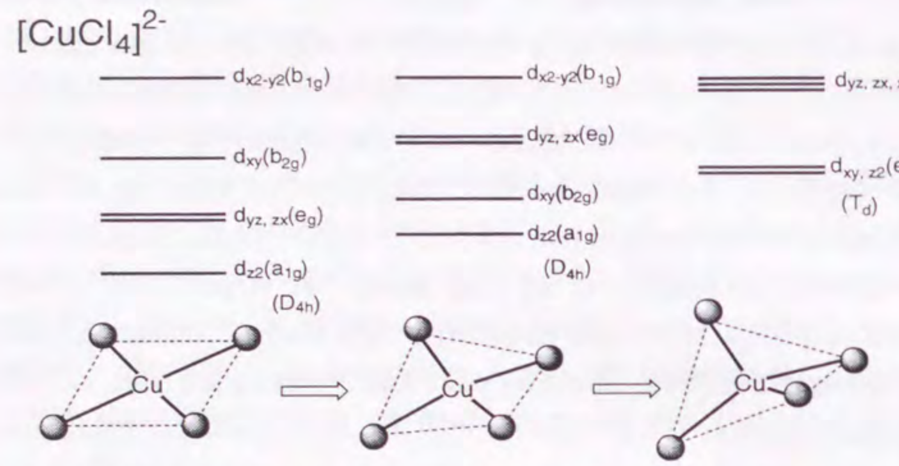
On the other hand, it is worth noting that certain monodenate nitrogen ligands yield square planar [CuN_4] complexes, although they are free from steric effects of the ligands. Characteristic electronic effects of the ligands may contribute to the formation of these square planar complexes. Deprotonated cyclic imides (hereafter abbreviate as 'imidate') act as a monodentate ligand, and generally give red or reddish violet complexes having a square planar [CuN_4] chromophore in the solid states. Two types of these complexes, such as M_2[Cu(imidate)$_4$] (M^+ = alkali metal ions)[11] and *trans*-[Cu(imidate)$_2$(amine)$_2$][12], reported by Tschugaeff in 1904. About 50 years later, Yamada and Miki studied their electronic spectra in detail in 1963,[13] however, the discrepancy between crystal axes and molecular plane was not considered because of the lack of crystallographic data in those days. The electronic states of the related complexes have been assigned tentatively by Walsh and Hathaway in 1984,[14] but the detailed electronic states of these complexes have not been elucidated clearly so far.



1.2 3d Electronic States of Square Planar Copper(II) Complexes.

As mentioned above, 3d electronic states of square planar [CuN_4] complexes with imidate ligands have not been established reasonably. Yamada and Miki proposed that tentative assignment was $d_{x2\text{-}y2}$ (b_{1g}) > d_{z2} (a_g) > d_{xy} (b_{2g}) > d_{yz}, d_{zx} (e_g) for K_2[Cu(succim)$_4$]·6H_2O (D_{4h} point group).[13] Although the polarized crystal spectra appeared dichroism finely, selection rules could not be applied to interpret spectra properly, since discrepancy between crystal axes and molecular planes was disregarded. On the other hand, Walsh and Hathaway determined the polarized crystal spectra of structurally characterized Cs_2[Cu(succim)$_4$]·2H_2O[15] and proposed that tentative assignment was $d_{x2\text{-}y2}$ (b_{1g}) > d_{xy} (b_{2g}) > d_{z2} (a_g) > d_{yz}, d_{zx} (e_g) (D_{4h} point group).[14] The spectrum in xy polarization shows a peak at 19800 cm^{-1} with a shoulder at 15800 cm^{-1}, while the spectrum in z polarization appears a broad band with two peaks at 19800 cm^{-1}

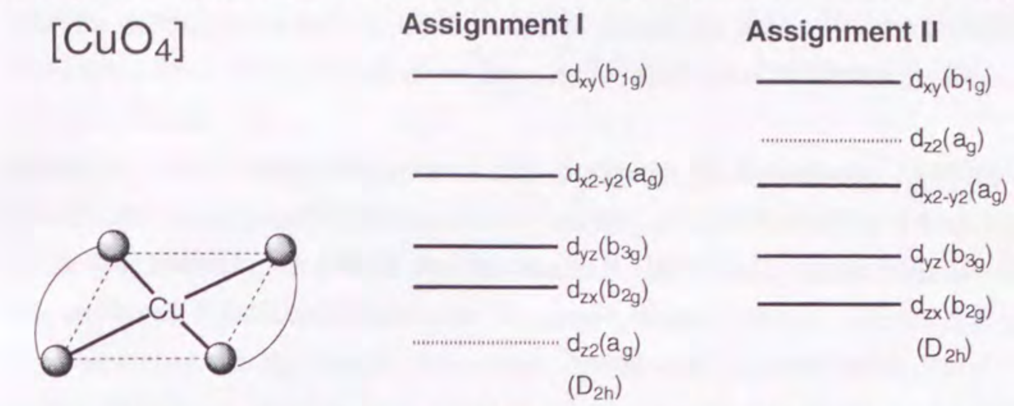
and 18400 cm^{-1}. Qualitatively speaking, it is reasonable that d_{yz} and d_{zx} orbitals exists in the lowest level, however, the order of d_{xy} and d_{z2} orbitals are not determined unequivocally. Both groups pointed out characteristic π–bonding interaction due to succinimidate ligand which affected the level of d_{xy} orbital. Thus it is difficult to assign d-d transitions for square planar $[CuN_4]$ complexes certainly.



On the other hand, reliable assignment of d-d transitions were established for square planar $[CuCl_4]^{2-}$ anions exceptionally by means of polarized crystal spectra and AOM calculations. At first, tentative assignment for bis(ethylammonium)$[CuCl_4]$ were reported to be d_{x2-y2} (b_{1g}) > d_{xy} (b_{2g}) > d_{z2} (a_g) > d_{yz}, d_{zx} (e_g) (D_{4h} point group)[16] on the basis of polarized crystal spectra at low temperature. Next, however, polarized crystal spectra of bis(methylphenethylammonium)$[CuCl_4]$ were assigned to be d_{x2-y2} (b_{1g}) > d_{xy} (b_{2g}) > d_{yz}, d_{zx} (e_g) > d_{z2} (a_g) (D_{4h} point group).[17] Because of suitable crystal packing, each transition could be specified in each polarization so that the highest energy band could be assigned to be $d_{z2}\rightarrow d_{x2-y2}$ transition. The experimental results were in agreement with the calculated transition energies to be set appropriate AOM parameters. This is consistent with the assignment of other square planar $[CuCl_4]^{2-}$ complexes, such as bis(methadonium)$[CuCl_4]$ and bis(creatimium)$[CuCl_4]$.[18] On the assumption of D_{4h} symmetry, 3d orbital order was assigned to be d_{x2-y2} (b_{1g}) > d_{xy} (b_{2g}) > d_{yz}, d_{zx} (e_g) > d_{z2} (a_g). Additionally, the assignment was also established for compressed tetrahedral $[CuCl_4]^{2-}$ anions.[19]

In contrast, a controversy of two different assignments was summarized for $Cu(acac)_2$ (acac = acethylacetonato) and related complexes having a square planar $[CuO_4]$ chromophore by Atanasov and Hitchman in 1993.[20] Two possible assignments are as follows: assignment I is d_{xy} (b_{1g}) > d_{x2-y2} (a_g) > d_{yz} (b_{3g}) > d_{zx} (b_{2g}) > d_{z2} (a_g), whereas assignment II is d_{xy} (b_{1g}) > d_{z2} (a_g) > d_{x2-y2} (a_g) > d_{yz} (b_{3g}) > d_{zx} (b_{2g}) (D_{2h} point group). Assignment I seems to be reasonable with respect to similar π–bonding parameters for all the complexes. This agree with experimental results as far as the lowest d_{z2} level is considered, but differs in the assignment of the other states. In contrast, assignment II

seems unlikely because π–bonding parameters for the acac ligands differ significantly among the complexes. Moreover, too small ds-mixing parameter seems to be implausible.



In this way, the assignment of electronic spectra and the order of 3d orbitals of square planar copper(II) complexes has long been the subject of controversy.[21] The primary reason for this problem is that individual orbital levels are so close that spectra appear as a broad band. Additionally, two problems have been pointed out with respect to both experiments and calculations. First, vibronic selection rules allow each transition so that individual d-d transitions are hard to be assigned on the basis of absence of certain transitions with particular polarization. Moreover, so called 'packing problem' may emerge. If a crystal contains two molecules of which molecular planes are perpendicular to each other, selection rules of electronic dipole transitions become inefficient for any polarization. Therefore polarized crystal spectra do not necessarily provide useful information on assignment for square planar transitions. Second, it is quite a burden to treat d_{z2} (a_g in D_{4h} point group) orbital in AOM calculations [23] for square planar complexes. Configuration interaction between $3d_{z2}$ and 4s orbitals, which are a_g character in D_{4h} point group, (ds-mixing)[24] contributes to vary the level of $3d_{z2}$ orbitals especially for square planar complexes, but the magnitude of ds-mixing cannot be estimated unless the band involved the $d_{z2}\rightarrow d_{x2-y2}$ transition is observed separately.

1.3 The Purpose of This Thesis.

On the basis of the preceding mentioned background, the author aims at the following purposes throughout this course study:

(1) Development of a series of copper(II) complexes having imidate and amine ligands with various coordination geometries and arrangement of the ligands.

(2) Discussion on the reasons for formation of various related complexes in view of both steric effects and electronic properties of the ligands.

(3) Assignment of d-d transitions for square planar [CuN_4] complexes having imidate and amine ligands. Related complexes with different distortion of [CuN_4] chromophore and different combination of imidate and amine ligands will be compared to establish reliable assignment and elucidate particular electronic property of imidate ligands.

In chapter 2, geometrical differences in chiral isomers of meso, optically active, and racemic *trans*-[Cu(phent)$_2$(phenea)$_2$] (phent = 5,5-diphenylhydantoinate and phenea = 1-phenylethyamine) are described. Three isomers afford a distorted square planar [CuN_4] coordination geometry, and the largest degree of tetrahedral distortion is found in the meso form due to steric factors of chirality of 1-phenylethylamine ligands.

In chapter 3, tetrahedral distortion of a [CuN_4] chromophore induced by steric factors of monodentate ligands are discussed by comparing between distorted square planar *trans*-[Cu(phent)$_2$(1,2-diphenea)$_2$]·2$CHCl_3$ and square planar *trans*-[Cu(succim)$_2$(1,2-diphenea)$_2$] (1,2-diphenea = 1,2-diphenylethylamine). The distortion of [CuN_4] chromophore may be explained by steric repulsion between phenyl group of 1,2-diphenylethylamine.

In chapter 4, relationship between the numbers and arrangement of imidate and amine ligands and axial coordination is described. The formation of [Cu(succim)$_2$(N-Eten)(H_2O)$_2$] (N-Eten = N-ethylethylenediamine) and comparison among related complexes suggest that comparison of related complexes suggests that imidate acts as a good donor ligand to retain four-coordinated square planar [CuN_4] coordination geometry.

In chapter 5, structures and electronic spectra of bidentate diimine complexes [Cu(succim)$_2$(phen)H_2O]·H_2O and [Cu(succim)$_2$(bpy)H_2O] with square pyramidal [CuN_4O] chromophore (phen = 1,10-phenanthoroline and bpy = 2,2'-bipyridine) are described.

In chapter 6, polarized crystal spectra of square planar *trans*-[Cu(phent)$_2$(R-chea)(S-chea)] and *trans*-[Cu(phent)$_2$(R-chea)$_2$], distorted square planar *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] and *trans*-[Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$], and square planar Rb_2[Cu(succim)$_4$]·2H_2O were determined and the d-d transitions were assigned reasonably (chea = 1-cyclohexylethylamine). All complexes can be described by consistent AOM parameters because $d_{z2} \rightarrow d_{x2-y2}$ transition appeared separately for *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)].

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Chapter 2.

Differences in Distortion of $[CuN_4]$ Chromphores Induced by Chiral Ligands. Selective Preparations of *Meso*, *Optically Active*, and *Racemic* Bis(5,5-diphenylhydantoinato)bis(1-phenylethylamine) copper(II) Complexes.

Abstract.

Three forms of crystals, *meso*, *optically active*, and *racemic trans*-bis(5,5-diphenylhydantoinato)bis(1-phenylethylamine)copper(II) complexes, were prepared and the crystal structures were determined. Blue violet *meso* form of *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) (phent = 5,5-diphenylhydantoinate, phenea = 1-phenylethylamine) was obtained solely by using *racemic* 1-phenylethylamine. Both a large amount of reddish violet prismatic crystals of *optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$] (**2**) (or *trans*-[Cu(phent)$_2$(R-phenea)$_2$] (**4**)) and a little amount of reddish violet plate-like *racemic* crystals of [Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (**3**) were obtained on treatment with *optically active* 1-phenylethylamine. The crystal **3** was identified to be a *racemic* crystal with X-ray crystallography and CD spectroscopy. It was confirmed with powder X-ray diffraction that the three forms of crystals were selectively prepared depending on the e.e. values of 1-phenylethylamine during preparation. Especially, *racemic* crystals were formed predominantly in the range from 80 to 70 % e.e.. All three forms afford a distorted square planar $[CuN_4]$ coordination geometry. The angles of imidate N-Cu-N and amine N-Cu-N are 154.9(2) and 159.8(2) ° for **1**, 168.1(5) and 162.3(5) ° for one of the two molecules in the asymmetric unit of **2**, 165.7(5) and 163.1(5) ° for the other molecule of **2**, and 166.6(2) and 163.2(2) ° for **3**, respectively. With the aid of space-filling models, the reason for the largest distortion of **1** can be explained in terms of steric repulsion between 5,5-diphenylhydantoinate and 1-phenylethylamine ligands. The electronic spectra of *meso* and *optically active* forms in the solid state showed a peak at 17300 and 18400 cm^{-1}, respectively. The spectra undergo low wave number shift accompanied by tetrahedral distortion of the $[CuN_4]$ chromophores.

2.1 Introduction

Trans-[Cu(imidate)$_2$(amine)$_2$] complexes have been studied systematically to investigate their electronic spectral properties responsible for $[CuN_4]$ chromophores.[1-3] In the solid state, most of these complexes are red or reddish violet and have a square planar [CuN$_4$] coordination goemetry.[4-9] But *trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)] (*meso* form) and *trans*-[Cu(hyd)$_2$(R-phenea)$_2$] (*optically active* form) exceptionally afford a distorted square planar [CuN$_4$] coordination geometry.[9] Distorted square planar *trans*-[Cu(imidate)$_2$(phenea)$_2$] complexes are the subject of interest in view of the spectral shifts due to the tetrahedral distortion of [CuN$_4$] chromophores. The formation factors of distorted square planar [CuN$_4$] complexes will be discussed in chapters 2 and 3.

A pair of diastereomeric complexes with respect to chiral R- and S-amine ligands will provide a suitable example to discuss geometrical effects on 3d electronic states regardless of electronic properties of coordination atoms of the ligands. But few systematic studies have been carried out to obtain diastereomeric isomers as far as copper(II) complexes to date. For example, only *meso* form has been isolated for *trans*-[Cu(succim)$_2$(phenea)$_2$], while only *optically active* form has been isolated for *trans*-[Cu(hyd)$_2$(phenea)$_2$]. In contrast, several diastereomeric isomers have been prepared for analogous palladium(II) complexes. The structures of *trans*-[Pd(succim)$_2$(R-phenea)(S-phenea)] and *trans*-[Pd(succim)$_2$(S-phenea)$_2$] have been reported.[10]

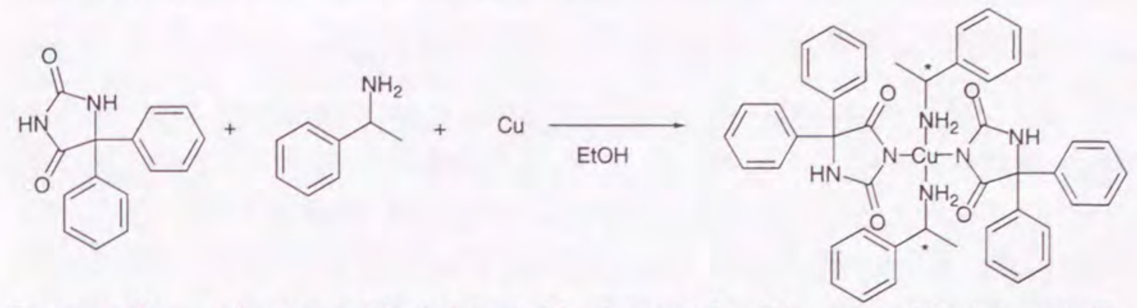
In chapter 2, preparations and structural comparison among distorted square planar [CuN$_4$] *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)], *optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$] (or *trans*-[Cu(phent)$_2$(R-phenea)$_2$]), and *racemic* [Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] forms are described. 5,5-diphenylhydantoinate enabled us to obtain above three chiral isomers. The formation conditions giving the three forms were also investigated in detail, and *racemic* crystals could be selectively obtained depending on the ratio of R- to S-1-phenylethylamine during preparations.

2.2 Experimental Section

General Procedures. R-1-phenylethylamine and S-1-phenylethylamine, of which purity was claimed to be better than 98 %, were purchased from Tokyo Kasei Kogyo Co. Ltd.. The other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. These were used as received without further purification. Elemental analyses were carried out at the Liberal Arts and Sciences Organization, Osaka University.

Preparation of *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (1). To a solution of 5,5-diphenylhydantoin (2.52 g, 10.0 mmol) in ethanol (100 cm^3), copper powder (0.318 g, 5.00 mmol) and *racemic* 1-phenylethylamine (1.82 g, 15.0 mmol) were added and the solution was stirred for 11 h at 50 °C. Gradually blue violet precipitates appeared in the reaction mixture. The blue violet precipitates were filtered off by suction and were recrystallized from chloroform-methanol (4:1, v/v). The resulting precipitates were washed with petroleum ether and were dried in a silica gel desiccator

overnight. Blue violet prismatic single crystals of **1** suitable for X-ray crystallography were obtained from chloroform-methanol (4:1, v/v) solution being allowed to stand in a refrigerator for several days. Yield: 68 %. Found: C, 68.34; H, 5.53; N, 10.29. Calcd for $C_{46}H_{44}N_6CuO_4$: C, 68.34; H, 5.49; N, 10.40.



Preparation of *trans*-[Cu(phent)$_2$(S-phenea)$_2$] (2) and [Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (3). To a solution of 5,5-diphenylhydantoin (2.52 g, 10.0 mmol) in ethanol (100 cm^3), copper powder (0.318 g, 5.00 mmol) and S-1-phenylethylamine (1.21 g, 10.0 mmol) were added and the suspension was stirred for 11 h at 50 °C to give a reddish-violet precipitates. They were collected by filtration and were recrystallized from chloroform-methanol (4:1, v/v). The resulting microcrystals were washed with petroleum ether and were dried in a silica gel desiccator overnight. Reddish violet single crystals were grown from a chloroform-methanol (4:1, v/v) solution being allowed to stand for a few days at room temperature. Yield: 59 %. Found: C, 68.67; H, 5.61; N, 10.41. Calcd for $C_{46}H_{44}N_6CuO_4$: C, 68.34; H, 5.49; N, 10.40. The resulting reddish violet crystals consisted of two types. The major products were prismatic crystals (*trans*-[Cu(phent)$_2$(S-phenea)$_2$] (**2**)) and the minor products were plate-like ones ([Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (**3**)). From this batch the prismatic crystal **2** was selected for X-ray analysis as a sample of *optically active* crystal.

Preparation of [Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (3) and *trans*-[Cu(phent)$_2$(R-phenea)$_2$] (4). The crystals **3** and **4** were prepared by the similar procedure to **2** using R-1-phenylethylamine (1.21 g, 10.0 mmol) in place of S-1-phenylethylamine. In analogy with **2**, the resulting reddish violet crystals also consisted of a large amount of prismatic crystals *trans*-[Cu(phent)$_2$(R-phenea)$_2$] (**4**) and a little amount of plate-like crystals [Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (**3**). Yield: 64 %. Found: C, 68.14; H, 5.56; N, 10.40. Calcd for $C_{46}H_{44}N_6CuO_4$: C, 68.34; H, 5.49; N, 10.40. The plate-like crystal **3** from this batch was selected for X-ray analysis as a sample of *racemic* crystal.

X-ray Crystallography. The X-ray diffraction intensity data were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with nickel-filtered CuKα (λ = 1.5418 Å) for **1**, with graphite-monochromated CuKα (λ = 1.5418 Å) for **2**, and with graphite-monochromated MoKα (λ = 0.7107 Å) for **3** at 296K. Calculations were carried out on an SGI Indy workstation with a CrystanGM[11] software package for **1**, on an SGI Indy workstation with a teXsan[12] software package for **2**, and on an SGI Indigo workstation with a teXsan software package for **3**. Empirical absorption corrections based on Ψ scans were applied for **2** and **3** (transmission factors 0.742-1.000 and 0.503-1.000, respectively). No significant decays in the intensities of three standard reflections (maximum 3.7, 3.8, and 2.9 % for **1**, **2**, and **3**, respectively) were observed throughout the data collection. The structures were solved using SIR 92[13] for **1** and SHELXS-86[14] for **2** and **3**, and were expanded by Fourier techniques. For **2**, the systematic absences, 0k0; k=2n+1, indicated the possible space groups $P2_1$ and $P2_1/m$. The space group $P2_1$ was adopted because of the less R values than that for $P2_1/m$ in the subsequent refinement. The structures of **1** and **2** were refined on F by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The hydrogen atoms H(2), H(3A), H(3B), H(6A), H(6B), and H(50) of **1** were located from difference Fourier syntheses and the residual ones of **1** were located at geometrically and all were refined isotropically. All the hydrogen atoms of **2** were fixed at geometrically calculated positions. The slightly distorted shape of the phenyl groups may be attributed to structural disorder for **2**. The disordered phenyl groups were unsuccessful in separating owing to the shortage of the number of reflections for the number of parameters. In the complex **3**, after anisotropic refinement of the non-hydrogen atoms, two 1-phenylethylamine ligands showed evidence of disorder, which was manifested in larger carbon displacement parameters, significant residual electron densities between the carbon atomic positions in a phenyl group, and unreasonable conformation of asymmetric carbons. Therefore, the following disordered models were tried in the refinement: one of them has two disordered methyl groups (C(17) and C(47)), and the other has two disordered phenyl groups (C(41) through C(46) and C(41), C(49) through C(53)) having a common C(41) bonded to two disordered asymmetric carbon atoms (C(39) and C(48)). An occupancy factor of each disordered atom was fixed at 0.5, which was consistent with the results of CD spectra. The results suggest that **3** is a *racemic* crystal. All hydrogen atoms of 5,5-diphenylhydantoinate ligands and the hydrogen atoms of a phenyl group in ordered 1-phenylethylamine ligand were added at geometrically calculated positions using riding models, with $U_{iso}(H) = 1.2U_{eq}(C)$. The carbon atoms C(16), C(17) and C(39) through C(53) were refined isotropically and the residual non-hydrogen atoms anisotropically. Restraints were applied to the disordered phenyl groups and to the distances and angles around the asymmetric C(16), C(39), and C(48) atoms. The ghost peak of the maximum difference density 1.14 e $Å^{-3}$ near C(16) is considered to be due to the failure to separate into two optically active ligands and due to the isotropic refinement of C(16).

Measurements. X-ray powder diffraction data were measured on a Rigaku Geigerflex RAD-IA diffractometer using nickel-filtered CuKα (λ = 1.5418 Å) radiation in the range of 5 ° < 2θ < 30 °. The electronic spectra of **1** and **4** in the solid state were measured on a Hitachi U-3400 UV/VIS/NIR spectrophotometer equipped with a diffuse reflectance attachment. Circular dichroism (CD) spectra of chloroform solutions of **2** and **4** in 1 mmol dm^{-3} concentration and chloroform solutions dissolved a crystal of **3** and **4** were recorded on a JASCO J-500C spectrophotometer. Thermogravimetry (TG) and differential thermal analysis (DTA) were measured simultaneously on a SEIKO Instruments. Inc. SSC-5000 thermal analysis system in static air at a heating rate of 20 °C/min. The amounts of α-alumina as a reference and the samples of **1** and **4** were 10.0 mg.

2.3 Results and Discussion

Description of the Structures. The crystallographic data for **1**, **2**, and **3** are summarized in Table 2-1, and the selected bond distances and angles are listed in Table 2-2. The molecular structures of **1**, **2**, and **3** with the adopted numbering scheme are illustrated in Figures 2-1, 2-2, and 2-3, respectively. The asymmetric unit of the crystal **2** consists of two independent molecules, **2(1)** and **2(2)**.

The central copper(II) ion has a distorted square planer $[CuN_4]$ geometry for **1**, **2**, and **3**. The geometry is a characteristic feature for *trans*-$[Cu(imidate)_2(amine)_2]$ complexes having 1-phenylethylamine ligands.[9] While most of the analogous *trans*-$[Cu(imidate)_2(amine)_2]$ complexes afford a square planar $[CuN_4]$ coordination geometry.[4,5,9]

The Cu-N(imidate) (Cu(1)-N(1) or Cu(1)-N(4)) bond distances for **1**, **2**, and **3** range from 1.99(1) to 2.07(1) Å (average 2.01 Å) and the Cu-N(amine) (Cu(1)-N(3) or Cu(1)-N(6)) bond distances from 1.97(1) to 2.07(1) Å (average 2.02 Å). No significant difference is observed between Cu-N(imidate) and Cu-N(amine) bond distances. According to the CSD,[15] the average bond lengths Cu-N(imidate) and Cu-N(amine) are 1.99 and 2.03 Å, respectively. Both the Cu-N(imidate) and Cu-N(amine) bond distances are similar to the related complexes regardless of the distortion of the $[CuN_4]$ coordination environment.

The most relevant difference between the structures of **1**, **2**, and **3** is the degree of the distortion of $[CuN_4]$ coordination environment. The *trans*-N(imidate)-Cu-N(imidate) (N(1)-Cu-N(4)) and *trans*-N(amine)-Cu-N(amine) (N(3)-Cu-N(6)) bond angles are 154.9(2) and 159.8(2) ° for **1**, 168.1(5) and 162.3(5) ° for **2(1)**, 165.7(5) and 163.1(5) ° for **2(2)**, and 166.6(2) and 163.2(2) ° for **3**, respectively. The degree of the distortion from a regular square planar geometry for **1** is larger than that of **2** or **3**, while that of **2** is similar to **3**. The N(imidate)-Cu-N(imidate) and N(amine)-Cu-N(amine) bond angles are

153.0(1) and 149.1(1) ° for *trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)], and 171.8(2) and 169.7(2) ° for *trans*-[Cu(hyd)$_2$(R-phenea)$_2$], respectively.[9] The order of the distortion is as follows: *trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)] > **1** > **2** and **3** > *trans*-[Cu(hyd)$_2$(R-phenea)$_2$]. The present 5,5-diphenylhydantoinate complexes **1**, **2**, and **3** have intermediate degree of distortion in a series of the distorted square planar [CuN_4] complexes with 1-phenylethylamine ligands.

Structural differences derived from chirality of 1-phenylethylamine ligands may be responsible for various degree of distortion of the [CuN_4] coordination environment. The complex **1**, which has the largest distorted square planar [CuN_4] chromophore, is coordinated by both R- and S-1-phenylethylamine ligands, whereas **2** and **3** by identical ligands in chirality (S and S or R and R). As indicated in Figure 2-4, when the *trans*-position (torsion angle 180 °) of one of the 1-phenylethylamine ligands is occupied by a phenyl group, the *trans*-position of another side of 1-phenylethylamine ligands is occupied by a methyl group and *vice versa* for both **1** and **2**, and the conformation of phenyl and methyl groups of **1** is identical with **2**. The difference in the distortion of the [CuN_4] chromophores can not be explained only with the steric factors of 1-phenylethylamine ligands.

Space-filling models of **1** and **2(1)** are employed to explain the difference in the distortion of [CuN_4] chromophores. As shown in Figure 2-5, the arrangement of the substituent groups of 1-phenylethylamine ligands around the central copper atom of **1** is as follows:

methyl-phenyl-(copper) -methyl-phenyl

The arrangement of **2** (and also **3**) is:

methyl-phenyl-(copper)-phenyl-methyl

The largest distortion of **1** is due to the torsion of 5,5-diphenylhydantoinate ligands caused by steric repulsion among this crowded alternative arrangement of the substituents. As depicted in Figure 2-6, two phenyl groups face each other in the molecule of **2** (and also **3**). The situation reduces steric strains of 5,5-diphenylhydantoinate ligands inside of phenyl groups of 1-phenylethylamine ligands on both sides. For this reason, the difference in the degree of the distortion can be explained by steric interaction between 1-phenylethylamine and 5,5-diphenylhydantoinate ligands. Intramolecular and intermolecular N-H•••O=C hydrogen bonds are formed in all the crystals, and the possible hydrogen bonding distances and angles are summarized in Tables 2-3 and 2-4, respectively.

Intramolecular hydrogen bonds are formed between amino hydrogen atoms of 1-phenylethylamine (N(3)-H and N(6)-H) and carbonyl oxygen atoms of 5,5-diphenylhydantoinate (O(1), O(2), O(3), and O(4)) (Table 2-3). Each complex potentially possesses four sets of proton-donor sites (N-H) and acceptor sites (C=O) available for

intramolecular hydrogen bonds. Judging from the statistical criterion by Taylor and Kennard,[16] however, only two of the four (for **1**) or three of the four (for **2** and **3**) sites are involved in intramolecular hydrogen bonds. Not all four intramolecular hydrogen bonds are formed because of the distortion of the coordination environment of the copper atom.

In all three crystals, the molecules are linked to the adjacent ones through double anti-parallel intermolecular hydrogen bonds between donor nitrogen atoms (N(2)-H or N(5)-H) and acceptor oxygen atoms (O(1) or O(3)) of 5,5-diphenylhydantoinate ligands (Table 2-4). The complementary double intermolecular hydrogen bonds give rise to infinite linear chains in the crystals. The intermolecular hydrogen bonding pattern may be classified as "lactam-lactam" type,[17] which is regarded as one of the dominant interactions to determine molecular arrangement in crystals.[18]

The crystal structure of **1** viewed down from nearly the *b* axis is shown in Figure 2-7. Each molecule is connected to the adjacent molecules by the double anti-parallel intermolecular hydrogen bonds along the *a* axis direction. Stacked ring moieties result in a column structure along the *b* axis direction.

On the other hand, the crystal **2** has no column structures as displayed in Figure 2-8. Intermolecular hydrogen bond networks run on the *ac* plane in the similar fashion to **1**. In this way, steric effects due to chirality of 1-phenylethylamine ligands affect the difference in crystal packing fashions as well as molecular structures of individual complexes.

Identification of Three Forms. Three forms, *meso*, *optically active*, and *racemic* forms have been obtained, and the isolation is the first example for *trans*-[Cu(imidate)$_2$(phenea)$_2$] system. We are going to discuss a formation process of these isomers depending on the difference in chirality of 1-phenylethylamine during preparations. The reaction in the presence of *optically active* S-1-phenylethylamine gave reddish violet products consisting of not only a large amount of prismatic crystals **2** (*optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$]) but also a little of plate-like crystals **3**. The reaction with *optically active* R-1-phenylethylamine also gave mixed products **3** and **4** (*optically active trans*-[Cu(phent)$_2$(R-phenea)$_2$]).

For the disordered structure of the plate-like crystal **3**, following two ordered molecular structures are considered; one is a polymorphic form of the *meso* form, and the other is a *racemic* crystal composed of a 1:1 mixture of *trans*-[Cu(phent)$_2$(R-phenea)$_2$] and *trans*-[Cu(phent)$_2$(S-phenea)$_2$]. No peaks due to phase transition were observed in the TG-DTA curves in the range from 20 °C to decomposition point (about 250 °C) for **1** and **4**, which suggested less possibility of polymorphism. No appreciable differences in individual molecular structures are observed between **2** and **3**. *Optically active* complex is sterically favored as a component of crystal **3**.

CD spectroscopy was used for inspection. The CD spectra were recorded for 1 mmol dm^{-3} chloroform solutions of random sampling precipitates of **2** and **4** (Figure 2-9). The spectrum of **2** showed two peaks at about 16000 ($\Delta\varepsilon$ = -0.50 mol^{-1} dm^3 cm^{-1}) and 19000 cm^{-1} ($\Delta\varepsilon$ = 0.38 mol^{-1} dm^3 cm^{-1}). The spectrum of **4** was quite similar to **2** except for the signs of $\Delta\varepsilon$, which proved that **2** and **4** were *optically active* enantiomers.

The CD spectra were measured for chloroform solutions of a single crystal of **3**, the identical crystal used for X-ray crystallography, and a single crystal of **4**. The concentration of the solutions was about 0.1 and 0.2 mmol dm^{-3} for **3** and **4**, respectively. The spectrum of the single crystal was similar to that of the random sampling precipitate of **4**, however, no peak appeared for a single crystal of **3**. The results provide the evidence that the prismatic crystal **4** is *optically active* crystal and the plate-like crystal **3** is *racemic*.[19]

Formation Condition of Three Forms. For searching formation condition of *racemic* crystals, preparations were carried out in the presence of various ratio of R- and S-1-phenylethylamine. At first, the products were confirmed qualitatively by appearance of the resulting crystals (color and shape). Since the resulting crystals were mixed products, predominant crystals were used for the judgment of main component of the resulting crystals. The predominant resulting crystals are reddish violet prismatic in the range of 60 to 70 and 90 to 100 % e.e., reddish violet plate-like in the range of 70 to 80 % e.e., and blue violet prismatic in the range of 0 to 20 % e.e., that corresponds to *optically active*, *racemic*, and *meso* crystals, respectively.[20] Additionally, changes in the products were examined by the powder X-ray diffraction given in Table 2-5. Since crystal structure of *optically active* crystal is similar to that of *racemic*, distinction between both patterns is obscure, however, *meso* is distinguishable from *optically active* or *racemic*. Intensity of the patterns has no quantitative accuracy, so that the peaks can be assigned by the diffraction angles. Characteristic peaks of both *optically active* **2** and *racemic* **3** such as at 9.8, 13.8, 17.7, 18.4, 19.5, 22.5, 25.1, and 27.6 ° appear in the ratio of R:S = 0:10 (100 % e.e., i.e. *optically active* 1-phenylethylamine) to R:S = 2:8 (60 % e.e.). While the peaks of *meso* crystals **1** such as at 13.6, 14.2, 16.8, 18.6, 20.0, 20.6, 21.8, 22.3, 23.4, 24.9, and 26.8 ° are observed in the range of R:S = 4:6 (20 % e.e.) to 5:5 (0 % e.e., i.e. *racemic* 1-phenylethylamine), and the peaks due to *optically active* or *racemic* crystals vanish in this range. When the amount of the produced *meso* form increase as the e.e. values decrease, the peaks of *optically active* or *racemic* form will decrease. In practice, however, the peaks *optically active* or *racemic* form increased in spite of the decrease in the e.e. values from 80% to 70%. Therefore the behavior of the peaks can be interpreted as a consequence of the formation of *racemic* crystals.

Consequently, the way of selective preparations of these forms is established by varying the ratio of R- to S-1-phenylethylamine during preparations as follow:

Meso form was obtained in the range of 0 to 20% e.e..

Optically active form was predominantly obtained in the range of 60 to 70 and 90 to 100 % e.e..

Racemic crystal was predominantly obtained in the range of 70 to 80% e.e..

On the contrary, the three crystals cannot be prepared by mixing various ratio of complexes **2** and **4**. For example, when solutions of **2** and **4** are mixed in a 1:1 ratio, only crystals **1** are obtained as a result of exchange of 1-phenylethylamine ligands.

In general, reaction of racemic ligands yields *meso* complexes. On the other hands, the phenomenon that racemic ligands afforded the complex consisted of a copper atom with R- and S- ligands, that is *optically active* complexes of *racemic* mixture complexes, was found for bis-α-hydroxy-α-phenylbuthylamidinie copper(II)[25] exceptionally. The present case was novel in view of the formation of *racemic* crystal (*racemic* compound) but *meso* complexes were not given by partially mixed *optically active* amine ligands. Thus the present system can be classified into intermediate phenomenon of novel type.

The reason and the mechanism for formation of the *racemic* form have not been clear and no evidence for the formation of it could be given directly, since the following attempts fail to detect the reason experimentally. On doping R-1-phenylethylamine, S-phenylethylamine ligands in the molecules of the *trans*-$[Cu(phent)_2(S\text{-}phenea)_2]$ will be replaced to give *trans*-$[Cu(phent)_2(R\text{-}phenea)_2]$ by R-1-phenylethylamine, that will cause increase in $\Delta\varepsilon$ values of 10 $mmol^{-1}$ dm^3 chloroform solution of **4**. The increase in $\Delta\varepsilon$ values related to S-1-phenylethylamine contained is estimated about 5 %. Moreover, the reaction of 5,5-diphenylhydantoin and 1-phenylethylamine without copper powder did not result in racemization of 1-phenylethylamine.

Electronic Spectra. The diffuse reflectance spectra of **1** and **4** in the solid state are shown in Figure 2-10. The spectra of **1** (blue violet) and **4** (reddish violet) exhibit a broad peak of ligand field band at 17300 and 18400 cm^{-1}, respectively. The band shapes of the spectra are similar to those of analogous distorted square planar *trans*-$[Cu(imidate)_2(phenea)_2]$ complexes. Difference in peak wave number between **1** and **4** is ascribed to only the degree of the distortion of the $[CuN_4]$ chromophore regardless of ligand field strength, because these complexes are diastereomeric isomers with identical ligands in view of electronic properties

The order of distortion of $[CuN_4]$ chromophores and the peaks of reflectance spectra (figures in parentheses denotes peak wave numbers of reflectance spectra) of the related 1-phenylethylamine complexes is as follows: *trans*-$[Cu(succim)_2(R\text{-}phenea)(S\text{-}phenea)]$ (16700 cm^{-1}), **1** (17300 cm^{-1}), **4** (18400 cm^{-1}), and *trans*-$[Cu(hyd)_2(R\text{-}phenea)_2]$ (18650 cm^{-1}). Square planar *trans*-$[Cu(imidate)_2(amine)_2]$ complexes exhibit the main peak of ligand field band at about 20000 cm^{-1} with a shoulder over the range of 16000 - 17000 cm^{-1}. In this way, as the $[CuN_4]$ chromophore is distorted from a square planar geometry toward a tetrahedral geometry, the peak shifts to lower wave number. The accurate assignment of d-d transitions must be carried out on a basis of polarized single crystal spectra and that will be described in chapter 6.

2.4 Conclusion.

Meso, *optically active*, and *racemic trans*-bis(5,5-diphenylhydantoinato)bis(1-phenylethylamine)copper(II) complexes were prepared and the crystal structures were determined. Each complex assumes a distorted square planar [CuN_4] coordination geometry, and tetrahedral distortion from square planar of *meso* form is larger than those of *optically active* and *racemic* forms. The largest distortion of *meso* form is due to the torsion of 5,5-diphenylhydantoinate ligands caused by steric repulsion of the crowded alternative arrangement of the substituents. Three forms of crystals were selectively obtained depending on the ratio of R- to S-1-phenylethylamine during preparations as follow:*Meso* form was obtained in the range of 0 to 20% e.e., *optically active* form was predominantly obtained in the range of 60 to 70 and 90 to 100 % e.e., and *racemic* crystal was predominantly obtained in the range of 70 to 80% e.e..

Table 2-1. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
Formula	$C_{46}H_{44}N_6O_4Cu$	$C_{46}H_{44}N_6O_4Cu$	$C_{46}H_{44}N_6O_4Cu$
Formula weight	808.44	808.44	808.44
Color of crystal	blue violet	reddish violet	reddish violet
Crystal size/mm	0.25x0.20x0.20	0.20x0.20x0.20	0.30x0.10x0.70
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1$	$P2_1/n$
a / Å	19.643(3)	13.993(1)	13.992(5)
b / Å	9.018(4)	18.277(2)	18.277(6)
c / Å	22.853(3)	16.167(1)	16.163(5)
β / °	93.97(1)	100.16(1)	100.15(3)
V / Å^3	4038(2)	4070(1)	4068(2)
Z	4	4	4
D_c /gcm^{-1}	1.650	1.319	1.320
μ /cm^{-1}	11.39	11.69	5.88
$2\theta_{max}$/°	120.0	120.1	60.0
Temperature/K	298	296	295
Measd reflcns	6109	6573	12683
Reflcns used in refine	3513 ($I \geq 3.0\sigma(I)$)	4591 ($I \geq 3.0\sigma(I)$)	5468 ($I \geq 3.5\sigma(I)$)
No. of parameters	576	1026	470
G.O.F.	2.65	2.93	1.17
R[†]	0.044	0.050	0.071
R_w[‡]	0.046	0.040	0.088

[†] $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, [‡] $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/\sigma^2(F_o)$

Table 2-2. Selected bond distances(Å) and angles(°) for **1**, **2**, and **3**.

Bond Distances

	1	2(1)	2(2)	3
Cu(1)-N(1)	1.988(3)	2.00(1)	2.02(1)	2.009(4)
Cu(1)-N(3)	2.012(3)	1.97(1)	1.97(1)	2.026(4)
Cu(1)-N(4)	1.997(3)	2.03(1)	2.02(1)	2.026(4)
Cu(1)-N(6)	2.019(3)	2.07(1)	2.06(1)	2.030(4)
O(1)-C(1)	1.233(4)	1.21(1)	1.23(1)	1.241(6)
O(2)-C(2)	1.219(4)	1.20(1)	1.22(1)	1.217(6)
O(3)-C(24)	1.235(4)	1.26(1)	1.20(2)	1.227(6)
O(4)-C(25)	1.217(4)	1.19(1)	1.23(2)	1.214(5)
N(1)-C(1)	1.394(4)	1.33(1)	1.42(1)	1.403(5)
N(1)-C(2)	1.361(4)	1.32(2)	1.36(2)	1.370(6)
N(3)-C(16)	1.488(6)	1.53(2)	1.50(1)	1.417(9)
N(4)-C(24)	1.392(4)	1.40(2)	1.41(2)	1.381(5)
N(4)-C(25)	1.352(5)	1.38(2)	1.33(2)	1.352(6)
N(6)-C(39)	1.483(5)	1.48(2)	1.49(2)	1.472(9)
C(16)-C(17)	1.526(6)	1.49(2)	1.56(2)	1.44(1)
C(39)-C(40)	1.480(8)	1.46(2)	1.49(2)	1.56(1)

Bond Angles

	1	2(1)	2(2)	3
N(1)-Cu(1)-N(3)	91.9(2)	89.2(5)	90.2(5)	93.2(2)
N(3)-Cu(1)-N(4)	92.6(2)	94.2(5)	92.5(5)	89.4(2)
N(4)-Cu(1)-N(6)	91.8(2)	93.4(5)	92.0(5)	88.5(2)
N(6)-Cu(1)-N(1)	92.4(2)	86.6(5)	89.5(5)	92.7(2)
N(1)-Cu(1)-N(4)	154.9(2)	168.1(5)	165.7(5)	166.6(2)
N(3)-Cu(1)-N(6)	159.8(2)	162.3(5)	163.1(5)	163.2(2)
C(2)-N(1)-C(1)	108.4(3)	110(1)	111(1)	107.1(4)
Cu(1)-N(3)-C(16)	118.0(3)	124.4(9)	116.2(7)	123.9(4)
C(24)-N(4)-C(25)	108.8(3)	105(1)	111(1)	108.7(4)
Cu(1)-N(6)-C(39)	120.1(3)	110.9(8)	116.8(8)	112.5(4)
N(3)-C(16)-C(17)	110.4(4)	108(1)	111(1)	119.3(7)
N(6)-C(39)-C(40)	110.0(4)	112(1)	109(1)	109.2(5)

Table 2-3. Proposed intramolecular hydrogen bond distances(Å) and angles(°).

	N•••O/Å	H•••O/Å	N-H•••O/°
1			
N(3)-H•••O(2)*	2.87(1)	2.21	134.5
N(3)-H•••O(3)*	2.84(1)	2.02	154.7
N(6)-H•••O(4)	2.90(1)	2.32	118.5
N(6)-H•••O(1)	2.86(1)	2.13	93.7
2(1)			
N(3)-H•••O(1)*	2.84(1)	1.98	149.8
N(6)-H•••O(4)*	2.81(1)	2.07	133.2
N(6)-H•••O(3)*	2.77(1)	1.98	138.6
N(3)-H•••O(2)	3.08(1)	2.36	132.4
2(2)			
N(3')-H•••O(3')*	2.78(1)	2.09	133.9
N(3')-H•••O(1')*	2.96(1)	2.28	128.0
N(6')-H•••O(4')*	2.71(1)	1.82	128.0
N(6')-H•••O(2')	3.24(1)	2.83	106.5
3			
N(3)-H•••O(1)*	2.76(1)		
N(3)-H•••O(3)*	2.91(1)		
N(6)-H•••O(2)*	2.76(1)		
N(6)-H•••O(4)	3.15(1)		

Bonds marked with *'s would be considered to form intramolecular hydrogen bonds. Poor quality of data made impossible to calculate geometries involved in hydrogen positions for **3**.

Table 2-4. Proposed intermolecular hydrogen bond distances(Å) and angles(°).

	N•••O/Å	H•••O/Å	N-H•••O/°
1			
N(5)-H•••O(1)$^{a)}$	2.93(1)	2.14	157.6
N(2)-H•••O(3)$^{a)}$	2.86(1)	2.07	162.8
2			
N(2)-H•••O(2')$^{b)}$	2.88(1)	1.97	162.9
N(5)-H•••O(1')$^{c)}$	2.81(1)	1.94	150.4
N(2')-H•••O(3)$^{d)}$	2.91(1)	2.01	138.6
N(5')-H•••O(1)$^{b)}$	2.87(1)	2.00	132.4
N(2)-H•••O(3)$^{e)}$	2.84(1)	1.95	151.5
N(5)-H•••O(1)$^{f)}$	2.90(1)	1.99	158.5
3			
N(2)-H•••O(3)$^{g)}$	2.84(1)		
N(5)-H•••O(1)$^{f)}$	2.90(1)		

Symmetry operations $^{a)}$(1/2-x, 1/2+y, -z), $^{b)}$(x, y, z), $^{c)}$(x+1, y, Z+1) $^{d)}$(x-1, y, z-1), $^{e)}$(-1/2+x, 1/2-y, -1/2-z), $^{f)}$(1/2+x, 1/2-y, 1/2+z), $^{g)}$(-1/2+x, 1/2-y, -1/2+z).

Poor quality of data made impossible to calculate geometries involved in hydrogen positions for **3**.

Table 2-5. Characteristic powder X-ray diffraction peaks and color, shape, and type of predominant crystals for **1**, **2**, and **3**, and products with various ratio of R- and S-1-phenylethylamine. The figures denote normalized intensity of each XRD pattern.

	2θ/°	*racemic* 3	*optically active* 2						*meso* 1
e.e.			100%e.e.	90%e.e.	80%e.e.	70%e.e.	60%e.e.	20%e.e.	0%e.e.
predominant crystal color		reddish violet	reddish violet	reddish violet	reddish violet	reddish violet	reddish violet	blue violet	blue violet
predominant crystal shape		plate-like	prismatic	prismatic	plate-like	plate-like	prismatic	prismatic	prismatic
predominant crystal type				*optically active*	*racemic*	*racemic*	*optically active*	*meso*	
	7.8	**64**	**85**	46	100	61	100	100	**100**
	9.8	**93**	**99**	74	73	100	60		
	10.4	**25**	**12**	22	15		54	27	**74**
	12.5	**56**	**100**	44	48	47	27	17	**73**
	13.0	**34**	**19**	24	29	35			
	13.6						53	20	**43**
	13.8	**75**	**58**	88	96	90	30		
	14.2						25	10	**40**
	14.8	**26**	**12**	19	15	28		3	**22**
	15.3						32	14	**22**
	15.7	**42**	**37**	55	34	42	23		**22**
	16.3	**66**	**58**	69	62	80	12		
	16.8							7	**31**
	17.7	**60**	**25**	28	48	46	10		
	18.4	**78**	**63**	69	59	66	13		
	18.6							11	**31**
	19.2				24	27	20	11	**33**
	19.5	**56**	**33**	40	30	49			
	20.0						23	5	**39**
	20.6						59	27	**50**
	21.8						45	64	**67**
	22.3							24	**34**
	22.5	**100**	**47**	100	68	92	21		
	23.4				29		40	21	**28**
	24.9					43		25	**23**
	25.1	**44**	**68**	30	30				
	25.7	**29**	**20**	20	15	29	16		
	26.8						20	26	**32**
	27.6	**29**	**39**	22		23			

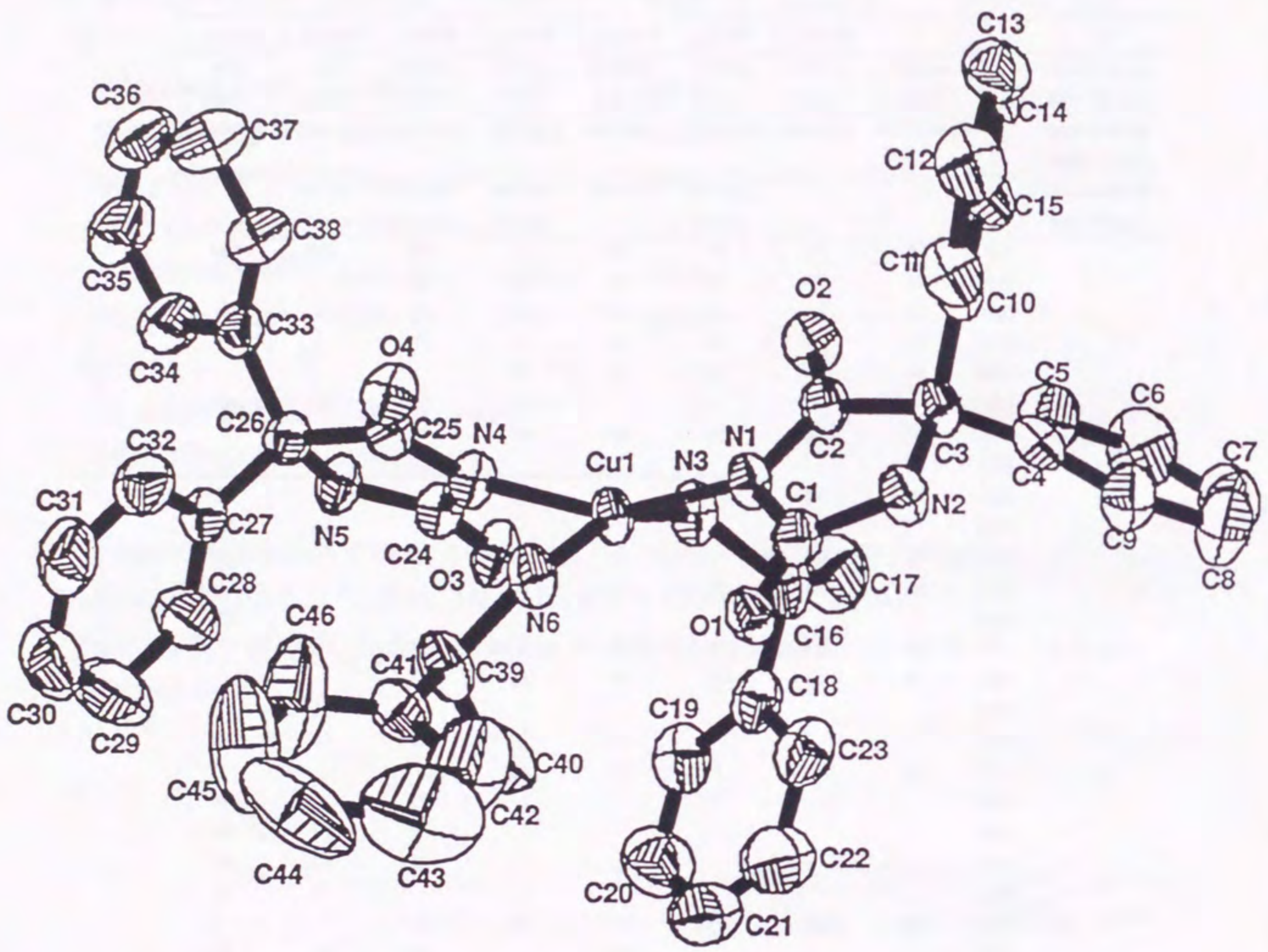


Figure 2-1. Molecular structure of *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**).

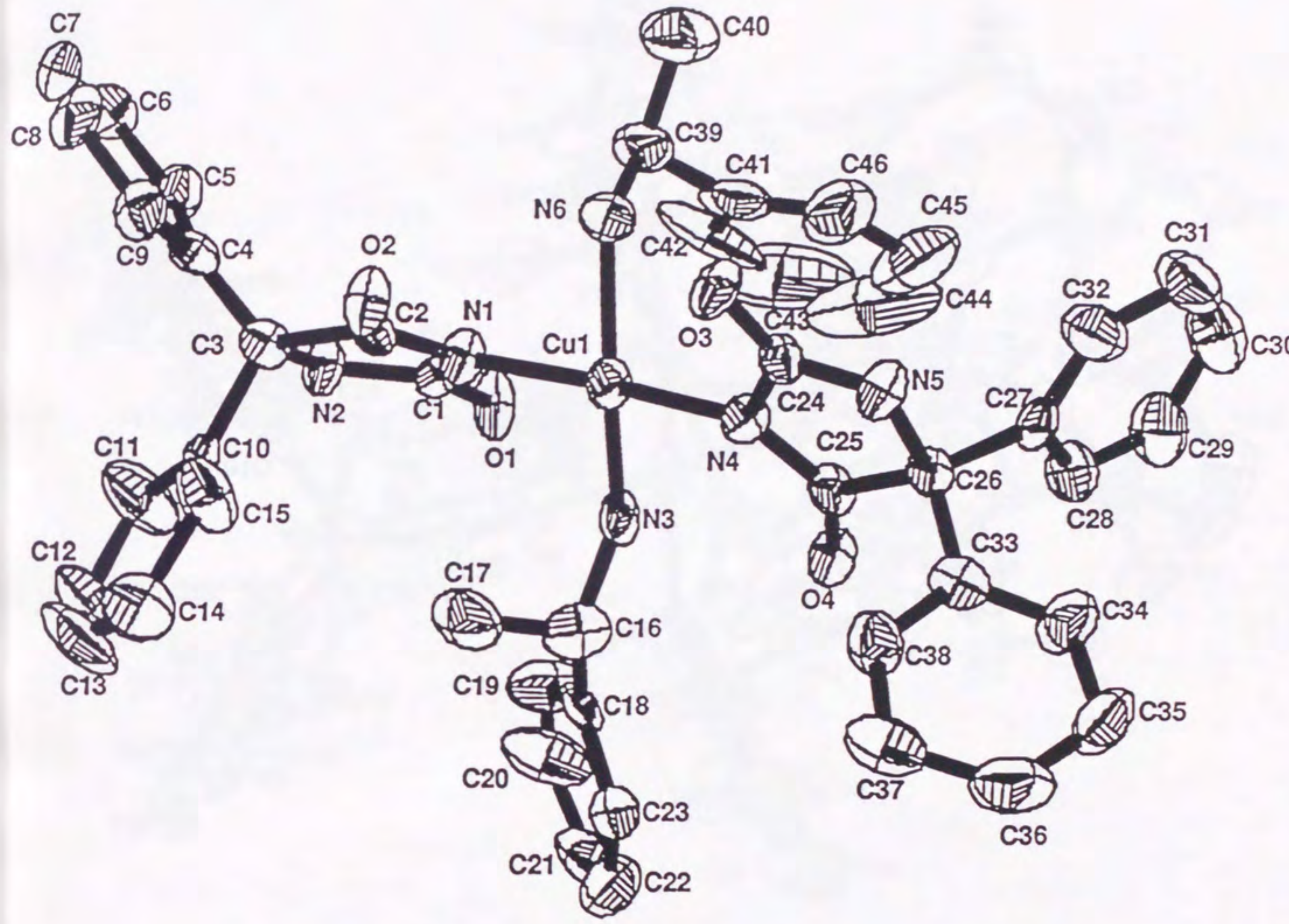


Figure 2-2-a. Molecular structures of *optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$] (**2**(**1**)).

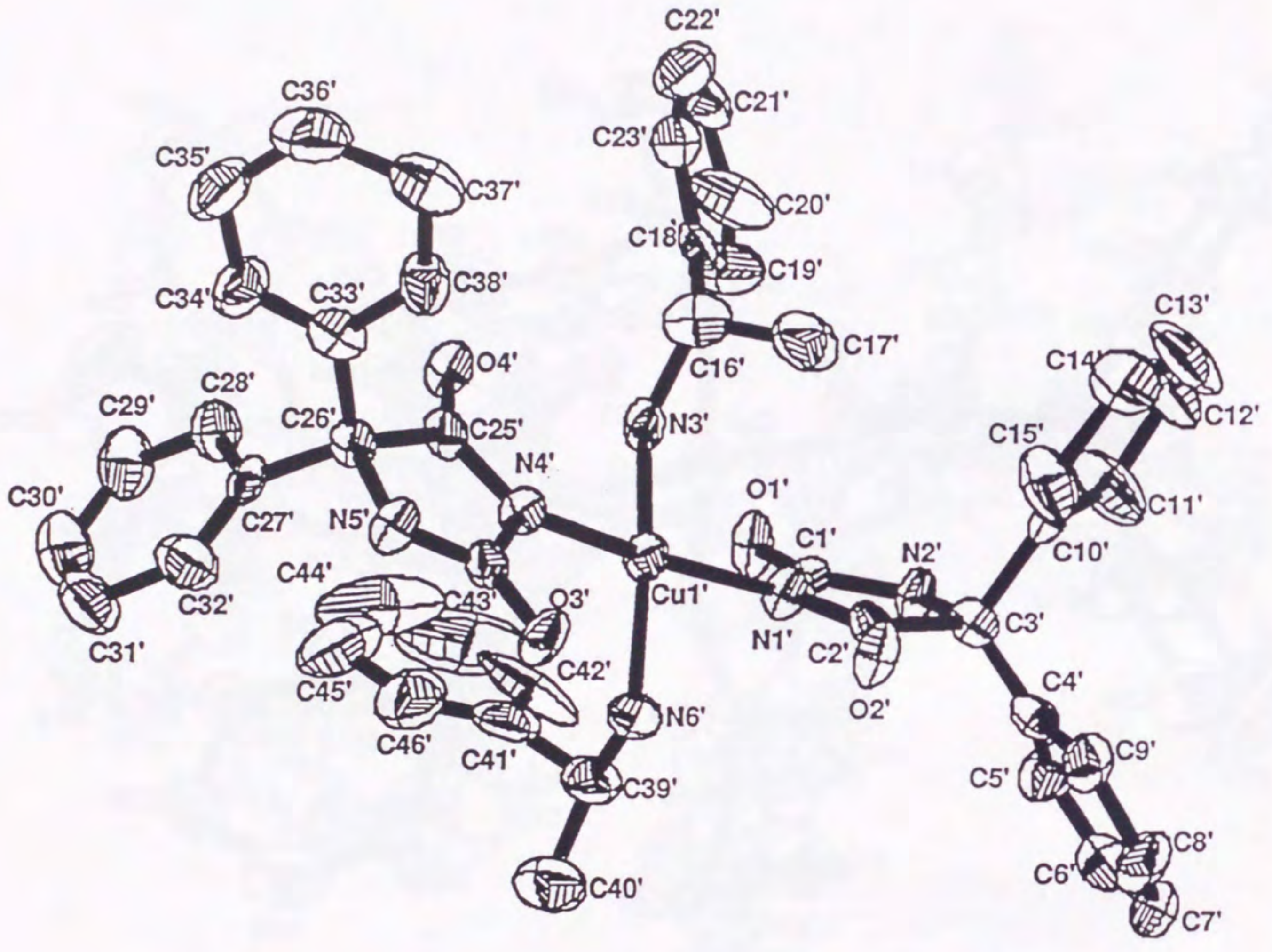


Figure 2-2-b. Molecular structures of *optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$] (2(2)).

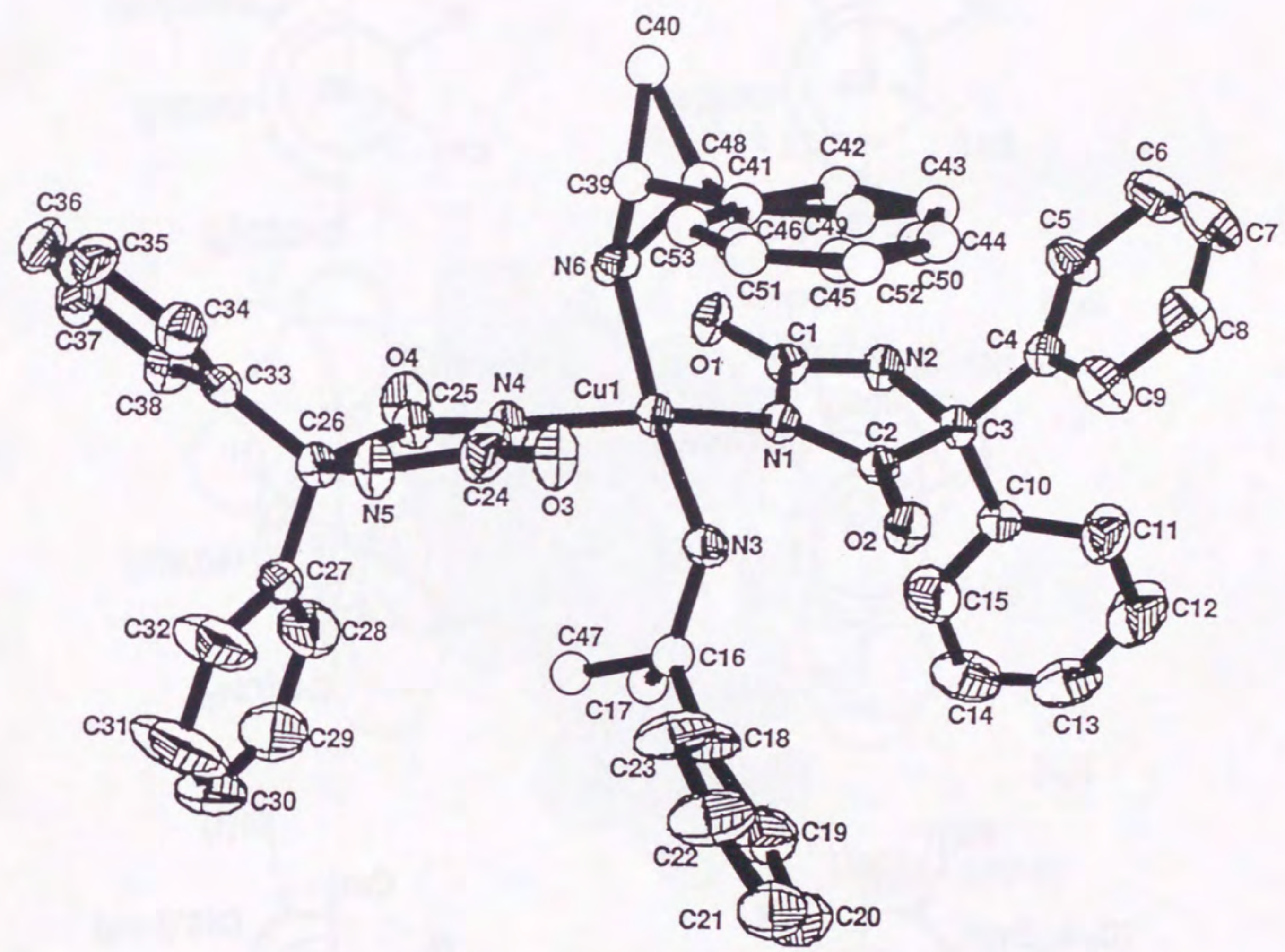


Figure 2-3. Molecular structure of *racemic* [Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (3).

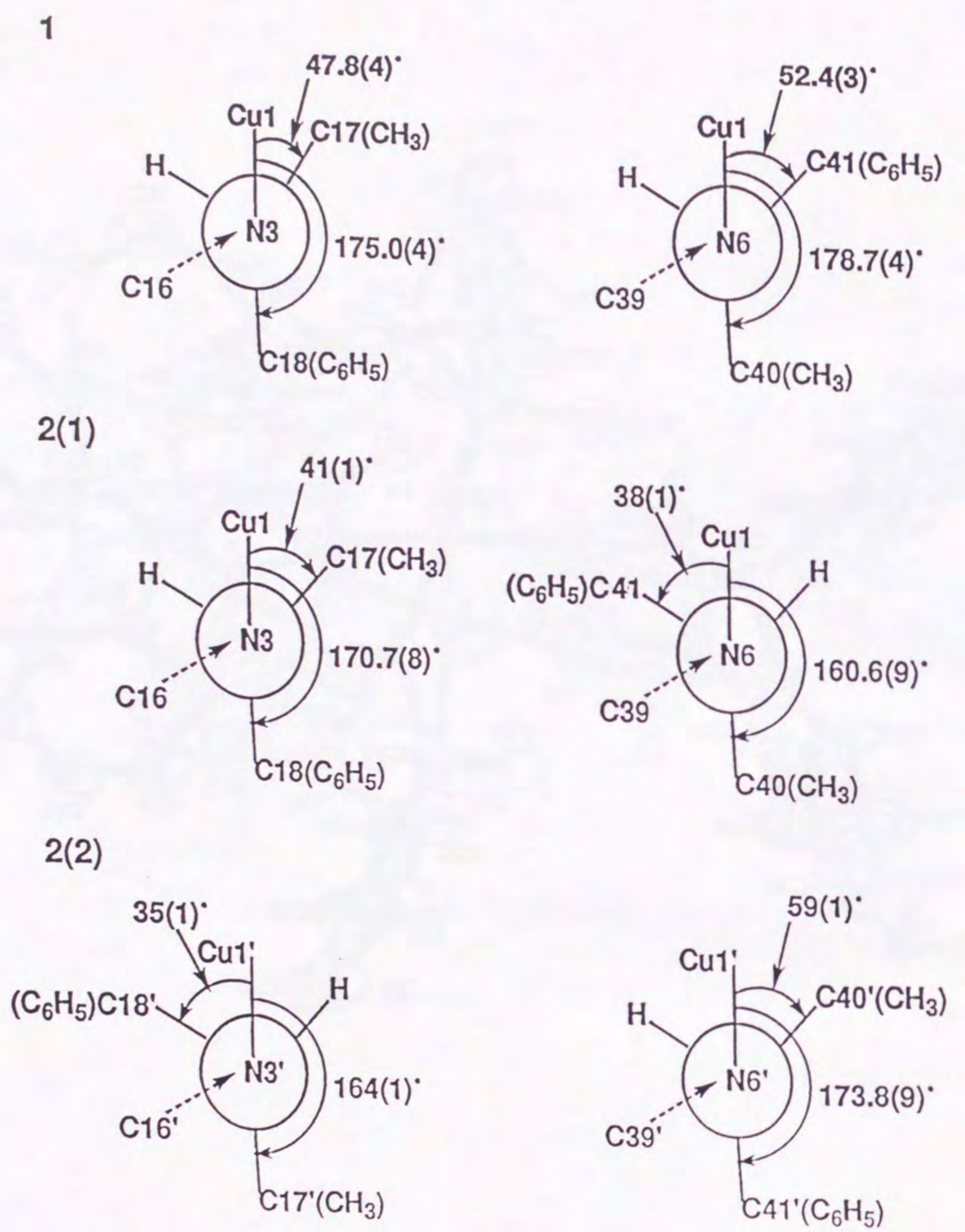


Figure 2-4. Newman projections around the N(phenea)-C(asymmetric carbon) axes for **1**, **2(1)**, and **2(2)**.

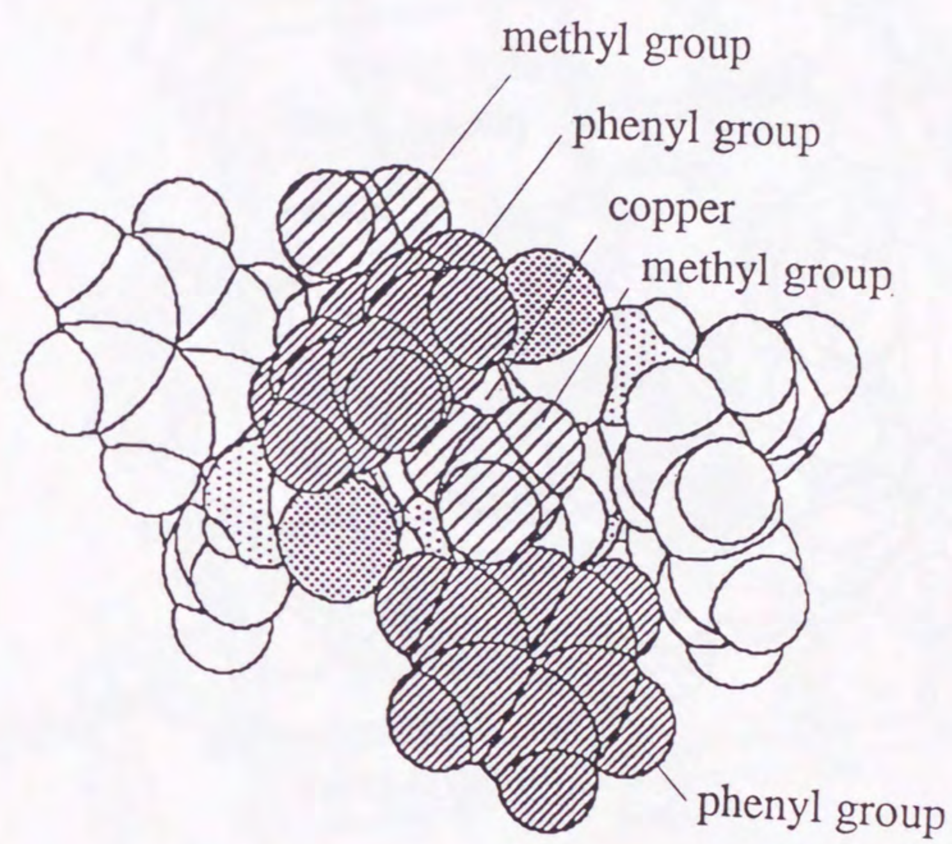


Figure 2-5. Space-filling model of *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**). Methyl and phenyl groups of 1-phenylethylamine ligands are highlighted by hatching.

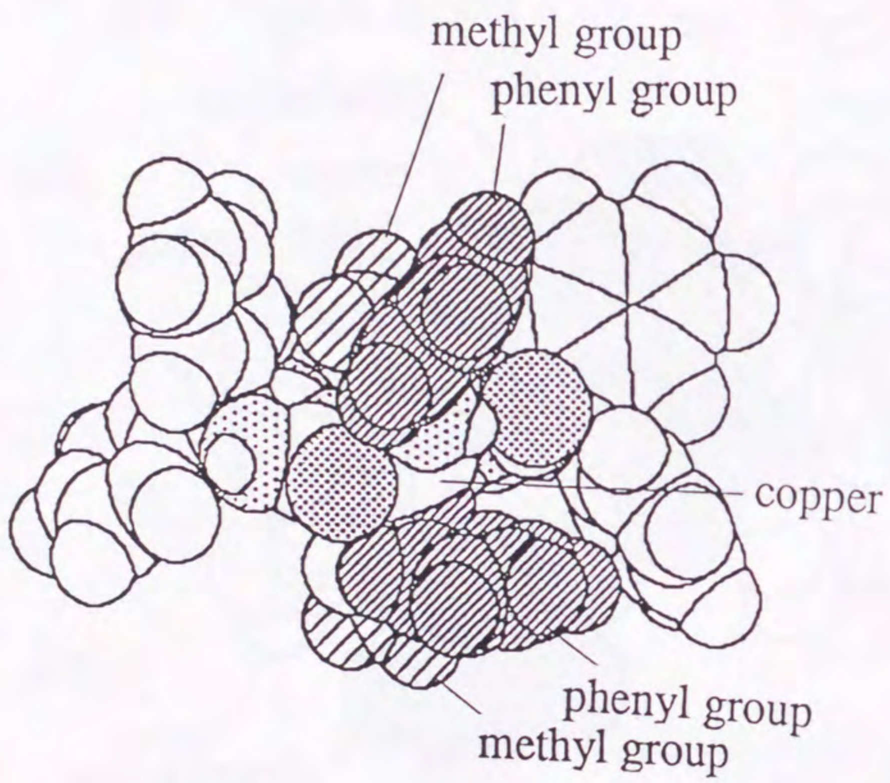


Figure 2-6. Space-filling model of *optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$] (**2**(**1**)). Methyl and phenyl groups of 1-phenylethylamine ligands are highlighted by hatching.

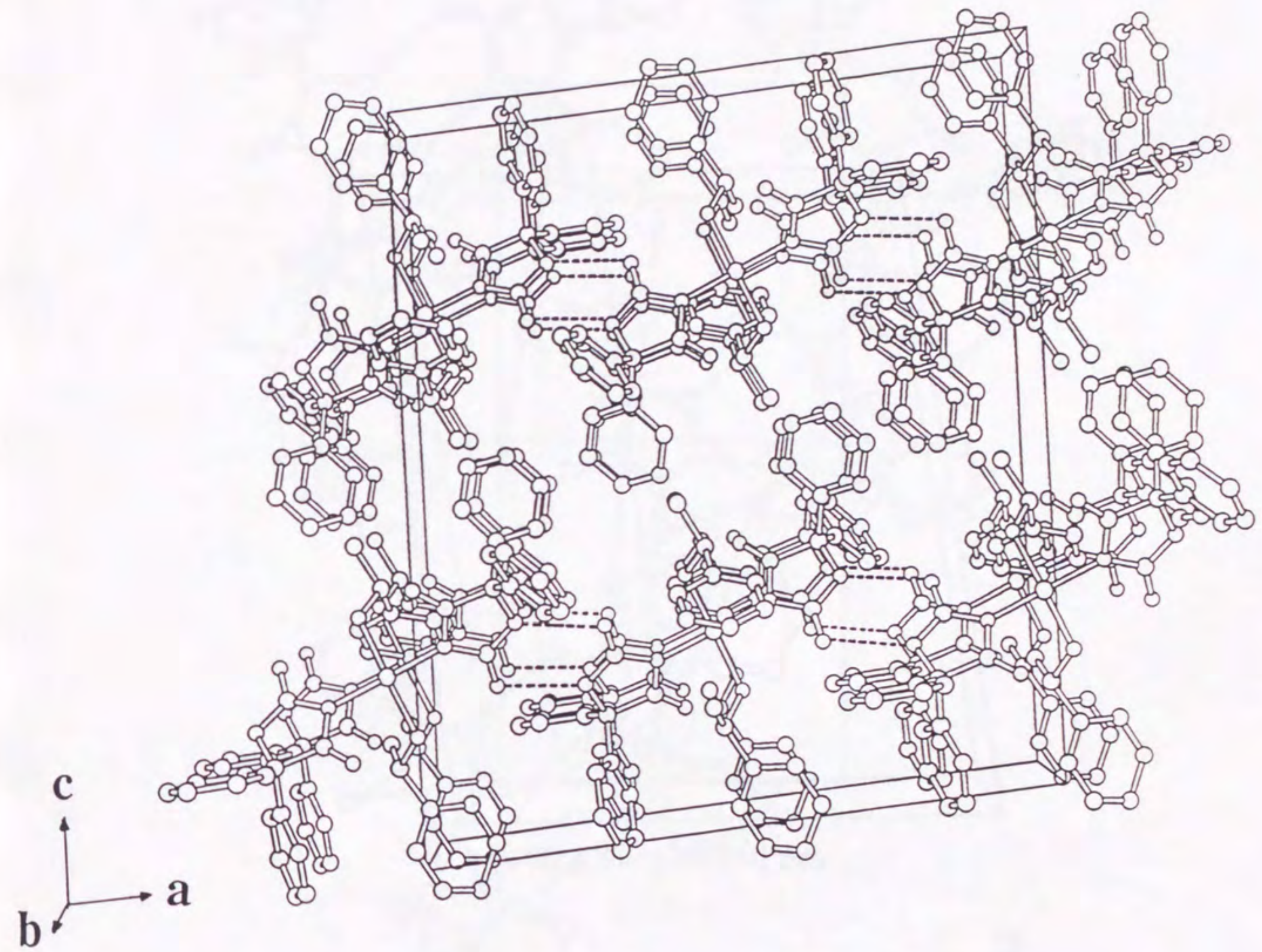


Figure 2-7. Crystal structure of *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) viewed down from nearly the *b* axis. Dashed lines denote intermolecular hydrogen bonds (N-H•••O=C).

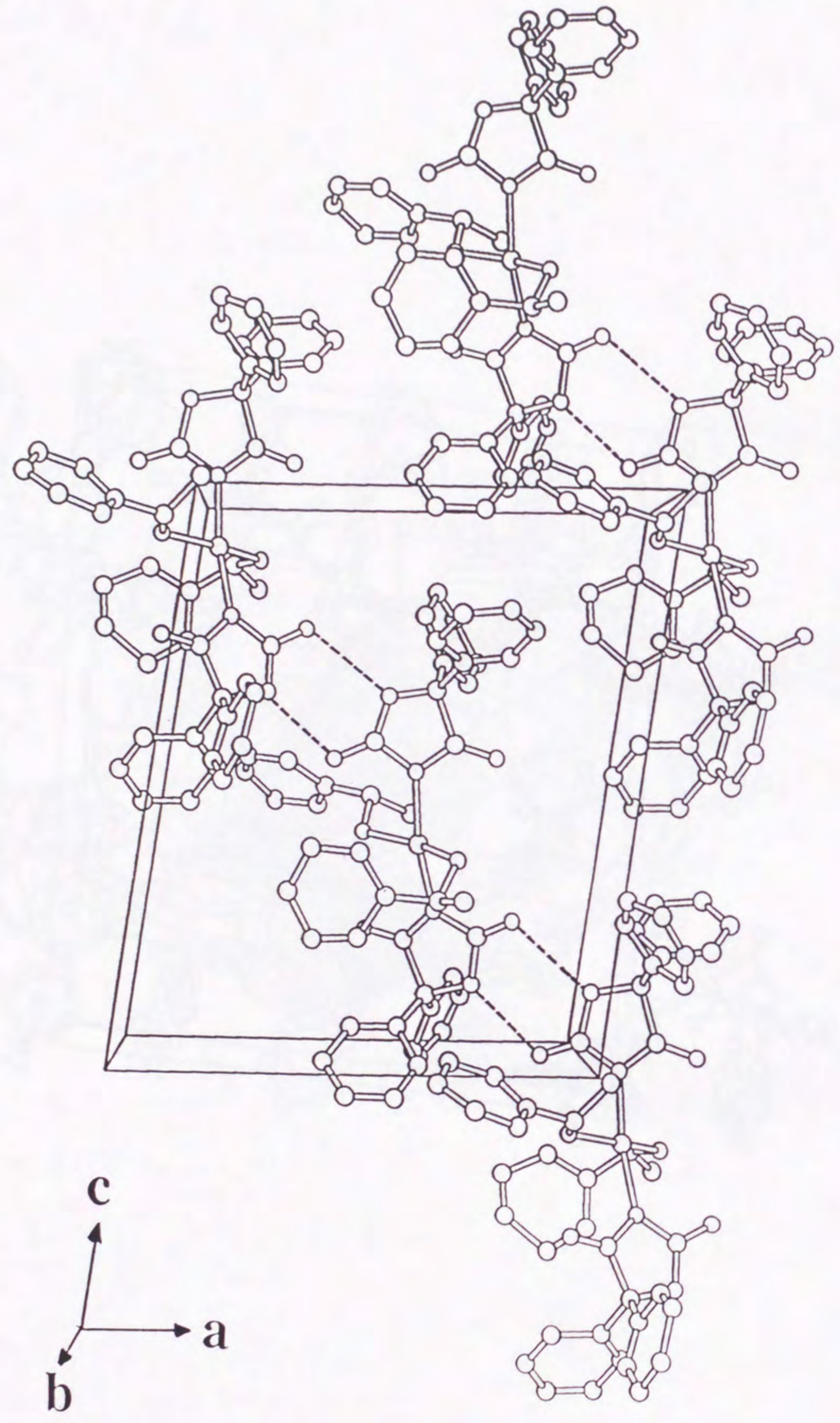


Figure 2-8. Crystal structure of *optically active trans*-[Cu(phent)$_2$(S-phenea)$_2$] (**2**) viewed down from nearly the *b* axis. Dashed lines denote intermolecular hydrogen bonds (N-H•••O=C).

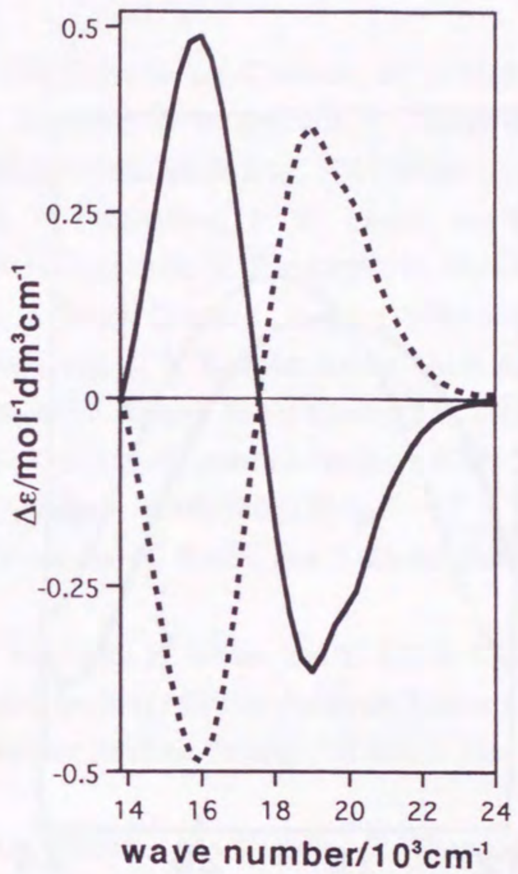


Figure 2-9. The CD spectra of *trans*-[Cu(phent)$_2$(R-phenea)$_2$] (**4**) (solid line) and *trans*-[Cu(phent)$_2$(S-phenea)$_2$] (**2**) (dotted line) in 10 mmol dm^{-3} chloroform solutions.

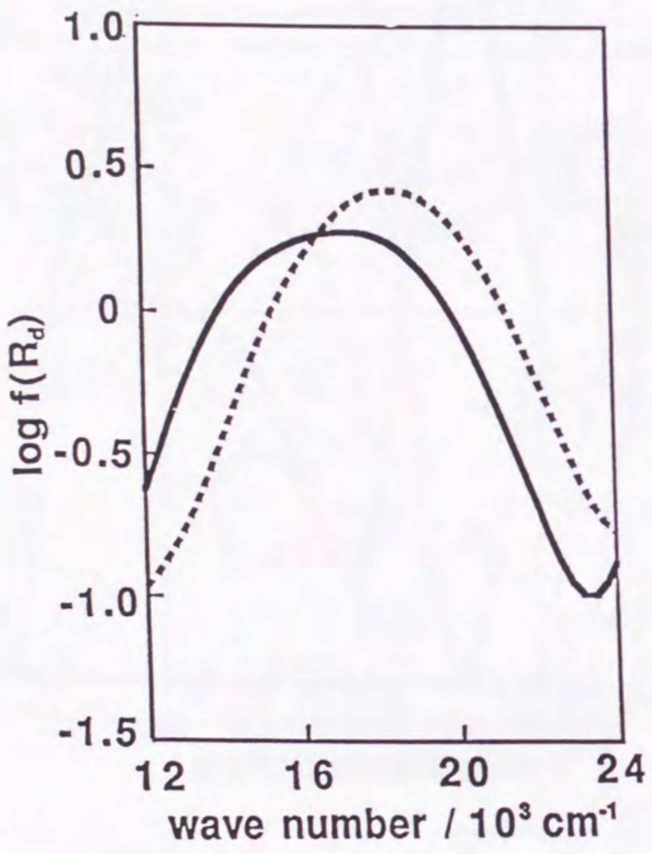


Figure 2-10. The diffuse reflectance spectra of *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) (solid line) and *optically active trans*-[Cu(phent)$_2$(R-phenea)$_2$] (**4**) (dotted line).

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19) Two formation processes of *racemic* crystals may be proposed: (1) Racemization of *optically active* 1-phenylethylamine during preparation reaction. (2) Contamination of opposite *optically active* 1-phenylethylamine in the starting ligands. Despite some attempts to specify the reasons to form *racemic* crystals, no definitive evidence could be obtained experimentally.

20) The resulting precipitates was mixture of *optically active* and *meso* that could not be specified the predominant component for 40 % e.e..

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Chapter 3.

Distortion of $[CuN_4]$ Chromophores Caused by Steric Factors of Monodentate Ligands. *Trans*-bis(imidato)bis(1,2-diphenylethylamine)copper(II) Complexes.

Abstract.

Two new copper(II) complexes, *meso trans*-$[Cu(phent)_2$(R-1,2-diphenea)(S-1,2-diphenea)]·$2CHCl_3$ (**5**) and *meso trans*-$[Cu(succim)_2$(R-1,2-diphenea)(S-1,2-diphenea)] (**6**) (phent = 5,5-diphenylhydantoinate, succim = succinimidate, and 1,2-diphenea = 1,2-diphenylethylamine) were prepared and the crystal structures were determined. Crystal data for **5** are triclinic with space group $P\bar{1}$; a = 13.909(4), b = 17.370(5), c = 13.700(4) Å; α = 112.50(2), β = 104.67(3), γ = 89.08(3) °; V = 2946(1) $Å^3$; Z = 2. Crystal data for **6** are monoclinic with space group $P2_1/n$; a = 12.577(2), b = 8.962(4), c = 15.097(3) Å; β = 111.24(1) °; V = 1586.1(7) $Å^3$; Z = 2. Complex **5** affords a distorted square planar $[CuN_4]$ coordination geometry with imidate and amine *trans*-N-Cu-N bond angles are 156.6(2) and 161.4(2) °, respectively. While complex **6** affords a square planar $[CuN_4]$ coordination geometry with both *trans*-N-Cu-N bond angles are 180.0 ° because of crystallographic center of symmetry. Complexes **5** and **6** differ in degree of distortion of $[CuN_4]$ chromophores by changing imidate ligands, though both complexes have the same 1,2-diphenylethylamine ligands. Moreover, it should be noted that **6** was the first example of the square planar $[CuN_4]$ complexes with 1-phenyl substituted ethylamine derivatives. Discussion will be made to explain the reasons for distortion of square planar $[CuN_4]$ complexes based on steric effects. Structural features are compared among **5**, **6**, and previously reported distortered square planar *meso trans*-$[Cu(phent)_2$(R-phenea)(S-phenea)] (**1**) and *meso trans*-$[Cu(succim)_2$(R-phenea)(S-phenea)] (**7**) (phenea = 1-phenylethylamine) complexes with imidate and amine *trans*-N-Cu-N bond angles are 154.9(2) and 159.8(2) ° for **1**, whereas 153.0(1) and 149.1(1) ° for **7**, respectively. Tetrahedral distortion of $[CuN_4]$ chromophores mainly results from steric repulsion between monodentate ligands caused by*egde-to-face* arrangement of phenyl group on the 1-position of amine ligands. Additionally, it was also elucidated that difference in distortion of $[CuN_4]$ chromophores between **5** and **6** reflected on the difference in the conformation of 1,2-diphenylethylamine ligands related to the rotation of two phenyl groups. Therefore it can be concluded that the distortion of square planar $[CuN_4]$ chromophores in a series of *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes is caused by the steric effects of the monodenatate ligands.

3.1 Introduction.

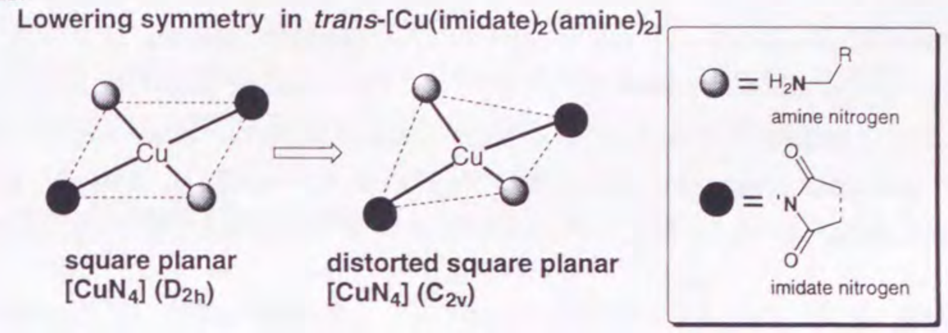
In general, imidates are capable to act as a monodentate ligand *via* deprotonated nitrogen atom giving rise to four-coordinated square planar [CuN_4] complexes in the solid state.[1,2] However, deviations from a square planar [CuN_4] coordination geometry to a tetrahedral one may emerge under particular circumstance.

For example, coordination geometries of M_2[Cu(succim)$_4$] complexes can be changed by the size of M^+ ions (counter alkali cations); small lithium[3] ion yields a distorted square planar [CuN_4] complexes, while large potassium,[3] rubidium,[4] and cesium[5] ions yield genuine square planar [CuN_4] ones. Additionally, it is stated that [$CuCl_4$]$^{2-}$ anions afford a square planar coordination geometry only with the aid of intermolecular hydrogen bonds between [$CuCl_4$]$^{2-}$ anions and co-crystallizing bulky organic cations, otherwise they afford a compressed tetrahedral geometry sterically preferred for monoatomic Cl^- ligand.

In contrast, circumstance is more complicated for *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes. These complexes also afford a square planar [CuN_4] coordination geometry in the solid state generally, though the combination of five-membered imidate and 1-phenylethylamine ligands yield distorted square planar [CuN_4] complexes, for example, *trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)] and *trans*-[Cu(hyd)$_2$(R-phenea)$_2$] (succim = succinimidate, hyd = hydantoinate, and phenea = 1-phenylethylamine). As shown in chapter 2, the structures of three chiral isomers of *trans*-[Cu(phent)$_2$(phenea)$_2$] (phent = 5,5-diphenylhydantoinate) were determined and the results indicated that the chirality of 1-phenylethylamine ligands could vary the degree of distortion of [CuN_4] coordination geometry.[8]

But dominating factors of the [CuN_4] coordination geometry of the complexes with monodentate imidate ligands is still ambigous and it is necessary that one should examine the reasons for distortion in detail. Then in order to investigate the steric effects caused by monodentate imidate and amine ligands, we prepared a pair of copper(II) complexes with 1,2-diphenylethylamine, which are distorted square planar *trans*-[Cu(phent)$_2$(1,2-diphenea)$_2$]·2$CHCl_3$ (**5**) and square planar *trans*-[Cu(succim)$_2$(1,2-diphenea)$_2$] (**6**). Although both complexes contain 1,2-diphenylethylamine ligands, they differ in coordination geometries depending on the imidate ligands. Complex **5** is the first square planar complex which has 1-phenyl substituted amine ligands. Therefore, these are suitable for examination of the distinguishing factors between a distorted square planar [CuN_4] and a genuine square planar [CuN_4] coordination geometry.

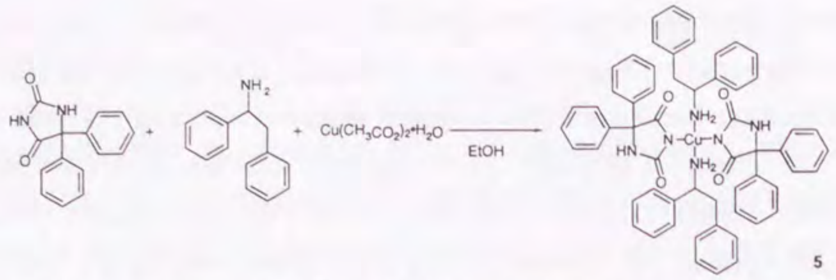
Chapter 3 describes preparations and structures of **5** and **6**. And their structural features are compared with including the analogous distorted square planar [CuN_4] copper(II) complexes *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) and *meso trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)] (**7**). And the reasons for lowering effective symmetry with respect to [CuN_4] chromophores from D_{2h} (square planar) to C_{2v} (distorted square planar) are discussed being focused on steric factors around 1-phenyl substituted amine ligands and intramolecular and intermolecular hydrogen bonds in the crystals.



3.2 Experimental Section.

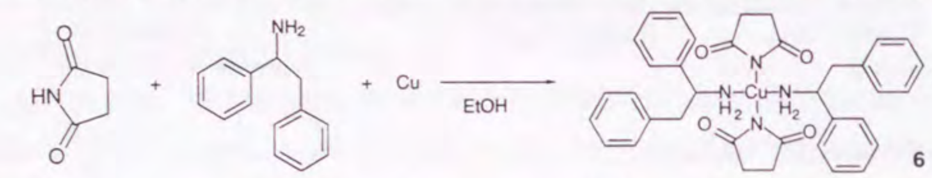
General Procedures. Racemic 1,2-diphenylethylamine were purchased from Aldrich Chemical Company, Inc. and the other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Methanol and chloroform were dried over molecular shieve 3A. Unless otherwise stated, commercial grade chemicals were used as received without further purification or resolution of optical isomers. Elemental analyses were carried out at the Liberal Arts and Sciences Organization, Osaka University.

Preparation of *meso* *trans*-[Cu(phent)$_2$(R-1,2-diphenea)(S-1,2-diphenea)]·2$CHCl_3$ (5). To a solution of copper(II) acetate monohydrate (0.499 g, 2.50 mmol) and 5,5-diphenylhydantoin (1.261 g, 5.00 mmol) in ethanol (50 cm^3), racemic 1,2-diphenylethylamine (0.986 g, 5.00 mmol) was added slowly and was stirred for 2h at 50 °C to give a deep blue solution. The resulting deep blue violet suspension was filtered and the precipitates were recrystallized from a chloroform-methanol (1:1, v/v) to obtain blue violet precipitate of *trans*-[Cu(phent)$_2$(R-1,2-diphenea)(S-1,2-diphenea)]·$CHCl_3$, for which formula the yield and the elemental analysis were calculated. Yield: 22.6 %. Found: C, 65.62; H, 4.95; N, 7.73%. Calcd for $C_{59}H_{53}N_6Cl_6CuO_4$: C, 65.62; H, 4.95; N, 7.78%. IR (Nujol, cm^{-1}) $\nu_{C=O}$ 1636. Single crystals suitable for X-ray crystallography (*meso trans*-[Cu(phent)$_2$(1,2-diphenea)(1,2-diphenea)]·2$CHCl_3$ (**5**)) were grown from chloroform-methanol-hexane (1:1:1, v/v/v). The blue violet prismatic crystal **1** immediately lost their clarity in an atmosphere.



5

Preparation of *meso trans*-[Cu(succim)$_2$(1,2-diphenea)(1,2-diphenea)] (6). To a suspension containing copper powder (0.318 g, 5.00 mmol) and succinimide (0.991 g, 10.0 mmol) in ethanol (50 cm^3), racemic 1,2-diphenylethylamine (1.973 g, 10.0 mmol) was added and was stirred for 2h at 50 °C. The resulting deep blue solution was filtered off and prismatic reddish violet crystals obtained from the filtrate were dried in a silica gel desiccator overnight. Yield: 75.8 %. Found: C, 66.05; H, 5.94; N, 8.57%. Calcd for $C_{36}H_{38}N_4CuO_4$: C, 66.09; H, 5.85; N, 8.56%. IR (Nujol, cm^{-1}) $\nu_{C=O}$ 1629.



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Measurements. Infrared spectra were recorded on a Perkin-Elmer 983G Infrared Spectrometer in the region of 4000-180 cm^{-1} on Nujol mulls with CsI plates.

Crystal Structure Determination. The intensy data were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with nickel-filtered CuKα radiation (λ = 1.5418 Å). Calculations were carried out on an SGI O2 workstation with a teXsan[9] software package. Empirical absorption corrections based on Ψ scans were applied for **5** and **6** (transmission factors 1.000-0.649 and 1.000-0.726, respectively). The crystal of **1** were coated with epoxy. Decays in the intensities of three standard reflections were observed throughout the data collection for **5** and **6** (maximum 9.4 % and 20.0 % for **5** and **6**, respectively), and decay correction was applied appropriately. Despite attempts of the measurements with an imaging plate at low temperature, the quality of data was not improved. The structures were solved using SIR 92[10] and were expanded by Fourier techniques. The structures of **5** and **6** were refined on F by full-matrix least-squares methods anisotropically for non-hydrogen atoms N, O, Cu, and C except for C(18) and C(60) of **5**. The atom Cl(3), Cl(4), Cl(5), and Cl(7) are disordered exhibiting 0.5 occupancy factors. All the atoms of the two chloroform molecules (Cl(1) through Cl(8), C(18), and C(60)) were fixed after several cycles of the least-squares refinement. The hydrogen atoms H(1), H(2), H(4),and H(5) of **5** and H(1) and H(2) of **6** were located from difference Fourier syntheses and the residual ones were located at geometrically calculated positions. The hydrogen atoms of two chloroform molecules could not be added. All the other hydrogen atoms were refined isotropically.

Theoretical Calculations. The semiempirical calculations were carried out with the MOPAC 6.0[11] program using the PM3[12] Hamiltonian. The molecular modeling software package CAChe served as a facility to built up and edit starting geometries and visualize the results. The EF (eigenvalue follower) optimization method was used to obtain the minimum structures. Optimized structure of free R-1,2-diphenylethylamine and ligand based on the X-ray structure of **6** was used as a starting geometry. Using the predetermined geometries, the barrier to rotation about C(1)*-C(2) single bond was calculated by a stepwise variation of the torsion angles C(3)-C(1)*-C(2)-C(9) in 10 ° increments for **6**. At each step, the remaining degrees of freedom were held constant to maintain the starting structure. No such calculation is possible for copper containing fragments since parameters for copper(II) are lacking.

3.3 Results and Discussion.

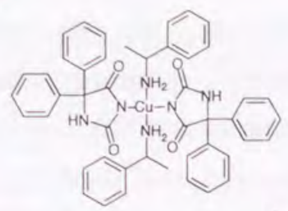
Description of Structures. The crystallographic data for **5** and **6** are summarized in Table 3-1. Selected bond distances and angles for **5**, **6**, **1**, and **7** are listed in Table 3-2. Molecular structures of **5** and **6** are shown in Figure 3-1 and 3-2, respectively.

Complex **5** affords a distorted square planar [CuN$_4$] coordination geometry, whereas **6** affords a square planar [CuN$_4$] coordination geometry. The copper atom of **6** is located on the crystallographic center of symmetry. Generally, *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes have a square planar [CuN$_4$] coordination geometry, however, a distorted square planar [CuN$_4$] coordination geometry has been limited only the complexes with 1-phenylethylamine and five-membered imidate ligands complexes.[6] As for the present complexes **5** and **6**, the variation of distortion of [CuN$_4$] coordination geometry depends on different imidate ligands, especially **6** is the first example that has a square planar [CuN$_4$] coordination geometry with 1-phenyl substituted ethylamine derivative ligands.

The Cu-N(imidate) bond distances are 1.975(5) and 1.986(5) Å for **5** and 1.961(3) Å for **6**. By contrast, the Cu-N(amine) bond distances fall in the range form 2.029(5) to 2.032(4) Å, which are slightly longer than that of imidates regardless of distortion. According to the CSD,[13] the corresponding average bond distances are 1.971 and 2.031 Å for imidate and amine, respectively.

The imidate and amine *trans*-N-Cu-N bond angles are 156.6(2) and 161.4(2) ° and 180.0 and 180.0 ° for **5** and **6**, respectively. The corresponding imidate and amine *trans*-N-Cu-N bond angles are 153.0(1) and 149.1(1) ° for **7**, 171.8(2) and 169.7(2) ° for *trans*-[Cu(hyd)$_2$(R-phenea)$_2$],[7] and 154.9(2) and 159.8(2) ° for **1**, respectively. Therefore the order of the tetrahedral distortion of [CuN$_4$] environment is as follows: **7** > **5** > **1** >

trans-[Cu(hyd)$_2$(R-phenea)$_2$] >> **6** (square planar). Thus complex **5** has intermediate degree of distortion.



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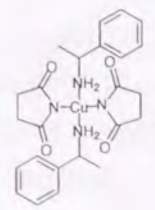

7

Intramolecular hydrogen bonds occur between amine hydrogens of 1,2-diphenylethylamine and carbonyl oxygens of imidate, which are also found generally in square planar *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes. Two of the four possible N-H···O=C intramolecular hydrogen bonding sites in diagonal positions are formed for **5** and **6**. The distance of N(1)-H(1)···O(1) is 2.892(9)Å with N-H···O angles 131.0 ° and N(4)-H(17)···O(4) is 2.916(6) Å with 122.2° for **5**, and N(1)-H(2)···O(1*) 2.966(4) Å with 133.0 ° for **6**. Possibility of hydrogen bonding was judged by the statistical criterion proposed by Taylor and Kennard.[14]

The adjacent molecules in **5** are linked through double anti-parallel N-H···O=C intermolecular hydrogen bonds between amine hydrogens and carbonyl oxygens of 5,5-diphenylhydantoinate ligands to give rise to one dimensional chains in the crystals. The N···O non-contact distances are 2.855 and 2.848 Å between the molecules expanded by symmetry operations (1-x, -y, 1-z) and (1-x, 1-y, 1-z), respectively. As for **6**, no intermolecular hydrogen bonds are formed between succinimidate ligands.

Steric Factors for Distortion. In order to investigate steric factors for distortion of [CuN$_4$] chromophores in detail, the molecular structures are compared with known distorted square planar complexes *meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) and *meso trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)] (**7**) shown in Figure 3-3 and 3-4. All these four complexes are *meso* diastereomers with respect to chirality of amine ligands, in which copper atoms are coordinated by one R- and one S-amine ligands.

Here discussion on steric factors for distortion will be made. At first, we deal with intramolecular hydrogen bonds. All *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes possess four pairs of proton-donor and acceptor sites being ready for N-H···O=C intramolecular hydrogen bonds. These interactions contribute to be brought close together for imidate and amine ligands in *cis*-position, because they may affect tetrahedral distortion of a [CuN$_4$] chromophore. Although **5**, **1**, and **7** afford a distorted square planar [CuN$_4$] geometry, they show different intramolecular hydrogen bonding fashions. Complexes **5** and **1** have two sets of intramolecular hydrogen bonds, whereas **7** has only one. On the contrary, both distorted square planar **5** and square planar **6** have the same pattern in which two of the four bonds are formed in a diagonal arrangement. Thus, intramolecular hydrogen bonds are irrelevant to the distortion, al least they are not determining factor for a distorted square planar [CuN$_4$] coordination geometry.

Secondly, we take up intermolecular hydrogen bonds. Two types of intermolecular hydrogen bonding fashions are depicted schematically in Figure 3-5. The complementary double anti-parallel hydrogen bonding fashion is called a '*lactam-lactam*' type[15] which are found in 5,5-diphenylhydantoinate complexes commonly. Moreover, this hydrogen bonding fashion have also been observed in other complexes with hydantoinate derivative ligands even if the complexes with a five-coordinated square pyramidal [CuN$_4$O] coordination geometry.[16] Thus, intermolecular hydrogen bonds of the *lactam-lactam* type are irrelevant to the coordination geometry, rather than common factor for molecular arrangement in the crystals.

An interesting feature of the double linear N-H···O=C intermolecular hydrogen bonds are observed for **7**, by which *coupled* structures are formed in the crystal exceptionally. The *column* type intermolecular hydrogen bonds may be attributed to the largest distortion of **7**, because they are formed in appropriate positions for stabilization of a distorted square planar [CuN$_4$] chromophores of two neighboring two complex molecules.

Finally, we shall examine the arrangement of 1-position phenyl group of amines and five-membered ring moiety of imidate and their steric interaction. Three ring moieties, *e.g.* 1-position phenyl group, five-membered ring moiety of succinimidate, and 2-position phenyl group, are stacked in parallel arrangement for **6**, as space-filling model indicated (Figure 3-2). In both sides of **6**, ring moieties are in *face-to-face* arrangement, which is favorable for a square planar geometry of **6**.

As for **5**, which has also 1,2-diphenylethylamine, however, steric hindrance due to two phenyl groups of 5,5-diphenylhydantoinate prevents both two 1,2-diphenylethylamine ligands from taking *face-to-face* arrangement like **6**. And then 1-position phenyl group and five-membered imidate ring are arranged in *edge-to-face* fashion. In this way, steric repulsion due to *edge-to-face* fashion causes distortion of [CuN$_4$] coordination environment. For this reason, **5** affords a square planar [CuN$_4$] coordination geometry. Therefore the difference in geometry of 1,2-diphenylethylamine in **5** and **6** is attributed to the arrangements (*face-to-face* or *edge-to-face*) of substituted groups of imidate ligands, and the resulting crowded coordination sphere results from two different conformations of 1,2-diphenylethylamine ligands (see next section).

On the other hand, as for 1-phenylethylamine complexes, both **1** and **7** have a distorted square planar [CuN$_4$] geometry. Both sides of ligands of **1** take *edge-to-face* arrangement owing to steric hindrance of 5,5-diphenylhydantoinate like **5**, thus **1** affords a distorted square planar [CuN$_4$] geometry. In the case of complex **7** with succinimidate ligands, a pair of ring moieties are stacked in *face-to-face* arrangement similar to **6**, whereas another pair is in *edge-to-face* arrangement. The *edge-to-face* arrangement results in the distortion of [CuN$_4$] coordination sphere. Unlike to 1,2-diphenylethylamine, 1-

phenylethylamine can not take several sterically favored conformations with respect to rotation of two phenyl groups because 1-phenylethylamine has only one phenyl group. Therefore, both **1** and **7** affords a distorted square planar [CuN_4] geometry solely.

Conformation of 1,2-diphenylethylamine. As mentioned above, it can be expected that steric features of 1,2-diphenylethylamine ligand may be responsible for possibility of forming both distorted square planar (**5**) and square planar (**6**) [CuN_4] complexes. To rationalize the steric features of 1,2-diphenylethylamine ligand, conformational energies (heat of formation) of a free ligand were calculated as a function of C(3)-C(1)*-C-(2)-C(9) torsion angle (Figure 3-6) and the energies relative to the global minimum value are plotted in Figure 3-7.

For R-1,2-diphenylethylamine (Figure 3-6), global minimum of the potential energy profile appears at around -160 °, which is corresponding to *trans*-position with respect to the two phenyl groups giving the lowest energy. The second stable conformation is found at -70 ° and the third at +80 °. The largest peak and the second peak appear at around 0 ° and 120 °, respectively, in which 1-position phenyl group comes close to 2-position phenyl group and amine group, respectively. Inverted profile with respect to the sign of the torsion angle would be expected for S-1,2-diphenylethylamine.

The experimental values of torsion angles are as follows: C(21)-C(19)*-C(20)-C(27) = -175 ° (R-configuration) and C(3)-C(1)*-C(2)-C(9) = +67 ° (S) for **5** and C(3)-C(1)*-C(2)-C(9) = -171 ° (R) and C(3*)-C(1*)*-C(2*)-C(9*) = +171 ° for **6**. The profile shows that both two 1,2-diphenylethylamine ligands preserve their most stable conformation for **6**, which is corresponding to the two *face-to-face* arrangement. On the other hand, as for **5**, one of the two 1,2-diphenylethylamine ligands is in the most stable conformation corresponding to the *face-to-face* arrangement, whereas the other is in the second stable conformation corresponding to *edge-to-face* arrangement. Two conformations found in **5** result from more crowded distorted square planar [CuN_4] coordination environment. In this way, the possibility of forming both distorted square planar and square planar [CuN_4] complexes is also elucidated by the favorable conformations of 1,2-diphenylethylamine ligand.

3.4 Conclusion.

Meso trans-[Cu(phent)$_2$(R-1,2-diphenea)(S-1,2-diphenea)]·2$CHCl_3$ (**5**) and *meso trans*-[Cu(succim)$_2$(R-1,2-diphenea)(S-1,2-diphenea)] (**6**) are prepared and the crystal structures have been determined by X-ray crystallography. Complex **5** affords a distorted square planar geometry, whereas **6** affords a square planar geometry. The latter is the first example of square planar complexes regardless of the amine ligands with the phenyl

group on the 1-position. Steric factors for distortion of [CuN_4] chromophores are deduced by comparing with **5**, **6**, and known distorted square planar complexes with 1-phenylethylamine ligands (*meso trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) and *meso trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)] (**7**)) and calculations with regard to the conformation of 1,2-diphenylethylamine ligand. It can be concluded that the main factor for the distortion of the [CuN_4] chromophores in **5**, **1**, and **7** is steric hindrance arising from characteristic *edge-to-face* arrangement of imidate ring moiety and phenyl group of amine ligands. And differences in distortion of **5** and **6** may correspond to the conformation of 1,2-diphenylethylamine. Thus it is indicated that the tetrahedral distortion from square planar of [CuN_4] coordination geometry can be induced by appropriate steric factors of monodentate imidate and amine ligands.

Table 3-1. Crystallographic data for **5** and **6**.

	5	**6**
Formula	$C_{60}H_{54}N_6Cl_6CuO_4$	$C_{36}H_{38}N_4CuO_4$
Molecular weight	1199.39	654.27
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$(#2)	$P2_1/n$ (#14)
a / Å	13.909(4)	12.577(2)
b / Å	17.370(5)	8.962(4)
c / Å	13.700(4)	15.097(3)
α / °	112.50(2)	
β / °	104.67(3)	111.24(1)
γ / °	89.08(3)	
V / Å^3	2946(1)	1586.1(7)
Z	2	2
D_c	1.352	1.370
F(000)	1238	686
μ(Cu Kα)/ mm^{-1}	34.35	13.42
$2\theta_{max}$ / °	120.0	120.0
Crystal dimensions / mm	0.20 x 0.20 x 0.10	0.20 x 0.20 x 0.10
Temperature / K	300	298
No. of measured reflections	8224	2117
No. of unique reflections	7880	2010
No. of reflections used in refinement	5464 [$I>3.0\sigma$ (I)]	1444 [$I>2.0\sigma$ (I)]
No. of parameters	627	282
g. o. f.	3.44	1.54
R [a]	0.080	0.038
R_w [b]	0.098	0.047

[a] $R=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b] $R_w=(\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$.

Weighting scheme: $w = 1/(\sigma^2(F_o)+0.000144F_o^2)$ for **5** and $w = 1/(\sigma^2(F_o)+0.0004F_o^2)$ for **6**.

Table 3-2. Selected bond distances (Å) and angles (°) for **5**, **6**, **1**, and **7**.

	5	**6**	**1** [b]	**7** [c]
Bond Distances				
Cu(1)-N(2) (imidate)	1.986(5)	1.961(3)	1.988(3)	1.984(3)
Cu(1)-N(5) (imidate)	1.975(5)		1.997(3)	1.970(3)
Cu(1)-N(1) (amine)	2.029(5)	2.032(4)	2.012(3)	1.995(3)
Cu(1)-N(4) (amine)	2.029(5)		2.019(3)	2.021(3)
Bond Angles				
N(imidate)-Cu-N(amine)				
N(1)-Cu(1)-N(2)	90.4(2)	88.5(1)	91.9(2)	94.3(1)
N(1)-Cu(1)-N(2*) [a]		91.5(1)		
N(1)-Cu(1)-N(5)	93.1(2)		92.6(2)	92.7(1)
N(2)-Cu(1)-N(4)	91.2(2)		91.8(2)	94.3(1)
N(4)-Cu(1)-N(5)	92.7(2)		92.4(2)	92.9(1)
N(imidate)-Cu-N(imidate)				
N(2)-Cu(1)-N(5)	156.6(2)		154.9(2)	153.0(1)
N(2)-Cu(1)-N(2*) [a]		180.0		
N(amine)-Cu-N(amine)				
N(1)-Cu(1)-N(4)	161.4(2)		159.8(2)	149.1(1)
N(1)-Cu(1)-N(1*) [a]		180.0		

[a] Atoms labeled with * are expanded by symmetry operation (-x, -y, -z).
[b] ref. 8
[c] ref. 7

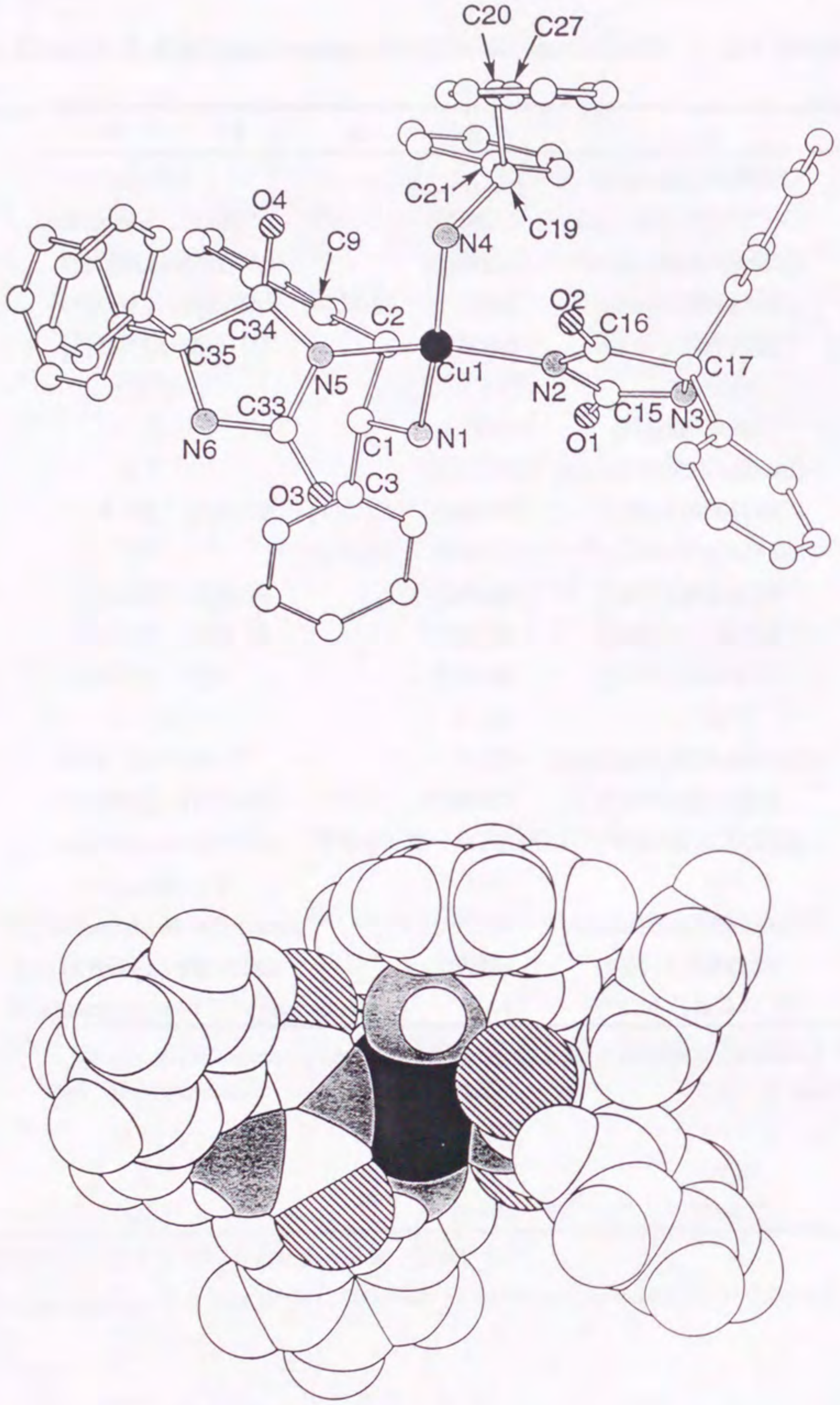

Figure 3-1. Molecular structures of *trans*-[Cu(phent)$_2$(1,2-diphenea)$_2$]·2CHCl$_3$ (**5**) as a ball-and-stick (above) and a space-filling (below) representation with the atom numbering scheme. Hydrogen atoms and two chloroform molecules of the crystalline solvent are omitted for clarity.

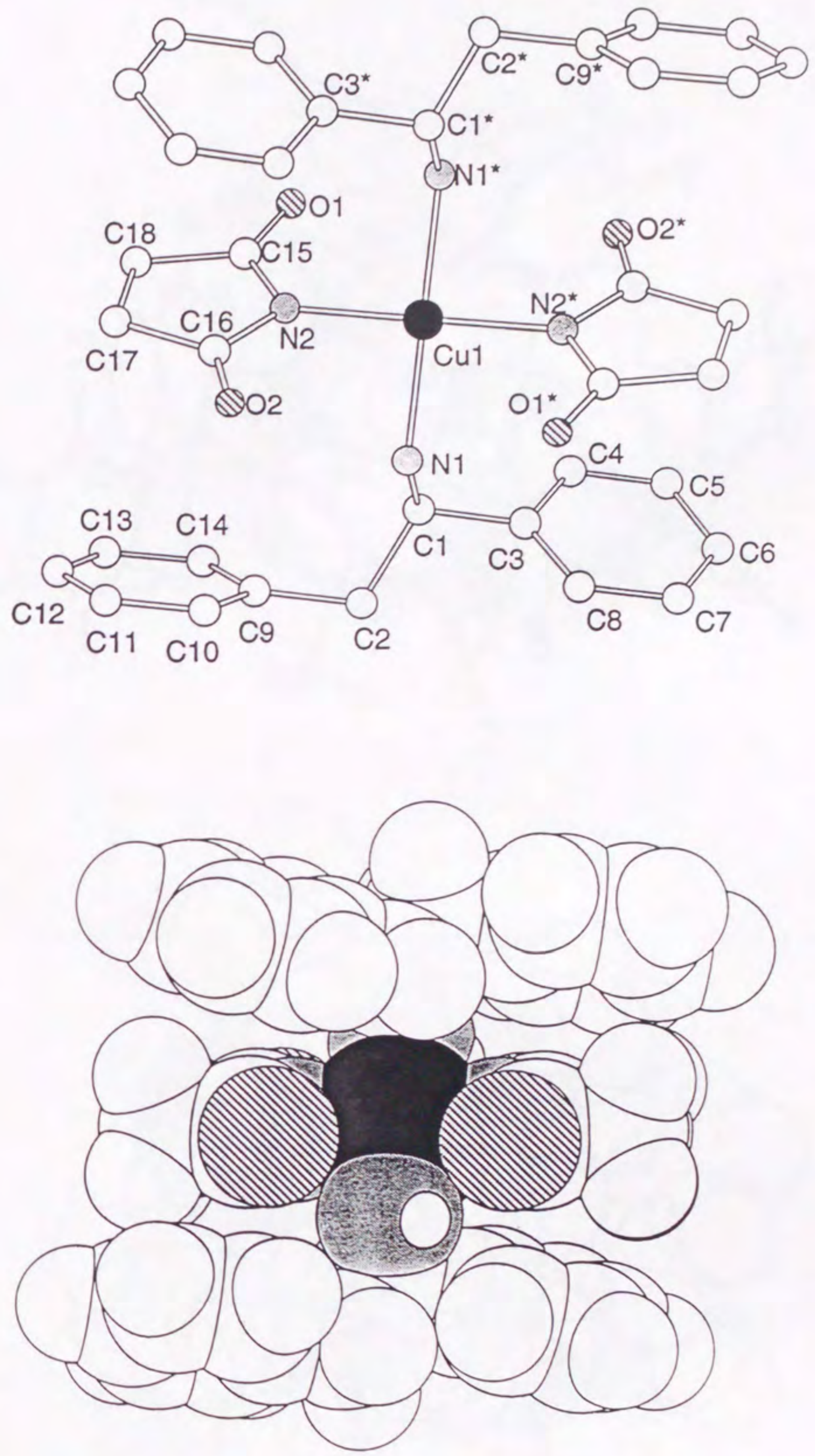

Figure 3-2. Molecular structures of *trans*-[Cu(succim)$_2$(1,2-diphenea)$_2$] (**6**) as a ball-and-stick (above) and a space-filling (below) representation with the atom numbering scheme. Hydrogen atoms are omitted for clarity.

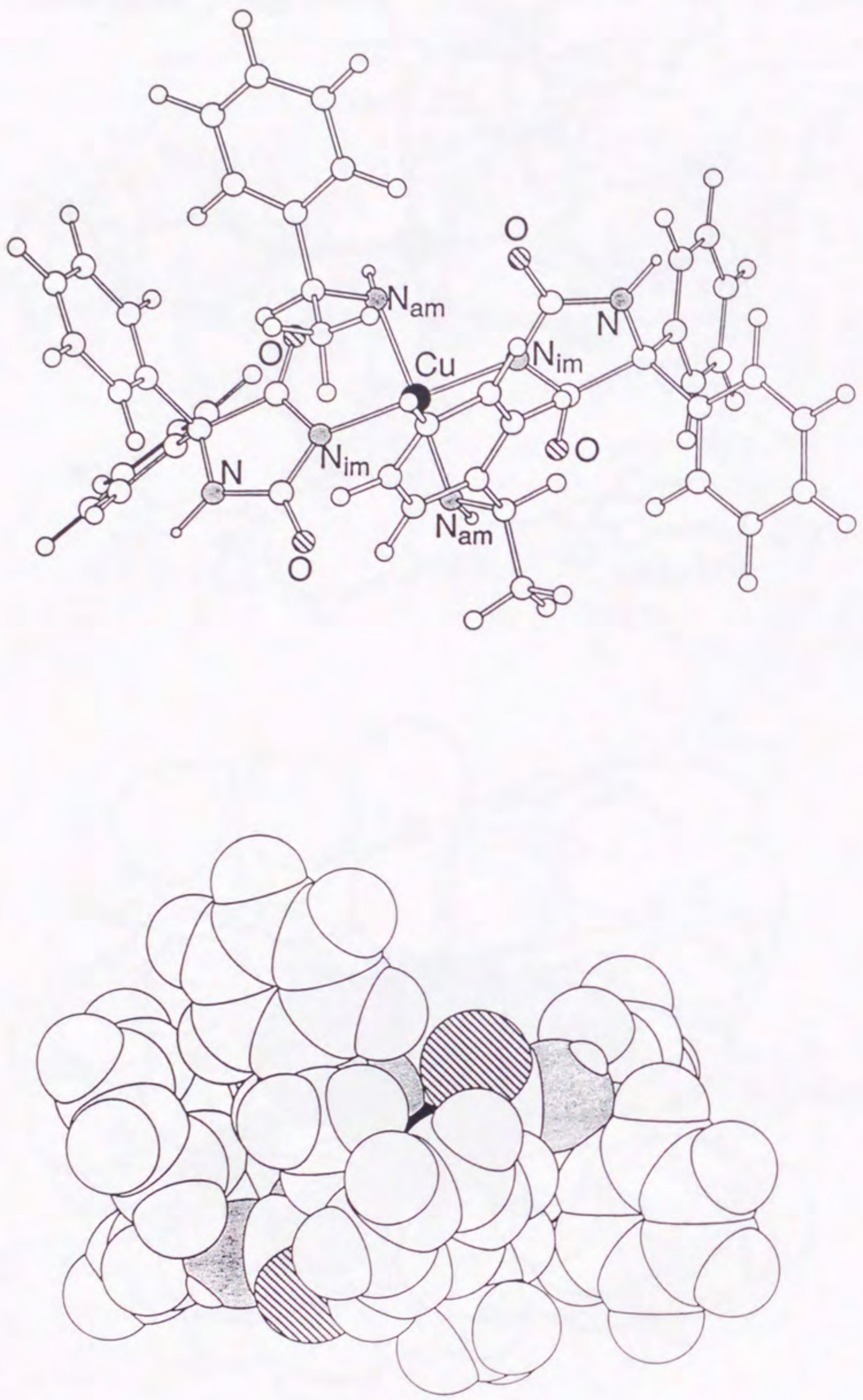

Figure 3-3. Molecular structures of *trans*-[Cu(phent)$_2$(phenea)$_2$] (**1**) as a ball-and-stick (above) and a space-filling (below) representation.

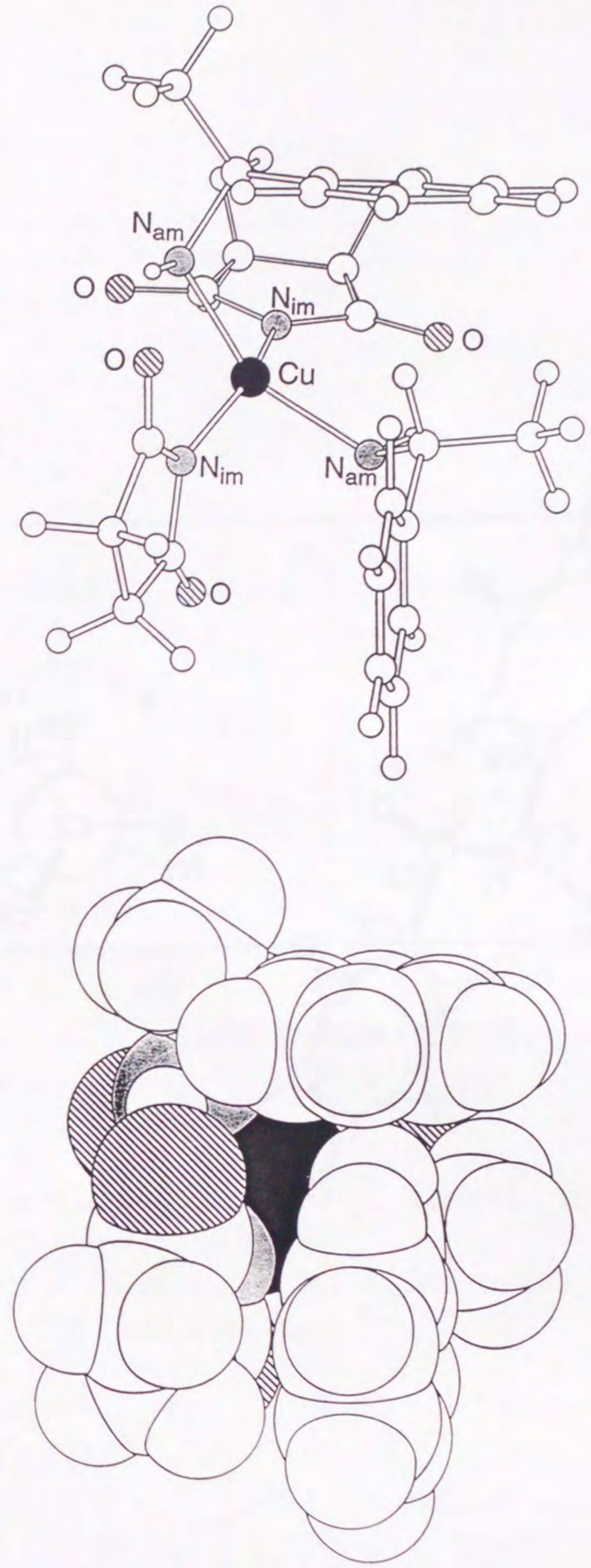

Figure 3-4. Molecular structures of *trans*-[Cu(succim)$_2$(phenea)$_2$] (**7**) as a ball-and-stick (above) and a space-filling (below) representation.

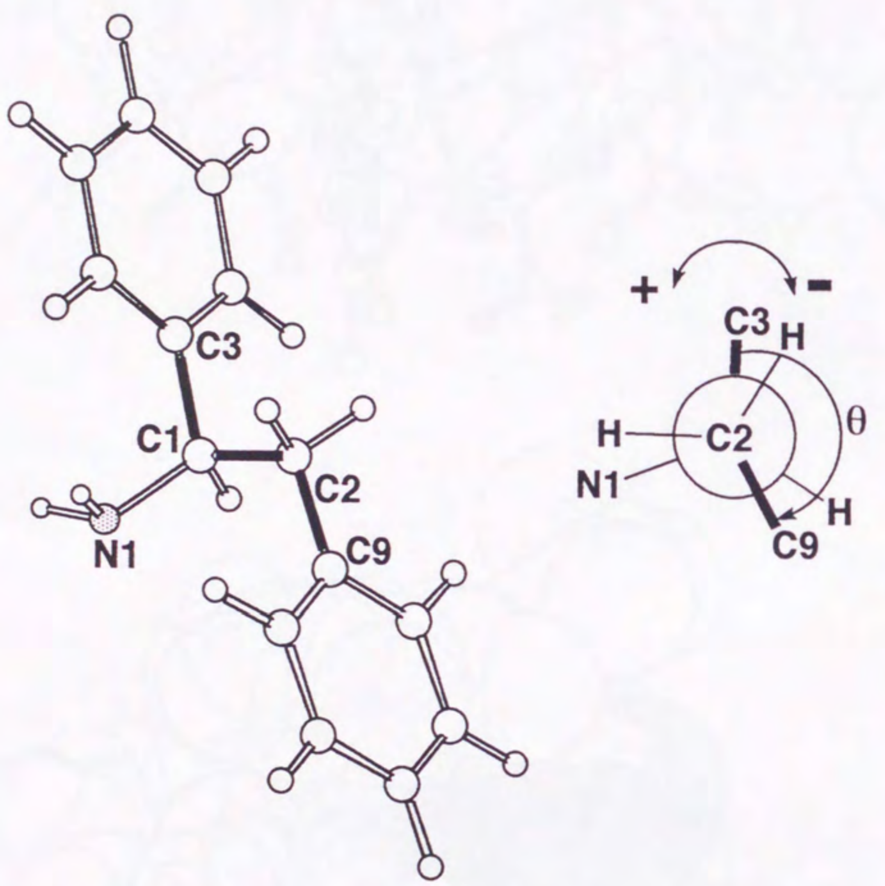

Figure 3-5. Definition of the C(3)-C(1)*-C(2)-C(9) torsion angle (θ) of R-1,2-diphenylethylamine optimized with PM3 calculation.

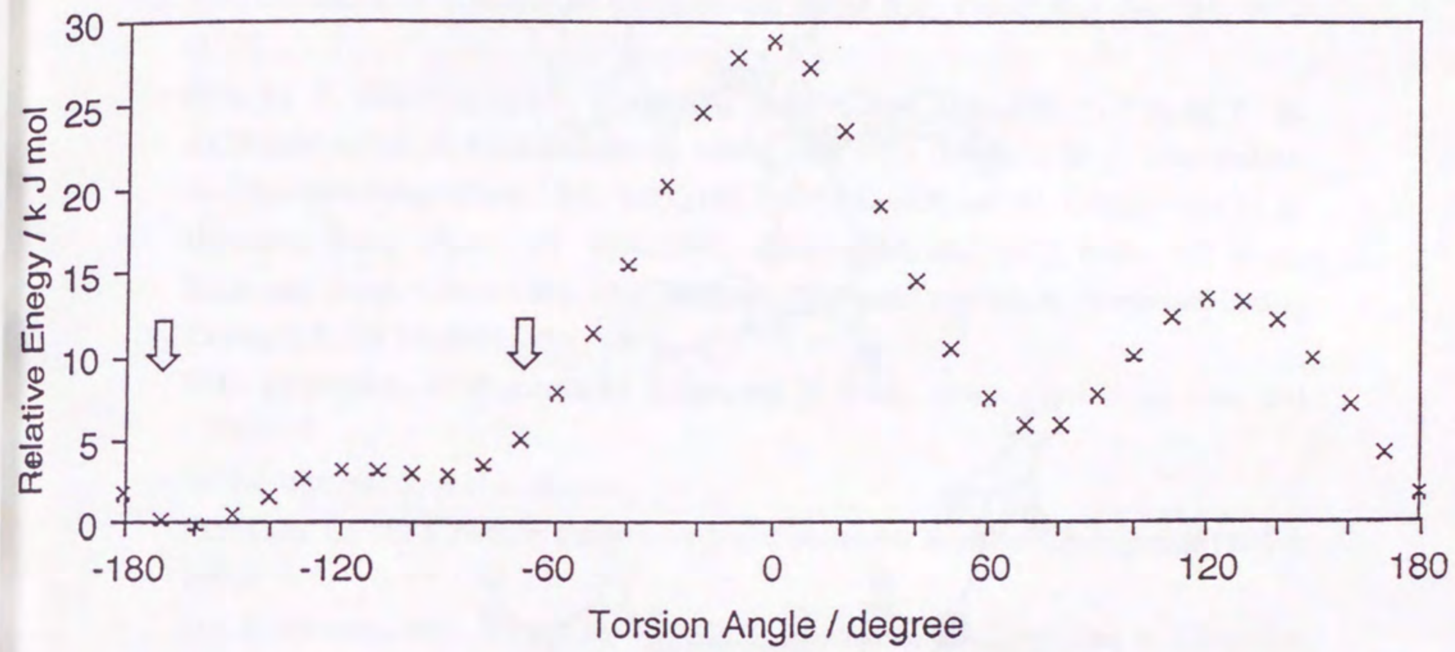

Figure 3-6. Potential energy (in $kJmol^{-1}$ relative to the global minimum) of optimized R-1,2-diphenylehylamine as a function of the C(3)-C(1)*-C(2)-C(9) torsion angles (θ in Figure 3-5).

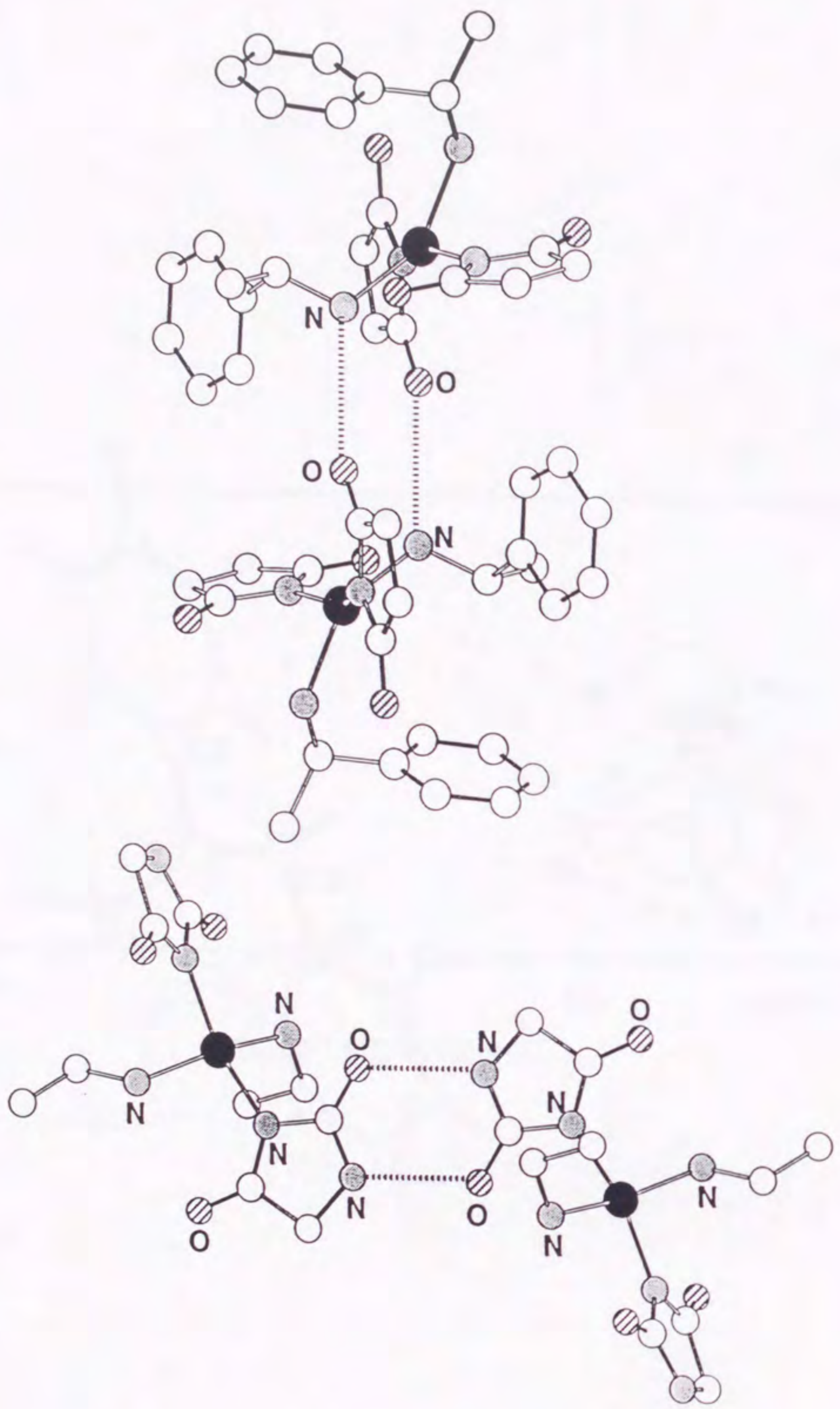

Figure 3-7. Schematic representation of N-H···O=C intermolecular hydrogen bonds. (top) *Coupled* structured hydrogen bonds formed between 1-phenylethylamine and succinimidate ligands characteristic for *trans*-[Cu(succim)$_2$(phenea)$_2$] (**7**). (bottom) Anti-parallel complementary double hydrogen bonds between hydantoin derivative ligands so called '*lactam-lactam*' type of *trans*-[Cu(phent)$_2$(phenea)$_2$] (**1**). Phenyl groups are omitted for clarity.

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Chapter 4.

Imidate and Amine Ligands Arrangement and Axial Coordination Ability.

Abstract.

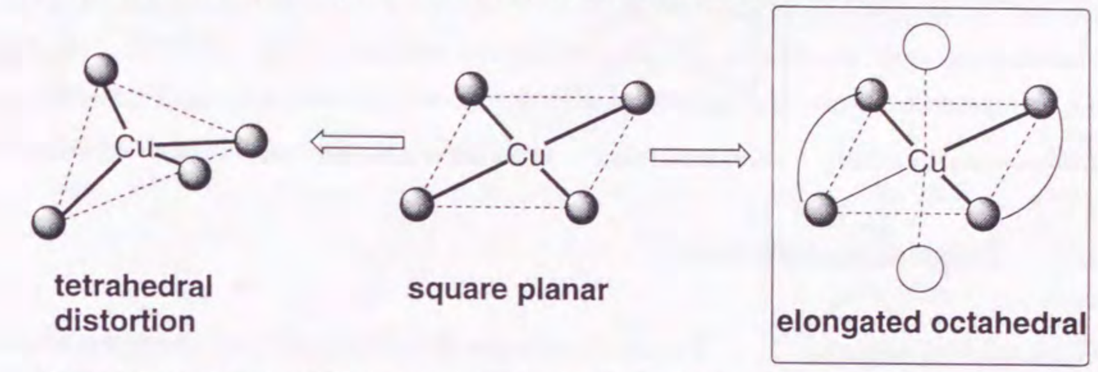
The crystal structure of $[Cu(en)_2](SCN)_2$ (**8**) and $[Cu(succim)_2(N\text{-}Eten)(H_2O)_2]$ (**9**) has been determined (en = ethylenediamine, succim = succinimidate and N-Eten = N-ethylethylenediamine). Crystal data for **8** are triclinic with space group $P\bar{1}$; a = 7.285(2), b = 7.627(1), c = 6.568(1) Å; α = 107.73(1), β = 113.75(2), γ = 77.48(2) °; V = 316.3(1) Å^3; Z = 1. Crystal data for **9** are triclinic with space group $P\bar{1}$; a = 7.303(2), b = 15.625(2), c = 7.2115(7) Å; α = 91.211(8), β = 90.54(1), γ = 83.59(1) °; V = 817.5(2) Å^3; Z = 2. Complex **8** affords a square planar $[CuN_4]$ coordination which consists of four amine nitrogen atoms with Cu-N = 2.010(5) and 2.003(5) Å. Complex **8** also has two considerably long Cu···S contacts with 3.173(2) Å on both axial sites but they can not be classified into so called semi-coordination. Complex **9** affords an elongated distorted octahedral $[CuN_4O_2]$ coordination geometry with two long axial Cu-O bond lengths (2.725(4) and 2.672(4) Å). The $[CuN_4O_2]$ coordination structure of **9** consists of two succinimidate nitrogens in *cis*-position, two amine nitrogens in *cis*-position, and two water oxygen atoms in *trans*-axial sites, respectively. In order to examine the relationship between the axial coordination ability and the arrangement of imidate and amine ligands, the structures of several related complexes are compared. Apparently, as the number of imidate ligand decrease, a complex is subjected to accept the axial coordination. It can be estimated that the stronger donor character of electron rich imidate ligands than amine ligands results in protection of the axial coordination of the central copper atom. The formation of **9** suggests that the donation effect of two imidate ligands is more stronger in *trans*-position than in *cis*-position.

4.1 Introduction.

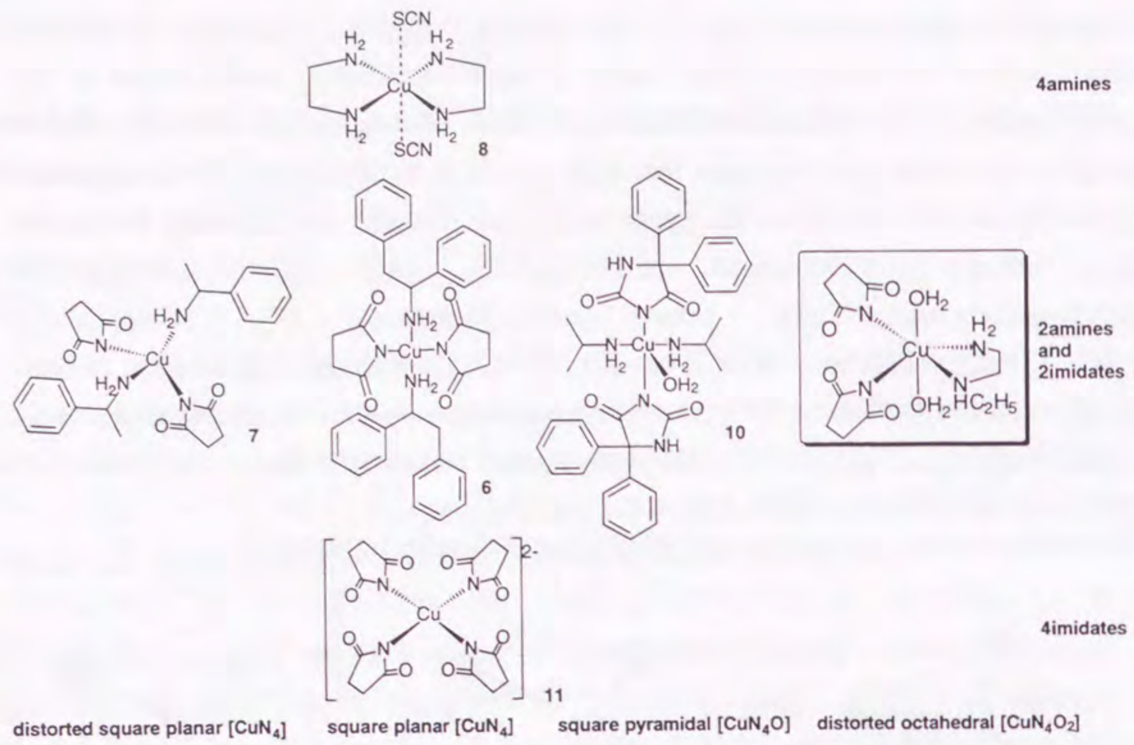
Deprotonated cyclic imide (abbreviated as 'imidate') acts as a monodenate ligand through its nitrogen atom and gives rise to square planar $[CuN_4]$ complexes such as $M_2[Cu(imidate)_4]$[1] (M^+ denotes alkali ions) and *trans*-$[Cu(imidate)_2(amine)_2]$[2] complexes in the solid states. Besides these square planar $[CuN_4]$ones, several distorted square planar $[CuN_4]$ complexes such as *trans*-$[Cu(succim)_2(phenea)_2]$(**7**)[3] and *trans*-$[Cu(phent)_2(phenea)_2]$ (**1**, **2**, **3**, and **4**)[4] have been known. Moreover, five-coordinated square pyramidal $[CuN_4O]$ complexes such as $[Cu(phent)_2(i\text{-}PrNH_2)_2(H_2O)]\cdot 2CHCl_3$

(**10**) and $[Cu(phent)_2(EtNH_2)_2(H_2O)]$[5] have been also reported. Therefore, it has been desired that the examination of the variety of these coordination modes related to the imidate ligands in view of steric and electronic factors of these ligands. Thus, in order to elucidate the relationship between the axial coordination ability and the arrangement (numbers and their positions) of imidate and amine ligands, the following complexes were selected and examined: $[Cu(en)_2](SCN)_2$ (**8**),[6] *trans*-$[Cu(succim)_2(1,2\text{-}diphenylethylamine)_2]$ (**6**),[7] *trans*-$[Cu(succim)_2(phenea)_2]$ (**7**),[3] $[Cu(phent)_2(i\text{-}PrNH_2)_2(H_2O)]\cdot 2CHCl_3$ (**10**),[5] $[Cu(succim)_2(N\text{-}Eten)(H_2O)_2]$ (**9**), and $Rb_2[Cu(succim)_4]\cdot 2H_2O$ (**11**)[8] (en = ethylenediamine, succim = succinimidate, 1,2-diphenylethylamine, phenea = 1-phenylethylamine, phent = 5,5-diphenylethylamine, *i*-$PrNH_2$ = 2-propylamine, and N-Eten = N-ethylethylamine).

Deviation from a square planar $[CuN_4]$ coordination geometry



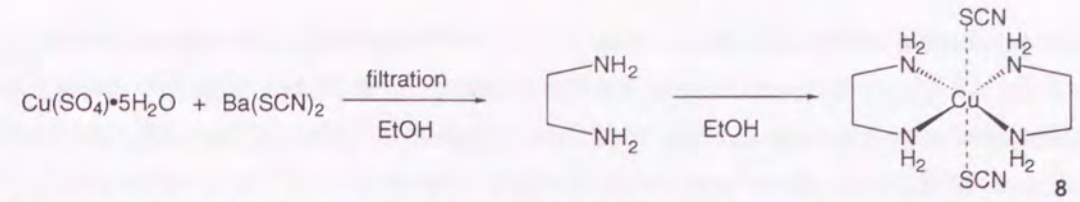
In these complexes, $[Cu(succim)_2(N\text{-}Eten)(H_2O)_2]$ (**9**) employing a bidentate amine ligand has been newly reported, in addition, the structure of $[Cu(en)_2](SCN)_2$ (**8**) has been redetermined. Then, the reasons for stabilization of low coordination numbers are discussed above mentioned imidate complexes.



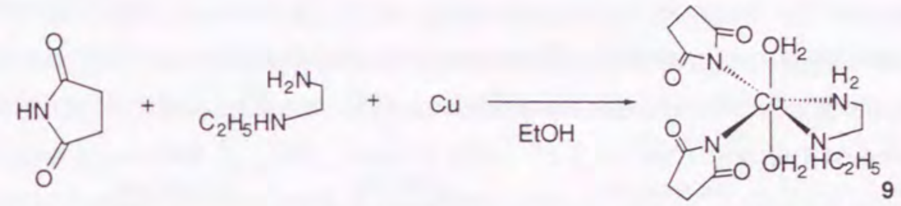
4.2 Experimental Section.

General Procedures. Barium thiocyanate dihydrate and N-ethylethylenediamine were purchased from Kishida Chemical Co. Ltd. and Tokyo Kasei Kogyo, Co. Ltd., respectively. The other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Methanol was dried over molecular shieve 3A. Unless otherwise stated, commercial grade chemicals were used as received without further purification. Elemental analyses were carried out at the Liberal Arts and Sciences Organization, Osaka University.

Preparation of [Cu(en)$_2$](SCN)$_2$ (8). Blue plate-like crystals of **8** were prepared according to the literature[6] with slight improvement. To a solution of copper(II) sulfate pentahydrate (1.248 g, 5.00 mmol) in ethanol (20 cm^3) at 30 °C were added ethylenediamine (0.601 g, 10.0 mmol) and barium thiocyanate dihydtate (1.448 g, 5.00 mmol), and the blue violet suspension containing white precipitate was stirred for 5 min at 30 °C. After filtration, the blue filtrate was concentrated to dryness in a silica-gel desiccator *in vacuo*. Crystals suitable for X-ray crystallography were obtained from methanol solution kept stand in a calcium chloride desiccator at room temperature for several days. Found: C, 23.74; H, 5.17; N, 27.91%. Calcd for $C_6H_{16}N_6CuS_2$: C, 24.03; H, 5.38; N, 28.02%.



Preparation of [Cu(succim)$_2$(N-Eten)(H$_2$O)$_2$] (9). To a suspension of copper powder (0.635 g, 10.0 mmol) in ethanol (20 cm^3) at 50 °C were added N-ethylethylenediamine (0.882 g, 10.0 mmol) and succinimide (1.982 g, 20.0 mmol). The reaction was continued for 7h at 50 °C. As the reaction proceeds, the suspension changed into a deep blue solution. Blue plate-like crystals sufficiently suitable for X-ray crystallography deposited from the solution. The resulting crystals were washed with ethanol and petroleum ether and were dried in a silica gel desiccator overnight. Yield: 7.58%. Found: C, 27.34; H, 6.30; N, 14.74%. Calcd for $C_{12}H_{24}N_4CuO_6$: C, 27.55; H, 6.00; N, 14.59%. The condition of preparation to coordinate two monodenate succinimidate ligands is quite delicate, unless [Cu(N-Eten)$_2$]$^{2+}$ easy to yield bacause of the chelate effect.



Electronic Spectra. The diffuse reflectance spectra in the solid state were measured at room temperature on a Hitachi U-3400 UV/VIS/NIR spectrophotometer equipped with an integrating sphere.

Crystal Structure Determination. The X-ray diffraction intensity data were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with nickel-filtered CuKα radiation (λ = 1.5418 Å) for **8** and **9**. Calculations were carried out on an SGI O2 workstation with a teXsan[9] software package for each complex. Empirical absorption corrections based on Ψ scans were applied for **8** and **9** (transmission factors 0.4715-0.9761 and 0.3598-1.0000 for **8** and **9**, respectively). No significant decays in the intensities of three standard reflections were observed throughout the data collection (decrease in intensity within 0.66% and 0.52% for **8** and **9**, respectively). The structures were solved by direct methods using an SIR92[10] program and were expanded by Fourier techniques. The structures of **8** and **9** were refined on F by full-matrix least-squares methods anisotropically for all the non-hydrogen atoms. All the hydrogen atoms were located at geometrically calculated positions for **8**. The hydrogen atoms H(9), H(14), H(15), H(21), H(22), H(23), H(24) were located form difference Fourier syntheses and the residual ones were located at geometrically calculated positions for **8**. All the hydrogen atoms were refined isotropically for each complex.

Theoretical Calculations. Formal charges were evaluated by the extended

Huckel molecular orbital (EHMO)[11] method for coordination nitrogen atoms of the free ligands and copper and coordination nitrogen atoms of the complexes. The molecular modeling software package CAChe served as a facility to build up and edit calculated geometries, which were determined by X-ray crystallography.

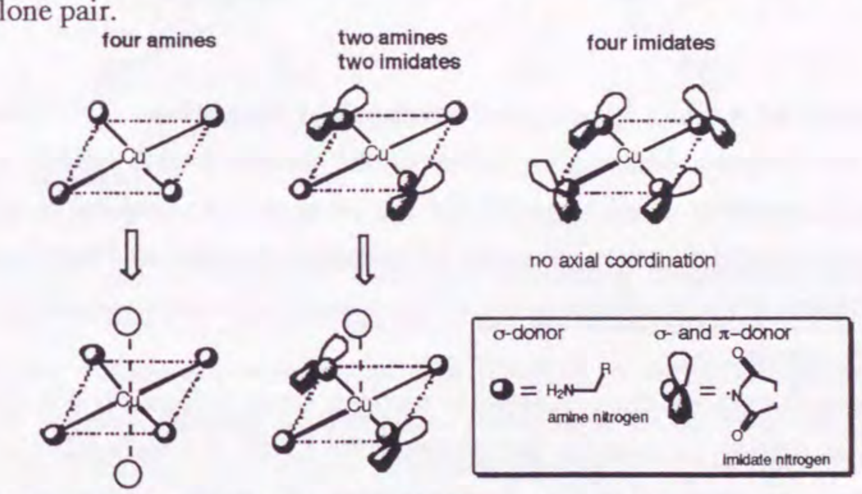
4.3 Results and Discussion.

Molecular Structure of 8. The crystallographic data for **8** and **9** are summarized in Table 4-1. Selected bond lengths and angles are listed in Table 4-2. Molecular structure and crystal structure viewed down from the crystallographic *b* axis are depicted in Figure 4-1 and 4-2, respectively. Complex **8** has crystallographic imposed square planar $[CuN_4]$ configuration with Cu(1)-N(1) = 2.010(5) Å and Cu(1)-N(2) = 2.003(5) Å bond distances which are in agreement with that of copper(II) complexes having ethylenediamine ligands (average 2.03 Å found in the CSD[12]). The axial bond distance is Cu(1)···S(1) = 3.173(2) Å (3.27 Å in the earlier structural analysis[7]), which is out of the range expected for the axial Cu-S coordination bonds (2.56 - 2.82 Å).[15] Therefore, the thiocyanate anions are not subjected to semi-coordination, that is also supported by electronic spectra.[16] For semi-coordinated $[Cu(en)_2]^{2+}$ complexes, the axial bond lengths are reported as follows: Cu-F = 2.56 Å for $[Cu(en)_2](BF_4)_2$[16] and Cu-N = 2.73 Å for $[Cu(en)_2](SCN)(ClO_4)$.[17] Thus, to our knowledge, **8** is the only example of square planar copper(II) complexes without axial semi-coordination containing only amine ligands. Torsion angle with N(1)-C(1)-C(2)-N(2) = 50.0(8) ° for **8** suggests that the ethylenediamine ligands are in stable conformation. No appreciable intramolecular and intermolecular hydrogen bonding interactions are found in **8** within Taylor and Kennard's statistical criterion.[18]

Molecular Structure of 9. Selected bond lengths and angles are listed in Table 4-3 and molecular structure is shown in Figure 4-3. Complex **9** affords a six-coordinated distorted octahedral $[CuN_4O_2]$ coordination geometry, which consists of two succinimidate and two amine nitrogens in *cis* positions and two oxygens in axial sites. The imidate and amine Cu-N bond lengths are similar to that of analogous complexes except for Cu(1)-N(4) (2.070(4) Å) which is elongated by steric hindrance of the ethyl group. The *cis* N(1)-Cu(1)-N(2) (90.0(2) °) bond angles are larger than N(3)-Cu(1)-N(4) (84.2(2) °), which is due to steric restriction of chelate ligand, and N(1)-Cu(1)-N(4) (95.6(2) °) is larger than N(2)-Cu(1)-N(3) (91.0(2) °), which is due to steric hindrance of the ethyl group. In sufficient space made by large N(1)-Cu(1)-N(2) bond angles, two axial water ligands coordinate to copper with the bond angle of O(5)-Cu(1)-O(6) = 172.3(1) °. Furthermore, *trans* N(1)-Cu(1)-N(3) (173.3(2) °) and N(2)-Cu(1)-N(4) (170.6(2) °) are also smaller than 180 °, which result in distortion of $[CuN_4O_2]$

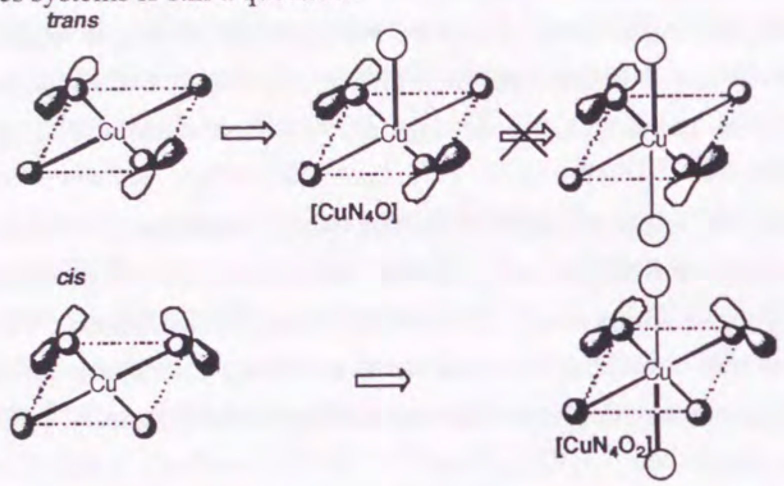
coordination geometry. The axial Cu-O bond distances of analogous complexes are as follows: six-coordinated distorted octahedral $[CuN_4O_2]$ **9** (Cu(1)-O(5) = 2.725(4) Å and Cu(1)-O(6) = 2.672(4) Å), five-coordinated square pyramidal $[CuN_4O]$ with diimine $[Cu(succim)_2(bpy)H_2O]$[5] (2.673(4) Å) and $[Cu(succim)_2(phen)H_2O]\cdot H_2O$[5] (2.548(5) Å), five-coordinated square pyramidal $[CuN_4O]$ with amine $[Cu(phent)_2(EtNH_2)_2H_2O]$[4] (2.436(9) Å) and $[Cu(phent)_2(i\text{-}PrNH_2)_2H_2O]$[4] (2.362(10) Å), and five-coordinated square pyramidal $[CuN_4O]$ with 4-methylpyridine $[Cu(succim)_2(4Mepy)_2H_2O]$[19] (2.282 Å). Thus, the axial Cu-O bond distances are elongated as the coordination numbers increase. Torsion angle of N-ethylethylenediamine moiety is N(3)-C(9)-C(10)-N(4) = 54.5(5) ° which is similar to that of **8**. Two intramolecular hydrogen bonds are proposed (O(6)-H(21)···O(2) = 2.800(5) and O(5)-H(24)···O(4) = 2.775(5) Å) between imidate carbonyl oxygens and the axial water ligands. No intermolecular hydrogen bonds are observed in **9**.

Arrangement of Ligands and Coordination Numbers. As instinctively expected, imidates and amines are different in the character of coordination nitrogen atoms. Deprotonated imidates act as an anionic ligand which forms Cu-N coordination bonds with not only σ-bonding lone pair but also a filled p lone pair perpendicular to five-membered ring, whereas amines act as a neutral ligand which forms Cu-N bonds with σ-bonding lone pair.



At first, we consider the number of imidate and amine ligands. As the number of σ- and π-donor imidate ligands increase, acceptability of axial ligands is weaken. Indeed, although **8** has no semi-coordinated axial ligands exceptionally, complexes containing four amine ligands are subjected to axial coordination commonly. *trans*-$[Cu(imidate)_2(amine_2)]$ complexes indicate intermediate character which can also form distorted square planar $[CuN_4]$ complexes like **7** examined in chapters 2 and 3 or square pyramidal $[CuN_4O]$ complexes like **10**, if steric condition permits. Complexes with four imidate lignads such as **11** are difficult to accept an axial ligand, which is also supported by the existence of $K_2[Cu(biuret)_2]\cdot 2H_2O$[20] which contains four σ- and π-donor coordination nitrogens.

Secondly, we compare the difference between *cis* and *trans* configuration in the series of two imidate and two amine complexes. In the case of *trans* complexes, not only four-coordinated square planar [CuN_4] complexes but also five-coordinated square pyramidal [CuN_4O] complexes such as **10** can be formed, however, six-coordinated [CuN_4O_2] complexes have not been known no matter how steric conditions permitted for the sixth axial coordination. On the contrary, in the case of *cis* configuration, even six-coordinated [CuN_4O_2] complex **9** can be formed, and the determination factor of the maximum coordination numbers between *cis* and *trans* arrangement of the two imidates and two amines systems is still a question.



Acceptability of Axial Ligands and Strength of Donation. In this section, we focus on electronic donating properties of the present several imidate and amine ligands and acceptability of axial ligands. For this purpose, we calculated roughly formal charges on the coordination nitrogen atoms of imidates and amines as a free ligand and on the copper atoms of the complexes to assist the qualitative preceding considerations about the series of complexes.

Formal charges on the coordination nitrogen atoms (q[ligand]) for various free ligands are as follows (in au unit): succinimidate (-1.1276), 5,5-diphenylhydantoinate (-1.1886), and anmonia (-0.6620), 2-propylamine (-0.7476), 1-phenylethylamine (-0.7344), 1,2-diphenylethylamine (-0.7497), 1-cyclohexylethylamine (-0.7424), ethylenediamine (-0.6952), N-ethylethylenediamine (-0.7703 for EtNH side and -0.7241 for NH_2 side), respectively. As far as the precision of this calculations, inductive effects by substitution groups are negligible. The q[ligand] values indicate that imidates are stronger donor than amines which is in agreement with a qualitative expectation.

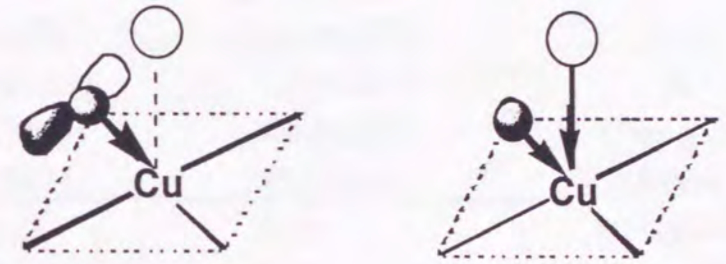
The strength of donation are estimated from the difference formal charge Δq defined as follow:

$$\Delta q = q[complex] - q[ligand]$$

where q[complex] denotes the formal charge on the coordination nitrogen atom in

complexes, and q[ligand] denotes that of free ligands. The small Δq value (large in absolute value) indicates the strong donation from nitrogen to copper. The charge on copper atom of complexes, q[complexes], and Δq values are listed in Table 4-4.

For all the complexes containing both imidate and amine ligands, the Δq values for imidate are smaller than that of amines, which is in harmony with the fact that imidates are stronger donor than amines. In the four-coordinated square planar [CuN_4] complexes **8**, **6**, and **11**, the formal charge on the copper of **11**, containing four imidates, is the smallest. As increase of strong donor imidates, the charges on copper atom decrease and the four-coordination is stabilized. As for **7**, **10**, and **9**, containing two imidates and two amines, the complexes with low coordination number indicate large charge on copper atom, which results from the fact that imidates act as to decrease the change on copper atom in *cis* coordination than in *trans* coordination. In this way, a new coordination structure of **9**, which belongs to the two imidates and two amines system, can be controlled in view of the electroneutrality principle[22] of the copper(II) atoms by means of weak donation caused by *cis* arrangement of imidate ligands.



4.4 Conclusion.

A new type of copper(II) complexes containing imidate and amine ligands, [$Cu(succim)_2(N\text{-}Eten)(H_2O)_2$] were prepared and the crystal structure were determined. The complex affords a distorted octahedral [CuN_4O_2] coordination geometry, which consists of two succinimidate and two amine nitrogens in *cis* positions and two oxygens in axial sites. According to structural comparison among analogous four-, five-, and six-coordinated complexes with imidate and amine ligands in various arrangement, it is suggested that imidate ligands, acting as a stronger donor than amine ligands, contribute to stabilization of low coordination numbers and donating property of imidate is stronger in *trans* arrangement than *cis* arrangement. In this way, in a series of complexes, the numbers and the arrangement of different strength donor, *e.g.* imidates and amine, can control acceptability of the axial ligands to satisfy the electroneutrality principle.

Table 4-1. Crystallographic data for **8** and **9**.

	8	**9**
Formula	$C_6H_{16}N_6CuS_2$	$C_{12}H_{24}N_4CuO_6$
Molecular weight	299.90	383.89
Color of crystal	blue	blue
Crystal size / mm	0.30x0.20x0.20	0.20x0.20x0.10
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a / Å	7.285(2)	7.303(2)
b / Å	7.627(1)	15.625(2)
c / Å	6.568(1)	7.2115(7)
α / °	107.73(1)	91.211(8)
β / °	113.75(2)	90.54(1)
γ / °	77.48(2)	83.59(1)
V / Å^3	316.3(1)	817.5(2)
Z	1	2
D_c / g cm^{-3}	1.574	1.559
F(000)	155	402
μ(Cu Kα) / cm^{-1}	53.70	22.23
$2\theta_{max}$ / °	123.8	120.0
Temperature / K	296	296
No. of measured reflections	1012	2648
No. of unique reflections	640	2426
No. of reflections used in refinement	882 [I>2.0σ (I)]	2128 [I>3.0σ (I)]
No. of parameters	71	209
R [a]	0.062	0.050
R_w [b]	0.099	0.058

[a] $R=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b] $R_w=(\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$.

Weighting scheme: $w = 1/(\sigma^2(F_o))$

Table 4-2. Selected bond lengths (Å) and angles (°) for **8**.

	8
Bond Lengths	
Cu(1)···S(1)	3.173(2)
Cu(1)-N(1)(amine)	2.010(5)
Cu(1)-N(2)(amine)	2.003(5)
N(1)-C(1)	1.474(9)
N(2)-C(2)	1.469(9)
C(1)-C(2)	1.50(1)
Bond Angles	
N(1)-Cu(1)-N(1*)	180.0
N(2)-Cu(1)-N(2*)	180.0
N(1)-Cu(1)-N(2)	84.6(2)
N(1)-Cu(1)-N(2*)	95.4(2)
Cu(1)-N(1)-C(1)	109.8(4)
Cu(1)-N(2)-C(2)	107.6(4)
N(1)-C(1)-C(2)	108.6(5)
N(2)-C(2)-C(1)	108.2(6)

Table 4-3. Selected bond lengths (Å) and angles (°) for **9**.

	9
Bond Lengths	
Cu(1)-N(1)(imidate)	1.944(4)
Cu(1)-N(2)(imidate)	2.006(4)
Cu(1)-N(3)(amine)	2.019(4)
Cu(1)-N(4)(amine)	2.070(4)
Cu(1)-O(5)	2.725(4)
Cu(1)-O(6)	2.672(4)
Bond Angles	
N(1)-Cu(1)-N(2)	90.0(2)
N(1)-Cu(1)-N(4)	95.6(2)
N(2)-Cu(1)-N(3)	91.0(2)
N(3)-Cu(1)-N(4)	84.2(2)
N(1)-Cu(1)-N(3)	173.3(2)
N(2)-Cu(1)-N(4)	170.6(2)
O(5)-Cu(1)-O(6)	172.3(1)

Table 4-4. Formal charges on copper and nitrogen atoms for complexes and difference formal charges (Δq) of nitrogen atoms.

complexes	formal charge of complex (on Cu) / au	nitrogen type	formal charge of complex (on N) / au	difference formal charges(Δq)/ au
8	2.7279	amine	-0.6733	-0.0219
6	2.7112	imidate	-1.0829	-0.0447
		amine	-0.7262	-0.0235
7	2.7038	imidate	-1.0800	-0.0476
		amine	-0.7285	-0.059
10	2.7396	imidate	-1.1282	-0.096
		amine	-0.7430	-0.046
9	2.8096	imidate	-1.0765	-0.0511
		amine(NH_2)	-0.6918	-0.053
		amine(EtNH)	-0.7243	-0.0460
11	2.4026	imidate	-1.0483	-0.0793

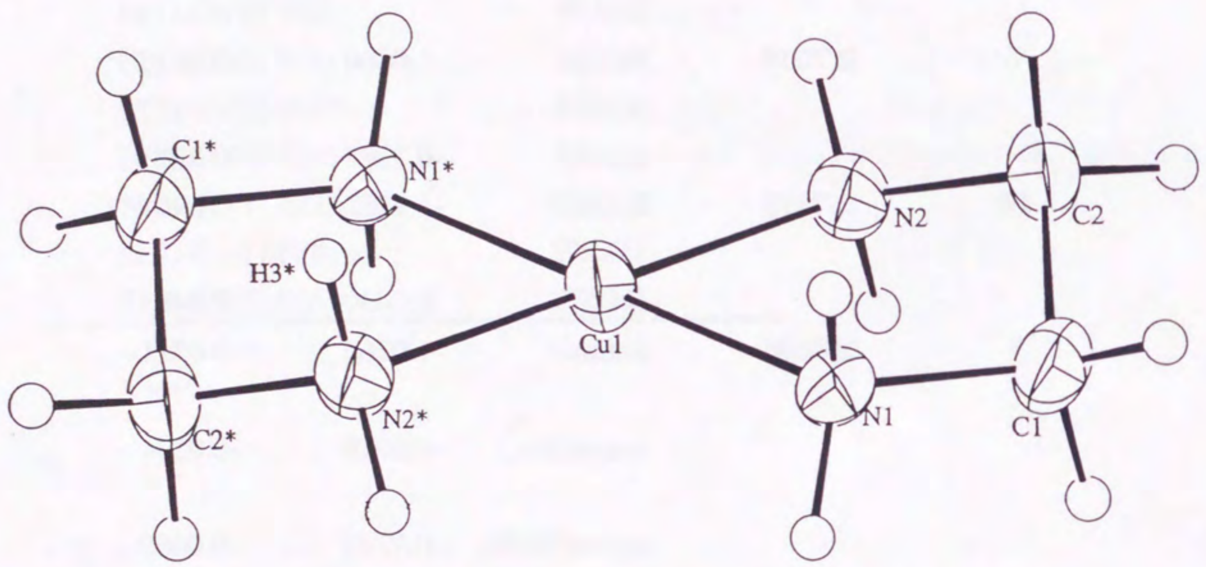


Figure 4-1. Molecular structure of $[Cu(en)_2](SCN)_2$ (**8**) with the atom numbering scheme. Two SCN^- anions are omitted for clarity.

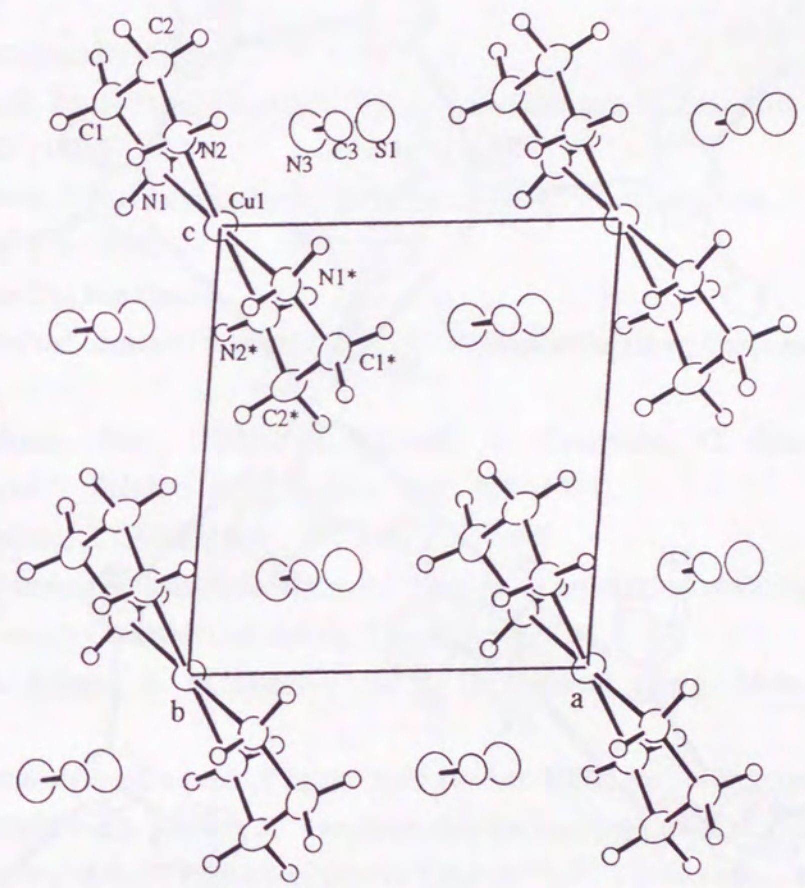


Figure 4-2. Crystal packing of $[Cu(en)_2](SCN)_2$ (**8**) viewed down along the crystallographic *b* axis.

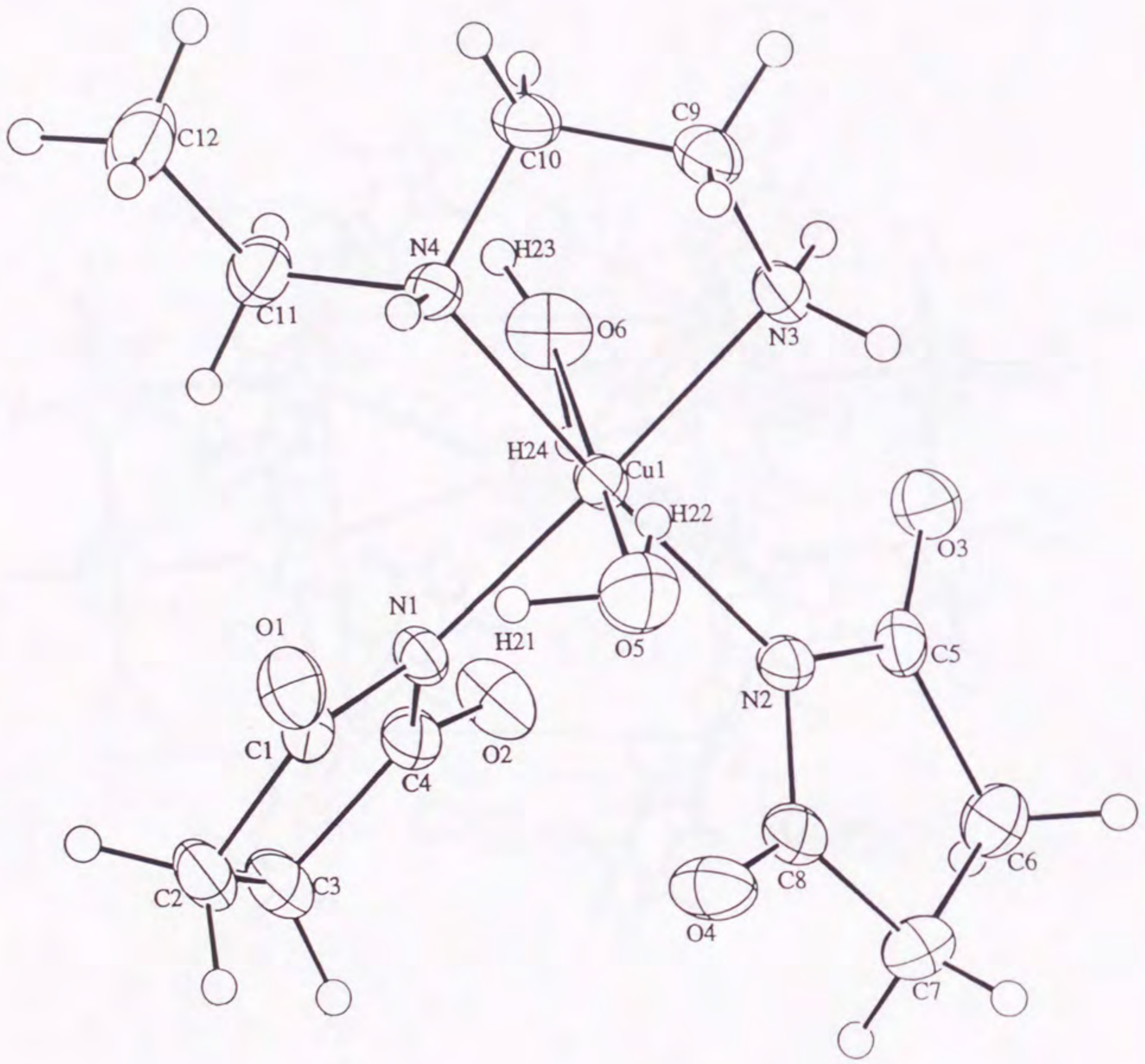


Figure 4-3. Molecular structure of $[Cu(succim)_2(N\text{-}Eten)(H_2O)_2]$ (**9**) with the atom numbering scheme.

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14) Complex **8** shows the peak of ligand field band at 18800 cm^{-1} with broad half width (half width 5800 cm^{-1}). Choi et al.[16] reported that the spectrum of $[CuL(SCH_3)_2]\cdot 2H_2O$ (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo $[14,4,0^{1.18},0^{7.12}]$ docosane), which has a $[CuN_4S_2]$ chromophore with Cu-S = 2.659(1) Å, appeared the sulfur-to-copper(II) charge transfer transition at 416 and 435 nm. In contrast, the spectrum of $[CuL]Cl_2\cdot 2H_2O$ having axial water with Cu···O = 2.649(2) Å show a similar spectrum to **8**. Therefore, the spectrum of **1** suggests no axial Cu···S interaction in **8**.

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Chapter 5.

Square Pyramidal [CuN_4O] Chromophore with Two Imidate Ligands in *cis*-Position: Aquadiiminebis(succinimidato)copper(II) Complexes.

Abstract.

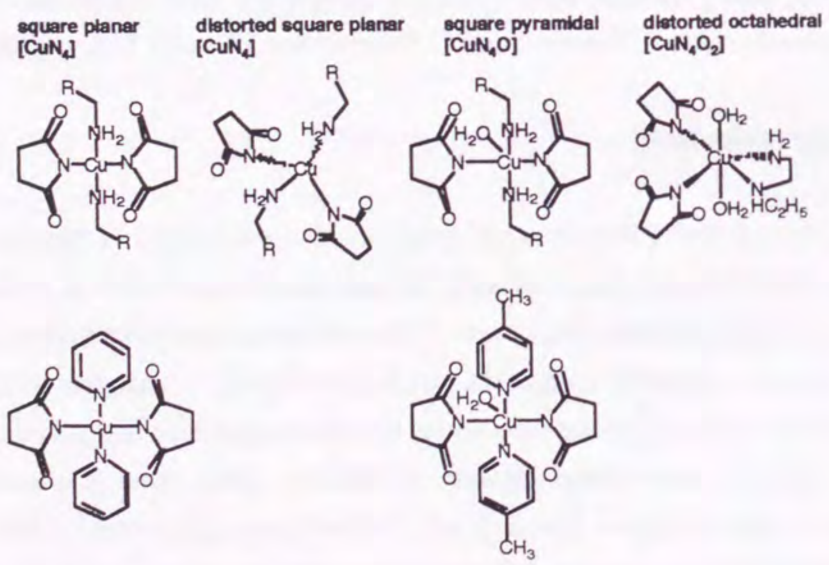
Copper(II) complexes [Cu(succim)$_2$(phen)H_2O]·H_2O (**12**) (succim = succinimidate, phen = 1,10-phenanthroline) and [Cu(succim)$_2$(bpy)H_2O] (**13**) (bpy = 2,2'-bipyridine) were prepared and the crystal structures were determined by X-ray crystallography. The coordination geometries are found to be five-coordinated slightly distorted square-based pyramidal [CuN_4O] with two succinimidate nitrogen atoms in *cis*-positions, two bidentate diimine nitrogens in *cis*-positions, and water oxygen atom in axial site for each complex. Crystal data for complex **12** are monoclinic with space group $P2_1/n$; a = 9.602(4), b = 12.003(4), c = 17.618(4) Å; β = 100.38(3) °; V = 1997(1) Å^3; Z = 4. Crystal data for complex **13** are monoclinic with space group $P2_1/n$; a = 9.616(2), b = 11.616(3), c = 15.871(2) Å; β = 90.61(2) °; V = 1772.8(6) Å^3; Z = 4. The [CuN_4] basal plane of these complexes are considerably distorted with *trans*-N(succim)-Cu-N(diimine) bond angles are 168.2(2) and 173.6(2) ° for **12** and 164.7(1) and 173.2(1) ° for **13**, respectively. The axial Cu-O(water) bond distances of the present complexes (2.548(5) Å for **12** and 2.673(4) Å for **13**) are appreciable longer than those of other square pyramidal *trans*-[CuN_4O] complexes. The diffuse reflectance spectra show a broad peak at 17900 cm^{-1} and 17500 cm^{-1} for **12** and **13**, respectively.

5.1 Introduction.

Conventionally, deprotonated cyclic imides (abbreviated as 'imidate') are known to act as a monodentate ligand through nitrogen atom and are liable to give square planar [CuN_4] complexes in the solid states.[1,2] Nevertheless, various coordination geometries on the related copper(II) complexes can be developed by changing steric effects and electronic properties of imidate and amine ligands as described the preceding chapters.

Imidate and amine ligands commonly yield *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes with a square planar [CuN_4] coordination geometry.[3,4] Moreover, *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes with a distorted square planar [CuN_4] coordination geometry can be obtained by suitable steric effect of amine ligands as mentioned in chapters 2 and 3 in detail.[5-7] Five-coordinated square pyramidal [CuN_4O] complexes can be obtained when axial coordination is permitted by sufficient space around axial coordination sites.[8] Additionally, bidentate chelate amine gives six-coordinated distorted octahedral [CuN_4O_2] complex [Cu(succim)$_2$(N-Eten)(H_2O)$_2$] (**9**) (N-Eten = N-ethylethylenediamine) with two succinimidate ligands on *cis*-positions.[9] In this way, the variation of coordination geometries have been indicated as far as the related complexes with amine ligands.

On the other hand, pyridine derivative ligands are different from amine ligands in the following points: (1) electronic property (possibility for π-acceptor) of coordination nitrogen atoms differs from that of amine, (2) hydrogen bonds involving amine hydrogens cannot be formed for these ligands, and (3) these ligands can not possess structural variation due to bulky substituents like ethylamine derivative ligands. A few complexes having imidate and pyridine derivative ligands have been reported and characterized structurally such as *trans*-[Cu(succim)$_2$(py)$_2$][10] (py = pyridine) with a square planar [CuN_4] coordination geometry and [Cu(succim)$_2$(4mepy)$_2$ H_2O][11] (4mepy = 4 methylpyridine) with a square pyramidal [CuN_4O] coordination geometry. What type of the complex will be formed by using bidentate chelate diimine ligands? Thus, we focused on chelate diimine ligands such as phen and bpy (phen = 1,10-phenanthroline and bpy = 2,2'-bipyridine), indeed many [Cu(diimine)$_2$X] complexes have been studied so far. Molecular structures were reported for compressed tetrahedral [CuN_4] complexes with phen[12] or bpy,[13] and square pyramidal [CuN_4O] complexes with various distorted geometries, reflecting differences in flexibility between phen[14] and bpy.[15] In this chapter we report preparation, structural determinations, and electronic spectra of [Cu(succim)$_2$(phen)H_2O]·H_2O (**12**) and [Cu(succim)$_2$(bpy)H_2O] (**13**).

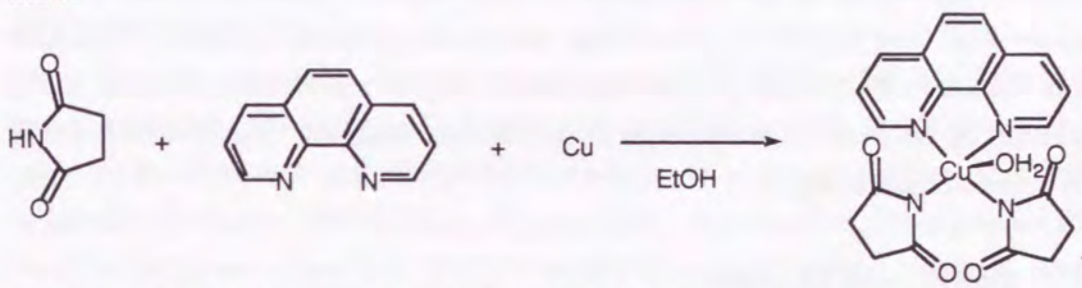


5.2 Experimental Section.

General Procedures. All of the reagents and solvents were purchased from

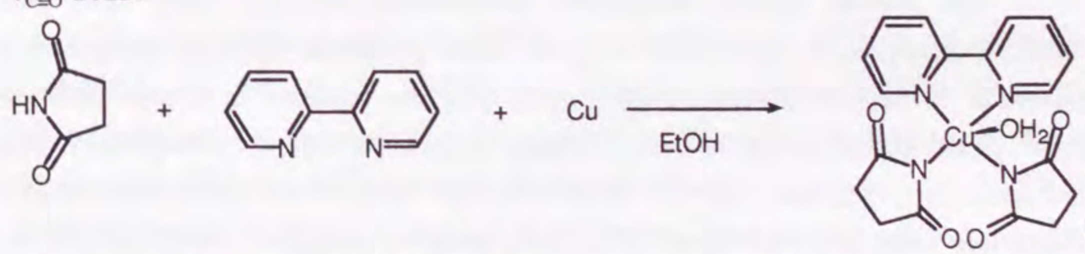
Wako Pure Chemical Industries, Ltd. and were used as received without further purification. Elemental analyses were carried out at the Liberal Arts and Sciences Organization, Osaka University.

Preparation of [Cu(succim)$_2$(phen)H_2O]·H_2O (12). To a suspension containing copper powder (0.635 g, 10.0 mmol) and succinimide (2.477 g, 25.0 mmol) in ethanol (25 cm^3) at 50 °C, 1,10-phenanthroline (1.982 g, 10.0 mmol) was added. The suspension was stirred for 7h, then kept at 50 °C to yield a dark green solution. Then the solution was filtered off, and dark blue precipitates ([Cu(succim)$_2$(phen)H_2O]·0.5H_2O (**12'**)) appeared. Dark blue prismatic crystals suitable for X-ray crystallography ([Cu(succim)$_2$(phen)H_2O]·H_2O (**12**)) were obtained from ethanolic solution. Yield: 55.4 %. Found: C, 51.52; H, 4.12; N, 12.01%. Calcd for $C_{20}H_{19}N_4CuO_{5.5}$: C, 51.45; H, 4.10; N, 12.00%. (calculated based on the formula of **12'**) IR (Nujol, cm^{-1}) $\nu_{C=O}$ 1616.



12

Preparation of [Cu(succim)$_2$(bpy)H_2O] (13). To a suspension of copper powder (0.318 g, 5.00 mmol) and succinimide (0.991 g, 10.0 mmol) in ethanol (20 cm^3) at 50 °C, 2,2'-bipyridine (0.781 g, 5.00 mmol) was added. The suspension was stirred for 4h to give a dark green solution. The resulting solution was filtered off and blue precipitates were obtained. Single crystals suitable for X-ray crystallography were grown from hot ethanolic solution. Yield: 40.3 %. Found: C, 49.85; H, 4.32; N, 12.91%. Calcd for $C_{18}H_{18}N_4CuO_5$: C, 19.83; H, 4.18; N, 12.91%. IR (Nujol, cm^{-1}) $\nu_{C=O}$ 1623.



13

Measurements. The diffuse reflectance spectra of the complexes in the solid state were measured on a Hitachi U-3400 UV/VIS/NIR spectrophotometer equipped with an integrating sphere. Infrared spectra were obtained on a Perkin-Elmer 983G Infrared Spectrometer in the region of 4000-180 cm^{-1} on Nujol mulls with CsI plates. The thermogravimetry (TG) and the differential thermal analyses (DTA) were recorded simultaneously on a SEIKO Instruments Inc. SSC-5000 thermal analysis system in static air at a heating rate of 20 °Cmin^{-1}. α-alumina (10.0 mg) was used as reference material, and the amounts of the samples examined were 10.0 mg for **12** and **13**.

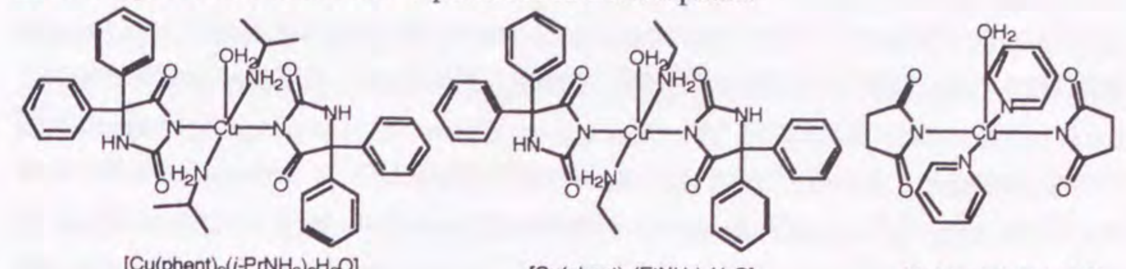
Crystal Structure Determination. The X-ray diffraction intensity data were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with nickel-filtered CuKα (λ = 1.5418 Å) for **12** and **13**. Calculations were carried out on an SGI O2 workstation with a teXsan[16] software package for each complex. Empirical absorption corrections based on Ψ scans were applied for **12** and **13** (transmission factors 0.778-0.997 and 0.699-0.993, respectively). No significant decays in the intensities of three standard reflections were observed throughout the data collection. The structures were solved using SIR 92[17] and expanded by Fourier techniques. The structures of **12** and **13** were refined on F by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The hydrogen atoms H(17) and H(18) of **12** and H(17) and H(18) of **13** were located from difference Fourier syntheses and the residual ones were located at geometrically calculated positions, except for hydrogen atoms connected to crystalline solvent O(6) of **12**. H(17) and H(18) of **12** and H(17) and H(18) of **13** were not included for the refinement, while the other hydrogen atoms were refined isotropically.

5.3 Results and Discussion.

Preparation of Complexes. It is well known that metal copper reacts in the presence of imidates with *monodentate* primary amines to give *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes, while *cis*-[Cu(imidate)$_2$(amine)$_2$] complexes are unknown so far. The oxidation reaction of metal copper with oxygen in the air is common, but the reaction mechanism has not been elucidated. The present study proves that the reaction also occurs by treatment with diimines.

The present diimine complexes [Cu(succim)$_2$(phen)H$_2$O]·H$_2$O (**12**) and [Cu(succim)$_2$(bpy)H$_2$O] (**13**) afford a square based pyramidal [CuN$_4$O] coordination structure as revealed by X-ray crystallography (see later section). In a basal plane, a diimine ligand coordinates as a *chelate* ligand, and the *cis*-sites are occupied by two *monodentate* succinimidate ligands. Conventionally, most *monodentate* imidate and *monodentate* amine afforded *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes. In addition, five-coordinated *trans*-[CuN$_4$O] complexes, such as [Cu(phent)$_2$(*i*-PrNH$_2$)$_2$H$_2$O],[8] [Cu(phent)$_2$(EtNH$_2$)$_2$H$_2$O][8] (phent = 5,5-diphenylhydantoinate), and [Cu(succim)$_2$(4mepy)$_2$H$_2$O][11] (4mepy = 4-methylpyridine) were known and the structures were determined. On the contrary, treatment of *chelate* diimine and succinimide ligands gave solely five-coordinated *cis*-[CuN$_4$O] complexes with an axial water molecule. In this way, the present complexes are the first examples in which

imidate ligands coordinate on *cis*-positions in a basal plane.



[Cu(phent)$_2$(*i*-PrNH$_2$)$_2$H$_2$O] [Cu(phent)$_2$(EtNH$_2$)$_2$H$_2$O] [Cu(succim)$_2$(py)$_2$H$_2$O]

Thermal Behavior of an Axial Water. The DTA curve of [Cu(phent)$_2$(*i*-PrNH$_2$)$_2$H$_2$O] exhibited a broad endothermic peak at 171 °C, and the TG curve showed a weight loss of 2.15 % corresponding to 1 mol of water per 1 mol of complex (Calcd. 2.64 %).[8] The change of the diffuse reflectance spectra suggested that [Cu(phent)$_2$(*i*-PrNH$_2$)$_2$H$_2$O] lost the axial water to afford four-coordinated square planar *trans*-[Cu(phent)$_2$(*i*-PrNH$_2$)$_2$]. Addition and elimination reaction of the axial water was reversible (Scheme 5-1).

In contrast to this, the present complexes [Cu(succim)$_2$(phen)H$_2$O]·H$_2$O (**12**) and [Cu(succim)$_2$(bpy)H$_2$O] (**13**) decomposed irreversibly at about 150 and 170 °C, respectively. Since each step of the thermal decomposition was ambiguous, we failed to isolate intermediate or final products. Consequently, an attempt to obtain genuine four-coordinated square planar *cis*-[CuN$_4$] complex has not succeeded yet with thermal methods.

Crystal Structures. The crystallographic data for **12** and **13** are summarized in Table 5-1. Selected bond distances and angles are listed in Table 5-2. The ORTEP drawings of **12** and **13** are shown in Figure 5-1 and 5-2, respectively.

The coordination geometries of the two complexes are slightly distorted square-based pyramidal [CuN$_4$O]. The [CuN$_4$] basal plane is composed of a *chelate* diimine ligand and two *monodentate* succinimidate ligands on the *cis*-positions. Additionally, a water molecule connects from one of the axial sites.

The Cu-N(succim) (N(1) or N(2)) bond distances for **12** and **13** range from 1.964(4) to 1.971(4) Å and 1.962(3) to 1.990(3) Å, respectively. The values are in good agreement with those of other copper(II) complexes with imidate ligands. The Cu-N(aromatic) (N(3) or N(4)) bond distances of **12** and **13** range from 2.027(4) to 2.052(4)Å and 2.024(3) to 2.049(3) Å, respectively. These are comparable to analogous complexes [Cu(succim)$_2$(4mepy)$_2$H$_2$O][11] and *trans*-[Cu(succim)$_2$(py)$_2$],[10] regardless of *cis*- or *trans*- arrangement of the imidate ligands in a basal plane.

The bond angles of *trans*-N(succim)-Cu-N(aromatic) (N(1)-Cu(1)-N(3) or N(2)-Cu(1)-N(4)) are 168.2(2) ° and 173.6(2) ° for **12**, and 164.7(1) ° and 173.2(1) ° for **13**, respectively. These values indicate that the basal planes are distorted somewhat for each complex. The *trans*-N(succim)-Cu-N(succim) and the *trans*-N(aromatic)-Cu-

N(aromatic) bond angles are 175.1° and 165.0 ° for $[Cu(succim)_2(4mepy)_2H_2O]$, and the *trans*-N(succim)-Cu-N(succim) and *trans*-N(aromatic)-Cu-N(aromatic) bond angles are 180.0 ° and 180.0 ° for $[Cu(phent)_2(i\text{-}PrNH_2)_2H_2O]$ and 177.8(3) ° and 165.0(3) ° for $[Cu(phent)_2(EtNH_2)_2H_2O]$. Therefore the basal plane of $[Cu(succim)_2(4mepy)_2H_2O]$ is closer to regular planar $[CuN_4]$ than those of **12** and **13**.

The axial Cu-O(water) bond distances of the present complexes (2.548(5) Å for **12** and 2.673(4) Å for **13**) are considerably longer than those of $[Cu(phent)_2(i\text{-}PrNH_2)_2H_2O]$ (2.362(10) Å), $[Cu(phent)_2(EtNH_2)_2H_2O]$ (2.436(9) Å), and $[Cu(succim)_2(4mepy)_2H_2O]$ (2.282 Å).

Intramolecular hydrogen bonds (C=O···H-O) are observed in **12** and **13** between carbonyl groups of succinimidate ligands and an axial water. The hydrogen bonding distances O(4)···O(5) are 2.761 Å for **12** and 2.728 Å for **13**, which are within the range of the statistical criterion about hydrogen bonds presented by Taylor and Kennard.[18] The long Cu-O(water) bond lengths may be attributed to only one intramolecular hydrogen bonds, because two intramolecular bonds are formed in the conventional *trans*-$[CuN_4O]$ complexes with short Cu-O(axial water) bond distances. It is assumed that the intramolecular hydrogen bonds play an important role in stabilizing the axial coordination.[8] However, the TG-DTA measurement shows that they does not result in stepwise decomposition by dessociation of axial water. On the other hand, no appreciable intermolecular hydrogen bonds are observed in **12** and **13**.

Dihedral angles defined between the $[CuN_4]$ basal plane and the five-membered ring moieties of succinimidate ligands are 114.46 ° (the $[CuN_4]$ mean plane and the plane of succinimidate containing N(1)) and 87.17 ° (N(2)) for **12**, and 112.15 ° (N(1)) and 109.06 ° (N(2)) for **13**, respectively. The two succinimidate ligands of **13** are aligned in parallel arrangement to each other, so that the succinimidate ligands are free from steric hindrance. Complex **12**, on contrast, has a water molecule as crystalline solvent in the space between two succinimidate ligands, therefore two succinimidate ligands of **12** arrange in non-parallel fashion to each other.

In the crystals, neighboring molecules are packed together with their diimine ligands stacked (Figures 5-3 and 5-4). As shown in Figure 5-4, the $[CuN_4O]$ coordination geometry around central copper(II) ion of **13** was compressed because of the aromatic stacking of bpy ligands. As a consequence of the absence of intermolecular hydrogen bonds or electrostatic interactions, the predominant factor to determine the crystal packing may be intermolecular van der Waals contact such as $\pi-\pi$ stacking of aromatic conjugated ring systems. Recently, crystal structures of $[MnCl_2(bpy)_2]\cdot 2H_2O\cdot EtOH$ and $[MnCl_2(phen)_2]$ were reported,[19] and the importance of $\pi-\pi$ stacking of the conjugated ring systems (bpy and phen) for the crystal packing was stated by McCann *et al.* In the present complexes, the stacking diimine moieties

characterized by the interplanar distances are about 3.6 Å and 3.7 Å for **12** and **13**, respectively. These stacking distances are in agreement with several manganese and platinum ($[Pt(phen)_2]Cl_2\cdot 3H_2O$ and $[Pt(bpy)_2]Cl_2$)[20] complexes with phen and bpy ligands.

Electronic Spectra. The diffuse reflectance spectra of **12**, **13** and square planar *trans*-$[Cu(succim)_2(py)_2]$ in the solid state are shown in Figure 5-5. We could not measure polarized crystal spectra of **12** and **13** because of the lack of appropriate samples.

The present complexes **12** and **13** involving a $[CuN_4O]$ chromophore show the peak of ligand field band at 17900 cm^{-1} and 17500 cm^{-1} with broad half width. Intensities over 22000 cm^{-1} are attributed to the $\pi-\pi*$ absorption of diimine ligands. In respect to the d-d band region, the spectra are similar to those of *trans*-square pyramidal $[CuN_4O]$ complexes, $[Cu(phent)_2(i\text{-}PrNH_2)_2H_2O]$ (17750 cm^{-1}) and $[Cu(phent)_2(EtNH_2)_2H_2O]$ (17150 cm^{-1}). The spectrum of reddish violet *trans*-$[Cu(succim)_2(py)_2]$ complexes shows a main peak at about 20500 cm^{-1} and with a shoulder over the range of 16000-17000 cm^{-1} which is simlar to that of square planar $[CuN_4]$ complexes with four midate ligands.

5.4 Conclusion.

By using *chelate* diimine ligands (phen and bpy), dark blue $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**12**) and blue $[Cu(succim)_2(bpy)H_2O]$ (**13**) were prepared and the molecular structures were determined by X-ray crystallography. The coordination geometries of the complexes were found to be square-based pyramidal $[CuN_4O]$. In the basal plane, two succinimidate ligands coordinated on *cis*-positions. And an axial site was occupied by a water molecule. The Cu-O bond distances were considerably longer than those of *trans*-square pyramidal $[CuN_4O]$ complexes. The reflectance spectra of the complexes contained broad bands at 17900 cm^{-1} and 17500 cm^{-1}, which were attributed to the square-based pyramidal $[CuN_4O]$ chromophores.

Table 5-1. Crystallographic data for **12** and **13**.

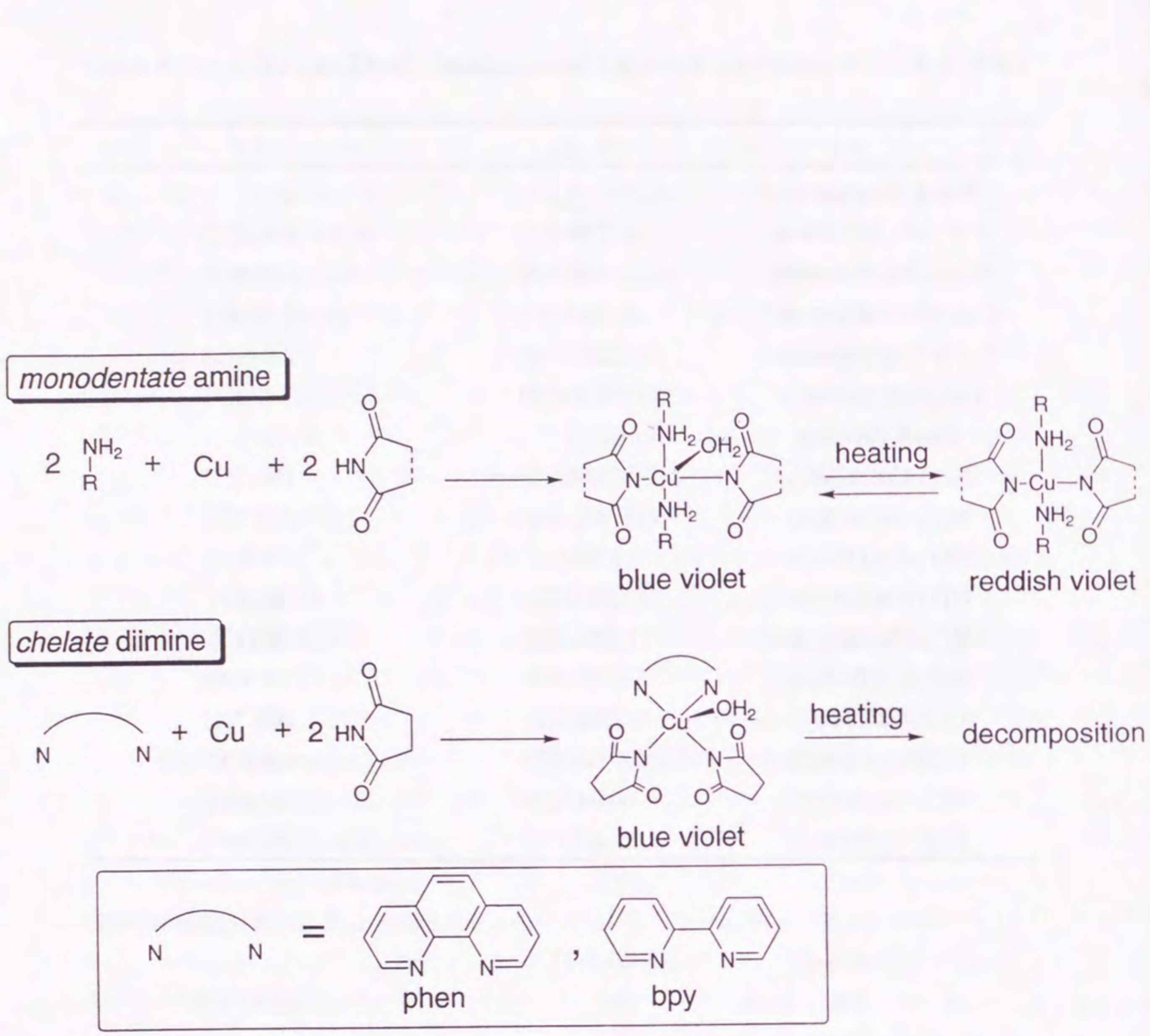
	12	**13**
Formula	$C_{20}H_{20}N_4CuO_6$	$C_{18}H_{18}N_4CuO_5$
Molecular weight	475.95	433.91
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / Å	9.602(4)	9.616(2)
b / Å	12.003(4)	11.616(3)
c / Å	17.618(4)	15.871(2)
β / °	100.38(3)	90.61(2)
V / Å^3	1997(1)	1772.8(6)
Z	4	4
D_c / g cm^{-3}	1.583	1.626
F(000)	980	892
μ(Cu Kα) / cm^{-1}	19.63	21.02
$2\theta_{max}$ / °	120.0	120.0
Crystal dimensions / mm	0.25x0.20x0.20	0.25x0.25x0.20
Temperature / K	300	300
No. of measured reflections	2800	2945
No. of unique reflections	2648	2764
No. of reflections used in refinement	2172 [I>2.0σ (I)]	2169 [I>2.0σ (I)]
No. of parameters	345	318
g. o. f.	3.24	2.39
Δ / σ_{max}	0.03	0.09
$\Delta\rho_{max}$ / eÅ^{-3}	0.55	0.34
R [a)]	0.058	0.040
R_w [b)]	0.081	0.041

[a)] $R=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b)] $R_w=(\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$.

Weighting scheme: $w = 1/(\sigma^2(F_o))$

Table 5-2. Selected bond distances (Å) and angles (°) for **12** and **13**.

	12	**13**
Bond Distances		
Cu(1)-N(1) (succim)	1.964(4)	1.962(3)
Cu(1)-N(2) (succim)	1.971(4)	1.990(3)
Cu(1)-N(3) (aromatic)	2.052(4)	2.024(3)
Cu(1)-N(4) (aromatic)	2.027(4)	2.049(3)
Cu(1)-O(5) (water)	2.548(5)	2.673(4)
Bond Angles		
N(1)-Cu(1)-N(3)	168.2(2)	164.7(1)
N(2)-Cu(1)-N(4)	173.6(2)	173.2(1)
N(1)-Cu(1)-N(2)	92.1(2)	92.8(1)
N(1)-Cu(1)-N(4)	93.6(2)	90.6(1)
N(2)-Cu(1)-N(3)	93.0(2)	96.0(1)
N(3)-Cu(1)-N(4)	80.8(2)	79.4(1)
O(5)-Cu(1)-N(1)	95.3(2)	107.7(1)
O(5)-Cu(1)-N(2)	94.1(2)	89.5(1)
O(5)-Cu(1)-N(3)	94.9(2)	84.8(1)
O(5)-Cu(1)-N(4)	88.2(2)	95.0(1)



Scheme 5-1. Schematic representations of preparations of $[CuN_4O]$ complexes with imidate ligands by using *monodentate* amine and *chelate* diimine and the results of their thermal reactions.

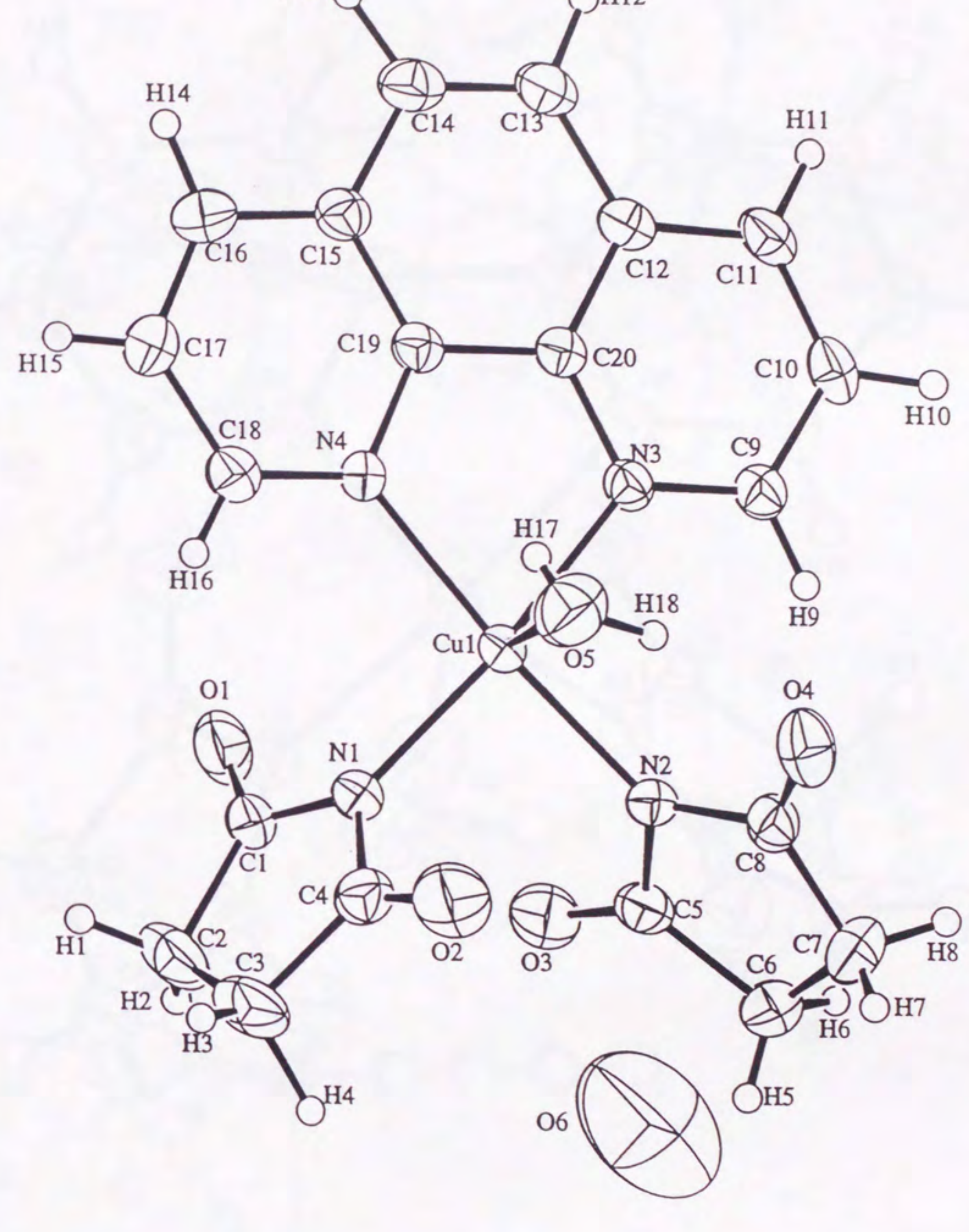


Figure 5-1. An ORTEP drawing of $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**12**) with the atom numbering scheme.

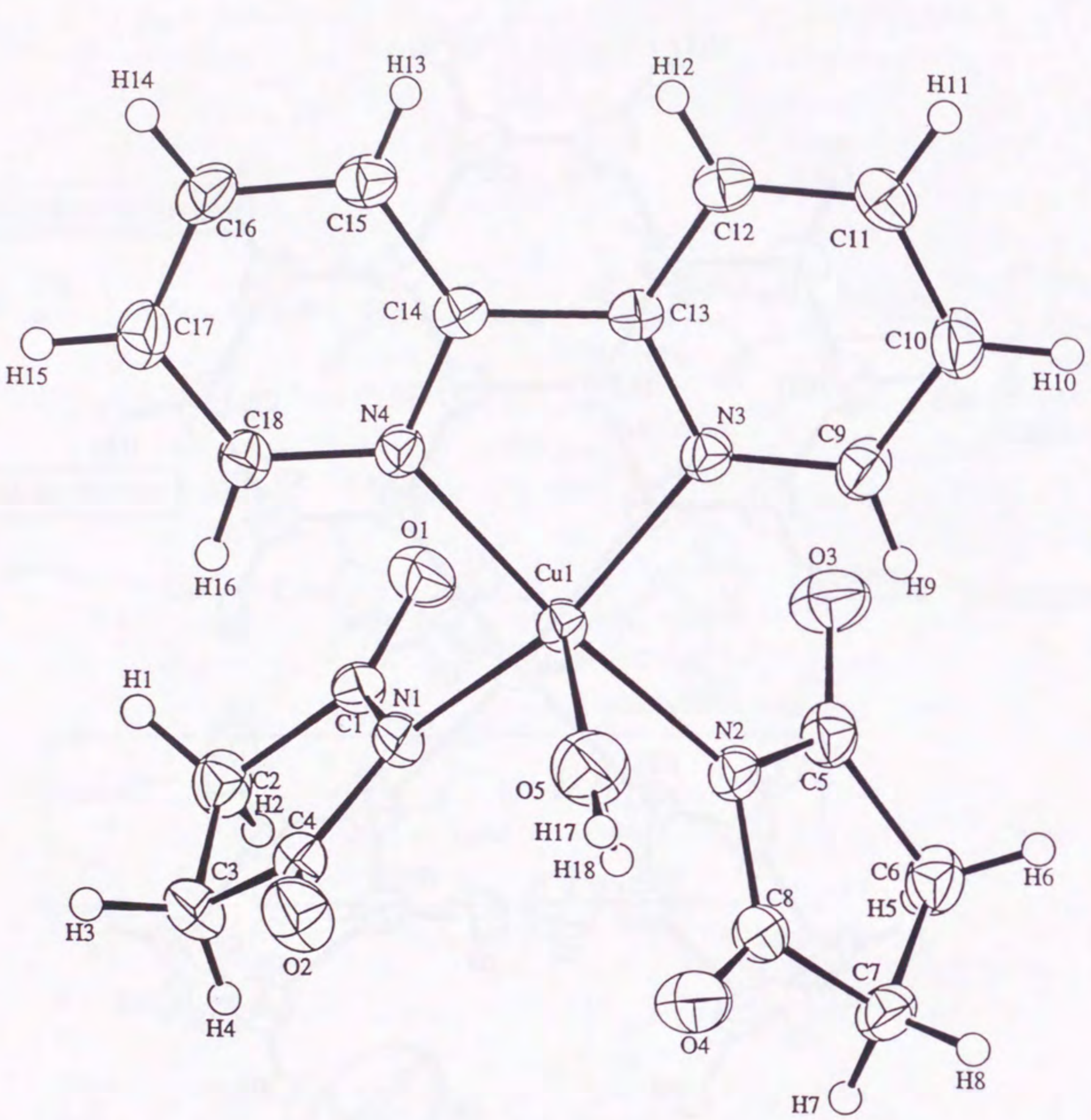


Figure 5-2. An ORTEP drawing of [Cu(succim)$_2$(bpy)H_2O] (**13**) with the atom numbering scheme.

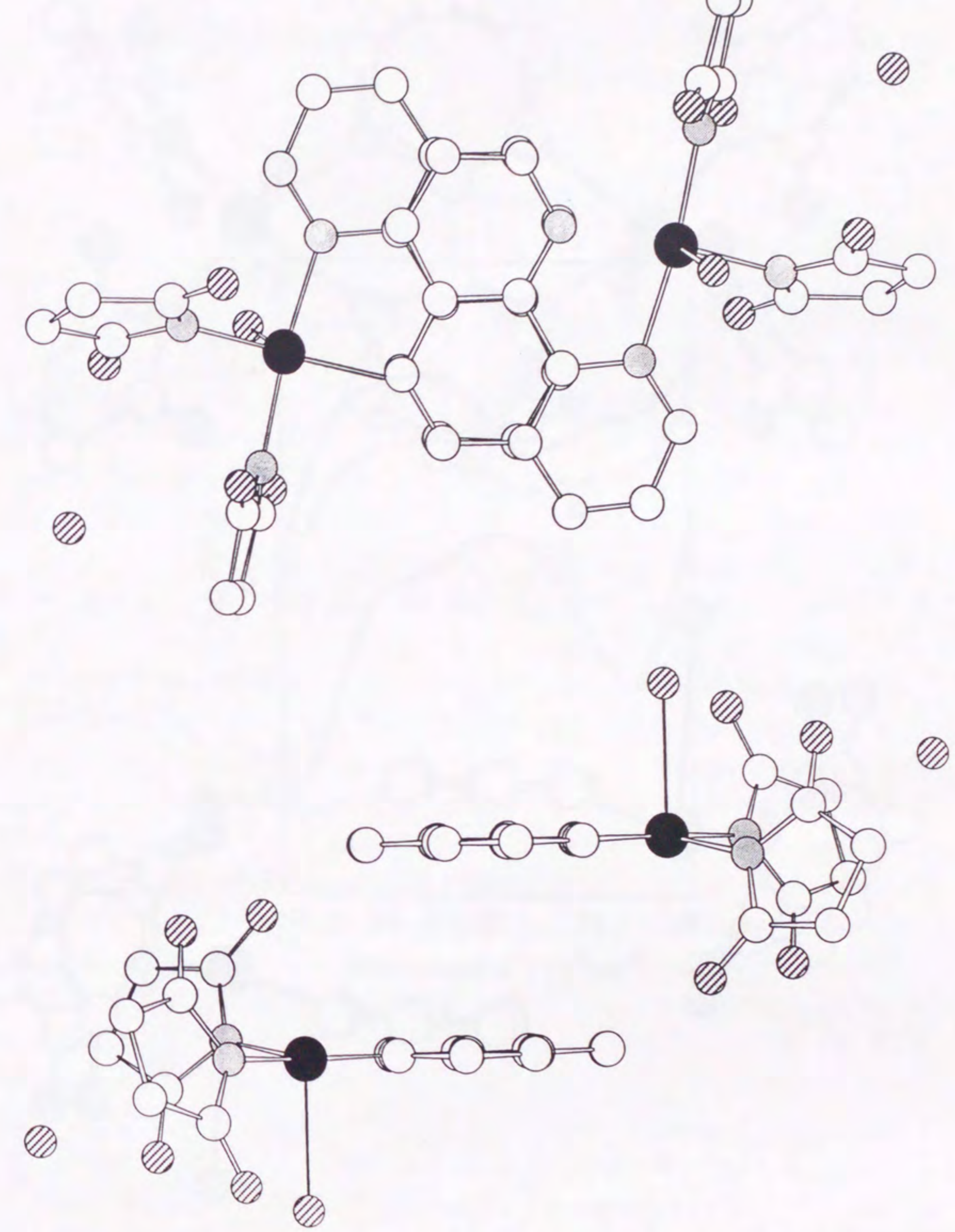


Figure 5-3. Perspective view of [Cu(succim)$_2$(phen)H_2O]·H_2O (**12**) showing a stacking structures with phen. (Above) Top view. (Below) Side view.

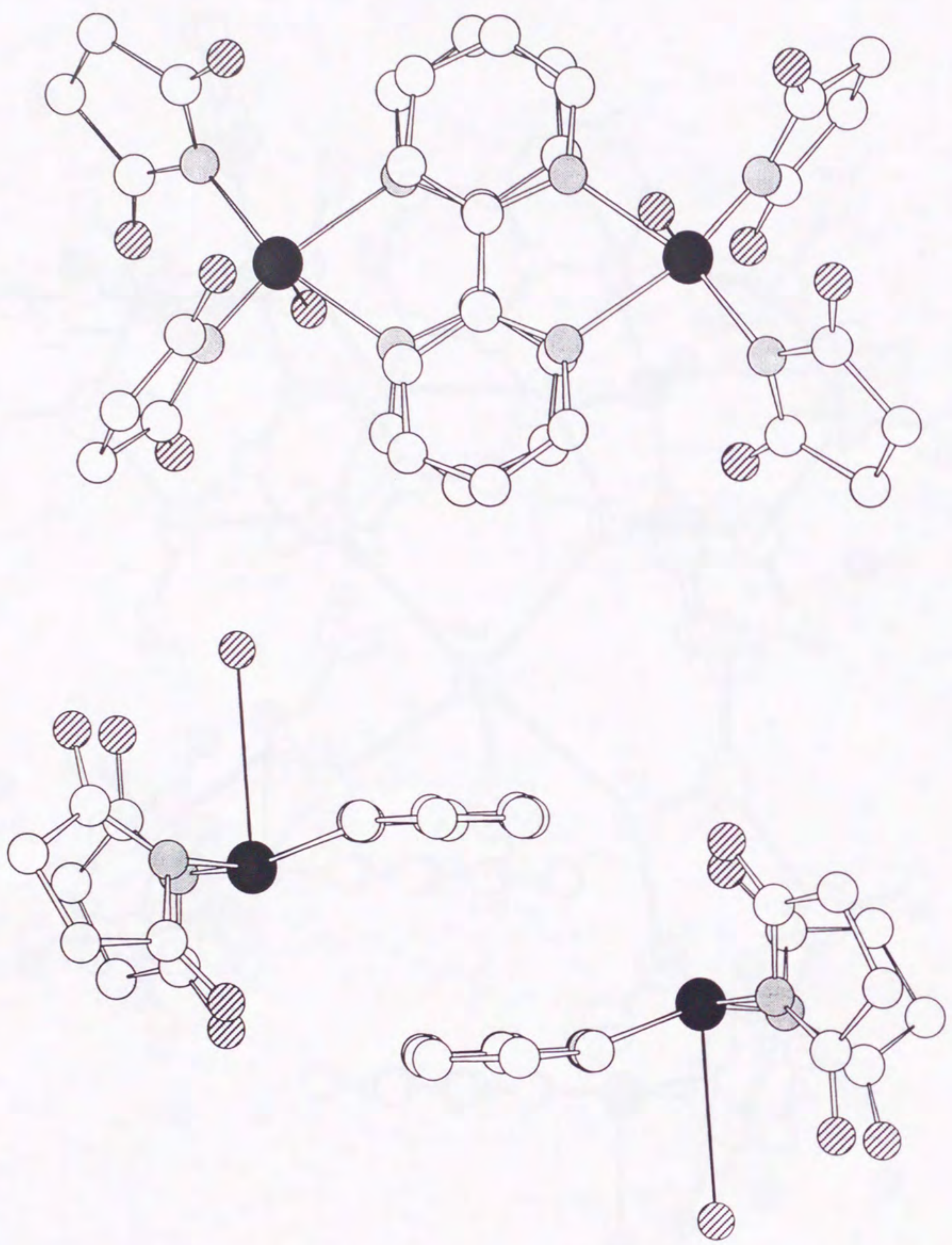


Figure 5-4. Perspective view of [Cu(succim)$_2$(bpy)H$_2$O] (**13**) showing a stacking structures with bpy. (Above) Top view. (Below) Side view.

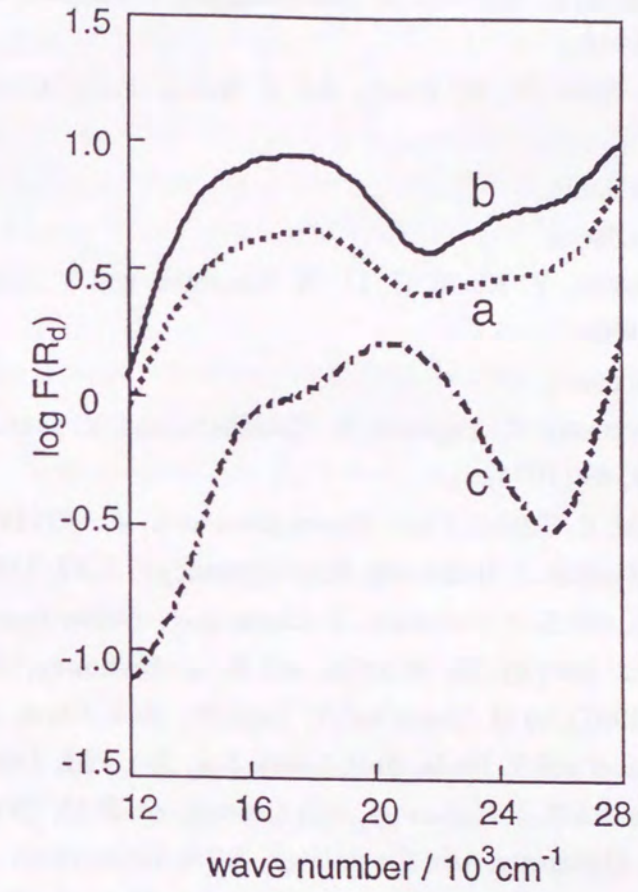


Figure 5-5. The diffuse reflectance spectra in the solid state. (a) [Cu(succim)$_2$(phen)H$_2$O]·H$_2$O (**12**), (b) [Cu(succim)$_2$(bpy)H$_2$O] (**13**), and (c) *trans*-[Cu(succim)$_2$(py)$_2$].

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Chapter 6.

Assignment of d-d Transitions of Square Planar $[CuN_4]$ Complexes with Imidate and Amine Ligands.

Abstract.

Square planar $[CuN_4]$ copper(II) complexes, *trans*-$[Cu(phent)_2(R\text{-}chea)(S\text{-}chea)]$ (**14**), *trans*-$[Cu(phent)_2(R\text{-}chea)_2]$ (**15**), $Rb_2[Cu(succim)_4]\cdot 2H_2O$ (**11**), $K_2[Cu(phent)_4]\cdot 8H_2O$ (**16**), $Rb_2[Cu(phent)_4]\cdot 6H_2O$ (**17**), and $Cs_2[Cu(phent)_4]\cdot 10H_2O$ (**18**) (phent = 5,5-diphenylhydantoinate, chea = 1-cyclohexylethylamine, and succim = succinimidate), were prepared and the crystal structures were determined for **14**, **15**, and **11**. Crystal data for **14** are monoclinic with space group $P2_1/c$; a = 8.485(2), b = 9.7854(8), c = 26.334(4) Å; β = 92.83(1) °; V = 2483.8(5) Å^3; Z = 2. Crystal data for **15** are monoclinic with space group $P2_1$; a = 8.472(2), b = 9.803(2), c = 26.331(6) Å; β = 92.67(2) °; V = 2184.6(8) Å^3; Z = 2. Crystal data for **11** are monoclinic with space group $C2/m$; a = 16.279(4), b = 8.382(3), c = 8.297(3) Å; β = 93.13(3) °; V = 1130.4(6) Å^3; Z = 2. The electronic polarized single crystal spectra were measured for **14**, **15**, and **11** and distorted square planar $[CuN_4]$ complexes *trans*-$[Cu(phent)_2(R\text{-}phenea)(S\text{-}phenea)]$ (**1**) and *trans*-$[Cu(phent)_2(R\text{-}phenea)_2][Cu(phent)_2(S\text{-}phenea)_2]$ (**3**) (phenea = 1-phenylethylamine). These spectra were analyzed by Gaussian curve fitting into three band components expected by the selection rules. The sequences of 3d orbitals were determined to be $d_{x2\text{-}y2}$ (a_{1g}) > d_{xy} (b_{1g}) > d_{z2} (a_{1g}) > d_{yz} (b_{3g}), d_{zx} (b_{1g}) for square planar **14** and **15** (D_{2h} point group), $d_{x2\text{-}y2}$ (b_{1g}) > d_{xy} (b_{2g}) > d_{z2} (a_{1g}) > d_{yz},d_{zx} (e_g) for square planar **11** (D_{4h} point group), and $d_{x2\text{-}y2}$ (a_1) > d_{xy} (a_2) > d_{z2} (a_1) > d_{yz} (b_2) >d_{zx} (b_1) for distorted square planar **1** and **3** (C_{2v} point group) on the basis of the angular overlap model (AOM) calculations. Since $d_{z2}\rightarrow d_{x2\text{-}y2}$ transition was observed separately for **1** in z polarization, accurate assignment could be carried out. Tetrahedral distortion of $[CuN_4]$ chromophores decreases the peak wave numbers for *trans*-$[Cu(imidate)_2(amine)_2]$ complexes, that is explained by the change of individual decreasing in the transition energies. Moreover, by comparing between the square planar *trans*-$[Cu(imidate)_2(amine)_2]$ and $M_2[Cu(imidate)_4]$ complexes, it can be estimated that the imidates p-lone pair forms a π-character coordination bond, which decreases $d_{xy}\rightarrow d_{x2\text{-}y2}$ transition energy.

6.1 Introduction.

The assignment of d-d transitions for four-coordinated square planar copper(II)

complexes has been the subject of controversy. Reasonable assignment has been established by Hitchman et al. only for various $[CuCl_4]^{2-}$ anions.[1] The sequence of 3d orbital level of $[CuCl_4]^{2-}$ was determined to be $d_{x2\text{-}y2}$ (b_{1g}) > d_{xy} (b_{2g}) > d_{zx},d_{yz} (e_g) > d_{z2} (a_{1g}) for square planar $[CuCl_4]^{2-}$ anions (D_{4h} point group). Gradual tetrahedral distortion of $[CuCl_4]^{2-}$ anion decreases individual transition energies, and results in a crossover of the levels to give $d_{x2\text{-}y2}$ (b_{1g}) > d_{zx},d_{yz} (e_g) > d_{xy} (b_{2g}) > d_{z2} (a_{1g}) sequence for distorted square planar $[CuCl_4]^{2-}$ anions.[2] This assignment could be established successfully for two reasons: (1) A band of $d_{z2}\rightarrow d_{x2\text{-}y2}$ transition can be observed separately in the highest wave number region of the spectra. (2) Because of adequate crystal packing, individual transitions can be assigned from the selection rules. The transitions of $d_{yz}\rightarrow d_{x2\text{-}y2}$, $d_{zx}\rightarrow d_{x2\text{-}y2}$, and $d_{xy}\rightarrow d_{x2\text{-}y2}$ are forbidden in x, y, and z polarization, respectively, while $d_{z2}\rightarrow d_{x2\text{-}y2}$ transition is allowed in all polarization. The agreement between observed and calculated energy of $d_{z2}\rightarrow d_{x2\text{-}y2}$ transition is still obscure because of the ds-mixing[3] problem of AOM[4] calculations.

In the case of $Cu(acac)_2$ molecule (acac = acetylacetonate) and related complexes with square planar $[CuO_4]$ chromophores, the polarized crystal spectra have been determined for several ones.[5] However, these spectra provide little information on assignment of d-d transitions. One of the reasons for this difficulty may be 'packing problem'; there are two molecules of which the $[CuO_4]$ molecular planes are orthogonal to each other in the crystal, so that vibronic selection rule is invalidated. In fact, three transitions are observed for $Cu(acac)_2$ itself,[6] while all four transitions are observed for two other complexes.[7] Individual bands could not be resolved for all these spectra. Then two types of possible assignment are proposed for these complexes (D_{2h} point group):[5] assignment I is d_{xy} (b_{1g}) > $d_{x2\text{-}y2}$ (a_g) > d_{yz} (b_{3g}) > d_{zx} (b_{2g}) > d_{z2} (a_g), while assignment II is d_{xy} (b_{1g}) > d_{z2} (a_g) > $d_{x2\text{-}y2}$ (a_g) > d_{yz} (b_{3g}) > d_{zx} (b_{2g}). It can be considered that the assignment I is reasonable because all the complexes can be explained by using the same AOM e_π parameter, and the d_{z2} (a_g) lies in the lowest level. On contrary, assignment II is consistent with the experimental results,[8] however, the assignment remains two serious problems with respect to the AOM calculations. (1) Different complexes are described by different e_π parameters though these are composed of the same $[CuO_4]$ chromophores. (2) The value of ds-mixing parameter is too small in comparison with e_σ and e_π parameters. In conclusion, there has not been established exactly the assignment of d-d transitions for square planar $[CuO_4]$ complexes.

On the other hand, genuine square planar $[CuN_4]$ complexes is fairly rare in particular for amine ligands. The fifth and sixth additional axial ligands are usually found and octahedral arrangement are formed.[9] Exceptionally, $[Cu(en)_2](SCN)_2$[10] (en = ethylenediamine) and complexes with N-substituted ethylenediamine ligands[11] are known to be a four-coordinated square planar $[CuN_4]$ coordination. In contrast to amine complexes, it is well known that biuret or biguanide derivatives give rise to four-coordinated square planar [CuN_4] complexes for example bis(biureto)copper(II) potassium salt[12] and bis((methoxycarboimido)aminato)copper(II).[13] Walsh et al. measured the polarized crystal spectra of several square planar [CuN_4] complexes and assigned their d-d transitions tentatively.[11] The reported 3d orbital sequences are d_{x2-y2} (b_{1g}) > d_{xy} (b_{2g}) > d_{z2} (a_{1g}) > d_{xy},d_{yz} (e_g) (D_{4h} point group) for Cs_2[Cu(succim)$_4$]·$2H_2O$.[14] Thus, the exact assignment of d-d transitions for square planar [CuN_4] complexes have not still been established by measuring the polarized crystal spectra and using a reliable AOM calculations. The primary difficulty is preparations of suitable single crystals for measurement of polarized crystal spectra. It can be expected that the imidate ligands are possible to give rise to the copper(II) complexes with various distortion from genuine square planar [CuN_4][14,15] to distorted square planar [CuN_4] geometry.[16,17]

The aim of this chapter is establishment of reasonable assignment of d-d transition of the square planar and distorted square planar [CuN_4] complexes containing imidate and amine ligands based on the polarized single crystal spectra and the AOM calculations. For this purpose, the differences in the distortion of [CuN_4] chromophores and in the Cu-N bonding characters of imidates and amines are discussed in detail. The preparations of square planar bis(imidato)bis(amine)copper(II) complexes *trans*-[Cu(phent)$_2$(R-chea)(S-chea)] (**14**) and *trans*-[Cu(phent)$_2$(R-chea)$_2$] (**15**), and square planar tetrakis(imidato)copper(II) complexes Rb_2[Cu(succim)$_4$]·$2H_2O$ (**11**), K_2[Cu(phent)$_4$]·$8H_2O$ (**16**), Rb_2[Cu(phent)$_4$]·$6H_2O$ (**17**), and Cs_2[Cu(phent)$_4$]·$10H_2O$ (**18**) are described. The electronic polarized crystal spectra of **14**, **15**, **11**, and distorted square planar*trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**) and *trans*-[Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (**3**) were measured and analyzed.[17] The excited-state energies are elucidated to establish the assignment of d-d transitions by using AOM calculations.

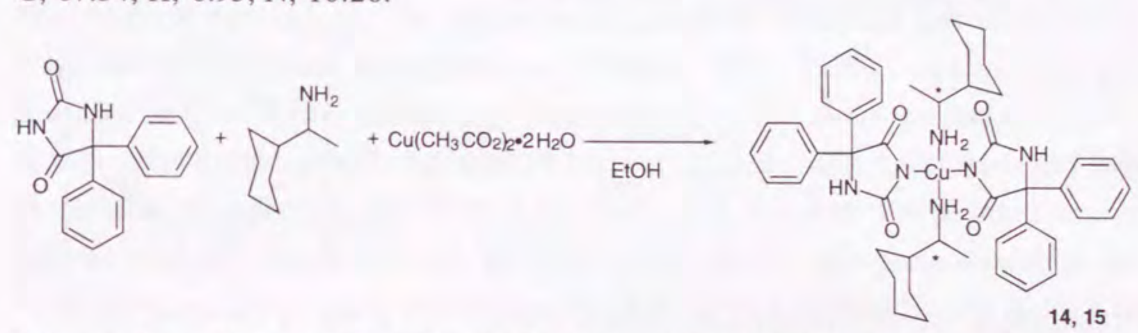
6.2 Experimental Section.

General Procedures. R- and S-1-cyclohexylethylamine and S-1-phenylethylamine were purchased from Fulka Fine Chemicals and Tokyo Kasei Kogyo Co. Ltd., respectively. The other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Methanol and chloroform were dried over molecular sieves, type 3A. Unless otherwise stated, commercial grade chemicals were used without further purification. Elemental analyses were carried out at the Liberal Arts and Sciences Organization, Osaka University.

Preparation of *meso trans*-[Cu(phent)$_2$(R-chea)(S-chea)] (14). To a solution of copper(II) acetate monohydrate (1.00 g, 5.00 mmol) in ethanol (100 cm^3) at

50 °C, 5,5-diphenylhydantoin (2.52 g, 10.0 mmol) was added to give rise to a greenish blue solution. Equimolar mixture of R-1-cyclohexylethylamine (0.64 g, 5.00 mmol) and S-1-cyclohexylethylamine (0.64 g, 5.00 mmol) was added to the solution, the resulting deep blue solution was kept stirred for 1h at 50 °C. Gradually reddish violet precipitates were filtered off and they were recrystallized from chloroform-methanol (4:1, v/v). The reddish violet precipitates **14** obtained were washed with petroleum ether and were dried in a silica gel desiccator overnight. Yield: 15.2 %. Reddish violet prismatic crystals suitable for X-ray crystallography and the measurement of polarized crystal spectra were obtained by slow diffusion of hexane into a chloroform-methanol (4:1, v/v) solution at room temperature for several weeks. Anal. Calcd for $C_{46}H_{56}N_6CuO_4$: C, 67.34; H, 6.68; N, 10.24. Found: C, 67.16; H, 6.92; N, 10.24.

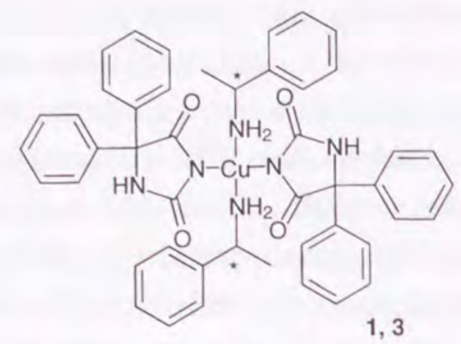
Preparation of *optically active trans*-[Cu(phent)$_2$(R-chea)$_2$] (15). Complex **15** was prepared in a similar manner as **14** using only R-1-cyclohexylethylamine (1.27 g, 10.0 mmol) in the place of equimolar mixture of 1-cyclohexylethylamine. Yield: 11.5 %. Reddish violet plate-like crystals suitable for X-ray crystallography and the measurement of polarized crystal spectra were obtained by slow diffusion of hexane into a chloroform-methanol (4:1, v/v) solution at room temperature for several weeks. Anal. Calcd for $C_{46}H_{56}N_6CuO_4$: C, 67.34; H, 6.68; N, 10.24. Found: C, 67.34; H, 6.93; N, 10.26.



14, 15

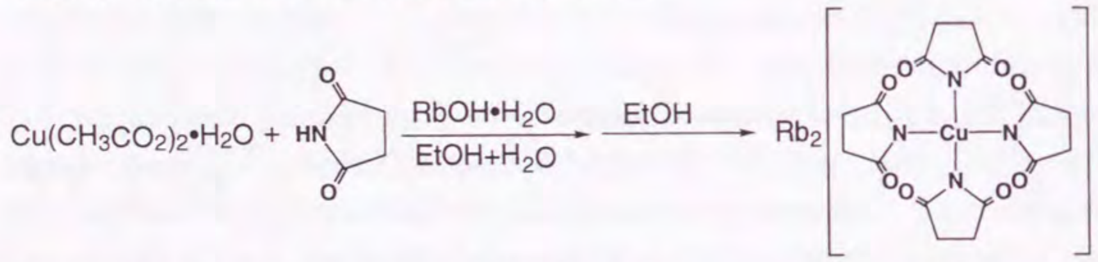
Preparation of *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (1). Blue violet prismatic crystals **1** (meso diastereomer) suitable for the measurement of polarized crystal spectra were prepared in chapter 1[17] and these had a satisfactory analysis. Anal. Calcd for $C_{46}H_{44}N_6CuO_4$: C, 68.34; H, 5.49; N, 10.40. Found: C, 68.34; H, 5.53; N, 10.29.

Preparation of *trans*-[Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (3). Violet prismatic crystals **3** (racemic crystal) suitable for the measurement of polarized crystal spectra were prepared in chapter 1[17] and these had a satisfactory analysis. Anal. Calcd for $C_{46}H_{44}N_6CuO_4$: C, 68.34; H, 5.49; N, 10.40. Found: C, 68.14; H, 5.56; N, 10.40.



1, 3

Preparation of $Rb_2[Cu(succim)_4]\cdot 2H_2O$ (11). Reddish violet prismatic crystals of **11** suitable for X-ray crystallography and the measurement of polarized crystal spectra were prepared according to Tschugaeff's method[19] with slight modification. To a solution of succinimide (4.00 g, 40.0 mmol) and copper(II) acetate monohydrate (1.00 g, 5.00 mmol) in ethanol (50 cm^3) and water (5 cm^3) at 50 °C, aqueous solution of rubidium hydroxide monohydrate (3.18 g, 26.0 mmol) was added dropwise to give rise to a deep blue violet solution. Immediately after filtration of the solution, 30 cm^3 of hot ethanol (about 30 °C) was added to the solution. The solution was cooled slowly at room temperature, and reddish violet crystals appeared in the solution. The resulting reddish violet crystals are slightly hygroscopic. Anal. Calcd for $C_{16}H_{20}N_4CuO_{10}Rb_2$: C, 28.99; H, 3.04; N, 8.45. Found: C, 28.84; H, 2.87; N, 8.53.



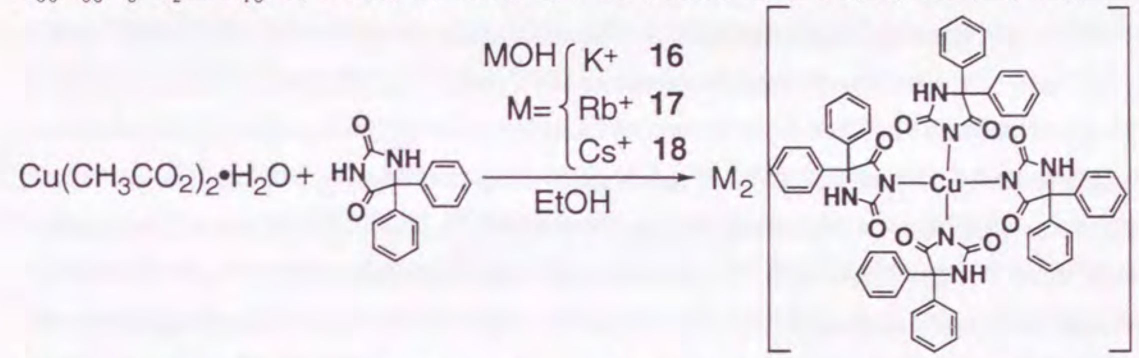
11

Preparation of $K_2[Cu(phent)_4]\cdot 8H_2O$ (16). To a solution of 5,5-diphenylhydantoin (1.26 g, 5.00 mmol) and copper(II) acetate monohydrate (0.25 g, 1.25 mmol) in ethanol (50 cm^3) at 50 °C, 1.6 cm^3 of aqueous solution of potassium hydroxide (2.00 g was dissolved in 10.0 cm^3 water at 50 °C) was added dropwise. The solution was stirred for 10 min at 45 °C to give rise to brown precipitates. The suspension was filtered off, and the resulting brown precipitates were washed with ethanol and were dried in a silica gel desiccator overnight. Yield: 87 %. Anal. Calcd for $C_{60}H_{64}N_8CuK_2O_{16}$: C, 55.65; H, 4.98; N, 8.65. Found: C, 55.86; H, 4.34; N, 8.47.

Preparation of $Rb_2[Cu(phent)_4]\cdot 6H_2O$ (17). To a solution of 5,5-diphenylhydantoin (1.26 g, 5.00 mmol) and copper(II) acetate monohydrate (0.25 g, 1.25 mmol) in ethanol (50 cm^3) at 50 °C, 1.3 cm^3 of aqueous solution of rubidium hydroxide (2.50 g was dissolved in 5.0 cm^3 water at 50 °C) was added dropwise. Immediately reddish violet precipitates emerged and the suspension was stirred for 15 min at 45 °C. The suspension was filtered off, and the resulting reddish violet precipitates

were washed with ethanol and were dried in a silica gel desiccator overnight. Yield 79 %. Anal. Calcd for $C_{60}H_{60}N_8CuO_{16}Rb_2$: C, 53.32; H, 4.47; N, 8.29. Found: C, 53.60; H, 4.10; N, 8.23.

Preparation of $Cs_2[Cu(phent)_4]\cdot 10H_2O$ (18). To a solution of 5,5-diphenylhydantoin (1.26 g, 5.00 mmol) and copper(II) acetate monohydrate (0.25 g, 1.25 mmol) in ethanol (50 cm^3) at 50 °C, 2.0 cm^3 of aqueous solution of cesium hydroxide (2.50 g was dissolved in 6.0 cm^3 water at 50 °C) was added dropwise. The solution was stirred for 10 min at 45 °C to give rise to beige precipitates. The suspension was filtered off, and the resulting beige precipitates were washed with ethanol and were dried in a silica gel desiccator overnight. Yield 60 %. Anal. Calcd for $C_{60}H_{68}N_8Cs_2CuO_{18}$: C, 47.46; H, 4.51; N, 7.38. Found: C, 47.84; H, 4.19; N, 7.39.



Electronic Spectra. The single crystal polarized absorption electronic spectra were measured at room temperature on a Hitachi model ESP-3T spectrometer and specially designed micro-spectroscopic equipment. The light beam passed thorough a Rochon quartz polarizer and condensed by two concave mirrors onto a pinhole (0.1 mm in diameter) in an indium plate where a thin crystal was mounted. The polarized crystal spectra were determined with the electronic vector parallel and perpendicular to the crystallographic *b* axis on the well-developed (001) face for **14**, **15**, **1**, and **3** or (100) face for **11**. The orientation of the crystal axes of the samples mounted was characterized by oscillation X-ray photographs. Crystals with dimensions of 0.40 x 0.25 (face) x 0.11 (thickness) mm for **14**, 0.40 x 0.20 x 0.09 mm for **15**, 0.30 x 0.18 x 0.028 mm for **1**, 0.78 x 0.40 x 0.03 mm for **3**, and 0.10 (thickness) mm for **11** were used for the measurements. The pinhole was covered completely by the sample crystal. The reference beam was appropriately attenuated so that the absorbance was adjusted to zero. Baseline correction was made on the basis of the corresponding diffuse reflectance spectra. The diffuse reflectance spectra of the complexes in the solid states were measured at room temperature on a Hitachi U-3400 UV/VIS/NIR spectrophotometer equipped with an integrating sphere attachment.

Crystal Structure Determination. The X-ray diffraction intensity data were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with nickel-filtered CuKα (λ = 1.5418 Å) for **14** and **15** and graphite monochromated MoKα (λ =

0.71069 Å) for **11**. Calculations were carried out on an SGI O2 workstation with a teXsan[20] software package for each complex. Empirical absorption corrections based on Ψ scans were applied for **14**, **15**, and **11** (transmission factors 0.8099-0.9987, 0.9333-0.9992, and 0.6459-1.0000, respectively). No significant decays in the intensity of the three standard reflections were observed throughout the data collection. The structures were solved using SIR92[21] and expanded by Fourier techniques. The structure of **14** and **11** were refined on F by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The carbon atoms of **15** as members of phenyl and cyclohexyl groups such as C(4) through C(9), C(10) through C(15), C(18) through C(23), C(27) through C(33), C(34) through C(38), and C(41) through C(46) were refined isotropically under constraint restrictions. The other atoms of **15** were refined anisotoropically. After final cycle of the least-squares refinement, noticeable large displacement parameters were found and the maximum shift/error values still did not indicated to be convergent completely because of considerable thermal motion of the carbon atoms of cyclohexyl and phenyl groups. Further attempts of refinement using fixed parameters did not result in improvement of the models. The hydrogen atoms H(12), H(13), H(40), and H(41) of **15** were located from difference Fourier syntheses and the residual ones were located at geometrically calculated positions. Two hydrogen atoms connected to crystalline solvent O(3) of **11** could not be found and the atoms were omitted from the analysis. These crystal structure analyses provided sufficiently satisfactory results for the purpose of the present study.

6.3 Results and Discussion.

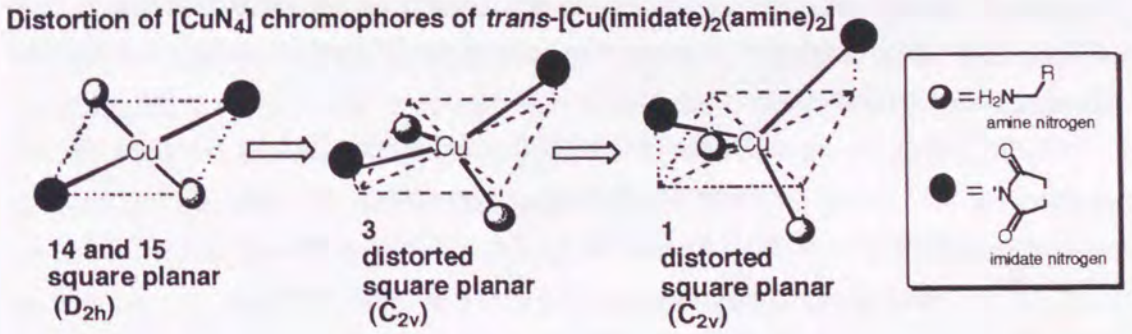
Crystal Structures. The crystallographic data for **14**, **15**, and **11** are summarized in Table 6-1. Selected bond distances and angles for **14**, **15**, **1**, **3**, and **11** are listed in Table 6-2. The molecular and crystal structures of **14**, **15**, **1**, **3**, and **11** are depicted in Figures 6-1, 6-2, 6-3, 6-4, and 6-5, respectively.

Complexes **14** and **15** afford a square planar $[CuN_4]$ coordination geometry, that is common feature for analogous *trans*-$[Cu(imidate)_2(amine)_2]$ complexes. The imidate and amine Cu-N bond distances fall in the range 1.97(1) to 2.02(1) Å and 2.01(1) Å to 2.05(1) Å, respectively, and these are equal within experimental errors. These bond distances are in agreement with the average Cu-N bond distances found in CSD[22] (1.97 and 2.03 Å for imidate and amine, respectively). The imidate and amine *trans*-N-Cu-N bond angles are exactly 180.0 ° for **14** by virtue of center of symmetry, whereas 178.2(6) and 176.6(6) ° for **15**. The deviation from exact square planar 180.0 °can be ignored, so that these square planar $[CuN_4]$ chromophores may be treated in point group D_{2h}.

On the other hand, **1** and **3** afford a distorted square planar $[CuN_4]$ coordination geometry, of which tetrahedral distortion of **1** are larger than that of **3** depending on chirality of 1-phenylethylamine ligands.[17] The imidate and amine Cu-N bond distances fall in the range from 1.988(3) to 2.026(4) Å and 1.997(3) to 2.030(4) Å, respectively. No noticeable differences in Cu-N bond distances are observed regardless of tetrahedral distortion. The imidate and amine *trans*-N-Cu-N bond angles are 154.9(2) and 159.8(2) ° for **1** and 163.2(2) and 163.2(2) ° for **3**, in addition, imidate and amine ligands coordinate in *trans* arrangement, so that effective symmetry may be lowered to C_{2v} for **1** and **3**.

In this way, a series of these *trans*-$[Cu(imidate)_2(amine)_2]$ complexes vary their $[CuN_4]$ coordination geometries from square planar (**14** and **15**) to distorted square planar (**1** and **3**). Nevertheless these complexes differ in the degree of distortion of $[CuN_4]$ coordination geometry, these $[CuN_4]$ chromophores are composed of two imidate and amine nitrogens in *trans* arrangement. Therefore gradual shifts of electronic spectra may be attributed to only geometries of the $[CuN_4]$ chromophores with less changes in electronic properties by ligands. In order to describe the degree of distortion of $[CuN_4]$ chromophores, distortion angles θ_{im} and θ_{am} are defined with a molecular coordinates as illustrated in Figure 6-6. Here the molecular x axis is a projection of the Cu-N(imidate) vector onto the $[CuN_4]$ mean plane, the molecular y axis is a projection of the Cu-N(amine) vector onto the $[CuN_4]$ mean plane, and the molecular z axis is normal to both x and y axis. Distortion angles θ_{im} and θ_{am} are 0.0 ° and 0.0 ° and for **14** and **15**, 12.5 ° and 10.1 ° for **1**, and 6.6 ° and 8.4 ° for **3**, and these values are used for AOM calculations. Since effective symmetry D_{2h} are applied for **15**, slight deviation from exactly square planar (θ_{im} = 1.6 ° and θ_{am} = 1.0 °) can be negligible for AOM calculations. Moreover, rotation angles (ψ) around the Cu-N(imidate) bond axes are fixed at 90 °, in which p-lone pair of a imidate ligand exsists on the $[CuN_4]$ coordination plane when the complex adopts a square planar coordination geometry.

Distortion of $[CuN_4]$ chromophores of *trans*-$[Cu(imidate)_2(amine)_2]$



Complex **11** affords a square planar $[CuN_4]$ coordination geometry coordinated by four succinimidates. The imidate Cu(1)-N(1) and Cu(1)-N(2) bond distances are 1.996(4) and 1.993(4) Å, respectively, which are equal within experimental errors and smilar to analogous complexes.[14,23] Because of center of symmetry, two *trans*-N-Cu-N bond angles are 0.0 °, so that two distortion angles of *trans*-N-Cu-N = 180.0 ° corresponding to the definition in Figure 6-6 are used for AOM calculations. Coordination geometry of **11** can be treated in the point group D_{4h}. The coordination number of Rb(1) and Rb(2) ions are eight and six, respectively. Rb(1) is coordinated by eight carbonyl oxygens of succinimidate ligands(O(1) and O(2)), whereas Rb(2) is coordinated by both four carbonyl oxygens (O(1)) and two crystalline water oxygens (O(3)). The Rb-O bond distances are as follows: Rb(1)-O(1) = 3.042(3), Rb(1)-O(2) = 3.028(3), Rb(2)-O(1) = 2.888(3), and Rb(2)-O(3) = 2.992(6) Å, respectively.

Crystal packing schemes of each complex is also shown in Figure 6-1, 6-2, 6-3, 6-4, and 6-5. As depicted in Figures, the crystallographic axes systems are not in agreement with the molecular coordinates for all the complexes.

Electronic Spectra. The polarized single crystal spectra are shown in Figure 6-7. The spectra of **14** and **15** measured in the (001) face with the electric vector (E) parallel (E//*b*) and perpendicular (E⊥*b*) to the *b* crystal axis appear a band maximum at about 20000 cm^{-1} with a shoulder around 16000-17000 cm^{-1} and no dichroism is observed for two spectra. The polarized crystal spectra of **3** were measured in the (001) face with E//*b* and E⊥*b* polarized light, and the two spectra showed distinct dichroism. The E//*b* spectrum appears a weak band at about 16000 cm^{-1}, while the E⊥*b* spectrum appears an intense band at about 18000 cm^{-1}. The spectra of **3** measured in the (001) face with E//*b* and E⊥*b* polarized light appear a broad peak at about 18000 cm^{-1} without dichroism. The spectra of **11** determined in the (100) face with E//*b* and E⊥*b* polarized lights are slightly different from each other. The E⊥*b* spectrum exhibits a high energy band maximum at about 20000 cm^{-1}. The E//*b* spectrum shows a remarkable shoulder in the low energy region.

Molecular Projections. In general, the direction of the crystallographic axes (*a, b, c*) are not in agreement with that of the molecular coordinates (x, y, z) of $[CuN_4]$ chromophores. In order to resolve the discrepancy, the squares of the molecular projections,[6] which means the squares of the direction cosine of the electric vectors onto the molecular axes, averaged over the two molecules in the monoclinic unit cell are evaluated as described bellow:

14 (001)	$0.0755\ x^2 + 0.1506\ y^2 + 0.7738\ z^2$	(E⊥*b*)
	$0.7142\ x^2 + 0.1148\ y^2 + 0.1710\ z^2$	(E // *b*)
15 (001)	$0.0712\ x^2 + 0.01611\ y^2 + 0.7677\ z^2$	(E⊥*b*)
	$0.7141\ x^2 + 0.1154\ y^2 + 0.1705\ z^2$	(E // *b*)
1 (001)	$0.8782\ x^2 + 0.1218\ y^2 + 0.0001\ z^2$	(E⊥*b*)
	$0.0007\ x^2 + 0.0025\ y^2 + 0.9968\ z^2$	(E // *b*)
3 (001)	$0.0972\ x^2 + 0.5185\ y^2 + 0.3843\ z^2$	(E⊥*b*)
	$0.0104\ x^2 + 0.4543\ y^2 + 0.5354\ z^2$	(E // *b*)
11 (100)	$0.8086\ x^2 + 0.1915\ y^2 + 0.0000\ z^2$	(E⊥*b*)
	$0.0000\ x^2 + 0.0000\ y^2 + 1.0000\ z^2$	(E // *b*)

It should be noted that the squares of molecular projections are mainly z polarized for **14** and **15** exceptionally, while all three molecular axes have significant components for the other complexes. This implies that the *b* crystal axis is almost or exactly parallel to the molecular z axis for **14** and **15**, respectively.

Selection Rules. Since **14** and **15** (effective symmetry D_{2h}) and **11** (effective symmetry D_{4h}) are centrosymmetric, the d-d transitions obey a vibronic mechanism, by which transitions are allowed by coupling with ungerade normal vibrations. On the other hand, the d-d transitions are allowed or forbidden only by the symmetry of ground and excited states and electric vector for non-centrosymmmtric complexes **1** and **3** (effective symmetry C_{2v}). Selection rules for D_{2h}, D_{4h}, and C_{2v} point groups are summarized in Table 6-3. Figure 6-7 also shows band components deconvoluted by Gaussian functions and their composite spectra.

On account of the misalignment of the crystallographic axes and the molecular axes, all four possible transitions are vibronically allowed in both E//*b* and E⊥*b* polarized spectra for **14** and **15**. Since four nitrogens coordinate to copper atom along the molecular x and y axes, $d_{x2-y2}(a_{1g})$ orbital should be the highest half-filled orbital, while $d_{yz}(b_{3g})$ and $d_{zx}(b_{2g})$ orbitals should be in the lowest level. Whether the component of the lower energy shoulder is $d_{xy}(b_{1g})$ or $d_{z2}(a_{1g})$ is still uncertain at present. The $d_{yz}(b_{3g})$ and $d_{zx}(b_{2g})$ orbitals could not be separated by AOM calculations as well as desolution of the observed spectra, so that these orbitals were treated as accidentally degenerated orbitals. Thus the spectra are expected to be consist of three components, $^2B_{1g}(xy)\leftarrow{}^2A_{1g}(x^2\text{-}y^2)$, $^2A_{1g}(z^2)\leftarrow{}^2A_{1g}(x^2\text{-}y^2)$, and accidentally degenerated $^2B_{2g}(zx)\leftarrow{}^2A_{1g}(x^2\text{-}y^2)$ and $^2B_{3g}(yz)\leftarrow{}^2A_{1g}(x^2\text{-}y^2)$.

The spectra of **1** show dichroism clearly resolved depending on the polarizations. Selection rule for C_{2v} point group requires $^2A_2(xy)\leftarrow{}^2A_1(x^2\text{-}y^2)$ transition to be forbidden in all x, y, and z polarizations. The molecular projections imply that the electric vector of E//*b* spectrum is almost parallel to the molecular z axis, while the electric vector of E⊥*b* spectrum lies on a molecular xy plane. The weak 16000 cm^{-1} band in the E//*b* spectrum can be assigned to be $^2A_1(z^2)\leftarrow{}^2A_1(x^2\text{-}y^2)$ transition, because only this transition is allowed and the rest of the transitions are forbidden in z polarization. On the contrary, $^2A_1(z^2)\leftarrow{}^2A_1(x^2\text{-}y^2)$ and $^2A_2(xy)\leftarrow{}^2A_1(x^2\text{-}y^2)$ transitions are absent in the E⊥*b* spectrum, so that the intense 18000 cm^{-1} band in E⊥*b* spectrum may be composeed of $^2B_1(zx)\leftarrow{}^2A_1(x^2\text{-}y^2)$ and $^2B_2(yz)\leftarrow{}^2A_1(x^2\text{-}y^2)$ transitions which are allowed in x and y poralizations, respectively. In summary, the spectrum of **1** contains three bands: $^2A_1(z^2)\leftarrow{}^2A_1(x^2\text{-}y^2)$ of the lowest energy band, and $B_1(zx)\leftarrow{}^2A_1(x^2\text{-}y^2)$ and $^2B_2(yz)\leftarrow{}^2A_1(x^2\text{-}y^2)$ transitions.

In contrast to **1**, the misalignment between the crystal and molecular axes enables three $^2A_1(z^2)\leftarrow{}^2A_1(x^2-y^2)$, $B_1(zx)\leftarrow{}^2A_1(x^2-y^2)$, and $^2B_2(yz)\leftarrow{}^2A_1(x^2-y^2)$ to be allowed for the spectra of **3** with both *E//b* and E⊥*b* polarized lights. Selection rules for C_{2v} point group also request the absence of the forbidden $A_2(xy)\leftarrow{}^2A_1(x^2-y^2)$ transition in any polarization. No further information on assignment or orbital sequences can be given from these polarized crystal spectra.

The spectra of **11** show slight anisotropy in virtue of the agreement with the crystallographic *b* axis and the molecular z axis. On the assumption of D_{4h} point group, three transitions of $^2A_{1g}(z^2)\leftarrow{}^2B_{1g}(x^2-y^2)$, $^2B_{2g}(xy)\leftarrow{}^2B_{1g}(x^2-y^2)$, and $^2E_g(yz,\ zx)\leftarrow{}^2B_{1g}(x^2-y^2)$ are vibronically allowed in x and y polarizations, while two transitions of $^2A_{1g}(z^2)\leftarrow{}^2B_{1g}(x^2-y^2)$ and $^2E_g(yz,\ zx)\leftarrow{}^2B_{1g}(x^2-y^2)$ are vibronically allowed in z polarization. The *E//b* spectrum having low energy shoulder with z polarization is composed of three $A_{1g}(z^2)\leftarrow{}^2B_{1g}(x^2-y^2)$, $^2B_{2g}(xy)\leftarrow{}^2B_{1g}(x^2-y^2)$, and $^2E_g(yz,\ zx)\leftarrow{}^2B_{1g}(x^2-y^2)$ transitions. The shoulder disappears for the E⊥*b* spectrum which contains two vibronically allowed transitions $^2A_{1g}(z^2)\leftarrow{}^2B_{1g}(x^2-y^2)$ and $^2E_g(yz,\ zx)\leftarrow{}^2B_{1g}(x^2-y^2)$ in x and y polarizations. Hence the pronounced shoulder at 16000-17000 cm^{-1} can be assigned to $^2B_{2g}(xy)\leftarrow{}^2B_{1g}(x^2-y^2)$ transition. That four coordination nitrogen atoms lie on the molecular x and y axes suggests that the ground state is $^2E_g(yz,\ zx)$. Therefore 3d orbital sequence of **11** is tentatively determined to be $d_{x2-y2}(b_{1g}) > d_{xy}(b_{2g}) > d_{z2}(a_{1g}) > d_{yz,zx}(e_g)$ on the basis of the polarized crystal spectra.

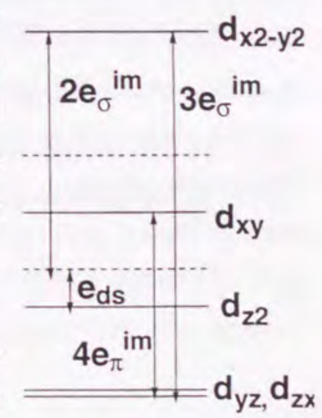
Assignment of d-d Transitions by AOM. The diffuse reflectance and polarized single crystal spectra are desolved using Gaussian function into several band components estimated by selection rules. Table 6-4 gives observed transition energies by polarized crystal spectra and calculated transition energies by AOM. Details of deconvolution of polarized crystal spectra by Gaussian curve fitting are summarized in Table 6-5, and the diffuse reflectance spectra are also deconvoluted in a similar way to the polarized crystal spectra.

In order to determine detailed assignment of individual d-d transitions, calculated transition energies were evaluated by using AOM to reproduce observed transition energies from polarized crystal spectra not to conflict the tentative assignment. The following points are prerequisite for determination of respective AOM parameters.

For a series of *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes (**14**, **15**, **1**, and **3**), the degree of distortion of [CuN_4] choromophores from square planar to distorted square planar should be taken into consideration for AOM calculations.[24] Distortion angles θ_{im} and θ_{am} defined in Figure 5-6 are used for description of degree of distortion. These values are set on the ground of their crystal structures. In contrast, rotation angles (ψ) around the Cu-N(imidate) bond axes are fixed to $\psi = 90\ ^\circ$.

Ligand field strength of imidates and amines are described by e_σ^{im}, e_π^{im}, and e_σ^{am} parameters. The e_σ^{im} and e_σ^{am} parameters are related to σ-bonding interaction along the Cu-N coordination bond for imidates and amines, respectively, while e_π^{im} parameter is related to π-bonding of Cu-N coordination bonds formed by p-lone pair distributing perpendicular to imidate ring. The π-bonding interaction being perpendicular to the direction of e_π^{im} parameter was not considered, and anisotropy of π-bonding interaction made by imidate ligands was described by single e_π^{im} parameter. Moreover, the π-bonding interaction was negligible for amine ligands. For the present calculations, transferability of AOM parameters are accepted, in other words, the same ligands of the different complexes are described by the same values of e parameters similarly to assignment I for Cu(acac)$_2$ complexes. The variation in θ_{im} and θ_{am} for fixed values of e_σ^{im}, e_π^{im}, and e_σ^{am} parameters and $\theta_{im}=\theta_{am}$ are shown in Figure 6-9 calculated for *trans*-[Cu(phent)$_2$(phenea)$_2$] complexes. The e_σ^{im} and e_π^{im} values used are 7200 cm^{-1} and 1700 cm^{-1} for 5,5-diphenylhydantoinate and 7100 cm^{-1} and 1500 cm^{-1} for succinimidate, respectively. As for e_σ^{am} parameter, the values $e_\sigma^{am} = 6300\ cm^{-1}$ and 6700 cm^{-1} are set for 1-phenylethylamine and 1-cyclohexylethylamine, respectively.

An extra parameter e_{ds} should be used for AOM calculations to account for ds-mixing, that is configuration interaction between $3d_{z2}$ (a_{1g}) and 4s (a_{1g}) orbitals (D_{4h} point group). The e_{ds} parameters are difficult to estimate because they decrease the energies of $d_{z2}\rightarrow d_{x2-y2}$ which is hard to separate in any polarization of polarized crystal spectra. Hence ambiguities related to the transition remain for the assignment of $[CuCl_4]^{2-}$ or [CuO_4] chromophores. Fortunately, the separated band observed in the *E//b* spectrum of **1** in z polarization is assigned to $^2A_1(z^2)\leftarrow{}^2A_1(x^2-y^2)$ transition. From this clue, the e_{ds} parameter is determined to be 2900 cm^{-1} for **1** using the rest parameters of constant values. The ds-mixing is especially important for the square planar complexes and tetrahedral distortion reduce the interaction. In fact less distorted square planar complex **3** is set $e_{ds} = 4000\ cm^{-1}$, and as for square planar complexes, $e_{ds} = 6300\ cm^{-1}$ for **14** and **15**, $e_{ds} = 4500\ cm^{-1}$ for **11**, and $e_{ds} = 4000\ cm^{-1}$ for **16**, **17**, and **18**.

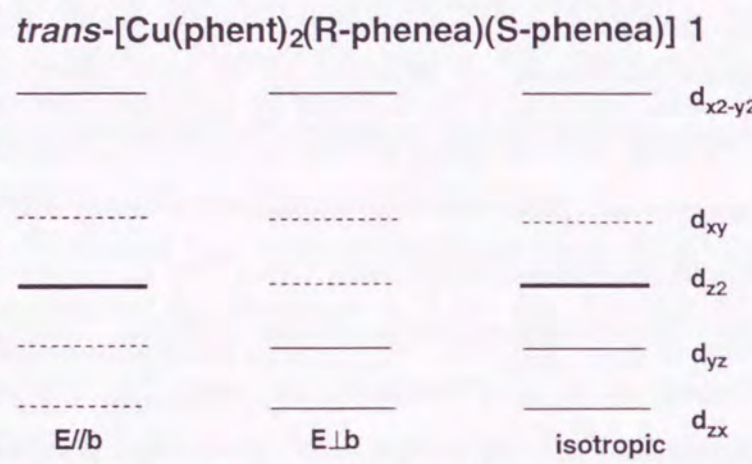


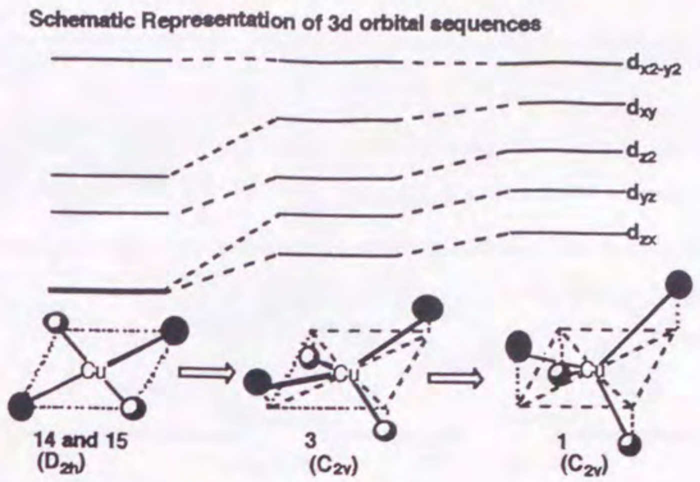
For example, transition energies of each orbital of square planar $Rb_2[Cu(succim)_4]\cdot 2H_2O$ (**11**) having four imidate lignads, can be written within the AOM framework by substitution of geometric and electronic parameters as follows:

$$E(d_{xy}) = 3e_\sigma^{im} - 4e_\pi^{im},\ E(d_{z2}) = 2e_\sigma^{im} + e_{ds},\ E(d_{yz,zx}) = 3e_\sigma^{im}.$$

Using the values as mentioned above, we obtained calculated transition energies and establish the assignment of d-d transitions given in Table 6-4. The agreement between experimental and calculated values are excellent for each complex.

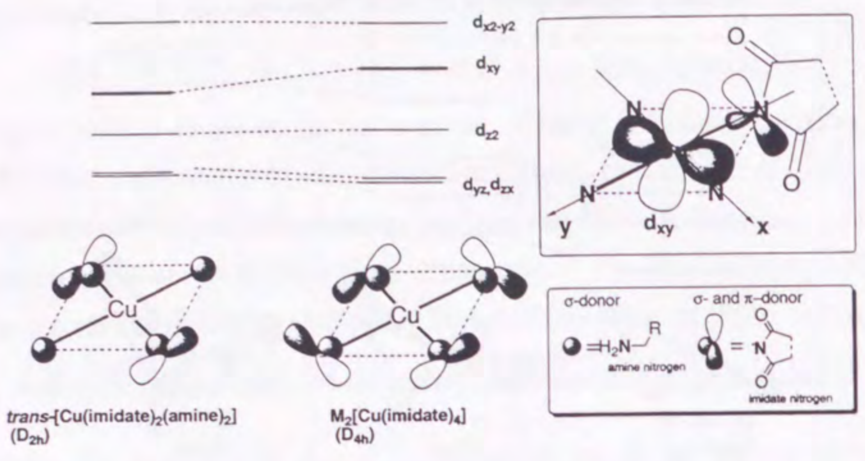
3d Electronic States and Bonding Property. The primary difficulty in establishing the assignment of square planar copper(II) complexes is the determination of $d_{z2} \rightarrow d_{x2-y2}$ transition related to AOM ds-mixing parameters(e_{ds}). In the case of $[CuCl_4]^{2-}$ chromophores, the band due to $d_{z2} \rightarrow d_{x2-y2}$ transition lies in the highest energy region separately, that enables to be assigned the band. In contrast, $[CuO_4]$ or $[CuN_4]$ complexes appear a single broad band containing all the three transitions. Our strategy to separate and assign the transition is lowering the effective symmetry by gradual distorting the $[CuN_4]$ chromophores for a series of *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes. Square planar complexes **14** and **15** (effective symmetry D_{2h}) obey vibronic mechanism, while distorted square planar **1** and **3** (effective symmetry C_{2v}) obey orbital symmetry selection rules. The former activates all the three transitions, however, the latter may enable to be assigned each transition by individual polarizations. Fortunately, the strategy was valid to decrease the number of allowed transition, in fact, the spectrum of **1** with *E//b* polarization appear the $d_{z2} \rightarrow d_{x2-y2}$ transition separately, because of appropriate crystal packing with approximately agreement between the *b* crystal axis and z molecular axis. On the basis of certain assignment for **1**, square planar complexes (**14** and **15**) could be also assigned without changing the 3d orbital sequences. The ratios of e_{ds}/e_σ^{im} are 0.88 for **14**(and **15**), 0.40 for **1**, 0.56 for **3**, 0.63 for **11**, and 0.56 for **16** (and **17**, and **18**), which also implies that ds-mixing is effective for square planar complexes.





For all the present complexes, the same ligand could be described by the same AOM parameters. The variation of the structures such as geometrical distortion of the $[CuN_4]$ chromophores (as mentioned above) and the combination of imidates and amines (*e.g. trans*-[Cu(imidate)$_2$(amine)$_2$] and M_2[Cu(imidate)$_4$]) could be described consistently. If the values of these parameters are varied, the transition energies will be changed as indicated in Figure 6-8 for example for **11**. To out knowledge, the present study is the first case which treats imidate ligands, and the e_σ^{im} and e_π^{im}parameters are determined emprically for the first time. The present e_σ^{am} parameters for 1-phenylethylamine (6300 cm^{-1}) and 1-cyclohexylethylamine (6700 cm^{-1}) are consistent with the value for general primary amine (6400 cm^{-1}) reported by Comba et al.[25] that may also support the validity of transferability of AOM parameters for copper(II) complexes.

In this context, it is reasonable that two imidate ligands are described by similar e_σ^{im} and e_π^{im} values and the ratio of $e_\sigma^{im}/e_\pi^{im} = 4.24$ and 4.73 for 5,5-diphenylhydantoinate and succinimidate, respectively. The e_π^{im} parameters correspond to p-lone pair which is perpendicular to a imidate ring. The imidate p-lone pair forms π-bonding being oriented at d_{xy} orbital and that in-plane of $[CuN_4]$ coordination plane which lower the energy of $d_{xy} \rightarrow d_{x2-y2}$ transition (see Table 6-4). The increase in the numbers of imidates by two *trans*-[Cu(imidate)$_2$(amine)$_2$] to M_2[Cu(imidate)$_4$] results in remarkable shoulder of the spectra of **11**. The present resultes is in agreement with the comparison of the spectra of [Cu(deen)$_2$](NO$_3$)$_2$ (four amine nitrogens) and Cs_2[Cu(succim)$_4$]·2H_2O reported by Walsh et al..[11)] The in-plane π-bonding is a characteristic feature for monodentate imidate ligands, because the nitrogen atoms are directed to out-of the $[CuN_4]$ coordination plane for chelate ligands such as biuret or macrocyclic ligands. Hathaway et al. stated that the π-bonding donor character contributed to the formation of a square planar $[CuN_4]$ coordination geometry, and this was also to be electronic reason for the present complexes.



6.4 Conclusion.

Copper(II) complexes *trans*-[Cu(phent)$_2$(R-chea)(S-chea)] (**14**), *trans*-[Cu(phent)$_2$(R-chea)$_2$] (**15**), and Rb_2[Cu(succim)$_4$]·$2H_2O$ (**11**) have been prepared and the crystal structures have been determined. The electronic polarized single crystal spectra were determined for **14**, **15**, *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (**1**), *trans*-[Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (3), and **11** and the corresponding diffuse reflectance spectra for these complexes and K_2[Cu(phent)$_4$]·$8H_2O$ (**16**) Rb_2[Cu(phent)$_4$]·$6H_2O$ (**17**), and Cs_2[Cu(phent)$_4$]·$10H_2O$ (**18**). Taking into account for molecular projections of electric vectors these spectra were deconvoluted three bands according to selection rules for each point group by means of Gaussian curve fitting. The following 3d orbital sequences are as follows: d_{x2-y2} (a_g) > d_{xy} (b_{1g}) > d_{z2} (a_{1g}) > d_{yz} (b_{3g}), d_{zx} (b_{1g}) for square planar **14** and **15** (D_{2h} point group), d_{x2-y2} (b_{1g}) > d_{xy} (b_{2g}) > d_{z2} (a_{1g}) > d_{yz}, d_{zx} (e_g) for square planar **11** (D_{4h} point group), and d_{x2-y2} (a_1) > d_{xy} (a_2) > d_{z2} (a_1) > d_{yz} (b_2) >d_{zx} (b_1) for distorted square planar **1** and **3** (C_{2v} point group). The $d_{z2} \rightarrow d_{x2-y2}$ transition related to ds-mixing could be observed separately in z polarization for **1**. That enabled us to establish reliable assignment for the present [CuN_4] complexes. Tetrahedral distortion of [CuN_4] chromophore results in decreasing the peak wave number of the spectra, and the detailed features were explained by each orbital level for a series of *trans*-[Cu(phent)$_2$(amine)$_2$] complexes (**14**, **15**, **1**, and **3**). As for square planar complexes, in-plane π−bonding character due to p-lone pair of imidate ligand were argued within AOM framework, that reflected the difference between *trans*-[Cu(imidate)$_2$(amine)$_2$] (**14** and **15**) and M_2[Cu(imidate)$_4$] (**11**, **16**, **17**, and **18**) complexes.

Table 6-1. Crystallographic data for **14**, **15** and **11**.

	14	**15**	**11**
Formula	$C_{46}H_{56}N_6CuO_4$	$C_{46}H_{56}N_6CuO_4$	$C_{16}H_{20}N_4CuO_{10}Rb_2$
Molecular weight	820.53	820.53	662.84
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1$ (#4)	$C2/m$ (#12)
a / Å	8.485(2)	8.472(2)	16.279(4)
b / Å	9.7854(8)	9.803(2)	8.382(3)
c / Å	26.334(4)	26.331(6)	8.297(3)
β / °	92.83(1)	92.67(2)	93.13(3)
V / Å^3	2183.8(5)	2184.6(8)	1130.4(6)
Z	2	2	2
D_c / g cm^{-3}	1.248	1.247	1.947
F(000)	870	870	2616
μ/ cm^{-1}	10.90	10.89	211.84
	(Cu Kα)	(Cu Kα)	(Mo Kα)
$2\theta_{max}$ / °	119.9	119.9	55.0
Crystal dimensions / mm	0.25x0.20x0.10	0.20x0.20x0.20	0.30x0.30x0.20
Temperature / K	298	298	296
No. of measured reflections	3140	2916	1485
No. of unique reflections	2878	2652	1393
No. of reflections used in refinement	2323	2190	1027
	[I>2.0σ(I)]	[I>2.0σ(I)]	[I>3.0σ(I)]
No. of parameters	260	335	86
g. o. f.	4.95	4.08	1.64
R [a)]	0.068	0.080	0.030
R_w [b)]	0.076	0.074	0.033

[a)] $R=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b)] $R_w=(\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$.

Weighting scheme: $w = 1/(\sigma^2(F_o))$

Table 6-2. Selected bond distances (Å) and angles (°) for **14**, **15**, **1**, **3**, and **11**.

	14	**15**	**1**	**3**		**11**
Bond Distances					**Bond Distances**	
Cu(1)-N(1) (imidate)	1.980(4)	2.02(1)	1.988(3)	2.009(4)	Cu(1)-N(1) (imidate)	1.996(4)
Cu(1)-N(3) (amine)	2.022(4)	2.05(1)	2.012(3)	1.993(3)	Cu(1)-N(2) (imidate)	1.970(3)
Cu(1)-N(4) (imidate)		1.97(1)	1.997(3)	1.993(3)		
Cu(1)-N(6) (amine)		2.01(1)	2.019(3)	2.030(4)		
Bond Angles					**Bond Angles**	
N(1)-Cu(1)-N(3)	90.8(2)	90.7(6)	91.9(2)	93.2(2)	N(1)-Cu(1)-N(2)	91.6(2)
N(1)-Cu(1)-N(6)		89.2(5)	92.4(2)	92.7(2)	N(1)-Cu(1)-N(2*)	88.4(2)
N(3)-Cu(1)-N(4)		89.6(5)	92.6(2)	89.4(2)		
N(1*)-Cu(1)-N(3)	89.2(2)					
N(4)-Cu(1)-N(6)		90.6(6)	91.8(2)	88.5(2)		
N(1)-Cu(1)-N(4)		178.2(6)	154.9(2)	166.6(2)		
N(1)-Cu(1)-N(1*)	180.0				N(1)-Cu(1)-N(1*)	180.0
N(3)-Cu(1)-N(6)		176.6(6)	159.8(2)	163.2(2)		
N(3)-Cu(1)-N(3*)	180.0				N(2)-Cu(1)-N(2*)	180.0

Table 6-3. Selection rule of vibronic coupling (D_{2h} and D_{4h}) orbital symmetry (C_{2v}) mechanism. $\langle\phi_e|r_i|\phi_g\rangle$ means direct product of wave functions for ground (ϕ_g) and excited (ϕ_e) state and direction of electronic dipole moment (r_i; i=x, y, and z). The transition of which product contains totally symmetry representation is allowed in terms of orbital symmetry. As for centrosymmetric point group (D_{2h} and D_{4h}), the transitions are allowed by coupling with ungerade vibrations in the polarization of the direction of electronic dipole moment.

D_{2h} Symmetry

transitions	$\langle\phi_e|r_i|\phi_g\rangle$			vibration modes			
	i= x	y	z	B_{1u}	A_u	B_{2u}	B_{3u}
$^2A_{1g}(z^2)\leftarrow{}^2A_g(x^2-y^2)$	B_{3u}	B_{2u}	B_{1u}	z	-	x	y
$^2B_{1g}(xy)\leftarrow{}^2A_g(x^2-y^2)$	B_{2u}	B_{3u}	A_u	-	z	y	x
$^2B_{3g}(yz)\leftarrow{}^2A_g(x^2-y^2)$	A_u	B_{1u}	B_{2u}	y	x	-	z
$^2B_{2g}(zx)\leftarrow{}^2A_g(x^2-y^2)$	B_{1u}	A_u	B_{3u}	x	y	z	-

D_{4h} Symmetry

transitions	$\langle\phi_e|r_i|\phi_g\rangle$		vibration modes		
	i= z	x, y	A_{1u}	B_{2u}	E_u
$^2A_{1g}(z^2)\leftarrow{}^2B_{1g}(x^2-y^2)$	B_{2u}	E_u	-	z	x, y
$^2B_{2g}(xy)\leftarrow{}^2B_{1g}(x^2-y^2)$	A_{1u}	E_u	-	-	x, y
$^2E_g(yz, zx)\leftarrow{}^2B_{1g}(x^2-y^2)$	E_u	$A_{1u}+A_{2u}B_{1u}+B_{2u}$	x, y	x, y	z

C_{2v} Symmetry

transitions	$\langle\phi_e|r_i|\phi_g\rangle$		
	i= x	y	z
$^2A_1(z^2)\leftarrow{}^2A_1(x^2-y^2)$	B_1	B_2	A_1
$^2A_2(xy)\leftarrow{}^2A_1(x^2-y^2)$	B_2	B_1	A_2
$^2B_2(yz)\leftarrow{}^2A_1(x^2-y^2)$	A_2	A_1	B_2
$^2B_1(zx)\leftarrow{}^2A_1(x^2-y^2)$	A_1	A_2	B_1

Table 6-4. Observed transition energies (cm^{-1}) deconvoluted by Gaussian curve fitting of polarized crystal spectra and reflectance spectra and calculated transition energies (cm^{-1}) by AOM.

14		$^2B_{3g}(yz),^2B_1(zx)\leftarrow^2A_g(x^2-y^2)$	$^2A_{1g}(z^2)\leftarrow^2A_g(x^2-y^2)$	$^2B_{1g}(xy)\leftarrow^2A_g(x^2-y^2)$
	E⊥*b*	20900	20100	17300
	E//*b*	20900	20100	17400
	reflectance	21400	20700	17500
	AOM	*20900*	*20200*	*17500*
15		$^2B_{3g}(yz),^2B_1(zx)\leftarrow^2A_g(x^2-y^2)$	$^2A_{1g}(z^2)\leftarrow^2A_g(x^2-y^2)$	$^2B_{1g}(xy)\leftarrow^2A_g(x^2-y^2)$
	E⊥*b*	20900	20100	17200
	E//*b*	20900	20100	17300
	reflectance	21400	20700	17500
	AOM	*20900*	*20200*	*17500*
1		$^2B_1(zx)\leftarrow^2A_1(x^2-y^2)$	$^2B_2(yz)\leftarrow^2A_1(x^2-y^2)$	$^2A_1(z^2)\leftarrow^2A_1(x^2-y^2)$
	E⊥*b*	18400	17900	-
	E//*b*	-	-	16100
	reflectance	18800	17400	15700
	AOM	*18900*	*17700*	*16100*
3		$^2B_1(zx)\leftarrow^2A_1(x^2-y^2)$	$^2B_2(yz)\leftarrow^2A_1(x^2-y^2)$	$^2A_1(z^2)\leftarrow^2A_1(x^2-y^2)$
	E⊥*b*	19500	18500	17500
	E//*b*	19500	18500	17500
	reflectance	19400	18800	17700
	AOM	*19800*	*18900*	*17500*
11		$^2E_g(yz, zx)\leftarrow^2B_{1g}(x^2-y^2)$	$^2A_{1g}(z^2)\leftarrow^2B_{1g}(x^2-y^2)$	$^2B_{2g}(xy)\leftarrow^2B_{1g}(x^2-y^2)$
	E⊥*b*	21000	19000	15800
	E//*b*	20900	18700	-
	reflectance	21200	19000	15800
	AOM	*21300*	*18700*	*15300*
16	reflectance	21200	18700	15600
17	reflectance	21200	18800	15700
18	reflectance	21600	18800	15500
	AOM	*21600*	*18400*	*14800*

Table 6-5. Deconvoluted components (maximum wave numbers (cm^{-1}), absorbance in arbitrary unit(the spectra are expanded and parallel translated values for calculations), and half width (cm^{-1})) by Gaussian curve fitting of polarized crystal spectra for **14**, **15**, **1**, **3**, and **11**.

complexes	spectra	wave number /cm^{-1}	arbitrary absorbance	half width /cm^{-1}
14	E⊥*b*	17300	18.16	2700
		20100	19.66	3600
		20900	23.12	3500
	E//*b*	17400	24.81	2700
		20100	25.58	3600
		20900	26.94	3400
15	E⊥*b*	17200	43.79	2800
		20100	46.91	3700
		20900	41.11	3700
	E//*b*	17300	17.61	2600
		20100	24.04	3500
		20900	19.71	3600
1	E⊥*b*	17900	88.06	4700
		18400	88.86	2900
	E//*b*	16100	68.17	3800
3	E⊥*b*	17500	18.72	4000
		18500	18.32	3200
		19500	18.26	5000
	E//*b*	17500	10.37	3000
		18500	27.05	4300
		19500	30.00	3500
11	E⊥*b*	15800	47.06	2500
		19000	80.75	2600
		21000	136.29	3300
	E//*b*	18700	18.35	3200
		20900	12.50	3700

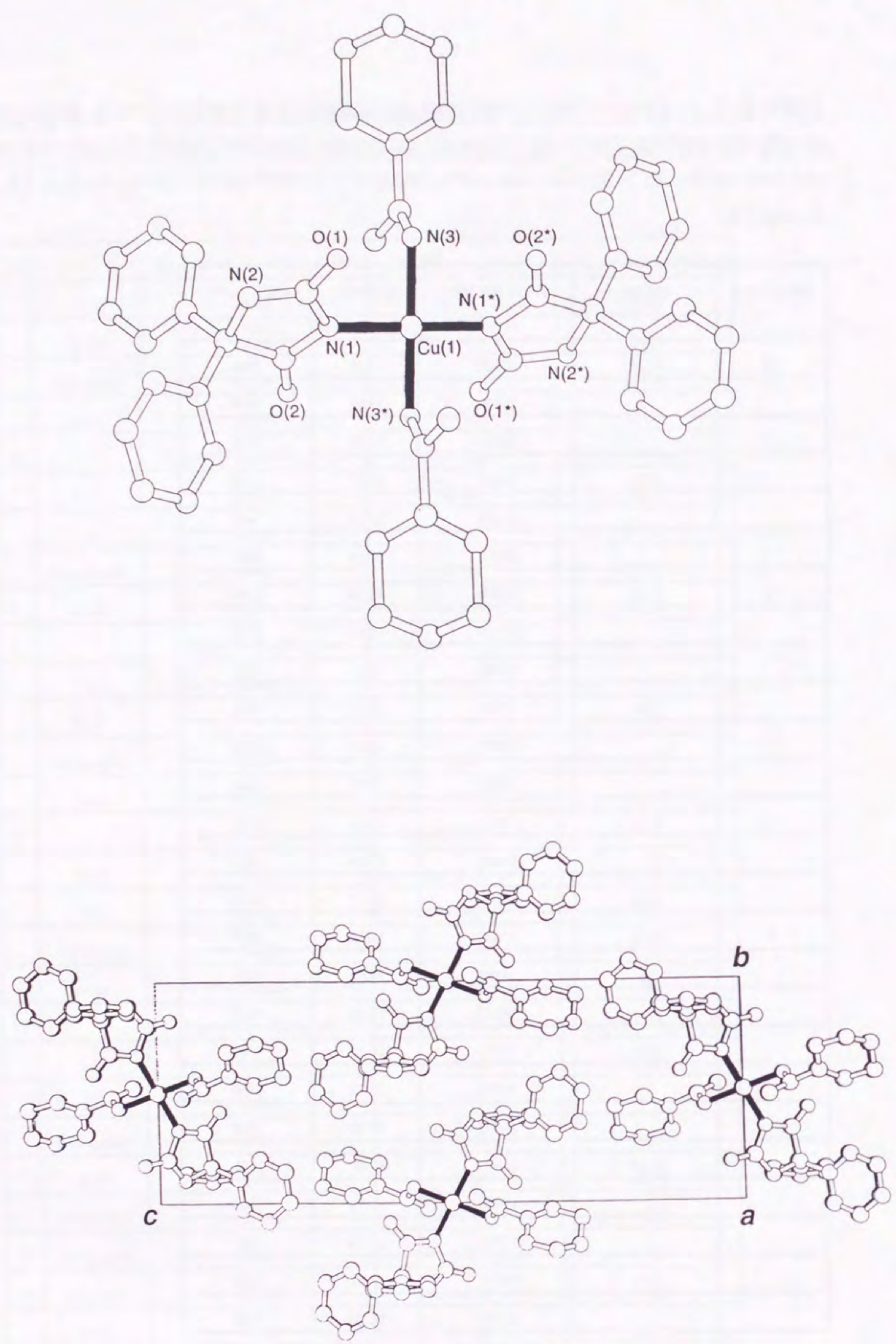


Figure 6-1. Molecular structure of *trans*-[Cu(phent)$_2$(R-chea)(S-chea)] (*meso* form) (**14**) [above], and crystal structure of **14** viewed down the crystallographic *a* axis [below].

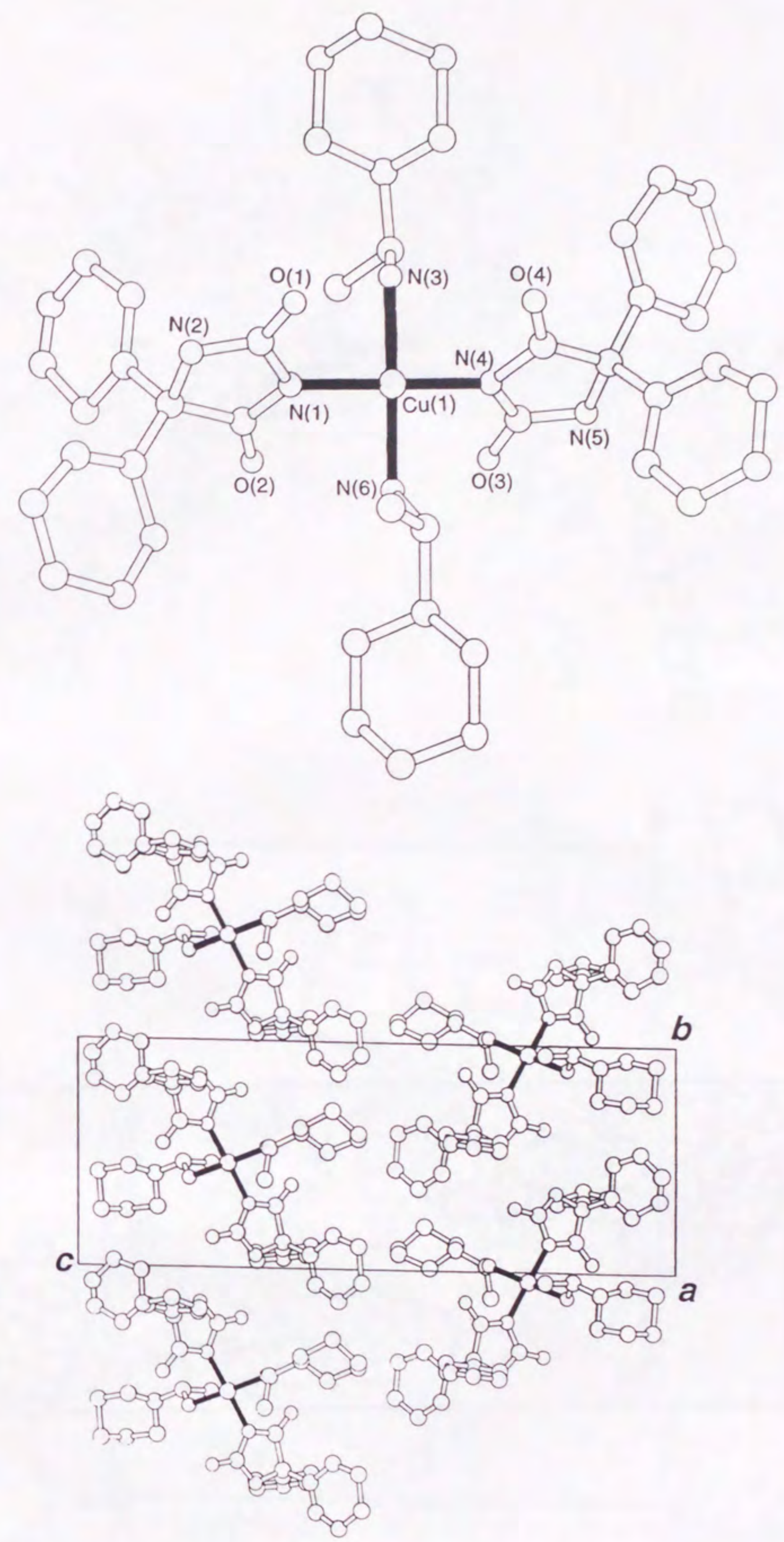


Figure 6-2. Molecular structure of *trans*-[Cu(phent)$_2$(R-chea)$_2$] (*optically active* form) (**15**) [above], and crystal structure of **15** viewed down the crystallographic *a* axis [below].

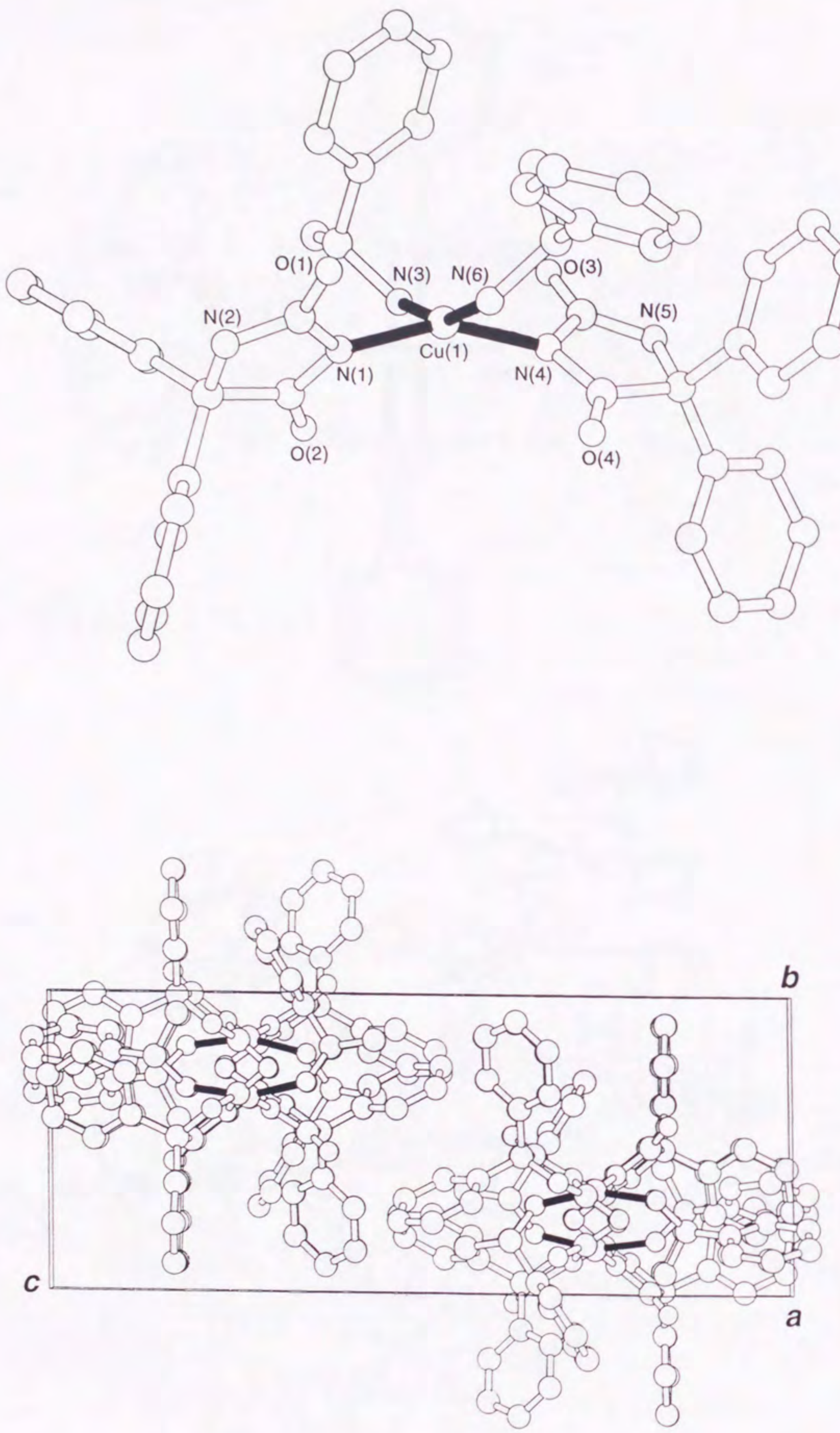


Figure 6-3. Molecular structure of *trans*-[Cu(phent)$_2$(R-phenea)(S-phenea)] (*meso* form) (**1**) [above], and crystal structure of **1** viewed down the crystallographic *a* axis [below].

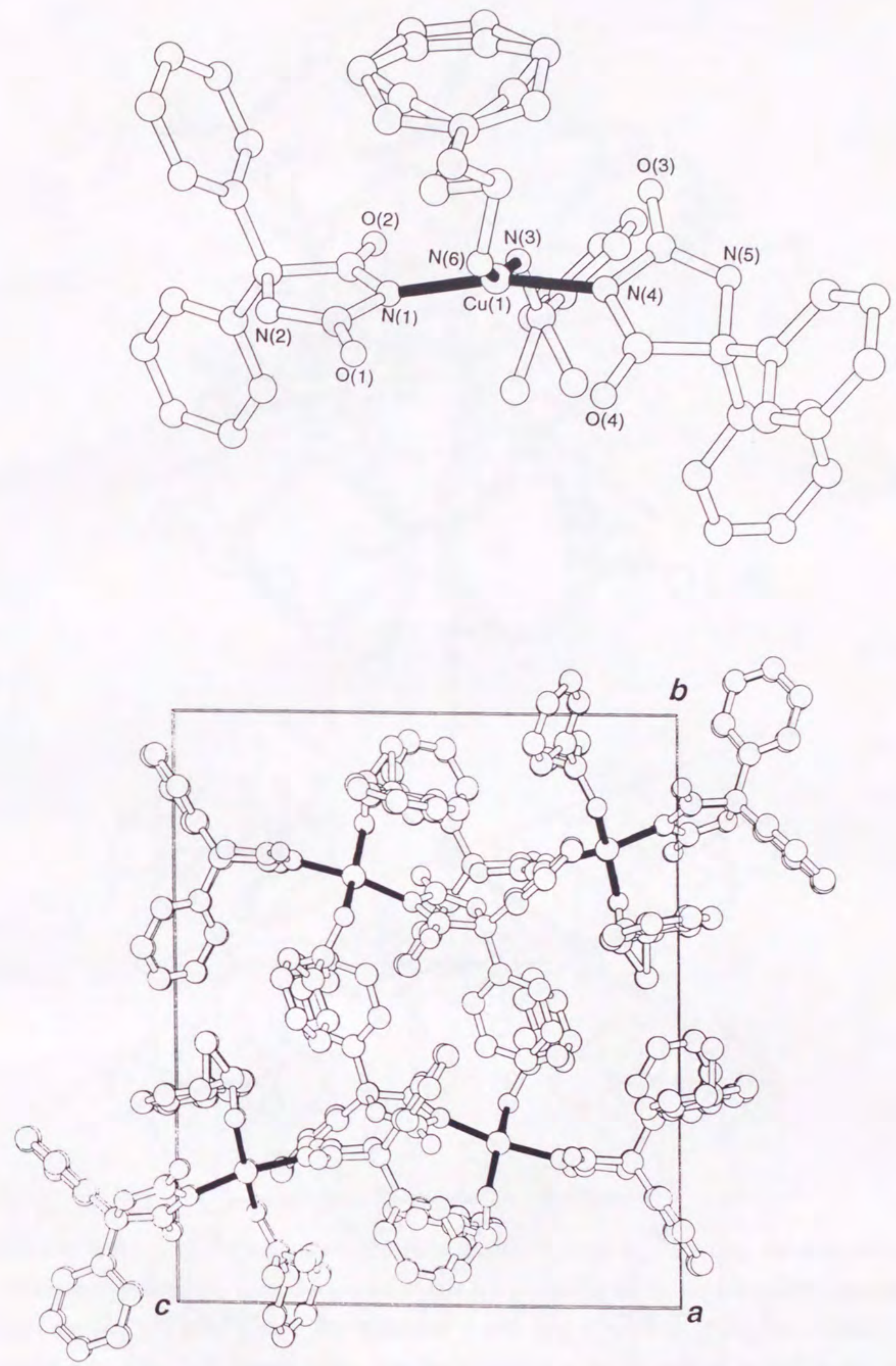


Figure 6-4. Molecular structure of *trans*-[Cu(phent)$_2$(R-phenea)$_2$][Cu(phent)$_2$(S-phenea)$_2$] (*racemic* form) (**3**) [above], and crystal structure of **3** viewed down the crystallographic *a* axis [below].

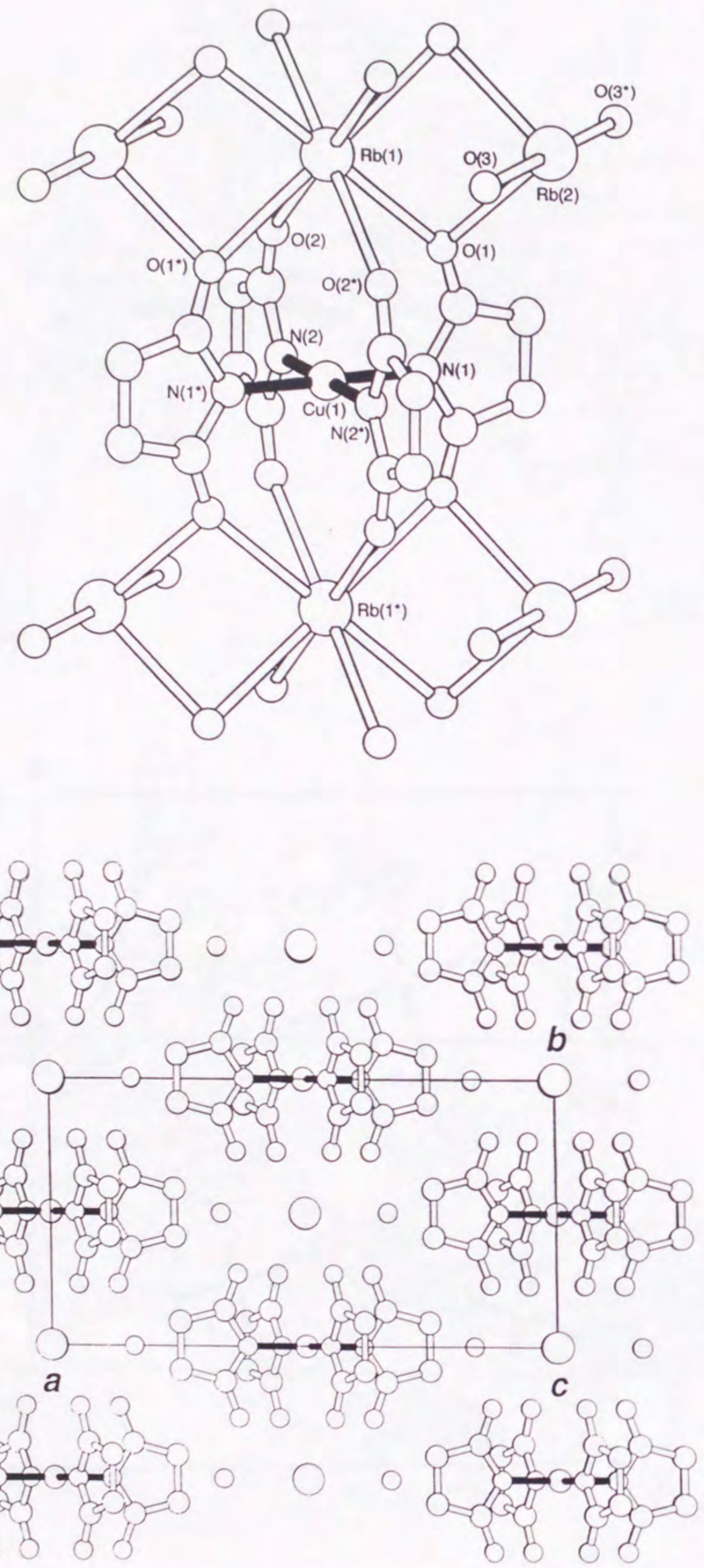


Figure 6-5. Molecular structure of $Rb_2[Cu(succim)_4]\cdot 2H_2O$ (**11**) [above], and crystal structure of **11** viewed down the crystallographic *a* axis [below].

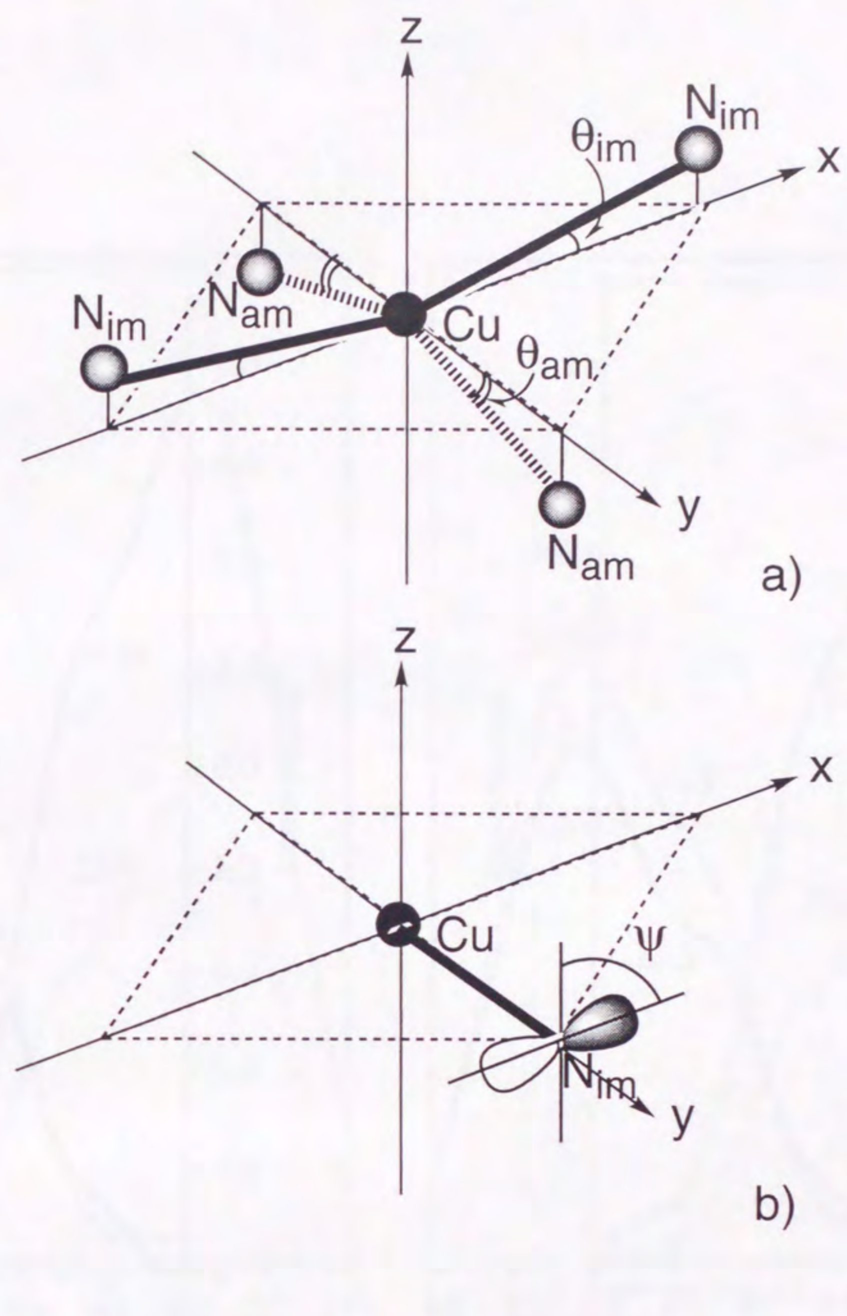


Figure 6-6. a) Definitions of distortion angles θ_{im} and θ_{am} showing the molecular coordinate systems (x, y, z). Molecular x axis is a projection of the Cu-N(imidate) vector onto the $[CuN_4]$ mean plane, the molecular y axis is a projection of the Cu-N(amine) vector onto the $[CuN_4]$ mean plane, and the molecular z axis is normal to both x and y axis. The distortion angles θ_{im} and θ_{am} describe angles between the Cu-N(imidate) vector and the x axis and the Cu-N(amine) vector and the y axis, respectively. b) Definition of distortion angles ψ around the Cu-N(imidate) axes.

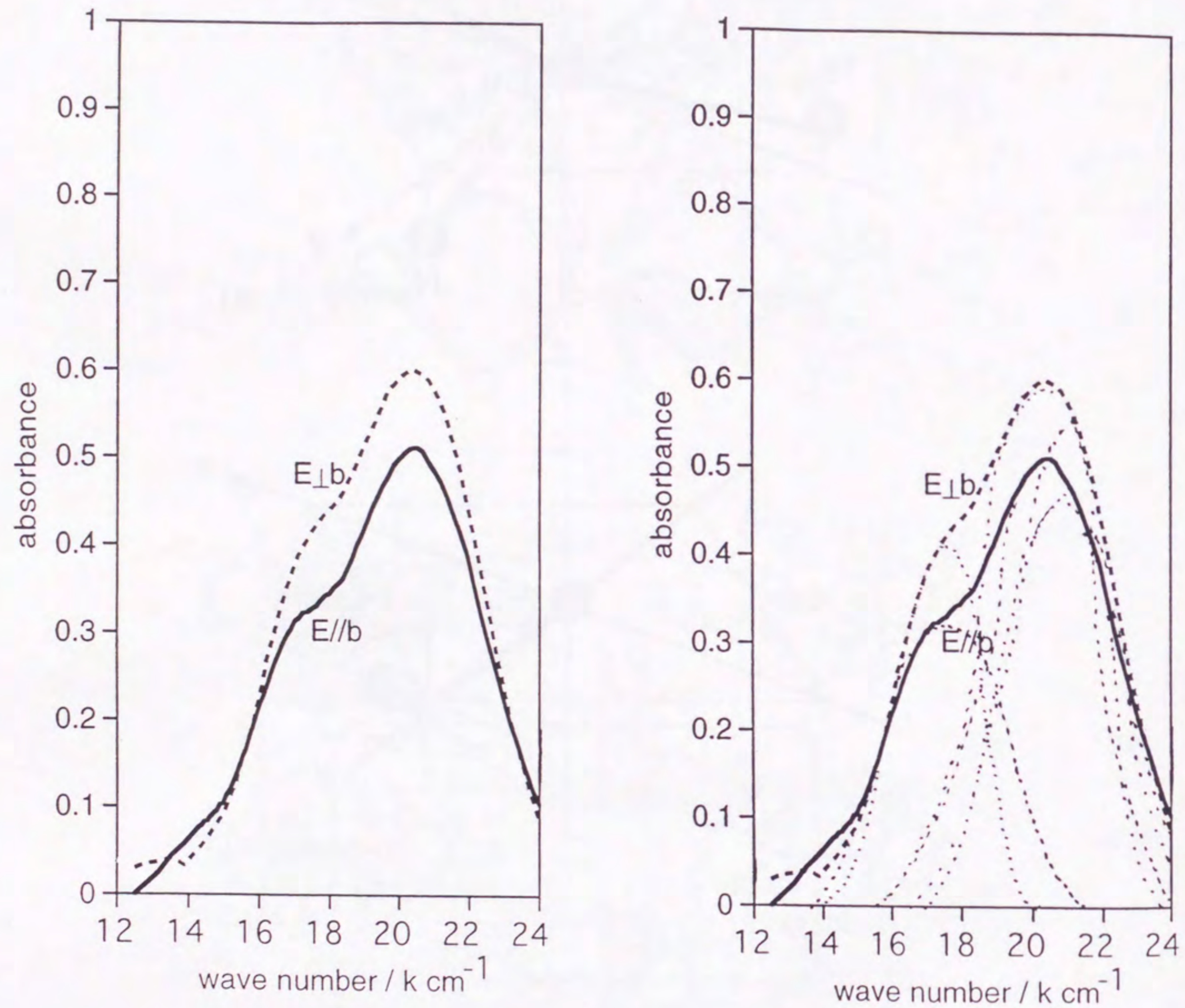


Figure 6-7-a. The polarized crystal spectra of **14** determined from (001) face with E//*b* and E⊥*b* polarizations.

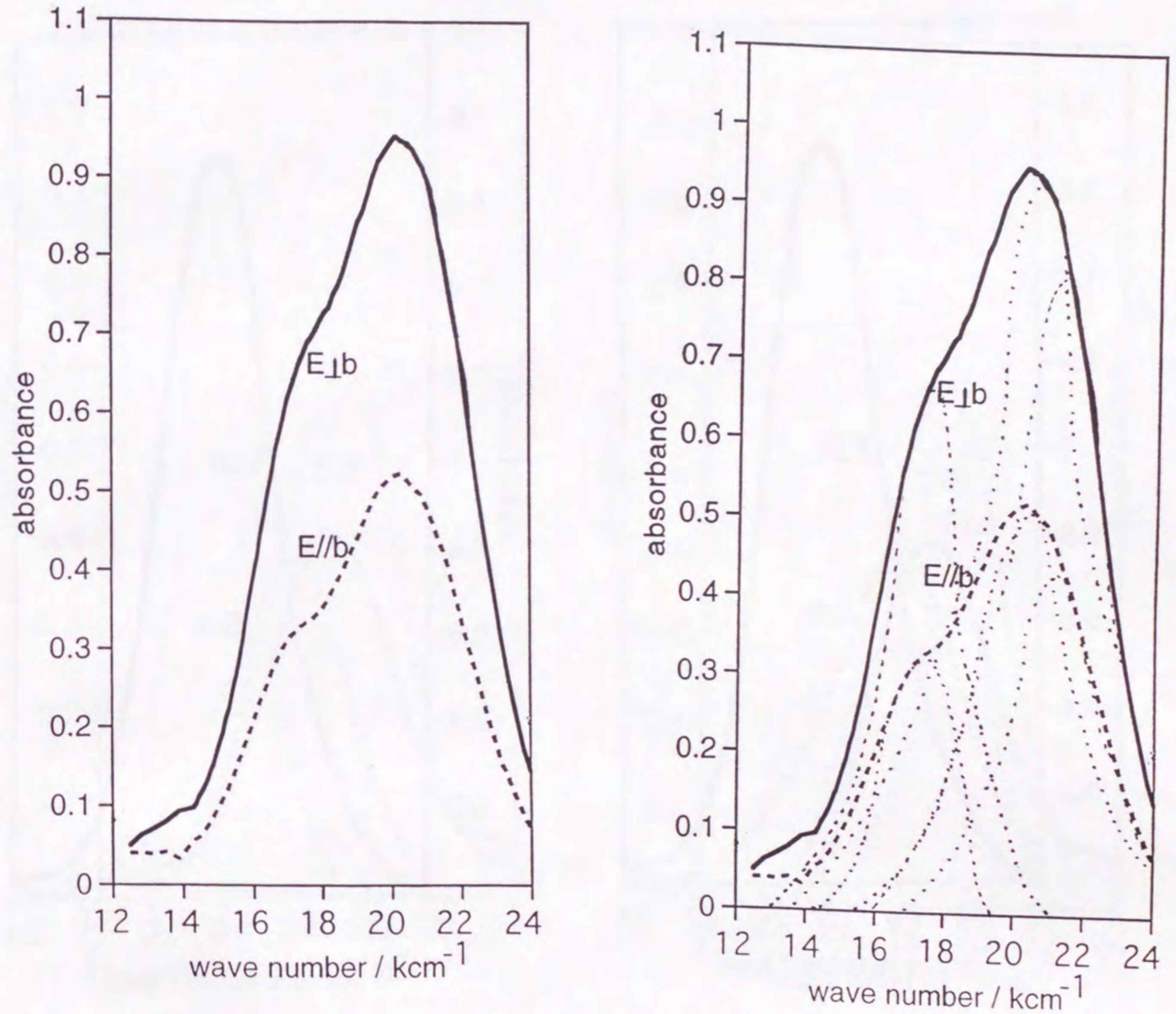


Figure 6-7-b. The polarized crystal spectra of **15** determined from (001) face with E//*b* and E⊥*b* polarizations.

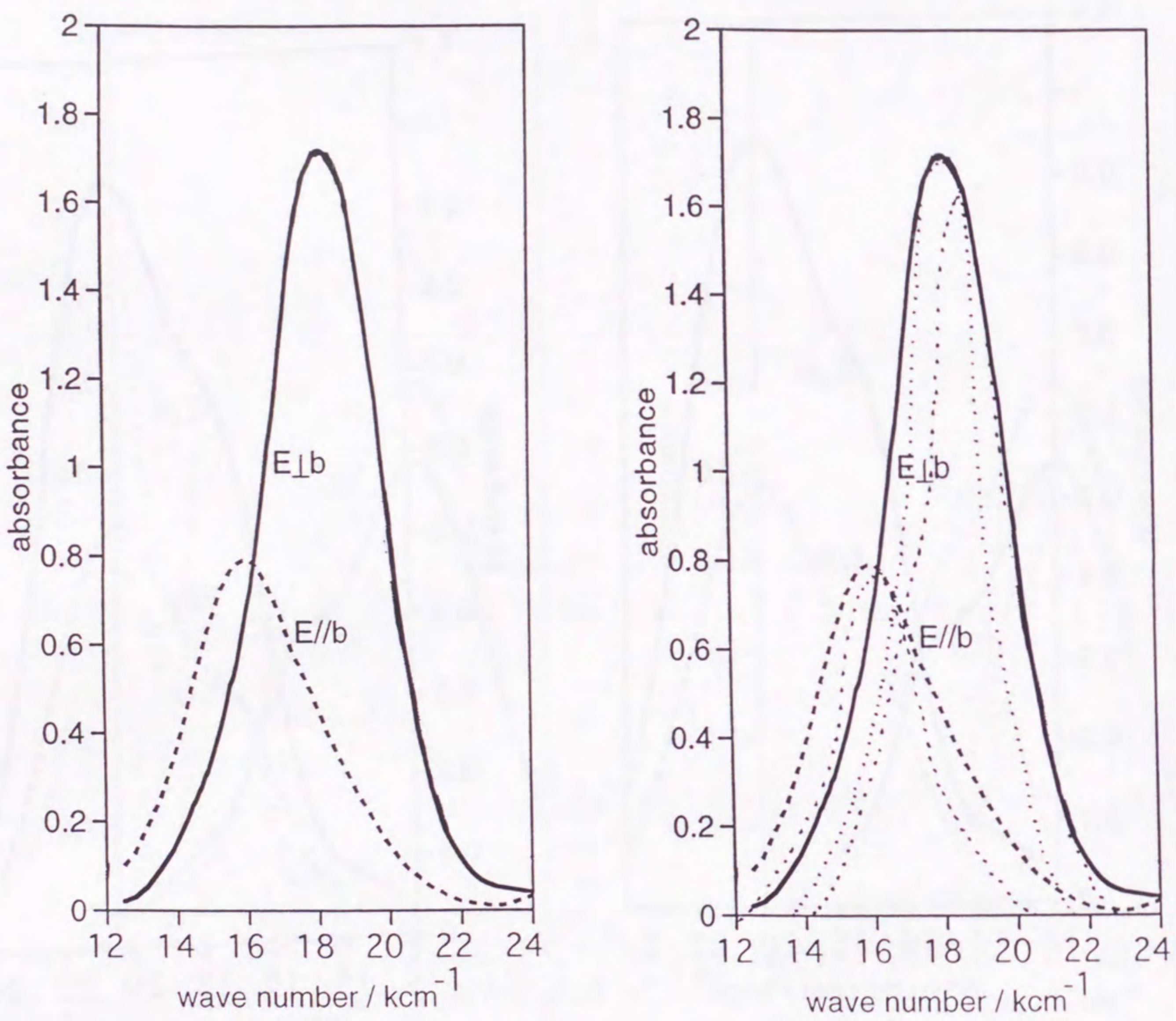


Figure 6-7-c. The polarized crystal spectra of **1** determined from (001) face with E//*b* and E⊥*b* polarizations.

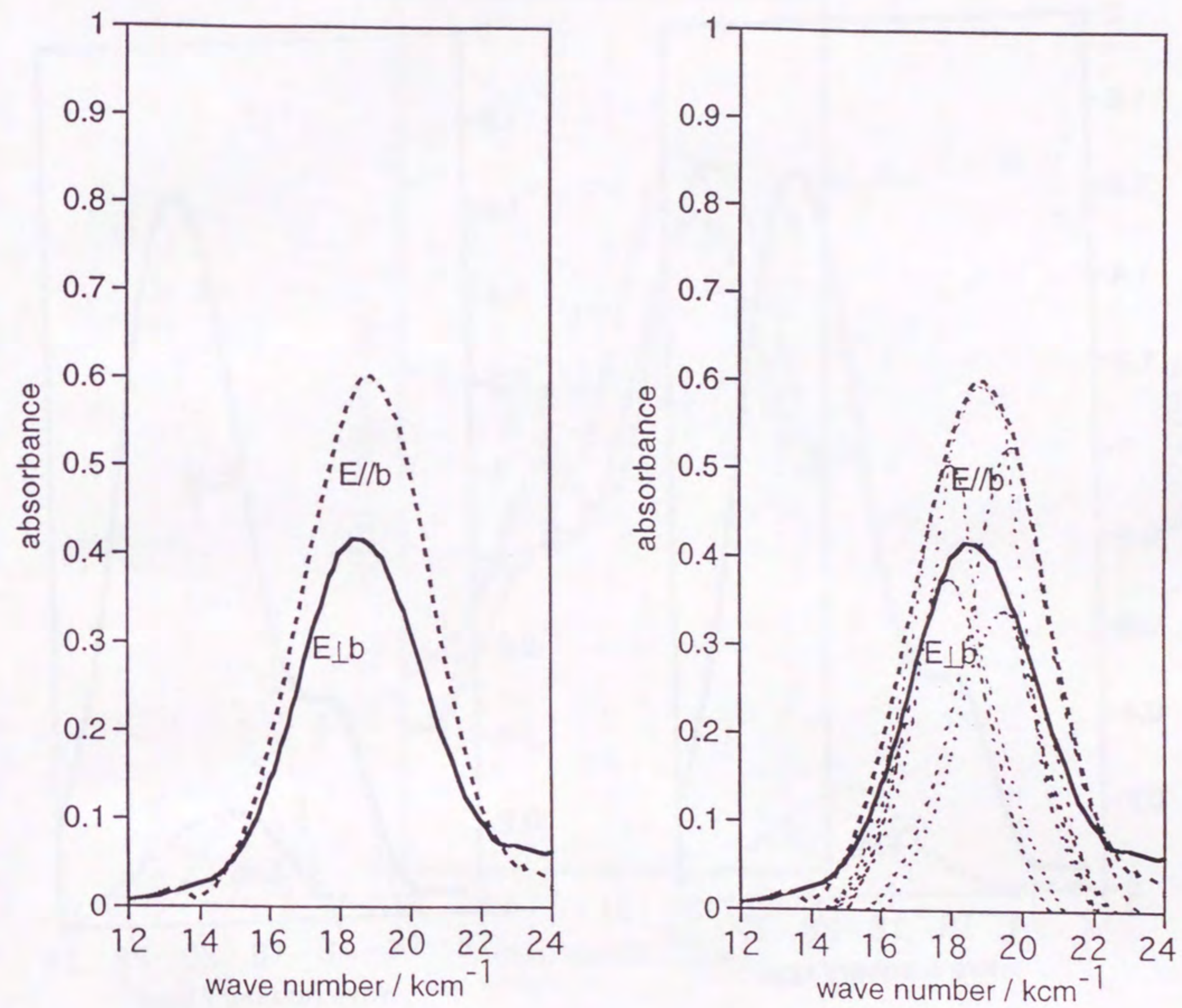


Figure 6-7-d. The polarized crystal spectra of **3** determined from (001) face with E//*b* and E⊥*b* polarizations.

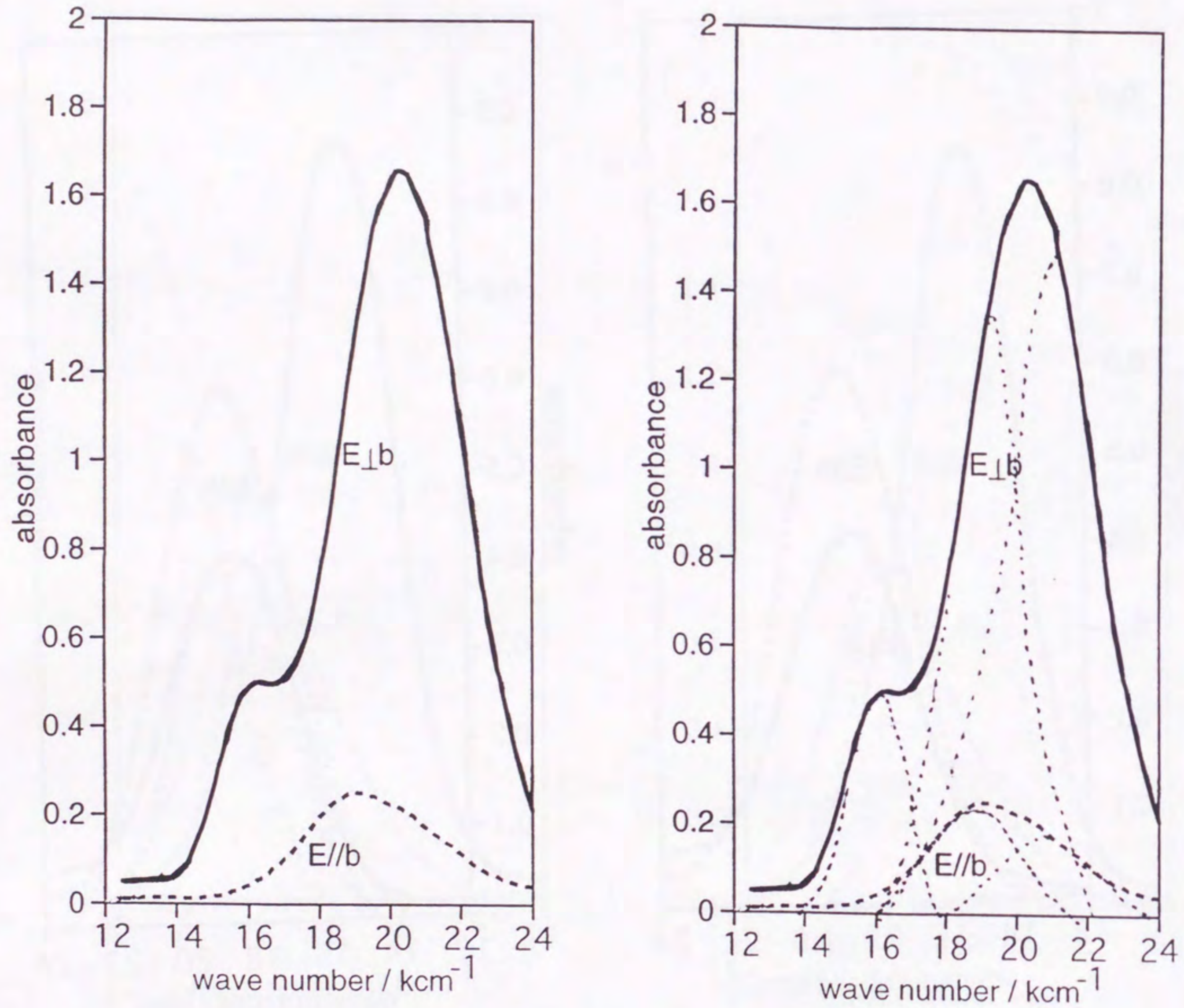


Figure 6-7-e. The polarized crystal spectra of **11** determined from (100) face with E//*b* and E⊥*b* polarizations.

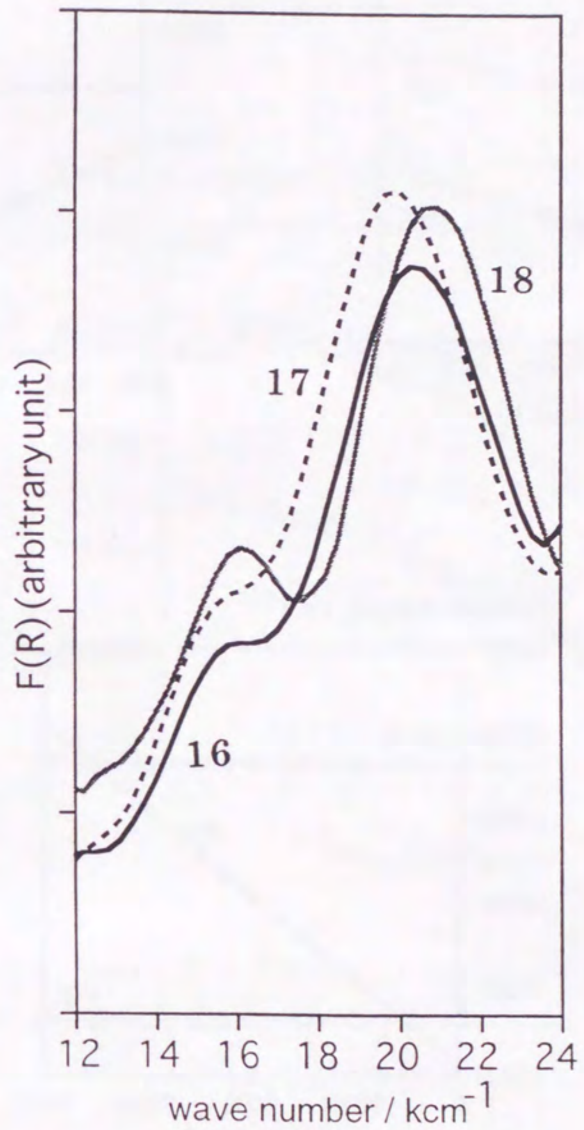


Figure 6-7-f. The reflectance spectra of **16**, **17**, and **18**.

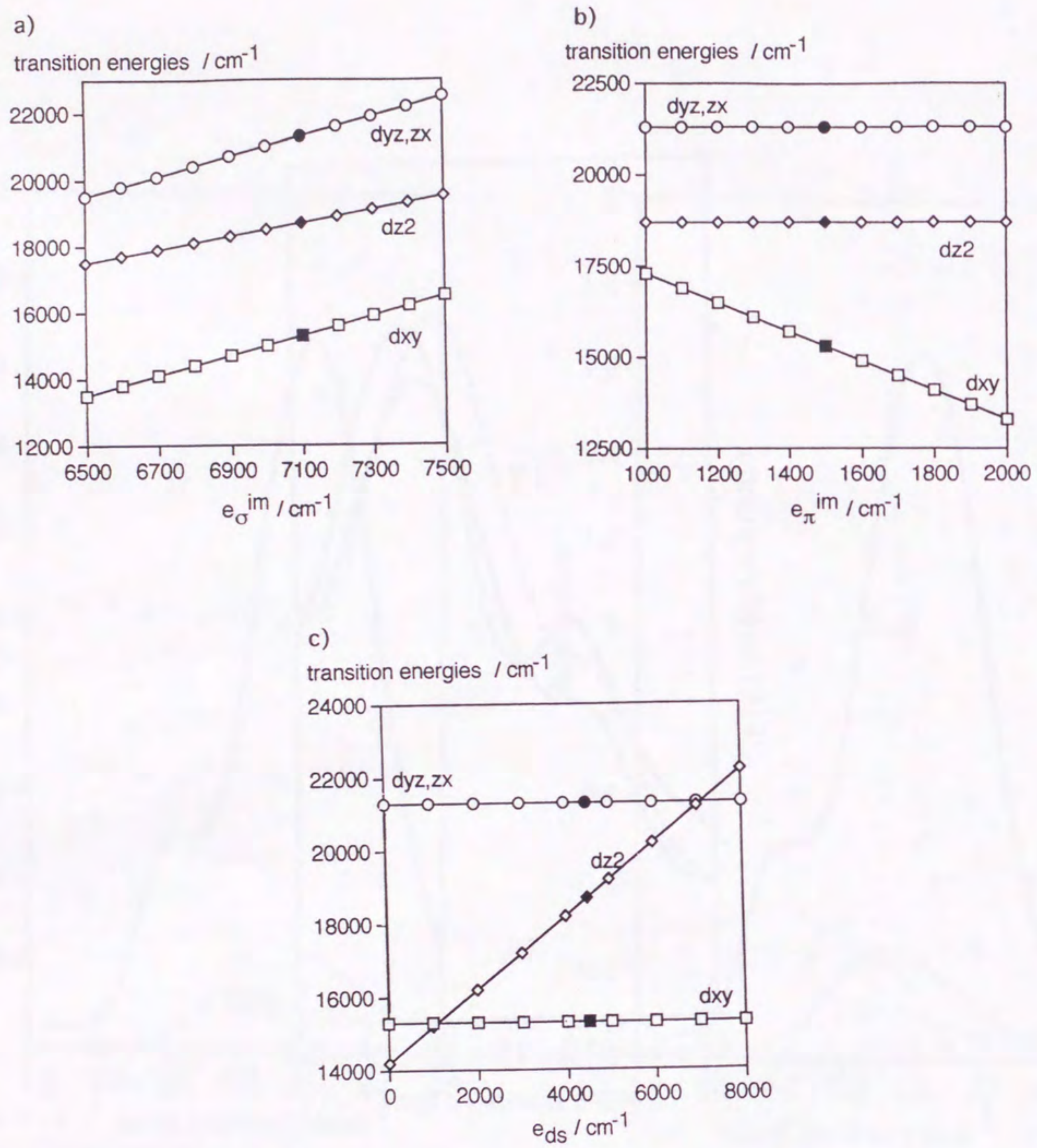


Figure 6-8. The variation of transition energies to d_{x2-y2} orbital as a function of a) e_σ^{im}, b) e_π^{im}, and c) e_{ds} parameters for **1 1**. The optimized values e_σ^{im} = 7100 cm^{-1}, e_π^{im} = 1500 cm^{-1} and e_{ds} = 4500 cm^{-1} are depicted as filled marks.

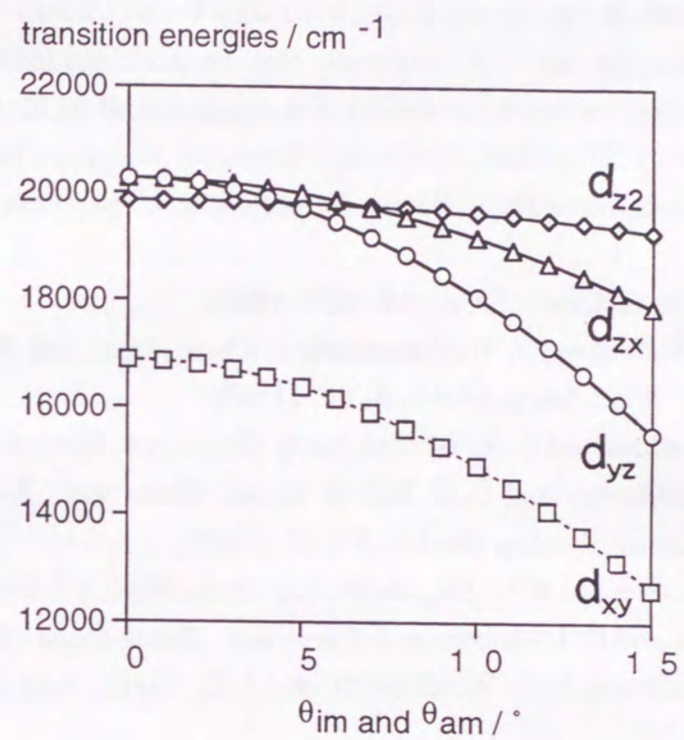


Figure 6-9. The variation of transition energies to d_{x2-y2} orbital as a function of θ_{im} and θ_{am} (θ_{im}=θ_{am}) parameters for *trans*-[Cu(phent)$_2$(phenea)$_2$] (**1** and **3**). The values e_σ^{im} = 7200 cm^{-1}, e_π^{im} = 1700 cm^{-1}, e_σ^{am} = 6300 cm^{-1} and e_{ds} = 6300 cm^{-1} (fixed) are used.

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Chapter 7.

General Conclusion.

In the present thesis, the author reported the preparations of copper(II) complexes containing various imidate, amine, or diimine ligands and their structures were determined by X-ray crystallography. As for five suitable complexes, polarized crystal spectra were measured and the assignment of d-d transitions for the related copper(II) having imidate and amine ligands with a [CuN_4] chromophore was established reasonably by means of AOM calculations.

In chapters 2, *meso*, *optically active*, and *racemic trans*-[Cu(phent)$_2$(phenea)$_2$] complexes were able to be isolated and their structures were determined for the first time. Three forms differs in degree of distortion of [CuN_4] chromophore due to the difference in chilality of 1-phenylethylamine ligands. Additionally, it was also found that three forms can be obtained selectively depending on the e.e. of 1-phenylehtylamine ligands during the preparation of the complexes.

In chapter 3, steric features were compared between distorted square planar *trans*-[Cu(phent)$_2$(1,2-diphenea)$_2$]·2$CHCl_3$ and square planar *trans*-[Cu(succim)$_2$(1,2-diphenea)$_2$] complexes. It was concluded that suitable *edge-to-face* arrangement between phenyl group on 1-position of amine ligands and five-membered imidate rings resulted in distortion of [CuN_4] chromophore, which also corresponded to unstable conformation of two phenyl groups of 1,2-diphenylethylamine.

In chapter 4, the relationship between the axial coordination ability and the arrangement of imidate and amine ligands were discussed by comparing the structures of several related complexes. Imidate ligands act as a good donor ligands which contribute to weaken the axial coordination ability of the ligands. Moreover, the formation of [Cu(succim)$_2$(N-Eten)(H_2O)$_2$] implies that the donation effect of imidate ligands is more stronger in *trans*-position than in *cis*-position.

In chapter 5, bidentate diimine ligands such as phen and bpy were introduced and these gave rise to [Cu(succim)$_2$(phen)H_2O]·H_2O and [Cu(succim)$_2$(bpy)H_2O] with a square pyramidal [CuN_4O] coordination geometry with succinimidate located on *cis*-position. The axial Cu-O bond distances of these complexes are appreciable longer than those of other square pyramidal [CuN_4O] complexes with imidate ligands located on *trans*-position.

In chapter 6, the assignment of d-d transition of square planar [CuN_4] complexes was descried. To lower effective symmetry of a [CuN_4] chromophore by tetrahedral distortion, $d_{z2} \rightarrow d_{x2-y2}$ transition could be observed separately and gradual geometrical changes could be treated reasonably by AOM calculations for *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes. Additionally, comparison between M_2[Cu(imidate)$_4$] and *trans*-[Cu(imidate)$_2$(amine)$_2$] showed that imidate ligands had a p-character lone pair perpendicular to imidate ring which destabilized the level of $d_{xy]}$ orbital. Therefore, the assignment of d-d transition was able to reasonably as follows: square planar *trans*-[Cu(phent)$_2$(chea)$_2$] d_{x2-y2} (a_g) > d_{xy} (b_{1g}) > d_{z2} (a_{1g}) > d_{yz} (b_{3g}), d_{zx} (b_{1g}) (effective symmetry D_{2h}), square planar M_2[Cu(imidate)$_4$] d_{x2-y2} (b_{1g}) > d_{xy} (b_{2g}) > d_{z2} (a_{1g}) > d_{yz},d_{zx} (e_g) (effective symmetry D_{4h}), and distorted square planar *trans*-[Cu(phent)$_2$(phenea)$_2$] d_{x2-y2} (a_1) > d_{xy} (a_2) > d_{z2} (a_1) > d_{yz} (b_2) >d_{zx} (b_1) (effective symmetry C_{2v}).

Acknowledgments.

The author would like to express his sincere acknowledgment to Professor Yoshihiko Kushi for his encouragement and guidance throughout the course of this work. He also wishes to express his sincere gratitude to Professor Sumio Kaizaki and Professor Shinnichiro Suzuki for their fruitful advice in refining throughout the expression in this thesis.

He would like to express his most sincere gratitude to Associate Professor Seiko Komorita for her direct instruction and valuable discussion throughout the course of this study for six years. He wishes to express his grate thanks to Associate Professor Hiro Kuma, Associate Professor Kazuaki Yamanari, and Dr. Tatsuya Kawamoto for their warm encouragement and helpful discussion.

Thanks are extended to Dr. Hatsue Tamura (Graduate School of Engineering, Osaka University) for her collaboration in X-ray crystallography and useful discussion, Mr. Ken-ichi Sakaguchi (Institute for Protein Research, Osaka University) for his help in use and maintenance of four-circle diffractometers, Professor Yasushi Kai, Dr. Nobuko Kanehisa, Dr. Chunmin Li, and Ms. Eiko Mochizuki (Graduate School of Engineering, Osaka University) for their collaboration in X-ray crystallography, Professor Akio Urushiyama (College of Science, Rikkyo University) for his collaboration in measurement of polarized single crystal spectra, and Dr. Takashi Komorita (Graduate School of Science, Osaka University) for his kindly providing of a program for AOM calculations and helpful discussion.

He gratefully acknowledges warm support and encouragement from all the fellows of the Laboratory for Coordination Chemistry, Department of Chemistry, Graduate School of Science, Osaka University.

Finally, the author expresses his heartfelt thanks to my family, Yoshiaki Akitsu, Reiko Akitsu, and Masashi Akitsu, for their warm support and constant encouragement.

February, 2000

秋津貴城
Takashiro Akitsu