

Assignment of d–d Transitions of Square Planar [$Cu^{II}N_4$] Complexes Containing Imidate and Amine Ligands by Means of Polarized Crystal Spectra.

Takashiro Akitsu,*,# Seiko Komorita, and Akio Urushiyama†

Department of Chemistry, Graduate School of Science, Osaka University,
1-16 Machikaneyama, Toyonaka, Osaka 560-0043

†Department of Chemistry, College of Science, Rikkyo University, 3 Nishi-Ikebukuro, Toshima, Tokyo 171-0021

(Received September 28, 2000)

Square planar [CuN_4] copper(II) complexes, Rb_2[Cu(succim)$_4$]•$2H_2O$ (**1**), *trans*-[CuL_2(*R*-chea)(*S*-chea)] (**2**), *trans*-[CuL_2(*R*-chea)$_2$] (**3**), (succim = succinimidate, L = 5,5-diphenylhydantoinate, and chea = 1-cyclohexylethylamine) were prepared and crystal structures were determined. Crystal data for **1** are monoclinic with space group *C*2/*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. Crystal data for **2** 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* = 2183.8(5) Å^3; *Z* = 2. Crystal data for **3** 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. The polarized crystal electronic spectra were determined for square planar [CuN_4] **1**, **2**, and **3** and distorted square planar [CuN_4] *trans*-[CuL_2(*R*-phenea)(*S*-phenea)] (**4**) and *trans*-[CuL_2(*R*-phenea)$_2$][CuL_2(*S*-phenea)$_2$] (**5**) (phenea = 1-phenylethylamine). These spectra were deconvoluted by Gaussian curve fitting by considering selection rules for electric dipole transitions. The 3d orbital orders were determined to be $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz}$,$d_{zx}$ for **1**, $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{zx}$ for **2** and **3**, and $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{zx}$ for **4** and **5** by means of polarized crystal spectra and angular overlap model (AOM) calculations. Since the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition could be observed separately for **4** for the first time, the present assignment could be established certainly. Distortion of [CuN_4] chromophores decreases the peak wave numbers for a series of *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes. The results of **1**, **2**, and **3** suggest that lone pairs of imidate ligands destabilize the d_{xy} orbital by distributing in the [CuN_4] plane.

Although various copper(II) complexes have been investigated for several decades, assignment of d–d transitions of square planar complexes has been the subject of controversy. At first, reliable assignment has been established only for several $[CuCl_4]^{2-}$ anions by Hitchman et al.,[1,2] which was a special case because of the following two reasons: (1) $d_{z^2} \rightarrow d_{x^2-y^2}$ band can be observed separately in the highest wave number region of the spectra; (2) because of appropriate crystal packing, individual transitions can be assigned by selection rules. However, the ds-mixing[3] parameter of AOM[4] is not still estimated certainty.

In the case of square planar [CuO_4] complexes, such as Cu(acac)$_2$ (acac = acetylacetonate) and their derivatives, several polarized crystal spectra have been reported.[5] Unfortunately, these spectra provide little information because of the so-called "packing problem"; there are two perpendicular [CuO_4] molecular planes in a crystal. Three transitions are observed for Cu(acac)$_2$,[6] while four transitions are observed for two derivatives,[7] and individual bands are not resolved clearly. Two kinds of assignment have been proposed[5] (D_{2h} point group): assignment I is d_{xy} (b_{1g}) > $d_{x^2-y^2}$ (a_g) > d_{yz} (b_{3g}) > d_{zx} (b_{2g}) > d_{z^2} (a_g), while assignment II is d_{xy} (b_{1g}) > d_{z^2} (a_g) > $d_{x^2-y^2}$ (a_g) > d_{yz} (b_{3g}) > d_{zx} (b_{2g}). Assignment I is reasonable in view of transferability of AOM parameters and the lowest d_{z^2} (a_g) level; While assignment II is more consistent with the experimental results better than assignment I,[8] but AOM parameters are doubtful.

On the other hand, genuine square planar [CuN_4] complexes are uncommon, because the fifth and sixth additional axial ligands are liable to coordinate to give semi-coordinated complexes.[9] Exceptionally, [Cu(en)$_2$](SCN)$_2$[10] (en = ethylenediamine) and *N*-substituted ethylenediamine complexes[11] are known to be in a four-coordinated square planar [CuN_4] coordination geometry. In contrast to amine ligands, it is well known that biuret or biguanide derivatives yield genuine four-coordinated square planar [CuN_4] complexes; for example, potassium bis(biuretato)cuprate(II)[12] and bis[(methoxycarboimido)aminato]copper(II).[13] Walsh and Hathaway measured polarized crystal spectra of several square planar [CuN_4] complexes and assigned d–d transitions tentatively on the basis of only the peaks and shoulders of polarized crystal spectra.[11] The reported tentative 3d orbital orders are $d_{x^2-y^2}$ (b_{1g}) > d_{xy} (b_{2g}) > d_{z^2} (a_{1g}) > d_{xy},d_{yz} (e_g) and $d_{x^2-y^2}$ (b_{1g}) > d_{z^2} (a_{1g}) > d_{xy} (b_{2g}) > d_{xy},d_{yz} (e_g) (D_{4h} point group) for Cs_2[Cu(succim)$_4$]•$2H_2O$[14] and [Cu(deen)$_2$](NO$_3$)$_2$ (deen = *N*,*N*-diethylethylenediamine), respectively. In this way, the assignment for

Present address: Division of Protein Crystallography, Institute for Protein Research, Osaka University, 3-2 Yamadaoka, Suita, Osaka 565-0871.

square planar [CuN_4] complexes has not been established certainly. The primary difficulty is preparation of suitable single crystals for polarized crystal spectra in view of both coordination geometries and crystal packings. Imidates, however, are suitable ligands for formation of copper(II) complexes of not only genuine square planar [CuN_4],[14,15] but also distorted square planar [CuN_4],[16,17] and five-coordinated square pyramidal [CuN_4O].[18] To make use of the advantage of imidate ligands due to in-plane anti-bonding π-bonding character, Yamada and Miki (Komorita) have employed K_2[Cu(succim)$_4$]•2H_2O and have assigned the order to be $d_{x^2-y^2}$ (b_{1g}) > d_{z^2} (a_{1g}) > d_{xy} (b_{2g}) > d_{xy},d_{yz} (e_g) (D_{4h} point group) tentatively by polarized crystal spectra.[15] But reliable assignment has not yet been established because no appropriate samples have been available.

The present study aims at reasonable assignment of d–d transitions for square planar (or distorted square planar) [CuN_4] complexes containing imidate and amine ligands. This paper describes preparations and crystal structures of square planar complexes Rb_2[Cu(succim)$_4$]•2H_2O (**1**),*trans*-[CuL_2(*R*-chea)(*S*-chea)] (**2**) and *trans*-[CuL_2(*R*-chea)$_2$] (**3**). Polarized crystal spectra of **1**, **2**, **3**, and distorted square planar complexes *trans*-[CuL_2(*R*-phenea)(*S*-phenea)] (**4**) and *trans*-[CuL_2(*R*-phenea)$_2$][CuL_2(*S*-phenea)$_2$] (**5**) were determined and were analyzed, taking into account the resolution of polarized light into molecular coordinates.[17] Each transition energy was calculated by AOM calculations.

Experimental

General Procedures. *R*- and *S*-1-cyclohexylethylamine and *S*-1-phenylethylamine were purchased from Fuluka 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 Rb_2[Cu(succim)$_4$]•2H_2O (1). Reddish violet prismatic crystals of **1** suitable for X-ray crystallography and 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, an 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%.

Preparation of *trans*-[CuL_2(*R*-chea)(*S*-chea)] (2). 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. An 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 1 h at 50 °C. Gradually reddish violet precipitates were filtered off and were recrystallized from chloroform–methanol (4:1, v/v). The reddish violet precipitates **2** (*meso* diastereomer) 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 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 *trans*-[CuL_2(*R*-chea)$_2$] (3). Complex **3** (*optically active* diastereomer) was prepared in a manner similar to that for **2** 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 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%.

Preparation of *trans*-[CuL_2(*R*-phenea)(*S*-phenea)] (4). Blue violet prismatic crystals **4** (*meso* diastereomer) suitable for polarized crystal spectra were prepared according to the literature[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*-[CuL_2(*R*-phenea)$_2$][CuL_2(*S*-phenea)$_2$] (5). Violet prismatic crystals **5** (*racemic* crystal) suitable for polarized crystal spectra were prepared according to the literature[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%.

Electronic Spectra. The single crystal polarized absorption spectra were measured at room temperature on a Hitachi model ESP-3T spectrometer and specially designed micro-spectroscopic equipment. The light beam was passed thorough a Rochon quartz polarizer and was condensed by two concave mirrors onto a pinhole (0.1 mm in diameter) in an indium plate where a thin crystal was placed. The polarized crystal spectra were determined with the electronic vector parallel and perpendicular to the crystallographic *b* axis on the well-developed (100) face for **1** and (001) face for **2**, **3**, **4**, and **5**. The orientation of the crystal axes of the samples mounted was characterized by oscillation X-ray photographs. Crystals with dimensions of 0.10 (thickness) mm for **1**, 0.40 × 0.25 (face) × 0.11 (thickness) mm for **2**, 0.40 × 0.20 × 0.09 mm for **3**, 0.30 × 0.18 × 0.028 mm for **4**, and 0.78 × 0.40 × 0.03 mm for **5** and were used for the measurement. 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 from the corresponding diffuse reflectance spectra.

Crystal Structure Determination. The X-ray diffraction intensity data were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with graphite monochromated Mo$K\alpha$ (λ = 0.71069 Å) for **1** and nickel-filtered Cu$K\alpha$ (λ = 1.5418 Å) for **2** and **3** and 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 **1**, **2**, and **3** (transmission factors 0.6459–1.0000, 0.8099–0.9987, and 0.9333–0.9992, respectively). No significant decay in the intensity of the three standard reflections was observed throughout the data collection. The structures were solved by using SIR 92[21] and expanded by Fourier techniques. The structures

Table 1. Crystallographic Data for **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{16}H_{20}N_4CuO_{10}Rb_2$	$C_{46}H_{56}N_6CuO_4$	$C_{46}H_{56}N_6CuO_4$
Molecular weight	662.84	820.53	820.53
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*m* (#12)	$P2_1$/c (#14)	$P2_1$ (#4)
a/Å	16.279(4)	8.485(2)	8.472(2)
b/Å	8.382(3)	9.7854(8)	9.803(2)
c/Å	8.297(3)	26.334(4)	26.331(6)
β/°	93.13(3)	92.83(1)	92.67(2)
V/Å^3	1130.4(6)	2183.8(5)	2184.6(8)
Z	2	2	2
D_c/g cm^{-3}	1.947	1.248	1.247
F(000)	2616	870	870
μ/cm^{-1}	211.84	10.90	10.89
	(Mo $K\alpha$)	(Cu $K\alpha$)	(Cu $K\alpha$)
$2\theta_{max}$/°	55.0	119.9	119.9
Crystal dimensions/mm	0.30 × 0.30 × 0.20	0.25 × 0.20 × 0.10	0.20 × 0.20 × 0.20
Temperature/K	296	298	298
No. of measured reflections	1485	3140	2916
No. of unique reflections	1393	2878	2652
No. of reflections used in refinement	1027	2323	2190
	[$I > 3.0\sigma(I)$]	[$I > 2.0\sigma(I)$]	[$I > 2.0\sigma(I)$]
No. of parameters	86	260	335
g.o.f.	1.64	4.95	4.08
R[a)]	0.030	0.068	0.080
R_w[b)]	0.033	0.076	0.074

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

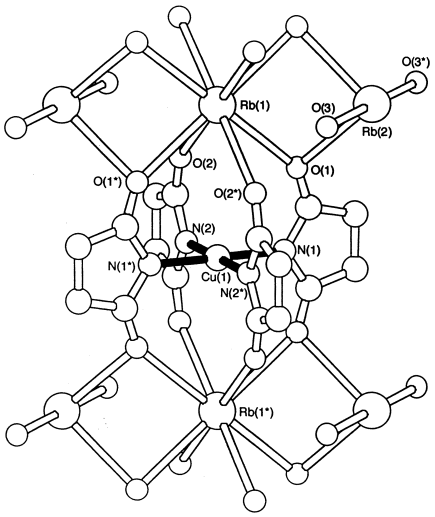
Table 2. Selected Bond Distances (Å) and Angles (°)

	1[a)]		**2**[a)]	**3**[a)]	**4**[b)]	**5**[b)]
Bond Distances		Bond Distances				
Cu(1)–N(1) (imidate)	1.996(4)	Cu(1)–N(1) (imidate)	1.980(4)	2.02(1)	1.988(3)	2.009(4)
Cu(1)–N(2) (imidate)	1.970(3)	Cu(1)–N(1) (amine)	2.022(4)	2.05(1)	2.012(3)	1.993(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(2)	91.6(2)	N(1)–Cu(1)–N(3)	90.8(2)	90.7(6)	91.9(2)	93.2(2)
N(1)–Cu(1)–N(2*)	88.4(2)	N(1)–Cu(1)–N(6)		89.2(5)	92.4(2)	92.7(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(2)–Cu(1)–N(2*)	180.0	N(3)–Cu(1)–N(3*)	180.0			

a) This work. b) Ref. 17.

of **1** and **2** were refined on F by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The carbon atoms of **3** as the 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 **3** were refined anisotoropically. After the final cycle of the least-squares refinement, noticeable large displacement parameters were found and the maximum shift/error values still did not indicate 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 **3** 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 **1** could not be found and the atoms were omitted from the analysis.

Despite the very poor quality of the crystals, the crystal structure analyses provided sufficiently satisfactory results for the pur-



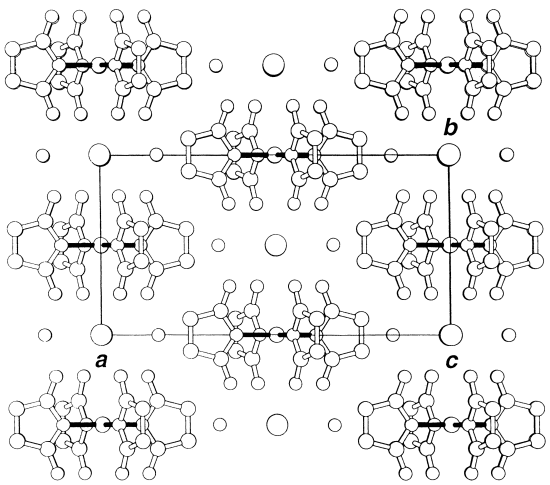
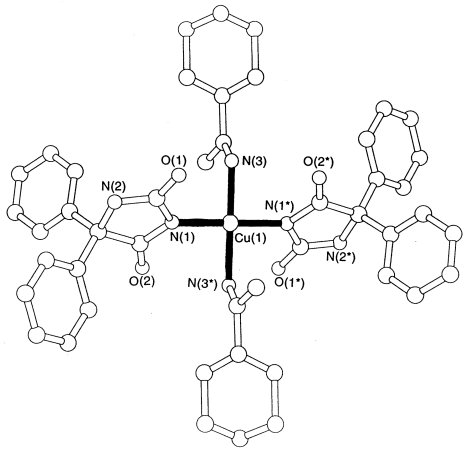


Fig. 1. Molecular structure of $Rb_2[Cu(succim)_4]\bullet 2H_2O$ (1) [above], and crystal structure of **1** viewed down the crystallographic *a* axis [below].



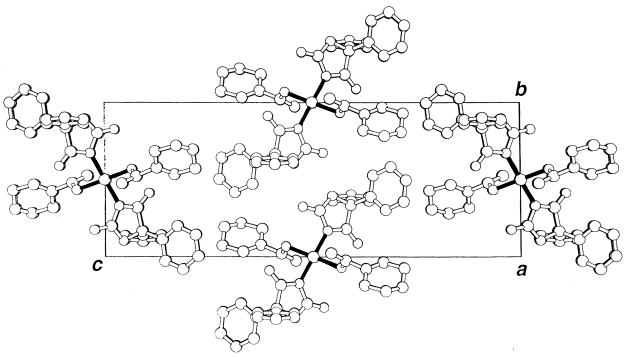


Fig. 2. Molecular structure of *trans*-[CuL_2(*R*-chea)(S-chea)] (*meso*) (**2**) [above], and crystal structure of **2** viewed down the crystallographic *a* axis [below].

pose of the present study.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 157849–157851.

Results and Discussion

Crystal Structures. The crystallographic data for **1**, **2**, and **3** are summarized in Table 1. The crystal structures of **4** and **5** have been determined previously.[17] Selected bond distances and angles are listed in Table 2. The molecular and crystal structures are depicted in Figs. 1–5. The list of atomic coordinates, anisotropic thermal parameters, and bond distances and angles are deposited as Document No. 74028 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Complex **1** with four succinimidates affords a square planar [CuN_4] coordination geometry. The imidate Cu(1)–N(1) and Cu(1)–N(2) bond distances are 1.996(4) and 1.993(4) Å, respectively. These values are equal within experimental errors and similar to analogous complexes.[14,23] The coordination numbers of Rb(1) and Rb(2) are eight and six, respectively. Rb(1) is coordinated by eight carbonyl groups of succinimidate ligands (O(1) and O(2)), whereas Rb(2) is coordinated by four carbonyl groups (O(1)) and two crystalline waters (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.

Complexes **2** and **3** afford a square planar [CuN_4] coordination geometry, which is a common feature for *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) to 2.05(1) Å, respectively. These are equal within experimental errors and 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 180.0 ° for **2**, and 178.2(6) and 176.6(6) ° for **3**, so the square planar [CuN_4] chromophores can be treated in point group D_{2h}.

On the other hand, **4** and **5** afford a distorted square planar [CuN_4] coordination geometry. The tetrahedral distortion of **4** is larger than that of **5** by the difference in chirality of 1-phenylethylamine ligands.[17] The imidate and amine Cu–N bond

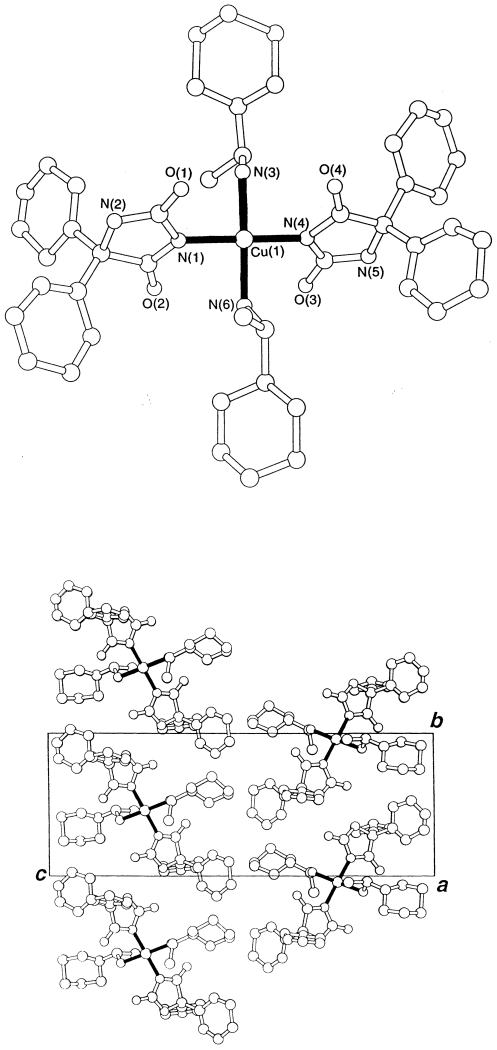


Fig. 3. Molecular structure of *trans*-[CuL_2(*R*-chea)$_2$] (*optically active*) (**3**) [above], and crystal structure of **3** viewed down the crystallographic *a* axis [below].

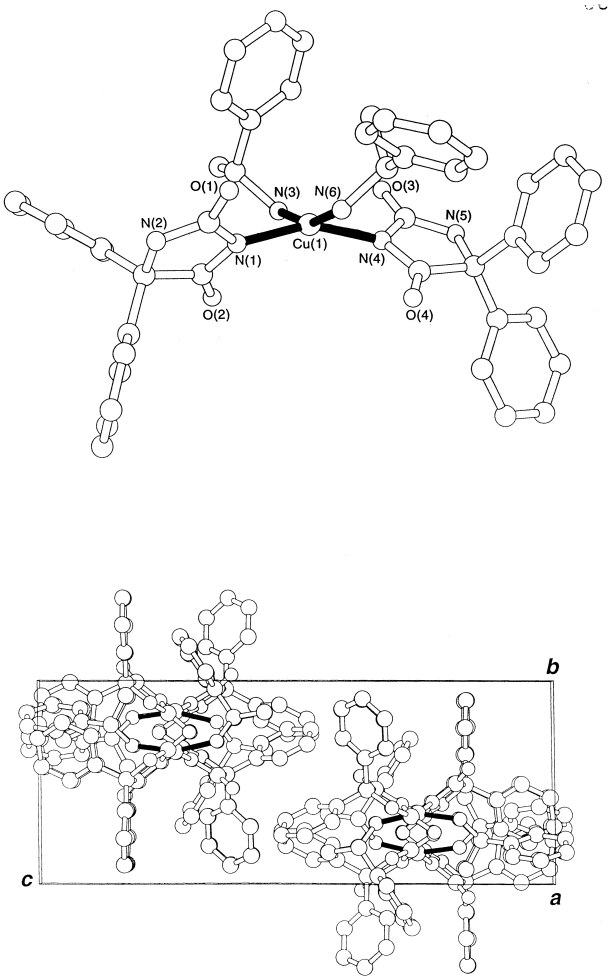


Fig. 4. Molecular structure of *trans*-[CuL_2(R-phenea)(*S*-phenea)] (*meso*) (**4**) [above], and crystal structure of **4** viewed down the crystallographic *a* axis [below].

distances fall in the range from 1.988(3) to 2.009(4) Å and 1.993(3) to 2.030(4) Å, respectively. No noticeable differences in Cu–N bond distances are observed regardless of distortion. The imidate and amine *trans*-N–Cu–N bond angles are 154.9(2) and 159.8(2) ° for **4** and 166.6(2) and 163.2(2) ° for **5**, so that the effective symmetry is point group C_{2v}.

In this way, these four complexes vary their [CuN_4] coordination geometries from square planar (**2** and **3**) to distorted square planar (**4** and **5**). 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 Fig. 6. 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 axes. Distortion angles θ_{im} and θ_{am} using AOM calculations are 0.0 ° and 0.0 ° and for **2** and **3**, 12.5 ° and 10.1 ° for **4**, and 6.6 ° and 8.4 ° for **5**. Since effective symmetry D_{2h} are applied for **3**, slight deviation from square planar (θ_{im} = 1.6 ° and θ_{am} = 1.0 °) can be negligible for AOM calculations. Since two distortion angles are θ_{im} = 0.0 °, **1** can be treated in point group D_{4h}.

As shown in Figs. 1–5, crystallographic axes are not in agreement with molecular coordinates generally. The projections of electric vector of polarized light onto the molecular coordinates will be considered to resolve the misalignment of these two coordinate systems.

Electronic Spectra. The polarized crystal spectra are shown in Fig. 7. The spectra of **1** were determined in the (100) face. The $E \perp b$ spectrum exhibits a band maximum at about 20000 cm^{-1} with a shoulder around 16000–17000 cm^{-1}, however, the $E \parallel b$ spectrum shows the peak at about 20000 cm^{-1} only. The spectra of **2** and **3** measured in the (001) face with $E \parallel b$ and $E \perp b$ polarized light include a band maximum at about 20000 cm^{-1} with a shoulder around 16000–17000 cm^{-1}. The polarized spectra of **4** were measured in the (001) face, and the $E \parallel b$ spectrum included a weak band at about 16000 cm^{-1}, while the $E \perp b$ spectrum included an intense band at about 18000 cm^{-1}. The spectra of **5** measured in the (001) face with $E \parallel b$ and $E \perp b$ polarized light included a broad peak at about 18000 cm^{-1}.

Molecular Projections. The polarized crystal spectra were measured along the crystallographic axes, while the se-

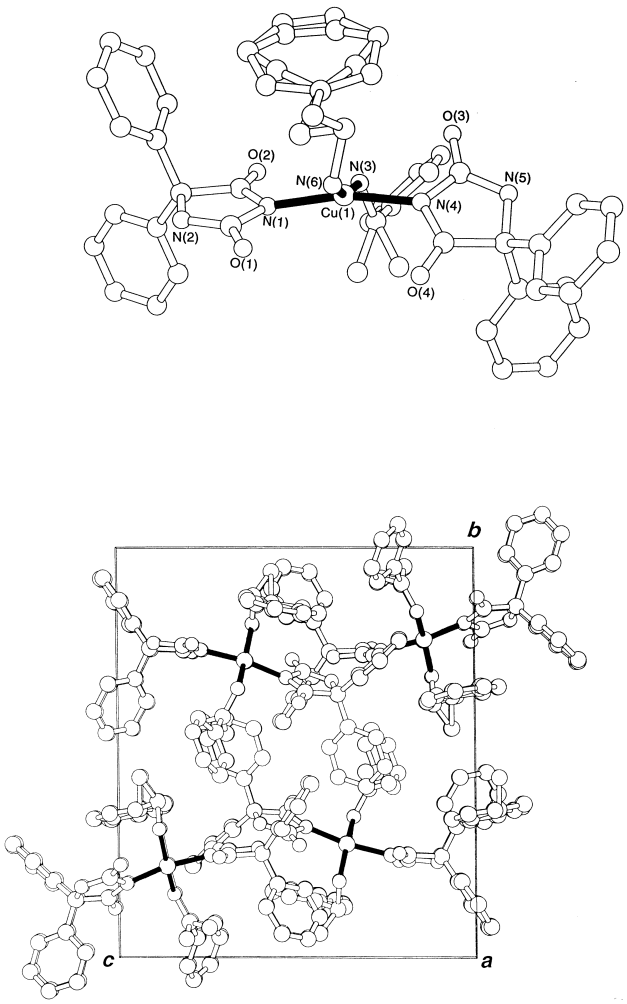


Fig. 5. Molecular structure of *trans*-[CuL$_2$(*R*-phenea)$_2$][CuL$_2$(*S*-phenea)$_2$] (*racemic*) (**5**) [above], and crystal structure of **5** viewed down the crystallographic *a* axis [below].

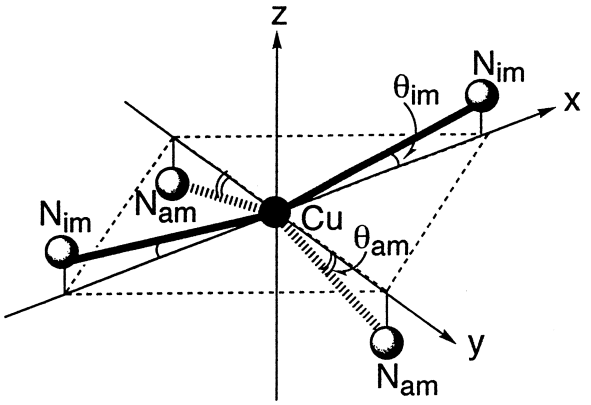


Fig. 6. Definitions of distortion angles θ_{im} and θ_{am} showing the molecular coordinate systems (x, y, z). Molecular *x* axis is a projection of the Cu–N(imidate) vector onto the [CuN$_4$] mean plane, the molecular y axis is a projection of the Cu–N(amine) vector onto the [CuN$_4$] mean plane, and 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.

lection rules of electronic dipole transition should be treated in molecular axes. In general, the crystallographic axes (*a*, *b*, *c*) are not in agreement with the molecular coordinates (x, y, z) of [CuN$_4$] chromophores. The squares of molecular projection (squares of cosine of electric vectors onto the molecular coordinates averaged over two molecules in monoclinic system) are described:

1 (100) $0.8085\,x^2 + 0.1915\,y^2 + 0.0000\,z^2$ ($E \perp b$)
$0.0000\,x^2 + 0.0000\,y^2 + 1.0000\,z^2$ (E // b)
2 (001) $0.0755\,x^2 + 0.1506\,y^2 + 0.7739\,z^2$ ($E \perp b$)
$0.7142\,x^2 + 0.1148\,y^2 + 0.1710\,z^2$ (E // b)
3 (001) $0.0712\,x^2 + 0.01611\,y^2 + 0.7677\,z^2$ ($E \perp b$)
$0.7141\,x^2 + 0.1154\,y^2 + 0.1705\,z^2$ (E // b)
4 (001) $0.8781\,x^2 + 0.1218\,y^2 + 0.0001\,z^2$ ($E \perp b$)
$0.0007\,x^2 + 0.0025\,y^2 + 0.9968\,z^2$ (E // b)
5 (001) $0.0972\,x^2 + 0.5185\,y^2 + 0.3843\,z^2$ ($E \perp b$)
$0.0104\,x^2 + 0.4543\,y^2 + 0.5353\,z^2$ (E // b)

It should be noted that the squares of molecular projections were considerably z-polarized for **1** and **4**, which suggested that the *b* crystal axis was parallel to the molecular *z* axis.

Selection Rules. Here we discuss selection rules for electric dipole transition in order to assign individual transitions. Since **1** (D_{4h}), **2** and **3** (D_{2h}) are centric, d–d transitions are forbidden by Laporte rules and they occur by vibronic mechanism coupled by ungerade normal vibrations. On the other hand, d–d transitions can be allowed by orbital symmetry for **4** and **5** (C_{2v}). Selection rules for D_{4h}, D_{2h}, and C_{2v} are summarized in Table 3. Generally, d–d transitions for acentric chromophores are dominated by orbital symmetry rather than vibronic coupling mechanism. If **4** and **5** are treated in vibronic coupling for C_{2v}, all four transitions will be allowed in any polarization, and both $E \perp b$ and E // b spectra will be similar to each other. However, this is in conflict with the results that the spectra indicate dichroism with $E \perp b$ and E // b polarizations. Therefore, intensity of **4** and **5** (C_{2v}) is not obtained by vibronic coupling, but orbital symmetry is considered for the analyses.

As for **1** (D_{4h}), three transitions, $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and d_{yz}, $d_{zx} \rightarrow d_{x^2-y^2}$, are vibronically allowed in x and y polarizations (E // b), while two transitions, $d_{z^2} \rightarrow d_{x^2-y^2}$ and d_{yz}, $d_{zx} \rightarrow d_{x^2-y^2}$, are vibronically allowed in z ($E \perp b$). Therefore the pronounced shoulder at 16000–17000 cm^{-1} can be assigned to be $d_{xy} \rightarrow d_{x^2-y^2}$ transition. Since four nitrogen atoms are located on the x and y axes, the lowest are degenerated d_{yz}, d_{zx} orbitals.

All four transitions are vibronically allowed in both E // b and $E \perp b$ polarized spectra for **2** and **3**. Since four nitrogen atoms were located on the molecular x and y axes, the $d_{x^2-y^2}$ (a_{1g}) orbital should be the ground state. Whether the shoulder is d_{xy}(b_{1g}) or d_{z^2}(a_{1g}) is still uncertain at present. In this way the spectra are expected to consist of four components, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{zx} \rightarrow d_{x^2-y^2}$, and $d_{yz} \rightarrow d_{x^2-y^2}$.

For **4** (C_{2v}), $d_{xy} \rightarrow d_{x^2-y^2}$ transition is forbidden in 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 $E \perp b$ spectrum lies on a

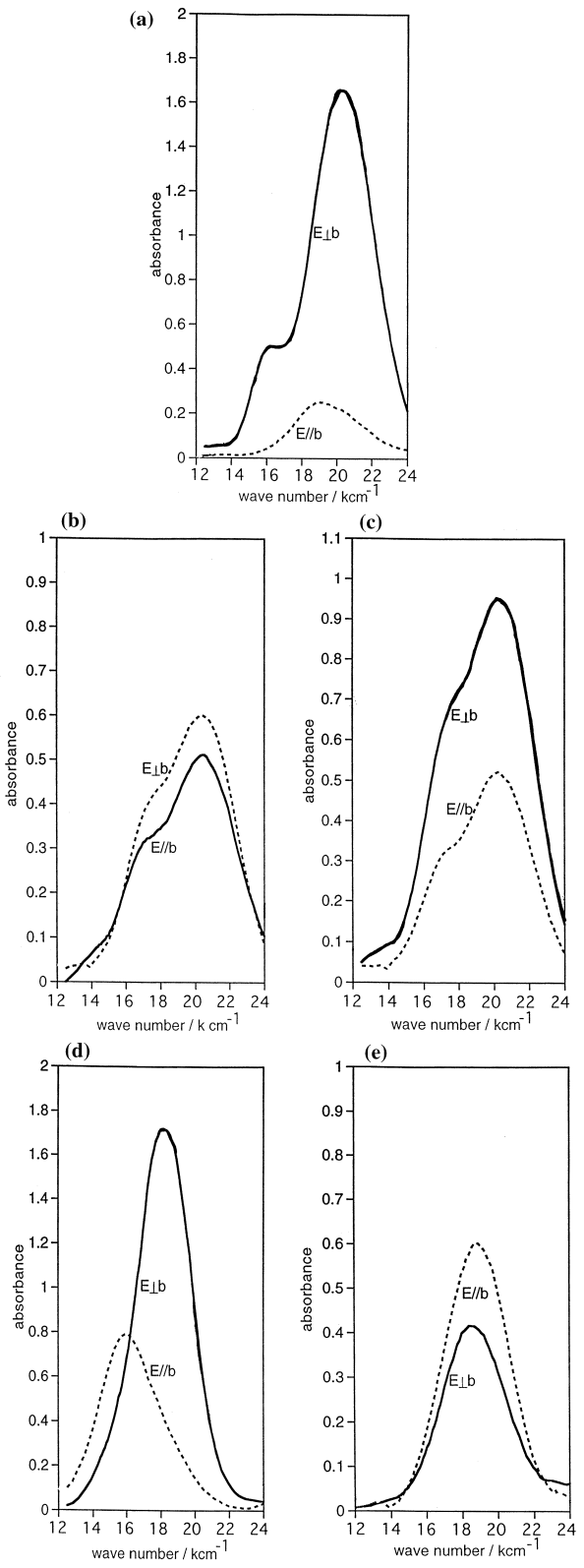


Fig. 7. The electronic polarized crystal spectra of **1** (a), **2** (b), **3** (c), **4** (d), and **5** (e).

molecular xy plane. The weak band at about 16000 cm^{-1} in the E // b spectrum can be assigned to be a $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, because only this is allowed and the others are forbidden in z polarization. The $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions are absent in the $E \perp b$ spectrum, because the intense band at about 18000 cm^{-1} in $E \perp b$ spectrum may be assigned to be $d_{zx} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions which are allowed in x and y polarizations, respectively. In summary, the spectrum of **4** contains three bands: $d_{z^2} \rightarrow d_{x^2-y^2}$ of the lowest energy among allowed ones, and $d_{zx} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions.

Three transitions: $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{zx} \rightarrow d_{x^2-y^2}$, and $d_{yz} \rightarrow d_{x^2-y^2}$, are allowed for **4** with both E // b and $E \perp b$ polarizations. Selection rules for C_{2v} make $d_{xy} \rightarrow d_{x^2-y^2}$ transition forbidden in any polarization.

The spectra are deconvoluted by Gaussian function into several band components[24] estimated by selection rules. Details of deconvolution by Gaussian curve fitting are summarized in Table 4.

Assignment of d–d Transitions. Table 5 gives the transition energy resulting from the deconvolution of the spectra and the transition energy calculated by AOM. Calculated transition energies reproduce deconvoluted transition energy, and these are not in conflict with the assignments discussed on the basis of selection rules.

For *trans*-[Cu(imidate)$_2$(amine)$_2$] complexes (**2**, **3**, **4**, and **5**), distortion angles θ_{im} and θ_{am} from crystal structures (Fig. 6) are used for AOM.[25] The rotation angles (ψ) around the Cu–N(imidate) bond axes are fixed at 90°.

As for ligand field strength, 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 the e_π^{im} parameter is related to the π-bonding character of Cu–N coordination bonds formed by a lone pair perpendicular to the imidate ring. Transferability of AOM parameters can be accepted, in other words, the same ligands of the different complexes are described by the same values of parameters similarly to assignment I for Cu(acac)$_2$ complexes.[5] These values are optimized to reproduce the transition energy by Gaussian deconvolution. The optimized e_σ^{im} and e_π^{im} values 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 optimized values e_σ^{am} = 6300 cm^{-1} and 6700 cm^{-1} are used for 1-phenylethylamine and 1-cyclohexylethylamine, respectively.

An e_{ds} parameter used for ds-mixing, the configuration interaction between 3 d_{z^2} (a_{1g}) and 4s (a_{1g}) orbitals (for D_{4h}), is difficult to estimate, because the transition energy of $d_{z^2} \rightarrow d_{x^2-y^2}$ is hard to separate in polarized crystal spectra. Fortunately, the band assigned to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition was observed separately in the E // b spectrum of **4** in z polarization for the first time, and the e_{ds} parameter is determined to be 2900 cm^{-1} using the rest parameters of the identical constant values. The ds-mixing is especially effective for the square planar complexes and tetrahedral distortions weaken this interaction. In fact, less distorted square planar complex **5** is described by e_{ds} = 4000 cm^{-1}, and as for square planar complexes, e_{ds} = 4500 cm^{-1} for **1** and e_{ds} = 6300 cm^{-1} for **2** and **3**.

In this way, we have obtained calculated transition energies and established assignment of d–d transitions given in Table 5. The optimized AOM parameters used for the calculations are listed in Table 6. The agreements between experimental and

Table 3. Selection Rule of Vibronic Coupling and Orbital Symmetry Mechanism
$\langle\phi_c|r_i|\phi_g\rangle$ means direct product of wave functions for ground (ϕ_g) and excited (ϕ_c) state and direction of electric 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_{4h} and D_{2h}), the transitions are allowed by coupling with ungerade vibrations in the polarization of the direction of electronic dipole moment.

D_{4h} Symmetry

Transitions	$\langle\phi_c\|r_i\|\phi_g\rangle$		Vibration Modes		
	i = z	x, y	A_{2u}	B_{2u}	E_u
$d_{z^2} \rightarrow d_{x^2-y^2}$	B_{2u}	E_u	—	z	x, y
$d_{xy} \rightarrow d_{x^2-y^2}$	A_{1u}	E_u	—	—	x, y
$d_{yz}, d_{zx} \rightarrow d_{x^2-y^2}$	E_u	$A_{1u} + A_{2u}B_{1u} + B_{2u}$	x, y	x, y	z

D_{2h} Symmetry

Transitions	$\langle\phi_c\|r_i\|\phi_g\rangle$			Vibration Modes			
	i = x	y	z	B_{1u}	A_u	B_{3u}	B_{2u}
$d_{z^2} \rightarrow d_{x^2-y^2}$	B_{3u}	B_{2u}	B_{1u}	z	—	x	y
$d_{xy} \rightarrow d_{x^2-y^2}$	B_{2u}	B_{3u}	A_u	—	z	y	x
$d_{yz} \rightarrow d_{x^2-y^2}$	A_u	B_{1u}	B_{2u}	y	x	—	z
$d_{zx} \rightarrow d_{x^2-y^2}$	B_{1u}	A_u	B_{3u}	x	y	z	—

C_{2v} Symmetry

Transitions	$\langle\phi_c\|r_i\|\phi_g\rangle$			Vibration Modes			
	i = x	y	z	A_1	A_2	B_1	B_2
$d_{z^2} \rightarrow d_{x^2-y^2}$	B_1	B_2	A_1	z	—	x	y
$d_{xy} \rightarrow d_{x^2-y^2}$	B_2	B_1	A_2	—	z	y	x
$d_{yz} \rightarrow d_{x^2-y^2}$	A_2	A_1	B_2	y	x	—	z
$d_{zx} \rightarrow d_{x^2-y^2}$	A_1	A_2	B_1	x	y	z	—

calculated values are excellent for each complex.

3d Electronic States and Bonding Properties. Here we confirm the present assignments in view of their physical meanings. The primary difficulty in assignment of square planar copper(II) complexes is the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition related to ds-mixing parameters. In the case of $[CuCl_4]^{2-}$ chromophores, the band due to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition lies in the highest energy region separately, which enables the band to be assigned.[1] In contrast, $[CuO_4]$ or $[CuN_4]$ complexes appear as a single broad band containing all the four transitions. Our strategy to separate the band and to assign the transition is lowering the effective symmetry by gradual distortion. Fortunately, with this strategy it was possible to limit the number of allowed transitions appropriately, in fact, the spectrum of **4** with *E* // *b* polarization the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition appear separately, because of appropriate crystal packing with approximately agreement between the *b* crystal axis and *z* molecular axis. On the basis of such a reliable assignment for **4**, square planar complexes (**2** and **3**) could be also assigned with gradual and slight distortion of $[CuN_4]$ chromophores. The ratios of e_{ds}/e_σ^{im} are 0.63 for **1**, 0.88 for **2** and **3**, 0.40 for **4**, and 0.56 for **5**, which also implies that ds-mixing is effective for square planar complexes.

For all the present complexes, the same ligands could be described reasonably by the identical AOM parameters. The variation of geometrical distortion of the $[CuN_4]$ chromophores and the combination of imidates and amines, namely, *trans*-[Cu(imidate)$_2$(amine)$_2$] and M_2[Cu(imidate)$_4$], could be described consistently. 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.,[26] which may also support the transferability of AOM parameters.

In this context, it is reasonable that two imidate ligands are described by similar e_σ^{im} and e_π^{im} values and that the ratio of e_σ^{im}/e_π^{im} = 4.24 and 4.73 for 5,5-diphenylhydantoinate and succinimidate, respectively. The e_π^{im} parameters correspond to a lone pair being perpendicular to imidate ring. The lone pair of imidates forms π-bonding being oriented at d_{xy} orbital and in-plane of $[CuN_4]$ coordination plane which lowers the $d_{xy} \rightarrow d_{x^2-y^2}$ transition energy. The increase of two imidates between *trans*-[Cu(imidate)$_2$(amine)$_2$] and M_2[Cu(imidate)$_4$] results in remarkable shoulder in the spectra of **1**. This feature 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$_2$O reported by Walsh and Hathaway.[11]

Concluding Remarks

Copper(II) complexes, Rb$_2$[Cu(succim)$_4$]•2H$_2$O (**1**), *trans*-[CuL$_2$(*R*-chea)(*S*-chea)] (**2**), and *trans*-[CuL$_2$(*R*-chea)$_2$] (**3**), have been prepared and the crystal structures have been determined. The electronic polarized single crystal spectra were determined for **1**, **2**, **3**, *trans*-[CuL$_2$(*R*-phenea)(*S*-phenea)] (**4**), and *trans*-[CuL$_2$(*R*-phenea)$_2$][CuL$_2$(*S*-phenea)$_2$] (**5**). Taking

Table 4. Components (Maximum Wave Numbers (cm^{-1}), Absorbance, and Half Width (cm^{-1})) by Gaussian Curve Fitting of the Polarized Crystal Spectra

	Polarization	Wave number/cm^{-1}	Absorbance	Half width/cm^{-1}
1	$E \perp b$	15800	0.47	2500
		19000	0.81	2600
		21000	1.36	3300
	$E // b$	18700	0.19	3200
		20900	0.14	3700
2	$E \perp b$	17300	0.35	2700
		19800	0.36	3100
		20900	0.27	3200
		21300	0.27	3200
	$E // b$	17400	0.28	2700
		19800	0.30	3300
		20900	0.23	3200
		21300	0.23	3200
3	$E \perp b$	17200	0.54	2800
		19800	0.57	3500
		20900	0.33	3300
		21300	0.33	3300
	$E // b$	17300	0.28	2600
		19800	0.30	3300
		20900	0.24	3200
		21300	0.24	3200
4	$E \perp b$	17900	0.88	4700
		18400	0.88	2900
	$E // b$	16100	0.78	3800
5	$E \perp b$	17500	0.09	4000
		18500	0.18	3200
		19500	0.18	5000
	$E // b$	17500	0.10	3000
		18500	0.27	4300
		19500	0.30	3500

Table 5. Transition Energy (cm^{-1}) Deconvoluted by Gaussian Curve Fitting of Polarized Crystal Spectra and Calculated Transition Energy (cm^{-1}) by AOM

D_{4h}		d_{yz},$d_{zx} \rightarrow d_{x^2-y^2}$	$d_{z^2} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{x^2-y^2}$
1	$E \perp b$	21000	19000	15800
	$E // b$	20900	18700	—
	AOM	21300	18700	15300

D_{2h}		$d_{zx} \rightarrow d_{x^2-y^2}$	$d_{yz} \rightarrow d_{x^2-y^2}$	$d_{z^2} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{x^2-y^2}$
2	$E \perp b$	21300	20900	19800	17300
	$E // b$	21300	20900	19800	17400
3	$E \perp b$	21300	20900	19800	17200
	$E // b$	21300	20900	19800	17300
	AOM	21300	20900	20200	17500

C_{2v}		$d_{zx} \rightarrow d_{x^2-y^2}$	$d_{yz} \rightarrow d_{x^2-y^2}$	$d_{z^2} \rightarrow d_{x^2-y^2}$
4	$E \perp b$	18400	17900	—
	$E // b$	—	—	16100
	AOM	18900	17700	16100
5	$E \perp b$	19500	18500	17500
	$E // b$	19500	18500	17500
	AOM	19800	18900	17500

Table 6. List of the AOM Parameters for the Complexes

	1	**2, 3**	**4**	**5**
θ_{im}/°	0.0	0.0	12.5	6.6
θ_{am}/°	—	0.0	10.1	8.4
e_σ^{im}/cm^{-1}	7100	7200	7200	7200
e_π^{im}/cm^{-1}	1500	1700	1700	1700
e_σ^{am}/cm^{-1}	—	6300	6700	6700
e_{ds}/cm^{-1}	4500	6300	2900	4000

into account for molecular projections of electric vectors, one can deconvolute these spectra according to selection rules by means of Gaussian curves. By means of selection rules and AOM calculations, 3d orbital orders can be assigned as follows: $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz}$,$d_{zx}$ for **1**, $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{zx}$ for **2** and **3**, and $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{zx}$ for **4** and **5**. The $d_{z^2} \rightarrow d_{x^2-y^2}$ transition could be observed separately in z polarization for **4** for the first time, and that enabled us to establish a reliable assignment for the present [CuN_4] complexes. Distortion of [CuN_4] chromophore resulted in decreasing the peak wave number of the spectra, and the detailed features were explained by individual orbital levels for **2**, **3**, **4**, and **5**.

The authors are grateful for Mr. Ken-ichi Sakaguchi (Institute for Protein Research, Osaka University) for the use of a diffractometer and his help with aspects of the X-ray studies. They also thank Dr. Takashi Komorita (Department of Chemistry, Graduate School of Science, Osaka University) for providing FORTRAN programs for angular overlap calculations, AOM 38 and Gaussian curve fitting, GA3.

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