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Structures of Bis(5,5-diphenylhydantoinato)copper(II) Complexes with Primary Amines Involving Square Pyramidal CuN_4O Chromophores

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Copper(II) complexes $[CuL_2(i\text{-}PrNH_2)_2\cdot H_2O]$ (**1a**), $[CuL_2(i\text{-}PrNH_2)_2]$ (**1b**), $[CuL_2(EtNH_2)_2\cdot H_2O]$ (**2a**), $[CuL_2(EtNH_2)_2]\cdot CHCl_3$ (**2b**), $[CuL_2(EtNH_2)_2\cdot H_2O]\cdot 2CHCl_3$ (**2c**), and $[CuL_2(EtNH_2)_2\cdot MeOH]$ (**2d**) (L = 5,5-diphenylhydantoinate) have been prepared. The crystal structures of **1a**, **2c**, and **2d** were determined by X-ray analysis. Each CuN_4O chromophore is a five-coordinated square-based pyramidal geometry. The axial Cu–O distances are Cu(1)–O(1)(water) = 2.362(10) Å, Cu(1)–O(1)(water) = 2.436(9) Å and Cu(1)–O(1)(MeOH) = 2.33(1) Å, for complexes **1a**, **2c**, and **2d**, respectively. Intramolecular hydrogen bonds are formed between the carbonyl oxygens and amino hydrogens (C=O···H–N) as well as the axial ligand (C=O···H–O). The latter hydrogen bonds stabilize the axial ligand for coordination. Moreover, double intermolecular hydrogen bonds link the 5,5-diphenylhydantoinate ligands (C=O···H–N) belonging to be adjacent complex molecules in all three complexes. The electronic spectra of the complexes in the solid state and in chloroform solutions were determined at room temperature, and a considerable change in ligand field bands was observed. The five-coordinated complexes in the chloroform solutions release their axial water ligand and the CuN_4O chromophore converts into a distorted tetrahedral CuN_4 chromophore.

Copper(II) complexes, which are able to take various coordination geometries, have been widely investigated.[1] There has been interested in the relationships between the structures of the coordination environment and their electronic states of bis(imidato)bis(amine)copper(II) complexes, where "imidato" denotes a cyclic imidate ion, such as succinimidate (abbreviated as succim) and hydantoinate (hyd).[2—5] Depending upon the combinations of imidates and amines, the following three types of complexes were obtained in the solid state (Fig. 1): (1) red complexes of the general formula $[Cu(imidato)_2(amine)_2]$ with square planar CuN_4 chromophores, (2) blue-violet or indigo-blue complexes of $[Cu(imidato)_2(amine)_2]$ with flattened tetrahedral CuN_4 chromophores, and (3) deep-blue complexes of $[Cu(imidato)_2(amine)_2\cdot H_2O]$ with square-based pyramidal CuN_4O chromophores. Most of the bis(imidato)bis(amine)-copper(II) complexes are type 1. The X-ray structure determinations of square-planar CuN_4 complexes have been reported on *trans*-$[Cu(succim)_2(n\text{-}PrNH_2)_2]$[6] and *trans*-[Cu-$(succim)_2(pyridine)_2]$.[7] When 1-phenylethylamine (phenea) was employed, *trans*-$[Cu(hyd)_2(R\text{-}phenea)_2]$ and *trans*-[Cu-$(succim)_2$(R-phenea)(S-phenea)] of type 2 were obtained.[5] On the other hand, the corresponding complexes of imidates with a six-membered ring, such as 3,3-dimethylglutarimidate (3,3-dimgluim) and glutarimidate, are type 1. In a previous paper, an X-ray analysis of *trans*-$[Cu(3,3\text{-}dimgluim)_2(R\text{-}phenea)_2]$ was reported.[5] Three examples of type 3 were obtained corresponding to bis(succinimidato)copper(II) complexes with cyclic amines (4-methylpyridine, 3,5-dimethylpyridine and piperidine).[3,4] The crystal structure of [Cu-$(succim)_2(4\text{-}methylpyridine)_2\cdot H_2O]$ was reported.[8]

The present paper deals with bis(5, 5- diphenylhydantoinato)copper(II) complexes. Since 5,5-diphenylhydantoinate contains two bulky phenyl groups, various steric effects are expected on bis(5,5-diphenylhydantoinato)-copper(II) complexes. The corresponding bis(1-phenylethylamine)copper(II) complex also has a flattened tetrahedral CuN_4 chromophore.[9] The complexes of bis(2-propylamine)-copper(II) and bis(ethylamine)copper(II) yield blue-colored crystals with the formula of $[CuL_2(amine)_2L_{ax}]$ (L = 5,5-diphenylhydantoinate, $L_{ax} = H_2O$ or MeOH). In contrast, the corresponding bis(succinimidato)copper(II) complexes involve the typical square-planar CuN_4 chromophore.[2] Judging from their color and formula, the blue-colored complexes would have CuN_4O chromophores. It is the first example of this series that a methanol molecule coordinates to the copper(II) ion, and no crystal structure of the primary amine complex of type 3 has been reported. Therefore, we have determined the structures of these complexes.

Experimental

Reagents. All of the reagents were purchased from Wako pure chemical industries, Ltd. and used without further purification.

Preparation of $[CuL_2(i\text{-}PrNH_2)_2\cdot H_2O]$ (1a). 5,5-Diphenylhydantoin (2.52 g, 10.0 mmol) and 2-propylamine (1.18 g, 20.0 mmol) were added to a solution of $Cu(CH_3CO_2)_2\cdot H_2O$ (1.00 g,

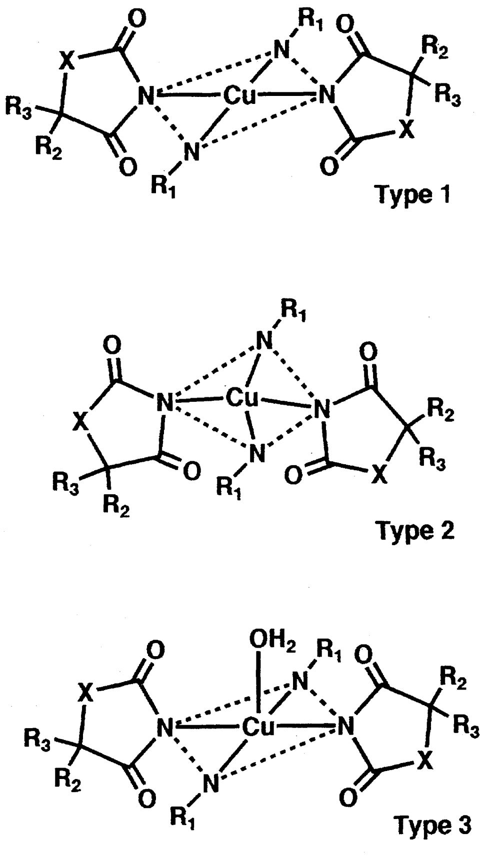

Fig. 1. Three types of chromophores of complexes: (1) [Cu(imidato)$_2$(amine)$_2$] with square planar CuN_4, (2) [Cu(imidato)$_2$(amine)$_2$] with flattened tetrahedral CuN_4, (3) [Cu(imidato)$_2$(amine)$_2$·H_2O] with square-based pyramidal CuN_4O.

5.00 mmol) in EtOH (100 cm^3) and stirred for 1 h at ca. 50 °C. During the reaction, blue precipitates gradually appeared in a deep-blue solution. The resulting suspension was filtrated by suction. The blue precipitates were recrystallized from $CHCl_3$–MeOH (4 : 1, v/v). Blue prismatic crystals were obtained. Found: C, 61.48; H, 6.00; N, 11.91%. Calcd for $C_{36}H_{42}N_6CuO_5$: C, 61.57; H, 6.03; N, 11.97%.

Preparation of [CuL$_2$(*i*-PrNH$_2$)$_2$] (1b). Blue precipitates **1a** were heated at ca. 130 °C in an evacuated desiccator. Heating was continued for 2 h until the blue monohydrate complexes turned completely into reddish micro-crystals. Being allowed to stand under the atmosphere, the reddish complex **1b** rapidly changed into the blue complex **1a**. Found: C, 63.19; H, 5.86; N, 12.24%. Calcd for $C_{36}H_{40}N_6CuO_4$: C, 63.19; H, 5.89; N, 12.28%.

Preparation of [CuL$_2$(EtNH$_2$)$_2$·H$_2$O] (2a). 5,5-Diphenylhydantoin (2.52 g, 10.0 mmol) and 70% aqueous solution of ethylamine (1.30 g, 20.0 mmol) were added to a solution of Cu(CH$_3$CO$_2$)$_2$·H$_2$O (1.00 g, 5.00 mmol) in EtOH (100 cm^3) and stirred for 1 h at ca. 50 °C. The resulting blue suspension was filtrated by suction. Recrystallization was carried out from $CHCl_3$–MeOH (1 : 1, v/v). Found: C, 60.26; H, 5.53; N, 12.30%. Calcd for $C_{34}H_{38}N_6CuO_5$: C, 60.57; H, 5.68; N, 12.46%.

Preparation of [CuL$_2$(EtNH$_2$)$_2$]·CHCl$_3$ (2b). The blue crude products of **2a** were stirred in $CHCl_3$–MeOH (2 : 1, v/v) for 30 min at ca. 50 °C in the presence of molecular sieves 3A. After filtration to remove the molecular sieves, the solution was allowed to stand for one month in a refrigerator. Reddish precipitates were deposited and collected by filtration and dried in a desiccator overnight. Found: C, 54.12; H, 4.84; N, 10.71%. Calcd for $C_{35}H_{37}N_6Cl_3CuO_4$: C, 54.20; H, 4.91; N, 10.84%.

Preparation of [CuL$_2$(EtNH$_2$)$_2$·H$_2$O]·2CHCl$_3$ (2c). Single crystals appropriate for an X-ray structure analysis were prepared by recrystallization of the crude products of **2a** from $CHCl_3$–MeOH (4 : 1, v/v). Only a very small amount of blue crystals were obtained which contained two chloroform molecules per complex molecule.

Preparation of [CuL$_2$(EtNH$_2$)$_2$·MeOH] (2d). Crude products of **2a** were stirred in $CHCl_3$–MeOH (4 : 1, v/v) with molecular sieves 3A in a round-bottomed flask attached to a silica gel dry tube. After filtration, the deep blue solution was slowly cooled to room temperature. Blue crystals of **2d** appropriate for an X-ray structure analysis were obtained from the filtrate. We have not been able to obtain a sufficient amount of analytically pure **2d**, due to its contamination by **2a** and other products.

Crystal Structure Determination. Each crystal of **1a**, **2c**, and **2d** was sealed in a glass capillary and used for an X-ray experiment. The diffraction data were measured on a Rigaku AFC5R diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ = 1.5418 Å) for **1a** and with Mo $K\alpha$ radiation (λ = 0.7107 Å) for **2c** and **2d**. The reflections were collected at 296 K using the ω–2θ scan technique over the range $2\theta < 120°$ for **1a** and over the range $2\theta < 55°$ for **2c** and **2d**.

On a SGI Indy workstation with a teXsan crystallographic software package,$^{10)}$ the structures of **1a**, **2c**, and **2d** were solved by heavy-atom methods, expanded using Fourier techniques, and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of H(011) and H(012) for **1a** and **2c** and H(01) for **2d** were located on a difference-Fourier-map. The other hydrogen atoms were fixed at a standard geometry. They were included, but not refined, except H(01) for **2d**.

Measurements. The differential thermal analysis and the differential thermal gravimetry measurement were recorded on a Seiko Instruments Inc. SSC-5000 thermal analysis system in the atmosphere at a heating rate of 20 °C min^{-1}. 10.0 mg of α-alumina was used as the reference sample, and the examined sample of **1a** was 10.0 mg.

The diffuse reflectance spectra of the complexes in the solid state were measured on a Hitachi U-3400 UV/vis/NIR spectrophotometer equipped with a diffuse reflectance attachment. The absorption spectra of the complexes in the chloroform solutions were measured in 1 mmol dm^{-3} concentration at room temperature with a Hitachi U-3400 UV/vis/NIR spectrophotometer.

Results and Discussion

Crystal Structures. The crystal data for **1a**, **2c**, and **2d** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. The ORTEP drawings of the complexes are shown in Fig. 2. Lists of atomic coordinates, anisotoropic thermal parameter, and bond distances and angles are deposited as Document No. 70013 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Two space groups, $P2_1$ and $P2_1/n$, could be considered for **1a**; each space group was examined. As a result, the R value for $P2_1/n$ was much better. The space group $P2_1/n$ has a crystallographic center of symmetry. Both axial positions were occupied by oxygen atoms. When their occupancy

Table 1. Crystal Data for **1a**, **2c**, and **2d**

	1a	**2c**	**2d**
Formula	$C_{36}H_{42}N_6CuO_5$	$C_{36}H_{40}N_6Cl_6CuO_5$	$C_{35}H_{40}N_6CuO_5$
Mol. wt.	702.31	913.01	688.28
Crystal size/mm	0.25 × 0.25 × 0.25	0.25 × 0.28 × 0.22	0.15 × 0.15 × 0.30
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (#14)	$C2$ (#5)	$P\bar{1}$ (#2)
a/Å	9.9390(9)	14.026(6)	13.628(3)
b/Å	8.968(1)	9.821(2)	14.302(5)
c/Å	20.993(1)	27.094(6)	10.093(4)
α/°			106.20(3)
β/°	103.183(9)	91.97(5)	97.55(3)
γ/°			64.87(2)
V/Å^3	1821.8(3)	3729(1)	1710(1)
Z	2	4	2
$D_c/g\,\mathrm{cm}^{-1}$	1.28	1.63	1.34
μ/cm^{-1}	12.40	10.68	6.89
$F(000)$	738	1876	722
No. data measured	3092	4724	7054
No. unique data	2906	4534	6710
No. observed data ($F_o \geq 3.0\sigma(F_o)$)	1804	3504	2445
$R^{a)}$	0.048	0.062	0.069
$R_w{}^{b)}$	0.050	0.057	0.055

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

factors were 1, the R value was about 8%, and was difficult to improve. However, when the equal occupancy factors for the two oxygen atoms were refined to 0.5, the R value decreased to about 4.8%. It was confirmed by the results of a differential thermal gravimetry measurement and elemental analysis that only one water molecule was contained in the **1a** molecule. Therefore, complex **1a** is not six-coordinated, but five-coordinated. In **1a**, atoms labeled without * show an independent moiety, and atoms labeled with * show an expanded moiety by a symmetry operation ($-x$, $-y$, $-z$).

The coordination geometries around the copper(II) ion in CuN_4O chromophores of **1a**, **2c**, and **2d** are square pyramidal. No considerable difference was found in the in-plane structure among the three complexes. The Cu–N(imidate) (N(1) or N(4)) and Cu–N(amine) (N(3) or N(6)) bond lengths range from 2.006(3) to 2.086(8) Å and 2.01(1) to 2.07(1) Å, respectively. The bond angles of N(imidate)–Cu–N(amine) range from 87.7(4) to 91.8(3) °, which are retained to be close to 90 ° for the three complexes. Each value is comparable with those of the analogous bis(imidato)bis(amine)copper(II) complexes for any types of their chromophores.

In the CuN_4O chromophores of **2c** and **2d**, the copper atom is deviated towards the axial oxygen atom from the basal N_4 plane. In the cases of **2c** and **2d**, the basal planes in the CuN_4O chromophores distort opposite to the axial oxygen atom, and the displacements of the copper atom from the N_4 mean plane are 0.080 and 0.088 Å, respectively. The bond angles of N(imidate)–Cu–N(imidate) (N(1)–Cu(1)–N(4)) are 177.8(3) and 175.4(5)°, N(amine)–Cu–N(amine) (N(3)–Cu(1)–N(6)) are 165.0(3) and 174.4(4)°, respectively.

The Cu(1)–O(1) bond distances between the copper atom and the axial oxygen atom in **1a**, **2c**, and **2d** are 2.362(10), 2.436(9), and 2.33(1) Å, respectively. As compared to [Cu(succim)$_2$(4-methylpyridine)$_2$·H_2O] (Cu–O is 2.282(3) Å)[8] and 166 samples of five-coordinate copper(II) complexes surveyed by Tahirov and Lu[11] with the Cambridge Structural Database,[12] the axial Cu–O bond lengths of the three complexes are comparable with other complexes.

The distance of Cu–O(MeOH) (2.33(1) Å in **2d**) is shorter than that of Cu–O(water) (2.436(9) Å in **2c**). Two examples of the five-coordinated copper(II) complexes containing the methanol on the axial site have been reported.[13,14] Castellani and Carugo[13] mentioned that the axial bond distance of Cu–O(MeOH) is longer than that of Cu–O(water), because it can be attributed to the weakness of methanol as a Lewis base. On the contrary, the results of complexes **2c** and **2d** show an opposite tendency. This indicates that the axial bond distances do not simply depend on the donor property of an axial ligand.

The corresponding bis(succinimidato)copper(II) complexes with 2-propylamine or ethylamine have square planar CuN_4 chromophores.[2] However, the present bis(5,5-diphenylhydantoinato)copper(II) complexes easily combine with another ligand, such as water, and consist of five-coordinated square pyramidal chromophores. It is expected that there would be few differences in the ligand field strength between bis(succinimidato)copper(II) complexes and bis(5,5-diphenylhydantoinato)copper(II) complexes with the same amine ligands. In spite of this, an additional fifth coordination is allowed for the bis(5,5-diphenylhydantoinato)copper(II) complexes. The copper atoms in the latter complexes have sufficient space to coordinate for the fifth ligand on the axial site, owning to the bulkiness of the phenyl groups of 5,5-diphenylhydantoinate ligands and the steric compact-

Table 2. Selected Bond Distances (Å) and Bond Angles (°) for **1a**, **2c**, **2d**

Bond distances	**1a**	**2c**	**2d**
Cu(1)–O(1)	2.362(10)	2.436(9)	2.33(1)
Cu(1)–N(1)	2.006(3)	2.016(7)	2.076(9)
Cu(1)–N(4)		2.024(7)	2.086(8)
Cu(1)–N(3)	2.049(6)	2.066(10)	2.01(1)
Cu(1)–N(6)		2.039(9)	2.01(1)
O(1)–C(35)			1.40(2)
N(1)–C(1)	1.393(6)	1.43(1)	1.39(2)
C(1)–O(2)	1.234(6)	1.22(1)	1.23(2)
C(1)–N(2)	1.341(5)	1.35(1)	1.36(1)
N(2)–C(3)	1.452(7)	1.46(1)	1.45(2)
C(3)–C(2)	1.554(6)	1.56(1)	1.54(2)
C(2)–O(3)	1.228(7)	1.22(1)	1.24(2)
C(2)–N(1)	1.354(6)	1.37(1)	1.36(2)
N(4)–C(18)		1.41(1)	1.39(2)
C(18)–O(4)		1.24(1)	1.24(2)
C(18)–N(5)		1.34(1)	1.36(1)
N(5)–C(20)		1.46(1)	1.46(2)
C(20)–C(19)		1.56(1)	1.58(2)
C(19)–O(5)		1.22(1)	1.22(2)
C(19)–N(4)		1.41(1)	1.35(2)
N(3)–C(16)	1.47(1)	1.53(2)	1.47(2)
C(16)–C(17)	1.51(3)	1.41(3)	1.43(3)
N(6)–C(33)		1.51(2)	1.47(2)
C(33)–C(34)		1.27(3)	1.52(2)
Bond angles	**1a**	**2c**	**2d**
N(1)–Cu(1)–N(3)	89.5(2)	89.6(3)	91.2(4)
N(3)–Cu(1)–N(4)		91.0(3)	87.7(4)
N(3)–Cu(1)–N(1*)[a]	90.5(2)		
N(4)–Cu(1)–N(6)		91.8(3)	89.8(4)
N(1*)–Cu(1)–N(3*)[a]	89.5(2)		
N(6)–Cu(1)–N(1)		88.1(3)	90.9(4)
N(3*)–Cu(1)–N(1)	90.5(2)		
N(1)–Cu(1)–N(4)		177.8(3)	175.4(5)
N(1)–Cu(1)–N(1*)[a]	180.0		
N(3)–Cu(1)–N(6)		165.0(3)	174.4(4)
N(3)–Cu(1)–N(3*)[a]	180.0		
Cu(1)–N(1)–C(1)	126.3(3)	123.2(6)	125.1(9)
Cu(1)–N(1)–C(2)	125.4(3)	126.8(6)	127.0(9)
Cu(1)–N(4)–C(18)		123.5(6)	127.7(9)
Cu(1)–N(4)–C(19)		127.5(6)	122.7(9)
C(2)–N(1)–C(1)	108.0(3)	110.0(8)	107.7(9)
N(1)–C(1)–O(2)	124.3(4)	123.6(9)	125(1)
N(1)–C(2)–O(3)	126.1(4)	126.4(9)	126(1)
C(19)–N(4)–C(18)		109.0(8)	109.6(10)
N(4)–C(18)–O(4)		124.7(9)	125(1)
N(4)–C(19)–O(5)		127.5(9)	128(1)
Cu(1)–N(3)–C(16)	123.2(8)	119.1(8)	114(1)
N(3)–C(16)–C(17)	116(1)	114(1)	114(1)
Cu(1)–N(6)–C(33)		117.4(8)	121(1)
N(6)–C(33)–C(34)		118(1)	114(1)

a) The atoms labeled with * are expanded by symmetry operation ($-x$, $-y$, $-z$).

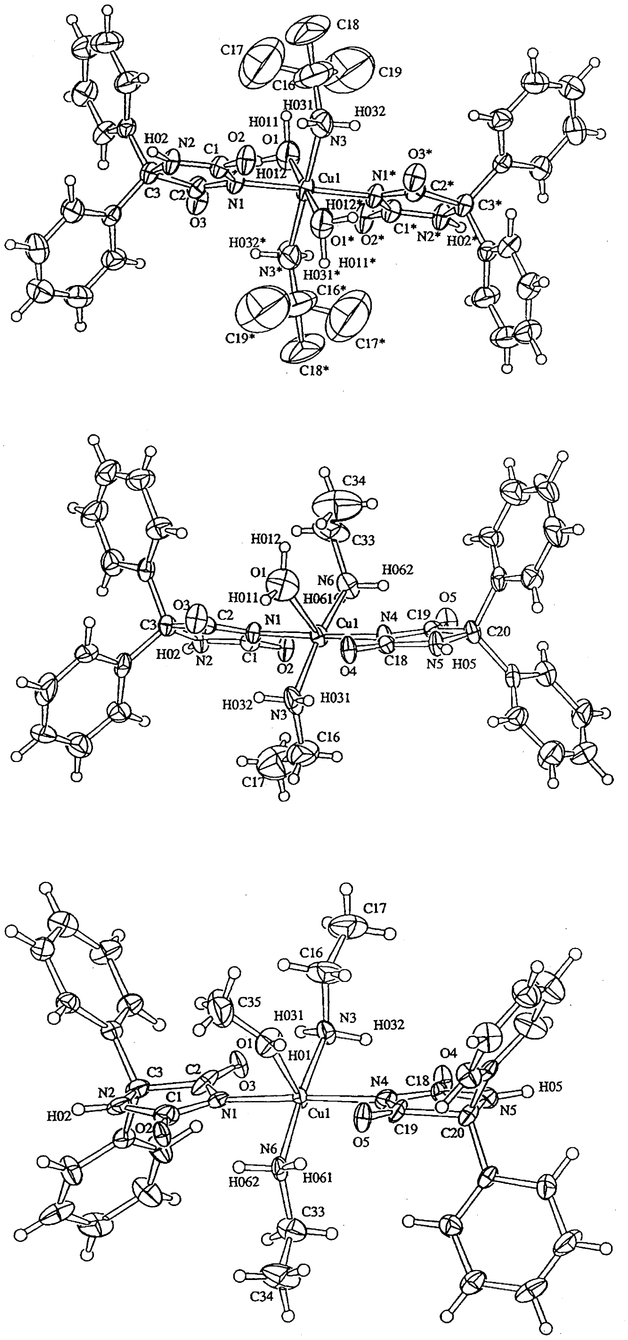

Fig. 2. ORTEP drawings of [$CuL_2(i\text{-}PrNH_2)_2 \cdot H_2O$] (**1a**) (Fig. 2a), [$CuL_2(EtNH_2)_2 \cdot H_2O$]·$2CHCl_3$ (**2c**) (Fig. 2b), and [$CuL_2(EtNH_2)_2 \cdot MeOH$] (**2d**) (Fig. 2c). For **2c**, two solvent $CHCl_3$ molecules are omitted for clarity.

ness of the amine ligands. Because of the steric requirement between the coordinated imidates and the amines, the five-membered rings of the imidate ions are perpendicular to the CuN_4 plane with the carbonyl groups facing in the direction of the axial ligand, which is preferable to form intramolecular hydrogen bonds. These two conditions lead the axial coordination to stabilize.

Intermolecular (C=O···H–N) and intramolecular (C=O···H–N and C=O···H–O) hydrogen bonds were observed in complexes **1a**, **2c**, and **2d**. The possible hydrogen-bond distances are listed in Table 3. The hydrogen bonds in a crystal of **2c** are shown in Fig. 3. Most of the bond distances, being in either intermolecular or intramolecular hydrogen bonds, are within the range of the statistical criterion by Taylor and Kennard.[15)]

Table 3. Possible Hydrogen Bond Distances (Å)

Intramolecular	N···O (N–H···O=C)		O···O (O–H···O=C)		N···O (N–H···O=C)
1a					
N(3)–H(031)···O(2)	2.960(5)	O(1*)$^{a)}$···O(2)	2.779(9)	N(2)–H(02)···O(2*)$^{a,b)}$	2.849(5)
N(3)–H(032)···O(3*)$^{a)}$	2.970(6)	O(1*)$^{a)}$···O(3)	2.876(9)		
2c					
N(3)–H(031)···O(4)	2.95(1)	O(1)···O(3)	2.67(1)	N(2)–H(02)···O(4)$^{c)}$	2.88(1)
N(6)–H(061)···O(2)	2.92(1)	O(1)···O(4)	2.81(1)	N(5)–H(05)···O(2)$^{d)}$	2.80(1)
N(6)–H(062)···O(5)	2.83(1)				
2d					
N(3)–H(031)···O(3)	2.78(1)	O(1)···O(5)	2.96(1)	N(2)–H(02)···O(4)$^{e)}$	2.91(1)
N(6)–H(032)···O(4)	2.84(1)			N(5)–H(05)···O(2)$^{f)}$	2.84(1)
N(6)–H(061)···O(3)	2.89(1)				
N(6)–H(062)···O(5)	2.82(1)				

a) For **1a**, the atoms labelled with * are expanded by symmetry operation $(-x, -y, -z)$.
b,c,d,e,f) Expanded by symmetry operations $(x+1, y, z)$, $^{b)}$ $(x, y+1, z)$, $^{c)}$ $(x, y-1, z)$, $^{d)}$ $(x, y, z-1)$, $^{e)}$ and $(x, y, z+1)$, $^{f)}$ respectively.

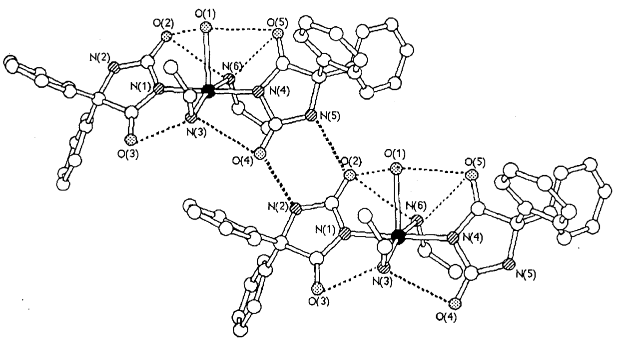

Fig. 3. Intramolecular and intermolecular hydrogen bonds observed in a crystal of [CuL$_2$(EtNH$_2$)$_2$·H$_2$O]·2CHCl$_3$ (**2c**). Two solvent CHCl$_3$ molecules are omitted for clarity.

There are two types of intramolecular hydrogen bonds in the present complexes. The first type is formed between amino hydrogens (N(3)–H, or N(6)–H) and carbonyl oxygens of 5,5-diphenylhydantoinate (O(2), O(3), O(4) or O(5)). These are commonly observed in analogous bis(imidato)bis(amine)copper(II) complexes involving the primary amine ligands. The second type is formed between carbonyl oxygens (O(2), O(3), O(4) or O(5)) and protons in the axial ligand (O(1)–H), represented as C=O···H–O. Similar hydrogen bonds between the imidate carbonyl groups and the hydrogens in the axial water molecule are also found in [Cu(succim)$_2$(4-methylpyridine)$_2$·H$_2$O].$^{8)}$ These intramolecular hydrogen bonds play an important role in stabilization for the axial coordination.

In the parallel double intermolecular hydrogen bonds, donor nitrogen atoms (N(2)–H or N(5)–H) and acceptor oxygen atoms (O(2) or O(4)) are alternate with each other. A similar conformation of the intermolecular hydrogen bonds was also observed in crystals of *trans*-[Cu(hyd)$_2$(R-phenea)$_2$].$^{5)}$ Judging from the fact that both 5,5-diphenylhydantoinate and hydantoinate are able to form double hydrogen bonds, the

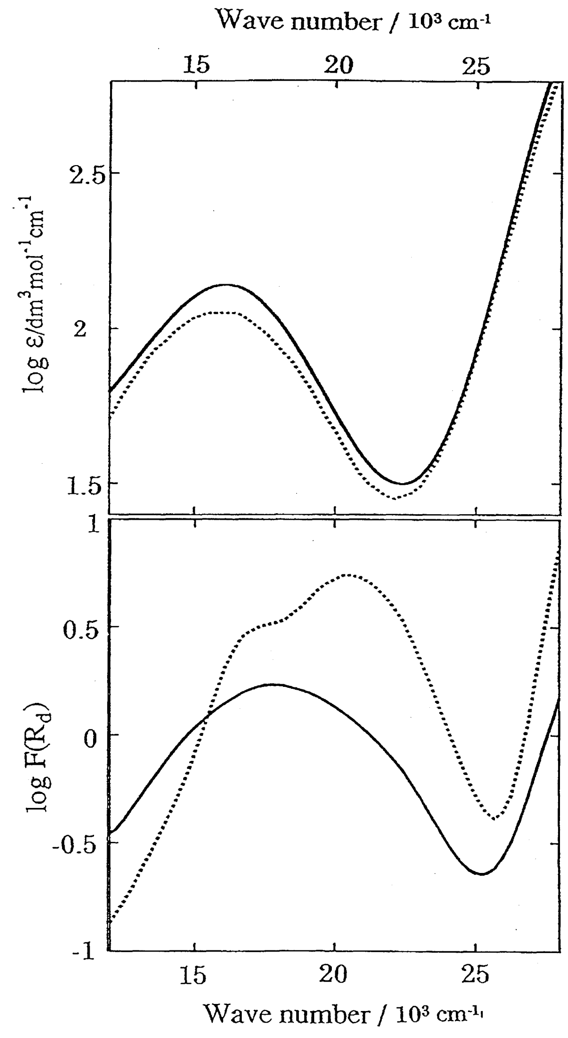

Fig. 4. Absorption spectra in CHCl$_3$ (1 mmol dm^{-3}) (above) and reflectance spectra (below) of [CuL$_2$(*i*-PrNH$_2$)$_2$·H$_2$O] (**1a**) (solid line) and [CuL$_2$(*i*-PrNH$_2$)$_2$] (**1b**) (dotted line).

Table 4. Peaks and Half widths of Electronic Spectra

	Reflectance spectra Peak/cm^{-1}	log $F(R_d)$	Band width/cm^{-1} a)
1a	17750	0.13	7280
1b	20590	0.74	4370
	16790	0.33	2930
2a	17150	0.23	6600
2b	19790	0.33	5190
	16270	−0.28	2530
	Absorption spectra Peak/cm^{-1}	log ε/dm^3 mol^{-1} cm^{-1}	Band width/cm^{-1} a)
1a	15650	2.00	6560
1b	15950	2.05	7200
2a	16100	2.00	6450
2b	16500	2.05	6660

a) Half width.

phenyl groups in 5,5-diphenylhydantoinate do not interfere with the intermolecular hydrogen bonds.

Thermal Analysis. A curve of the differential thermal analysis of complex **1a** exhibits a broad endothermic peak in the range from room temperature to 171 °C. A differential thermal gravimetry measurement shows a weight loss of 2.15% in the same temperature range. The weight loss amounts to 1 mol of water per 1 mol of complex (Calcd 2.64%). In addition to the result of the elemental analysis, the amount of weight loss is evidence that complex **1a** contains only one water molecule.

Electronic Spectra. The reflectance spectra of **1a** and **1b** in the solid state are shown in Fig. 4. Curve-fitting analyses were performed for the reflectance spectra of **1b** and **2b** using the GA3 program;[16] the resulting electronic spectral data of **1a**, **1b**, **2a**, and **2b** in the solid state are listed in Table 4.

The five-coordinated complex **1a** involving the CuN_4O chromophore shows the peak of ligand field band at 17750 cm^{-1} with a broad half width. The spectrum of this complex corresponds to those of [Cu(succim)$_2$(4-methylpyridine)$_2$·H_2O] and [Cu(succim)$_2$(3,5-dimethylpyridine)$_2$·H_2O],[3,8] which coordinate a water molecule on the axial site. Complex **2a** shows the band maximum at 17150 cm^{-1}, which is similar to those of complexes involving a CuN_4O chromophore. It is concluded that the complex of **2a** also has a CuN_4O chromophore. The reflectance spectra of the red complexes, **1b** and **2b**, show a main peak at about 20000 cm^{-1} and with a shoulder over the range of 16000—17000 cm^{-1}. These spectra are quite similar to those of the other red copper(II) complexes of type 1, which involve a square-planar CuN_4 chromophore.[2—5]

The red and blue crystals of the present complexes are dissolved in chloroform to form dark-blue solutions. The absorption spectra of the chloroform solutions of **1a**, **1b** are shown in Fig. 4 and the electronic spectral data of **1a**, **1b**, **2a**, and **2b** in the chloroform solutions are listed in Table 4. The maxima of their ligand field bands lie at 16000 cm^{-1} with a broad half width (7200—6500 cm^{-1}). The five-coordinated (**1a** and **2a**) and the four-coordinated (**1b** and **2b**) complexes indicate a similar spectra in chloroform solutions (Fig. 4). These ligand field bands are far lower than the wave-numbers of the bands of the same complexes in the solid state (Table 4). On the other hand, the reflectance spectrum of *trans*-[Cu(succim)$_2$(R-phenea)(S-phenea)], which involves a distorted tetrahedral CuN_4 chromophore (classified as type 2), shows the peak of the ligand field band at 16600 cm^{-1} with a broad half width.[5] This spectrum is relatively close to the absorption spectra of the present complexes in chloroform solutions. It is considered that the five-coordinated complexes in the chloroform solutions are free from any crystal-packing effects, and that the complex molecule releases the axial water ligand coordinating to the copper(II) ion. Thus, the coordination geometry of the complex is converted into a distorted tetrahedral CuN_4 chromophore. The detailed structure and band assignments were not established in the present study. Studies of these are now in progress, and will be reported elsewhere.

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