Structures and Electronic Spectra of Aquadiiminebis(succinimidato)copper(II) Complexes with Square Pyramidal [CuN_4O] Chromophores (Diimine = 1,10-Phenanthroline and 2,2′-Bipyridine)

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(Received October 28, 1998)

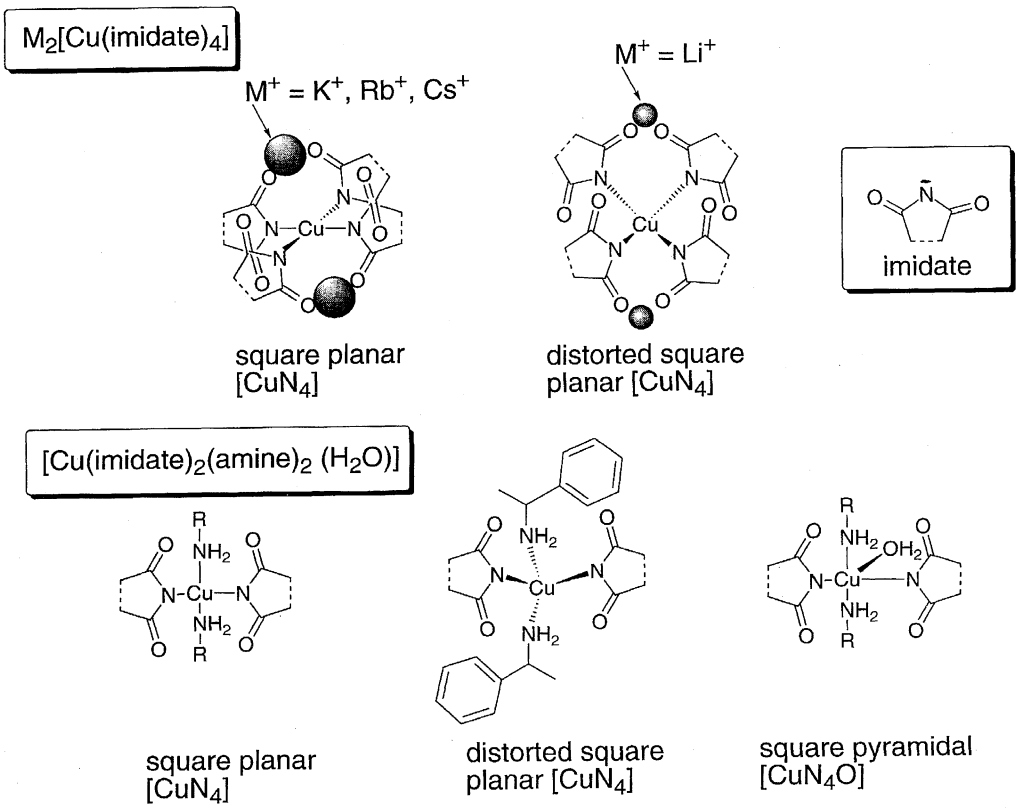
Copper(II) complexes $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**) (succim = succinimidate, phen = 1,10-phenanthroline) and $[Cu(succim)_2(bpy)H_2O]$ (**2**) (bpy = 2,2′-bipyridine) were prepared and the crystal structures were determined by X-ray crystallography. The coordination geometries are found to be five-coordinated square-based pyramidal [CuN_4O] for each complex. Crystal data for complex **1** 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 **2** 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 axial Cu–O(water) bond distances of the present complexes (2.548(5) Å for **1** and 2.673(4) Å for **2**) are appreciable longer than those of other square pyramidal *trans*-[CuN_4O] complexes. The diffuse reflectance spectra showing a broad peak at about 17000 cm^{-1} were analyzed by means of Gaussian curve fitting and angular overlap model (AOM) calculations with respect to d_{xy}, d_{yz}, and d_{zx} orbitals distributing in the [CuN_4] basal plane. According to the analyses, transferability of AOM parameters is valid for succim. The ligand field of bpy can be described by the same parameters as py (py = pyridine). However, it is necessary to set a larger π-bonding AOM parameter for phen than that of py to reproduce the experimental results. The reason for this is out-of-plane lone pairs and π-conjugation of phen. The assignment of the one-electron orbital sequences is presumed to be $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{yz} > d_{zx}$ based on the AOM calculations for each complex.

Copper(II) complexes exhibit a remarkable variety in their coordination numbers and geometries,[1] resulting from the lack of cubic symmetry of $3d^9$ electrons and electronic properties derived from characteristic $3d^9$ electron configurations: for instance, Jahn–Teller effects.[2] Changes of coordination geometries vary the electronic properties inevitably. Recently, many in the fields of electrochemistry[3] and photochemistry[4] are interested in studying how the electronic properties of copper(II) complexes depend on their coordination geometries.

In our studies on copper(II) complexes having various deprotonated cyclic imide ligands (abbreviated as 'imidate'), we have mainly dealt with a relationship between the coordination geometries and the $3d^9$ electronic states.[5,8,11,12] Imidate ligands have a peculiarity to form square planar [CuN_4] complexes in the solid state. This is an unusual feature for copper(II) complexes composed of only nitrogen-coordinating *monodentate* ligands.

In order to obtain various complexes with different coordination geometries, the following strategies have been developed (Scheme 1). For $M_2[Cu(imidate)_4]$ (M^+ = alkali metal ions) complexes,[5] distortion of [CuN_4] coordination geometry is controlled by the size of counter cations. When a small alkali metal cation (lithium) is employed,[6] the central copper atom has a distorted square planar [CuN_4] coordination. Using large counter cations such as potassium,[6] rubidium, and caesium,[7] will give square planar [CuN_4] complexes. On the other hand, steric effects of amine ligands are utilized for *trans*-$[Cu(imidate)_2(amine)_2]$ complexes.[8] Commonly, *monodentate* amine and imidate ligands yield square planar [CuN_4] complexes.[9,10] Distorted square planar [CuN_4] complexes, for example *trans*-$[Cu(succim)_2(phenea)_2]$ and *trans*-$[Cu(hyd)_2(phenea)_2]$ (hyd = hydantoinate), are obtained by using 1-phenylethylamine (phenea) and five-membered imidate ligands.[11] Furthermore, five-coordinated $[Cu(imidate)_2(amine)_2H_2O]$ complexes with a square pyramidal *trans*-[CuN_4O] chromophore are formed by using small amine and bulky imidate ligands. In these complexes, sufficient space is kept for an axial coordination of a water molecule. Recently, we reported structures and electronic spectra of $[Cu(phent)_2(i\text{-}PrNH_2)_2H_2O]$ and $[Cu(phent)_2(EtNH_2)_2H_2O]$ (phent = 5,5-diphenylhydantoinate).[12]

To date, *trans*-$[Cu(imidate)_2(amine)_2]$ complexes have been obtained without exception by using *monodentate* amine ligands. For the next step, we tried to design new type complexes with two imidate ligands coordinated on two *cis*-positions in a [CuN_4] coordination plane. In order to obtain the desired complexes, a *chelate* diimine ligand (phen or bpy) was introduced to protect two neighboring *cis*-sites. And that would lead two *monodentate* ligands to occupy the rest of the *cis*-sites.



Scheme 1. Schematic representations of known $M_2[Cu(imidate)_4]$, *trans*-$[Cu(imidate)_2(amine)_2]$, and $[Cu(imidate)_2(amine)_2H_2O]$ complexes and their steric effects on controlling the coordination geometries.

Many studies on $[Cu(diimine)_2X]$ complexes have been carried out by many authors. Molecular structures were reported for compressed tetrahedral $[CuN_4]$ complexes with phen[13] or bpy,[14] and square pyramidal $[CuN_4O]$ complexes with various distorted geometries, reflecting differences in flexibility of phen[15] and bpy.[16]

In this paper, we report preparations, structural determinations, and discussion of electronic spectra of $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**) and $[Cu(succim)_2(bpy)H_2O]$ (**2**).

Experimental

General Procedures. All of the reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. and used as received without further purification. Elemental analyses were carried out at the Liberal Arts and Sciences Organization, Osaka University.

Preparation of $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (1). 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 7 h, then kept at 50 °C to yield a dark green solution. Then the solution was filtered off, and dark blue precipitates ($[Cu(succim)_2(phen)H_2O]\cdot 0.5H_2O$ (**1′**)) appeared. Dark blue prismatic crystals suitable for X-ray crystallography ($[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**)) 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 **1′**) IR (Nujol) $\nu_{C=O}$ 1616 cm^{-1}.

Preparation of $[Cu(succim)_2(bpy)H_2O]$ (2). 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 4 h 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) $\nu_{C=O}$ 1623 cm^{-1}.

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 °C min^{-1}. α-Alumina (10.0 mg) was used as reference material, and the amounts of the samples examined were 10.0 mg for **1** and **2**.

Crystal Structure Determination. The X-ray diffraction intensities were collected using ω–2θ scan techniques on a Rigaku AFC-5R diffractometer with nickel-filtered Cu $K\alpha$ (λ = 1.5418 Å) for **1** and **2**. Calculations were carried out on an SGI O2 workstation with a teXsan[17] software package for each complex. Empirical absorption corrections based on Ψ scans were applied for **1** and **2** (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[18] and expanded by Fourier techniques. 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(17) and H(18) of **1** and H(17) and H(18) of **2** 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 **1**. H(17) and H(18) of **1** and H(17) and H(18) of **2** were not included for the refinement, while the other hydrogen atoms were refined isotropically.

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. 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 **1** and **2** afford a square based pyramidal [CuN_4O] 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_4O] complexes, such as [Cu(phent)$_2$-(*i*-PrNH$_2$)$_2$H$_2$O], [Cu(phent)$_2$(EtNH$_2$)$_2$H$_2$O][12] (phent = 5,5-diphenylhydantoinate), and [Cu(succim)$_2$(4mepy)$_2$H$_2$O][10] (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_4O] 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.

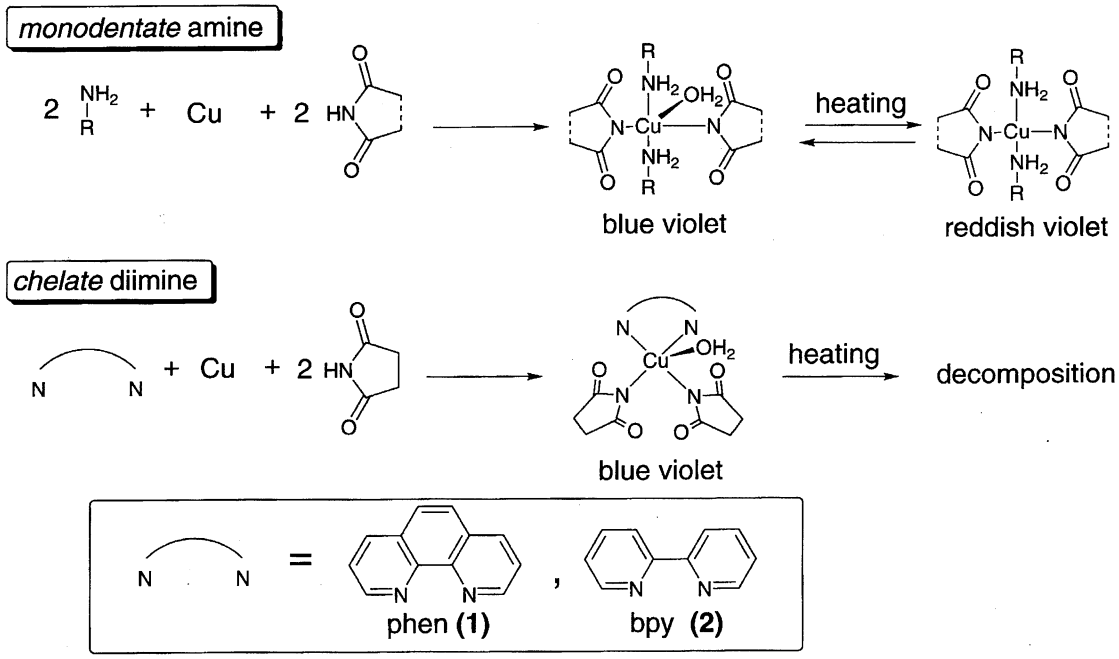
Thermal Behavior of an Axial Water. The DTA curve of [Cu(phent)$_2$(*i*-PrNH$_2$)$_2$H$_2$O] exhibited a broad endothermic peak at 171 °C, and the TG curve showed a weight loss of 2.15% corresponding to 1 mol of water per 1 mol of complex (Calcd 2.64%).[12] The change of the diffuse reflectance spectra 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 2).

In contrast to this, the present complexes **1** and **2** 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. For this reason **1** and **2** are different from [Cu(phent)$_2$(*i*-PrNH$_2$)$_2$H$_2$O] in bonding properties of the axial water ligand.

Crystal Structures. The crystallographic data for **1** and **2** are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The ORTEP drawings of **1** and **2** are shown in Figs. 1 and 2, respectively. Lists of atom coordinates, anisotoropic thermal parameter, and bond distances and angles are deposited as Document No. 72009 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The coordination geometries of the two complexes are slightly distorted square-based pyramidal [CuN_4O]. 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 **1**



Scheme 2. 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.

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

	1	**2**
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 $K\alpha$)/cm^{-1}	19.63	21.02
$2\theta_{max}$/°	120.0	120.0
Crystal dimensions/mm	$0.25 \times 0.20 \times 0.20$	$0.25 \times 0.25 \times 0.20$
Temperature/K	300	300
No. of measured reflections	2800	2945
No. of unique reflections	2648	2764
No. of reflections used in refinement	2172	2169
	$[I > 2.0\sigma(I)]$	$[I > 2.0\sigma(I)]$
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) $R = \sum||F_o| - |F_c||/\sum|F_o|$. b) $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Weighting scheme; $w = 1/(\sigma^2(F_o))$

Table 2. Selected Bond Distances (Å) and Angles (°) for **1** and **2**

	1	**2**
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)

and **2** 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.[6,7,9–12] The Cu–N(aromatic) (N(3) or N(4)) bond distances of **1** and **2** 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 $[Cu(succim)_2(4mepy)_2H_2O]$[10] and *trans*-$[Cu(succim)_2(py)_2]$,[9] regardless of *cis*- or *trans*-arrangement of the imidate ligands in a basal plane.

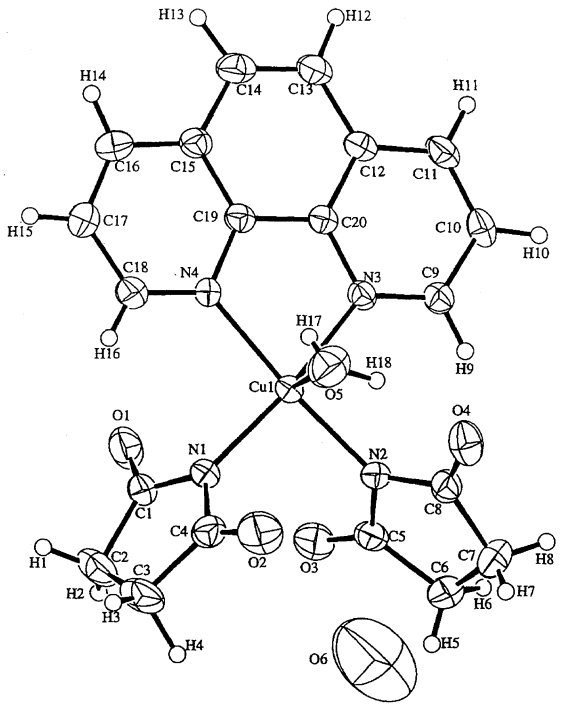


Fig. 1. An ORTEP drawing of $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**) with the atom numbering scheme.

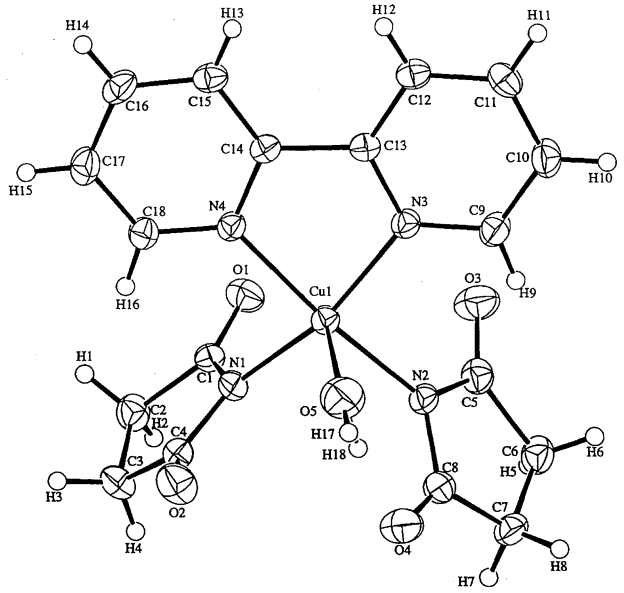


Fig. 2. An ORTEP drawing of $[Cu(succim)_2(bpy)H_2O]$ (**2**) with the atom numbering scheme.

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 **1**, and 164.7(1)° and 173.2(1)° for **2**, 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 **1** and **2**.

The axial Cu–O(water) bond distances of the present complexes (2.548(5) Å for **1** and 2.673(4) Å for **2**) 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 **1** and **2** between carbonyl groups of succinimidate ligands and an axial water. The non-contact distances O(4)···O(5) are 2.761 Å for **1** and 2.728 Å for **2**, which are within the range of the statistical criterion about hydrogen bonds presented by Taylor and Kennard.[19] 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.[12] However, no appreciable intermolecular hydrogen bonds are observed in **1** and **2**.

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 **1**, and 112.15° (N(1)) and 109.06° (N(2)) for **2**, respectively. The two succinimidate ligands of **2** arrange in parallel to each other, so that the succinimidate ligands are free from steric hindrance. Complex **1**, on contrast, has a water molecule as crystalline solvent in the space between two succinimidate ligands. Therefore two succinimidate ligands of **1** arrange in non-parallel fashion to each other.

In the crystals, neighboring molecules are packed together with their diimine ligands stacked (Figs. 3 and 4). As shown in Fig. 4, the $[CuN_4O]$ coordination geometry around central copper(II) ion of **2** 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 π–π 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,[20] and the importance of π–π 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 and 3.7 Å for **1** and **2**, respectively. These stacking distances are in agreement with several manganese and platinum ($[Pt(phen)_2]Cl_2\cdot 3H_2O$ and $[Pt(bpy)_2]Cl_2$)[21] complexes with phen and

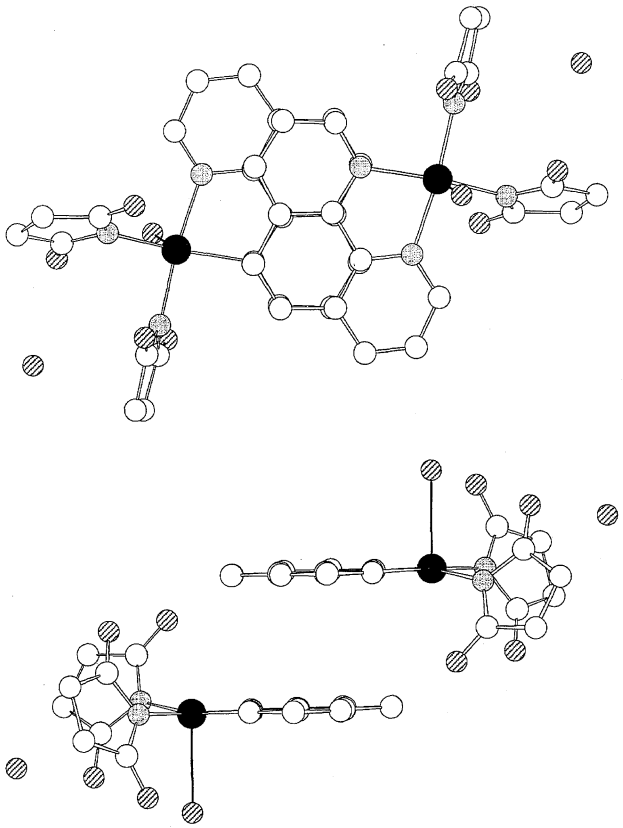


Fig. 3. Perspective view of $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**) showing a stacking structures with phen. (Above) Top view. (Below) Side view.

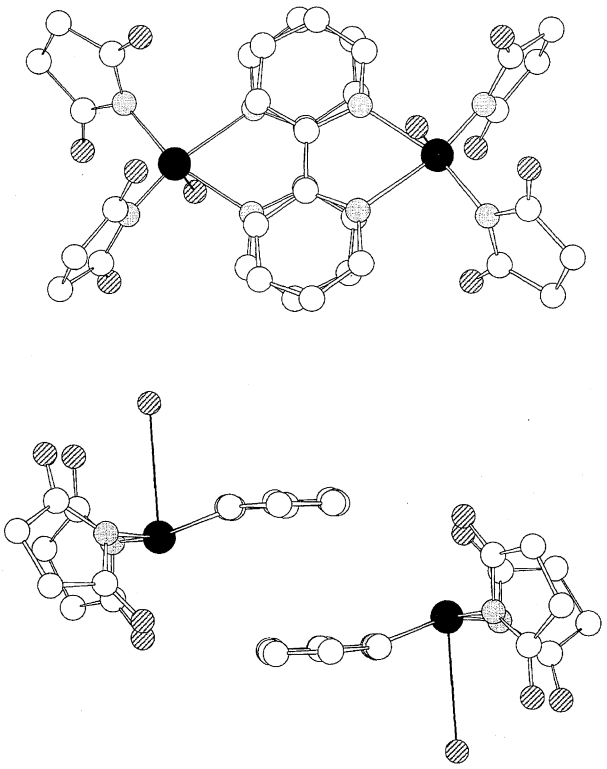


Fig. 4. Perspective view of $[Cu(succim)_2(bpy)H_2O]$ (**2**) showing a stacking structures with phen. (Above) Top view. (Below) Side view.

bpy ligands.

Electronic Spectra. The diffuse reflectance spectra of **1**, **2** and square planar *trans*-$[Cu(succim)_2(py)_2]$[8] in the solid state are shown in Fig. 5. We could not measure polarized crystal spectra of **1** and **2** because of the lack of appropriate samples.

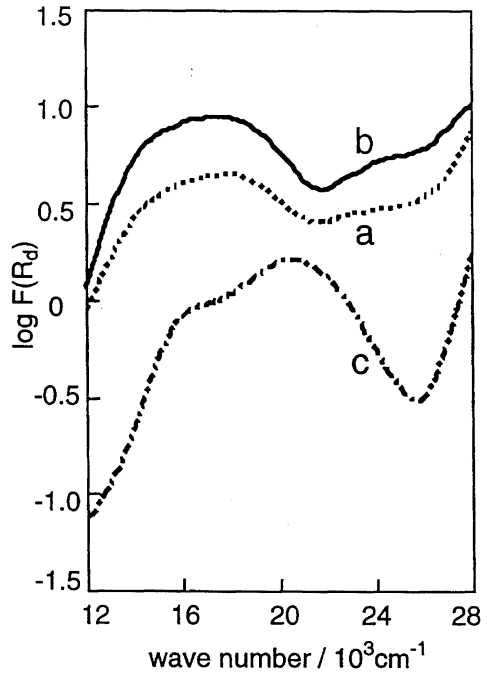


Fig. 5. The diffuse reflectance spectra in the solid state. (a) $[Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**), (b) $[Cu(succim)_2(bpy)\text{-}H_2O]$ (**2**), and (c) *trans*-$[Cu(succim)_2(py)_2]$.

The present complexes **1** and **2** involving a $[CuN_4O]$ chromophore show the peak of ligand field band at 17900 cm^{-1} (0.66) and 17500 cm^{-1} (0.95) (figures in parentheses denote $\log F(R_d)$ derived from Kubelka–Munk conversion) with broad half width. Intensities over 22000 cm^{-1} are attributed to the π–π^* 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} (0.13)) and $[Cu(phent)_2(EtNH_2)_2H_2O]$ (17150 cm^{-1} (0.23)).[12] The spectrum of reddish violet *trans*-$[Cu(succim)_2(py)_2]$ complexes shows a main peak at about 20500 cm^{-1} (0.21) and with a shoulder over the range of 16000—17000 cm^{-1}. Such a spectrum is characteristic of square planar $[CuN_4]$ complexes with imidate ligands.

To discuss 3d electronic states of the present complexes in the solid state, the electronic spectra were deconvoluted using Gaussian functions with a program GA3,[22] and analyzed by means of angular overlap model (AOM) calculations.[23] The AOM parameters of nitrogens used in the calculations were estimated from the analyses of polarized crystal spectra of square planar *trans*-$[Cu(succim)_2(py)_2]$.[24] The values are $e_\sigma^{im} = 7100\ cm^{-1}$ and $e_\pi^{im} = 1500\ cm^{-1}$ for succim, and $e_\sigma^{am} = 7100\ cm^{-1}$ and $e_\pi^{am} = 1000\ cm^{-1}$ for py, respectively. The AOM parameters of succim (e_σ^{im} and e_π^{im}) are more reliable, since the polarized crystal spectra of square planar $Rb_2[Cu(succim)_4]\cdot 2H_2O$[25] could be analyzed successfully by the same values.

Detailed discussion of d–d transitions of **1** and **2** is limited only for d_{xy}, d_{yz}, and d_{zx} orbitals distributing in the $[CuN_4]$ basal plane because of some difficulties: (1) To estimate the level of d_{z^2} orbital toward an axial water ligand, it is necessary to know appropriate AOM parameters associated with oxygen (σ and π). The AOM parameters related to oxygen vary as a function of the Cu–O bond distances with a $1/r^5$ or $1/r^6$ dependence.[26] (2) The energy level of d_{z^2} orbital is significantly influenced by configuration interaction with the 4s orbital, so called ds-mixing.[27] This effect may change the transition energy from d_{z^2} orbital to $d_{x^2-y^2}$ orbital (half filled orbital), independent of the axial ligand parameters.

AOM calculations were carried out with a program AOM38[28] based on the $[CuN_4O]$ geometrical parameters of **1** and **2**. The experimental (deconvoluted with Gaussian functions) and calculated transition energies are listed in Table 3. Tentatively, the σ and π parameters for oxygen were set 7100 and 1000 cm^{-1}, respectively, and ds-mixing was neglected.

C_s symmetry is assumed for $[CuN_4O]$ chromophores, and the coordinate system defined is shown in Fig. 6. The one-electron orbital sequences are suggested to be $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{yz} > d_{zx}$ for each complex. For complex **2**, the calculated transition energies from d_{xy}, d_{yz}, and d_{zx} orbitals are approximately in agreement with the experimental values. The results indicate that transferability of the AOM parame-

Table 3. Experimental (Deconvoluted by Gaussian Functions) and Calculated (AOM) Transition Energies (cm^{-1}).

Transition	1			2	
	Exp. (Gaussian)	Calcd e_π^{am} = 1000 cm^{-1}	Calcd e_π^{am} = 3000 cm^{-1}	Exp. (Gaussian)	Calcd e_π^{am} = 1000 cm^{-1}
$d_{z^2} \rightarrow d_{x^2-y^2}$	13100	—	—	13200	—
$d_{xy} \rightarrow d_{x^2-y^2}$	16200	18100	16800	16600	17800
$d_{yz} \rightarrow d_{x^2-y^2}$	17700	19100	18100	19000	19000
$d_{zx} \rightarrow d_{x^2-y^2}$	19600	20100	18600	20100	20200

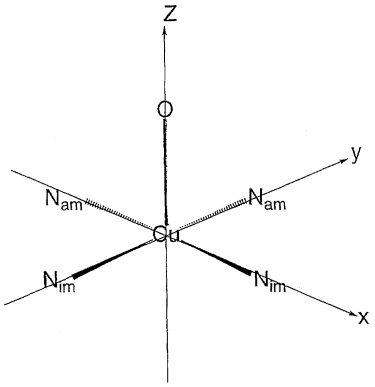


Fig. 6. Idealized geometry of the square pyramidal [CuN_4O] chromophores, showing the coordinate systems.

ters is valid for *monodentate* succim ligands. And the ligand field made by bpy can be described by the same AOM parameters as py. Noticeable deviations appear in **1**, where the three transition energies are too large to reproduce the experimental values. To reduce the calculated transition energies for **1**, AOM calculations were carried out as a function of π-donor strength of aromatic nitrogens e_π^{am}, where the other values were held constant (Fig. 7).

The results show a tendency that the calculated values come close to the experimental values when large e_π^{am} value is

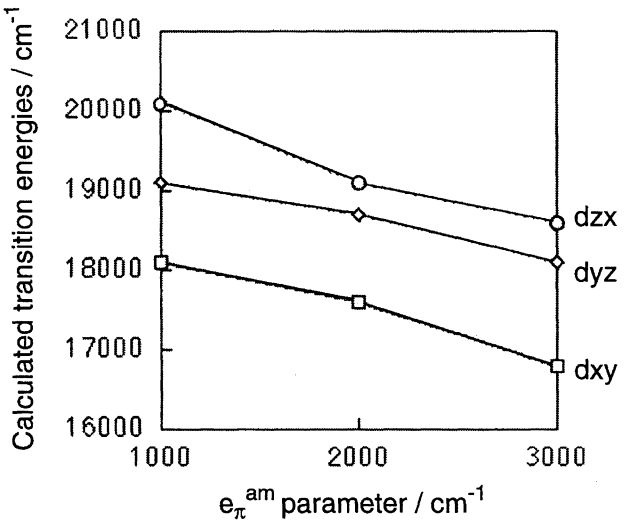


Fig. 7. Calculated transition energies from d_{xy}, d_{yz}, and d_{zx} orbitals to $d_{x^2-y^2}$ orbitals as a function of e_π^{am} parameters for [$Cu(succim)_2(phen)H_2O]\cdot H_2O$ (**1**).

set at about 3000 cm^{-1}. Thus the π-bonding strength of phen ligand is significantly larger than that of bpy, which suggests that the effect of spread π-conjugated system by out-of-plane lone pairs and their interactions is present for phen. Accurate treatments of π-conjugated *chelate* ligands are complicated for AOM calculations, and now some theoretical models are proposed to improve the problem.[29] The present study also gives evidence of the importance of π-conjugation of *chelate* ligands on ligand field splitting.

Concluding Remarks

By using *chelate* diimine ligands (phen and bpy), dark blue [$Cu(succim)_2(phen)H_2O]\cdot H_2O$ and blue [$Cu(succim)_2(bpy)$-H_2O] 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 and 17500 cm^{-1}, which were attributed to the square-based pyramidal [CuN_4O] chromophores. The assignments of the one-electron orbital sequences were presumed to be $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{yz} > d_{zx}$ by AOM calculations. Transferability of the AOM parameters is valid for succim and bpy. Reflecting the π-conjugated system of phen ligand, however, a large e_π^{am} value must be set to reproduce the experimental results.

The authors are grateful for Mr. Ken-ici Sakaguchi (Laboratory of Protein Informatics, Research Center for Structural Biology, 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 his providing a program for angular overlap calculations, AOM38.

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