High Axial Coordination in a *cis*-Coordinated Succinimidatocopper(II) Complex

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A copper(II) complex [Cu(succim)$_2$(N-Eten)(H$_2$O)$_2$] (succim = succinimidate and N-Eten = *N*-ethylethylenediamine) was prepared and characterized by X-ray crystallography and polarized crystal electronic spectra. The complex has a distorted octahedral [CuN$_4$O$_2$] chromophore. The π-donor succim ligands on *cis*-positions raise the potential of axial coordination up to six-coordination to maintain electroneutrality of the complex.

The structural chemistry of copper(II) complexes has received much attention as regards variations of their coordination environment.[1] In particular, easy changes of coordination numbers by addition of small molecules will also provide fundamentals of functional active sites of metalloproteins and catalysts. So far, we have systematically prepared various *trans*-[Cu(imidate)$_2$(amine)$_2$X] copper(II) complexes which afford square planar [CuN$_4$],[2,3] distorted square planar [CuN$_4$],[4,5] and distorted square pyramidal [CuN$_4$O][6,7] coordination geometries to investigate the electronic states of the complexes. Four-coordinated square planar [CuN$_4$] complexes are mainly obtained by making use of *trans*-coordinated π-donor imidate ligands avoiding axial coordination, while sufficient space for axial ligands (e.g. [Cu(phent)$_2$(EtNH$_2$)$_2$H$_2$O][6]) or bidentate diimine ligands (e.g. [Cu(succim)$_2$(bpy)H$_2$O][7]) enable five-coordinated distorted square pyramidal [CuN$_4$O] complexes (phent = 5,5-diphenylhydantoinate and bpy = 2,2′-bipyridine). However, few six-coordinated complexes have been known for analogous complexes. Herein, we describe the preparation as well as structural and spectroscopic characterization of [Cu(succim)$_2$(N-Eten)(H$_2$O)$_2$] (**1**) and we discuss the relationship between the axial coordination and the position of imidate ligands.

Treatment of succimH with N-Eten in ethanol containing copper powder afforded blue plate-like crystals of **1** in a very low yield, albeit to introduce *N*-ethyl groups somewhat prevented undesirable other products. The X-ray crystallography study reveals that **1** has a six-coordinated distorted octahedral [CuN$_4$O$_2$] coordination environment (Fig. 1). This is the first example of *cis*-coordinated succim complexes protected by a bidentate amine N-Eten ligand. Characteristic amide bands around 1700 cm^{-1} of IR spectrum result from monodentate coordination of succim ligands. The Cu–N bond distances: Cu(1)–N(1) = 1.994(4) Å, Cu(1)–N(2) = 2.006(4) Å, and Cu(1)–N(3) = 2.019(4) Å, and Cu(1)–N(4) = 2.070(4) Å, which is comparable to that of analogous complexes[4–7,10] except for Cu(1)–N(4) slightly elongated by bulky *N*-ethyl group. The axial Cu–O bond distances Cu(1)–O(5) = 2.725(4) Å and Cu(1)–O(6) = 2.672(4) Å are significantly elongated by Jahn–Teller effect. The *cis*-N–Cu–N bond angles can be classified into three categories: small N(3)–Cu(1)–N(4) = 84.2(2)°, moderate N(1)–Cu(1)–N(2) = 90.0(2)° and N(2)–Cu(1)–N(3) = 91.0(2)°, and large N(1)–Cu(1)–N(4) = 95.6(2)°. Furthermore, all the *trans*-bond angles, that is O(5)–Cu(1)–O(6) = 172.3(1)°, N(1)–Cu(1)–N(3) = 173.3(2)°, and N(2)–Cu(1)–N(4) = 170.6(2)°, are considerably smaller than 180°. Steric restriction arising from didentate N-Eten and monodentate succim ligands results in the distorted coordination environment.

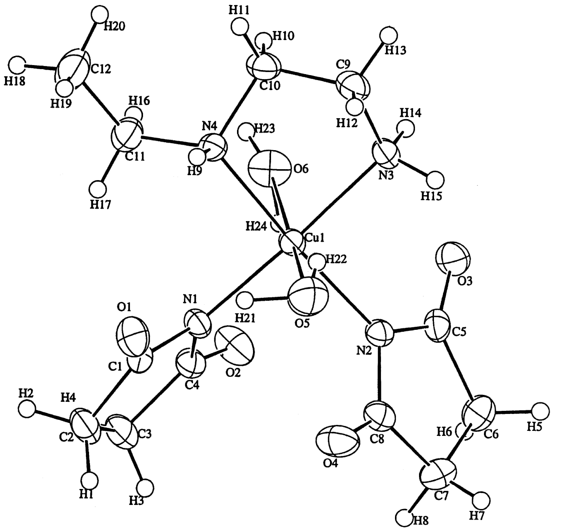

Fig. 1. Molecular structure of **1** with the atom numbering scheme.

Blue **1** exhibits a broad ligand field band at about 16000 cm^{-1} in both polarized crystal spectra (Fig. 2) similarly to the diffuse reflectance spectrum. Little anisotropy by polarization may be a result of triclinic crystal system in which all chromophores are parallel to each other. Compared with the square pyramidal [CuN$_4$O] complexes such as [Cu(succim)$_2$(bpy)-H$_2$O] exhibiting a peak at about 17000 cm^{-1},[7] the spectra of **1** are more sharp and show a peak in lower wavenumber region likewise common six-coordinated copper(II) complexes.[8]

EHMO calculations[9] reveal that the formal charge on copper(II) atom of **1** (2.81) is more positive than that of four-coordinated square planar *trans*-[Cu(succim)$_2$(diphenea)$_2$][5] (2.70) (diphenea = 1,2-diphenylethylamine). The fact suggests that characteristic π-donor property of succim ligand[10] is more effective in *trans*-coordination than in *cis*-coordination. Therefore, axial coordination up to six-coordination can be possible only for *cis*-coordination to maintain total electroneutrality of

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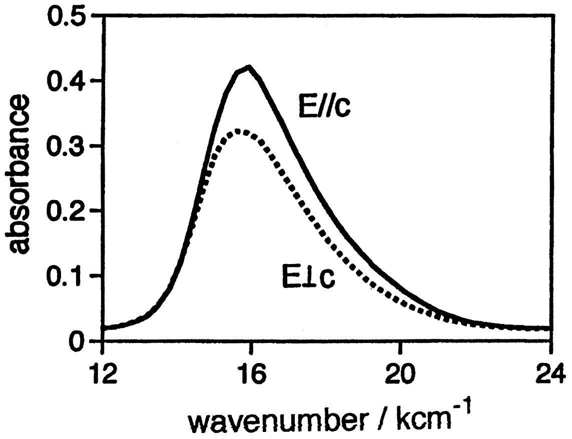

Fig. 2. The polarized crystal electronic spectra of **1** with polarized light parallel and perpendicular to *c* axis on (001) face.

the complexes.[11] The coordination fashion of π-donor imidate and amine ligands can affect axial coordination, indeed **1** provides a distinct example for high acceptability of axial ligands when succim ligands are in *cis*-coordination.

Experimental

Preparation of [Cu(succim)$_2$(N-Eten)(H$_2$O)$_2$] (1). To a suspension of copper powder (0.635 g, 10.0 mmol) in ethanol (20 cm^3) at 50 °C, *N*-ethylethylenediamine (0.882 g, 10.0 mmol) and succinimide (1.982 g, 20.0 mmol) were added and the suspension was stirred for 7 h. The suspension changed into a deep blue solution and blue plate-like crystals deposited from the solution. The crystals were washed with ethanol and petroleum ether and were dried in a silica gel desiccator. Yield: 7.58%. Found: C, 27.34; H, 6.30; N, 14.74%. Calcd for $C_{12}H_{24}N_4CuO_6$: C, 27.55; H, 6.00; N, 14.59%.

Measurements. The polarized crystal electronic spectra were recorded with polarized light parallel and perpendicular to the *c* axis on (001) face at room temperature on a Hitachi U-3400 UV/VIS/NIR spectrophotometer equipped with originally designed attachments.[12] The diffuse reflectance spectra were measured at room temperature 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. Elemental analysis was performed at Osaka University.

X-ray Crystallography. Intensity data were collected using ω–2θ scan on a Rigaku AFC-5R diffractometer with nickel-filtered Cu $K\alpha$ radiation (λ = 1.5418 Å). Empirical absorption corrections (ψ scans) were applied (transmission factor 0.3598–1.0000), and no significant decay was observed. The structure was solved by a direct method (SIR92[13]) and refined by a full-matrix least-squares on F with a teXsan.[14] H(9), H(14), H(15), H(21), H(22), H(23), and H(24) were located from difference Fourier syntheses and the residual H's were located by calculation. All the non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively. Crystal data: $C_{12}H_{24}N_4CuO_6$, Fw = 383.89, T = 300 K, triclinic, $P\bar{1}$, a = 7.303(2), b = 15.625(2), c = 7.2115(7) Å, α = 91.211(8), β = 90.54(1), γ = 83.59(1)°, V = 817.5(2) Å^3, Z = 2, D_{calcd} = 1.559 g m^{-3}, μ = 22.23 cm^{-1}, F(000) = 402, crystal size = 0.20×0.20×0.10 mm, $2\theta_{\max}$ = 120.0°, measured reflections 2648, independent reflections 2426, R_{int} = 0.027, 209 parameters, R = 0.050, and R_w = 0.058. Lists of atom coordinates, anisotropic thermal parameters, and bond distances and angles are deposited as Document No. 75019 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request by quoting the publication citation and the deposition number 179145.

Theoretical Calculations. Formal charges were evaluated by the extended Hückel molecular orbital (EHMO) method. A CAChe software served to build up and edit calculated geometry determined by X-ray crystallography.

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