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Copper(II)-Thioether Bondings in Multidentate N,S-Donor Ligand Complexes. Structural Dependence of the Chemical Properties of the Copper(II) Complexes of 1,5-Bis(2-pyridylmethylamino)-3-thiapentane and 2,6-Bis(2,6-dithiaheptyl)pyridine

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With a view to understanding the factors affecting the chemical properties of the copper sites in proteins, model copper(II) complexes of two multidentate ligands with nitrogen and sulfur atoms, 1,5-bis(2-pyridylmethylamino)-3-thiapentane (pmtp) and 2,6-bis(2,6-dithiaheptyl)pyridine (dthp), have been isolated as $[Cu(pmtp)][Cu(pmtp)ClO_4](ClO_4)_3$ (**1**) and $[Cu(dthp)(NO_3)_2]$ (**2**), respectively, and studied by X-ray diffraction, spectroscopic, and electrochemical methods. Complex **1** crystallizes in space group $P2_1/a$ of the monoclinic system with four $[Cu(pmtp)]^{2+}$ ions and four $[Cu(pmtp)(ClO_4)]^+$ ions in a cell of dimensions $a=24.180(7)$, $b=31.855(7)$, $c=9.760(3)$ Å, and $\beta=143.84(1)°$. The coordinations around the coppers in the two independent complexes are square-pyramidal and octahedral, respectively, with an amine nitrogen, two pyridine nitrogens, and a thioether sulfur at the equatorial positions (eq) and an amine nitrogen (and a perchlorate oxygen in addition in the octahedral complex) at the axial position(s) (ax); $Cu\text{-}N_{eq}=1.991(10)$, 2.001(14), and 2.009(9) Å, $Cu\text{-}S_{eq}=2.353(6)$ Å, $Cu\text{-}N_{ax}=2.276(8)$ Å for $[Cu(pmtp)]^{2+}$, and $Cu\text{-}N_{eq}=1.994(7)$, 2.002(6), and 2.013(14) Å, $Cu\text{-}S_{eq}=2.355(6)$ Å, $Cu\text{-}N_{ax}=2.306(10)$ Å, $Cu\text{-}O_{ax}=2.698(14)$ Å for $[Cu(pmtp)(ClO_4)]^+$. Complex **2** crystallizes in space group $P2_1/c$ of the monoclinic system with four $[Cu(dthp)(NO_3)_2]$ molecules in a cell of dimensions $a=18.492(5)$, $b=14.375(3)$, $c=8.554(2)$ Å, and $\beta=101.19(2)$ Å. The coordination around copper is distorted trigonal-bipyramidal with two thioether sulfurs and a nitrate oxygen in the trigonal plane and a pyridine nitrogen and a nitrate oxygen at the axial positions; $Cu\text{-}S_{eq}=2.344(2)$ and 2.402(2) Å, $Cu\text{-}O_{eq}=2.244(6)$ Å, $Cu\text{-}N_{ax}=1.982(6)$ Å, $Cu\text{-}O_{ax}=1.927(5)$ Å. The structures of these complexes in aqueous solution were concluded to be square-pyramidal from ESR and electronic spectra. Their reduction potentials ($E_{1/2}$ vs. NHE) were +0.062 V for **1** in CH_3CN with one coordinated S atom and +0.678 V for **2** in CH_2Cl_2 with two coordinated S atoms. The higher $E_{1/2}$ value for **2** has been interpreted as due to the presence of the two coordinated sulfur atoms and the flexibility of the ligand which can accomodate the structural changes accompanying the Cu(II)/Cu(I) redox reaction.

The copper sites in proteins hitherto elucidated invariably involve histidine imidazole nitrogens and in the blue copper proteins thiolate and thioether sulfurs in addition.[1] Whereas the type II and the type III copper center in superoxide dismutase and hemocyanin, respectively, and the type II and III centers in ascorbate oxidase have imidazole nitrogens as the main ligand atoms,[1,2] the type I copper center in plastocyanin[3] has two imidazole nitrogens, a thiolate (S^-) sulfur, and a thioether sulfur in a distorted tetrahedral geometry. The type I center in azurin[4] has the same set of donors and an additional peptide carbonyl oxygen atom present at about 3.1 Å in a distorted trigonal-bipyramidal geometry. The chemical properties of the copper centers and thus the roles of copper proteins are determined by the coordination geometry and donor set. The coordination environment for the type I copper with the above donor set is ideal for the Cu(II)/Cu(I) redox center with a high reduction potential (+0.23— +0.38 V vs. NHE), which makes plastocyanin and azurin electron-transfer proteins.

An important approach to the structures and functions of the copper centers is to develop model copper-multidentate ligand systems incorporating various nitrogen and sulfur donors. A number of studies[5] have been reported on Cu-N,S-donor ligand complexes as type I copper models including a few successful examples with a Cu(II)-thiolate(S^-) bond.[6] We have previously investigated[7a] the copper(II) complexes of multidentate N,S-ligands including 1,5-bis(2-pyridylmethylamino)-3-thiapentane (pmtp) and concluded from the stability constants and spectral properties that the thioether and the disulfide sulfur atom in the ligands coordinate to Cu(II) in the basal plane and that the stability decreases by *ca.* 4—4.5 log units when one of the nitrogens in an N_4 donor set is replaced with a sulfur to form an N_3S donor set. Cu(II)-sulfur bonding causes electronic effects on the complexes, which can be seen from the appearance of the S → Cu(II) charge transfer (LMCT) band and relatively high reduction potentials characteristic of the blue copper proteins.[5,8] Under certain conditions, the disulfide bond in bis[2-(2-pyridylmethylamino)-ethyl]disulfide suffers oxidative cleavage in the presence of Cu(II) to form the corresponding sulfinate complex by incorporating oxygen atoms from dioxygen.[9]

In order to obtain further information on the structural and chemical aspects of sulfur coordination, we isolated the Cu(II) complexes of pmtp with one sulfur and four nitrogens and 2,6-bis(2,6-dithiaheptyl)pyridine (dthp) with four sulfurs and one nitrogen (Fig. 1) as crystals and determined their crystal and molecular structures. We here report the syntheses and structures

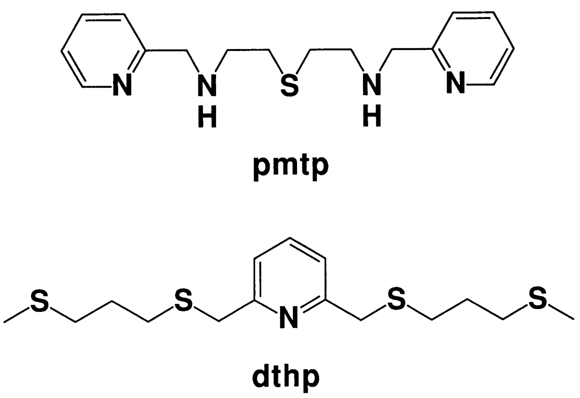


Fig. 1. Schematic structures of pmtp and dthp.

of these complexes in the solid state and in solution and their spectral and redox properties discussed on the basis of the molecular structures.

Experimental

Synthesis of [Cu(pmtp)(ClO$_4$)$_2$] (1). The ligand pmtp·4HCl (0.01 mol) synthesized in the manner reported previously[7a)] was added to an aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.01 mol) with stirring at room temperature. Greenish blue crystals which separated on standing at room temperature were collected and recrystallized from water to give analytically pure complex **1**.

Synthesis of [Cu(dthp)(NO$_3$)$_2$] (2). The ligand dthp (0.01 mol), which was synthesized according to the literature,[10)] was added to a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.01 mol) in hot methanol (15 ml). Green crystals which separated on standing at room temperature were collected and recrystallized from methanol to give analytically pure complex **2**.

Spectroscopic Measurements. Electronic spectra were taken on a Hitachi 330 and a Shimadzu UV-3101PC spectrophotometer at room temperature. X-Band electron spin resonance (ESR) spectra of the powdered copper(II) complexes and of the frozen solutions were obtained at 77 K by using a JEOL RE-1X ESR spectrometer.

Electrochemical Measurements. Cyclic voltammetric measurements were carried out using a Bioanalytical Systems (BAS) CV-27 Voltammograph equipped with a Graphtec X–Y WX2400 chart recorder. A 3-mm diameter glassy carbon working electrode (GCE; BAS) and a platinum wire counter eléctrode were used in a glass cell having a working compartment (approximately 3-ml in volume). All measurements were made at 25 °C under an argon atmosphere with tetrabutylammonium tetrafluoroborate (0.2 M, 1 M = 1 mol dm^{-3}) as a supporting electrolyte. Electrochemical potentials were measured relative to an Ag/AgCl electrode, and the nonaqueous electrochemical potentials were corrected for liquid-junction potentials via the use of the ferrocene/ferrocenium couple,[11)] and are reported vs. the normal hydrogen electrode (NHE) by addition of 222 mV.[11)]

X-Ray Structure Determinations. Diffraction data for **1** and **2** were obtained with a Rigaku AFC-5 and an AFC-5R four-circle diffractometer, respectively. Crystal data and experimental details for both crystals are summarized in Table 1. Three standard reflections for respective crystals were monitored every 100 measurements, and the decay of their intensities was within 2%. Reflection data were corrected for Lorentz and polarization effects. Absorption correction was not applied in either case, because the absorption coefficients for both crystals were very small.

Both structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix

Table 1. Crystallographic Data for [Cu(pmtp)][Cu(pmtp)(ClO$_4$)](ClO$_4$)$_3$ (**1**) and [Cu(dthp)(NO$_3$)$_2$] (**2**)

	1	**2**
Formula	$Cu_2S_2Cl_4O_{16}N_8C_{32}H_{44}$	$CuS_4O_6N_3C_{15}H_{25}$
F. W.	1129.78	535.19
Color	Greenish blue	Green
Crystal size/mm	0.20×0.15×0.10	0.02×0.10×0.48
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$
a/Å	24.180(7)	18.492(5)
b/Å	31.855(7)	14.375(3)
c/Å	9.760(3)	8.554(2)
β/deg	143.84(1)	101.19(2)
V/Å^3	4435.7	2230.6
Z	4	4
D_c/g cm^{-3}	1.692	1.593
λ/Å	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)
μ/cm^{-1}	13.69	13.75
F(000)	2312.0	1108.0
Scan method	ω–2θ	ω–2θ
2θ max/deg	60	60
Scan speed/deg min^{-1}	4	4
Scan range/deg	1.0+0.5 tan θ	1.0+0.5 tan θ
No. of data collected	9909	6800
No. of independent data with $\|F_o\|>3\sigma(F_o)$	3493	1539
R	5.45	3.74
R_w	6.41	4.58

least-squares calculations. Refinement was continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-Ray Crystallography.[12] Hydrogen atoms were located from difference Fourier maps, and their parameters were isotropically refined. The final R and R_w values were 0.0545 and 0.0641 for **1**, and 0.0374 and 0.0458 for **2**, respectively. The weighting scheme $w^{-1}=[\sigma^2(F_o)+(0.015F_o)^2]$ was employed for both crystals. The final difference Fourier maps did not show any significant features. The calculations were performed on a Hitachi M-680H computer at the Computer Center of the Institute for Molecular Science by using the program system UNICS III.[13]

Table 2. Fractional Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors for the Non-Hydrogen Atoms of $[Cu(pmtp)][Cu(pmtp)(ClO_4)](ClO_4)_3$ (**1**)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Cu(A)	160 (1)	3850 (1)	7991 (2)	3.1	C(1A)	2198 (7)	3694 (4)	12011 (18)	4.3
Cu(B)	4840 (1)	3849 (1)	2352 (2)	3.1	C(2A)	2997 (7)	3452 (4)	13421 (20)	5.9
S(A)	129 (2)	3642 (1)	10242 (5)	4.0	C(3A)	2912 (8)	3067 (4)	12761 (21)	5.7
S(B)	4873 (2)	3642 (1)	4732 (5)	4.0	C(4A)	2045 (8)	2892 (4)	10708 (20)	5.0
Cl(1)	3506 (2)	4719 (1)	1732 (4)	4.1	C(5A)	1282 (7)	3147 (3)	9388 (17)	3.8
Cl(2)	1427 (2)	6882 (1)	9195 (5)	4.5	C(6A)	310 (8)	2993 (4)	7081 (19)	5.6
Cl(3)	8504 (2)	5280 (1)	7288 (4)	4.2	C(7A)	−684 (8)	2972 (4)	7147 (20)	5.6
Cl(4)	8573 (2)	8119 (1)	8492 (5)	4.4	C(8A)	−87 (9)	3097 (4)	9539 (22)	6.2
O(1)	3175 (9)	5106 (5)	683 (24)	15.5	C(9A)	−994 (7)	3878 (4)	8412 (19)	4.8
O(2)	4025 (7)	4553 (3)	1693 (21)	10.0	C(10A)	−1562 (7)	4000 (4)	6030 (18)	4.5
O(3)	2847 (7)	4432 (4)	848 (21)	12.2	C(11A)	−1459 (7)	4311 (4)	3930 (17)	4.3
O(4)	4121 (10)	4800 (6)	3997 (19)	17.6	C(12A)	−751 (6)	4370 (3)	4219 (15)	3.3
O(5)	2083 (6)	6839 (3)	11610 (13)	6.4	C(13A)	−931 (7)	4600 (3)	2685 (16)	4.2
O(6)	1488 (7)	6542 (3)	8433 (15)	10.5	C(14A)	−247 (8)	4614 (3)	3020 (18)	4.4
O(7)	529 (7)	6920 (5)	7924 (18)	12.3	C(15A)	575 (8)	4409 (4)	4865 (19)	5.2
O(8)	1614 (8)	7239 (4)	8796 (18)	11.1	C(16A)	717 (7)	4200 (3)	6361 (17)	3.8
O(9)	9007 (7)	5446 (3)	9383 (15)	9.7	C(1B)	2788 (7)	3694 (3)	−1789 (17)	4.2
O(10)	7844 (7)	5557 (4)	5527 (15)	12.6	C(2B)	1994 (7)	3456 (4)	−3568 (19)	5.7
O(11)	9124 (10)	5207 (5)	7516 (27)	17.4	C(3B)	2075 (8)	3051 (4)	−3899 (18)	5.6
O(12)	8164 (9)	4906 (4)	6986 (21)	14.8	C(4B)	2944 (8)	2904 (3)	−2494 (19)	5.1
O(13)	7906 (5)	8165 (3)	8239 (14)	7.0	C(5B)	3722 (7)	3151 (4)	−720 (16)	4.0
O(14)	8385 (8)	7747 (3)	7376 (21)	10.9	C(6B)	4687 (8)	3001 (4)	843 (21)	5.7
O(15)	9480 (6)	8079 (5)	10810 (15)	11.7	C(7B)	5652 (8)	2980 (4)	4832 (19)	5.4
O(16)	8506 (8)	8458 (3)	7484 (22)	11.0	C(8B)	5080 (9)	3094 (4)	4909 (22)	6.0
N(1A)	1352 (5)	3534 (2)	10005 (13)	3.2	C(9B)	5977 (7)	3878 (4)	7354 (17)	4.5
N(2A)	−432 (6)	3200 (3)	6374 (13)	4.2	C(10B)	6547 (7)	4009 (3)	7246 (16)	4.1
N(3A)	−958 (5)	4197 (3)	6210 (13)	3.7	C(11B)	6443 (7)	4314 (3)	4742 (17)	4.0
N(4A)	61 (5)	4160 (2)	6017 (12)	3.0	C(12B)	5745 (7)	4367 (3)	2211 (16)	3.2
N(1B)	3639 (5)	3544 (2)	−416 (12)	3.1	C(13B)	5940 (7)	4601 (3)	1429 (18)	3.9
N(2B)	5435 (5)	3190 (3)	3107 (14)	4.1	C(14B)	5256 (8)	4614 (4)	−971 (19)	4.6
N(3B)	5961 (5)	4196 (3)	5055 (13)	3.7	C(15B)	4426 (8)	4408 (4)	−2434 (18)	4.7
N(4B)	4942 (5)	4167 (3)	779 (12)	3.1	C(16B)	4282 (7)	4187 (4)	−1524 (17)	4.4

Table 3. Fractional Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors for the Non-Hydrogen Atoms of $[Cu(dthp)(NO_3)_2]$ (**2**)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Cu	8238 (1)	4374 (1)	2503 (1)	2.9	C(2)	7271 (5)	8264 (6)	1283 (11)	5.7
S(1)	6633 (2)	8424 (2)	2590 (3)	5.7	C(3)	7911 (5)	7653 (6)	2024 (11)	5.0
S(2)	8438 (1)	5969 (1)	3311 (2)	3.1	C(4)	7719 (4)	6624 (5)	2038 (9)	3.4
S(3)	7499 (1)	3360 (1)	726 (2)	3.3	C(5)	9195 (4)	6064 (5)	2264 (8)	3.3
S(4)	5120 (1)	3395 (2)	280 (3)	6.3	C(6)	9055 (3)	5552 (5)	713 (8)	2.6
N(1)	8656 (3)	4758 (4)	637 (6)	2.6	C(7)	9312 (4)	5850 (5)	−610 (9)	3.4
N(2)	7226 (3)	4302 (4)	4473 (7)	3.6	C(8)	9170 (4)	5343 (5)	−1988 (8)	3.5
N(3)	9557 (3)	3301 (4)	3618 (8)	4.4	C(9)	8785 (4)	4516 (5)	−2029 (8)	3.5
O(1)	7863 (3)	3974 (3)	4341 (6)	3.9	C(10)	8529 (4)	4245 (5)	−673 (8)	2.8
O(2)	7006 (3)	4132 (4)	5702 (7)	5.9	C(11)	8105 (4)	3345 (5)	−688 (9)	3.7
O(3)	6900 (3)	4802 (4)	3413 (6)	5.4	C(12)	6754 (4)	4066 (5)	−358 (9)	3.8
O(4)	9344 (3)	4066 (4)	4023 (7)	6.3	C(13)	6211 (5)	3476 (7)	−1549 (9)	4.9
O(5)	10153 (3)	2994 (4)	4251 (7)	6.1	C(14)	5736 (4)	2841 (6)	−778 (10)	5.0
O(6)	9159 (4)	2870 (5)	2548 (8)	7.8	C(15)	4481 (5)	3874 (8)	−1246 (14)	8.2
C(1)	5887 (6)	8952 (7)	1231 (13)	7.0					

Table 4. Selected Intramolecular Bond Lengths (Å) and Angles (deg) for $[Cu(pmtp)][Cu(pmtp)(ClO_4)](ClO_4)_3$ (**1**)

Bond	Length	Bond	Length
Cu(A)-S(A)	2.353(6)	Cu(A)-N(1A)	2.009(9)
Cu(A)-N(2A)	2.276(8)	Cu(A)-N(3A)	1.991(10)
Cu(A)-N(4A)	2.001(14)	Cu(B)-S(B)	2.355(6)
Cu(B)-O(2)	2.698(14)	Cu(B)-N(1B)	2.002(6)
Cu(B)-N(2B)	2.306(10)	Cu(B)-N(3B)	1.994(7)
Cu(B)-N(4B)	2.013(14)		

Bond	Angle	Bond	Angle
S(A)-Cu(A)-N(1A)	92.7(5)	S(A)-Cu(A)-N(2A)	85.1(4)
S(A)-Cu(A)-N(3A)	85.9(5)	S(A)-Cu(A)-N(4A)	165.7(3)
N(1A)-Cu(A)-N(2A)	79.9(3)	N(1A)-Cu(A)-N(3A)	175.3(4)
N(1A)-Cu(A)-N(4A)	98.8(5)	N(2A)-Cu(A)-N(3A)	104.4(3)
N(2A)-Cu(A)-N(4A)	105.3(5)	N(3A)-Cu(A)-N(4A)	82.1(6)
S(B)-Cu(B)-O(2)	84.5(5)	S(B)-Cu(B)-N(1B)	92.9(5)
S(B)-Cu(B)-N(2B)	85.1(4)	S(B)-Cu(B)-N(3B)	85.6(5)
S(B)-Cu(B)-N(4B)	165.1(3)	O(2)-Cu(B)-N(1B)	95.5(4)
O(2)-Cu(B)-N(2B)	168.8(7)	O(2)-Cu(B)-N(3B)	78.8(4)
O(2)-Cu(B)-N(4B)	85.2(6)	N(1B)-Cu(B)-N(2B)	80.8(3)
N(1B)-Cu(B)-N(3B)	174.3(5)	N(1B)-Cu(B)-N(4B)	98.8(5)
N(2B)-Cu(B)-N(3B)	104.5(3)	N(2B)-Cu(B)-N(4B)	105.8(5)
N(3B)-Cu(B)-N(4B)	81.9(5)		

Table 5. Selected Intramolecular Bond Lengths (Å) and Angles (deg) for $[Cu(dthp)(NO_3)_2]$ (**2**)

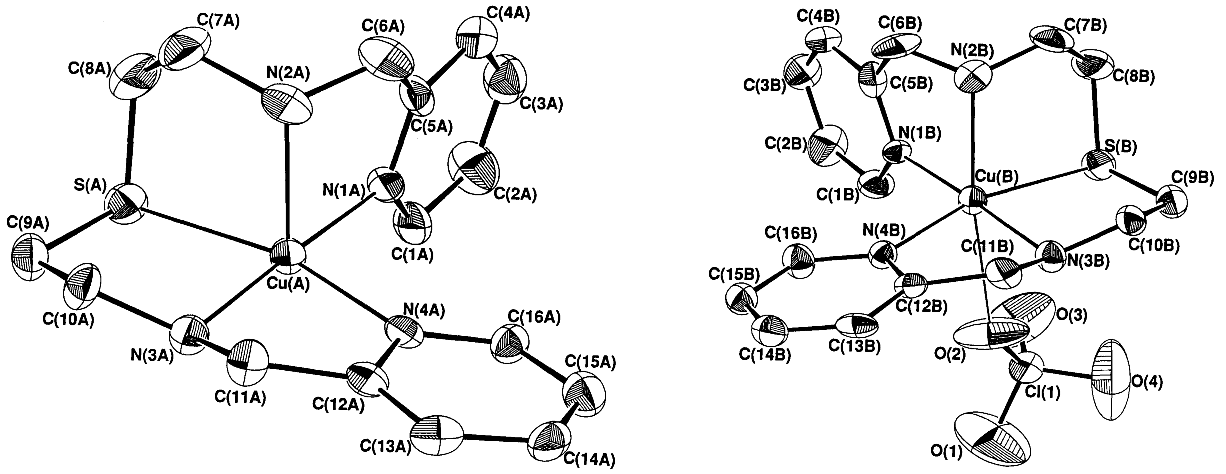
Bond	Length	Bond	Length
Cu-S(2)	2.402(2)	Cu-S(3)	2.344(2)
Cu-N(1)	1.982(6)	Cu-O(1)	1.927(5)
Cu-O(4)	2.244(6)		

Bond	Angle	Bond	Angle
S(2)-Cu-S(3)	144.8(1)	S(2)-Cu-N(1)	84.5(2)
S(2)-Cu-O(1)	96.3(2)	S(2)-Cu-O(4)	87.1(2)
S(3)-Cu-N(1)	85.4(2)	S(3)-Cu-O(1)	95.0(2)
S(3)-Cu-O(4)	127.2(2)	N(1)-Cu-O(1)	177.9(2)
N(1)-Cu-O(4)	93.9(2)	O(1)-Cu-O(4)	84.3(2)

The final atomic parameters for non-hydrogen atoms for **1** and **2** are given in Tables 2 and 3, respectively, and the selected bond lengths and angles are listed in Tables 4 and 5, respectively. Tables of the final parameters for all non-hydrogen atoms and positions of hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, torsion angles, and observed and calculated structure factor amplitudes (36 pages) are deposited as Document No.8983 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Molecular Structure of $[Cu(pmtp)][Cu(pmtp)(ClO_4)](ClO_4)_3$ (1). Figure 2 shows a perspective view of the two independent cations, $[Cu(pmtp)]^{2+}$ and $[Cu(pmtp)(ClO_4)]^+$, with the atomic labeling scheme in the asymmetric unit. The coordination polyhedrons about the respective Cu atoms can be described as a square-pyramid (A) (Fig. 2a) and an axially elongated octahedron (B) (Fig. 2b). The copper atom in complex A is coordinated by one S and three N atoms of pmtp in the equatorial positions (Cu(A)-S(A)=2.353(6), Cu(A)-N(1A)=2.009(9), Cu(A)-N(3A)=1.991(10), and Cu(A)-N(4A)=2.001(14) Å) and one N atom in the apical position (Cu(A)-N(2A)=2.276(8) Å). The octahedral copper atom in complex B is coordinated by one S and three N atoms of the ligand in the equatorial positions (Cu(B)-S(B)=2.355(6), Cu(B)-N(1B)=2.002(6), Cu(B)-N(3B)=1.994(7), and Cu(B)-N(4B)=2.013(14) Å) and one N atom of the ligand and one perchlorate oxygen in the axial positions (Cu(B)-N(2B)=2.306(10) and Cu(B)-O(2)=2.698(14) Å). The Cu-S lengths, 2.353(6) and 2.355(6) Å, are on the short side when compared with those reported for equatorial copper(II)-thioether bonds (2.31—2.48 Å).[5c,14-16] The short Cu-S length is probably caused by the chelating effect of the ligand. The apical monodentate perchlorate has a Cu-O length of 2.698(14) Å, which is within the range (2.26—2.88 Å) for the copper(II) complexes with the perchlorate anion.[15,16] The Cu-N(pyridine) lengths, 2.001—2.013 Å, are in the range hitherto reported (2.007—2.183 Å).[15] The Cu-N(amine) lengths in the equatorial positions, 1.991(10) and 1.994(7) Å, lie at the short end of the reported range (2.002—2.055 Å)[15] when the 3σ error range is taken into account. The Cu(B)-N(2B) bond in complex B is slightly elongated by the occupation of the perchlorate oxygen in comparison with that in complex A, although the geometries of the two molecules are very similar to each other. The mean planes defined by the atoms in the equatorial base are planar to within 0.04 and 0.03 Å for complexes A and B, respectively. The Cu atoms in A and B deviate from the coordination plane toward the axial nitrogen atom by 0.12 and 0.13 Å, respectively. The pyridine rings involving N(4A) and N(1A) in complex A are coordinated in the equatorial



(a) (b)

Fig. 2. Molecular structures of $[Cu(pmtp)]^{2+}$ (a) and $[Cu(pmtp)ClO_4]^{+}$ (b) ions, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity of presentation.

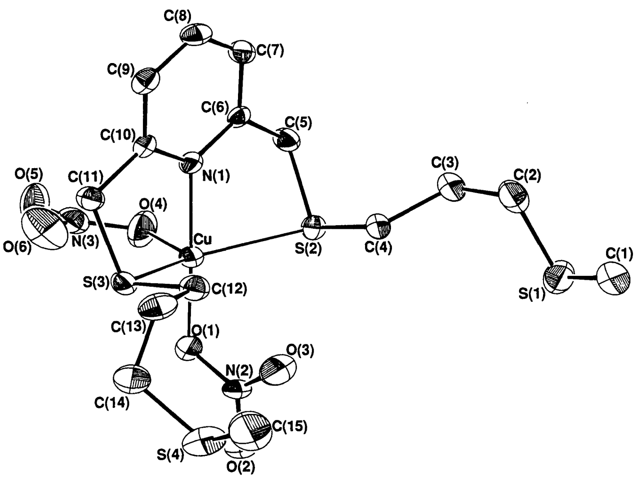


Fig. 3. Molecular structure of $[Cu(dthp)(NO_3)_2]$, showing the atomic numbering scheme (hydrogens omitted).

positions in parallel (13.2°) with and in perpendicular (88.0°) to the basal plane, respectively. Also, in complex B the pyridine ring containing N(4B) coordinates in parallel with the basal plane (12.2°), and the other one containing N(1B) coordinates in perpendicular to the basal plane (87.9°). The remaining three perchlorate anions are not involved in coordination.

Molecular Structure of $[Cu(dthp)(NO_3)_2]$ (2). The molecular structure of $[Cu(dthp)(NO_3)_2]$, also showing the atomic numbering scheme, is given in Fig. 3. The coordination geometry around the Cu atom is considered to be an axially compressed trigonal-bipyramid with the two thioether sulfurs and one nitrate oxygen in the trigonal plane (Cu–S(2)=2.402(2), Cu–S(3)=2.344(2), and Cu–O(4)=2.244(6) Å) and the pyridine nitrogen atom and another nitrate oxygen atom in the axial positions (Cu–N(1)=1.982(6) and Cu–O(1)=1.927 (5) Å). The Cu–S(3) length is also somewhat short for the copper–thioether bonds (2.31—2.48 Å), whereas the Cu–S(2) length lies in the middle of the range.[5c,14—16] The Cu(II)–nitrate bond in the trigonal-bipyramidal geometry is generally short in the axial position (1.964—2.037 Å) and long in the equatorial position (2.027—2.532 Å).[15] The equatorial Cu–O(4) length lies in the previously reported range, whereas the axial Cu–O(1) length is the shortest among those reported previously.[15,16] The pyridine nitrogen binds strongly to the copper(II) ion, which is seen from the bond lengths for usual copper complexes with coordinated pyridine (2.007—2.183 Å),[15] and this may be caused by the chelating effect of the ligand. The structure of **2** is not a perfect trigonal-bipyramid; the S(2)–Cu–S(3) (144.8°) and S(2)–Cu–O(4) (87.1°) angles clearly deviate from the value of the ideal trigonal angle (120°), though the N(1) and O(1) atoms are coordinated linearly (N(1)–Cu–O(1)=177.9°). To distinguish between a trigonal-bipyramid and a square-pyramid, Addison et al. proposed a structural parameter τ,[17] which is defined as equal to $(\beta-\alpha)/60$ with α and β being the two largest coordination angles ($\beta>\alpha$). In the perfect square-pyramidal geometry, τ equals 0, while it equals 1 in the case of the perfect trigonal-bipyramidal geometry. The τ value for **2** is 0.55, indicating that the structure is intermediate between trigonal-bipyramidal and square-pyramidal geometries. Since the powder ESR spectrum indicates a d_{z^2} ground state as described in the following section, the structure may be best described as a distorted trigonal-bipyramid. The Cu atom deviates by 0.12 Å from the trigonal plane toward the axial nitrate oxygen atom. The remaining two thioether sulfur atoms of the ligand do not participate in coordination but form a hydrophobic environment in the crystal structure, as shown in Fig. 4.

Table 6. Electronic and ESR Spectral Data for the Copper(II) Complexes

Complex	Absorption		ESR (77 K)	
	$\lambda_{\max}$/nm	ε/M^{-1} Cu^{-1} cm^{-1}	Solid	Solution
1[a] in H_2O (pH 7.0)	320	3500	$g_{/\!/}=2.152$	$g_{/\!/}=2.20$
	600	190	$g_{\perp}=2.081$	$g_{\perp}=2.07$
	850	81		$\lvert A_{/\!/}\rvert=175$[b]
2 in CH_2Cl_2	388	3300	$g_{/\!/}=2.019$	$g_{/\!/}=2.14$
	721	351	$g_{\perp}=2.145$	$g_{\perp}=2.03$
	951	182		$\lvert A_{/\!/}\rvert=170$[b]

a) Ref. 7. b) In 10^{-4} cm^{-1}.

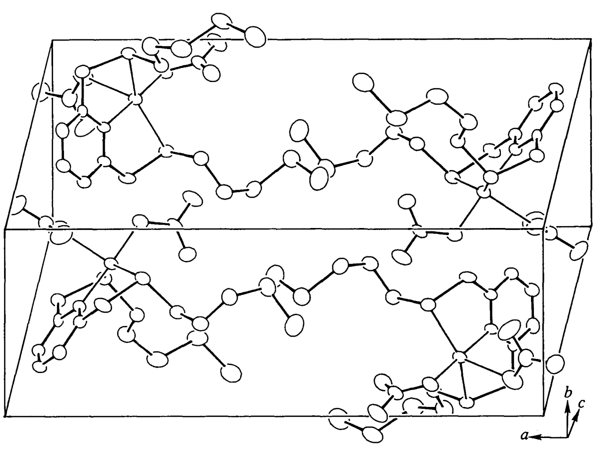


Fig. 4. Crystal structure of $[Cu(dthp)(NO_3)_2]$ (hydrogens omitted).

Electronic and ESR Spectra. Electronic and ESR spectral data for **1** and **2** are given in Table 6.

Both complexes exhibit three distinct absorption peaks of which the most intense one, at 320 and 388 nm for **1** and **2**, respectively, is assigned to the σ(S)→d(Cu) charge transfer,[8] and the two well-split bands, at 600 and 850 nm for **1** and 721 and 951 nm for **2**, are assigned to d–d transitions.[18] These bands indicate that **1** and **2** in solution have the S atom in an equatorial position[8] in the square-pyramidal geometry.[14,19] This is in agreement with the previous conclusions on pmtp from solution chemical[17a] and spectroscopic studies.[7b,20] The absorption band in the d–d region exhibited by **2** with two S atoms is enhanced in comparison with that by **1**, which suggests that the absorption also includes π(S)→d(Cu) charge transfer components.[18] All the peaks of **2** shift to the lower energy region as compared with those of **1**. The coordination of N atoms, whose p orbitals are at a lower energy level than the d-orbitals of Cu(II), may destabilize the energy level of the $d_{x^2-y^2}$ orbital through the interaction between them. This is shown by the fact that the copper complex with N-substituted pmtp has weaker absorption peaks at higher energy regions (590 nm (ε 150), 820 nm (ε 48)) than those for **1** and **2**.

The ESR spectrum of **1** observed in the polycrystalline state is essentially that of a $d_{x^2-y^2}$ ground state ($g_{/\!/}>g_{\perp}$),[21] although the crystal contains two different structures in the unit cell, a square-pyramid and an octahedron, the latter of which may be regarded as an axially elongated square-pyramid. The frozen-solution ESR spectrum also indicates clearly the same axial symmetry, which coincides with the conclusion from the electronic spectrum in solution.

Table 7. Electrochemical Parameters for One-Electron Reductions of the Copper Complexes[a]

Complex	E_{pc}/V	E_{pa}/V	$E_{1/2}$/V	ΔE_p/V
1 (in CH_3CN)	+0.028	+0.095	+0.062	0.067
2 (in CH_2Cl_2)	+0.64	+0.721	+0.678	0.087

a) Measured vs. Ag/AgCl and converted to the NHE scale by addition of +0.222.

The powder and solution ESR spectra of **2** are very different from each other and point to a d_{z^2} ground state ($g_{/\!/}<g_{\perp}$) in the solid state and a $d_{x^2-y^2}$ ground state ($g_{/\!/}>g_{\perp}$) in solution.[21] They are consistent with the structure in the solid state (distorted trigonal-bipyramid) (Fig. 3) and that in solution (square-pyramid) concluded from the electronic spectrum.

On the basis of the above results, we may assign the longer wavelength d–d bands to the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition and the shorter wavelength band to the d_{xy}, d_{yz}, $d_{zx}\rightarrow d_{x^2-y^2}$ transitions, because the d_{xy}, d_{yz}, d_{zx} orbital energy levels are lower than the d_{z^2} level in the square-pyramidal structures of **1** and **2** in solution.[21]

Electrochemistry. One of the aims of this study was to see how the redox properties of copper(II) complexes are affected by sulfur coordination and flexibility of complex structures. The results of cyclic voltammetric measurements are given in Table 7 for **1** in CH_3CN and **2** in CH_2Cl_2. Both complexes showed a reversible or a quasi-reversible cyclic voltammogram with a pair of cathodic and anodic waves of Cu(II)/Cu(I). The remarkable difference in the $E_{1/2}$ values detected between **1** (+0.062 V) and **2** (+0.678 V) seems to reflect the properties of the ligands, i.e., the difference of the number of S atoms coordinated and structural adaptability in coordinating to Cu(I) and Cu(II). This is particularly important when we consider the effect of the nitrate ion which tends to make the potential more negative. The Cu(II)/Cu(I) structural change is easily posssible for **2** by removing a nitrate anion, whereas it is difficult for **1** because of the tightly coordinated N and S atoms. The reduction potential for **1** is lower than that for **2** even in CH_3CN which stabilizes the Cu(I) state. The side chain sulfur atoms that are not coordinated in **2** may further stabilize the Cu(I) state by coordination to Cu(I) and/or by forming a hydrophobic environment. The fact that the reduction potential for **2** is more positive than that for **1** agrees well with the result that the $\sigma(S)\rightarrow d(Cu)$ LMCT in **2** occurs at a lower energy than that in **1**. Also, the lower energy S→Cu LMCT in **2** may account for the enhancement of the d–d band intensity through more effective intensity borrowing.

Relevance to Type I Copper Sites. The active site of plastocyanin[3] represents the structural and electronic requirements achieved by nature for the function of electron transfer. Both the distorted tetrahedral geometry and combination of soft and intermediate donor atoms, which give rise to the unique spectroscopic and electrochemical properties,[1] contribute to the adaptability of the copper center to the redox activity. In certain azurin,[4d] an extra carbonyl oxygen was found at a distance which may be taken to indicate a Cu(II)–O interaction, completing a distorted trigonal-bipyramidal geometry.

Studies on blue copper protein model complexes have revealed the following structural dependence of redox potentials: (i) Thioether sulfur coordination increases the redox potential in the order $CuS_4 > CuN_2S_2 > CuN_4$ where S and N refer to a thioether group and a secondary amino group, respectively.[22] (ii) Thiolate→thioether[6c,6e] and imidazole[20] or aliphatic amine[22]→pyridine[23] substitutions raise the redox potentials. (iii) The redox potential increases with the increasing chelate ring size,[22,24] suggesting that the flexible chelate rings can accomodate a pseudotetrahedral copper(I) geometry.

Although pmtp and dthp in **1** and **2**, respectively, are multidentate ligands having thioether sulfurs and nitrogen donors of different nature, the $E_{1/2}$ values of **1** and **2** shown in Table 7 are greatly different from each other, indicating that the number of coordinated sulfur atoms and the structural factors affect the redox properties. In an attempt to evaluate the effect of the structural flexibility on the $E_{1/2}$ value, we estimated the values for **1** and **2** from the average reduction potentials reported for several types of copper complexes. Such an attempt has already been made by Karlin el al.[25] by calculation of the contribution to the redox potentials $\Delta E(L)$ expected for individual donor groups L. We calculated the $\Delta E(L)$ values for L=secondary amine (N(am)), imidazole (N(im)), pyridine (N(py)), and thioether (S) from the following values: +0.68 V for CuS_4,[26] +0.60 V for $CuN(py)_2S_2$,[23a,24a,24c] +0.48 V for $CuN(im)_2S_2$,[23b,23c] +0.44 V for $CuN(py)N(am)S_2$,[24b] +0.15 V for $CuN(am)_2S_2$,[22,26] +0.02 V for $CuN(py)_2N(am)_2$,[24c] −0.43 V for $CuN(am)_4$,[27] and +0.15 V for Cu_2^+/Cu^+.[28] The tentative $\Delta E(L)$ values obtained are: $\Delta E(N(im)) = -0.08$ V, $\Delta E(N(py)) = +0.08$ V, $\Delta E(N(am)) = -0.15$ V, and $\Delta E(S) = +0.13$ V. By using these values we estimated the $E_{1/2}$ values to be +0.14 V and +0.45 V for **1** ($CuN(py)_2N(am)_2S$) and **2** ($CuN(py)OS_2$ (O: nitrate ion)), respectively, on the assumption that **1** and **2** are five- and four-coordinate, respectively; the $\Delta E(O)$ value used for **2** was that estimated by Karlin et al. (−0.04 V).[25] The reduction potential of **1**, +0.062 V, is slightly lower than expected, whereas that of **2**, +0.634 V, is considerably higher. This may be interpreted as due to the rigid structure of **1** with two pyridine nitrogens, two secondary amine nitrogens, and one thioether sulfur, and the very flexible structure of **2** with a pyridine nitrogen, two thioether sulfurs, an easily replaceable nitrate ion, and additional uncoordinated thioether groups.

These observations indicate that the redox properties of the copper center is subtly controlled by the geometry and nature of donor atoms and the flexibility of conformation around the copper ion. It is highly likely that the flexible environment is necessary for electron transfer, and this has been demonstrated for plastocyanin by the Cu-ligand distances that change with the Cu(II)/Cu(I) redox states.[3]

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