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Synthesis and Characterization of Dichloro and Dibromo(2-(dimethylaminomethyl)thiophene) Copper(II) Complexes

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The 2-(dimethylaminomethyl)thiophene (dmamt) complexes with copper(II) chloride and bromide were prepared and characterized by optical, EPR, XPS spectroscopies and magnetic susceptibility measurements. The low-energy absorption band above 850 nm and the relatively small EPR hyperfine coupling constant ($A_{\parallel} \approx 125$ G) indicate the pseudotetrahedral site symmetry around copper(II) ion both in $\text{Cu}(\text{dmamt})\text{Cl}_2$ and $\text{Cu}(\text{dmamt})\text{Br}_2$ complexes. The higher satellite to main peak intensity of Cu $2P_{3/2}$ core electron binding energy in XPS spectra also supports the pseudotetrahedral geometry around the copper(II) ions having CuNSX_2 chromophores. The distortion from square-planar to pseudotetrahedral symmetry is likely to arise from the steric hindrance of the bulky dmamt ligand in the complex. Magnetic susceptibility study shows that these compounds follow Curie-Weiss law in the temperature range of 77-300 K with positive Weiss constant exhibiting the ferromagnetic interaction between copper(II) ions in solid state.

Introduction

Blue copper proteins (Type 1) exhibit unusual spectral and chemical properties in comparison with those of other copper (II) complexes¹. Such unusual properties are presumably justified with not only the nature of the donor atoms of ligands coordinated to copper(II) but also with the distorted tetrahedral geometry around copper(II) site in the proteins^{1,2}. Therefore, The pseudotetrahedral copper(II) complexes have been used as model compounds for the copper proteins. The degree of distortion from square plane to tetrahedron is highly

variable, being strongly influenced by the nature of the ligands coordinated to copper(II). In any case, the spectral and chemical properties of the complexes usually provide useful informations concerning their stereochemistry.

We prepared previously (-)-sparteine-copper(II) halides, which have pseudotetrahedral geometry around copper site, and examined the thermal³, electrochemical⁴, structural and magnetic⁵ properties, and also reported the result of the mechanistic investigation of the hydrolysis of these complexes⁶. The unusual properties of (-)-sparteine-copper(II) halides complexes were discussed in terms of the coordination geo-

metry around copper(II) ion.

In this report, as the extension of the study of 4-coordinate distorted tetrahedral copper(II) complexes, we synthesized 2-(dimethylaminomethyl)-copper(II) halides complexes having CuSNX_2 chromophore. These compounds stimulate our interest since they contain sulfur and nitrogen donor atoms as in the blue copper proteins, although the coordination environment is somewhat different from that found in biological system. The compounds were characterized by optical, EPR, XPS spectroscopy, and by magnetic susceptibility measurements.

Experimental

Preparation of Complexes. The 2-(dimethylamino-methyl) thiophene (dmamt) complex with copper(II) chloride was prepared by the direct reaction of dmamt and anhydrous CuCl_2 . 1.0 mmole of anhydrous CuCl_2 was dissolved in a mixture of absolute methanol (50 ml) and trimethylorthoformate (10 ml). A solution of dmamt (ca. 1.0 mmol) in a mixture of methanol (50 ml) and trimethylorthoformate (10 ml) was added dropwise to the solution. The mixture was refluxed ca. 1-2 hr and refrigerated overnight. The brown precipitate was collected by filtration and washed successively with absolute methanol. The precipitate was dried in vacuum at room temperature. The analogous copper(II) bromide complex was prepared by the similar method using anhydrous CuBr_2 . The obtained compound was dark purple. Elemental analysis was performed by the Korea Research Institute of Chemical Technology, Daejeon, Korea.

$\text{Cu}(\text{dmamt})\text{Cl}_2$; Calcd, C; 30.50, H; 4.02, N; 5.08

Found C; 31.15, H; 4.10, N; 5.09

$\text{Cu}(\text{dmamt})\text{Br}_2$; Calcd, C; 23.06, H; 3.04, N; 3.84

Found C; 22.83, H; 3.70, N; 3.80

Physical Measurements. Electronic spectra were taken on a Hewlett Packard 8451A and Cary 17 Spectrophotometer in solution. EPR spectra of powdered samples were

obtained from a Varian E-3 X-band spectrometer (~9.5 GHz). The magnetic field was calibrated by using an NMR gaussmeter (Magnion Model G-502) and a Hewlett Packard precision frequency counter. The free radical DPPH ($g=2.0036$) was used as a field marker. The magnetic susceptibility data from 77 K to room temperature were collected using Faraday method with a Cahn 2000 electrobalance. The magnetometer was calibrated with $\text{HgCo}(\text{SCN})_4$.⁷ All data were corrected for the diamagnetism of the constituent atoms using Pascal's constant and for temperature-independent paramagnetism of copper(II) which was estimated to be 60×10^{-6} cgsu per atom. XPS spectra were recorded on a Perkin Elmer Physical Electronics Model 5400 X-ray photoelectron spectrometer equipped with a magnesium anode X-ray source and a hemispherical analyzer, at residual gas pressure of 5×10^{-9} torr. The samples were mounted on the fresh surface of an indium foil to make a good contact with the spectrometer. The binding energies (BE) were calibrated using Au $4f_{7/2}$ peak at 84.9 eV and the Cu $2P_{3/2}$ peak at 932.4 eV. The adventitious C 1s line at 284.6 eV was used for charge referencing.

Results and Discussion

Electronic spectra for $\text{Cu}(\text{dmamt})\text{X}_2$ were recorded from 250-1600 nm in chloroform solution. The results of the electronic spectra of the compounds and other pseudotetrahedral copper(II) complexes are summarized for comparison in Table 1. Only one broad band above 800 nm was observed in $\text{Cu}(\text{dmamt})\text{X}_2$ compounds. Such low-energy absorption bands are commonly found in the pseudotetrahedral copper(II) complexes. R. B. Wilson and coworkers¹⁰ assigned previously the band at 825 nm to $d_{xz} \leftarrow d_{xy}$ transition in pseudotetrahedral $\text{Cu}(\text{dmaep})\text{Cl}_2$ (dmaep=dimethylaminoethylpyridine) complex. The intense bands ($\epsilon > \sim 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) absorbed at 310-350 nm arise from the charge transfer. The band at around 310 nm is presumably due to sulfur-to-copper ($d_{z^2-y^2}$) cha-

Table 1. Electronic spectral data for some pseudotetrahedral copper (II) complexes

Compd.	Solvent	λ_{max} (nm)	References
$\text{Cu}(\text{dmamt})\text{Cl}_2$	chloroform	280 (3.40×10^3) ^a	this work
		315 (sh. 2.54×10^3)	
		352 (sh. 1.92×10^3)	
		860 (br. 1.72×10^2)	
$\text{Cu}(\text{dmamt})\text{Br}_2$	chloroform	310 (3.22×10^3)	this work
		880 (br. 1.72×10^2)	
$\text{Cu}(\text{dmaep})\text{Cl}_2$	dichloromethane	825 (133), 1050 (132)	(8)
	Nujol	400, 800, 1030	
$\text{Cu}(\text{dmaep})\text{Br}_2$	dichloromethane	860 (252), 1080 (247)	(8)
	Nujol	430, 495, 840, 1100	
$\text{Cu}((-)\text{-sparteine})\text{Cl}_2$	Nujol	780	(9)
$\text{Cu}((-)\text{-sparteine})\text{Br}_2$	Nujol	830	(9)

^aMolar absorptivity (ϵ) is in parenthesis.

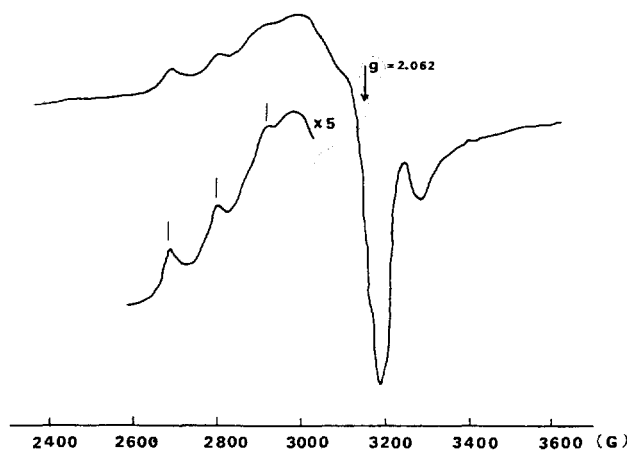


Figure 1. EPR spectrum of Cu(dmamt)Cl₂ doped into analogous ZnCl₂ (1%).

rge transfer since the complexes having CuN₂S₂ chromophore exhibit strong bands in the range of 300-400 nm while CuN₄ complexes display no band in this region¹¹⁻¹².

Figure 1 shows the room temperature EPR spectrum of polycrystalline Cu(dmamt)Cl₂ doped into the corresponding

diamagnetic Zn(II) complex (1%). It exhibits four hyperfine lines resulting from the coupling of the unpaired electron with the nuclear spin of copper(II) ion. EPR g and $A_{//}$ values are well resolved. The results are listed in Table 2. the $A_{//}$ values of Cu(dmamt)Cl₂ and Cu(dmamt)Br₂ are 125 and 130 gauss, respectively. These values are somewhat larger than that of blue copper proteins, but are comparable to those of some distorted tetrahedral copper(II) complexes. The values of less than 150G are observed for a variety of distorted tetrahedral copper(II) complexes¹³. The relatively small $A_{//}$ values in tetrahedral symmetry are explained by the fact that 4s and 4p orbitals in the ground state can be easily mixed in low symmetry complexes. The limiting case of this is given by the CuCl₄²⁻ anion in Cs₂(Zn, Cu)Cl₄($A_{//}$ ~ 25G)¹⁴. J. R. Wasson *et al.*¹³ pointed that the A-values decrease and g -values increase as the distortion from square-planar to tetrahedral symmetry increases. Such an effect was also observed in EPR spectrum of copper(II) complex with 2-methylamino-1-cyclopentene-1-dithiocarboxylate) anion in the diamagnetic host lattices¹⁵.

The binding energies of core electrons were investigated by X-ray photoelectron spectroscopy (XPS). The data are summarized in Table 3. The Cu 2p orbital is split into 2p_{3/2} and 2p_{1/2} levels. The binding energies of Cu 2p_{3/2} and Cu

Table 2. EPR and magnetic data for dmamt-copper halide complexes

Complex	EPR parameters*		Magnetic moment		Curie-Weiss fitting
	g	$A_{//}$ (gauss)	room temp.	liq N ₂ temp.	
Cu(dmamt)Cl ₂	$g_1 = 2.336$ $g_2 = 2.062$ $g_3 = 1.962$	125	2.03	2.46	$\langle g \rangle = 2.25$ $\theta = +25.3 \text{ K}$
Cu(dmamt)Br ₂	$g_1 = 2.197$ $g_2 = 1.970$ $g_3 = 1.916$	130	2.06	2.20	$\langle g \rangle = 2.33$ $\theta = +16.7 \text{ K}$

*EPR data were obtained in doping analogous zinc(II) halides.

Table 3. Binding energies of some copper(II) compounds (eV)

Compound	Copper				N (1s)	S (2p)	halide (2p)
	2P _{3/2}		2P _{1/2}				
	satellite	main	satellite	main			
Cu(dmamt)Cl ₂	941.2 943.9	933.6	962.6	953.7	399.4	163.4 164.4	197.5 (Cl) 199.0
CuCl ₂ · 2H ₂ O		936.6		956.6			200.8
CuCl ₂	942.0 944.6	934.6	963.2	954.4			
Cu(dmamt)Br ₂	941.4 942.7	933.7	962.6	952.2	399.7	163.9	68.5 (Br)
CuBr ₂	941.5 943.1	933.1	962.9	952.9			71.5

$2p_{1/2}$ core electrons for $\text{Cu}(\text{dmamt})\text{Cl}_2$ are 933.6 and 953.7 eV, respectively. The values are smaller than those of CuCl_2 by ~ 1.0 eV, indicating the lower positive charge density on copper ion for $\text{Cu}(\text{dmamt})\text{Cl}_2$. This smaller binding energy is comparable to the values found for nickel and other transition metal complexes with sulfur-containing ligand¹⁶. The compounds exhibited smaller binding energy than expected for a particular oxidation state of the metal due to the significant electron donating effect of the ligand. The shake-up satellite peaks were observed at an energy level of ~ 8 eV higher than the corresponding main peaks in the copper $2p_{3/2}$ and $2p_{1/2}$ levels. The presence of shake-up satellite peaks is known to be the characteristic phenomenon of paramagnetic copper(II) oxidation state due to the charge transfer from ligand to copper(II) ion¹⁷. The intensity of the shake-up satellite peaks is known to be affected by the different electronic environment such as the relative position of copper and ligand valence holes and by the amount of hybridization¹⁸. A. A. Gewirth and coworkers¹⁹ studied XPS spectra of square-planar (D_{4h}) and pseudotetrahedral (D_{2d}) CuCl_4^{2-} anions and correlated the satellite intensity to the geometry of copper site. The authors demonstrated that the ratio of the satellite peak intensity (I_s) to the main peak intensity (I_m) in D_{2d} symmetry is greater than that in D_{4h} symmetry. Cu $2p_{3/2}$ relative satellite intensity (I_s/I_m) values of 0.63 and 0.85 were reported for D_{4h} and D_{2d} CuCl_4^{2-} salts, respectively. It was concluded that the I_s/I_m values decrease as the tetrahedral distortion from the planar copper(II) site increases. The measured relative satellite intensity in $\text{Cu}(\text{dmamt})\text{Cl}_2$ and $\text{Cu}(\text{dmamt})\text{Br}_2$ were about 0.70 in both compounds, supporting the distorted tetrahedral geometry around copper(II) site. The N 1s binding energies are 399.4 and 399.7 eV whereas N 1s in NH_3 is 398.9 eV²⁰. This binding energy shift (~ 1 eV) is justified by the coordinated nitrogen atom in the complexes. Similar results were observed in the binding energy of halogen in the complexes. For example, the binding energy of Cl 2p in $\text{Cu}(\text{dmamt})\text{Cl}_2$ (197.5 eV) is less than that in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (200.8 eV). The S 2p peaks are slightly asymmetric with a shoulder at the low-binding energy side. S 2p binding energies in $\text{Cu}(\text{dmamt})\text{X}_2$ are similar to those of some copper protein model compounds (163.0–163.9 eV)²¹.

The magnetic susceptibility data were collected from 77 to 300 K and summarized in Table 2. Figure 2 shows the temperature dependence of the magnetic susceptibility for $\text{Cu}(\text{dmamt})\text{Cl}_2$. The data are well described by the Curie-Weiss law expressed by the equation

$$\chi = \frac{C}{T - \theta} = \frac{N g^2 \beta^2 s(s+1)}{3k(T - \theta)},$$

where the symbols have usual meanings. The solid line was calculated by the Curie-Weiss law with $\langle g \rangle = 2.25$, $\theta = +25.3$ K for $\text{Cu}(\text{dmamt})\text{Cl}_2$. It was fitted by using standard linear least-square method. The values of $\langle g \rangle = 2.23$ and $\theta = +16.7$ K were obtained for $\text{Cu}(\text{dmamt})\text{Br}_2$. The effective magnetic moments (μ_{eff}) are 2.03, and 2.06 BM at room temperature for $\text{Cu}(\text{dmamt})\text{Cl}_2$ and $\text{Cu}(\text{dmamt})\text{Br}_2$, respectively. It was calculated from the equation, $\mu_{\text{eff}} = 2.828 \sqrt{\chi \cdot T}$. It is known that the magnetic moments of a variety of pseudotetrahedral copper(II) complexes are around 2.0 BM at room temperature since the low-symmetry ligand fields are large compared to

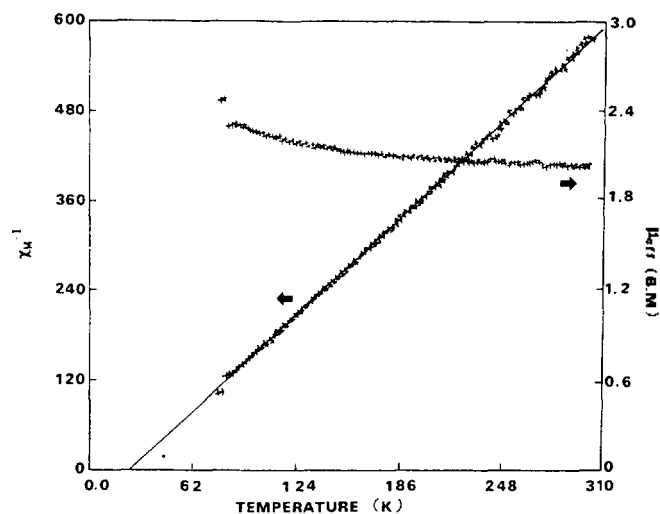


Figure 2. Temperature dependence of inverse magnetic susceptibility and magnetic moment of $\text{Cu}(\text{dmamt})\text{Cl}_2$: solid line is the best fit to the Curie-Weiss law with $\langle g \rangle = 2.25$ and $\theta = 25.3$ K.

the spin-orbit coupling of copper(II) metal²². The effective magnetic moment increases slowly as the temperature decreases, exhibiting 2.46 BM and 2.20 BM at 77 K for $\text{Cu}(\text{dmamt})\text{Cl}_2$ and $\text{Cu}(\text{dmamt})\text{Br}_2$, respectively. The observed temperature dependence of the magnetic moment and the positive value of the Weiss constant (θ) strongly imply the ferromagnetic exchange coupling between copper(II) ions. The magnetic data for $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ ²³ and $\text{Cu}[\text{O}(\text{CH}_2\text{CO}_2)_2]$ ²⁴ also showed the ferromagnetic interaction between copper(II) ions with positive Weiss constant.

In summary, the optical, EPR and XPS spectral properties reveal the pseudotetrahedral geometry around copper(II) site in $\text{Cu}(\text{dmamt})\text{Cl}_2$ and $\text{Cu}(\text{dmamt})\text{Br}_2$ complexes. The small values of the binding energy of Cu 2p core electrons indicate that sulfur atom coordinates strongly to copper metal as well as nitrogen atom having CuNSX_2 chromophores. The pseudotetrahedral geometry is arising from the steric hindrance of the bulky dimethylaminomethylthiophene ligand in the complexes. The magnetic study shows the ferromagnetic interaction between copper(II) ions in the solid state, although an X-ray structure determination in necessary for further elucidation of these subject matters.

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An NMR Study on Molecular Motions of $\alpha,2,6$ -Trichlorotoluene in Solution State

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Dynamics of CH_2Cl group in $\alpha,2,6$ -trichlorotoluene dissolved in CDCl_3 was studied by observing various relaxation modes for ^{13}C under proton uncoupled condition. Partially relaxed ^{13}C spectra were obtained at 34°C as a function of evolution time after applying various designed pulse sequences to this AX_2 spin system. It was found that nonlinear regression analysis of the relaxation data for these magnetization modes could provide the information about dipolar and spin-rotational auto-correlation and cross-correlation spectral densities for fluctuation of the ^{13}C - ^1H internuclear vector in CH_2Cl group. The results show that the effect of cross-correlation is comparable in magnitude to that of auto-correlation and the relaxation in this spin system is dominated by dipolar mechanism rather than spin-rotational one. From the resulting spectral density data we could calculate the bond angle $\angle\text{HCH}$ (105.1°) and elements of the rotational diffusion tensor for CH_2Cl group.

Introduction

The theory describing intramolecular nuclear magnetic relaxation phenomena in multispin systems is nowadays well established and has been shown to be a very powerful tool for the study of dynamics and structure of molecules in liquid.¹⁻⁴ For spin $1/2$ nuclei, such as ^1H and ^{13}C , in small molecules the most important relaxation mechanisms are known to be the inter- and intramolecular dipole-dipole interactions modulated by molecular reorientation and the

spin-rotation interactions modulated by random fluctuation in molecular rotational angular momenta. The dipolar mechanism is usually much more prevailing over the spin-rotational one, but if a system can easily undergo the change in rotational motions, then the contribution from the latter may be substantial.

In a previous investigation⁵ we have studied the spin-lattice relaxation of ^{13}C and ^1H spins in methyl group of 2,6-dichlorotoluene dissolved in CDCl_3 at 34°C . The result showed that the spin-rotational contribution to the total relaxation rate was found to be about 20%, which indicates that the internal rotation of methyl group is quite fast and facile in

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