Synthesis and Characterization of Pseudotetrahedral Copper(II) Dihalide Complexes with (s)-(−)-Nicotine

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Blue copper proteins (Type I) exhibit unusual spectral and chemical properties such as higher reduction potentials and small hyperfine coupling constants $A_{\parallel}$ in the EPR spectrum in comparison with other copper(II) complexes.[1] Such unusual properties are justified partly by the tetralhedral geometry around the copper(II) site and partly by the CuN_2S_2 chromophores in which the soft S atoms coordinate with the copper ions to stabilize the copper(I) state in the proteins.[1,2]

Recently we prepared neutral alkaloid (−)-*l*-sparteine complexes with copper(II) malonitrilodithiolate[3] and with coper(II) oxyanion complexes,[4] and suggested them as model compounds for the type I copper(II) site of blue copper proteins since their physicochemical properties mimic interesting spectral and redox behaviors in the blue copper centers. In the former compound, the copper atom adopted a distorted tetrahedral geometry with a dihedral angle of 68.07° between the CuN_2 and CuS_2 planes, and the distortion was caused from the steric hindrance of the bulky (−)-*l*-sparteine ligand in the reported Cu(sp)(mnt) complex.

We focussed on the copper coordination sphere as a first step in model studies on the copper proteins. Herein we prepared (s)-(−)-nicotine complexes with copper(II) halides since (s)-(−)-nicotine is another bulky ligand forming a distorted tetrahedral geometry around the copper(II) site. Furthermore, (s)-(−)-nicotine is a basic ligand possessing methylated pyrrolidine nitrogen and pyridine nitrogen to form a stable chelate with the copper(II) ion. The prepared compounds were characterized using spectroscopic (optical, EPR), electrochemical methods and magnetic susceptibility measurements, and the examined properties are discussed in relation to the geometry around the copper site.

Experimental Section

All of the reagents and solvents were purchased from either Aldrich or Sigma chemical companies and used without further purification. Cu(nic)Cl_2 was prepared by adding a (s)-(−)-nicotine solution (1 mmole) to a ethanol/triethylorthoformate solution of anhydrous $CuCl_2$ (1 mmole). The solution was refluxed at 60 °C for two hours under a nitrogen atmosphere. The solution changed to a dark green color immediately, and was refrigerated overnight. The resultant precipitates were collected and recrystallized in absolute ethanol. The collected precipitates were dried under vacuum at room temperature. Cu(nic)Br_2 was prepared by an analogous method using anhydrous $CuBr_2$. Elemental analyses were performed at the Korean Basic Science Center, and the results are listed below.

Anal. (%) Calcd. for Cu(nic)Cl_2 yellow: C, 40.48; H, 4.76; N, 9.44. Found: C, 40.78; H, 4.91; N, 9.22. Calcd. for Cu(nic)Br_2 brown: C, 31.15; H, 3.66; N, 7.27. Found: C, 31.47; H, 3.50; N, 7.43.

The electronic absorption spectra (200-1600 nm) were recorded on a Shimadzu UV-3101PC spectrophotometer in acetonitrile. Cyclic voltammograms were recorded on a BAS CV-50W Voltammetric Analyzer in a three-electrode system at 0.1 M tetraethylammonium perchlorate (TEAP) in DMF. EPR spectra measurements were carried out for the solution samples (DMF/CH_2Cl = 50/50) at 77 K using a ESP-300S EPR spectrometer at the X-band frequency. The field modulation frequency was 100 kHz and DPPH was used as a reference. Magnetic susceptibility data was collected from 4 K to 300 K by the SQUID method using the MPMS7 (Magnetic Property Measurement System) of U.S.A. Quantum Design. The data was corrected for the diamagnetism of the constituent atoms using Pascal's constants and for the temperature-independent paramagnetism of the copper estimated to be 60×10^{-6} cgsu/Cu atom.

Results and Discussion

The electronic spectra of the titled compounds were examined (200 nm-1600 nm) in an acetonitrile solution. Broad and unsymmetric absorption bands with a shoulder at around 1200 nm centered at 845 nm and 840 nm for Cu(nic)Cl_2 and Cu(nic)Br_2 respectively, which can be assigned to d-d transitions. Such low-energy absorption bands higher than 800 nm are commonly found in pseudotetrahedral copper(II) complexes.[5] According to the crystal field theory, the d-d transition absorption band envelope shifts to lower energy as the planar copper(II) complexes are twisted toward the distorted tetrahedral structure of D_{2d} or C_{2v} symmetry.[5] For example, the absorption peaks of the planar $CuCl_4^{2-}$ ion lie from 800 nm to 570 nm, whereas the

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Table 1. Electronic and magnetic properties of Cu(nic)X_2 complexes

Compounds	Electronic spectra λ_{max} (nm)	EPR parameters		Effective magnetic moment[c] μ_{eff} (B.M.)	Curie-Weiss parameters[d]	
		g	$A_{\|}$ ($\times 10^{-4}$ cm^{-1})		C	θ(K)
Cu(nic)Cl_2	845 [ν_1; 1198(4)[b], ν_2; 974(15), ν_3; 810(26)][a]	$g_{\|}$ = 2.065	119	1.85	0.40	+21.2
	285	$g_{\|}$ = 2.353				
Cu(nic)Br_2	840 [ν_1; 1158(24)[b], ν_2; 954(30), ν_3; 813(58)][a]	$g_{\|}$ = 2.069	130	1.90	0.43	+19.9
	300	$g_{\|}$ = 2.370				

[a]The absorption peak was resolved into three peaks by Gaussian analysis. [b]The calculated molar absorptivities ($M^{-1}cm^{-1}$) are in parentheses. [c]The effective magnetic moments were calculated at room temperature. [d]The Curie-Weiss parameters were examined form 100 K to room temperature.

regular tetrahedron $CuCl_4^{2-}$ in Cs_2CuCl_4 exhibited four transitions higher than 1000 nm. The prepared compounds can be represented as a CuN_2X_2 chromophore with a C_{2v} symmetry, which lead to four possible d-d transitions[5,6]; $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{yz}$, $d_{x^2-y^2} \rightarrow d_{xz}$. Among them, $d_{x^2-y^2} \rightarrow d_{xz}$ transition exhibits usually at low energy at around 1600 nm or less. No absorption peaks were examined at higher than 1400 nm for the present Cu(nic)X_2 compounds. Therefore we analyzed the observed asymmetric absorption (500-1400 nm) into three peaks by Gaussian resolution, and the obtained three bands (ν_1, ν_2, ν_3) were tentatively assigned to $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{yz}$ transitions respectively. The data is summerized in Table 1. The absorption peaks are comparable to those of pseudotetrahedral copper(II) complexes having a variety of chromophores.[4]

Both the Cu(nic)Cl_2 and the bromide analogue exhibited an intense band ($\varepsilon > 10^{-3}$ $M^{-1}cm^{-1}$) at around 300 nm [285 nm for Cu(nic)Cl_2 and 301 nm for Cu(nic)Br_2], which can be ascribed to the charge-transfer transition from the nitrogen to the copper(II) 3d orbital since the charge transfer transitions from the halogen donor site are expected to occur at *ca.* 400 nm.[7]

Cyclic voltammograms were examined in DMF solution versus a Ag/Ag+ electrode, and found to be well behaved. The $E_{1/2}$ potentials were estimated by averaging the anionic and cathodic peak potentials. The results are summarized in Table 2.

Cu(nic)Cl_2 showed only one peak at −0.05 V for the Cu^{+2}/Cu^{+1} couple, whereas Cu(nic)Br_2 exhibited two peaks at +0.36 V for the Cu^{+2}/Cu^{+1} couple and at −0.02 V for the Cu^{+1}/Cu^0 couple. These observed values are somewhat higher than those of $CuCl_2$ and $CuBr_2$ respectively and those of some planar CuN_2X_2 complexes.[8] Patterson *et al.*[8] discussed the correlation of the geometry around the copper(II) metal ion with redox potential, and concluded that the reduction potential shifted to higher values as distorted from a square planar to a tetrahedral symmetry since the distortion toward tetrahedral geometry makes the copper(II) ion easier to reduce. Therefore, the relatively higher $E_{1/2}$ potentials of Cu(nic)X_2 complexes indicate that the complexes are twisted toward a pseudotetrahedral geometry. The higher $E_{1/2}$ values of Cu(nic)Br_2 than those of Cu(nic)Cl_2 could be elucidated in terms of the better reduction ability of the bromide ligand than that of the chloride ligand.

Table 2. Electrochemical data of Cu(nic)X_2 complexes in DMF versus a Ag/Ag^+ electrode

Compounds	E_{pc}	$E_{1/2}$	E_{pa}	Process
$CuCl_2 \cdot 2H_2O$	−2.90	−0.07	0.16	Cu^{II}/Cu^{I}
Cu(nic)Cl_2	−0.27	−0.05	0.18	Cu^{II}/Cu^{I}
$CuBr_2$	0.54	0.63	0.71	–
	0.25	0.35	0.44	Cu^{II}/Cu^{I}
	−0.25	−0.09	0.03	Cu^{I}/Cu^{0}
Cu(nic)Br_2	0.59	0.70	0.80	–
	0.28	0.38	0.47	Cu^{II}/Cu^{I}
	0.20	−0.03	0.15	Cu^{I}/Cu^{0}

The X-band powdered EPR spectra exhibited a broad singlet at around <g> = 2 at room temperature. The EPR spectra showed well-defined four hyperfine lines for frozen glass samples at 77 K resulting from the coupling of the unpaired electron with the nuclear spin of copper(II). The typical EPR spectrum of Cu(nic)Br_2 is shown in Figure 1. The resulted data is summarized in Table 1.

The g values are $g_{\|} > g_{\perp} > 2.0023$, indicating that the copper(II) metal has a $d_{x^2-y^2}$ ground state. The $A_{\|}$ values were observed to be 119×10^{-4} and 130×10^{-4} cm^{-1} for Cu(nic)Cl_2 and Cu(nic)Br_2 respectively. These values are comparable to those of the distorted tetrahedral copper(II) complexes.[9,10]

Lee Y. M. *et al.*[11] reported the relationships between the structure and spectroscopic properties in tetrahedrally distorted Cu(sp)Cl_2 [sp = (−)-*l*-sparteine] complexes, and pointed out that the A values are quite sensitive to the small change in the dihedral angle between the $CuCl_2$ and CuN_2 planes in the Cu(sp)Cl_2 unit. The $A_{\|}$ values of Cu(sp)Cl_2 (115×10^{-4} cm^{-1}) in the frozen sample were reduced to 100 $\times$ 10^{-4} cm^{-1} as the dihedral angle increased by ~11° toward a tetrahedral symmetry in the Zn(II) host lattice. A similar effect was discussed in the Cu(acda) series.[12] acda = 2-amino-cyclopentene-carbodithionic acid, in which there was a ~15×10^{-4} cm^{-1} change in $A_{\|}$ for a 4.3° change in the twist angle. These reduced A values in tetrahedral symmetry are explained by the fact that the 4s and 4p orbitals in the ground state can be easily mixed in low symmetry complexes.[9,13] The EPR features of pseudotetrahedral copper(II) complexes

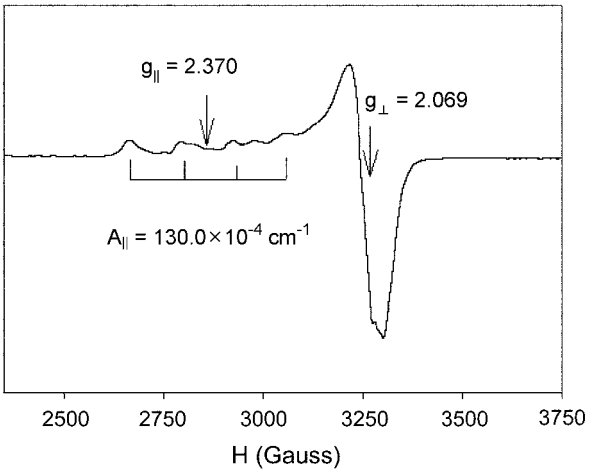

Figure 1. The X-band EPR spectrum of Cu(nic)Br_2 in solution (DMF/CH_2Cl_2 = 50 : 50) at 77 K.

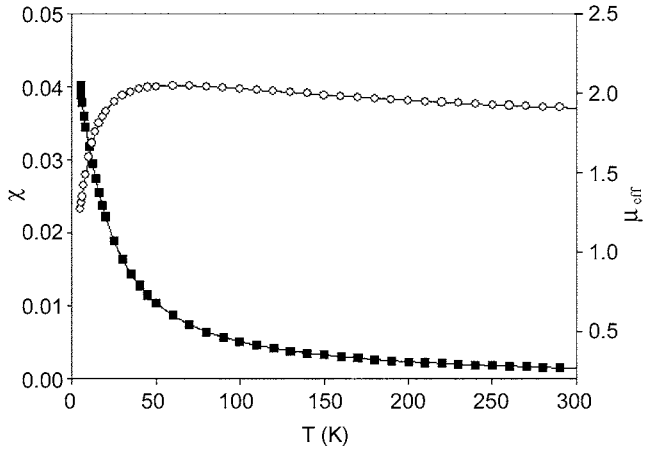

Figure 2. Temperature dependence of the magnetic susceptibilities (■) and the effective magnetic moments (○) of Cu(nic)Br_2.

usually show $A_{\|}$ values less than 150 × 10^{-4} cm^{-1}. Recently we[14] reported that the A value of Cu(sp)Br_2 which has a dihedral angle of 73.8° between the $CuBr_2$ and CuN_2 planes was 117 cm^{-1}, and suggested that the pseudotetrahedral symmetry at the copper site in Cu(sp)Br_2 arose from the steric hinderance of the bulky sparteine ligand. Therefore, on the basis of the observed spectral and electrochemical results, we suggest that there is a distortion from square planar to peudotetrahedal symmetry due to the crystal packing forces resulted from the existence of the bulky (s)-(−)-nicotine ligand in the cell. The lattice effect of the bulky nicotine ligand was reported in nicotinium tetrachlorocuprate(II), $(nicH_2)CuCl_4$ complex,[15] in which $CuCl_4^{2-}$ anions were distorted from square planar to D_{2d} symmetry as a result of the bulky nicotinium cations as well as the hydrogen bonding interactions between $CuCl_4^{2-}$ anions and nicotinium cations.

The magnetic susceptibility was examined from 4 K to room temperature by the SQUID method. The typical temperature dependence of the magnetic susceptibility for Cu(nic)Br_2 is shown in Figure 2. The magnetic susceptibility increases as the temperature decreases in a Curie-like tail, and the data follows the Curie-Weiss law of the form $\mu_{eff} = C/(T-\theta)$ from 100 K to room temperature. Below 100 K, however, there is a marked deviation from Curie-Weiss behavior, indicating that magnetic interactions are present between Cu(II) ions at low temperature. The obtained parameters of the Curie-Weiss fit (100 K ~ room temperature) are shown in Table 1. The Curie constants C=0.40 and 0.43 cm^3 K mol^{-1} were obtained for the Cu(nic)Cl_2 and Cu(nic)Br_2 compounds respectively. These values are normal for a complex with one unpaired electron, and are similar to the value (C=0.44 cm^3 K mol^{-1} for both compounds) calculated from the g tensors determined from the EPR experiments.[16] The effective magnetic moment (μ_{eff}) of Cu(nic)Br_2 calculated from the equation μ_{eff} = 2.828 $(\chi \cdot T)^{1/2}$ was 1.90 B.M. at room temperature. It rises slowly to a broad maximum value of 2.05 B.M. around 60 K and falls rapidly to 1.30 B.M. near 5 K as the temperature decreases. A similar behavior was found in an analogue chloride compound rising from 1.85 B.M. (300 K) to 1.95 B.M. (60 K) and falling to 1.32 B.M. (5 K). The calculated positive Weiss constants and the magnetic moments behaviors are indicative of the ferromagnetic interactions between the copper(II) ions in solid state and the examined effective magnetic moments are in a range similar to the other tetrahedral cupric compounds.[17]

Conclusions

We prepared dihalo[(s)-(−)-nicotine]copper(II) complexes having CuN_2X_2 chromophores, and the experimental data revealed that the prepared compounds have a pseudotetrahedral symmetry around the copper site resulting from the bulky (s)-(−)-nicotine ligand. The interesting spectral and electrochemical properties of the prepared complexes were caused from the particular geometry around the copper site, which could be related to the properties of blue copper proteins although the present complexes do not represent an active site of the copper proteins. The magnetic behaviors show that there are ferromagnetic interactions between copper(II) ions in solid state. No proper pathways for this ferromagnetic interactions are suggested at present time. This explanation should be elucidated from the structure determination, but we did not obtain the single crystal for an X-ray structure determination.

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