Notes

Magnetic and Electrochemical Properties of Dichloro-(2-(dimethylaminomethyl)thiophene) Copper(II) Complex

Young Inn Kim,* Sung Nak Choi[†], and Seong Bae Moon

Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea
[†]*Department of Chemistry, Pusan National University, Pusan 609-735, Korea*

Recently we studied the 2-(dimethylaminomethyl)thiophene (dmamt) complex with copper(II) chloride of the formula of Cu(dmamt)Cl$_2$, and mentioned that the coordination environment of copper(II) ion is distorted from square planar to pseudotetrahedral symmetry.[1] The magnetic property of the compound was especially interesting. The magnetic susceptibility data were well described by Curie-Weiss law with the positive Weiss constant from 77 K to room temperature. The effective magnetic moment increased slowly as decreasing the temperature. This results indicated the ferromagnetic interaction between copper(II) ions in the compounds. But the detailed magnetic interaction was not shown because the exchange interaction between the spins in copper(II) complexes is usually established at low temperatures. The magnetic interaction in copper(II) systems are of interest since many proteins and enzymes contain copper(II) magnetic interactions.[2] Hemocyanin and tyrosinase are well characterized examples of magnetically coupled binuclear metal sites.[2c] In this study, we investigate the magnetic interaction between copper(II) ions in Cu(dmamt)Cl$_2$ from 4 K to 90 K using VSM method and the electrochemical property of the compound in DMF solution. The small magnetic coupling constant and the relatively high reduction potential of the compound are discussed on the basis of the structural geometry of Cu(dmamt)Cl$_2$.

Results and Discussion

The magnetic susceptibility data were collected from 4 to 90 K and shown in Figure 1. The data obtained in the temperature range of 77 K to room temperature were represented by Curie-Weiss law, $\chi = C/T - \theta$ with the parameters $\langle g \rangle = 2.10$ and $\theta = +25.3$ K.[1] However, the data are deviated from the Curie-Weiss law below 70 K. We tried first to fit the magnetic data to the Heisenberg linear-chain theory, for which the Hamiltonian is

$$H = -2J \sum_i^\infty S_i S_{i+1}$$

However, the magnetic susceptibility data did not satisfy the one-dimensional Heisenberg model. Baker *et al.*[3] have developed a model for a ferromagnetic linear chain based on a
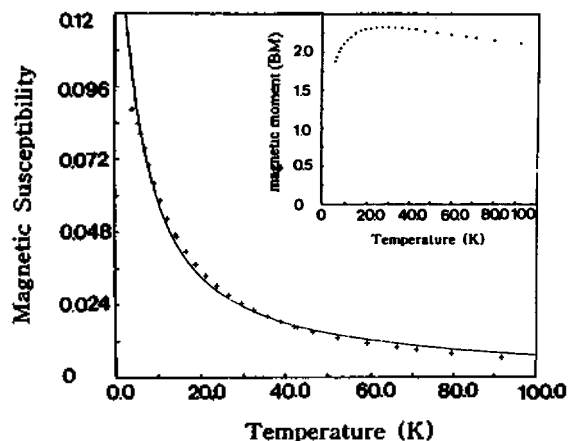

Figure 1. Temperature dependence of magnetic susceptibility and magnetic moment of Cu(dmamt)Cl$_2$.

high temperature Pada expansion technique. This expansion was modified with a correction for interchain interactions in the following manner.

$$\chi_m = \frac{\chi_H}{1 - 2zJ' \ \chi_H/Ng^2\beta^2}$$

where χ_H is the magnetic susceptibility of an isolated Heisenberg linear chain of $s = 1/2$ ions, z is the number of near neighbors in adjacent chains, and J' is the interchain exchange parameters. The above equation was fit to the experimental magnetic susceptibility and temperature data by using as the criterion of best fit the minimum value of $\sum_i (\chi_i^{cald} - \chi_i^{obs})^2 / \chi_i^{obs2}$. The best-fit values over the temperature range of 4-90 K are $J = 9.60 \times 10^{-1}$ cm^{-1}, $g = 2.34$, $zJ' = -1.89$ cm^{-1} for Cu(dmamt)Cl$_2$. The positive (+) value of J indicates the ferromagnetic interaction between copper(II) ions in the Heisenberg linear-chain (intrachain), and the negative (−) value of J' shows the antiferromagnetic interaction between the isolated linear chains (intrachain). The result of this fit is shown as the smooth curve in Figure 1. The effective magnetic moment increases slowly as the temperature decreases in the range of 90-10 K. The magnetic moment decrease sharply as decreasing temperature below 10 K. The increase in magnetic moment as the temperature decreases signals a ferromagnetic interactions, and the decrease of magnetic moment below 10 K is a result of the approaching saturation of the ferromagnetic system and a weak antiferromagnetic interaction between the chains.

The intrachain ferromagnetic exchange coupling constant (J) is smaller than those of halogen-bridged copper(II) clusters ($J = 2.7$-56 cm^{-1})[4] and some tetrachlorocuprate(II) ($J = 11.8$ cm^{-1}).[5] The observed small exchange coupling constant of Cu(dmamt)Cl$_2$ can be rationalized in terms of the structural aspect of the compound, which is the pseudotetrahedral geometry around the copper(II) ions. Hatfield[6] has demonstrated the effect of the bridged geometry on exchange coupling in chloro, bromo, and sulfur-bridged copper(II) dimers

Notes

Bull. Korean Chem. Soc. **1995**, *Vol. 16, No. 4* 371

and chains. He concluded that the exchange coupling constant decreased as the bridging angle (Cu-X-Cu) decreased. The small bridging angle is anticipated between the pseudotetrahedral copper(II) complex unit. This small bridging angle lead to the small exchange coupling constant between copper(II) ions in Cu(dmamt)Cl$_2$.

The pseudotetrahedral geometry around Cu(II) ion in Cu (dmamt)Cl$_2$ is supported by the electrochemical properties. Cyclic voltammogram was recorded in 0.1 M TEAP/DMF from -0.5 V to $+1.0$ V vs. Ag/AgCl electrode. Cu(dmamt)Cl$_2$ exhibited two cathodic (Epc) and anodic (Epa) peaks at $+0.74$ (Epc), $+0.88$ (Epa) and at $+0.09$ (Epc), $+0.44$ V (Epa). We were tentatively assigned as Cu^{II}/Cu^I and Cu^I/Cu^0 couples, respectively, in the central metal in Cu(dmamt)Cl$_2$. The potentials and the peak currents were not changed after scanning several times, indicating that these couples are reversible. In case of CuCl$_2$ in DMF, the voltammogram obtained in our work is shown only one oxidation-reduction peak at $+0.28$ (Epc) and $+0.64$ (Epa) at the same condition, which might be assigned to Cu^{II}/Cu^I couple. The mid-peak potentials of Cu(dmamt)Cl$_2$ were $+0.81$ (Cu^{II}/Cu^I) and $+0.27$ V (Cu^I/Cu^0). The mid-peak potential of Cu(dmamt)Cl$_2$ is somewhat higher than that of Cu(sp)Cl$_2$ ($E_{1/2} = +0.60$ for Cu^{II}/Cu^I couple in Cu(sp)Cl$_2$).[7] Choi *et al.*[7] demonstrated that the relatively high reduction potentials of Cu(sp)Cl$_2$ was due to the pseudotetrahedral symmetry around the copper(II) ion in Cu (sp)Cl$_2$. It is well known that the distortion from square planar to tetrahedral geometry makes the copper(II) ion easier to reduce because of the absence of Jahn-Teller energy.[8] The mid-peak potentials of Cu^{II}/Cu^I in Cu(dmamt)Cl$_2$ is also comparable to those of the blue copper proteins ($+0.2$-$+0.8$ V vs. SHE).[9] The relatively high reduction potential of the copper proteins has been interpreted as the pseudotetrahedral symmetry around copper(II) site as well as the nature of the donor atoms in the proteins (CuN$_2$S$_2$ chromophores).[2] The similar mid-peak value of Cu(dmamt)Cl$_2$ to the copper proteins supports the pseudotetrahedral coordination symmetry around the copper(II) site in Cu(dmamt)Cl$_2$, although an x-ray structure determination is necessary for the description of the subject matter.

Experimental

Cu(dmamt)Cl$_2$ was prepared by the direct reaction of dmamt and anhydrous CuCl$_2$ as described in the literature.[1] The brown precipitates were dried in vacuum oven at room temperature. Elemental analysis was performed by the Korea Research Institute of Chemical Technology, Daejeon, Korea. Calculated C; 30.50, H; 4.02, N; 5.08. Found C; 31.15, H; 4.10, N; 5.09.

Magnetic susceptibility measurements were obtained using a Princeton Applied Research vibrating-sample Magnetometer (VSM) operating at field strength of 10 kOe from 4 to 90 K. The magnetometer was calibrated against HgCo(NCS)$_4$. Finely ground polycyrstalline sample weighing 150 mg was housed in precision-milled Lucite sample holder. Temperatures were measured with a calibrated Ga-As diode. The output data were corrected for the diamagnetic of the sample holder and the constituent atoms using Pascals' constants. A value of 60×10^{-6} emu/mol was assumed for the temperature-independent paramagnetism (TIP) of copper(II) ion. Cy-

clic voltammogram was obtained using a PAR Model 273 Potentiostat in a three electrode configuration and recorded with Kipp & Zenon Model 13 BD XY recorder. The working electrode was a Pt disc electrode (0.38 cm^2) and the counter electrode was a Pt wire. Ag/AgCl electrode was used as a reference electrode. The working solution ($\sim 10^{-3}$ M) was prepared in 0.1M TEAP/DMF as a supporting electrolyte.

References

1. Kim, Y. I.; Choi, S. N.; Ro, C. U. *Bull. Kor. Chem. Soc.* **1994**, *15*, 549.
2. (a) Bertini, I.; Drago, R. S.; Luchinat, C. The Coordination Chemistry of Metalloenzyme. D. Reidel Pub. Comp., 1983. (b) Otsuka, S.; Yamanaka, T. Metalloproteins. Elsevier, 1988. (c) Spiro, T. G. Copper proteins. John-Wiley & Sons, 1981.
3. Baker, G. A.; Rushbrooke, G. S.; Gilbert, H. E. *Phys. Rev.* [A]. **1964**, *135*, 1272.
4. Estes, W. E.; Wassen, J. R.; Hall, J. W.; Hatfield, W. E. *Inorg. Chem.* **1978**, *17*, 3657.
5. Willet, R. D.; Wong, R.; Numata, M. *J. Magn. Mater.* **1980**, *15*, 717.
6. Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105.
7. Choi, S. N.; Park, J. H.; Kim, Y. I.; Shim, Y. B. *Bull. Kor. Chem. Soc.* **1991**, *12*, 276.
8. Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.
9. Malkin, R.; Malmstrm, B. G. *Advan. Enzymol.* **1970**, *33*, 177.

Benzylic Bromination of Alkylbenzenes with Sodium Bromate-Bromotrimethylsilane

Jong Gun Lee*, Jong Wha Seo, Ung Chan Yoon, and Kyung-Tae Kang

Department of Chemistry, College of Natural Sciences, Pusan National University, Pusan 609-735, Korea

Radical halogen substitution of carbon-hydrogen bonds has been considered to be one of the most important reactions for further funtionalization. Radical bromination on a benzylic position has been achieved using bromine[1] and N-bromosuccinimide.[2] In addition, bromine complex of styrene-vinylpyridine copolymer,[3] bromotrichloromethane,[4] and copper(II) bromide[5] were reported to be effective for benzylic bromination. For the majority of brominating agents, the presence of a peroxide or other radical initiator is required.

Recently, we reported that sodium halate-halotrimethylsi-