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The Magnetic Properties of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$

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From magnetic susceptibility and ESR measurements, it has been confirmed that polybis(μ-(2-picoline *N*-oxide)-chlorocopper(II)di-μ-chloro)diaquocopper, $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$, consists of alternating linear chains with diamagnetic $Cu_2Cl_4(C_6H_7NO)_2$ units and paramagnetic $CuCl_2 \cdot 2H_2O$ units joined by long Cu–Cl bonds. The two copper ions in the $Cu_2Cl_4(C_6H_7NO)_2$ unit are coupled together very strongly by antiferromagnetic exchange interaction and occupy almost entirely the diamagnetic singlet state below room temperature. This interpretation is appropriately supported by the observation of a half-field resonance near 1600 Oe in the ESR spectrum of the powdered sample. On the other hand, the copper ion in the $CuCl_2 \cdot 2H_2O$ unit isolated magnetically can account for the ESR spectrum due to $\Delta M = \pm 1$ transition and magnetic susceptibility, following the Curie law. The magnetic susceptibility of the dehydrate compound, $Cu_3Cl_6(C_6H_7NO)_2$, has also been measured.

There have been many reports on the physical properties of complexes formed between aromatic *N*-oxide and copper(II) halide compounds. They may be divided into general categories which reflect their chemical compositions and magnetic properties. One of them consists of magnetically subnormal substances which are composed of one aromatic *N*-oxide molecule and one $CuCl_2$ group (hereafter termed "1: 1 complexes"). Other well-known complexes with a normal magnetic moment belong to another category consisting of complexes which are formed between two aromatic *N*-oxide molecules and one $CuCl_2$ group ("2: 1 complexes").

Polybis(μ-(2-picoline *N*-oxide)-chlorocopper(II)di-μ-chloro)-diaquocopper, $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$, the complex formed between 2-picoline *N*-oxide and copper(II) halide, is an exceptional compound ("2: 3 complex"). From the magnetic properties and the crystallographical analysis of this complex, it was confirmed by Watson and his co-workers[1,2] that the structure of this complex consists of infinite linear chains containing both five- and six-coordinated copper(II) ions bridged by either chlorine of oxygen atoms. The structure can be regarded as an alternating linear chain consisting of $Cu_2Cl_4(C_6H_7NO)_2$ units and $CuCl_2\cdot 2H_2O$ units joined by long Cu–Cl bonds. Watson and his co-workers also proposed that the copper ions in the $Cu_2Cl_4(C_6H_7NO)_2$ unit interact antiferromagnetically through the bridging oxygens, while the copper ion in the $CuCl_2\cdot 2H_2O$ unit does not interact with those of the $Cu_2Cl_4(C_6H_7NO)_2$ units through the bridging chlorine atoms. However, a central problem in this interpretation is whether or not the magnetic ions in the $CuCl_2\cdot 2H_2O$ units really interact through the chlorine bridges.

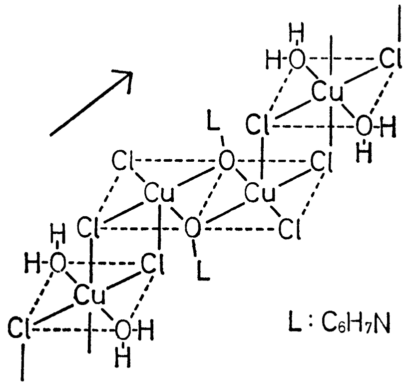

Fig. 1. Schematic crystal structure of $Cu_3Cl_6(C_6H_7NO)_2\cdot 2H_2O$. The arrow shows the *c*-axis direction.

In the present study, the magnetic susceptibilities of this complex have been measured down to 1.6°K in order to obtain experimental data on the existence of the metal-metal magnetic interaction in this complex. The ESR spectrum of a single crystalline sample has also been observed at room temperature, and that of a powdered sample, at room temperature, 77°K and 4.2°K.

Experimental

$Cu_3Cl_6(C_6H_7NO)_2\cdot 2H_2O$ (I) was prepared following the procedure of Watson and his co-workers. From the results of a chemical analysis, thermal analysis, infrared and far-infrared spectra measurements,[3] we confirmed the identity of the compound with reference to the preceding data. Found: C, 22.22; H, 2.74; N, 4.38%. Calcd: C, 22.0; H, 2.73; N, 4.27%. The single crystals were grown by the spontaneous evaporation of the solvent from the unsaturated solution. When dried for 50 hr at 100°C, this complex lost two water molecules to its dehydrate, $Cu_3Cl_6(C_6H_7NO)_2$ (II). Found: C, 23.19; H, 2.26; N, 4.56%. Calcd: C, 23.19; H, 2.27; N, 4.51%. The dehydrate (II) has not been reported in the literature, but the identity of this compound was confirmed by a chemical analysis of II and a thermal analysis of I. This complex was a little hygroscopic and reverted to the hydrate after several months. We found some differences in the X-ray powder patterns between I and II.

Results and Discussion

Magnetic susceptibilities were measured in the temperature range from 1.6°K to room temperature by means of a magnetic torsion balance described elsewhere.[4] Mn-Tutton salt was used to calibrate the carbon resistor and the thermocouple. The usual Pascal diamagnetic correction was within the range of experimental error at low temperatures. The X_m-T curves for the two complexes are compared in Fig. 2.

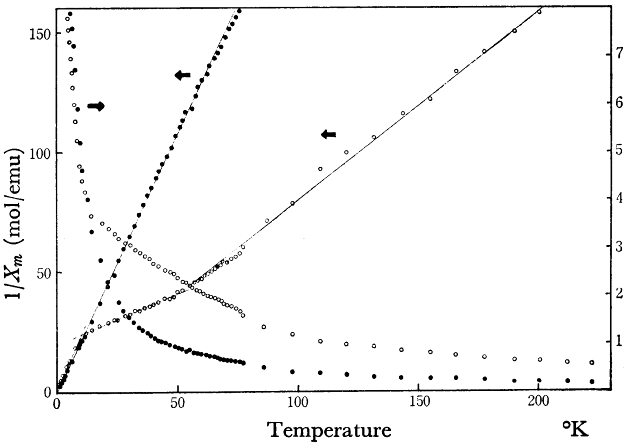

Fig. 2. Molar susceptibilities and their reciprocals as a function of temperature; ●: $Cu_3Cl_6(C_6H_7NO)_2\cdot 2H_2O$, ○: $Cu_3Cl_6(C_6H_7NO)_2$.

Assuming that $X_m = xNg^2\beta^2 s(s+1)/3k(T-\theta)$, with $s = 1/2$ and $g = 2.15$, a parameter, x, obtained from the slope of the $1/X_m - T$ plots can offer information about the magnetic state of these complexes. Here the assumption about the g-value is consistent with the ESR data to be described later. The most remarkable features of the magnetic data of the compound (I) are that the data obey the Curie law, with $x = 1.06$ from room temperature to 1.6°K, and that the molar magnetic susceptibilities can almost all be attributed to only one copper ion per molecule. On the other hand, the dehydrate (II) behaves very differently, as is shown in Fig. 2; this complex seems to be a magnetic trimer with mutual antiferromagnetic interaction.[5] It should be noted, in comparison with I, that the susceptibilities of the II have the values of three copper ions per molecule in the high-temperature range ($x = 2.8_3$).

ESR measurements of the hydrate were carried out by using an X-band spectrometer. The hyperfine separation (429.4 Oe) and the g-value (2.000) of Mn(II) in MgO were used to calibrate the magnetic field, and DPPH was also used as the magnetic-field indicator. The ESR spectrum of the powdered sample at room

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[1] R. S. Sager and W. H. Watson, *Inorg. Chem.*, **7**, 2035 (1968).

[2] M. R. Kidd, R. S. Sager, and M. H. Watson, *ibid.*, **6**, 946 (1967).

[3] R. Whymann and W. E. Harfield, *ibid.*, **6**, 1859 (1967).

[4] M. Mekata, *J. Phys. Soc. Japan*, **17**, 796 (1962).

[5] K. Kambe, *ibid.*, **5**, 48 (1949); J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford (1932).

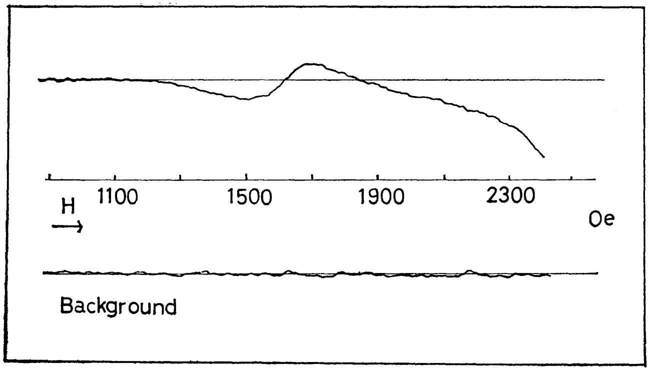

Fig. 3. Low field portion of the polycrystalline ESR spectrum of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$ at room temperature.

temperature exhibited one broad, asymmetric line caused by the anisotropy of the g-value centered at about 3250 Oe, with one additional weak line at about 1600 Oe, as is shown in Fig. 3. The line-shape of the main absorption at 3250 Oe did not show any appreciable change, even at temperatures of liquid nitrogen and helium, implying that the magnetic environment of this complex changes little with the temperature.

Single-crystal studies were undertaken in this complex's three mutually perpendicular planes. The principal values of the g-tensor obtained from the single-crystal measurements are: $g_1=2.302\pm0.005$, $g_2=2.084$, and $g_3=2.032$. The experimental errors are mainly due to the uncertainty of the crystal mounting on the sample holder. The principal values of the g-tensor can be attributed to those of the copper ions, the site symmetry of which is rhombic or approximately orthorhombic and the orbital ground state of which is $d_{x^2-y^2}$. This interpretation is supported by a crystallographic consideration of this complex.

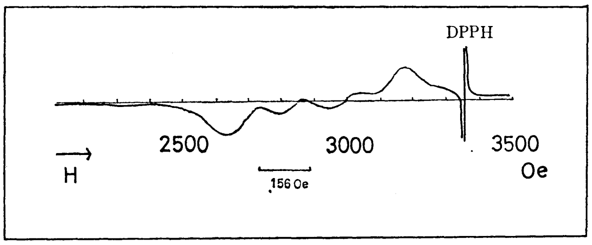

Fig. 4. ESR spectrum at a certain angle of $Cu_3Cl_6(C_6H_7NO)_2$ $2H_2O$ single crystal at room temperature.

The angular variation of the single crystalline ESR spectrum provides much interesting information about the electronic state of the paramagnetic copper(II) ion in this complex. At certain angles, for example, the sample gives an ESR spectrum with four hyperfine lines and a maximum separation between them are about 156 Oe, as is shown in Fig. 4. This splitting arises from copper ions with an electron spin of $s=1/2$ and a nuclear spin of $I=3/2$. The observation of the hyperfine splittings in the ESR spectrum of the single-crystal sample leads to the conclusion that this complex is similar to the magnetically diluted systems. This conclusion can be confirmed further from the results of the temperature variation of X_m with the values attributed to only one copper ion per molecule and with a Weiss constant nearly equal to zero. Other evidence of this consideration is that the dehydrate (II) shows the X_m values due to three copper ions per molecule in the high-temperature range. The absorption near 1600 Oe in the powder ESR spectrum is due to the $\Delta M=\pm2$ forbidden transition, which clearly indicates the existence of the dimer species in this complex, although its signal intensity is very weak. Therefore, it can be concluded that the copper ions of the $Cu_2Cl_4(C_6H_7NO)_2$ units are coupled together very strongly by antiferromagnetic exchange interaction and that they occupy almost entirely the diamagnetic singlet state below room temperature, while the copper ions of the $CuCl_2 \cdot 2H_2O$ units are isolated magnetically. Alternatively speaking, only the copper ions of the $CuCl_2 \cdot 2H_2O$ units diluted magnetically can account for the four hyperfine lines of the ESR spectrum and the molar susceptibilities due to one copper ion per molecule, while a few $Cu_2Cl_4(C_6H_7NO)_2$ units occupying the higher triplet state can give a half-field resonance. This conclusion is consistent with the invariability of the powder ESR line shapes in spite of the temperature variation.

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