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Magnetic Moments of Copper(II) Diethyldithiocarbamate and Related Compounds

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The X-ray crystal analysis of copper(II) diethyldithiocarbamate[1] and di-*n*-propyldithiocarbamate[2] has shown that the crystals are formed with a binuclear structure having the Cu-Cu distance equal to 3.38—3.59 Å as a unit. Each copper atom has a distorted tetragonal-pyramidal coordination involving four sulfur atoms from two diethyldithiocarbamate groups at the corners of a square and the fifth surfur atom belonging to the other monomeric unit at the apex of the tetragonal pyramid. At room temperature, copper(II) dialkyldithiocarbamates[3] show magnetic moments of 1.75—1.76 B. M., which are smaller than about 1.9 B.M. normally observed for magnetically dilute

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TABLE 1. EFFECTIVE MAGNETIC MOMENTS, μ_{eff}, WEISS CONSTANTS, θ, MAGNETIC MOMENTS, μ_C, CALCULATED FROM CURIE CONSTANTS, C, MAGNETIC MOMENTS IN CHLOROFORM, μ_{sol}, AND MAGNETIC MOMENTS, μ_{calc}, CALCULATED FROM SPECTROSCOPIC DATA, Δ_1, OF COPPER (II) DIETHYLDITHIOCARBAMATE AND RELATED COMPOUNDS

Compounds	μ_{eff}, B.M.	θ, °K	C, emu/mol	μ_C, B.M.	μ_{sol}, B.M.	Δ_1, $10^4\,cm^{-1}$	μ_{calc}, B.M.
$Cu[(CH_3)_2NCS_2]_2$	1.75 (23°C)	−4	0.387	1.76	—	2.30	1.79
$Cu[(C_2H_5)_2NCS_2]_2$	1.75 (21°C)	+1	0.380	1.74	1.72	2.28	1.79
$Cu[(n\text{-}C_3H_7)_2NCS_2]_2$	1.76 (21°C)	−1	0.390	1.77	1.74	2.28	1.79

copper(II) compounds. In view of the binuclear structure and the low effective magnetic moments, one would expect the presence of spin coupling within a pair of copper atoms. However, electron spin resonance studies[4,5] yielded $g_\parallel=2.1085$ and $g_\perp=2.0236$, which are smaller than those of a majority of copper(II) complexes. This fact suggests that the low magnetic moments are due to a strong crystal field leading to the quenching of orbital contribution. In order to clarify this point, we have determined the magnetic susceptibilities of copper(II) dimethyldithiocarbamate, diethyldithiocarbamate, and di-*n*-propyldithiocarbamate in the solid state by the Gouy method[6,7] in a temperature range of 80—300°K and also the magnetic moments of these compounds of chloroform solutions.

The materials were prepared from commercial samples of sodium dialkyldithiocarbamates and copper(II) acetate. They were recrystallized from chloroform by adding methanol. The X-ray powder patterns of copper(II) diethyldithiocarbamate and di-*n*-propyldithiocarbamate showed agreement with the data of the complete X-ray crystal analysis.[1,2]

The magnetic susceptibilities of the compounds obey the Curie-Weiss law in the whole range of temperature studied. The Weiss constant and the Curie constant are listed in Table 1. The observed susceptibilities of the solutions of copper(II) diethyldithiocarbamate and di-*n*-propyldithiocarbamate in chloroform at 20°C show a linear relation to the concentration over the range of 0.3—1.2% and 0.4—2.4% by weight, respectively. The magnetic moments of the copper(II) complexes in chloroform were calculated from the slope of the susceptibility *versus* concentration plot and are shown in Table 1. Copper(II) dimethyldithiocarbamate could not be investigated in solutions, because it is sparingly soluble in common solvents.

The very small values for Weiss constants indicate that spin interaction is negligible in spite of the binuclear structure and the low effective magnetic moments. The magnetic moments, $\mu_C=1.74$—1.76 B.M., calculated from the Curie constants are smaller than about 1.9 B.M. for common copper(II) compounds. Since an unpaired electron in the $d_{x^2-y^2}$ orbital gives rise to magnetic polarization, the g-factor is given by

$$g_\parallel = 2\left(1-\frac{4\lambda}{\Delta_1}\right)$$
$$g_\perp = 2\left(1-\frac{\lambda}{\Delta_2}\right) \qquad (1)$$

for a copper(II) ion in a crystal field having D_{4h} symmetry.[8] Here, λ is the spin-orbit coupling constant, and Δ_1 and Δ_2 are energy separations between b_{2g} and b_{1g} states and between e_g and b_{1g} states, respectively. For copper(II) complexes,[9] λ is negative, and its absolute value is 625 cm^{-1}. Since Δ_2 is much greater than Δ_1, the magnetic moments of copper(II) compounds are given by

$$\mu = \left[\frac{1}{3}(g_\parallel^2+2g_\perp^2)S(S+1)\right]^{1/2}\beta$$
$$= 3^{1/2}\left(1-\frac{4\lambda}{3\Delta_1}\right)\beta \qquad (2)$$

where S is the total spin of a copper(II) ion equal to 1/2 and β denotes the Bohr magneton. Although the crystal field has C_{4v} symmetry in these copper(II) complexes, it can be approximated by D_{4h} symmetry because of a long distance of the apical sulfur atom from the central copper atom. In fact, the magnetic moments of copper(II) diethyldithiocarbamate and di-*n*-propyldithiocarbamate in chloroform agree excellently with those in the solid state as shown in Table 1. We have taken the visible and ultraviolet spectra of the compounds in chloroform and estimated Δ_1 in order to evaluate the magnetic moments by Eq. (2). The good agreement between the observed and calculated magnetic moments indicates that the low magnetic moments are due to the effect of a strong crystal field rather than to spin interaction between copper atoms in the binuclear structure.

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