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The Magnetism of Potassium Dioxalatocuprate(II) Dihydrate and Ammonium Dioxalatocuprate(II) Dihydrate

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The magnetic susceptibilities of the potassium and ammonium salts of dioxalatocuprate(II) dihydrate have been measured in the temperature range 2.9-296°K. The electron paramagnetic resonance spectra give evidence for weak spin-spin coupling which is confirmed by the magnetic susceptibility data. The mechanism for the weak interaction is transmitted by the oxalate bridges.

Introduction

In a continuation of our investigations of the magnetic properties of polymeric copper(II) complexes which form near linear chains,[2-4] magnetic susceptibility and electron paramagnetic resonance studies have been undertaken on both the potassium and ammonium salts of dioxalatocuprate(II) dihydrate. The crystal structures of these complexes[5,6] contain two non-equivalent copper ions in distorted octahedral environments in the unit cell. Aggregates of these two copper ions which are weakly bridged together *via* the oxalate group are than linked into chains. In view of this unusual type of bridging and the question of superexchange mechanisms in electronic spin-spin coupling, it was of interest to determine the magnetic properties of these two compounds. The results of the magnetic studies are presented herein.

Experimental Section

Preparation of the compounds. Potassium dioxalatocuprate(II) dihydrate was prepared by the method of Kirschner[7] by mixing rapidly aqueous solutions of $CuSO_4 \cdot 5H_2O$ and $K_2C_2O_4 \cdot H_2O$ both of which were heated to 90°C. The resulting dark blue solution was cooled, and crystals of the complex precipitated. The precipitate was collected, washed with cold water, and dried over night at 50°C. A lustrous blue powder resulted. *Anal.* Calcd for $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$: C, 13.78%; H, 1.14%. Found: C, 13.70%; H, 0.98%.

Ammonium dioxalatocuprate(II) dihydrate was prepared by the method described in Gmelins.[8] To an aqueous solution of $(NH_4)_2C_2O_4$ was added $CuC_2O_4 \cdot nH_2O$. The solution was then digsted and finally evaporated until blue crystals formed. They were also collected, washed and dried. *Anal.* Calcd for $(NH_4)_2[Cu(C_2O_4)] \cdot 2H_2O$: C, 15.41%; H, 3.88%; N, 8.99%. Found: C, 15.29%; H, 3.92%; N, 8.83%.

Magnetic Measurements. In the temperature range 77.2-296°K the magnetic susceptibility of powdered samples were determined using a Faraday balance.[9] A Foner-type vibrating sample magnetometer[10] was used for measuremets in the temperature span 2.9 - 50.7°K. Mercury tetrathiocyanacobaltate(II) was used as a magnetic susceptibility standard[11] for both systems, and diamagnetic corrections for the substituent atoms were estimated from Pascal's constants.[12]

EPR Measurements. The EPR spectra of powdered samples of the two complexes were obtained at room temperature using a Jeolco Model JES-ME-3X X-band spectrometer operating at 9.49 GHz with a cylindrical cavity and 100 kHz modulation. Cylindrical quartz sample tubes were used.

Results

The plot of the temperature variation of the reciprocal magnetic susceptibility for $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ is shown in Figure 1, and the data for both compounds are collected in Tables I and II. As can be observed in these tables, there is little variation between the magnetism of the two salts. The data obey the Curie-Weiss law, $\chi = C/(T+\Theta)$, with $C = 0.445$ and $\Theta = 0.7°$ for $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ and $C = 0.438$ and $\Theta = 0.6°$ for $(NH_4)_2[Cu(C_2O_4)_2] \cdot 2H_2O$. Using the relationship for magnetic moment, $\mu_{eff} = 2.828\ C^{1/2}$, the calculated values are 1.89 and 1.87 B.M. respectively. The EPR spectra of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ are displayed in Figures 2 and 3. From

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Table I. The Magnetic Susceptibility for $K_2[Cu(C_2O_4)_2]$.-$2H_2O$.

Temperature (°K)	χ_m^{corr}($\times$10) c.g.s. units	$1/\chi_m^{corr}$	μ_{eff}(B.M.)
2.9	1.2910	7.7	1.73
3.1	1.2380	8.1	1.75
3.4	1.1650	8.6	1.78
4.2	0.9905	10.1	1.82
4.4	0.9903	10.1	1.86
4.9	0.9672	10.3	1.94
5.1	0.9305	10.7	1.94
5.3	0.8763	11.4	1.92
5.6	0.8207	12.2	1.91
6.1	0.7693	13.0	1.93
6.6	0.7156	14.0	1.94
7.2	0.6676	15.0	1.96
8.1	0.5986	16.7	1.96
9.6	0.5223	19.1	2.00
11.5	0.4524	22.1	2.04
14.3	0.3775	26.5	2.07
17.0	0.3160	31.6	2.07
18.3	0.2696	37.1	1.98
21.0	0.2245	44.5	1.94
28.8	0.1636	61.1	1.94
33.2	0.1398	71.5	1.92
50.7	0.0858	116.6	1.86
77.2	0.0547	182.9	1.83
195.0	0.0230	434.8	1.89
296.0	0.0150	666.7	1.88

Table II. The Magnetic Susceptibility Data for $(NH_4)_2[Cu(C_2O_4)_2]$. $2H_2O$.

Temperature (°K)	χ_m^{corr}($\times$10) cgs units	$1/\chi_m^{corr}$	μ_{eff}(B.M.)
3.1	1.2840	7.8	1.78
4.2	0.9964	10.0	1.82
5.0	0.9773	10.2	1.97
5.1	0.9736	10.3	1.93
5.5	0.9002	11.1	1.99
5.7	0.9683	11.5	1.99
6.4	0.8008	12.5	2.2
7.6	0.6888	14.5	2.04
9.5	0.5681	17.6	2.07
10.8	0.4734	21.1	2.02
12.9	0.3909	25.6	2.00
18.2	0.2816	35.5	2.02
22.0	0.2168	56.1	1.95
26.0	0.1763	56.7	1.91
37.0	0.1280	78.1	1.94
77.2	0.0549	182.8	1.84
195.0	0.0224	445.4	1.87
295.0	0.0148	674.8	1.87

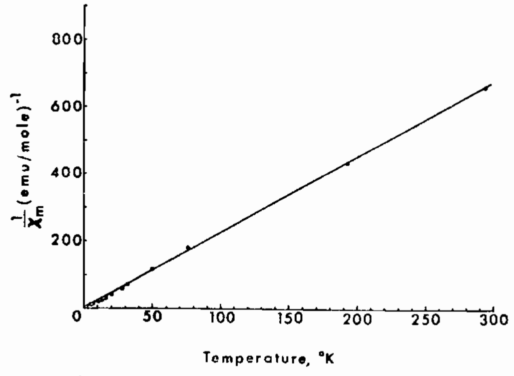

Figure 1. The temperature variation of the inverse susceptibility of the complex, $K_2[Cu(C_2O_4)_2]$. $2H_2O$ in the temperature range 2.9 - 296°K.

these spectra, on which there was a much earlier report[13] and the analogous spectrum for $(NH_4)_2[Cu(C_2O_4)_2]\cdot 2H_2O$, $g_{\parallel}$ = 2.31 and $g_{\perp}$ = 2.09 for the potassium salt and $g_{\parallel}$ = 2.31 and $g_{\perp}$ = 2.08 for the ammonium salt may be calculated. As shown in Figure 3, there is a definite absorption at about 1510 G (1550 G for NH_4^+). This line is held to be indicative of some magnetic interaction.

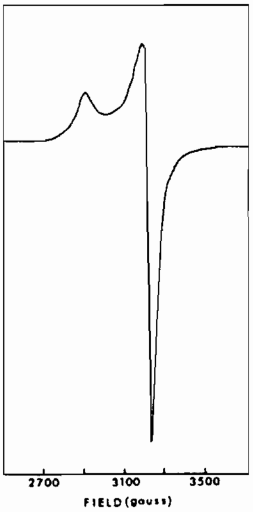

Figure 2. The EPR spectrum at room temperature of $K_2[Cu(C_2O_4)_2]$. $2H_2O$ in the region 2500 - 3700 G.

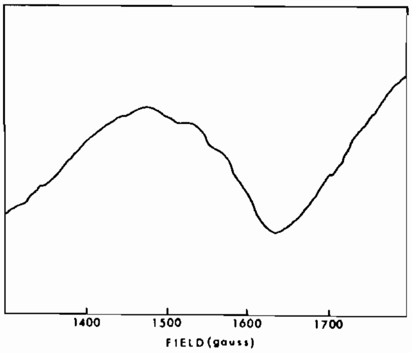

Figure 3. The EPR spectrum at room temperature of $K_2[Cu(C_2O_4)_2]$. $2H_2O$ in the region 1300 - 1800 G.

Discussion

A schematic representation of the coordination of the two non-equivalent copper(II) ions in the unit cell[5,6] is shown in Figure 4. In both environments the two oxalates are coplanar with a Cu-O distance of about 2 Å. In one of the sites the coordination about the copper ion is completed with two water molecules in the fifth and sixth positions at distances of 2.27 A (K^+) and 2.49 A (NH_4^+). The coordination about the other copper ion is completed by an oxalate oxygen from each of its two nearest neighbors which are both of the type first described. Units of these two differently coordinated copper(II) ions are then

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repeated along the chain. In both complexes there is extensive hydrogen bonding where the main portion is between adjacent chains. This interaction, however, occurs over a distance of more than 5 Å. Thus it is reasonable to consider that these two complexes consist of copper(II) ions bridged by oxalate groups into chains of ions which are somewhat similar in structure to diammine copper(II) carbonate.[14,15,16]

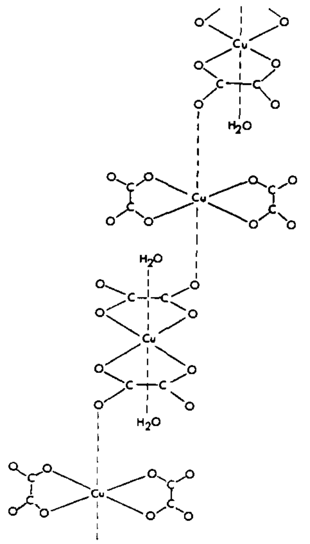

Figure 4. A schematic representation of the two non-equivalent copper(II) ions in the unit cell of $K_2[Cu(C_2O_4)_2]\ .2H_2O$ and $(NH_4)_2[CuC_2O_4)_2]\ .2H_2O$.

As in the case of $Cu(NH_3)_2CO_3$,[17] a two g-value EPR spectrum is observed for each complex as shown in Figure 2 for the potassium salt. Procter, Hathaway and Nicholls[18] have postulated that the ratio ($g_{\parallel}$ -2)/-$g_{\perp}$ -2) reflects the presence or absence of exchange coupling in polycrystalline samples. In $Cu(NH_3)_2CO_3$ the value of the ratio was 3.4 and this was considered to be evidence for an exchange interaction since the value of the ratio was less than four. In the present complexes the values are 3.4 (K^+) and 3.9 (NH_4^+) which, if the postulate holds, would also suggest that interactions are present here, although perhaps weaker in $(NH_4)_2[Cu(C_2O_4)]\cdot 2H_2O$ than in the potassium salt. In the oxalates, however, an added feature is present. The spectra of the complexes show lines in the half-field region at 1510 G (K^+) and 1550 G (NH_4^+). Such absorptions although sometimes seen for powdered samples of copper(II) dimers, are unusual for polymeric complexes. However, this absorption was also observed in the EPR spectrum of the chain complex copper(II) pyrazine nitrate.[2]

Even though the EPR spectra of these complexes suggest the existance of an exchange interaction, it is apparent from Figure 1 that if such is the case, it must be exceedingly weak since the magneti susceptibility data obey the Curie-Weiss law even at very low temperatures. This, however, is not unreasonable since the copper(II) ions along the chains are at least 4.5 Å apart along a direct pathway and even further *via* the path through the oxalate bridges. In comparison with $Cu(NH_3)_2CO_3$ where the direct Cu-Cu interchain distance is about 3.5 A and the carbonate brindging pathway is only about 0.5 A shorter than that in the oxalates, the susceptibility maximum was observed at approximately 11°K and the exchange energy is 6-0 cm^{-1} although the interaction route is uncertain. Since there are major structural differences between the oxalato-complexes and both copper(II) acetate monohydrate and diamine copper(II) carbonate,[14,15] and since all six coordination positions on each copper(II) ion are filled, it would seem most likely that any exchange interaction present in these oxalate salts occurs through the bridging ligands by a super-exchange mechanism. This conclusion further suggests that either a direct mechanism is operative in $Cu(NH_3)_2CO_3$ or that exchange is quite sensitive to small changes in the bridge length and substitution in such systems. Characterization of other similar systems will perhaps resolve this problem.

One additional observation about oxalate bridges should be made. The magnetism of copper(II) oxalate,[20] which is also likely to be polymeric, has been investigated and shown to have a susceptibility maximum at 260°K which is indicative of extensive exchange interaction. Our results would seem to indicate that the bridging in this system must involve a much more intimate arrangement than the out-of-plane bridging found in the complexes considered herein.

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