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Abstract

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MAGNETIC SUSCEPTIBILITY OF COPPER(II) OXALATE AND SUCCINATE

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Copper compounds with dicarboxylic acids, except malonic acid, at room temperature have effective magnetic moments considerably lower than the theoretical (spin-only) moment for the d^9 configuration ([1,2]). This anomaly has been explained by the formation of an infinite two-dimensional network, which gives rise to direct exchange between the nearest magnetically active ions. In other words, copper compounds with dicarboxylic acids, on the basis of the value of μ_{eff} at room temperature, were assigned to the class of substances with intramolecular antiferromagnetism. However, a detailed study of the magnetic susceptibility had not been carried out. In particular, we were unable to find in the literature information on the temperature dependence of the magnetic susceptibility.

This article reports the results of a study of the dependence of the magnetic susceptibility on temperature in the range 80—300°K for two copper compounds: oxalate and succinate.

Analysis for copper shows that, for the oxalate, the copper content is somewhat lower than that calculated for $\mathrm{CuC_2O_4}$ (40.3%), whereas for copper succinate it corresponds to the composition $\mathrm{Cu(C_4H_4O_4)}$. The reduced copper content in the oxalate may be explained by formation of a polymeric molecule with free terminal carboxyl groups, although it is not excluded that the succinate also has a polymeric structure.

Judging by the copper content, the following structure may be assigned to the oxalate:

$$\mathrm{H{-}O{-}C(=O) - [\,C(=O)O{-}Cu{-}OOC\,]_n - C(=O){-}O{-}H}$$

Copper oxalate hemihydrate has the same copper content. However, the water cannot be removed by ordinary drying. It may be assumed that the water of crystallization plays the role of a bridge between copper ions, as a result of which it is very strongly bound.

Measurement of the magnetic susceptibility in the range 80—300°K showed that, with decreasing temperature, it decreases for both compounds studied. However, the character of the change of $\chi = \varphi(I)$ is not the same. The maximum susceptibility of copper oxalate is observed at 260°K, and that of copper succinate at 280°K (Fig. 1, Table 1). If the dependence χ—I is calculated from the equation

$$\chi = \frac{2g^2 N\beta^2}{3kT}\left[1 + {}^1\!/_3 \exp(J/kT)\right]^{-1}, \tag{1}$$

using the values of the exchange integrals found from the relation $J = 1.6\,kT$ and equal to $J = 290$ cm^{-1} for copper oxalate and $J = 312$ cm^{-1} for the succinate, then, as is evident from Fig. 1, this curve agrees well with the experimental one in the case of copper oxalate and does not agree at all for ···

Table 1

Temp., °K	$\chi_r \cdot 10^6$	$\chi_{\mathrm{Cu}^{2+}} \cdot 10^6$	μ_{eff}	Temp., °K	$\chi_r \cdot 10^6$	$\chi_{\mathrm{Cu}^{2+}} \cdot 10^6$	μ_{eff}
Copper oxalate*				**Copper succinate****			
79	3,44	533	0,58	79	0,425	79,4	0,225
93	3,45	534	0,63	93	0,795	146	0,325
103	3,48	538	0,67	110	1,315	239	0,46
125	3,60	558	0,73	132	2,04	369	0,63
141	3,66	568	0,80	151	2,62	473	0,76
157	3,76	582	0,86	166	2,97	537	0,85
175	3,85	597	0,89	183	3,32	599	0,94
192	3,90	606	0,97	199	3,52	635	1,01
214	3,96	613	1,03	216	3,71	669	1,08
236	4,00	621	1,07	230	3,83	690	1,14
260	4,01	623	1,14	244	3,90	703	1,18
278	4,00	621	1,17	259	3,96	714	1,22
292	3,99	619	1,21	275	3,99	719	1,25
				286	3,99	712	1,29
				295	3,96	714	1,30

* $g = 2{,}17$, $\chi_{\mathrm{dia}} = -48 \cdot 10^{-6}$; $\chi_{\mathrm{TNP}} = 60 \cdot 10^{-6}$.
** $g = 2{,}16$, $\chi_{\mathrm{dia}} = -63 \cdot 10^{-6}$; $\chi_{\mathrm{TNP}} = 60 \cdot 10^{-6}$.

of copper oxalate. For copper succinate, equation (1) takes the form (1a):

$$\chi_{\mathrm{Cu}^{2+}} = \frac{0{,}583}{T}\left[1 + \frac{1}{3}\exp(458/T)\right]^{-1}. \tag{1a}$$

Thus, for copper succinate the temperature dependence of the susceptibility fits completely into the scheme of intramolecular antiferromagnetism, whereas for copper oxalate this dependence has a more complex character. Assuming, for both compounds, the possibility of formation of polymeric molecules, this difference in magnetic properties may be a consequence only of the nature of the anion. The δ bond resulting from direct exchange interaction between the copper ions of copper succinate is realized both for the dimer and for the polymer.

Fig. 1. **A**—dependence of magnetic susceptibility on temperature for copper oxalate: **a**—calculated from equation (1), **b**—experimental curve. **B**—the same for copper succinate: **a**—calculated from equation (1a), **b**—experimental curve.

If the assumption of a polymeric structure is valid, then the structure of copper oxalate and succinate can be represented as a two-layer polymeric network, allowing direct exchange interaction Cu–Cu (of the copper acetate type).

The structural features of the succinate ion, in which the carboxyl groups bonded to the paramagnetic ions are separated from one another by a dimethylene bridge, exclude other types of exchange interactions except direct ones. The situation is different in copper oxalate. The oxalate ion (C—C) can be regarded as a system with conjugated bonds, allowing the possibility of indirect exchange interactions between the paramagnetic ions. Consequently, in copper oxalate, in addition to the direct exchange interaction (Cu–Cu),

characterized by the exchange integral, other exchange interactions are also possible, in particular indirect exchange with J_2

$$\left(\mathrm{Cu}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{C}-\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{Cu}\right),$$

where, in the general case, each copper ion is linked by indirect exchange interaction with eight other copper ions. Obviously, such a character of the exchange interactions in copper oxalate leads to a more complicated dependence of the magnetic susceptibility on temperature. In particular, because of the great ability of the carboxyl groups of the oxalate ion to rotate about the C–C bond, the structure of copper oxalate may be such that the spin orientation is not strictly antiparallel. This will lead to the resultant spin differing from zero even at very low temperatures. Increasing the distance between the carboxyl groups decreases the probability of their disordered orientation in the crystal, and this leads to the magnetic behavior being determined only by an exchange interaction of one type. Then the paramagnetism of copper succinate will be due to the excited triplet state ($S = 1$), whose population, because J is comparable with kT, rapidly decreases as the temperature is lowered. On the other hand, it may be assumed that copper succinate is an ordinary dimer. Such an assumption can be substantiated by the fact that its composition corresponds to the simplest formula $Cu(COO)_2(CH_2)_2$, and also by the absence of resonance absorption in copper compounds with succinic acid ether.

Thus, the study of the magnetic susceptibility of copper oxalate and succinate makes it possible to conclude that the exchange interactions between copper ions in these compounds are of different nature. Consequently, information obtained on the magnetic properties of compounds with dicarboxylic acids at only one temperature is insufficient for an unambiguous conclusion, since the magnetic anomaly, as shown above, may have a very complex nature.

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CITED LITERATURE

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