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Abstract

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STUDY OF THE STRUCTURE OF CERTAIN COMPLEXES OF COPPER ACETATE AND CHLOROACETATES BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

(Presented by Academician A. E. Arbuzov, 12 VI 1961)

Amiel (^1) found that the paramagnetism of the Cu^2+ ion in salts of fatty acids amounts to approximately one half of the normal value. Guh (^2) showed that the paramagnetic susceptibility of copper acetate monohydrate $(CH_3COO)_2Cu \cdot H_2O$ passes through a maximum near room temperature and then rapidly decreases with decreasing temperature, becoming equal to zero at approximately 50°K. Lancaster and Gordy (^3) measured the electron paramagnetic resonance (e.p.r.) of copper acetate powder in the millimeter range and observed a single line with an effective g-factor approximately equal to four. Bleaney and Bowers (^4) studied the e.p.r. spectrum of a single crystal of this substance and proposed that the anomalous paramagnetism is due to the presence of isolated pairs in which the copper ions are bound by exchange forces. The interaction of two spins in this case leads to the appearance of an upper triplet state with parallel spins ($S = 1$) and a lower singlet state with antiparallel spins ($S = 0$).

An X-ray study of crystals of copper acetate monohydrate (^5) showed that dimeric molecules are indeed present in the crystal lattice. The six nearest neighbors of a copper atom are 4 oxygen atoms belonging to four different acetate groups, a copper atom, and a water molecule. These six atoms are located at the vertices of a distorted octahedron with the copper atom at the center. All distances between the copper atom and the oxygens of the carboxyl groups are approximately 1.97 Å. Each of the four acetate groups is individually planar. The distance between two neighboring copper atoms is very small and equals 2.64 Å, which is only slightly greater than the distance in metallic copper (2.56 Å). The $Cu—H_2O$ distance is 2.20 Å. Copper acetate monohydrate is a binuclear compound.

Study of the e.p.r. spectra of single crystals of copper propionate monohydrate $(CH_3CH_2COO)_2Cu \cdot H_2O$ (^6), copper n-butyrate monohydrate, and copper monochloroacetate monohydrate $(CH_2ClCOO)_2Cu \cdot H_2O$ (^7) showed that in these compounds the molecules are also dimeric. In the crystal lattice of copper trichloroacetate monohydrate $(CCl_3COO)_2Cu \cdot H_2O$ (^7) there are no isolated pairs of copper ions and therefore the e.p.r. spectrum of this compound does not exhibit a triplet state.

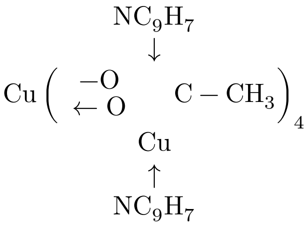
We obtained copper monochloroacetate in the form of dark-green prisms of composition $(CH_2ClCOO)_2Cu\cdot 2\frac{1}{2}H_2O$ and measured the e.p.r. spectrum of this salt. It proved to be due to transitions in a triplet state with effective spin $S = 1$. It is of interest to study by the e.p.r. method the structure of complex compounds that are products of addition of nitrogen-containing addends, such as ammonia, pyridine, and quinoline, to copper acetate and chlor acetates. Costăchescu and Ablov (⌢8) showed that copper acetate, mono-, di-, and trichloroacetate add quinoline, with copper acetate giving

the addition product with only one quinoline molecule, $(CH_3COO)_2Cu\cdot NC_9H_7$; copper mono- and dichloroacetate give addition products

$$\begin{array}{ll} (CH_2ClCOO)_2Cu\cdot NC_9H_7, & (CH_2ClCOO)_2Cu\cdot 2NC_9H_7; \\ (CHCl_2COO)_2Cu\cdot NC_9H_7, & (CHCl_2COO)_2Cu\cdot 2NC_9H_7, \end{array}$$

whereas copper trichloroacetate gives an addition product with only two quinoline molecules. It should be added that all monoquinolinates are green in color, whereas the diquinolinates are violet.

Study of the EPR spectra of some of these products in the polycrystalline state at a frequency of 9330 MHz (on a standard radiospectrometer of the RE type) showed that in the green monoquinolinates of copper acetate and copper monochloroacetate a triplet state is observed, analogous to that of copper acetate monohydrate. In these compounds the Cu–Cu bond is retained, and the green products are in fact dimeric molecules having the structure



$$\begin{array}{c} NC_9H_7 \\ \downarrow \\ Cu\left(\begin{array}{c} -O \\ \leftarrow O \end{array}\quad C-CH_3\right)_4 \\ Cu \\ \uparrow \\ NC_9H_7 \end{array}$$

Experiment showed that lowering the temperature from room temperature to 77° K leads to a decrease in the integral intensity of the resonance paramagnetic absorption. This confirms that the paramagnetism of these salts is due to an excited triplet state.

It is interesting to note that copper acetate monopyridinate $(CH_3COO)_2Cu\cdot NC_5H_5$, which is green in color, also exhibits a triplet state with effective spin $S = 1$.

It is known (4) that in copper acetate monohydrate the electric crystal field has almost axial symmetry and splits the triplet state into a singlet and a doublet, separated from one another by ~ 0.34 cm^{-1}. Therefore, in the 3-cm range two EPR lines are observed, one of which is located in a very weak magnetic field, and the second near 5000 oersted. In polycrystalline samples each of these lines represents the result of averaging the anisotropic parameters D and the g-spectrum.

Table 1

Positions of EPR lines and values of the fine-structure constant, D

Substance	1st line (H, oerst.)	2nd line (H, oerst.)	D, cm^{-1}
$(CH_3COO)_2Cu \cdot H_2O$	150	4460	0.34
$(CH_2ClCOO)_2Cu \cdot 2\frac{1}{2}H_2O$	390	4580	0.36
$(CH_3COO)_2Cu \cdot NC_5H_5$	360	4530	0.35
$(CH_3COO)_2Cu \cdot NC_9H_7$	340	4560	0.35
$(CH_2ClCOO)_2Cu \cdot NC_9H_7$	680	4630	0.40

If it is assumed that in the compounds we studied the fine splitting can also be characterized by a single parameter D, then its average value is readily estimated by comparing the EPR spectra of the substances studied with the spectrum of copper acetate monohydrate. From Table 1 it is seen that both lines in $(CH_3COO)_2Cu \cdot NC_9H_7$, $(CH_2ClCOO)_2Cu \cdot NC_9H_7$, and $(CH_3COO)_2Cu \cdot NC_5H_5$ are shifted toward stronger fields, which indicates an increase of the parameter D in these substances. The values of D given in Table 1 were determined

by relative distances from the lines observed in strong fields to the EPR signal of α,α-diphenyl-β-picrylhydrazyl.

It should be noted that the EPR spectra of the monoquinolinate and monopyridinate of copper acetate differ very little from one another both in the position and width of the lines and in the value of D. On comparing the EPR spectra of the compounds

$$(CH_3COO)_2Cu \cdot H_2O, \qquad (CH_3COO)_2Cu \cdot NC_9H_7;$$

$$(CH_2ClCOO)_2Cu \cdot 2\tfrac{1}{2}H_2O, \qquad (CH_2ClCOO)_2Cu \cdot NC_9H_7,$$

it is seen that replacement of hydrogen in the methyl group by chlorine leads to an increase in the fine splitting; moreover, in the case of the quinolinates it is manifested more strongly than in the case of the hydrates.

The EPR spectrum of the violet diquinolinates of copper monochloro- and trichloroacetate shows that here we have a singlet state with spin $S = 1/2$. This indicates that in these products there is no longer a Cu–Cu bond. The compounds most probably have the following structure

[[structural formula: a Cu center coordinated by two acetate groups and two NC_9H_7 ligands]]

It is also possible that the four vertices of the distorted octahedron (square bipyramid) are occupied by the oxygens not of two, but of four acetate groups. The values of the effective g-factors and line widths measured between the points of maximum slope are given in Table 2.

Table 2

g-factors and EPR line widths ΔH, measured between the points of maximum slope

Substance	g	ΔH, oerst.
$(CH_2ClCOO)_2Cu \cdot 2\,NC_9H_7$	2.06	28
$(CCl_3COO)_2Cu \cdot 2\,NC_9H_7$	2.08	170

The EPR spectrum of copper acetate diamminate, $(CH_3COO)_2Cu{\cdot}2NH_3$, which is violet in color, also reveals only a singlet state. The EPR signal is a very asymmetric line, the shape of which is preserved even after thorough grinding of the crystals. This is due to the large anisotropy of the g-factor and of the line width. At present, an X-ray structural investigation and a study of the EPR spectra of single crystals of this compound are being carried out in our laboratories.

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