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ELECTRON PARAMAGNETIC RESONANCE OF ANHYDROUS COPPER SALTS OF MONOCARBOXYLIC ACIDS

Copper salts of acetic acid and its higher homologues exhibit reduced paramagnetism. Bleaney and Bowers ([1]) studied the electron paramagnetic resonance (EPR) spectrum of a single crystal of copper acetate monohydrate and suggested that the anomalous paramagnetism is due to the presence of isolated pairs of copper ions in which these ions are bound by exchange forces. An X-ray study of this compound ([2]) confirmed this assumption and showed that dimeric molecules are present in the crystal lattice.

A study of the EPR spectra of single crystals of copper propionate monohydrate $(CH_3CH_2COO)_2Cu \cdot H_2O$ ([3]), copper *n*-butyrate monohydrate, and copper monochloroacetate monohydrate $(CH_2ClCOO)_2Cu \cdot H_2O$ ([4]) showed that in these compounds the molecules are likewise dimeric. Double molecules were detected by us ([5]), by the EPR method, in polycrystals of copper monochloroacetate hydrate $(CH_2ClCOO)_2Cu \cdot 2.5\,H_2O$, copper acetate monoquinolinates $(CH_3COO)_2Cu \cdot C_9H_7N$, copper monochloroacetate $(CH_2ClCOO)_2Cu \cdot C_9H_7N$, and copper acetate monopyridinate $(CH_3COO)_2Cu \cdot C_5H_5N$.

Since studies of EPR spectra had been carried out only on hydrates of copper salts of fatty acids, we undertook the study of anhydrous salts, both in the polycrystalline state and in solutions in the corresponding fatty acids. Salts of propionic, *n*-butyric, *n*-valeric, *n*-caproic ($C_6H_{12}O_2$), and *n*-capric ($C_{10}H_{20}O_2$) acids were studied.

Measurements were carried out at a frequency of 9320 MHz at room temperature and at 77° K on an RE-type radiospectrometer, which uses automatic frequency tuning to the working resonator and high-frequency modulation. The samples under study were placed in thin-walled glass ampoules. Therefore, in all recordings of the EPR spectra there is a signal from Fe^{3+} in the glass with $g \simeq 4$. The EPR spectra obtained were compared with spectra of polycrystalline samples of copper acetate and copper propionate monohydrates. The exchange interactions arising between closely spaced copper ions in the dimeric molecules of these compounds lead to the formation of a lower singlet with spin $S = 0$ and an upper triplet with $S = 1$. The combined action of the electric crystalline

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

field, anisotropic exchange, and dipole-dipole interactions leads (see, for example, ([6])) to splitting of the triplet state into a doublet and a singlet, equal to 0.34 cm^{-1}. Therefore the EPR spectrum of these salts in the 9000 MHz region consists of two lines, one of which (I) is located in a very weak magnetic field, and the second (II)—near 4500 Oe (Fig. 1a). In polycrystals, each of these lines is the result of averaging signals from three nonequivalent pairs of Cu^{2+} ions in the unit cell, possessing anisotropic values of the fine splitting and the g-factor.

Our studies showed that the anhydrous copper salts of fatty acids listed above exhibit a different picture. Let us consider it using anhydrous copper propionate as an example. Figure 1b shows a recording of the EPR spectrum of this salt at room temperature. On the clearly visible lines I and II there is superimposed an intense line III, having $g = 2.08 \pm 0.01$

and a width between inflection points of $\sim$ 800 Oe. The nature of the line becomes clearer if the sample is cooled to 77°K (Fig. 1b). Figure 2 shows group of lines III, recorded at 77°K in greater detail. It is not difficult to see that these lines constitute the hyperfine structure of the EPR spectrum of ordinary Cu^{2+} ions, due to the copper nuclear isotopes Cu^{63} and Cu^{65} with spin $I = 3/2$.

Fig. 1. EPR spectra of polycrystals of copper salts of fatty acids:
a —$(CH_3CH_2COO)_2Cu \cdot H_2O$ at 300°K; b —$(CH_3CH_2COO)_2Cu$ at 300°K; v — $(CH_3CH_2COO)_2Cu$ at 77°K.
Lines I and II are due to exchange-coupled pairs of Cu^{2+} ions; line III, to single Cu^{2+} ions.

In powdered $(CH_3CH_2COO)_2Cu$, the axes of the electric crystal fields at the sites of the Cu^{2+} ions are oriented randomly. Therefore, in this case the analysis given by Sands (7) for Cu^{2+} ions in silicate glasses is applicable. He showed that the large anisotropy of the g-factor and of the hyperfine-structure constant, characteristic of Cu^{2+} ions, leads, as a result of averaging over all angles between the directions of the Stark and magnetic fields, to a spectrum analogous to ours, consisting of two groups of 4 lines each.

Fig. 2. Hyperfine structure of the EPR spectrum in polycrystalline $(CH_3CH_2COO)_2Cu$ at 77°K, arising from single Cu^{2+} ions.

In our case, the series of four lines located around the value $H_0 = 3230$ Oe, which corresponds to $g_\perp = 2.04 \pm 0.01$, makes it possible to determine the constant $A = 35 \pm 3$ Oe, while the series grouped around $H_0 = 2870$ Oe ($g_\parallel = 2.30 \pm 0.01$)

gives the constant $B = 120 \pm 3$ Oe. We note that the values we found for group III of the g-factor and of the hyperfine-structure constants are very close to the corresponding values obtained in work (7).

Thus, it may be concluded that in the anhydrous salt $(CH_3CH_2COO)_2Cu$, in the crystalline state, there are both dimeric molecules with exchange-coupled pairs of copper ions having an effective spin $S = 1$, and single Cu^{2+} ions, apparently formed as a result of disruption of the exchange bond between neighboring copper ions. When comparing Figs. 1b and 1c, the fact that, upon lowering the temperature from room temperature to 77°K, there is a sharp decrease in the width of the EPR lines and a decrease in the integral intensity of the EPR lines of the single Cu^{2+} ions is noteworthy. If the decrease in line width with decreasing temperature is naturally attributed to an increase in the spin-lattice relaxation time under these conditions, then the second fact is quite unexpected. It may be assumed that, as the temperature is lowered, the dimeric molecules become energetically more favorable, which leads to a decrease in the number of unpaired molecules.

All that has been said also applies to the other anhydrous copper salts of fatty acids that were studied. In their EPR spectra, as in anhydrous copper propionate, the lines of types I and II are located at the same values of H_0 as in copper propionate monohydrate. This makes it possible to conclude, within the accuracy of our measurements, that the zero-field splitting of the spin triplet in these compounds has the same magnitude as in $(CH_3CH_2COO)_2Cu \cdot H_2O$, i.e., equal to 0.34 cm^{-1}. (The constant D in the anhydrous copper salts was determined from measurements made at 77°K.) Line III at room temperature in all these salts has approximately the same width and g-factor. Spectrum III at 77°K was measured only in anhydrous copper n-valerate $(C_5H_9O_2)_2Cu$. The following parameters were obtained: $g_\perp = 2.03 \pm 0.01$, $g_\parallel = 2.29 \pm 0.01$; $A = 39 \pm 3$ Oe and $B = 115 \pm 3$ Oe.

Tsutsida [8–10] found that monohydrates of copper acetate, copper propionate, and other copper salts of fatty acids in the crystalline state, as well as solutions of these salts in alcohol or chloroform, show, in addition to the band at 698 mμ, a specific absorption band at ~ 375 mμ, which was attributed to a possible Cu –Cu bond. From this it was concluded that all the listed salts have dimeric molecules both in the crystalline state and in solutions.

In this connection it was of interest to study the EPR of solutions of copper salts of fatty acids, since in this case paramagnetic resonance is apparently the most direct method for detecting a Cu–Cu bond. We measured the EPR of anhydrous salts $(CH_3COO)_2Cu$; $(C_3H_5O_2)_2Cu$; $(C_4H_7O_2)_2Cu$; $(C_5H_9O_2)_2Cu$ and $(C_6H_{11}O_2)_2Cu$, dissolved in the corresponding anhydrous fatty acids. Only in the solution of copper acetate was it not possible to obtain a measurable EPR effect, owing to its low solubility in acetic acid.

Figure 3 presents the EPR spectra of a solution of copper propionate in propionic acid saturated at 25°C, and of the same solution diluted with acid in ratios 1 : 1

Fig. 3. EPR spectra of solutions of $(CH_3CH_2COO)_2Cu$ in anhydrous propionic acid at 300° K: a –solution saturated at 25° C; b –anhydrous propionic acid diluted in the ratio 1 : 1; c –diluted in the ratio 1 : 5. Lines I and II are due to dimeric molecules, line III to monomeric molecules.

Figure 3: Fig. 3. EPR spectra of solutions of $(CH_3CH_2COO)_2Cu$ in anhydrous propionic acid at 300° K: a –solution saturated at 25° C; b –anhydrous propionic acid diluted in the ratio 1 : 1; c –diluted in the ratio 1 : 5. Lines I and II are due to dimeric molecules, line III to monomeric molecules.

and 1 : 5 (the narrow lines to the right of the central line are the signal of the free radical diphenylpicrylhydrazyl, used for calibration of the constant magnetic field). Similar spectra were also obtained for solutions of other copper salts of fatty acids in the corresponding anhydrous fatty acids.

The spectra obtained allow one to state that the solutions of the copper salts of fatty acids studied contain both dimeric and monomeric molecules. Since the paramagnetism of the dimeric molecules is due to the excited state and the integral intensity of their EPR signals is small, it is clear that the relative concentration of monomeric molecules in solution is very low. For example, in a saturated solution of anhydrous copper propionate in anhydrous propionic acid, the signal of the monomeric molecules in intensity corresponds to the EPR line of the paramagnetic salt $CuCl_2 \cdot 2H_2O$ in water, having a concentration of 0.003 mol/l.

It should be noted that lines I and II in the studied solutions of copper salts of fatty acids

are shifted toward weaker magnetic fields in comparison with their position in the EPR spectra of these salts in the crystalline state. For a saturated solution of $(CH_3CH_2COO)_2Cu$ in anhydrous propionic acid, the shifts of lines I and II are, respectively, ~ 90 and 240 oersted. Part of this shift, equal for line II to ~ 160 oersted, should be attributed to symmetrization of the EPR lines in solution as a result of averaging of the anisotropy of the g-factor during molecular motion. The second part of this shift may be

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explained by a decrease in the magnitude of the fine splitting of the spin triplet of copper propionate in solution. Analyzing this fact by the method described in paper ([5]), we conclude that the constant D in a saturated solution of $(CH_3CH_2COO)_2Cu$ in anhydrous propionic acid is smaller than in the crystalline state and is equal to ~ 0.33 cm^{-1}. From papers ([1],[6]) it follows that the value of D depends very strongly on the distance between copper ions; therefore the decrease in D can be explained by a slight increase in the distance between

copper ions in the dissolved molecules.

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Note: Figure translations are in progress. See original paper for figures.