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Abstract

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF OPTICALLY ACTIVE CHELATE COMPOUNDS OF COPPER WITH OXYALDIMINES AND OXYKETIMINES

Continuing the study of chelate compounds ([1]) containing the chelate unit A

[structural formula] $X = \mathrm{H},\ \mathrm{CH_3}$

(A)

we obtained copper and nickel chelates with optically active oxyaldimines and oxyketimines (the synthesis and optical-rotation dispersion curves of these compounds will be described separately). We found that the magnitude of optical rotation increases sharply on going from aldehyde derivatives ($X = \mathrm{H}$) to ketone derivatives ($X = \mathrm{CH_3}$) (Fig. 1). It was suggested that the change in molecular rotation is connected with different degrees of coplanarity of the chelate compounds.

Optically active molecules should be regarded as an aggregate of anisotropically polarizing groups and bonds ([2]). In the compounds studied, the greatest responsibility for optical activity is borne by the metal atom and the group

$$> C = N,$$

which participates in the formation of quasi-aromatic (chelate) rings. In these chelate compounds, dsp^2-hybridization occurs for the copper atom, characterized by the presence of an unpaired electron in a $3d$-orbital. Therefore, in copper

Fig. 1. Rotation-dispersion curves of copper chelate compounds

Figure 1: Fig. 1. Rotation-dispersion curves of copper chelate compounds

structural formula I

Figure 2: structural formula I

chelates the coplanarity of the molecule determines not only the degree of delocalization of the π-electrons of the entire system, but also the delocalization of the unpaired electron. It is known that

Fig. 1. Rotation-dispersion curves of copper chelate compounds:
a —bis-(salicylal)-(−)-propylenediimine-Cu (I),
b —bis-(o-oxyacetophenone-(−)-propylenediimine-Cu (II),
v —bis-(β-oxy-α-naphthal)-(−)-propylenediimine-Cu (III),
g —bis-(α-oxy-β-acetonaphth)-(−)-propylenediimine-Cu (IV),
d —bis-(acetylacetone-(−)-propylenediimine-Cu (V)

the degree of delocalization of the unpaired electron can be studied directly by the method of electron paramagnetic resonance (EPR). Thus, the same structural features of the molecules find their manifestation in optical activity and in EPR spectra. For this purpose, in the present work the EPR spectra of the indicated copper chelates were studied. The investigation was carried out on a superheterodyne EPR spectrometer at a frequency of 9455 MHz. The experimental results are given in Table 1 and in Figs. 2, 3.

Table 1

Line widths (ΔH, Oe), splitting between lines (ΔH^*, Oe), and values of the g-factor in the EPR spectra of copper chelate compounds*

Compound	g_1	g_2	g_3	g_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_1^*	ΔH_2^*	ΔH_3^*	g	ΔH
I	2.010	2.063	2.116	2.173	46	47	46	50	84	82	82	2.051	62
II	2.009	2.062	2.118	2.184	c	46	42	52	84	87	87	2.048	135
III	2.008	0.059	2.118	2.173	47	42	42	47	87	89	84	2.038	3
IV	2.009	2.059	2.117	2.171	c	46	46	50	84	91	80	2.033	47
V	2.008	0.059	2.114	2.172	c	42	39	44	84	84	84	2.067	73

* Accuracy of measurement of the line width: $±$5%; of the g-factor: $±$0.005; c —5 additional hfs lines with splitting 11 Oe.

I.

II.

III.

structural formula II

Figure 3: structural formula II

structural formula III

Figure 4: structural formula III

structural formula IV

Figure 5: structural formula IV

IV.

V.

All compounds in chloroform solutions give EPR spectra characterized by four lines of hyperfine structure (hfs), arising as a result of the interaction of the nuclear moment of the copper atom ($I_{\mathrm{Cu}} = 3/2$) with the magnetic spin moment of the unpaired electron. The line widths lie in the range 39-52 Oe, and the splitting between the lines is 82-91 Oe.

In the EPR spectra of compounds II, IV, V (Table 1 and Fig. 2b), in which there is the greatest possibility of violation of coplanarity of the molecule, an additional hfs of five lines is observed, clearly resolved on the most intense line ($I_z = -3/2$) of the main hfs spectrum and caused by interaction of the unpaired electron with two equivalent nitrogen atoms ($I_{\mathrm{N}} = 1$). In the EPR spectra of compounds I, III the additional hfs does not appear (Table 1 and Fig. 2a).

One could suppose that this is connected with the ability of chelates I and III, as more coplanar ones, to form associates. Indeed, formation of associates could lead to removal of the additional hfs.

as a result of the appearance of dipolar spin-spin interaction. However, study of the E.P.R. spectra of compound I in chloroform and dimethylformamide at various concentrations ($C = 2 \cdot 10^{-2}$—10^{-3} mole $\cdot$ l^{-1}), and also at $t = 130°$, showed that the additional h.f.s. does not appear.

Fig. 2. E.P.R. spectra of copper chelate compounds in chloroform:
a—bis-(salicylal)-(−)-propylenediimine-Cu (I),
b—bis-(o-oxyacetophenone)-(−)-propylenediimine-Cu (II).
The arrow indicates the DPPH absorption lines.

In order to minimize the possibility of association, the E.P.R. spectra of analogous chelate compounds containing substituents (Cl, Br, OCH_3) in the aldehyde component were also studied. But in these cases as well the character of the E.P.R. spectra did not change. Thus, the absence of additional h.f.s. in the E.P.R. spectra of chelates I, III is not connected with the formation of associates between molecules. The presence of additional h.f.s. in compounds II,

structural formula V

Figure 6: structural formula V

Fig. 2

Figure 7: Fig. 2

Fig. 3

Figure 8: Fig. 3

IV, V and its absence in chelates I, III can be explained only by peculiarities of the structure of the molecules, namely by a strong disturbance of their coplanarity when CH_3 groups are introduced instead of the hydrogen atom of the aldehyde group. Disturbance of coplanarity exerts a substantial influence on the distribution of the electron density of the unpaired electron in the molecule. Apparently, the largest fraction of the electron density of the unpaired electron falls on the Cu atom and a considerably smaller fraction on the atoms of the nearest

Fig. 3. E.P.R. spectra of copper chelate compounds in powder:
a—bis-(salicylal)-(−)-propylenediimine-Cu (I),
b—bis-(o-oxyacetophenone)-(−)-propylenediimine-Cu (II),
c—bis-(*β*-oxy-*α*-naphthal)-(−)-propylenediimine-Cu (III),
d—bis-(*α*-oxy-*β*-acetonaphth)-(−)-propylenediimine-Cu (IV),
e—bis-(acetylacetone)-(−)-propylenediimine-Cu (V).
The arrow indicates the DPPH absorption lines.

and more distant surroundings. With a more coplanar arrangement of atoms in molecules I, III, when delocalization of the unpaired electron is carried out most completely, i.e. its molecular orbital encompasses all nuclei, no additional h.f.s. from interaction with nitrogen nuclei, and still less with proton nuclei bound to carbon atoms, is observed in the E.P.R. spectra. With strong disturbance of the coplanarity of molecules II, IV, V, the degree of electron delocalization decreases, while the time of its residence in the field of neighboring nuclei increases. Under these conditions, interaction of the electron

of the copper atom with two nitrogen nuclei ($I_N = 1$) should lead to the appearance of an additional superhyperfine splitting consisting of five components (splitting magnitude $\simeq 11$ G). Differences in the coplanarity of compounds I, III and II, IV, V, caused by steric factors, are also distinctly manifested in the EPR spectra of the powders (Table 1, Fig. 3). The EPR spectra of the powders are characterized by single asymmetric lines of different width, which strongly depends on the structure of the chelate compound. As the steric factor increases, a sharp increase in the width of the EPR line occurs. A change in the overall conjugation chain also has a large influence on the width of the EPR lines. These facts can be explained as follows. It is known that paramagnetic molecules of solids are subject to the influence of the internal electric and magnetic fields of the crystal lattice. The various types of interaction that arise under these conditions (spin-lattice, dipolar spin-spin, and exchange) between paramagnetic

particles do not allow the hyperfine structure of EPR spectra to be observed, but they affect the width of the resonance absorption line in different ways. If spin-lattice and dipolar spin-spin interactions lead to line broadening (in accordance with the relation $\Delta E \cdot \Delta t \simeq \frac{h}{2\pi}$), then exchange interaction of the electrons of paramagnetic particles causes narrowing of the EPR line ([3,4,5]).

In powders of chelates I, III, whose molecules possess greater coplanarity, delocalization of the unpaired electron is effectively realized, promoting strong exchange interaction between molecules in crystals. This leads to averaging of the internal fields and, consequently, to narrowing of the EPR line in comparison with chelates II, IV. In the latter compounds, delocalization of the unpaired electron and exchange interaction are hindered because of the violation of molecular coplanarity. This is especially strongly manifested when comparing the EPR spectra of powders of the chelate compounds (naphthalene series) III and IV. With an increase in the effective length of the conjugated system, more rapid delocalization of the unpaired electron is accomplished, causing the participation of the entire molecule as a whole in the exchange interaction. This should lead to a sharper narrowing of the EPR line, which is indeed observed for compound III. In works ([6–9]), EPR spectra were described for some copper chelate compounds of analogous structure, but not possessing optical activity. The facts presented in these works confirm the main results of the present investigation. Thus, it may be concluded that the same structural features of the studied copper chelate compounds, associated with violation of coplanarity of the molecules under the influence of steric factors, determine the change in optical activity and in the EPR spectra of the compounds.

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