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Abstract

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Study of the Structure of Certain Inner-Complex Compounds by the Method of Electron Paramagnetic Resonance

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The study of electron paramagnetic resonance (EPR) spectra of inner-complex compounds can provide valuable information on the nature of the bond between the metal and the atoms of the ligand. Since application of this method is limited to paramagnetic compounds, we chose as the object of study inner-complex compounds (i.c.c.) of copper, whose atom contains an unpaired electron in the $3d$-orbital. There are a number of works in the literature devoted to the EPR spectra of copper i.c.c. McGarvey ([1–3]) investigated single crystals and solutions of copper acetylacetonate, 3-ethylacetylacetonate, acetylacetoacetate, and salicylalaminatocopper, as well as magnetically diluted single crystals of copper acetylacetonate. In works ([4,5]), EPR spectra of powders and solutions of copper complexes of certain azo compounds, acetylacetone, and acetoacetic ester were studied.

In the present work, EPR spectra were studied for a series of copper complexes formed by alkyl- and aryl-imines of salicylaldehyde, *o*-hydroxyacetophenone, and β-hydroxynaphthaldehyde, in the form of powders and solutions in chloroform. The general formulas of the compounds are given in Table 1. Such a set of compounds makes it possible to trace regularities in the spectra caused by the influence of the substituent, by the growth of the conjugated system of bonds in the molecule, and by the spatial arrangement of the ligands around the central metal atom. The investigation was carried out on a superheterodyne EPR spectrometer at a frequency of 9434 MHz. The data obtained are presented in Table 1.

Discussion of Results

From the data in Table 1 it is evident that, for polycrystalline samples of the compounds studied, single absorption bands of asymmetric shape are observed; in solution all compounds give a hyperfine structure (h.f.s.) consisting of four lines (Fig. 1). The splitting in the spectra of solutions is due to interaction of the unpaired electron with the nucleus of the copper atom, which has nuclear spin 3/2. In the case of copper *o*-hydroxyacetophenoniminate, we succeeded in

obtaining in solution an additional h.f.s. consisting of five bands separated from one another by 12 Oe. The additional h.f.s. was obtained on the most intense h.f.s. line ($I = -3/2$) and is due to interaction of the unpaired electron with two equivalent nitrogen atoms ($I - 1$) (see Fig. 2). The appearance of an additional h.f.s. indicates that the copper atom participates in formation of the copper–nitrogen bond not only with its free orbitals, but also gives its unpaired electron into common use with neighboring atoms. This leads to an increase in the bond order of the metal–nitrogen bond, which in turn promotes equalization of the bonds in the metallacycle.

For the other compounds it was not possible to resolve an additional h.f.s. in solutions, since the disordered orientation of the molecules leads to overlap of lines shifted relative to one another because of anisotropy of the g-factor and possible association of the molecules. However, evidence in favor of the fact that the unpaired electron in these compounds is also delocalized is provided–

Table 1

Widths of the bands (ΔH), splitting between the bands (ΔH^*), and g-factor values in the EPR spectra of inner-complex copper compounds

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
1	salicylaldehyde-type Cu/2 complex, R at imine nitrogen, formyl H	H	2.064	177	2.023	2.075	2.124	2.177	79	44

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
2	salicylaldehyde-type Cu/2 complex, *R* at imine nitrogen, formyl H	CH_3	2.034	106	–	–	–	–	–	–
3	salicylaldehyde-type Cu/2 complex, *R* at imine nitrogen, formyl H	CH_3	2.064	145	2.032	2.075	2.115	2.158	66	41
4	salicylaldehyde-type Cu/2 complex, *R* at imine nitrogen, formyl H	C_2H_5	2.145	175	2.037	2.079	2.130	2.174	65	44

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
5	salicylaldehyde type Cu/2 complex, R at imine nitrogen, formyl H	C_4H_9	2.092	180	2.035	2.083	2.125	2.159	63	42
6	salicylaldehyde type Cu/2 complex, R at imine nitrogen, formyl H	$-(CH_2)_6-$	2.092	173	2.039	2.079	2.119	–	65	50
7	salicylaldehyde type Cu/2 complex, R at imine nitrogen, formyl H	C_6H_5	2.052	40	2.051	2.084	2.124	2.158	55	40

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
8	salicylaldehyde type Cu/2 complex, R at imine nitrogen, formyl H	$-(CH_2)_2-$	2.081	87	2.010	2.074	2.105	2.152	74	53
9	salicylaldehyde type Cu/2 complex, R at imine nitrogen, formyl H	$-(CH_2)_3-$	2.063	60	2.012	2.062	2.112	2.156	76	58

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
10	*o*-hydroxyacetophenone-type Cu/2 complex, *R* at imine nitrogen, CH_3 at carbon	H	2.073	106	–	–	–	–	84	57
11	*o*-hydroxyacetophenone-type Cu/2 complex, *R* at imine nitrogen, CH_3 at carbon	C_2H_5	2.058	99	2.038	2.081	2.125	2.165	65	52

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
12	*o*-hydroxyacetophenone-type Cu/2 complex, *R* at imine nitrogen, CH_3 at carbon	$-(CH_2)_2-$	2.063	45	–	–	–	–	–	–
13	*β*-hydroxynaphthaldehyde-type Cu/2 complex, *R* at imine nitrogen, formyl H	H	2.103	145	–	–	–	–	–	–

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
14	β-hydroxynaphthaldehyde-type Cu/2 complex, R at imine nitrogen, formyl H	C_2H_5	2.053	50	2.034	2.073	2.122	2.156	61	37
15	β-hydroxynaphthaldehyde-type Cu/2 complex, R at imine nitrogen, formyl H	C_4H_9	2.048	66	2.033	2.075	2.120	2.149	60	39

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
16	β-hydroxynaphthaldehyde-type Cu/2 complex, R at imine nitrogen, formyl	$-(CH_2)_6-$	2.058	140	–	–	–	–	–	–
17	β-hydroxynaphthaldehyde-type Cu/2 complex, R at imine nitrogen, formyl	C_6H_5	2.058	33	2.045	2.084	2.125	2.156	56	36

No.	General formula	R	Powder: g	Powder: ΔH, gauss	Solution in chloroform: g_1	g_2	g_3	g_4	ΔH^*, gauss	ΔH, gauss
18	β-hydroxynaphthaldehyde-type Cu/2 complex, R at imine nitrogen, formyl	H	2.071	89	–	–	–	–	–	–

* Accuracy of measuring the line width: ±5%; of the g-factor: ±0.001.

corresponds to the dependence of the magnitude of the splitting between the h.f.s. lines on the structure of the ligand. From Table 1 it is seen that, in the salicylaldehyde series, when a phenyl radical is introduced into the molecule, the distance between the h.f.s. bands (ΔH) decreases by approximately 10 gauss relative to alkyl substituents. This is explained by an increase in the conjugated system of bonds in the molecule and, accordingly, by a greater delocalization of the electron density. At the same time, the time spent by the unpaired electron at the copper atom decreases, which leads to a decrease in the distance between the h.f.s. bands. Replacement of alkyl radicals by hydrogen increases the splitting by 10–15 gauss. In addition to the structure of the ligand, the spectrum is also affected by the geometrical configuration of the molecule, as is evident from the data for ethylenediamine and 1,2-diaminopropane derivatives.

The value of the g-factor, on the contrary, increases on going from $R = H$ to alkyl and aryl substituents; moreover, for alkyls it remains almost unchanged (2.032–2.039). Unfortunately, we were unable to obtain spectra of solutions of some derivatives of o-hydroxyacetophenone and β-hydroxynaphthaldehyde because of their poor solubility (in this case the data are absent from Table 1). However, from the available data it is evident that the regularities observed for these compounds are analogous to those that occur for derivatives of salicylaldehyde. In addition, a certain narrowing of the distance between the h.f.s. bands is observed owing to an increase in the conjugated system on going to derivatives

Fig. 1. EPR spectrum of the copper complex of salicylalphenylimine in chloroform solution. Recording of the first derivative of the absorption band

Figure 1: Fig. 1. EPR spectrum of the copper complex of salicylalphenylimine in chloroform solution. Recording of the first derivative of the absorption band

of β-hydroxynaphthaldehyde. Consideration of the widths of the EPR bands of the inner-complex compounds studied in solutions shows that it does not depend on the size of the substituent and on the magnitude of the conjugated system.

In the solid state, strong exchange interactions do not allow observation of h.f.s.; however, some regularities can be derived by comparing the width of the EPR line (ΔH^*) with the structure of the inner-complex compounds. The data of Table 1 may be interpreted as follows: the width of the EPR line in the solid state is determined by the magnitude of exchange interactions between paramagnetic particles in the crystal; as the size of the substituent increases, the volume of the molecule and the steric hindrances to dense packing increase.

packing, which leads to a decrease in exchange interactions and, in the case of equivalent packing of paramagnetic particles in the crystal, to a narrowing of the EPR line; an increase in the conjugated system of bonds in the molecule leads in this case to line broadening, since not only the unpaired electron itself but also the entire π-electron system of the molecule participates in the transfer of exchange interactions.

In the light of these considerations, let us first consider derivatives of salicylaldehyde. According to available X-ray structural data [(6)], salicylaldehyde compounds with $R = H, CH_3$ (brown form), C_2H_5, C_4H_9, and C_6H_5 form centrosymmetric crystals with equivalent packing of molecules. For them, as the size of the substituent increases from methyl to butyl, the line width increases owing to an increase in molecular volume and a decrease in exchange interactions. The hexamethylenediamine derivative has a line width close to that of the alkyl derivatives. The copper complex of salicylaliminamine, as well as the imine complexes of the other compounds considered, falls outside the general series, which may be explained by their ability to form hydrogen bonds involving imine hydrogen. When an aromatic substituent is introduced into the molecule, the line width decreases sharply because exchange interactions increase as the system of conjugated bonds in the molecule becomes larger.

Fig. 1. EPR spectrum of the copper complex of salicylalphenylimine in chloroform solution. Recording of the first derivative of the absorption band.

Molecules possessing a planar cis-configuration (derivatives of ethylenediamine and 1,2-diaminopropane) must pack in the crystal in a manner different from centrosymmetric molecules. Accordingly, for them a narrowing of the absorption band is observed in comparison with the alkyl derivatives.

Fig. 2. Additional h.f.s. of the EPR band of *o*-oxyacetophenoniminate copper in chloroform solution. Recording of the first derivative of the absorption band

Figure 2: Fig. 2. Additional h.f.s. of the EPR band of *o*-oxyacetophenoniminate copper in chloroform solution. Recording of the first derivative of the absorption band

Fig. 2. Additional h.f.s. of the EPR band of *o*-oxyacetophenoniminate copper in chloroform solution. Recording of the first derivative of the absorption band.

When considering complexes of derivatives of β-oxynaphthaldehyde, it must be taken into account that, in comparison with the derivatives of salicylalimine, the molecules of these compounds contain an additional benzene ring, which, on the one hand, increases the volume of the molecule, leading to a decrease in exchange interactions, and, on the other hand, increases the conjugated system in the molecule, thereby strengthening such interaction. Apparently, the second factor is predominant, since for these compounds a narrowing of the absorption bands is observed in comparison with the corresponding derivatives of salicylaldehyde. The general regularities in the series of β-oxynaphthaldehyde are analogous to those observed in the series of salicylaldehyde. For the ethylenediamine derivative of β-oxynaphthaldehyde the band width is somewhat greater than for its alkyl derivatives and is close to that observed for copper salicylalethylenediiminate. Probably in this case, with the change in molecular symmetry, steric factors acquire greater importance, compensating the gain in the magnitude of exchange interactions achieved through increased conjugation.

In derivatives of *o*-oxyacetophenone, the additional methyl group creates certain obstacles to the packing of molecules in the crystal and

decreases exchange interactions. Experiment shows, however, not a broadening but a narrowing of the absorption band for these substances in comparison with salicylaldehyde derivatives, which may be explained by nonequivalent packing of the molecules in the crystal. Unfortunately, we do not have structural data for these compounds; however, the infrared spectrum of copper *o*-oxyacetophenoniminate, in which three absorption bands are observed in the region of the stretching vibrations of N—H, whereas with an equivalent arrangement of molecules in the crystal only one band would be observed, supports such an assumption.

Copper salicylaliminate crystallizes in two forms: green and brown. The brown isomer gives centrosymmetric crystals with coordination number 4. In the green form the coordination number is increased owing to the formation of intermolecular copper—oxygen bonds (7). The formation of such a bond increases exchange interactions and narrows the EPR absorption band from 145 G in the brown form to 106 in the green.

The absence of any dependence, in solutions, of the line width on the size of the substituent and on the magnitude of the conjugated system indicates that

the width of the absorption line in the solid state is indeed determined by interactions in the crystal.

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