Chemistry

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1964

SovietRxiv

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Abstract

Full Text

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Study of the E.P.R. Spectra of α-Thiopicolinanilide Cu(II)

Many works have been devoted to the study of the chemical properties of chelate polymers$^{(1-4)}$; however, investigation of the E.P.R. spectra of chelate polymers has only just begun$^{(5)}$. In work$^{(2)}$ it was shown that the catalytic properties of chelate polymers are determined by the presence of a metal ion in the chelate unit, and that these properties are modified by selecting the appropriate structure of the organic part, which affects the electronic state of the metal. Therefore it is of considerable interest to determine the electronic structure of the chelate unit on the basis of a study of the corresponding monomeric complex.

It is known that the presence of a covalent bond between the central atom of transition metals and the nearest atoms of the ligands leads in some cases to resolved hyperfine structure from the ligand nuclei, if they possess a nuclear magnetic moment. However, the number of compounds in which resolved hyperfine structure has been observed is small$^{(6-8)}$.

Fig. 1. Structure of α-thiopicolinanilide Cu(II)

In the present work results are presented for the study of the E.P.R. spectra of α-thiopicolinanilide Cu(II)–(TPA–Cu(II)) in the polycrystalline state and in solutions. This complex is a monomeric analogue of chelate polymers that have already been studied$^{(5)}$; its structure is shown in Fig. 1. The complex, in the form of a crystalline brown precipitate, was obtained by interaction of α-thiopicolinanilide$^{(4)}$ with cupric acetate in a methanol medium. It was recrystallized from benzene and acetone. T_{m} 210-211°. Analysis for Cu and N corresponds to the structure in Fig. 1. Measurements were carried out on a standard radiospectrometer RE-13-01.

The E.P.R. spectrum of the polycrystalline sample of TPA–Cu(II) is shown in Fig. 2. It is characterized by the values of the g tensor $g_{\parallel} = 2.11$, $g_{\perp} = 2.042$ and is due to transitions within a Kramers doublet with spin $s = 1/2$. Analysis

Fig. 2. EPR spectrum of a polycrystalline TPA–Cu(II) sample at room temperature.

Figure 2: Fig. 2. EPR spectrum of a polycrystalline TPA–Cu(II) sample at room temperature.

Fig. 3. EPR spectrum of a solution of TPA–Cu(II) in benzene at room temperature.

Figure 3: Fig. 3. EPR spectrum of a solution of TPA–Cu(II) in benzene at room temperature.

of the E.P.R. line shape of this compound in the polycrystalline state, carried out by the method of(9), showed that in this case there is no resolved hyperfine structure. Since no change in the line width at liquid-nitrogen temperature, as compared with the line width at room temperature, was observed, it may be assumed that indirect exchange interactions are absent in this case(10).

The values of the g-tensor quantities in this case are substantially smaller than for Cu(II) salts having similar symmetry. This fact makes it possible to assume that in the present case covalent bonds of the metal ion with the nearest atoms of nitrogen and sulfur play a major role. To verify this supposition, the E.P.R. spectra of TPA–Cu(II) were studied in solutions at concentrations not greater than 0.01 mol. Such concentrations ensured the absence of dipole-dipole interaction in solution. As solvents–

benzene, dioxane, and chloroform were used as solvents. All measurements were carried out at room temperature.

The EPR spectrum of TPA–Cu(II) in benzene is shown in Fig. 3 and consists of two spectra with resolved hyperfine structure. The principal hyperfine structure, with splitting a_{Cu}, is caused by the interaction of the unpaired electron with the nuclear moment of copper, which has spin $I_{\mathrm{Cu}} = 3/2$. The width of each of these four lines $(2I_{\mathrm{Cu}}+1) = 4$ depends on the projection m_I of the nuclear spin of copper, $I_{\mathrm{Cu}} = 3/2$.

Fig. 2. EPR spectrum of a polycrystalline TPA–Cu(II) sample at room temperature

Fig. 3. EPR spectrum of a solution of TPA–Cu(II) in benzene at room temperature

The principal hyperfine structure is additionally split into several lines. Analysis showed that the additional splitting a_N is associated with the interaction of the unpaired electron with the nitrogen nuclei of the nearest environment. The spin of the nitrogen nucleus is $I_N = 1$, and, provided that two nitrogens are equivalent, the number of additional components will be equal to five $(2 \cdot n \cdot I_N + 1 = 5)$. It should be noted that the multiplicity of the splitting of the hyperfine lines by nitrogen nuclei is observed for all projections of the nuclear spin of copper m_I.

The resolution of these hyperfine structures evidently worsens toward smaller values of the constant magnetic field H_0, but even on the copper hyperfine line corresponding to $m_I = +3/2$ such a hyperfine structure is observed. For a solution of TPA—Cu(II) in benzene, $a_{\mathrm{Cu}} = 65$ oersted, $a_N = 16$ oersted.

In addition, an additional splitting of each of the a_N components into two lines is observed for the value of the projection of the nuclear spin of copper equal to $m_I = -3/2$. This splitting appears as a consequence of the presence of two copper isotopes, Cu^{63} and Cu^{65}, which have the same spin but somewhat different magnetic moments $\mu = 2.22\mu_n$, $= 2.379\mu_n$, with abundances of 69 and 31%, respectively.

It is evident that the additional hyperfine structure from nitrogen nuclei is due to the contact interaction of the unpaired electron with the nuclear spins $I_N = 1$ of nitrogen atoms and is a direct indication of the presence of a covalent bond of the Cu(II) ion with the surrounding ligands. Such interaction of the unpaired electron with the nitrogen nucleus indicates that, in the molecular orbital of the unpaired electron, there is an admixture of an orbital of *s*-symmetry of the ligand atom. Such an admixture is ensured by the presence of sp^2-hybridization of nitrogen. It follows from the spectrum that there is an equal and nonzero probability of finding the unpaired electron on two nitrogen nuclei. Pri-

whereas the value a_N is constant for all the solvents used, which proves the invariance of the copper—nitrogen bond.

Since $g_x \approx g_y$, it may be assumed that there is a covalent bond of copper with the sulfur atom. To verify this assumption, a complex was synthesized in which the sulfur was enriched to 21% with the isotope S^{33}, which has nuclear spin $I_S = 3/2$. The EPR spectrum of a polycrystalline sample of such a complex did not change (Fig. 2). It has not yet been possible to obtain a resolved additional hyperfine structure from the sulfur nucleus, which proves the absence of *sp*-hybridization of sulfur. Thus, the covalency of the copper—sulfur bond is due to the participation of the pure *p*-orbital of sulfur.

The results presented make it possible to conclude that TPA—Cu(II) is a coplanar complex in which the copper—nitrogen and copper—sulfur bonds are covalent to a considerable degree.

The authors consider it a pleasant duty to thank the staff of the firm "Izotop" for the rapid delivery of the sulfur isotope.

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Received
1 VIII 1964

CITED LITERATURE

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