Reports of the Academy of Sciences of the USSR

R. Kh. Timerov, Yu. V. Yablokov, Academician of the Academy of Sciences of the Moldavian SSR A. V. Ablov

1963

SovietRxiv

Fig. 1. EPR spectrum of polycrystalline $Cu(DH)_2$ at room temperature

Figure 1: Fig. 1. EPR spectrum of polycrystalline $Cu(DH)_2$ at room temperature

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1953. Volume 152, No. 1

PHYSICAL CHEMISTRY

R. Kh. Timerov, Yu. V. Yablokov, Academician of the Academy of Sciences of the Moldavian SSR A. V. Ablov

STUDY OF BIS-DIMETHYLGLYOXIMATO-COPPER (II) BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

Analysis of the spectra of electron paramagnetic resonance (EPR) of complex compounds makes it possible to investigate the covalent bonds of the central atom of transition metals with the nearest atoms of the ligands ($^{1-3}$). Nevertheless, the number of copper compounds studied in which the presence of covalent bonds leads to a resolved hyperfine structure from the nuclei of the ligands is very limited ($^{3-7}$).

We investigated* the EPR spectra of bis-dimethylglyoximato-copper (II) ($Cu(DH)_2$) in the crystalline state and in solutions. The measurements were carried out at a frequency of 9320 MHz on a standard radio spectrometer of the RE-1301 type. An X-ray structural study of bis-dimethylglyoximato-copper showed (^{9}) that, in contrast to bis-dimethylglyoximatonickel, whose structure is planar (^{10}), the two organic radicals DH bonded to the copper atom do not lie in one plane, but form an angle of $180^\circ - 21^\circ 44'$. The copper atom is bonded to four nitrogen atoms of two organic radicals DH (mean distance $Cu - N = 1.94$ Å) and to an oxygen atom of a neighboring $Cu(DH)_2$ molecule ($Cu - O = 2.43$ Å) and, consequently, in the crystal lattice bis-dimethylglyoximato-copper forms dimeric molecules $Cu_2(DH)_4$. The coordination number of copper is five. The copper atom is displaced from the plane of the four N atoms in the direction toward the oxygen atom of the neighboring $Cu(DH)_2$.

Fig. 1. EPR spectrum of polycrystalline $Cu(DH)_2$ at room temperature

The EPR signal of crystalline bis-dimethylglyoximato-copper is shown in Fig. 1. It is characterized by the values of the g tensor: $g_{\|} = 2.155$ and $g_{\perp} = 2.035$ and

Fig. 2. EPR spectrum of a solution of $Cu(DH)_2$ in dioxane at room temperature

Figure 2: Fig. 2. EPR spectrum of a solution of $Cu(DH)_2$ in dioxane at room temperature

Fig. 3. Theoretical spectrum of 9 Gaussian components with intensities 1:4:10:16:18:16:10:4:1 at $\Delta H/a_N = 1$ (half of the spectrum)

Figure 3: Fig. 3. Theoretical spectrum of 9 Gaussian components with intensities 1:4:10:16:18:16:10:4:1 at $\Delta H/a_N = 1$ (half of the spectrum)

is due to transitions within a Kramers doublet with $S = 1/2$. The presence of dimers with $Cu - N - O - Cu$ bonds made it possible to expect that indirect exchange interactions might be possible, which could lead to pairing of the electron spins of the copper atoms ([11]). Experiment shows that in the dimers $Cu_2(DH)_4$ such exchange interactions are absent.

Of unquestionable interest was the study of the nature of the bonds of the copper atom with the four nearest nitrogen atoms N^{14}. It is known that information of this kind can be obtained from analysis of the hyperfine structure of the EPR spectrum ([1-7]). Water, methanol, and dioxane were used as solvents. All measurements were performed in solutions of concentration 0.01 mol/l at room temperature. In all solvents there is observed the EPR spectrum characteristic of solutions of Cu^{2+} salts, consisting of four hyperfine lines, the width of which shows a distinct dependence on the projections m_I of the nuclear spin $I = 3/2$ (Fig. 2). In addition, each such hyperfine line (let us call it a principal one) is further split into several components. Their resolution naturally worsens toward smaller values of the constant magnetic field H; however, the additional structure is noticeable even on the principal line corresponding to $m_I = +1/2$. Obviously, this additional structure is due to the contact interaction of the magnetic electron with the nuclear spins $I_N = I$ of the nitrogen atoms and is direct evidence for the presence of a covalent bond of the Cu^{2+} ion with the ligands. One might have expected that in the $Cu(DH)_2$ molecule the four nitrogen atoms are pairwise nonequivalent and that contact interaction occurs with only two of them. In this case the additional structure would consist of five lines (see, for example, ([5])). However, the number of observed additional lines is clearly greater than five. To interpret the experimental data we constructed theoretical absorption curves

Fig. 2. EPR spectrum of a solution of $Cu(DH)_2$ in dioxane at room temperature

Fig. 3. Theoretical spectrum of 9 Gaussian components with intensities $1 : 4 :$

* Reported at the Conference on the Application of Physical Methods to the Study of Complex Compounds. Kishinev, September 1962 ([8]).

$10 : 16 : 18 : 16 : 10 : 4 : 1$ at $\Delta H/a_N = 1$ (half of the spectrum)

$$I(H) = \sum_{i=1}^{9} I(\Delta H, a, m_N, H)$$

in a spectrum consisting of 9 Gaussian components with an intensity ratio

$$1 : 4 : 10 : 16 : 18 : 16 : 10 : 4 : 1,$$

corresponding to hyperfine interaction with four equivalent N nuclei (Fig. 3). From comparison of Figs. 3 and 2 it is seen that the theoretical spectrum agrees well with the experimental one at $\Delta H/a_N = 1$ (here a_N is the hyperfine splitting due to I_N). Calculations of the function $I(H)$ were performed on an M-3M electronic computer. The determined values of a_{Cu}, a_N, and g_0—the factor of the center of the spectrum—for various solvents are given in Table 1.

The analysis performed shows that in $\mathrm{Cu(DH)_2}$ there is an equal and nonzero probability of finding the unpaired electron on the four nitrogen atoms. Apparently, it may be considered that in solution the dinuclear structure characteristic of crystalline $\mathrm{Cu_2(DH)_4}$ is not preserved. Nevertheless, the actual coordination of the copper ion is not fourfold: the change in g_0 and a_{Cu} indicates interaction of the copper ion with solvent molecules. However, the constancy of the constant a_N of the additional hyperfine structure in all the solvents used makes it possible to conclude that the character of the Cu—N bonds is not changed.

This circumstance allows us to use the theoretical analysis of the EPR spectra of chelate copper compounds employed by Maki and McGarvey ([3]) and developed by Kivelson and Neiman ([6]). We proceed from the assumption that the $^{14}\mathrm{N}$ nuclei form a plane square, at the center of which the Cu^{2+} ion is located, and we assume that each of the four nitrogen atoms can provide $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals for the formation of molecular orbitals with the $3d$-orbitals of the Cu^{2+} ion. In the field of symmetry D_{4h} the unpaired electron is located in the nonbonding orbital B_{1g} ([6,11]).

$$B_{1g} = N\{\alpha d_{x^2-y^2} - (1-\alpha^2)^{1/2}(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2\}, \qquad (1)$$

where

$$\sigma^{(i)} = np^{(i)} \mp (1-n^2)^{1/2} S^{(i)}, \qquad 0 \leqslant n \leqslant 1. \qquad (2)$$

(Here the four nitrogen atoms are placed on the $\pm x$ and $\pm y$ axes and are numbered starting from $+x$ counterclockwise.)

In addition, the normalization of B_{1g} gives:

$$N^2 = \left[1 - 2\alpha(1-\alpha^2)^{1/2} S\right]^{-1}, \tag{3}$$

where S is the overlap integral

$$S = \left\langle d_{x^2-y^2} \mid \left(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}\right) \mid 2 \right\rangle = 2\left\langle d_{x^2-y^2} \mid -\sigma_x^{(1)} \right\rangle. \tag{4}$$

We further assume that the atomic $3d$-orbitals of Cu^{2+} do not produce any appreciable spin density at the nuclei of the nitrogen atoms. Then, for the energy of the isotropic hyperfine interaction of the unpaired electron with the nuclei N^{14}, we have:

$$E_N = a_N S^2 I_N^z = \left\{ \frac{4\pi}{9} \beta g_N \beta_N \left[N^2(1-\alpha^2)\right] \left|\rho_N(0)\right|^2 \right\} S^z I_N^z. \tag{5}$$

Table 1

g-factors (determined from the center of the spectrum) and hyperfine-structure constants of $Cu(DH)_2$ *solutions*

Solvent	g_0	a_{Cu}, oerst.	a_N, oerst.
Water	2.086	87.5	15.0
Methanol	2.084	81.0	15.0
Dioxane	2.077	89.0	15.0

Here $\rho_N(0)$ is the value of the $2S$-function at the N^{14} nucleus; β and β_N are the electron and nuclear magnetons, and g_N is the nuclear g-factor for N^{14}.

The anisotropic part of the hyperfine interaction, due to the magnetic dipole-dipole interaction of the magnetic moments of the unpaired electron and the N^{14} nuclei, is averaged in a liquid and in our experiments appears only in the width ΔH of the additional hyperfine lines.

By measuring the constant a_N of the additional hyperfine structure, one can determine the constants α and N in the molecular wave function B_{1g} with the aid of formulas (5) and (3). According to the estimates of Maki and McGarvey (^{3}), $|\rho_N|^2 = 33.4 \cdot 10^{24}$ cm^{-3}. For a distance of the order of 1.9 Å one may put $S = 0.093$ (^{3}). If, in addition, $n = (2/3)^{1/2}$, which corresponds to sp^2 hybridization in the ligands, then from (5) and (3), at $a_N = 15$ oerst., we find:

$$\begin{aligned} N^2\alpha^2 &= 0.77; & N^2(1-\alpha^2) &= 0.32; \\ \alpha^2 &= 0.71; & 1-\alpha^2 &= 0.29. \end{aligned} \tag{6}$$

Although these coefficients determine the character of the molecular orbital only of the unpaired electron in the complex under study, they also make it possible

Structural diagram of $Cu(DH)_2$ showing a planar CuN_4 core and two short symmetrical $O \cdots H \cdots O$ hydrogen bonds between the DH residues.

Figure 4: Structural diagram of $Cu(DH)_2$ showing a planar CuN_4 core and two short symmetrical $O \cdots H \cdots O$ hydrogen bonds between the DH residues.

to judge the character of the Cu–N bond. In particular, comparing our results (the upper line of (6)) with the data of work (^{6}), we arrive at the conclusion that the distribution of the cloud of the unpaired electron on the antibonding orbit B_{1g} in $Cu(DH)_2$ is analogous to the distribution of the unpaired electron in the case of copper etioporphyrin and copper phthalocyanine.

The observed equivalence of the four nitrogen atoms coordinated with the copper atom in $Cu(DH)_2$ can be explained by assuming that the atoms CuN_4 lie in one plane and that between the oxygen atoms of the two DH residues there are symmetrical short hydrogen bonds:

Such a short hydrogen bond was detected spectroscopically (^{13}) for one pair of O atoms (the O–O distance is 2.53 Å (^{9})) in the crystall-

···crystalline $Cu_2(DH)_4$; in the other pair of oxygens such a bond is disrupted as a result of the coordination of one of the O atoms with the copper atom of the second $Cu(DH)_2$ molecule of the dimer. Therefore, in dimeric crystalline $Ni(DH)_2$ the four nitrogen atoms cannot, in principle, be equivalent. It is also known that in crystalline $Ni(DH)_2$ short symmetric hydrogen bonds are characteristic of pairs of oxygen atoms (^{14}), and, in accordance with this, $Ni(DH)_2$ is a monomeric compound.

Thus, the established equivalence of the four nitrogen atoms in bis(dimethylglyoximato)copper indicates that in solutions this compound is monomeric. In solution the copper atom completes its coordination by means of the oxygen atoms of two coordinated solvent molecules.

The authors consider it their pleasant duty to express their gratitude to Prof. B. M. Kozyrev for his constant interest in this work, and to I. B. Bersuker for the very valuable comments made during discussion of the results.

Physico-Technical Institute
of the Kazan Branch of the Academy of Sciences of the USSR

Institute of Chemistry
of the Academy of Sciences of the Moldavian SSR

Received
30 V 1963

CITED LITERATURE

[1] K. W. H. Stevens, Proc. Roy. Soc. (London), **A219**, 542 (1953).
[2] J. Owen, Proc. Roy. Soc. (London), **A227**, 183 (1955).
[3] A. H. Maki, B. R. McGarvey, J. Chem. Phys., **29**, 31, 35 (1958).
[4] E. M. Roberts, W. S. Koski, J. Am. Chem. Soc., **82**, 3006 (1960).
[5] A. K. Piskunov, D. N. Shigorin et al., DAN, **136**, 871 (1961).
[6] D. Kivelson, R. Neiman, J. Chem. Phys., **35**, 149 (1961).
[7] H. R. Gersmann, J. D. Swalen, J. Chem. Phys., **36**, 3221 (1962).
[8] R. Kh. Timerov, Yu. V. Yablokov, A. V. Ablov, ZhNKh, **8**, 1291 (1963).
[9] E. Frasson, R. Bardi, S. Bezzi, Acta crystallogr., **12**, 201 (1959).
[10] L. E. Godycki, R. E. Rundle, Acta crystallogr., **6**, 487 (1953).
[11] J. Owen, J. Appl. Phys., Suppl. **32**, 213 (1961).
[12] I. B. Bersuker, A. V. Ablov, *Chemical Bonding in Complex Compounds*, Kishinev, 1962, p. 62.
[13] K. Nakamoto, M. Margoshes, R. E. Rundle, J. Am. Chem. Soc., **77**, 6480 (1955).
[14] R. E. Rundle, M. Parasol, J. Chem. Phys., **20**, 1487 (1952).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.