

# E.P.R. PHENOMENA IN POLYMERS WITH COORDINATION BONDS

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## Abstract

## Full Text

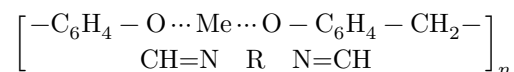
### PHYSICAL CHEMISTRY

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## E.P.R. PHENOMENA IN POLYMERS WITH COORDINATION BONDS

(Presented by Academician I. V. Obreimov on 12 VII 1961)

We obtained electron paramagnetic resonance spectra of coordination polymers containing elements of the transition group—iron and cadmium. Polymers of the following type were studied:



As  $R$ , the groups  $(-\text{CH}_2-)_2$ ,  $(-\text{CH}_2-)_6$ , and



were used. Compounds in which the group  $R$  was absent were also considered. The following polymers were studied: 5,5'-methylene-bis-salicylalethylenediimine (I), 5,5'-methylene-bis-salicylal-hexamethylenediimine (II), 5,5'-methylene-bis-salicylal-*o*-phenylenediimine (III), and methylene-bis-salicylaldimine (IV), and these same polymers containing Cu, Ni, Fe, Co, Zn, Cd. The preparations were obtained in the Laboratory of Special Organic Synthesis of the Chemistry Faculty of Moscow State University by E. G. Rukhadze and V. V. Rod. The samples were finely dispersed powders, poorly soluble in dimethylformamide and tetrahydrofuran.

The e.p.r. spectra were measured on a spectroscope made in the Optical Laboratory of the Institute of Scientific and Experimental Optical Studies of the Academy of Sciences of the USSR by V. A. Kolbasov, M. M. Mukhina, and V. P. Nazarov. During operation the sensitivity of the instrument was not less than  $10^{-11}$  mole of DPPH. Recording was carried out at a klystron frequency of 9035 MHz, with variation of the magnetic field in the range from 0 to 5000 oersted.

### Table 1

	$R$ absent (IV)	$R = (-\text{CH}_2-)_2$ (I)	$R = (-\text{CH}_2-)_6$ (II)	$R = \text{C}_6\text{H}_4$ (III)
Copper				
$g$	2.10	Not studied	2.10	2.0
$\delta H$ , oerst.	150	Not studied	100	210
$P$	1	Not studied	0.8	0.4
Nickel	No signal	No signal	No signal	No signal
Iron				
$g$	2.01	4.14	2.03	No signal
$\delta H$ , oerst.	830	390	650	No signal
$P$	1	$2 \cdot 10^{-3}$	1.6	No signal
Cobalt	Existence of a signal doubtful	No signal	No signal	Not studied
Zinc				
$g$	2.00	2.00	2.00	2.00
$\delta H$ , oerst.	13	12	13	13
$P$	1	0.2	0.1	0.1
Cadmium				
$g$	2.00	No signal	No signal	2.00
$\delta H$ , oerst.	13	No signal	No signal	13
$P$	1	No signal	No signal	0.7

The results obtained are summarized in Table 1. Figure 1 shows the EPR spectra of IV Zn at room temperature and at the temperature of liquid nitrogen. As is seen from Table 1, in polymers with nickel and cobalt, with the exception of IV Co, no resonance absorption was observed. We cannot speak with certainty about the existence of a signal in polymer IV Co, since the presumed absorption line had low intensity, and its position coincided with the position of the signal from the empty resonator. In all the substances studied that contain Cu and Fe, except III Fe, resonance absorption was observed. Polymer IFe gave a very weak signal, which disappeared when the temperature was lowered to that of nitrogen. In polymers with Zn and Cd, despite the absence of paramagnetic metals, a narrow ( $\delta H = 13$  oersted) signal with a  $g$ -factor equal to 2.00 was found. None of the polymers not containing a metal gave resonance. In addition to the compounds listed in Table 1, copper and nickel salicylaldimine monomers were studied. The first of these gave an intense signal with  $\delta H = 190$  oersted and  $g = 2.10$ ; in the second no signals were detected.

**Fig. 1.** EPR signal from polymer IV Zn at room temperature (a) and at the temperature of liquid nitrogen (b)

In Table 1 the intensities of the EPR signals in the series for each metal are compared qualitatively by the amplitude of the derivative signal ( $P$ ). The am-

Fig. 1. EPR signal from polymer IV Zn at room temperature (a) and at the temperature of liquid nitrogen (b)

Figure 1: Fig. 1. EPR signal from polymer IV Zn at room temperature (a) and at the temperature of liquid nitrogen (b)

plitude of the derivative signal (IV) of each metal is taken as unity; there also is given the half-width of the absorption line in oersteds ( $\delta H$ ) (the distance between the points of maximum slope). As indicated above, we were dealing with powder samples; therefore, from the EPR data obtained for polymers, which give only certain average values of the constants of the spin Hamiltonian, one cannot judge unambiguously the configuration of the nearest environment of the metal. However, relying on results obtained for single crystals of similar compounds, it is possible to speak about whether the monomolecular configuration is retained or not retained.

X-ray structural analysis, as well as the work of Maki and McGarvey (1) on the study of EPR in crystals of diamagnetically diluted copper salicylaldehyde, make it possible to assume that the nearest environment of Cu forms a plane square with distances from Cu to N and O equal to 1.94 Å, where nitrogen and oxygen occupy equivalent positions, so that the symmetry of the complex is  $D_{4h}$ .

In work (1) the values  $g_x = 2.04$ ,  $g_y = 2.05$  and  $g_z = 2.20$  were obtained. From these values one can calculate the mean value of the  $g$ -factor for the powder. The calculation gives 2.11. In our measurements  $g = 2.10$ , and is close to  $g$  determined on the basis of averaging. This agreement gives grounds to assert that in the polymer with Cu the symmetry of the complex is preserved and the groups R have almost no influence on the internal configuration. We believe that the symmetry of the complex  $D_{4h}$  is also preserved for nickel; then the absence of signals in nickel compounds can be explained by the fact that in a strong  $D_{4h}$  field the spin triplet is split into two levels, one of which will be degenerate. The initial splitting between the nondegenerate and degenerate levels may be much greater than  $0.3 \text{ cm}^{-1}$ , and in the 3-cm range we shall not observe resonance absorption.

The absence of resonance signals in polymers with cobalt can be explained— can be explained either by the fact that below there is a doublet ( $3/2, -3/2$ ), the transition intensity within which will be small because of selection rules, or by the presence of strong spin-lattice relaxation.

The high intensity of the signals in polymers II Fe and IV Fe compared with I Fe and the absence of a signal in III Fe indicate a sharp difference between the spatial configuration of the nearest environment of II Fe and IV Fe and the configuration of I Fe and III Fe. In a distorted strong field of tetrahedral symmetry, the spin quintet of iron, because of the large separation of the orbital levels from the ground state, is split only weakly. Therefore, when a magnetic

field is applied, the level will behave as a purely spin level and will split into a series of almost equidistant sublevels, transitions between which will correspond to  $g$ -factors close to 2.00. A similar value was observed by us experimentally. This permits the assumption that in compounds IV Fe and II Fe the nearest environment has tetrahedral symmetry. In compounds I Fe and III Fe, however, the symmetry of the complex is lowered to  $D_{4h}$  (a planar square). A field of axial symmetry splits the spin quintet into two doublets (2, -2), (1, -1) and a singlet (0), lying higher (<sup>2, 3</sup>). The disappearance of the signal at  $T = 78^\circ\text{K}$  indicates that the observed resonance transition in I Fe occurs at the (1, -1) level with  $\Delta M = 2$ . In such a transition the  $g$ -factor is close to 4 (in our case 4.14). The strong weakening of the intensity can be explained by a decrease in the population of the level and by the presence of selection rules for transitions with  $\Delta M = \pm 2$ .

In polymers containing Zn and Cd, when the temperature was lowered to that of liquid nitrogen, neither the intensity nor the width of the absorption lines changed. It is possible that here we are dealing with Pauli-type paramagnetism of free electrons.

Thus, analysis of the EPR data has shown that the configuration of the nearest environment of the metal atom in compounds with copper has  $D_{4h}$  symmetry. In polymers VI Fe and II Fe the complex has tetrahedral symmetry, while in I Fe and III Fe it has  $D_{4h}$  symmetry. No definite conclusions about the compounds with Co could be drawn.

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## CITED LITERATURE

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

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