

EPR SPECTROSCOPIC STUDY OF METALLOCOMPLEXES OF
3,6-DICHLOROPICOLINIC ACID

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EPR measurements have been made to obtain the magnetic resonance parameters of cobalt, nickel, manganese, iron, zinc, magnesium, and molybdenum bidentate complexes of 3,6-dichloropicolinic acid (the active ingredient of the herbicide Lontrel) in the solid state and in solution. Upon dissolution in water under normal conditions, all of the complexes preserve the coordination environment of the central ion, thus existing in the undissociated state under native conditions. The broadening of the signals of water-dissolved samples at 300 K indicates partial pairing of electrons and the joining of two or more molecules into polymeric chains.

Pyridinecarboxylic acids play a major role in the vital activity of animal and vegetable organisms [1]. The adjacency of the nitrogen atom and the carboxyl group in picolinic acids is manifested in a capability for complex formation and isolation of metals from metal-containing enzyme systems, and also the capability of curtailing the pool of free metals in a plant. Complexation, particularly with the trace elements that are necessary for the vital activity of a plant cell, may be the reason for the phytotoxicity of a number of compounds [2], including picolinic acids such as fusaric acid and 3,6-dichloropicolinic acid (3,6-DCPA). The possibility of forming bidentate complexes of 3,6-DCPA with Fe, Co, Mo, Ni, Mn, Mg, and Zn was demonstrated in [3]. Complexes of the type $M(3,6-DCPA)_2$ were synthesized under laboratory conditions and isolated in the individual state. However, since all processes in biological systems proceed in a liquid phase, it was of interest to study the behavior of these compounds in aqueous solutions.

In the present work, we have examined the possibility of existence, under native conditions, of seven metallocomplexes of 3,6-DCPA (the active ingredient of the herbicide Lontrel), on the basis of a study of their electronic structure.

EXPERIMENTAL

The synthesis and purification of the complexes $Co(3,6-DCPA)_2$ (I), $Mn(3,6-DCPA)_2$ (II), $Ni(3,6-DCPA)_2$ (III), $Fe(3,6-DCPA)_2$ (IV), $Zn(3,6-DCPA)_2$ (V), $Mg(3,6-DCPA)_2$ (VI), and $Mo(3,6-DCPA)_2$ (VII) were carried out in accordance with [3]. Elemental analyses indicated the following contents of impurities in the samples: Mn in original $Co(ac)_2 \approx 10^{-11}$ to 10^{-12} M; Fe in original Zn and Mo $\approx 10^{-10}$ M. No impurities could be detected in the synthesized complexes.

The EPR spectra were taken on a Varian E-104 spectrometer (3-cm range), on powders at 300 K and aqueous solutions at 77 and 300 K. Calibration of the g-factors was performed using the reference substance DPPH with $g = 2.0036$.

RESULTS AND DISCUSSION

In Fig. 1 we show the EPR spectrum of a finely dispersed sample of $Co(ac)_2$, which was the starting substance in synthesizing the complex (I), and also the EPR spectrum of the complex (I). The original $Co(ac)_2$ had the following magnetic resonance parameters: $g_{\perp} = 2.268$, $g_{\parallel} = 1.934$, $g_{av} = 2.157$. These values are consistent with those reported in the literature for complexes of cobalt with other ligands [4]. The EPR spectrum of (I) is a doublet with $g = 3.0825$ and $a = 305$ Oe. Such a transformation of the EPR spectrum indicates significant structural-conformational changes in the coordination sphere of the central ion. Apparently, however, upon dissolution in water, the complex (I) preserves its structure. In the EPR

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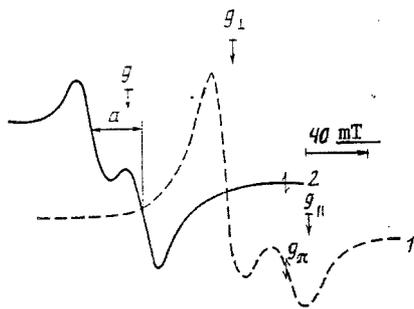


Fig. 1. EPR spectra of original $\text{Co}(\text{ac})_2$ (1) and complex $\text{Co}(3,6\text{-DCPA})_2$ (2) in finely dispersed state.

spectrum of an aqueous solution of (I) we observe six equidistant lines with $g = 2.00$ and $a = 84$ Oe, possibly from traces of manganese ion. The EPR spectrum of this sample at 77 K is a doublet with $g = 2.332$ and $a = 710$ Oe [5]. Apparently, in solution at room temperature, changes take place in the environment of the paramagnetic center as a result of solvation, changes that are partly reversed upon cooling.

The EPR spectrum of finely dispersed $\text{Mn}(\text{ac})_2$ powder is two-component, with $g_1 = 2.186$ and $g_2 = 1.822$, and with a distance between components 600 Oe [6]. The complex (II) synthesized from this material gives a spectrum with $g = 2.112$ and $\Delta H = 430$ Oe. Such a change could result from an increased contribution of the orbital moment of motion of the unpaired electron. Upon dissolution of (II) in water, a sextet of lines is registered, with $g = 2.001$ and $a = 73$ Oe (300 K), indicating localization of the unpaired electron on the central nucleus of the complex, with a considerable distance between ions [7]. On this basis we can assume that compound (II) partially dissociates in water.

In Fig. 2 we show EPR spectra of the original $\text{Ni}(\text{ac})_2$ and the complex (III) synthesized from this material. At 300 K, the spectrum of the original material is a broad singlet ($\Delta H = 720$ Oe) with $g = 2.123$, which is characteristic for compounds of similar type [8]. On the background of this singlet, a weakly resolved triplet is observed, with $g = 2.069$ and $a = 150$ Oe (Fig. 2). The EPR spectrum of the complex (III) is essentially no different in form from that of the original compound; the only observable difference is a slight decrease in width of the individual components of the spectrum and an increase in the g -factor of the triplet to 2.123, which may indicate a slight change in environment of the paramagnetic ion. Upon dissolution of the complex (III) in water, we observe an EPR spectrum with $g = 2.019$ and $\Delta H = 356$ Oe. These are close to the values reported in the literature for Ni compounds with other ligands [9]. When the temperature is lowered to 77 K, the EPR spectrum of (III) is shifted downfield ($g = 2.580$) and broadened to 530 Oe; this is probably due to "superparamagnetic" properties of the sample [10] as a result of a certain structurization of the immediate environment of the central ion; this may lead to a certain change in conformation of the complex.

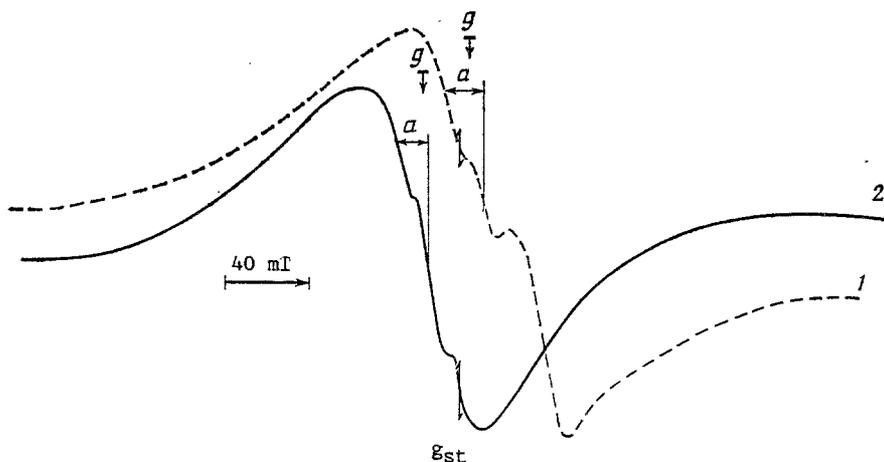


Fig. 2. EPR spectra of original $\text{Ni}(\text{ac})_2$ (1) and complex $\text{Ni}(3,6\text{-DCPA})_2$ (2) in finely dispersed state.

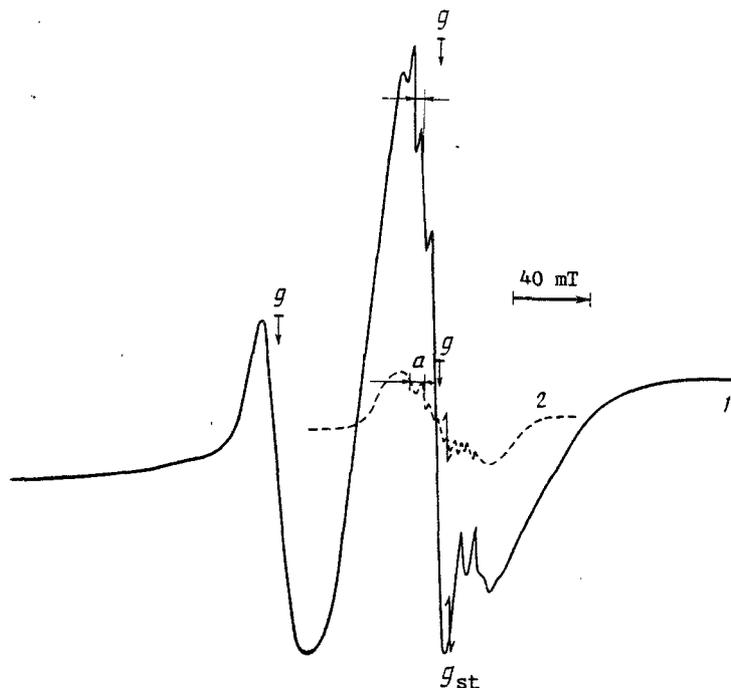


Fig. 3. EPR spectra of complex $\text{Mg}(3,6\text{-DCPA})_2$ in finely dispersed state (1) and in solution (2).

The EPR spectrum of powdered $\text{Fe}(\text{lactate})_2$ at 300 K is an exchange-broadened singlet ($\Delta H = 920$ Oe) with $g = 2.018$. The signal of the finely dispersed complex (IV) has an axial g-tensor with $g_{\parallel} = 1.803$, $g_{\perp} = 2.228$, and $g_{\text{av}} = 2.080$. Such a change in the magnetic resonance parameters indicates structural and conformational changes of the iron ion in the synthesis: the transition ($\text{Fe}^{2+} \rightarrow \text{Fe}^{4+}$). Upon dissolving (IV) in water at 300 K, its EPR spectrum is transformed to a broad singlet (600 Oe) with $g = 2.052$; this can be explained by molecular motions of some sort of "clusters" of 10-20 complexes in the dissolved sample. Upon cooling the solution of the complex (IV) to 77 K, its EPR spectrum is shifted downfield ($g = 2.075$) and narrowed to 242 Oe; this can be explained by a change in the electron relaxation times and by weak manifestation of anisotropy of the g-tensor. The magnetic resonance parameters obtained for all iron samples are in agreement with what has been reported in the literature [11, 12].

The symmetric singlet of the complex (V) has a line width of 850 Oe and $g = 2.147$. Upon dissolving this sample in water (300 K), the spectrum is shifted upfield ($g = 2.019$) and narrowed to $\Delta H = 540$ Oe. Dissolution leads to an increase of the S-contribution to the molecular orbital occupied by the unpaired electron, and to a decrease in exchange electron interaction. Cooling the solution of (V) to 77 K narrows its EPR line to 77 Oe and changes the g-factor slightly (2.066); this may be due to a change in electron relaxation times and a certain modification of the MO of the unpaired electron [13].

In Fig. 3 we show EPR spectra of the complex (VI) in the finely dispersed state (continuous curve) and in aqueous solution. At 300 K, the spectrum of the powdered sample is a doublet with $g = 2.314$ and $a = 790$ Oe. After dissolving the sample in water, the EPR spectrum is converted to a symmetric, exchange-broadened singlet with $g = 2.021$ and $\Delta H = 470$ Oe with a superposed weak sextet with $g = 2.012$ and $a = 67$ Oe. The substantial difference of the g-factor from the pure spin factor and the form of the spectrum indicate a significant contribution from orbital magnetic moment to the overall magnetic moment of the unpaired electron, i.e., a contribution from p- and d-orbitals of the ligand and metal atoms to the orbital occupied by the unpaired electron. At 77 K, the spectrum of the solution is shifted upfield ($g = 2.063$) without any significant change in line width. This fact may indicate that the coordination spheres of the crystalline and water-dissolved samples are not identical [14].

In Fig. 4 we show EPR spectra of the complex (VII) in the finely dispersed state and in solution. The spectrum of the powdered (VII) represents a superposition of individual spectra of nonequivalent paramagnetic centers: a broad singlet (45 Oe) with $g = 1.925$ and a

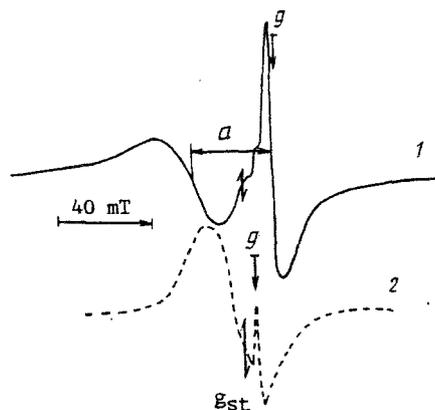


Fig. 4. EPR spectra of complex $\text{Mo}(3,6\text{-DCPA})_2$ in finely dispersed state (1) and in solution (2).

doublet with $g = 2.034$ and $a = 290$ Oe. Upon dissolving the sample in water, a broad singlet (217 Oe) is registered with $g = 2.026$, with a superposed narrower singlet ($\Delta H = 22$ Oe) with $g = 1.967$. Such a transformation of the spectrum indicates that the braking of molecular motions of the complex has been released as a result of dissolution [15]. The EPR spectrum of the frozen (77 K) aqueous solution of (VII) represents a superposition (the same as in the case of the finely dispersed sample) of a broad doublet with $g = 2.000$ and $a = 240$ Oe, and a singlet with $g = 1.928$ and $\Delta H = 90$ Oe. Thus, we can say that the structural-conformational features of sample (VII) have been preserved, and that this complex has a considerable mobility in the dissolved state.

On the basis of the data obtained in this work, we can assume that stable metallocomplexes of 3,6-DCPA are formed as a result of the synthesis. These complexes differ from the original salts in the structure of the coordination sphere of the central ion, and are probably analogous to the complex $\text{Cu}(3,6\text{-DCPA})_2$ [16]. Upon dissolution in water, all of the complexes, with the possible exception of (II), apparently preserve the coordination environment of the central nucleus, as is evident from the EPR spectra of the frozen solutions. Water may enter into the immediate environment of the central ion at the expense of unused coordination sites of the metal, thus increasing the degree of freedom of the solvated complex. The slight broadening of the signals of the water-dissolved samples at 300 K indicates partial pairing of electrons, i.e., a joining of two or more molecules into polymeric chains, possibly analogous to what was described in [16].

Thus, these metallocomplexes, under native conditions, exist as a single unit, participating in the undissociated state in further complexation up to complete filling of the coordination sphere of the metal.

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