

ESR spectra of copper(II) complexes in the solids

M. VALKO, P. PELIKÁN, S. BISKUPIČ, and M. MAZÚR

*Department of Physical Chemistry, Faculty of Chemical Technology,
Slovak Technical University, CS-812 37 Bratislava*

Received 27 February 1990

Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

The ESR spectra of $\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{sal})_2(2\text{-pycar})_2$ and $\text{Cu}(\text{sal})_2(3\text{-pycar})_2$ (sal = salicylate ion; pycar = pyridinemethanol) at 77 K were studied. The spin Hamiltonian parameters indicate that the unpaired electron is in the antibonding ψ_{b1g} molecular orbital. The ESR spectra of pentacoordinated Cu(II) complexes of the $[\text{Cu}(\text{phen})_2\text{X}]\text{ClO}_4$ (phen = 1,10-phenanthroline; X = Cl, Br) exhibit axial symmetry. The compressed trigonal-bipyramidal (TBP) configuration with D_{3h} symmetry points ($|z^2 >$ ground electronic state) is consistent with the spin Hamiltonian parameters of the ESR spectra. The ESR spectra of the pentacoordinated complex of $[\text{Co}(1,3\text{-diaminopropane})_3][\text{CuCl}_5] \cdot 3\text{H}_2\text{O}$ have been studied in the temperature range 100–290 K. At higher temperature ($T > 160$ K) the ESR spectra change their symmetry into the orthorhombic one, the square pyramidal (SP) structure of $[\text{CuCl}_5]^{3-}$ polyhedrons is violated and a dynamical transition between the SP and TBP structures takes place.

Изучены ЭПР спектры $\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{sal})_2(2\text{-pycar})_2$ и $\text{Cu}(\text{sal})_2(3\text{-pycar})_2$ (sal = ион салицилата; пycар = пиридинметанол) при 77 К. Спиновые параметры Гамильтона показывают, что неспаренный электрон находится в антисвязующем ψ_{b1g} молекулярном орбитале. ЭПР спектры пентакоординированных Cu(II) комплексов $[\text{Cu}(\text{phen})_2\text{X}]\text{ClO}_4$ (phen = 1,10-фенантролин; X = Cl, Br) показывают аксиальную симметрию. Сжатая тригональнوبيрамидальная (ТБП) конфигурация с D_{3h} симметричными пунктами ($|z^2 >$ основное электронное состояние) совпадает со спиновыми параметрами Гамильтона ЭПР спектров. ЭПР спектры пентакоординированного комплекса $[\text{Co}(1,3\text{-диаминопропан})_3][\text{CuCl}_5] \cdot 3\text{H}_2\text{O}$ были изучены в температурном диапазоне 100–290 К. При повышенной температуре ($T > 160$ К) ЭПР спектры изменяют свою симметрию в орторомбическую, причем состоится превращение квадратно пирамидальной (КП) структуры $[\text{CuCl}_5]^{3-}$ полигедронов в нарушенную и динамически переходную между КП и ТБП структурами.

The basic object of ESR studies in the transition metal complexes is to obtain as much information as possible about the metal-to-ligand bond, the unpaired electron distribution and the order of the energy levels. Measurements on

complexes of many transition metals have resulted in a large quantity of data, and a reasonably good picture of the bonding in many groups of complexes now available.

Many inorganic chemists are now using ESR measurements for studying copper(II) complexes in the solid state [1—4]. Electron spin resonance (ESR) plays an important role in the deeper understanding of the copper with respect to its physiological significance in copper-containing compounds [5].

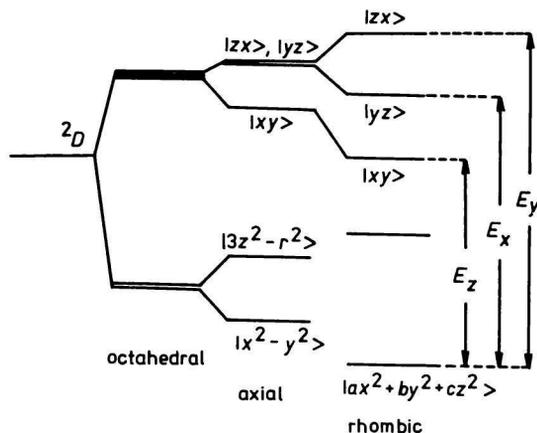
Generally, the greatest amount of information concerning nuclear or paramagnetic sites in solids can be obtained from measurements in single crystals. However, there are two fundamental reasons for using powdered materials in magnetic resonance studies. Firstly, the most obvious is that some materials are available only in powdered form. Secondly, frozen solutions, glasses and amorphous materials are inherently “powders” in the sense that they can be viewed as an ensemble of randomly oriented paramagnetic sites. Experiments on single crystals, although more precise, can be time-consuming and unnecessarily tedious when compared to the speed and simplicity possible with powdered samples.

In a single crystal, the resonance field or frequency depends on its orientation with respect to the applied magnetic field. The resonance condition is calculated from the energy eigenvalues of the spin Hamiltonian. In polycrystalline materials, powders or glasses the paramagnetic sites are randomly oriented with respect to the applied field. Then the magnetic resonance spectrum, referred to as a “powder pattern”, is an average over the resonance conditions for all possible orientations of the paramagnetic site.

For copper(II) in most environments, the ground state magnetism is essentially spin only and the orbital motion is said to be “quenched”. Since copper(II) has one unpaired electron in its $3d^9$ configuration, the “effective” spin is equal to the actual spin of the free ion $S = 1/2$. The Zeeman splitting, or g factors are shifted from the free-electron value of 2.0023 by spin-orbit coupling of the ground state to excited states.

The 2D free ion ground state of copper(II) ($3d^9$) may be split by an octahedral crystal field to give a doublet state lowest and triplet state uppermost in a $3d^1$ “hole” formalism. In a real representation, the orbitals may be written as $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ for the doublet and $|xy\rangle$, $|xz\rangle$ and $|yz\rangle$ for the triplet (Fig. 1). The doublet splitting is attributed to the Jahn—Teller effect [6, 7], which results from a coupling of electronic and vibrational states, but it may also be due in part simply to a low symmetry crystal field arising from the symmetry of the arrangement of atoms about the copper(II) ion. In orthorhombic symmetry the ground state must be a linear combination of $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$.

Fig. 1. Schematic energy level diagram for copper(II) considered as a $3d^1$ hole configuration in octahedral, tetragonal (axial) and orthorhombic fields.



Analysis of the ESR spectra of Cu(II) complexes

In frozen solutions or powder samples, it is assumed that all orientations of the complexes with respect to the applied magnetic field are possible. Thus the general expression for the ESR line shape must be averaged over the elementary angular volume $d\Omega = \sin\Theta d\Theta d\Phi$. Therefore for the total line shape we may write the following expression [8]

$$f(B) = N \sum_i \sum_{\Theta} \sum_{\Phi} P(\Theta, \Phi, i) G(B, \Theta, \Phi, i) \Delta \cos \Theta \Delta \Phi \quad (1)$$

where N is normalization constant, $P(\Theta, \Phi, i)$ is the probability of the i -th spectral transition, $G(B, \Theta, \Phi, i)$ is the line shape function (for the ESR spectra Lorentz or Gauss type derivative function can be used); B is the value of external magnetic field induction, Θ and Φ are polar angles which define orientation of the crystal with respect to the external magnetic field.

It has proved difficult to obtain an exact match between experimental and computer simulated curves in every detail of line position or line shape. This problem can be overcome using the optimization procedure. This procedure can be based on the minimization of the error function according to the relation [8]

$$\Psi = \sum_B (f_{\text{exp}}(B) - f(B))^2 \quad (2)$$

where $f_{\text{exp}}(B)$ are the experimental spectra points, and $f(B)$ theoretical points given by eqn (1).

Analysis of the g -tensor of hexacoordinated copper(II) complexes allows an unambiguous assignment of the ground state and the nature of the distortion. Let us consider the simple case of a tetragonal distortion which may either shorten or lengthen the axial copper—ligand bonds. If there is a lengthening of the bond, the $|z^2\rangle$ orbital is stabilized and the unpaired electron will be in an orbital of b_{1g} symmetry (mainly $|x^2 - y^2\rangle$). The g -values are given by

$$g_{\perp} = g_e - 2\lambda/\Delta E(b_{1g} - e_g) \quad (3)$$

$$g_{\parallel} = g_e - 8\lambda/\Delta E(b_{1g} - b_{2g}) \quad (4)$$

where λ is spin-orbit constant and $g_{\parallel} > g_{\perp} > g_e$. An example of this is $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ where $g_{\parallel} = 2.400$ and $g_{\perp} = 2.099$ [9].

On the other hand, if there is a shortening of the bond, the $|z^2\rangle$ orbital will be destabilized and will contain the unpaired electron. The g -values are then given by

$$g_{\parallel} = g_e \quad (5)$$

$$g_{\perp} = g_e - 6\lambda/\Delta E(a_{1g} - e_g) \quad (6)$$

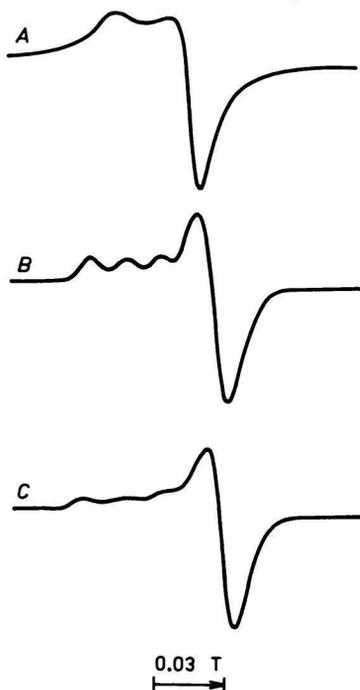


Fig. 2. ESR spectra of the $\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$ (A); $\text{Cu}(\text{sal})_2(2\text{-pycar})_2$ (B); $\text{Cu}(\text{sal})_2(3\text{-pycar})_2$ (C).

So $g_{\perp} > g_{\parallel} \approx g_e$. Examples of this case are rather rare, but the effect is present when Cu^{2+} ions are substituted for Zn in ZnWO_4 [10].

Considerable attention has been paid to the study of carboxylato-copper(II) complexes from the chemical and biological point of view. We studied the ESR spectra of $\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{sal})_2(2\text{-pycar})_2$ and $\text{Cu}(\text{sal})_2(3\text{-pycar})_2$ (sal = salicylate ion; pycar = pyridinemethanol). The spectra were recorded at 77 K and are presented in Fig. 2. They showed effective axial symmetry and were interpreted using the spin Hamiltonian [11]

$$\hat{H} = \beta B g \hat{S} + \hat{I} A \hat{S} \quad (7)$$

where the symbols have their usual meaning [11]; $S = 1/2$ and $I = 3/2$ for Cu^{2+} .

The spectral parameters obtained using the above-mentioned optimization method are summarized in Table 1. Spin Hamiltonian parameters of all compounds under study show $g_{\perp} < g_{\parallel}$. This indicates that the unpaired electron is in the antibonding ψ_{b1g} molecular orbital, which clearly demonstrates an elongated tetragonal bipyramidal coordination around Cu(II), which is in good agreement with X-ray data [12].

Table 1

ESR parameters of the copper(II) complexes $\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$ (I), $\text{Cu}(\text{sal})_2(2\text{-pycar})_2$ (II), and $\text{Cu}(\text{sal})_2(3\text{-pycar})_2$ (III)

Compound	g_{\perp}	g_{\parallel}	$\frac{ A_{\perp} \cdot 10^4}{\text{cm}^{-1}}$	$\frac{ A_{\parallel} \cdot 10^4}{\text{cm}^{-1}}$
I	2.065	2.310	—	—
II	2.075	2.304	12.9	154.1
III	2.060	2.310	10.2	170.0

While the tendency to form tetracoordinated or hexacoordinated compounds is a dominant feature of the structure chemistry of copper(II), the synthesis and properties of pentacoordinated copper(II) compounds have attracted interest only recently [3, 4].

In pentacoordinated Cu(II) complexes of the $[\text{Cu}(\text{phen})_2\text{X}]\text{ClO}_4$ (phen = 1,10-phenanthroline; X = Cl, Br), distortion of the CuN_4X chromophore from the trigonal bipyramidal geometry (TBP) to the square pyramidal geometry (SP) is conceivable [13]. In the case of the compressed configuration of the coordination polyhedron, the perpendicular and parallel components of

the axially symmetrical g -tensor can be described in the crystal field theory approximation, by the equations [14]

$$g_{\perp} = g_e + 6\lambda/\Delta E(a'_1 - e'') \quad (8)$$

$$g_{\parallel} = g_e \quad (9)$$

The shape of the ESR spectra of the systems investigated (Fig. 3) indicates that all of them exhibit axial symmetry and the relation $g_{\perp} > g_{\parallel} \approx g_e$ holds for the components of the axial g -tensor of all the spectra (Table 2). The compressed TBP configuration with D_{3h} symmetry points ($|z^2| >$ ground electronic state) is consistent with the parameters of the ESR spectra obtained, which satisfy the above-mentioned relation.

The ESR spectra of pentacoordinated complex of $[\text{Co}(1,3\text{-diaminopropane})_3][\text{CuCl}_3] \cdot 3\text{H}_2\text{O}$ in polycrystalline state have been studied in the temperature range 100—290 K.

As it was mentioned above the $\text{Cu(II)}L_5$ polyhedrons can occur in two different geometric arrangements: 1. in trigonal bipyramidal structure (TBP) (symmetry D_{3h}); 2. in tetragonal pyramidal structure (SP) (symmetry C_{4v}). These

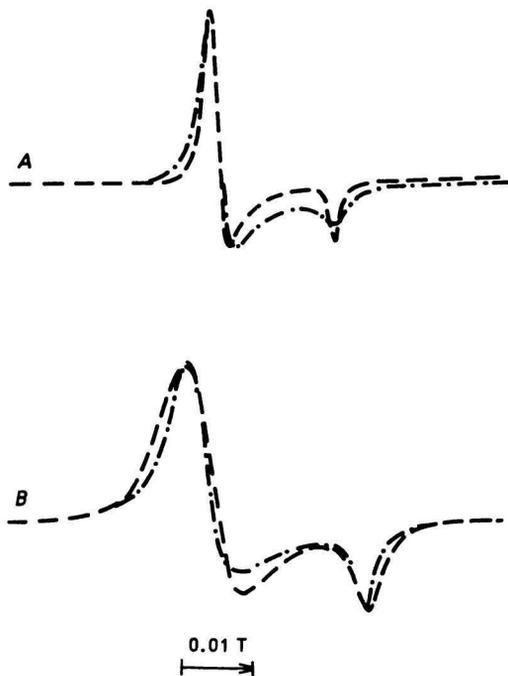


Fig. 3. Experimental (—) and simulated (---) spectra of $[\text{Cu}(\text{bipy})_2\text{Cl}]\text{ClO}_4$ (A) and $[\text{Cu}(\text{bipy})_2\text{Br}]\text{ClO}_4$ (B).

Table 2

Spin Hamiltonian parameters of the ESR spectra of $[\text{Cu}(\text{phen})_2\text{Cl}]\text{ClO}_4$ (I) and $[\text{Cu}(\text{phen})_2\text{Br}]\text{ClO}_4$ (II)

Compound	g_{\perp}	g_{\parallel}	$\frac{\Delta B_{\perp} \cdot 10^4}{\text{T}}$	$\frac{\Delta B_{\parallel} \cdot 10^4}{\text{T}}$
I	2.184	2.008	22.7	12.1
II	2.178	2.023	40.3	18.9

two configurations can pass from one to other by the Berry rotation [15] mechanism. The activated state of this rotation has C_{2v} symmetry.

Fig. 4 presents some examples of the measured ESR spectra of the $[\text{Co}(1,3\text{-diaminopropane})_3][\text{CuCl}_5] \cdot 3\text{H}_2\text{O}$ complex in polycrystalline state obtained at different temperatures.

The principal values of the g -tensor elements obtained for the $[\text{Co}(1,3\text{-diaminopropane})_3][\text{CuCl}_5] \cdot 3\text{H}_2\text{O}$ (Table 3) imply an axially symmetric system of the SP structure of the $[\text{CuCl}_5]^{3-}$ ion as the relation $g_{\parallel} > g_{\perp} > g_e$ is fulfilled. A very small temperature dependence of the values g_{\perp} and g_{\parallel} points out a considerable rigidity of the SP structure of the $[\text{CuCl}_5]^{3-}$ ions which is stabilized

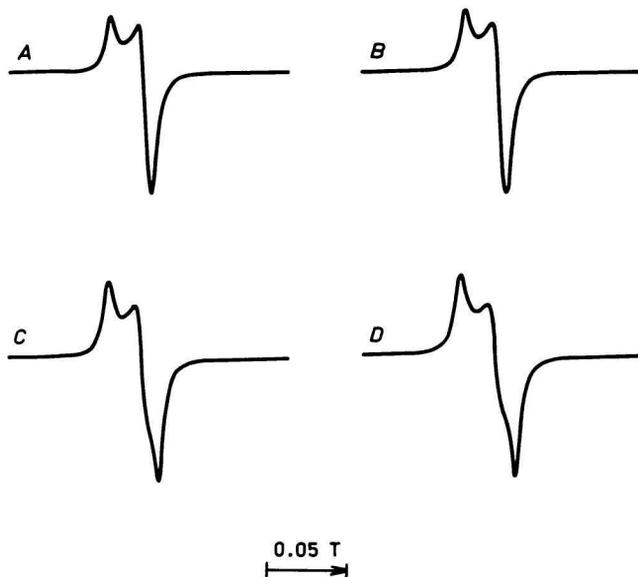


Fig. 4. ESR spectra of the $[\text{Co}(1,3\text{-diaminopropane})_3][\text{CuCl}_5] \cdot 3\text{H}_2\text{O}$ measured at different temperatures: 100 K (A), 160 K (B), 220 K (C), 290 K (D).

Table 3

Temperature dependence of the ESR parameters of $[\text{Co}(\text{1,3-diaminopropane})_3][\text{CuCl}_5] \cdot 3\text{H}_2\text{O}$

T/K	g_1	g_2	g_3 or	ΔB_1	ΔB_2	ΔB_3 or
	g_{\perp}		g_{\parallel}	$\frac{\Delta B_{\perp}}{10^{-4} \text{ T}}$		$\frac{\Delta B_{\parallel}}{10^{-4} \text{ T}}$
100		2.106	2.248	52.24		43.04
140		2.107	2.248	54.83		43.53
160	2.105	2.107	2.248	64.44	55.34	46.07
180	2.082	2.108	2.249	66.24	56.79	50.94
220	2.069	2.107	2.250	66.52	63.15	55.02
260	2.068	2.107	2.249	72.36	71.49	56.07
290	2.063	2.109	2.261	78.20	72.21	60.09

by the weak hydrogen bonds of diaminopropane (contained in the complex cation) to chlorine atoms of the $[\text{CuCl}_5]^{3-}$ anion.

At higher temperatures ($T > 160 \text{ K}$) the ESR spectra change their symmetry into the orthorhombic one and the SP structure of $[\text{CuCl}_5]^{3-}$ polyhedrons is violated (under simultaneous breaking of the weak hydrogen bonds) and a dynamical transition (Berry rotation) between the SP and TBP structures takes place. At every temperature a certain equilibrium of the SP and TBP polyhedrons is established to which the incident orthorhombic ESR spectrum corresponds. The portion of the TBP polyhedrons increases with the increased temperature, which manifests itself in increasing asymmetry of the ESR spectra.

Acknowledgements. The authors wish to thank Professor M. Melník for some of the specimens used in this investigation. The art work for the figures was provided by D. Valková, for which we are especially grateful.

References

- Hoffman, S. K., Goslar, J., and Szczepaniak, L. S., *Phys. Rev.* B37, 7331 (1988).
- Maki, A. H. and McGarvey, B. R., *J. Chem. Phys.* 29, 31 (1958).
- Reinen, D. and Friebel, C., *Inorg. Chem.* 23, 791 (1984).
- Pelikán, P., Valko, M., Kováčik, I., Mazúr, M., and Staško, A., *Chem. Papers* 44, 477 (1990).
- Melník, M., *DrSc. Thesis*. Slovak Technical University, Bratislava, 1987.
- Jahn, H. A. and Teller, E., *Proc. R. Soc. London*, A161, 220 (1937).
- Boča, R., Breza, M., and Pelikán, P., *Structure and Bonding* 71, 57 (1989).
- Valko, M., Pelikán, P., Biskupič, S., and Staško, A., to be published.
- Lewis, W. B., Alei, M., and Morgan, L. O., *J. Chem. Phys.* 45, 4003 (1966).
- Sroubek, Z. and Zdanský, K., *J. Chem. Phys.* 44, 3078 (1966).

11. Abragam, A. and Bleaney, B., *Electron Paramagnetic Resonance of Transition Ions*. Clarendon Press, Oxford, 1970.
12. Valach, F., Hoang, N., Dunaj-Jurčo, M., and Melník, M., *Proceedings of the 12th Conference on Coordination Chemistry*. Smolenice, 1989.
13. Ray, N., Hulett, L., Sheahan, R., and Hathaway, B. J., *Inorg. Nucl. Chem. Lett.* 14, 305 (1978).
14. Ballhausen, C. J., *Introduction to Ligand Field Theory*. McGraw-Hill, New York, 1962.
15. Berry, S., *J. Chem. Phys.* 32, 933 (1960).

Translated by M. Valko