Polycrystalline ESR spectra
of the [Co(1,3-diaminopropane)₃][CuCl₅] · 3H₂O complex

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The ESR spectra of the [Co(1,3-diaminopropane)₃][CuCl₅] · 3H₂O complex in polycrystalline state are the subject of the present study. Their analysis indicates the pentacoordinate configuration of the Cu(II) ion. The CuCl₅ chromophore forms tetragonal pyramidal polyhedrons stabilized by the hydrogen bonds with diaminopropane (included in the complex cation). At higher temperatures ($T > 160$ K) a dynamic transition from tetragonal pyramidal to trigonal bipyramidal structure takes place. This transition results in a change of the ESR spectra line shape from the axial to the orthorhombic symmetry.

ЭПР спектры [Co(1,3-диаминопропан)₃][CuCl₅] · 3H₂O комплекса в поликристаллическом состоянии являются предметом данного исследования. Анализ показывает пентакоординационную конфигурацию Cu(II) иона. Хромофор CuCl₅ образует тетрагонально-пирамидальные полигедроны, стабилизированные водородными связями с диаминопропаном (включенного в катионный комплекс). При повышенных температурах ($T > 160$ К) осуществляется динамический переход от тетрагонально-пирамидальной к тригонально-бипирамидальной структуре. Этот переход способствует изменению формы линии ЭПР спектра от аксиальной к орторомбической симметрии.

The Cu(II) compounds form a wide series of polyhedrons of different symmetry. These polyhedrons are usually distorted owing to the Jahn—Teller effect [1, 2]. That is why the considerable attention has been paid to the structure of the Cu(II) complexes. The number of the investigated pentacoordinated complexes of the Cu(II) ion is relatively small at present, because the Cu(II) ions incline to form hexacoordinated or tetracoordinated compounds. Moreover, the majority of the pentacoordinated Cu(II) compounds were prepared only in polycrystalline powder form and this makes the use of X-ray spectroscopy to determine the crystal structure of such compounds impossible.

In the paper presented here the ESR spectra of the [Co(1,3-diaminopropane)$_3$][CuCl$_5$] · 3H$_2$O complex in polycrystalline state have been studied. From the results obtained a structure model of this complex is suggested.

Experimental

The compound [Co(1,3-diaminopropane)$_3$]Cl$_3$ was prepared in the reaction of the CoCl$_2$ · 6H$_2$O aqueous solution with 1,3-diaminopropane in weakly acidic medium (HCl) under the simultaneous oxidation of Co(II) to Co(III) by air oxygen [3].

The [Co(1,3-diaminopropane)$_3$][CuCl$_5$] · 3H$_2$O complex was obtained as a product in the reaction of CuCl$_2$ · 2H$_2$O and [Co(1,3-diaminopropane)$_3$]Cl$_3$ in weakly acidic (HCl) aqueous solution. The reaction gave rise to a clear dark-orange solution. By precipitation with ethanol a yellow-orange precipitate was formed. It was filtered on a glass frit S3, washed with ethanol and dried over solid KOH. The composition of the formed compound was confirmed by the elemental chemical analysis and with the spectra in visible and near infrared region. These spectra exhibit a broad band in the region of $\tilde{v} = 8000$—$11\,000$ cm^{-1}. The absence of bands at $\tilde{v} = 12\,000$—$14\,000$ cm^{-1} excludes a possible existence of tetra- or hexacoordination of the Cu(II) [4, 5].

The ESR spectra of the investigated system were measured on a Bruker 200E-SRC spectrometer in the X-band region with variable temperature unit.

Results

The ESR spectra of the investigated system were measured at various temperatures in the range from 100 to 290 K. The obtained spectra were numerically evaluated using the automatic optimization procedure based on the minimization of the functional [6]

$$F = \sum_B (f_{\exp}(B) - f(B))^2 = \min \tag{1}$$

where $f_{\exp}(B)$ are the experimental spectrum points and $f(B)$ are the theoretical points given by the equation

$$f(B) = N \sum_i \int_\Theta \int_\Phi P(\Theta, \Phi, i)\, G(B, \Theta, \Phi, i) \sin \Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi \tag{2}$$

In this equation N is the normalization constant; the summation over i involves all spectral transitions; $G(B, \Theta, \Phi, i)$ is the line shape function (the Lorentz form was used); B is the value of external magnetic field induction; Θ and Φ are polar angles defining the orientation of the system under study to the external magnetic field; $P(\Theta, \Phi, i)$ is the spectral i-th transition probability. This transition probability is given by the equation

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$$P(\Theta, \Phi, i) = g_1^2 g_2^2 \sin^2 \Theta + g_2^2 g_3^2 (\sin^2 \Theta + \cos^2 \Theta \cos^2 \Phi) + \\ + g_3^2 g_1^2 (\cos^2 \Phi + \cos^2 \Theta \sin^2 \Phi) \tag{3}$$

where g_1, g_2, and g_3 are the principal elements of g-tensor.

Functional (2) can be transformed into a more convenient form for numerical optimization by replacing the double integral by double summation and using the identity $\sin \Theta \, d\Theta = -d(\cos \Theta)$

$$f(B) = -N \sum_i \sum_\Theta \sum_\Phi P(\Theta, \Phi, i) \, G(B, \Theta, \Phi, i) \, \Delta\cos \Theta \, \Delta\Phi \tag{4}$$

As $\Delta\cos \Theta$ and $\Delta\Phi$ may be chosen equidistantly, they can be included into the normalization constant. Then the line shape function suitable for computer optimization may be written in the form

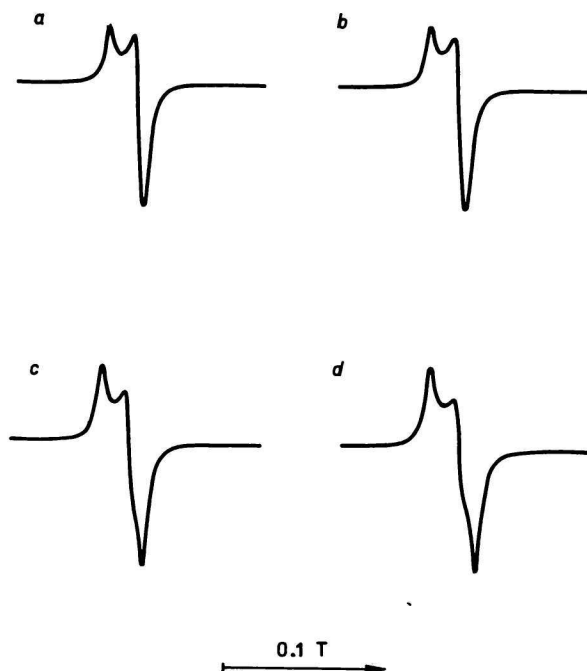$$f(B) = N^* \sum_i \sum_\Theta \sum_\Phi P(\Theta, \Phi, i) \, G(B, \Theta, \Phi, i) \tag{5}$$

Fig. 1. ESR spectra of the [Co(1,3-diaminopropane)$_3$][CuCl$_5$] · 3H$_2$O complex measured at different temperatures: a) $T = 100$ K; b) $T = 160$ K; c) $T = 220$ K; d) $T = 290$ K.

where N^* is the normalization constant including the equidistant values of $\Delta\cos\Theta$ and $\Delta\Phi$. The gradient method according to *Fletcher—Powell* [7] was used as optimization method.

Fig. 1 presents some examples of the measured ESR spectra of the [Co(1,3--diaminopropane)$_3$][CuCl$_5$] · 3H$_2$O complex in polycrystalline state obtained at different temperatures. The principal values of the g-tensor elements as well as the values of the spectral line shape half-widths are given in Table 1. This table involves also some statistical characteristics which correspond to the visually obtained spin Hamiltonian parameters. This table illustrates the necessity of numerical optimization of these parameters. It should be mentioned here that the interpretations of the ESR spectra of randomly oriented radicals in solids based on computer optimization procedure are rare up to this time. The values of the numerically optimized spin Hamiltonian parameters and their standard deviations are listed in Table 2.

Discussion

The Cu(II)L$_5$ (L = NH$_3$, Cl$^-$, Br$^-$) polyhedrons represent a relatively rare case of pentacoordinated Cu(II) complexes with homogeneous monodentate

Table 1

Parameters of ESR spectra of the [Co(1,3-diaminopropane)$_3$][CuCl$_5$] · 3H$_2$O complex as a function of temperature[a]

T K	Type[b]	g_1 $g_\perp$	g_2	g_3 or g	ΔB_1 $\Delta B_\perp$	ΔB_2	ΔB_3 or ΔB	Correlation coefficient	R factor
100	R	2.091		2.246	50.00		40.00	0.6517	0.608
	O	2.106		2.248	52.24		43.04	0.9003	0.079
140	R	2.091		2.246	50.00		40.00	0.6427	0.679
	O	2.107		2.248	54.83		43.53	0.8868	0.072
160	R	2.091		2.246	50.00		40.00	0.6478	0.634
	O	2.105	2.107	2.248	64.44	55.34	46.07	0.8178	0.202
180	R	2.091		2.246	50.00		40.00	0.6478	0.634
	O	2.082	2.108	2.249	66.24	56.79	50.94	0.8023	0.487
220	R	2.055	2.126	2.258	70.00	70.00	65.00	0.6447	0.761
	O	2.069	2.107	2.250	66.52	63.15	55.02	0.8188	0.401
260	R	2.055	2.126	2.258	70.00	70.00	65.00	0.6447	0.761
	O	2.068	2.107	2.249	72.36	71.49	56.07	0.8247	0.451
290	R	2.055	2.126	2.258	70.00	70.00	65.00	0.6394	0.791
	O	2.063	2.109	2.261	78.20	72.21	60.09	0.7563	0.429

a) Half-widths of spectral lines are given in 10^{-4} T.

b) R — Parameters read visually; O — optimized parameters.

Optimum parameters of ESR spectra of the $[Co(1,3-diaminopropane)_3][CuCl_5] \cdot 3H_2O$ complex and their standard deviations[a]

T/K	g_1	$g_\perp$	g_2	g_3 or $g_\parallel$	ΔB_1	$\Delta B_\perp$	ΔB_2	ΔB_3 or $\Delta B_\parallel$
100		2.1056		2.2476		52.24		43.04
		(0.00005)		(0.00004)		(0.003)		(0.008)
140		2.1068		2.2478		54.83		43.53
		(0.00005)		(0.00004)		(0.003)		(0.007)
160	2.1052	2.1068	2.1068	2.2481	64.44	55.34		46.07
	(0.0001)	(0.0001)		(0.0001)	(0.008)	(0.007)		(0.020)
180	2.0821		2.1081	2.2492	66.24	56.79		50.94
	(0.0001)		(0.0001)	(0.0002)	(0.004)	(0.002)		(0.020)
220	2.0693		2.1072	2.2503	66.52	63.15		55.02
	(0.0003)		(0.0004)	(0.0004)	(0.03)	(0.02)		(0.03)
260	2.0682		2.1071	2.2485	72.36	71.49		56.07
	(0.0004)		(0.0004)	(0.0004)	(0.02)	(0.02)		(0.05)
290	2.0634		·2.1095	2.2614	78.20	72.21		60.09
	(0.0004)		(0.0004)	(0.0004)	(0.02)	(0.02)		(0.06)

a) Half-widths of spectral lines are given in 10^{-4} T.

ligand sphere [4, 8, 9]. The results of the structural analysis [5, 8, 10, 11], the electrostatic calculations [12—14] as well as the results of the ESR spectroscopy measurements [9, 15—17] have shown that the $Cu(II)L_5$ polyhedrons can occur in the different geometric arrangements:

i) In trigonal bipyramidal structure (TBP) (symmetry $\mathbf{D}_{3h}$) where the distances of axial ligands are shorter in comparison with equatorial ligands distances [8, 10, 11, 18].

ii) In tetragonal pyramidal structure (SP) (symmetry $\mathbf{C}_{4v}$) where the distance of apical ligand is longer in comparison with equatorial ligands distances [4]. In addition the Cu(II) ion is shifted above the equatorial ligands plane.

These two configurations can pass one to other by the *Berry* rotation [19] mechanism. The activated state of this rotation has $\mathbf{C}_{2v}$ symmetry. The scheme of the d-electron levels splitting of the above-mentioned geometries is shown in Fig. 2. The ground electron state for SP structure ($\dot{\mathbf{C}}_{4v}$) is $|B_1\rangle = |x^2 - y^2\rangle$ while for TBP structure ($\mathbf{D}_{3h}$) it is $|A_1\rangle = |z^2\rangle$. This difference in electron ground state is unambiguously reflected in the ESR spectra which exhibit axial symmetry [9, 15] because:

i) $g_\perp > g_\parallel \approx g_0$ in the case of TBP structure;

ii) $g_\parallel > g_\perp > g_0$ in the case of SP structure.

The ESR spectra of the $K[Cu(NH_3)_5](PF_6)_3$ complex in polycrystalline state are axially symmetric ($g_\parallel = 2.26$; $g_\perp = 2.06$) at low temperatures ($T < 300$ K) and reflect the real molecular structure of the four $[Cu(NH_3)_5]^{2+}$ SP polyhedrons which are placed in one unit cell. The apical Cu—N bonds of these polyhedrons [5] have parallel or antiparallel orientations ("ferrodistortive order"). The line shape of ESR spectra indicates a rather small exchange coupling of individual polyhedrons. At the temperatures above 300 K the spectrum gets isotropic [9] because of the complete pseudorotation of the $[Cu(NH_3)_5]^{2+}$ polyhedron. This rotation evokes full dynamical averaging of the Cu—N bonds.

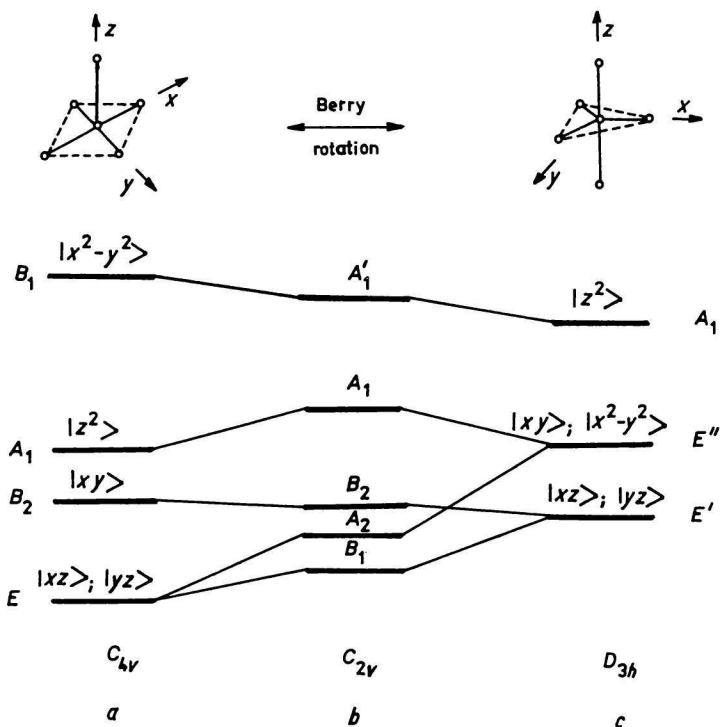*Fig. 2.* Diagram of the *d*-energy levels splitting of the pentacoordinated Cu(II) ion in the fields of different symmetry: *a)* tetragonal pyramidal structure (symmetry C_{4v}); *b)* transition state structure (symmetry C_{2v}); *c)* trigonal bipyramidal structure (symmetry D_{3h}).

The results of X-ray structure analysis of the $[T(III)(NH_3)_6][CuCl_5]$ complexes (T = Cr, Co) [10, 11] suggest a TBP structure of the $[CuCl_5]^{3-}$ ion. The thermochemical measurements indicate a phase transition of the first order at $T_c = 280.8$ K [14]. The ESR spectra of the complexes in polycrystalline state at

298 K show an isotropic signal. If the temperature decreases the ESR spectra acquire axial symmetry and the spectral anisotropy ($g_\perp/g_\parallel$) increases with the temperature decrease. Below 120 K the ESR spectra do not change anymore and $g_\perp = 2.17$, $g_\parallel = 2.07$. Although these results suggest a TBP structure of the $[CuCl_5]^{3-}$ ion, the authors of paper [9] assume that the obtained principal values of the g-tensor at $T < 280$ K are a result of the dynamical averaging of the four SP polyhedrons occurring in an eighth of unit cell giving rise to the effective TBP structure. At higher temperatures ($T > 280.8$ K) the authors of paper [9] suppose a distortion of the SP structure leading to the TBP structure which is formed increasingly with the rising temperature. The observation that the exchange coupling changes the spectral line shape, but it does not change the principal values of the g-tensor is in contradiction with the proposed mechanism. In addition, the energy necessary for the transition from the SP structure to the TBP structure (Berry rotation) is much smaller [19] in comparison with the energy of dynamical averaging of the four SP polyhedrons to the effective TBP structure.

However, the results of ESR spectroscopy investigations of the $[Co(NH_3)_6][CuCl_5]$ complex may be explained in a simpler and more unambiguous way. The ESR spectra obtained at low temperature correspond to the frozen TBP configuration [5, 19] of the $[CuCl_5]^{3-}$ polyhedrons, which is confirmed by the ESR spectra line shape indicating a weak exchange coupling.

At higher temperatures ($T > 280.8$ K) a dynamical transition (Berry rotation) from the SP structure to the TBP structure takes place and the individual Cu—Cl bonds are averaged, which results in the observed isotropic ESR spectrum.

The above-mentioned model is supported also by the ESR investigations of the $[N\text{-}(2\text{-amet})pipzH_3][CuCl_5]$ complex which gives an orthorhombic ESR spectrum [9] in the temperature range 130—290 K ($g_1 = 2.18$, $g_2 = 2.16$, $g_3 = 2.06$ at 130 K; $g_1 = 2.18$, $g_2 = 2.17$, and $g_3 = 2.06$ at 290 K). This spectrum is only slightly different from the axially symmetric spectrum ($g_1 = g_2 \neq g_3$) corresponding to the ideal SP structure of the $[CuCl_5]^{3-}$ polyhedron.

Owing to the relatively strong and nonequivalent —NH···Cl hydrogen bonds of equatorial Cl ligands, as well as the HOH···Cl hydrogen bond of apical Cl ligand with crystal water [4] a slight distortion of the SP structure of the $[CuCl_5]^{3-}$ ion takes place. This distortion is manifested by a slight orthorhombic distortion of the ESR spectrum. The temperature independence of the ESR spectra is also a consequence of a considerable rigidity of the roughly SP structure of the $[CuCl_5]^{3-}$ polyhedron which is significantly favoured by the above-mentioned hydrogen bonds.

The principal values of the g-tensor elements obtained for the $[Co(1,3\text{-diaminopropane})_3][CuCl_5] \cdot 3H_2O$ complex (Table 1) imply an axially symmetric sys-

tem of the SP structure of the $[CuCl_5]^{3-}$ ion at low temperatures ($T < 160$ K) as the relation $g_\parallel > g_\perp > g_0$ 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 $[CuCl_5]^{3-}$ ions which is stabilized by the weak hydrogen bonds of diamino-propane (contained in the complex cation) to chlorine atoms of the $[CuCl_5]^{3-}$ anion. At higher temperatures ($T > 160$ K) the ESR spectra change their symmetry into the orthorhombic one and the SP structure of $[CuCl_5]^{3-}$ 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 corresponds the incident orthorhombic ESR spectrum. The portion of the TBP polyhedrons increases with increased temperature, which manifests itself in increasing asymmetry of the ESR spectra.

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