

**POWDER ESR SPECTRA OF THE COMPLEXES [Cu(phen)₂X]ClO₄
AND [Cu(bipy)₂I]ClO₄**

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The ESR spectra of the polycrystalline [Cu(phen)₂X]ClO₄ and [Cu(bipy)₂I]ClO₄ complexes (phen 1,10-phenanthroline, bipy 2,2'-bipyridyl, X = Cl, Br, I) were studied. The values of the optimized parameters of the spin Hamiltonian of the experimental ESR spectra indicate that the CuN₄X chromophor has the shape of a compressed trigonal bipyramid with the *D*_{3h} symmetry, and its structure involves the |z²⟩ ground electronic state of the unpaired electron of the Cu(II) ion.

Cu(II) compounds exhibit interesting stereochemical variability. For a description of the nonrigid properties of Cu(II) complexes, the coordination polyhedron plasticity concept has been introduced^{1,2} to account for the occurrence of their distortion isomers¹⁻³. 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 recently⁴⁻⁶.

In pentacoordinated Cu(II) complexes of the [Cu(phen)₂X]ClO₄ and [Cu(bipy)₂X]ClO₄ types (phen 1,10-phenanthroline, bipy 2,2'-bipyridyl, X = Cl, Br, I), distortion of the CuN₄X chromophor from the trigonal bipyramid geometry (TBP) to the square pyramid geometry (SP) is conceivable⁷. The ESR spectra of these systems in the polycrystalline state are interpreted in the present paper; the ground electronic state of copper(II) and the structure of the CuN₄X chromophor are discussed based on the optimized parameters of the spin Hamiltonian of the experimental spectra.

EXPERIMENTAL

[Cu(bipy)₂I]ClO₄ was synthesized in solution containing Cu(bipy)₂(ClO₄)₂ (ref.⁸) at a concentration of 5 · 10⁻³ mol dm⁻³ in 105 cm³ of the acetone-water 1 : 1 mixture, to which a solution of KI (c = 5 · 10⁻³ mol dm⁻³) in 10 cm³ of this solvent mixture was added; the precipitate formed was filtered out, rinsed with the acetone-water mixture and dried in a desiccator. The [Cu(phen)₂X]ClO₄ complexes with X = Cl, Br, I were synthesized by reacting Cu(phen)₂(ClO₄)₂

(ref.⁸) at a concentration of $5 \cdot 10^{-3}$ mol dm⁻³ in 237 cm³ of the acetone–water mixture with KX in 10 cm³ of this mixture. The subsequent treatment was as above. The composition of the substances obtained was confirmed by chemical analysis.

The ESR spectra of the polycrystalline substances were measured at room temperature on a BRUKER ER-200E-SRC spectrometer in the X-band.

THEORETICAL

The theoretically calculated points of the spectral line shape function can be described by the equation⁹

$$f(B) = N \sum_i \int_{\theta} \int_{\phi} P(\theta, \phi, i) G(B, \theta, \phi, i) \sin \theta \, d\theta \, d\phi, \quad (1)$$

where N is the normalization constant, the summation over i involves all spectral transitions, $G(B, \theta, \phi, i)$ is the derivative shape of the spectral line (the Lorentz function is used to describe the spectral line), B is the external magnetic field induction, θ and ϕ are polar angles defining the orientation of the system with respect to the external magnetic field, and $P(\theta, \phi)$ is the probability of the i -th spectral transition, which is given by the equation

$$P(\theta, \phi) = g_1^2 g_2^2 \sin^2 \theta + g_2^2 g_3^2 (\sin^2 \phi + \cos^2 \theta \cos^2 \phi) + g_3^2 g_1^2 (\cos^2 \phi + \cos^2 \theta \sin^2 \phi), \quad (2)$$

where g_1 , g_2 and g_3 are the principal components of the \mathbf{g} -tensor.

The differential volume element $\sin \theta \, d\theta \, d\phi$, through which function (1) is integrated, can be replaced by the product $-\Delta \cos \theta \cdot \Delta \phi$ for the numerical processing on computers. If $\Delta \cos \theta$ and $\Delta \phi$ are chosen equidistant, the line shape function transforms into a form suitable for application in the optimization by means of computers, viz.

$$f(B) = N^* \sum_i \sum_{\theta} \sum_{\phi} P(\theta, \phi, i) G(B, \theta, \phi, i), \quad (3)$$

where the double integral is replaced by double summation over θ and ϕ ; N^* is the normalization constant involving the equidistant values of $\Delta \cos \theta$ and $\Delta \phi$.

The experimental ESR spectra were processed by using the automated optimization procedure based on the minimization of the functional⁹

$$F = \sum_B [f^{\text{exp}}(B) - f(B)]^2, \quad (4)$$

where $f^{\text{exp}}(B)$ are points in the experimental spectrum and $f(B)$ are those calculated theoretically by means of Eq. (3). The Fletcher–Powell gradient optimization procedure was employed¹⁰.

RESULTS AND DISCUSSION

The experimental ESR spectra and the simulated spectra corresponding to the optimized parameters of the spin Hamiltonian of the complexes studied are shown in Fig. 1, the values of the principal components of the g -tensor, the spectral half line widths, some statistical characteristics as well as the values obtained by conventional visual reading from the experimental spectra are given in Table I, the

TABLE I

Parameters of ESR spectra of *I* [Cu(phen)₂Cl]ClO₄, *II* [Cu(phen)₂Br]ClO₄, *III* [Cu(phen)₂I]ClO₄, *IV* [Cu(bipy)₂I]ClO₄: visually read parameters (upper rows) and optimized parameters (lower rows)

| Complex | g_{\perp} | g_{\parallel} | ΔB_{\perp} mT | ΔB_{\parallel} mT | Correlation coefficient | R-factor |
|------------|-------------|-----------------|--------------------------|------------------------------|----------------------------|----------|
| <i>I</i> | 2.199 | 2.015 | 4.03 | 4.03 | 0.9045 | 0.211 |
| | 2.184 | 2.008 | 2.27 | 1.21 | 0.9877 | 0.162 |
| <i>II</i> | 2.194 | 2.015 | 6.00 | 4.00 | 0.9725 | 0.271 |
| | 2.178 | 2.023 | 4.03 | 1.89 | 0.9782 | 0.266 |
| <i>III</i> | 2.171 | 2.026 | 6.00 | 4.00 | 0.9543 | 0.199 |
| | 2.168 | 2.037 | 3.77 | 2.43 | 0.9905 | 0.160 |
| <i>IV</i> | 2.174 | 2.037 | 6.00 | 4.00 | 0.9794 | 0.181 |
| | 2.166 | 2.041 | 4.55 | 5.19 | 0.9973 | 0.043 |

TABLE II

Parameters of the spin Hamiltonian of the ESR spectra (upper rows) and their deviations (lower rows) for the complexes *I*–*IV* (for the complex numbering see Table I)

| Complex | g_{\perp} | g_{\parallel} | ΔB_{\perp} mT | ΔB_{\parallel} mT |
|------------|-------------------|-------------------|--------------------------|------------------------------|
| <i>I</i> | 2.1841 | 2.0085 | 2.27 | 1.21 |
| | $1 \cdot 10^{-4}$ | $2 \cdot 10^{-4}$ | 0.3 | 0.6 |
| <i>II</i> | 2.1775 | 2.0226 | 4.03 | 1.89 |
| | $5 \cdot 10^{-4}$ | $8 \cdot 10^{-4}$ | 0.9 | 2 |
| <i>III</i> | 2.1680 | 2.0370 | 3.78 | 2.43 |
| | $2 \cdot 10^{-4}$ | $1 \cdot 10^{-3}$ | 0.8 | 6 |
| <i>IV</i> | 2.1657 | 2.0411 | 4.55 | 5.19 |
| | $3 \cdot 10^{-4}$ | $2 \cdot 10^{-3}$ | 0.4 | 1 |

deviations of the spin Hamiltonian parameters are given in Table II. This table demonstrates that although applied rarely in ESR laboratories, optimization of parameters of ESR spectra of this kind is actually necessary.

Basic structure information on crystalline complexes is derived by X-ray structure analysis. Although pentacoordinated Cu(II) compounds have been largely prepared in the polycrystalline form, X-ray data for some systems involving the CuN_4X chromophor are available¹¹⁻¹³.

X-ray structure analysis of compounds of the $[\text{Cu}(\text{bipy})_2\text{X}]\text{Y}$ type involving the CuN_4X chromophor has revealed¹⁴⁻¹⁶ that this chromophor may be distorted from the nearly regular TBP structure to the SP structure, as shown in Fig. 2. The course of this distortion can be treated in terms of Berry's twisting mechanism¹⁷, interpreting the conversion from the regular TBP structure to the regular SP structure via normal vibrational modes of the MX_5 chromophor of the C_{2v} symmetry (Fig. 3).

The study of the effect of the anion Y on the distortion of the $[\text{Cu}(\text{bipy})_2\text{Cl}]^+$ cation has shown that the structure of $[\text{Cu}(\text{bipy})_2\text{Cl}]\text{Cl}\cdot 6\text{H}_2\text{O}$ is nearly regular TBP (ref.¹⁵) whereas $[\text{Cu}(\text{bipy})_2\text{Cl}]\text{ClO}_4$ exhibits a rather marked distortion. The extreme case of the SP structure occurs with the $\text{CuN}_2\text{N}'_2\text{N}''$ chromophor¹⁸. Also for the complexes of the $[\text{Cu}(\text{phen})_2\text{X}]\text{Y}$ type where $\text{X} = \text{I}, \text{Cl}, \text{Br}, \text{NH}_3$ or H_2O and $\text{Y} = \text{NO}_3, \text{I},$ or BF_4 , X-ray structure analysis revealed¹⁹⁻²² that their coordination geometry is partly distorted TBP. Hence, in compounds of the general formula $[\text{CuL}_2\text{X}]$ where L is an N,N'-aromatic bidentate ligand (2,2'-bipyridyl or 1,10-phenanthroline) and X is a monodentate ligand (H_2O , halogen), the cation has a nearly regular TBP structure.

The TBP crystal field of the D_{3h} symmetry splits the 2D spectral term as shown in Fig. 4. 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 equations²³

$$g_{\perp} = 2.0023 + 6\lambda/\Delta E(a'_1 \rightarrow e'') \quad (5)$$

$$g_{\parallel} = 2.0023, \quad (6)$$

where λ is the spin-orbital interaction constant of the Cu(II) ion. It will be clear that for a compressed TBP structure we have $g_{\perp} > g_{\parallel} \approx g_0$ (g_0 is the g -factor of the free electron).

The shape of the ESR spectra of the systems investigated (Fig. 1) indicates that all of them exhibit axial symmetry, and a considerable dipole-dipole interaction occurs between the Cu ions in the elementary cell. The relation $g_{\perp} > g_{\parallel} \approx g_0$ holds for the components of the axial g -tensor of all the spectra (Table I).

In the elongated TBP configuration of the Cu(II) ion, the ground electronic state is the doubly degenerate e' state. According to the Jahn-Teller theorem^{24,25}, this

orbital degeneracy of the ground state must be removed. Thus, any distortion leads to a new electronic state, either $|x^2 - y^2\rangle$ or $|xy\rangle$. The compressed TBP configuration with the D_{3h} symmetry points to the $|z^2\rangle$ ground electronic state. This is consistent with the parameters of the ESR spectra obtained, which satisfy the relation $g_{\perp} > g_{\parallel} \approx g_0$. It can be inferred from the values of the principal \mathbf{g} -tensor components that the distortion of the TBP structure of the CuN_4X chromophore increases in order $[\text{Cu}(\text{phen})_2\text{Cl}]\text{ClO}_4 < [\text{Cu}(\text{phen})_2\text{Br}]\text{ClO}_4 < [\text{Cu}(\text{phen})_2\text{I}]\text{ClO}_4 <$

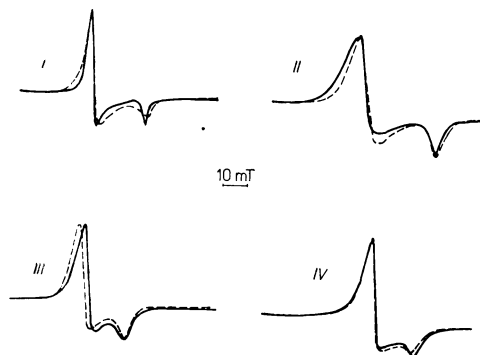


FIG. 1

Experimental spectra (—) and simulated spectra with optimized parameters of the spin Hamiltonian (---) of I $[\text{Cu}(\text{phen})_2\text{Cl}]\text{ClO}_4$, II $[\text{Cu}(\text{phen})_2\text{Br}]\text{ClO}_4$, III $[\text{Cu}(\text{phen})_2\text{I}]\text{ClO}_4$, IV $[\text{Cu}(\text{bipy})_2\text{I}]\text{ClO}_4$

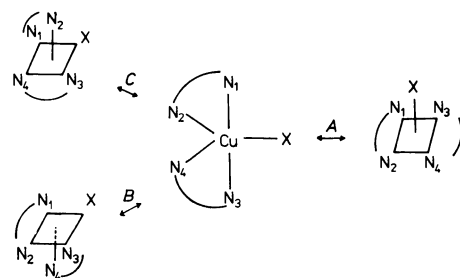


FIG. 2

Transitions of the trigonal bipyramidal structure to various square pyramidal structures

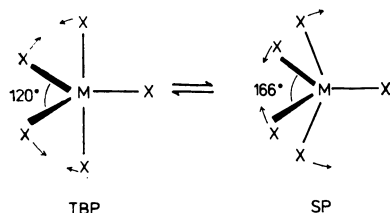


FIG. 3

The Berry twisting mechanism

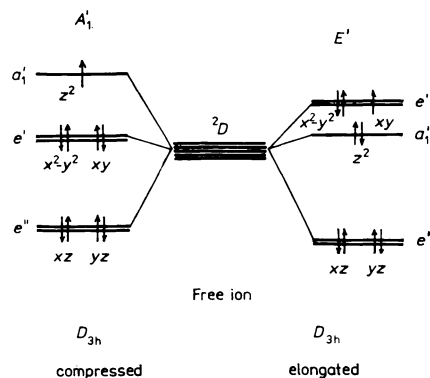


FIG. 4

Splitting of d -orbitals in trigonal-bipyramidal crystal fields of the D_{3h} symmetry

$< [\text{Cu}(\text{bipy})_2\text{I}]\text{ClO}_4$, i.e., with decreasing electronegativity of halogen X (the Cu—X bond length increases as compared to Cu—N), hence, with increasing covalency difference between the Cu—N and Cu—X bonds.

It is a well-known fact that the synthesis of compounds of copper(II) with directly bonded ligands possessing reduction properties (I^- , CN^- , thiourea, etc.) meets with difficulties because copper is easily reduced and complexes of copper(I) emerge. In the complexes studied in this work, the stability of the Cu(II) oxidation state can be explained in terms of the ligand being localized in the equatorial plane, owing to which its overlap with the potential electron acceptor orbital (singly occupied $|z^2\rangle$ orbital) is weak, so that no favourable conditions exist for the reducing action of the ligand X (ref.²⁶).

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