

INVESTIGATION OF AROMATIC SCHIFF BASE Cu^{2+} -CHELATES BY ELECTRON PARAMAGNETIC RESONANCE*

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Electron paramagnetic resonance and optical spectra of quadridentate Cu^{2+} -chelates with aromatic Schiff bases are studied on powders, solutions and single crystals. Principal values of spectroscopic splitting and hyperfine tensors as well as the spin density on the central ion are determined. EPR is seen as a method permitting to study the nature of the ligand with which the paramagnetic ion coordinates and yielding information on the crystal structure.

Introduction

Chelates of ions of metals belonging to the transition groups with aromatic, quadridentate Schiff bases are the object of investigation in the domain of extraction now conducted at the Institute of Nuclear Physics at Cracow [1]. They are interesting from the radiospectroscopical viewpoint, since salicylaldehydeimine ligands form paramagnetic complexes of various coordination numbers [2, 3]. This provides the possibility of establishing what influence the coordination number and structure of the complex have on the mechanism of spin density distribution between the central ions and atoms of the ligand a task especially well adapted to nuclear (NMR) [3] and electron paramagnetic resonance (EPR). The present paper contains the results of a systematical investigation of Cu^{2+} -complexes with aromatic Schiff bases carried out by EPR in the Radiospectroscopy Laboratory of the Institute of Physics of the Polish Academy of Sciences in Poznań.

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Experimental

Materials. Investigation concerned four chelates of copper involving the following Schiff bases:

1. bis-salicylaldehyde-ethylenediimine, BSEDI-Cu(II)
2. the 3-methoxy derivative of the latter, B-3-Mox-SEDI-Cu(II)
3. bis-3-methoxy-salicylaldehyde-propylenediimine, B-3-Mox-SPDI-Cu(II)
4. bis-3-methoxy-salicylaldehyde-phenylenediimine, B-3-Mox-SPhDI-Cu(II).

The Schiff bases were prepared by condensation of salicylaldehyde or 3-methoxy-salicylaldehyde with ethylenediimine or *o*-phenylenediimine and crystallisation of the product from ethanol.

EPR measurements. EPR spectra were studied with a JEOL JES-3BX spectrometer at room temperature. Powders, solutions in chloroform and, in the case of B-3-Mox-SPDI-Cu(II), the single crystal, were investigated. For determining the hyperfine interaction constants, EPR spectra of powders in which the paramagnetic Cu²⁺ ions had been diluted with diamagnetic Zn²⁺ ions the ratio Zn:Cu \approx 10:1 were obtained.

UV measurements. Electronic absorption spectra were measured in the 200–600 nm region with a Unicam A-700 spectrophotometer. These were spectra of solutions of Schiff bases in chloroform and in pyridine, as well as of single crystals of B-3-Mox-SPDI-Cu(II) that had crystallized on the walls of the spectrophotometer cuvette.

Results and discussion

The results are assembled in Table I.

Spectra of powdered chelates

From a study of the powdered substances, values of the spectroscopic splitting factors g_{\parallel} and g_{\perp} were determined and the width of the individual resonance line $\Delta H_{1/2}$ evaluated.

The EPR spectra are shown in Figs 1 and 2.

The spectrum of a B-3-Mox-SPDI-Cu(II) sample as shown in Fig. 1*a*, is a typical example of spectra deriving from paramagnetic complexes with axial symmetry of the crystal field. With regard to the large value of the anisotropy parameter $\delta = (H_{\parallel} - H_{\perp})/\Delta H_{1/2} > 5$ (where H_{\parallel} and H_{\perp} are the resonance field strengths respectively parallel and perpendicular to the direction of the crystal field and $\Delta H_{1/2}$ the halfwidth of the line) one can determine H_{\parallel} and H_{\perp} directly from the shape of the spectrum [4]. Indeed, H_{\perp} corresponds to that value of the magnetic field at which the derivative of the EPR is maximal, and H_{\parallel} to the field value of the additional minimum of the line. The values thus obtained amount to $g_{\parallel} = 2.206$ and $g_{\perp} = 2.052$. The spectrum of Fig. 1*a* was obtained in a substance with 100 per cent concentration of copper ions. On diluting the latter with diamagnetic zinc ions, one obtains the spectrum shown in Fig. 1*b* (at dilution Zn:Cu = 100:1). Here, owing to the decrease in dipole interaction between the paramagnetic centres, a hyperfine structure is apparent due to interaction between the unpaired spin of Cu²⁺ (which has electron configuration 3*d*⁹) and the nucleus with spin $I = 3/2$. The spectrum permits a determination of the hyperfine

TABLE I

Compound	B-3-Mox-SEDI -Cu(II)	B-3-Mox-SPDI -Cu(II)	B-3-Mox-SPhDI -Cu(II)	BSEDI-Cu(II)
Powder				
g_{\parallel}	$g_1 = 2.205$	2.206	2.175	2.170
g_{\perp}	$g_2 = 2.060$ $g_3 = 2.047$	2.052	2.052	2.035
Line width $\Delta H_{1/2}$	35 Gs	20-50 Gs	25-110 Gs	45-100 Gs
Hyperfine splitting parameters:				
A		$1.50 \times 10^{-2} \text{ cm}^{-1}$		
B		$0.38 \times 10^{-2} \text{ cm}^{-1}$		
Single crystal				
g_{\parallel}		2.210		
g_{\perp}		2.050		
$\Delta H_{1/2}^{(1)}$		20 Gs		
$\Delta H_{1/2}^{(2)}$		42 Gs		
Solution		in chloroform	in chloroform	
g_{av}		2.093	2.093	
A_{av}		$0.72 \times 10^{-2} \text{ cm}^{-1}$	$0.84 \times 10^{-2} \text{ cm}^{-1}$	
α^2		0.70	0.77	
UV — bands (nm)				
	282.5	285.4	251.4 324.7 344.8	301.1
	374.6	380.1	363.3	369.0
	505.0		444.4	

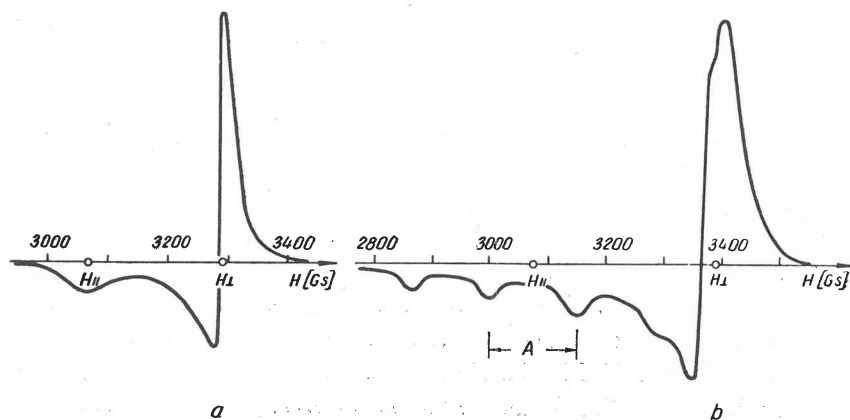


Fig. 1. EPR spectrum of powdered sample B-3-Mox-SPDI-Cu(II). *a*) at 100 per cent concentration of Cu^{2+} ions; *b*) at dilution with zinc ion, $\text{Zn}:\text{Cu} = 100:1$

interaction constant A , which characterizes this interaction when the external magnetic field is parallel to the symmetry axis of the crystal field. Its value is $A = 1.50 \times 10^{-2} \text{ cm}^{-1}$.

The EPR spectrum of B-3-Mox-SEDI-Cu(II) shown in Fig. 2a proves that the symmetry of the crystal field of the paramagnetic complex deviates from axial symmetry. Here, g_1

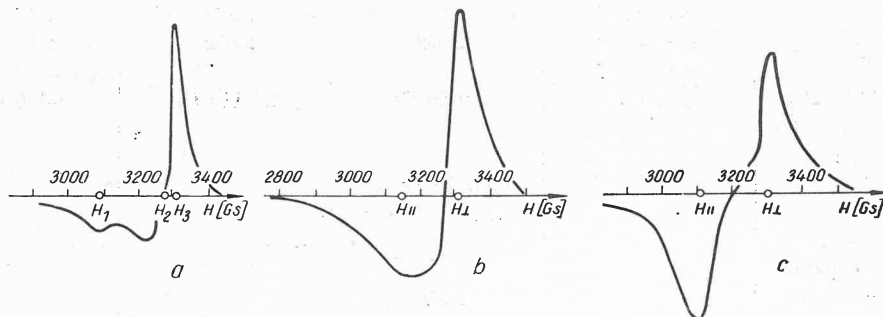


Fig. 2. EPR spectra for powdered samples: a) for B-3-Mox-SEDI-Cu(II); b) for B-3-Mox-SPhDI-Cu(II); c) for BSEDI-Cu(II)

and g_3 can be determined from the spectrum as in the previous case, whereas the remaining coefficient g_2 corresponds approximately to that resonance field at which the EPR line derivative becomes zero [5]. The g -values thus obtained are:

$$g_1 = 2.205; \quad g_2 = 2.060; \quad g_3 = 2.047.$$

The EPR spectra of B-3-Mox-SPhDI-Cu(II) and BSEDI-Cu(II) (Figs 2b and 2c) point to the presence of nonequivalent position of the Cu^{2+} -ions in the lattice [6] and of strong exchange interaction between the paramagnetic centres [5]. Line shape analysis of these spectra performed by methods described in Ref. [7] shows that the crystal field has the axial symmetry and that the g -values of the two substances differ but slightly:

$$g_{||} = 2.175; \quad g_{\perp} = 2.052 \quad \text{for B-3-Mox-SPhDI-Cu(II)}$$

and

$$g_{||} = 2.170; \quad g_{\perp} = 2.035 \quad \text{for BSEDI-Cu(II)}$$

Exchange interactions between paramagnetic centers lead to a dependence of the resonance linewidth on the mutual orientation of the magnetic field and crystal field symmetry axis of the complex. A dependence of this kind is exhibited by the EPR spectra of three of the substances under investigation. Thus, in B-3-Mox-SPDI-Cu(II), the individual resonance linewidth evaluated according to Ref. [7] varies in the interval 20–50 Gs; whereas in B-3-Mox-SPhDI-Cu(II) and BSEDI-Cu(II) the orientation-dependent change in width is stronger, ranging from 25 to 110 Gs and 45 to 100 Gs respectively. B-3-Mox-SEDI-Cu(II) fails to exhibit exchange interaction, and the width is constant (35 Gs) and independent of the orientation.

Spectra of solutions of chelates in chloroform

B-3-Mox-SPDI-Cu(II) and B-3-Mox-SPhDI-Cu(II) dissolve easily in chloroform. Consequently, EPR studies were extended to their solutions. The spectra obtained were similar (Fig. 3) and served for determining mean spectroscopic splitting factors g_{av} and mean hyperfine splitting factors A_{av} , as follows:

$$g_{av} = 2.093 \text{ in solutions of either compound,}$$

$$A_{av} = 0.72 \times 10^{-2} \text{ cm}^{-1} \text{ in the solution of B-3-Mox-SPDI-Cu(II)}$$

$$A_{av} = 0.84 \times 10^{-2} \text{ cm}^{-1} \text{ in that of B-3-Mox-SPhDI-Cu(II).}$$

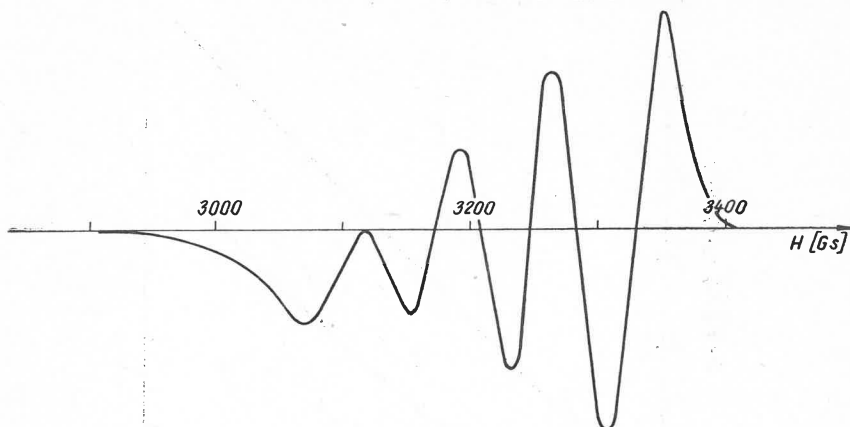


Fig. 3. EPR spectrum of B-3-Mox-SPDI-Cu(II) solution in chloroform

The relation $A_{av} = (A + 2B)/3$ allows to calculate the constant of hyperfine interaction B once A is known from the spectrum of the powder. This calculation, performed for B-3-Mox-SPDI-Cu(II), yielded $B = 0.38 \times 10^{-2} \text{ cm}^{-1}$. On comparing the g -values for the solid and the solution, one finds the structure of the complex retains its stability when in the solvent, since the relation $g_{av} = (g_{\parallel} + 2g_{\perp})/3$ is fulfilled strictly.

When the mean parameters of the EPR spectrum of the solution are known, one can calculate the spin density α^2 on the central ion of the complex by the theory of Kivelson and Neiman [8] from the formula

$$\alpha^2 = \frac{7}{3} \left[\frac{A_{av}}{P} + (g_{av} - 2) \right] + 0,02. \quad (1)$$

where P is a constant amounting to 0.036 cm^{-1} in the case of Cu^{2+} [10]. The following spin densities resulted:

$$\alpha^2 = 0.70 \text{ for } \text{Cu}^{2+} \text{ in B-3-Mox-SPDI}$$

and

$$\alpha^2 = 0.77 \text{ for } \text{Cu}^{2+} \text{ in B-3-Mox-SPhDI}$$

pointing to a more covalent nature of the Cu-ligand bond in the former and to a more ionic nature of the bond in the latter complex.

Fig. 3 shows the EPR spectrum of B-3-Mox-SPDI-Cu(II) in chloroform. It characteristically exhibits a dependence of the amplitude of the hyperfine structure line on the magnetic field strength. By the theory of EPR in solutions [9], the transversal relaxation time T_2 of the electron spin depends on the spin I_z of the nucleus:

$$\frac{1}{T_2^2} = \frac{32\pi}{45} \left(\frac{\Delta g \beta H_0 + b I_z}{h} \right) \operatorname{arctg} \frac{2\tau_c}{T_2} \quad (2)$$

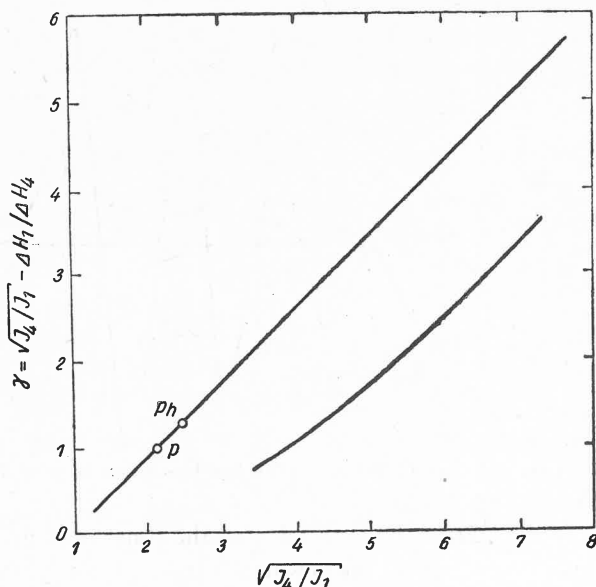


Fig. 4. Characteristics of ligand atoms; lower curve: complexes with oxygen ligands, straight line: complexes with nitrogen ligands. Point *P* — B-3-Mox-SPDI-Cu(II), point *Ph* — B-3-Mox-SPhDI-Cu(II)

with $\Delta g = g_{\parallel} - g_{\perp}$, $b = A - B$, and τ_c — the correlation time. Since the resonance linewidth is directly related with T_2 , the conclusion from Eq. (2) is that it should differ from one hyperfine component to another and that these components should fulfil the relation:

$$J_j(\Delta H_j)^2 = J_k(\Delta H_k)^2 \quad (3)$$

with $J_{j,k}$ are intensities and $\Delta H_{j,k}$ linewidths of the j -th and k -th hyperfine components. Owing to overlapping of hyperfine components and to the presence of a hyper-hyperfine structure due to interaction between the central ion and the nuclei of atoms of the ligand, the effective intensities and widths of hyperfine lines can differ from the real ones, and Eq. (3) can fail to be fulfilled. In such case, investigation of the degree of overlapping permits to assess whether the paramagnetic ion coordinates with ligands involving containing atoms whose nuclei possess magnetic moment (nitrogen, sulphur) or solely atoms having non-magnetic nuclei (oxygen). The presence of but a single magnetic nucleus in the coordination

neighbourhood of the paramagnetic ion suffices for causing a deviation from Eq. (3). On assuming the quantity

$$\gamma = \sqrt{\frac{J_4}{J_1} - \frac{\Delta H_1}{\Delta H_4}} \quad (4)$$

as a measure of the overlapping (the indices of hyperfine lines grow with the magnetic field) a calculation of the functions $\gamma = (J_4/J_1)^{1/2}$ leads to Fig. 4, where curve is for the case of complexes with oxygen ligands whereas the straight line represent that of ones with nitrogen ligands. The EPR spectra of the chloroform solutions investigated by us shown a hyperfine linewidth independent of I_z and constant for the extremal lines, amounting to 46 Gs. The overlapping parameters computed from the spectra are:

$$\gamma = 1.1; (J_4/J_1)^{1/2} = 2.1 \text{ for B-3-Mox-SPDI-Cu(II)}$$

and

$$\gamma = 1.4; (J_4/J_1)^{1/2} = 2.4 \text{ for B-3-Mox-SPhDI-Cu(II).}$$

These parameters yield points (marked P and Ph) lying on the straight line of Fig. 4, thus confirming that the Cu^{2+} -ions coordinate with ligands involving nitrogen in the compounds under investigation.

Spectra of single crystal B-3-Mox-SPDI-Cu(II)

The chelate B-3-Mox-SPDI-Cu(II) crystallizes from ethanol in well-defined single crystals of the shape of elongated plates. A single crystal $0.6 \times 0.3 \times 0.1$ mm in size was taken for studying the anisotropy of the g -factor in three planes. The orthogonal reference frame was chosen in accordance with the crystallographical axes, namely axis Z and Y lying in the larger plane of the plate and Z parallel to its longer edge. The results for the anisotropy of g

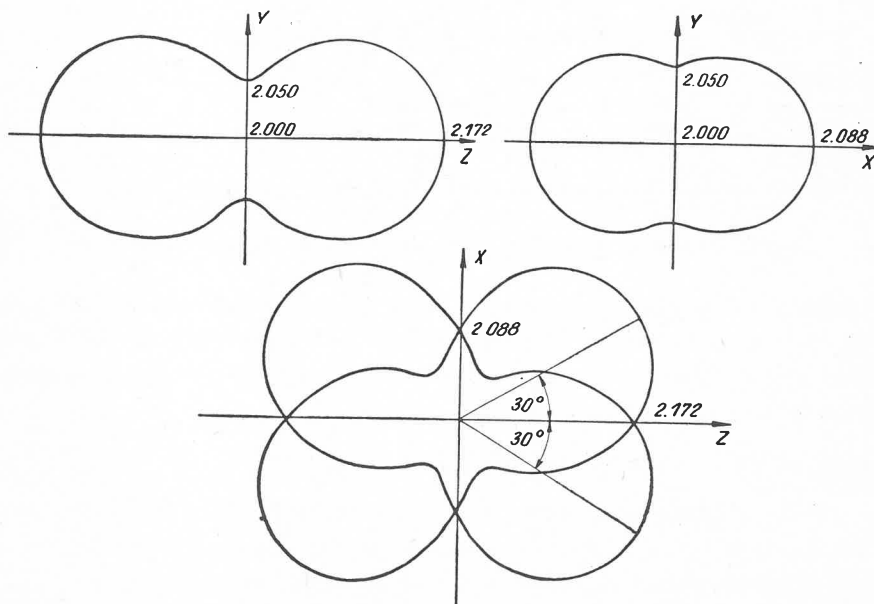


Fig. 5. Anisotropy of the g -factor in B-3-Mox-SPDI-Cu(II) crystal

are shown in Fig. 5. The principal values of the g -tensor are: $g_{\parallel} = 2.210$ and $g_{\perp} = 2.050$. The angular dependence of g permits the conclusion that B-3-Mox-SPDI-Cu(II) single crystal present two distinctly oriented complexes whose principal directions $g_{\parallel}^{(1)}$ and $g_{\parallel}^{(2)}$ lie in the XZ -plane and subtend on angle of 60° with one another. These directions deviate by $\pm 30^{\circ}$ from the XY -plane. Since the molecules of aromatic Schiff bases are planar [11] and since the principal direction of the crystal field of the square coordination of Cu^{2+} is perpendicular to the coordination plane, the planar molecules of B-3-Mox-SPDI-Cu(II) can be thought of as deviating from the XY -plane by an angle of $\pm 30^{\circ}$. This leads to the conclusion that the crystal structure of B-3-Mox-SPDI-Cu(II) resembles the structures of BSEDI-Co(II) [11] and BSEDI-Cu(II) established by X-ray methods. For the sake of comparison, the structure of cobalt chelate with BSEDI is represented in Fig. 6.

The crystal structure of complexes of metals and Schiff bases is characterized by the presence of layers flat molecules. These layers are linked to one another by a specific inter-

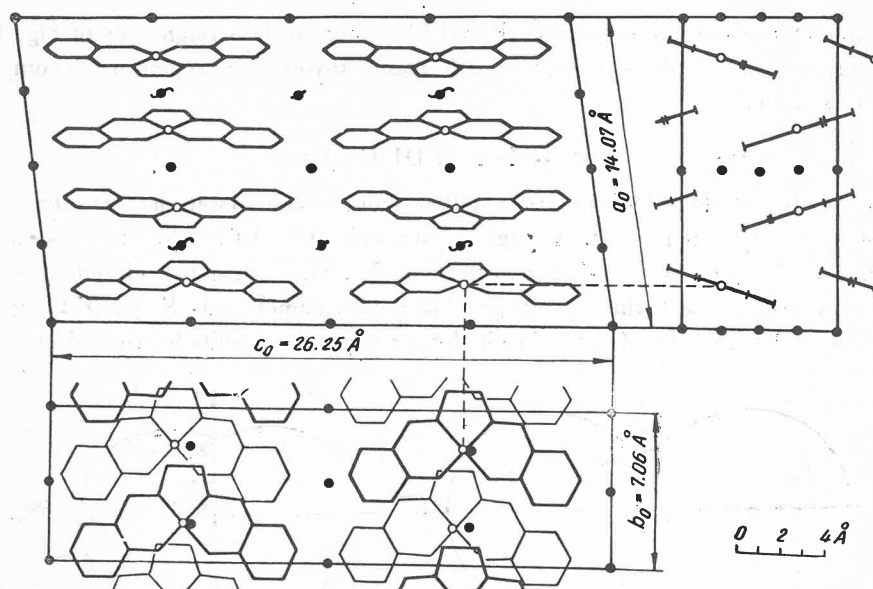


Fig. 6. Disposition of BSEDI-Co(II) molecules in the elementary cell [11]

action occurring between the metal ions [12]. This type of crystal structure is explained by the strong exchange interactions between (*e.g.* Cu^{2+}) ions apparent in the EPR spectra as a dependence of the resonance linewidth on orientation, as the case in the substances under investigation here.

Electronic (UV) spectra of solutions of chelates

With the aim of determining the distances between orbital levels of Cu^{2+} in the complexes, the optical bands of the solutions were studied. The solution of B-3-Mox-SPDI-Cu(II) in chloroform presents absorption bands in UV at the wavelengths (Fig. 7a):

$$380.1 \text{ nm} \quad \text{and} \quad 285.4 \text{ nm}$$

Optical bands were also studied in B-3-Mox-SPDI-Cu(II) single crystal (Fig. 7b) obtained from ethanol, on the wall of the spectrophotometer cuvette. The bands were found to coincide with those of chloroform solution.

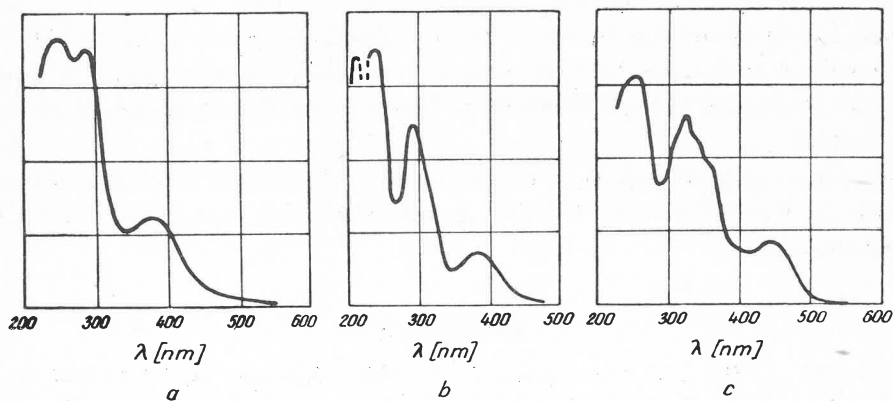


Fig. 7. Optical spectra in UV: a) B-3-Mox-SPDI-Cu(II) dissolved in chloroform; b) B-3-Mox-SPDI-Cu(II) single crystals; c) B-3-Mox-SPhDI-Cu(II) dissolved in chloroform

B-3-Mox-SPhDI-Cu(II) in chloroform exhibits absorption at:

444.4 nm 363.3 nm 344.8 nm 324.7 nm and 251.4 nm

The bands of this solution are shown in Fig. 7c.

B-3-Mox-SEDI-Cu(II) in pyridine absorbs in UV at:

505.0 nm 374.6 nm and 282.5 nm

The spectrum is shown in Fig. 8a.

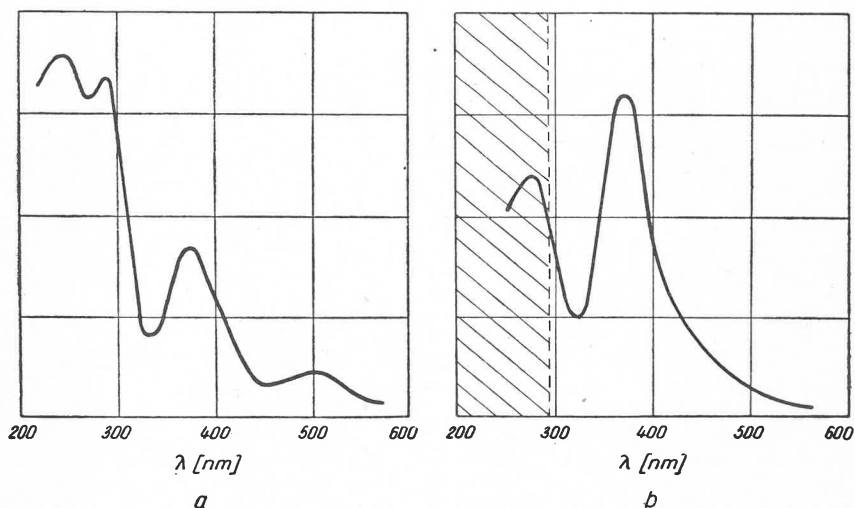


Fig. 8. Optical spectra in UV: a) for a solution of B-3-Mox-SEDI-Cu(II) in chloroform; b) for a solution of BSEDI-Cu(II) in pyridine; the shaded area shows the region of absorption of the solvent (pyridine)

BSEDI-Cu(II) in pyridine is found to exhibit absorption at the wavelengths:

369.0 nm and 301.1 nm

The spectrum is shown in Fig. 8b.

These optical spectra fail to reveal distinct absorption bands in the visible region from orbital level transitions of the copper ion. Presumably, the absorption is so weak that these bands, belonging to the visible region, disappear in the wing of the UV absorption of the ligand.

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