

Copper(II) complexes with organic ligands

XXII. Spectral and magnetic properties of phenoxy- and methylphenoxyacetatocopper(II) complexes with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide*

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Received 24 February 1982

Paper published on the occasion of the 30th anniversary of the foundation
of the Faculty of Pharmacy, Komenský University, Bratislava

Copper(II) complexes of the composition $\text{Cu}(\text{R}-\text{COO})_2\text{L}_n$ were prepared by the reactions of pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide with corresponding phenoxy-, 2- and 3-methylphenoxyacetatocopper(II) hydrates. Their e.s.r. spectra, electronic spectra, and magnetic properties were studied. When R—COO is the 2-methylphenoxyacetate anion and L is the pyridine-*N*-oxide, then n equals 2. This is a magnetically diluted complex of tetragonal symmetry. In all other cases n equals 1. The complex $\text{Cu}(\text{phoac})_2(\text{pyo})$ is antiferromagnetic and its susceptibility data have been fitted to various models for polynuclear complexes. The spectral and magnetic data of other complexes of this group indicate that the complexes are dimeric with bridging carboxyl groups and *N*-oxide bound monodentately in the axial positions of the complex molecule.

Реакциями соответствующих гидратов феноксиацетата меди и 2- или 3-метилфеноксиацетатов меди с *N*-оксидом пиридина и *N*-оксидом 2-метилпиридина были приготовлены и, затем, охарактеризованы с помощью ЭПР и электронной спектроскопии комплексы состава $\text{Cu}(\text{R}-\text{COO})_2\text{L}_n$. Были также изучены их магнитные свойства. В случае, когда R—COO

* For Part XXI see Ref. [10].

phoac — phenoxyacetate anion

2-mephoac — 2-methylphenoxyacetate anion

4-mephoac — 4-methylphenoxyacetate anion

pyo — pyridine-*N*-oxide

2-mepyuo — 2-methylpyridine-*N*-oxide

представляет собой 2-метилфеноксиацетат-анион, а L — *N*-оксид пиридина, *n* равнялось 2. Этот комплекс относится к числу магнитно разбавленных комплексов с тетрагональной симметрией. Во всех остальных случаях *n* = 1. Комплекс Cu(phoac)₂(pyo) является антиферромагнитным; были испробованы различные модели для объяснения его магнитной восприимчивости. Обнаруженные спектральные и магнитные свойства других комплексов этой группы свидетельствуют об их двухъядерной структуре с карбоксильными мостиками и *N*-оксидами в аксиальных положениях молекулы комплекса.

The aryloxyacetate anions form less frequently dimeric Cu(II) complexes with various types of molecular ligands (mainly H₂O) than the alkancarboxylate anions of similar basicity do. For example the complex Cu(phoac)₂(H₂O) is magnetically diluted [1]. The complexes Cu(phoac)₂(H₂O)₃ and Cu(phoac)₂(H₂O)₂ are penta- and hexacoordinated and they have tetragonal symmetry [2—4]. In the case of Cu(phoac)₂(H₂O)₃ the phenoxyacetate anion is monodentate and is bound via the oxygen atom of the carboxyl group [2, 3]. The phenoxyacetate anion is able to attach itself also as a chelate ligand simultaneously through the carboxylic and etheric oxygen atoms, e.g. in the complex Cu(phoac)₂(H₂O)₂ [4]. The coordinated H₂O molecules in these complexes participate in the system of hydrogen bonds in the crystal structure.

The formation of various structural types of aryloxyacetatocopper(II) complexes was studied also in dependence on the substituents present on the aromatic ring [1, 5—7]. Whereas 2- and 3-methyl derivatives form complexes of the composition Cu(R—COO)₂(H₂O)₂, 4-methylphenoxyacetate anion forms preferentially Cu(R—COO)₂(H₂O)₃. The composition and properties of these complexes are similar to those of the corresponding phenoxyacetatocopper(II) complexes.

The H₂O molecules located in the base of the square pyramidal complex Cu(phoac)₂(H₂O)₃ [2, 3] can be substituted by pyridine molecules and the complex Cu(phoac)₂(py)₂(H₂O) is formed [8]. The isomeric methylphenoxyacetate anions form analogical Cu(II) complexes with pyridine and H₂O [9]. On the other hand, the coordination of 2-methylpyridine leads to the formation of “magnetically condensed” phenoxy- and methylphenoxyacetatocopper(II) complexes of the composition Cu(R—COO)₂(2-mepy) with properties of dimeric, carboxylato bridged copper(II) complexes [9]. This indicates the important influence of molecular ligands on the manner of coordination of aryloxyacetate ions in copper(II) complexes.

Herein we report studies on the formation and properties of phenoxy-, 2-methylphenoxy-, and 4-methylphenoxyacetatocopper(II) complexes with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide. In copper(II) complexes *N*-oxide molecular ligands (like the carboxylate anions) are capable to coordinate either monodentately or as bridging ligands.

Experimental

Preparation of complexes

The mole ratios in the reaction systems were $x(\text{Cu}(\text{R}-\text{COO})_2 \cdot (\text{H}_2\text{O})_n)/x(\text{N-oxide}) = 1:4$. For preparation of methylphenoxyacetatocopper(II) complexes it was necessary to add 0.5 mol of corresponding acid to the reaction systems. All complexes were dried in air at room temperature. The results of analyses are listed in Table 1.

Table 1

Analytical data of the prepared complexes (w/mass %)

Complex	Calculated/found			
	Cu	C	H	N
Cu(phoac) ₂ (pyo)	13.79	54.73	4.15	3.04
	13.79	54.70	3.96	3.00
Cu(phoac) ₂ (2-mepyo)	13.38	55.64	4.46	2.95
	13.40	55.52	4.60	3.03
Cu(2-mephoac) ₂ (pyo) ₂	10.88	57.53	4.83	4.79
	10.86	57.20	4.77	4.77
Cu(2-mephoac) ₂ (2-mepyo)	12.63	57.25	5.00	2.78
	12.46	57.45	5.09	2.89
Cu(4-mephoac) ₂ (pyo)	12.99	56.49	4.74	2.86
	13.00	56.64	4.98	2.91
Cu(4-mephoac) ₂ (2-mepyo)	12.63	57.25	5.00	2.78
	12.60	57.41	5.19	2.80

Cu(phoac)₂(pyo)

The solution of phenoxyacetatocopper(II) trihydrate (4.2 g) in dioxan (40 cm³) at 50°C was added to the solution of pyridine-*N*-oxide (3.8 g) in ethanol (200 cm³). The reaction system was heated up to boiling. The resulting solution was filtered, allowed to cool and a light green product was deposited. The complex was recrystallized from butyl alcohol.

Cu(phoac)₂(2-mepyo)

When phenoxyacetatocopper(II) trihydrate (4.2 g) was moderately heated with 2-methylpyridine-*N*-oxide (4.4 g) a suspension was formed. Acetone (60 cm³) was added and the reaction system was heated up to boiling. The green solution was filtered and then cooled down to room temperature. A green powder was deposited and then it was recrystallized from acetone.

$\text{Cu}(2\text{-mephoac})_2(\text{pyo})_2$

The reaction system was prepared by dissolving pyridine-*N*-oxide (3.8 g) in propyl alcohol (15 cm³) containing 2-methylphenoxyacetatocopper(II) dihydrate (4.3 g) and 2-methylphenoxyacetic acid (0.8 g). The system was heated up to boiling. The resulting solution was filtered and allowed to cool. A blue complex was deposited and washed with ether.

 $\text{Cu}(2\text{-mephoac})_2(2\text{-mepyo})$

The ligand (2-methylpyridine-*N*-oxide) (4.4 g) was dissolved in ethanol solution (50 cm³) of 2-methylphenoxyacetatocopper(II) dihydrate (4.3 g) and 2-methylphenoxyacetic acid (0.8 g). The solution was brought to boiling and filtered. After the solution had cooled down, the green product was deposited and washed with ether.

 $\text{Cu}(4\text{-mephoac})_2(\text{pyo})$

4-Methylphenoxyacetatocopper(II) trihydrate (4.5 g) and 4-methylphenoxyacetic acid (0.8 g) were dissolved in hot ethanol (200 cm³) and added to a 70 cm³ solution of pyridine-*N*-oxide (3.8 g). The reaction system was heated up to boiling. From the resulting solution a green complex was deposited and washed with ether.

 $\text{Cu}(4\text{-mephoac})_2(2\text{-mepyo})$

2-Methylpyridine-*N*-oxide (4.4 g) was dissolved in ethanol (80 cm³) containing 4-methylphenoxyacetatocopper(II) trihydrate (4.5 g) and 4-methylphenoxyacetic acid (0.8 g). The reaction system was heated up to boiling and filtered. A green complex crystallized immediately. The product was recrystallized from butyl alcohol.

Physical measurements

Electron spin resonance spectra of polycrystalline solids were recorded on a Varian E-4 spectrometer in X band ($\nu \sim 9.1$ GHz) employing 100 kHz modulation in the temperature range 77—293 K. DPPH was used as a standard for the determination of *g* values.

Electronic spectra of mullied solids were registered on a Specord UV VIS (Zeiss, Jena) in the range 13 000—28 000 cm⁻¹, and in the case of the complex $\text{Cu}(\text{phoac})_2(\text{pyo})$, also on UNICAM SP-700 in the range 10 000—28 000 cm⁻¹.

The values of magnetic susceptibility were determined by the Gouy method on a commercial equipment (Newport Instruments Ltd.) at room temperature and in the case of $\text{Cu}(\text{phoac})_2(\text{pyo})$, in the temperature range 92—337 K. The measurement conditions were as previously reported [10]. The effective magnetic moments were calculated using the equation $\mu_{\text{eff}} = F[(\chi'_M - N_a)T]^{1/2}$, where $F = 798 \text{ m}^{-3/2}$

$K^{-1/2} \text{ mol}^{1/2}$ and χ'_M is the molar susceptibility corrected for diamagnetism [11]. The value of temperature independent paramagnetism N_a was taken as $75 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ for the magnetically diluted complex $\text{Cu}(2\text{-mephoac})_2(\text{pyo})_2$ and in all other cases of complexes with magnetic interactions as $94 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ [12].

Susceptibility equations

The magnetic data of $\text{Cu}(\text{phoac})_2(\text{pyo})$ were fitted to various models for polynuclear complexes. In all cases the possibility of a proportion of magnetically diluted complex was considered. The best fit was obtained by a mapping routine, minimizing the value $\sigma = \left[\sum^n (\chi'_{\text{calc}} - \chi'_{\text{exp}})^2 / n \right]^{1/2}$. The following models were considered:

a) Bleaney—Bowers equation for $S = 1/2$ coupled dimers [13, 14]

$$\chi'_M = (1-x) \frac{\mu_0 N_A \beta^2 g^2}{kT} [3 + \exp(-U(J)/kT)]^{-1} + x \frac{0.448 \text{ m}^3 \text{ mol}^{-1} \text{ K}}{T} + N_a \quad (1)$$

Here x is the mole fraction of monomer, $U(J)$ is the energy of the singlet triplet separation characterized by the exchange constant J , and the other remaining symbols have their usual meaning.

b) Tetramer involving a distorted (D_{2d}) cluster of copper(II) atoms probably consisting of two dimers associated via out of plane bridging [15, 16]

$$\chi'_M = (1-x) \frac{\mu_0 N_A \beta^2 g^2}{12kT} \frac{12 + 6K_1^2 K_2^{-2} + 30K_1^2 K_2^2}{6 + K_1^{-2} + K_1^2 K_2^{-4} + 3K_1^2 K_2^{-2} + 5K_1^2 K_2^2} + x \frac{0.448 \text{ m}^3 \text{ mol}^{-1} \text{ K}}{T} + N_a \quad (2)$$

where $K_1 = \exp(U(J_1)/kT)$, $K_2 = \exp(U(J_2)/kT)$.

In this equation J_{11} is the exchange constant for in plane interaction within each dimeric unit and J_2 is the constant for out of plane interaction between dimeric units.

c) Ising equation for linear polymer of copper(II) atoms [17]

$$\chi'_M = (1-x) \frac{\mu_0 N_A \beta^2 g^2}{12kT} \frac{\exp(4K) + (2 + K^{-1}) \exp(2K) - K^{-1} \exp(-2K) + 5}{\exp(2K) + \exp(-2K) + 2} + x \frac{0.448 \text{ m}^3 \text{ mol}^{-1} \text{ K}}{T} + N_\alpha \quad (3)$$

where $K = U(J)/kT$ and J is the exchange constant.

Results and discussion

Studying the reactions of phenoxy-, 2-methylphenoxy-, and 4-methylphenoxy-acetato-copper(II) complexes with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide we prepared green compounds of the composition $\text{Cu}(\text{R}-\text{COO})_2\text{L}$ (L is pyridine-*N*-oxide or 2-methylpyridine-*N*-oxide), the only one exception being a blue complex $\text{Cu}(\text{2-mephoac})_2(\text{pyo})_2$. This fact is remarkable, because there was an excess of the molecular ligand in the reaction system and consequently formation of complexes with higher content of bonded *N*-oxide was in principle possible.

The complex $\text{Cu}(\text{2-mephoac})_2(\text{pyo})_2$ shows an axial e.s.r. spectrum (Fig. 1) with $g_{\parallel} = 2.312$, $g_{\perp} = 2.070$, and $\bar{g} = 2.154$. The values of $g_{\perp} > 2.04$ and $G = 4.5$ [$G = (g_{\parallel} - 2)/(g_{\perp} - 2)$] allow us to classify this complex as a tetragonal Cu(II) system with parallel aligned local tetragonal axes and a ground state $d_{x^2-y^2}$ [18]. The exchange interactions are not significant and the experimental g factors reflect in a satisfactory way the local microsymmetry of the complex unit. In accordance with the e.s.r. spectrum the magnetic moment at room temperature is $\mu_{\text{eff}} = 1.92 \mu_B$, a value typical of magnetically diluted copper(II) complexes.

In the electronic spectra of $\text{Cu}(\text{2-mephoac})_2(\text{pyo})_2$ (Table 2) the maximum of the broad ligand field absorption band is at $\tilde{\nu}_{\text{max}} = 14\,600 \text{ cm}^{-1}$. A shoulder of another

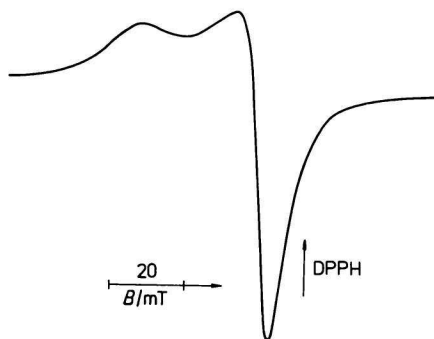


Fig. 1. Electron spin resonance spectrum of the complex $\text{Cu}(\text{2-mephoac})_2(\text{pyo})_2$ at 77 K.

Table 2

Spectral and magnetic properties

Complex	Electronic spectra		Magnetic properties		
	$\tilde{\nu}_{\max} \cdot 10^{-3}/\text{cm}^{-1}$	T/K	$\frac{\chi'_M \cdot 10^{11}}{\text{m}^3 \text{mol}^{-1}}$	μ_{eff}/μ_B	J/cm ⁻¹
Cu(phoac) ₂ (pyo)	26.5 sh 12.8 10.3 sh	287	1516	1.61	—
Cu(phoac) ₂ (2-mepyo)	26.8 sh 13.8	293	1029	1.32	-335
Cu(2-mephoac) ₂ (pyo) ₂	27.1 sh 14.6	293	2076	1.93	—
Cu(2-mephoac) ₂ (2-mepyo)	26.5 sh 13.5	293	1079	1.36	-315
Cu(4-mephoac) ₂ (pyo)	26.8 sh 13.4	293	1088	1.36	-315
Cu(4-mephoac) ₂ (2-mepyo)	26.7 sh 13.1	293	1079	1.36	-315

sh — shoulder.

intensive band can be observed at $\tilde{\nu}_{\text{sh}} \sim 27\,100\text{ cm}^{-1}$. With regard to magnetic properties of the complex this band is considered to be caused by some kind of common mechanism of the metal—ligand charge transfer.

The composition, spectral and magnetic properties of the complex Cu(2-mephoac)₂(pyo)₂ show that its symmetry is tetragonal with *trans*-planar coordination of anionic and molecular ligands completed by donor oxygen atoms from the crystal structure to a distorted octahedral coordination polyhedron. With regard to the possibility of the anionic ligand to form chelate complexes [4], the completing of coordination polyhedron with etheric oxygen of 2-methylphenoxyacetate anion is possible also within the same complex molecule.

The complexes Cu(phoac)₂(2-mepyo), Cu(2-mephoac)₂(2-mepyo), Cu(4-mephoac)₂(pyo), and Cu(4-mephoac)₂(2-mepyo) exhibit a significant similarity in their spectral and magnetic properties. The e.s.r. spectra of these complexes (Fig. 2) are typical of spin—spin interacting binuclear copper(II) complexes with bridging ligands, where a ground state is a diamagnetic singlet ($S = 0$), while the

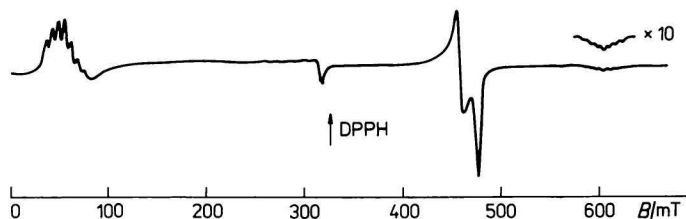


Fig. 2. Electron spin resonance spectrum of the complex Cu(4-mephoac)₂(2-mepyo) at 103 K.

excited, thermal populated state is a triplet ($S = 1$). The e.s.r. spectra are due to the resonance transitions in the triplet state. The spin-Hamiltonian for triplet state dimeric copper(II) complexes may be written as [19, 20]

$$\hat{H}_S = g_{\parallel}\beta B_z \hat{S}_z + g_{\perp}\beta(B_x \hat{S}_x + B_y \hat{S}_y) + U(D)[\hat{S}_z^2 - 1/3 \cdot S(S+1)] + U(E)(\hat{S}_x^2 - \hat{S}_y^2) + U(A_{\parallel})\hat{I}_z \hat{S}_z \quad (4)$$

where $S = S_1 + S_2 = 1$, $I = I_1 + I_2 = 3$

The parameters of this Hamiltonian for the studied complexes are given in Table 3. The zero field splitting parameters D , E and parallel and perpendicular components of the g tensor were obtained using a procedure based on the analysis of the e.s.r. spectra of randomly oriented molecules in triplet state [21].

Table 3

Spin-Hamiltonian parameters for the dimeric complexes

Complex	g_{\perp}	g_{\parallel}	\bar{g}	D/cm^{-1}	E/cm^{-1}	$A_{\parallel}/\text{cm}^{-1}$	α^2
Cu(phoac) ₂ (2-mepyo)	2.075	2.385	2.183	0.370	0.001	0.0067	0.83
Cu(2-mephoac) ₂ (2-mepyo)	2.070	2.379	2.178	0.370	0.005	0.0072	0.85
Cu(4-mephoac) ₂ (pyo)	2.074	2.388	2.181	0.376	0.002	0.0067	0.83
Cu(4-mephoac) ₂ (2-mepyo)	2.071	2.379	2.179	0.370	0.005	0.0067	0.82

All the studied complexes exhibit very similar values of the zero field splitting parameter D ($D \in \langle 0.370 \text{ cm}^{-1}, 0.376 \text{ cm}^{-1} \rangle$). Since under our operative conditions $U(D)$ is larger than $h\nu$ it is not possible to observe the half field transition " $\Delta M_S = 2$ ".

The experimentally determined zero-field splitting parameter D can be considered a sum of magnetic dipole interaction D_{DD} and a pseudodipolar term D_{pseudo} originating from the spin-orbital interaction

$$|D_{exp} \doteq D_{DD} + D_{pseudo}|$$

For dimeric complexes with the copper(II) acetate structure the D_{DD} contribution has been estimated in the range from -0.12 to -0.20 cm^{-1} [22, 23]. The pseudodipolar term is given approximately by [22]

$$D_{pseudo} = -\frac{J'}{32} [(g_{\parallel} - 2.0023)^2 - 4(g_{\perp} - 2.0023)^2] \quad (5)$$

Thus an estimation of exchange interactions in the excited electronic state J' can be made using these equations and our experimental data. For the complexes under investigation the J' values are in the range from -124 to -148 cm^{-1} , depending

on the used value of D_{DD} . These values are consistent with the J' values known for dimeric carboxylatocopper(II) complexes [22—24]. Generally, J' is smaller than the singlet-triplet separation in ground electronic state ($J' \sim J/2$).

The perpendicular component of the e.s.r. line at 460 mT is more or less split at 103 K. This is an evidence for the nonzero value of the spin-Hamiltonian parameter E , and consequently, for the rhombic distortion of the coordination polyhedron. The trend in E values indicates that the deviation from axial symmetry around the paramagnetic unit increases in the order $\text{Cu}(\text{phoac})_2(2\text{-mepyo}) < \text{Cu}(4\text{-mephoac})_2(\text{pyo}) < \text{Cu}(2\text{-mephoac})_2(2\text{-mepyo}) \sim \text{Cu}(4\text{-mephoac})_2(2\text{-mepyo})$.

The expected seven-line hyperfine splitting (with the ratios of intensities 1:2:3:4:3:2:1) from two equivalent copper(II) nuclei was observed on the high and low field lines (H_{z_1} and H_{z_2}) at 103 K. It was not possible to recognize the hyperfine splitting on the perpendicular components of the spectrum (the H_x and H_y lines), because its value is low in comparison with the e.s.r. line width.

In addition in all e.s.r. spectra weak absorptions near 330 mT were also observed. Since the intensities of these absorptions increase with a decreasing temperature, they have been assigned to a small percentage of magnetically diluted ($S = 1/2$) monomeric complex units. The parameters of the axial spectra with $g_{\perp} < g_{\parallel}$ are shown in Table 4. The well resolved hyperfine structure in the parallel direction is approximately twice as large as in the case of corresponding dimeric complexes.

For the dimeric complexes, as well as for their monomeric impurities the bonding parameters α^2 were calculated using the equation [25]

$$\alpha^2 = \frac{A_{\parallel}}{0.036 \text{ cm}^{-1}} + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04 \quad (6)$$

These parameters reflect the covalency of metal—ligand bond. In the case of dimeric complexes the value A_{\parallel} was taken as twice that experimentally observed [24]. The obtained α^2 values (Tables 3 and 4) are within the range from 0.77 to 0.85 and are typical of copper(II) complexes with oxygen ligands [24].

Table 4

Electron spin resonance parameters derived from monomer impurity signals

Parent complex	g_{\perp}	g_{\parallel}	\bar{g}	$A_{\parallel}/\text{cm}^{-1}$	α^2
$\text{Cu}(\text{phoac})_2(2\text{-mepyo})$	2.047	2.366	2.159	0.0145	0.83
$\text{Cu}(2\text{-mephoac})_2(2\text{-mepyo})$	2.056	2.291	2.137	0.0149	0.77
$\text{Cu}(4\text{-mephoac})_2(\text{pyo})$	2.052	2.317	2.144	0.0151	0.80
$\text{Cu}(4\text{-mephoac})_2(2\text{-mepyo})$	2.040	2.316	2.136	0.0151	0.79

The spin-Hamiltonian parameters for the complexes $\text{Cu}(\text{phoac})_2(2\text{-mepyo})$, $\text{Cu}(2\text{-mephoac})_2(2\text{-mepyo})$, $\text{Cu}(4\text{-mephoac})_2(\text{pyo})$, and $\text{Cu}(4\text{-mephoac})_2(2\text{-mepyo})$ correspond to the values usually found for dimeric carboxylatocopper(II) complexes [26].

The results of the e.s.r. spectral study prove unambiguously the dimeric structure of these complexes. The two copper(II) atoms in the dimeric molecule are linked by four bridging carboxylate groups and the *N*-oxide molecules are bound monodentately in the axial positions of the complex unit. In the complexes under investigation such a coordination of *N*-oxide molecules (a consequence of a σ donor and π acceptor ability of molecular ligands together with the properties of corresponding anionic ligands including steric effects), causes the charge on the Cu_2O_{10} fragment to reach the optimum value for the formation of dimeric complex molecule.

The results of electronic spectra and magnetic data of the four dimeric complexes are in accordance with the results obtained on the basis of e.s.r. study (Table 2). The effective magnetic moments ($\mu_{\text{eff}} = 1.32\text{--}1.36 \mu_B$) are significantly subnormal at room temperature. The value of the separation between the singlet and triplet states J was found using the Bleaney—Bowers equation (1) (where $x = 0$), in which for g the g factor values found from e.s.r. spectra were taken. The obtained values of J are in the range from -315 to -335 cm^{-1} in accordance with the assumed dimeric structure with bridging carboxyl groups.

In the electronic spectra of the complexes under investigation the ligand field transition band with a maximum in the range $\tilde{\nu}_{\text{max}} = 13\,100\text{--}13\,800 \text{ cm}^{-1}$ appears. This fact is in agreement with the assumed tetragonal-pyramidal ligand field around Cu(II). The absorption band at $\tilde{\nu}_{\text{sh}} \sim 27\,000 \text{ cm}^{-1}$ could not be taken as an evidence for an antiferromagnetic spin—spin coupling, since similar absorption bands were found also for magnetically diluted parent aquacomplexes [7] and for $\text{Cu}(2\text{-mephoac})_2(\text{pyo})_2$.

The magnetic and spectral properties of $\text{Cu}(\text{phoac})_2(\text{pyo})$ differ considerably from those of the above complexes, although the composition of all these

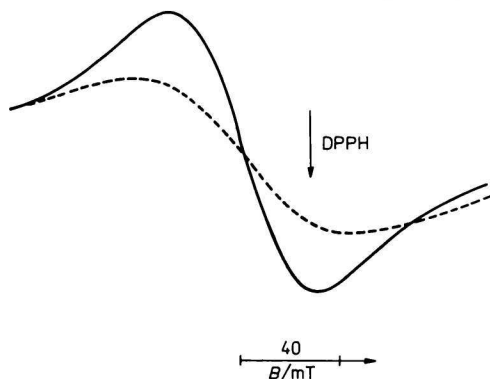


Fig. 3. Electron spin resonance spectrum of the complex $\text{Cu}(\text{phoac})_2(\text{pyo})$ at 253 K (dashed line) and at 103 K (full line).

complexes is very similar. In the electronic spectrum of this light green complex the ligand field transition is shifted to the range of lower energies with a maximum at $\tilde{\nu}_{\max} = 12\,800\text{ cm}^{-1}$ and with a good resolved shoulder at $\tilde{\nu}_{\text{sh}} \sim 10\,300\text{ cm}^{-1}$.

A broad symmetrical singlet signal with $g_0 = 2.173$ can be observed in the e.s.r. spectrum of $\text{Cu}(\text{phoac})_2(\text{pyo})$ (Fig. 3). The shape of line indicates an exchange interaction. The line width decreases markedly with the decreasing temperature ($\Delta B = 91\text{ mT}$ at 295 K and $\Delta B = 58\text{ mT}$ at 103 K). The half field transition " $\Delta M_S = 2$ " could not be observed.

The results of magnetic susceptibility measurements of $\text{Cu}(\text{phoac})_2(\text{pyo})$ in the temperature range 92–337 K are listed in Table 5. The found value of the effective magnetic moment ($\mu_{\text{eff}} = 1.61\ \mu_B$) at room temperature is subnormal. With the decreasing temperature the value of μ_{eff} decreases significantly to $\mu_{\text{eff}} = 0.84\ \mu_B$ at 92 K. The susceptibility passes through a flat maximum at $T_N \sim 205\text{ K}$ (Fig. 4), which is an evidence for an antiferromagnetic interaction between the paramagnetic centres in the structure of the complex.

Table 5

Magnetic properties of the complex $\text{Cu}(\text{phoac})_2(\text{pyo})$

T/K	$\chi_M \cdot 10^{11}/\text{m}^3\text{ mol}^{-1}$	μ_{eff}/μ_B
337	1406	1.68
308	1509	1.67
287	1516	1.61
261	1553	1.56
241	1642	1.54
208	1660	1.44
192	1646	1.38
162	1598	1.25
141	1548	1.14
111	1384	0.95
92	1299	0.84

The susceptibility vs. temperature data have been fitted to various polynuclear models. Reasonable fits within experimental error were obtained in cases discussed below. The equations for these models are given in Experimental and the best fitting parameters are listed in Table 6.

A good fit to the Bleaney—Bowers equation for $S = 1/2$ coupled dimers can be obtained only if a presence of comparatively large proportion ($x = 0.09$) of monomeric impurity is assumed. As no e.s.r. signal of such an impurity was observed, the dimeric structure for $\text{Cu}(\text{phoac})_2(\text{pyo})$ seems to be improbable.

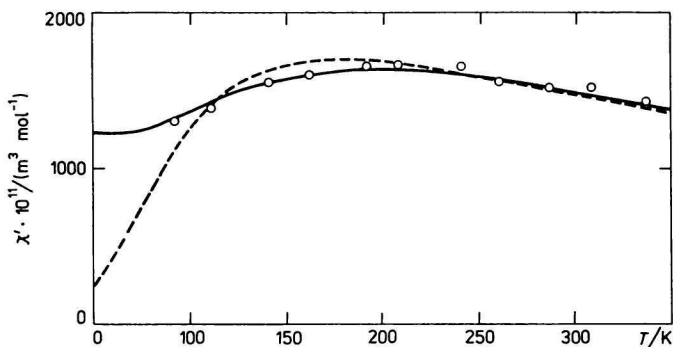


Fig. 4. Temperature dependence of magnetic susceptibility for the complex $\text{Cu}(\text{phaoac})_2(\text{py})$. Experimental points are indicated by circles. The full line represents the calculated values for the Ising model ($g = 2.50$, $J = -150 \text{ cm}^{-1}$) and the dashed line the calculated values for the tetramer (D_{2d}) of coppers ($g = 2.32$, $J_1 = -100 \text{ cm}^{-1}$, $J_2 = -30 \text{ cm}^{-1}$).

For a tetramer structure involving a distorted (D_{2d}) cluster of $\text{Cu}(\text{II})$ atoms, possibly consisting of two dimers associated *via* out of plane bonding, a reasonable fit within the experimental error can be obtained, if we assume that both the interactions within the dimers and those between the dimeric units are of antiferromagnetic nature (Fig. 4).

If an interaction of $\text{Cu}(\text{II})$ centres along a chain is assumed, the magnetic data can be fitted to the Ising model for linear antiferromagnetism (Fig. 4). In this case the value of $g = 2.50$, necessary for a good fit is unreasonably high for a $\text{Cu}(\text{II})$ complex, though such g values were recently reported [27] for fitting of magnetic properties of some linear polymer $\text{Cu}(\text{II})$ complexes.

Table 6

The best fits of magnetic data of the complex $\text{Cu}(\text{phaoac})_2(\text{py})$ to various polynuclear models^a

Model (eqn No.)	g	$\frac{J \text{ (or } J_1)}{\text{cm}^{-1}}$	$\frac{J_2}{\text{cm}^{-1}}$	Mole fraction of the monomer	$\frac{\sigma \cdot 10^{11}}{\text{m}^3 \text{ mol}^{-1}}$
				x	
Dimer (1)	2.17	-220	—	0.09	66
Distorted tetrahedron of coppers (2)	2.32	-100	-30	0.00	71
Ising linear polymer (3)	2.50	-150	—	0.00	40

a) The way of fitting and the appropriate equations are given in Experimental.

On the basis of the obtained results the dimeric structure with bridging carboxyl groups for the complex $\text{Cu}(\text{phoac})_2(\text{pyo})$ can be ruled out. The complex is more likely of tetrameric or polymeric structure, involving a proper bridging system required for the antiferromagnetic exchange. If the magnetic properties of this complex are to be explained in more detail, the information on the crystal structure would be necessary.

We have shown that phenoxy-, 2-methylphenoxy-, and 4-methylphenoxyacetato anions form preferentially dimeric, tetrameric or polynuclear $\text{Cu}(\text{II})$ complexes with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide, while the analogous cresotatocopper(II) complexes are mostly monomeric [28]. This is a further contribution to the investigation on the mutual influence of anionic and molecular ligands on the formation of carboxylatocopper(II) complexes of different structures.

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Translated by G. Plesch