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EPR Study of Local and Cooperative Symmetry Effects in *N*-Salicylideneglycinatocopper(II) Complexes*

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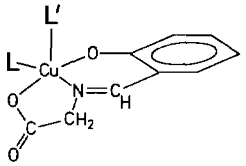
Abstract

N-Salicylideneglycinatocopper(II) complexes of the composition Cu(salgly)(L)$(H_2O)_x$ with L = imidazole, $x = 0$ (**I**); L = 2-propylimidazole, $x = 1$, (**II**); L = pyridine, $x = 0$ (**III**); L = pyrazole, $x = 1$ (**IV**) and L = 3,5-dimethylpyrazole, x = 1 (**V**) were synthesized. The EPR and ligand field spectra of these compounds as well as of *N*-salicylideneglycinatothioureacopper(II) (**VI**) give evidence for a square-pyramidal Cu(II) coordination. The EPR spectra of **I**, **II** and **III** can be reasonably interpreted using axial molecular *g* tensors, whereas the molecular *g* tensors of **IV**, **V** and **VI** exhibit orthorhombic symmetry. The experimental EPR spectrum of **VI** shows molecular *g* values in accordance with the ferrodistortive order found previously by X-ray structural analysis. In **V** no exchange interactions between crystallographically non-equivalent Cu(II) ions were found. The complexes **I**–**IV** show exchange coupled *g* parameters, corresponding to an antiferrodistortive (**I**, **III**) or disturbed antiferrodistortive ordering (**II**, **IV**). The alkyl-substitution on the neutral ligand and the presence of water in the crystal structure strongly influence the exchange interactions between Cu(II) ions.

Introduction

Copper(II) complexes with N-salicylideneaminoacidato tridentate Schiff bases are interesting from the view of bioinorganic chemistry, since they serve as models for the catalytic intermediates in reactions of pyridoxalphosphate with aminoacids [1–3]. Much attention has been devoted to the study of copper(II) complexes with *N*-salicylideneglycinato ligand. In all Cu(II) complexes with this ligand, which were examined by X-ray structural analysis, square pyramidal coordination around the Cu(II) ion was found [4–6].



The donor atoms (O N O) of the tridentate ligand are bound in the base of the coordination polyhedron. In *N*-salicylideneglycinatoaquocopper(II) tetrahydrate [4] the remaining site in the plane as well as the apex of the pyramide are occupied by water molecules. In *N*-salicylideneglycinatoaquocopper(II) hemihydrate [5] a water molecule is bound in the base, whereas a carboxyl oxygen atom of the neighbouring molecule lies in the apical site. The reaction of *N*-salicylideneglycinatoaquocopper(II) hemihydrate with thiourea leads to *N*-salicylideneglycinatothioureacopper(II) complex [6]. In the base of its coordination polyhedron the donor atoms of the tridentate ligand and the sulphur atom of thiourea are bound. In this case the apices of two adjacent pyramids are formed each by a phenolic oxygen atom of the neighbouring molecule, thus providing $[Cu(salgly)(tu)]_2$ dimers. Nevertheless the magnetic susceptibility obeys the Curie–Weiss law

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in the range 90–330 K ($\theta = 0.3$ K) [6]. The substitution of basal water molecule in *N*-salicylideneglycinatoaquocopper(II) hemihydrate by pyridine and its derivatives has been reported in ref. 7. While the EPR spectra of most complexes described [7] are axial with $g_\parallel > g_\perp$, the spectra of adducts with 3-methyl- and 4-methylpyridine are 'inverted' ($g_\perp > g_\parallel$).

In order to study the influence of neutral ligands on the structure of Cu(II) complexes with tridentate Schiff bases, we prepared *N*-salicylideneglycinatocopper(II) complexes with imidazole, its isomer pyrazole, some of their alkyl-derivatives and pyridine (the non-hydrated complex). EPR and ligand field spectra of these new compounds as well as of *N*-salicylideneglycinatothioureacopper(II) were studied. In particular the EPR spectroscopic investigations yield valuable informations about local and cooperative symmetry effects in these complexes.

TABLE I Analytical Data of *N*-Salicylideneglycinatocopper-(II) Complexes

Compound[a]	*Anal.* calc. (found) (%)		
	C	H	N
Cu(salgly)(Iz)	46.68 (46.63)	3.59 (3.41)	13.60 (13.61)
Cu(salgly)(2-Pr-Iz)(H_2O)	48.84 (49.00)	5.19 (5.34)	11.39 (11.39)
Cu(salgly)(Pz)(H_2O)	44.10 (43.70)	4.00 (4.00)	12.85 (13.15)
Cu(salgly)(3,5-dMe-Pz)(H_2O)	47.38 (47.41)	4.83 (4.86)	11.84 (11.81)
Cu(salgly)(Py)	52.58 (52.68)	3.78 (3.70)	8.76 (8.68)
Cu(salgly)(tu)	37.91 (37.39)	3.50 (3.48)	13.26 (13.02)

[a] salgly = *N*-salicylideneglycinato anion; Iz = imidazole; 2-Pr-Iz = 2-propylimidazole; Pz = pyrazole; 3,5-dMe-Pz = 3,5-dimethylpyrazole; tu = thiourea; Py = pyridine.

Experimental

N-Salicylideneglycinatothioureacopper(II) and *N*-salicylideneglycinatoaquocopper(II) hemihydrate were prepared according to refs. 6 and 10, respectively. The adducts with imidazole, pyrazole and their derivatives were synthesized in diluted ethanol (ethanol:water = 3:1). 1.38 g (0.5×10^{-3} mol) of *N*-salicylideneglycinatoaquocopper(II) hemihydrate were dissolved in 140 cm^3 of solvent, heated up to boiling, and 1×10^{-2} mol of ligand (0.68 g of imidazole or pyrazole, or 0.96 g of 3,5-dimethylpyrazole, or 1.1 g of 2-propylimidazole) were added. The resulting hot solutions were filtered and allowed to cool down to room temperature. The green or dark green crystalline products were deposited, washed with cool solvent and dried in air. *N*-salicylideneglycinatopyridinecopper(II) was prepared in an analogical way by the reaction of non-recrystallized *N*-salicylideneglycinatocopper(II) hydrate [10] (1 g) with pyridine (2.95 g) in 50 cm^3 of hot water. The analytical data of the obtained compounds are given in Table I.

The ligand field reflectance spectra of finely powdered samples were scanned in the range 4000–28 000 cm^{-1} with the Zeiss DMR-21 spectrometer at room temperature and at 77 K. Sr_2ZnTeO_6 and MgO were used as standards in the 4000–13 000 and 13 000–28 000 cm^{-1} ranges, respectively.

The EPR powder spectra were recorded with the Varian E-15 spectrometer at Q-band frequency (34.4 GHz) at room temperature and at 130 K. There were no significant changes in the spectra scanned at both temperatures. The EPR data given in Table II were obtained from the measurements at room temperature. DPPH was used as an internal standard.

TABLE II. Ligand Field Bands and EPR Data (Molecular *g* Values) of *N*-Salicylideneglycinatocopper(II) Complexes

Compound	Electronic spectra $\times 10^{-3}$ (cm^{-1})		EPR data (±0.002)			
	±0.2	±0.5	g_x $g_\perp$	g_y	g_z $g_\parallel$	$\bar{g}$[a]
Cu(salgly)(tu)	15.0	17.0sh	2.035	2.064	2.220	2.106
Cu(salgly)(Pz)(H_2O)[b]	15.8		2.038	2.078	2.247	2.121
Cu(salgly)(3,5-dMe-Pz)(H_2O)	15.0		2.038	2.081	2.257	2.125
Cu(salgly)(Py)	15.0	17.5sh	2.054		2.252	2.120
Cu(salgly)(Iz)	15.5	17.8sh	2.053		2.245	2.117
Cu(salgly)(2-Pr-Iz)(H_2O)	15.3	17.8sh	2.057		2.262	2.125

[a] $\bar{g} = 1/3\,(g_x + g_y + g_z) = 1/3\,(2g_\perp + g_\parallel)$. [b] Uncertainty in *g* values ±0.01 (see text).

Results and Discussion

The ligand field spectra of *N*-salicylideneglycinatocopper(II) complexes with thiourea, pyridine, imidazole and 2-propylimidazole consist of a broad asymmetric band with a shoulder on the side of lower wavelengths (Table II). The maximum is probably composed of the $d_{x^2-y^2} \leftarrow d_{z^2}$ and $d_{x^2-y^2} \leftarrow d_{xy}$ transitions. The shoulder may be assigned to the $d_{x^2-y^2} \leftarrow d_{xz}$, d_{yz} transition. In the spectra of adducts with pyrazole and 3,5-dimethylpyrazole the shoulder was not clearly resolved and an approximately symmetrical band, which involves probably all three d–d transitions, was observed (Table II). At 77 K some narrowing of the bands occurred, but the resolution did not significantly improve even at this temperature.

The *N*-salicylideneglycinatothioureacopper(II) complex shows an orthorhombic EPR spectrum with $g_z = 2.220$, $g_y = 2.064$ and $g_x = 2.035$ (Fig. 1a). These values are in accordance with the data reported in ref. 6, however, the anisotropy between g_x and g_y could not be observed at X-band frequency. Taking for simplicity $g_\perp \simeq (g_x + g_y)/2 = 2.050$, a parameter of $G = 4.5$ ($G = (g_\parallel - 2.002)/(g_\perp - 2.002)$) [11] is obtained. This value indicates that the experimental data correspond to molecular g values. It is in accordance with the results of X-ray structural analysis of this compound [6], which shows a ferrodistortive order of complex molecules in the crystal. The sharp EPR lines indicate weak exchange interactions between crystallographically equivalent Cu(II) ions in dimers $[Cu(salgly)(tu)]_2$ (Cu···Cu = 349 pm).

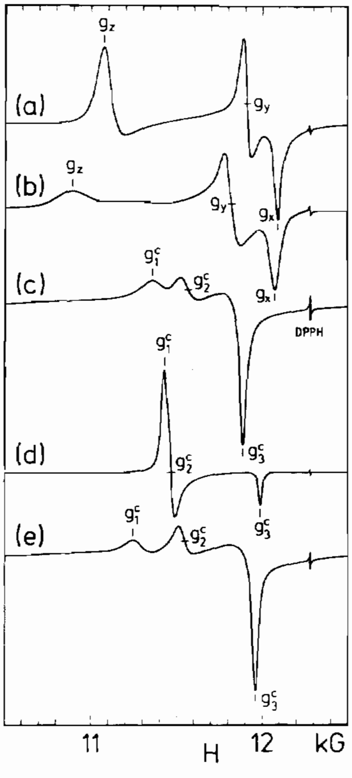

Fig. 1. EPR powder spectra (34.4 GHz, room temperature) of (a) Cu(salgly)(tu), (b) Cu(salgly)(3,5-dMe-Pz)(H_2O), (c) Cu(salgly)(Pz)(H_2O), (d) Cu(salgly)(Iz), (e) Cu(salgly)(2-Pr-Iz)(H_2O).

An orthorhombic EPR spectrum with $g_z = 2.257$, $g_y = 2.081$, $g_x = 2.038$ was also observed for *N*-salicylideneglycinato-3,5-dimethylpyrazolecopper(II) monohydrate (Fig. 1b). In the same way as above, values of $g_\perp \simeq 2.060$ and $G = 4.4$ are obtained. These data again indicate that molecular g parameters are measured. In this case, however, exchange interactions are to be excluded, because in measurements on single crystals more than one angular dependent signal was observed [12]. It is noteworthy that the g_x value is almost the same as that found for the adduct with thiourea, but the g_z and g_y components of both compounds differ distinctly (Table II). The reduction of g_z and g_y in the complex with a sulphur donor atom is probably caused by π-bonding of sulphur with d_{xy} and d_{xz} metal orbitals.

The EPR spectrum of *N*-salicylideneglycinatopyrazolecopper(II) monohydrate is orthorhombic with $g_1^c = 2.166$, $g_2^c = 2.128$, $g_3^c = 2.069$ (Fig. 1c). Apparently this spectrum cannot be interpreted in the same way as that of the adduct with 3,5-dimethylpyrazole (such interpretation would lead to $G = 1.7$). This in this case crystal g values (g^c) are observed. When the unit cell contains two sets of crystallographically non-equivalent axial complex molecules with the main axes canted by an angle 2γ ($90° < 2\gamma < 180°$), the equations for crystal g values are given by [9, 13]

$$g_1^c = \sin^2\gamma g_\parallel + \cos^2\gamma g_\perp$$

$$g_2^c = \cos^2\gamma g_\parallel + \sin^2\gamma g_\perp \qquad (1)$$

$$g_3^c = g_\perp$$

The above expressions yield $g_\perp = 2.069$, $g_\parallel = 2.225$. These values result in $G = 3.3$, which is unreasonably low [11]. It leads to the conclusion that the complex under investigation exhibits some deviation from axial symmetry. For such case the expressions (1) are not fully valid and no analytical equations for crystal g values are available [11]. The molecular g values can be estimated, if we approximate that G reaches the same value ($G = 4.4$) as in the analogical adduct with 3,5-dimethylpyrazole. Further we assume that g_x equals 2.038 (a g_x which was found for adducts with 3,5-dimethylpyrazole and thiourea). The average g value, $\bar{g} = 1/3(g_1^c + g_2^c + g_3^c) = 1/3\ (g_x + g_y + g_z)$, which is determined by the ligand field, is not affected by the above transformations. With these conditions, the following molecular g values, $g_x = 2.038$, $g_y = 2.078$, $g_z = 2.247$, are obtained. In this case the uncertainity in molecular g parameters is estimated to be not greater than 0.01. So far it is apparent that the alkyl-substitution on pyrazole remarkably influences the exchange interactions in the solid state. Thus in a complex with the more bulky ligand 3,5-dimethylpyrazole no exchange interactions between crystallographically non-equivalent Cu(II) ions could be observed. Similar results were obtained in earlier investigations [7]. Whereas *N*-salicylideneglycinatocopper(II) adducts with 2,4-dimethylpyridine and quinoline showed axial EPR spectra with $g_\parallel > g_\perp$, the spectra of adducts with 3-methyl- and 4-methylpyridine were significantly influenced by exchange interactions ($g_\perp > g_\parallel$).

The *N*-salicylideneglycinatopyridinecopper(II) and *N*-salicylideneglycinatoimidazolecopper(II) complexes show similar EPR patterns. The spectrum of Cu(salgly)(Py) is 'inverted' axial with $g_\perp^c = 2.153$, $g_\parallel^c = 2.054$. The complex Cu(salgly)(Iz) shows a nearly axial EPR spectrum with $g_1^c = 2.152$, $g_2^c = 2.145$, $g_3^c = 2.053$ ($g_\perp^c \simeq (g_1^c + g_2^c)/2 = 2.149$, $g_\parallel^c \simeq g_3^c$) (Fig. 1d). Such spectra are typical of antiferrodistortively ordered Cu(II) polyhedra with the main axes aligned at the angle $2\gamma = 90°$ [8, 9]. In that case for the crystal g values the following equations hold [8, 9]

$$g_\parallel^c = g_\perp$$

$$g_\perp^c = \frac{g_\perp + g_\parallel}{2} \tag{2}$$

From these expressions the molecular g parameters $g_\perp = 2.054$, $g_\parallel = 2.252$ for Cu(salgly)(Py) and $g_\perp = 2.053$, $g_\parallel = 2.245$ for Cu(salgly)(Iz) are obtained. The resulting G values of 4.8 for both compounds are quite reasonable [11]. The spectral parameters of the adduct with pyridine resemble closely the data observed for the imidazole complex. Apparently the bonding properties of both ligands are very similar. Whereas Cu(salgly)(Py) shows an 'inverted' EPR pattern with crystal g values, for Cu(salgly)(Py)(H_2O) an axial EPR spectrum with $g_\parallel > g_\perp$ has been reported [7]. This fact is in agreement with the spectra of *N*-salicylideneglycinatocopper(II) adducts with methylpyridines [7]. In the case of monohydrates axial spectra with $g_\parallel > g_\perp$ have been found. On the other hand, the anhydrous complexes have shown 'inverted' EPR spectra. The water molecule apparently strongly influences the order in the crystal structure.

The EPR spectrum of *N*-salicylideneglycinato-2-propylimidazolecopper(II) monohydrate is orthorhombic with exchange coupled g components $g_1^c = 2.188$, $g_2^c = 2.131$, $g_3^c = 2.057$ (Fig. 1e). Equations (1) for disturbed antiferrodistortive order yield the following molecular g values $g_\perp = 2.057$, $g_\parallel = 2.262$. With these parameters $G = 4.7$ is calculated, which is a quite reasonable value. The canting angle 2γ between the principal axes follows from eqns. (1)

$$\cos 2\gamma = \frac{g_2 - g_1}{g_\parallel - g_\perp} = \frac{g_2 - g_1}{g_2 + g_1 - 2g_3} \tag{3}$$

In our case we obtain $2\gamma = 106°$. The alkyl-substitution on the pyrazole ligand (or/and the presence of water in the crystal structure) causes the change in the ordering of molecules.

Conclusions

The spectral data of *N*-salicylideneglycinatothioureacopper(II), in which a square-pyramidal Cu(II) coordination was previously found by X-ray structural analysis [6], are essentially consistent with the data obtained for remaining complexes under investigation. Therefore for all studied compounds a square-pyramidal coordination of the Cu(II) ion can be assumed. The base is then formed by three donor atoms of the tridentate ligand and one of the neutral ligand. However, on the basis of our spectral results it is not possible to decide whether the carboxyl or phenolic donor oxygen from the adjacent molecule (or in some cases oxygen from water molecule) lies in the apex of the pyramide.

The EPR spectra of *N*-salicylideneglycinatocopper(II) adducts with pyridine, imidazole and its 2-propyl-derivative can be reasonably interpreted using molecular g tensors of axial symmetry. On the other hand the spectra of complexes with thiourea, pyrazole and 3,5-dimethylpyrazole show molecular g tensors of orthorhombic symmetry. This fact can be explained by distortions in the base of the square pyramide. Such distortions are the consequence of intramolecular N–H···O bonds. They were actually found by X-ray structural analysis in *N*-salicylideneglycinatothioureacopper(II) [6]. In the case of adducts with pyridine, imidazole and 2-propylimidazole those hydrogen bonds cannot be realized (in imidazole and its 2-propylderivative from steric grounds), and the base of the pyramid is more regular.

From the fact that a consistent interpretation of molecular g values was achieved, it is evident that the local symmetry of the coordination polyhedra is mainly determined by the tridentate ligand. However, small changes on the neutral ligand, such as alkyl substitution, and a presence of water in the crystal structure cause significant changes in the cooperative symmetry (ordering) of complex molecules.

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