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COORDINATION GEOMETRIES AND COOPERATIVE ORDERING EFFECTS IN COPPER(II) COMPLEXES WITH TRIDENTATE SCHIFF BASE DIANIONS—III. EPR STUDY ON N-SALICYLIDENEGLYCINATOCOPPER(II) COMPLEXES WITH THIOUREA DERIVATIVES*

G. PLESCH†

Department of Inorganic Chemistry, Faculty of Natural Sciences, Komensky University,
84215 Bratislava, Slovak Republic

and

C. FRIEBEL†

Department of Chemistry, Philipps University, D-35032 Marburg, Germany

and

O. ŠVAJLENOVÁ and J. KRÄTSMÁR-ŠMOGROVIČ

Department of Inorganic and Organic Chemistry, Faculty of Pharmacy,
Komensky University, 83232 Bratislava, Slovak Republic

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Abstract—N-Salicylideneglycinatocopper(II) complexes of the composition Cu(salgly)$(L_s)(H_2O)_x$ were synthesized with L_s = thiourea, N-methylthiourea, N,N,N′,N′-tetramethylthiourea, N-ethylthiourea, N,N′-diethylthiourea, N-(2-chlorphenyl)thiourea, N,N′-diphenylthiourea, N,N′-ethylenethiourea, N,N′-phenylenethiourea [≡1,3-dihydrobenzimidazole-2-thione]; and $x = 0$ or 1. The EPR spectra gave evidence for square-pyramidal coordination around Cu^{II}, however, with a different strength of axial interaction originating from an oxygen atom from the adjacent complex molecule. In the case of monohydrates bonding of a water molecule is also possible. In two examples, even square-planar geometry, without any significant axial interaction can be assumed. The great variety of cooperative ordering phenomena in the structure, which is caused mainly by the extraordinary flexibility of the Schiff base ligand, results in coupling patterns ranging from ferrodistortive to antiferrodistortive. These patterns are remarkably influenced by the substitutions on thiourea. Both the global and local symmetry effects are analysed with the aid of EPR spectroscopy.

In recent years much attention has been devoted to studies on Cu^{II} complexes with tridentate Schiff base dianions (TSB^{2-}) of N-salicylideneaminoalkanoate type. These complexes are of great interest from the point of view of bioinorganic chemistry, since they may serve as models for some metalloenzymes. For example, complexes of this group have been shown to exhibit superoxodismutase-like activity.[1] For this reason they justify our interest in complexes with thiourea derivatives. Other points of interest are the structure and spectral properties of these compounds in the solid state. In spite of the fact that in all these

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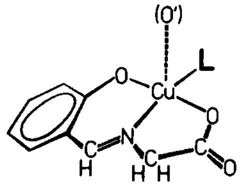
* For part II, see Ref. 8.

† Authors to whom correspondence should be addressed.

complexes the three-ring unit consisting of a roughly planar N-salicylideneaminoalkanoate ligand meridionally bound by three donor atoms (O,N,O) to Cu^{II} constitutes a nearly constant structural element (**I**), complexes with various degree of tetragonality and of orthorhombic distortion in the plane may be prepared. If an additional monodentate ligand L is present, it occupies the fourth position in the basal plane of a usually square-pyramidal coordination polyhedron. The apical site is then occupied by a suitable oxygen donor atom O′ (phenolic or carboxylic) from the adjacent complex molecule.[2–4] Bonding of a water molecule (if present) in the apex of the pyramid has been reported too.[5] In such a way monomeric square-pyramidal Cu^{II} coordination polyhedra,[3] ferrodistortively ordered dimeric units,[4] or even polymeric zigzag chains of complex molecules are formed.[2] Less frequently a square-planar arrangement of donor atoms around Cu^{II} has been found.[6]



(I)

The most striking fact is the extraordinary richness of the coupling patterns ranging from ferrodistortive to antiferrodistortive, which has been found in (TSB)–Cu^{II} complexes.[7–9] Coupling phenomena between the single molecules, between the molecules within a dimer (intradimeric coupling), between the dimeric units (interdimeric coupling) and between the molecules arranged in a zigzag chain have been reported. The exceptionally large flexibility of the tridentate ligand caused by attractive forces via hydrogen bonds and via π–π interactions, together with the presence of more than one kind of oxygen atom, which can be potentially coordinated at the apical site, leads to stabilization of a great multitude of chemically similar Cu^{II} complexes with a surprising diversity of cooperative orderings in the solid state. In this case the correlation of data on crystal and molecular structure obtained by X-ray diffraction method, with the results of EPR measurements on monocrystals yields a great amount of information.[2] However, EPR spectroscopy also on non-diluted polycrystalline material is a valuable tool for investigations on coupling patterns between Cu^{II} centres in differently aligned coordination polyhedra in the structure. Frequently, from the coupled g values the calculation of molecular g components is possible, resulting in information on local symmetry around the Cu^{2+} ions.

In a previous paper of this series it has been shown that the EPR spectra of polycrystalline samples of imidazole adducts of N-salicylideneglycinatocopper(II) complexes with non-parallel aligned coordination polyhedra can be interpreted in terms of a simple model of two canted g tensors of *axial* symmetry.[8] Detailed EPR investigations on monocrystals combined with structural data have shown, however, that the assumption of axial symmetry was arbitrary and strictly speaking not compulsory.[2] In this paper we report the results of EPR studies on N-salicylideneglycinatocopper(II) adducts with thiourea derivatives. A model for the interpretation of EPR powder spectra resulting from coupled g values of *orthorhombic* symmetry is proposed. The local and global symmetry of the complexes under investigation characterizing molecular and crystal structure, respectively, is discussed.

EXPERIMENTAL

The N-salicylideneglycinato(thiourea)copper(II) complex was synthesized according to Ref. 4. Water-free N-salicylideneglycinatocopper(II) adducts $Cu(salgly)L_s$ with thiourea derivatives L_s were prepared by reaction of $Cu(salgly)(OH_2)\cdot 0.5\ H_2O$ with L_s = N-methylthiourea (MeTu), N,N′-diethylthiourea (diEtTu), N-(2-chlorphenyl) thiourea (ClPhTu), N,N′-ethylenethiourea (etenTu), and N,N′-phenylenethiourea (phenTu).[10] The ratio of Cu : L_s in the reaction mixture was 1 : 1.5. Cu(salgly) $(H_2O)_{1.5}$ (2.7 g, 10 mmol) was dissolved in 400 cm^3 of diluted ethanol (ethanol–water = 2 : 1), heated to $\approx$ 55–60°C for 30 min and filtered. An amount of 15 mmol of L_s dissolved in ethanol was added. The resulting solution was allowed to cool, green crystals (with a tinge to grey) were deposited, washed with ethanol and dried in a desiccator.

In case of L_s = N,N′-diphenylthiourea (diPhTu), N-ethylthiourea (EtTu), and N,N,N′,N′-tetramethylthiourea (ttMeTu), green compounds (with a tinge to blue) of the composition $Cu(salgly)\ (L_s)\cdot(H_2O)$ were obtained in an analogous way. For the preparation of the adduct with ttMeTu an excess of L_s as high as 3.75 had to be used.

The analytical data obtained for the complexes are given in Table 1.

The EPR spectra of polycrystalline samples were measured in the Q band (34.7 GHz) at room temperature with a Varian E-15 spectrometer. DPPH was used as an internal standard.

The electronic spectra of the finely powdered samples were recorded in the range 4000 to 30,000 cm^{-1}

Table 1. Analytical data for N-salicylideneglycinatocopper(II) complexes, Cu(salgly)(L_s)$(H_2O)_x$

L_S[a]	x	Formula	Elemental analysis (%)—Found (calc.) C	H	N
MeTu	0	$C_{11}H_{13}CuN_3O_3S$	40.1 (39.9)	4.1 (4.0)	12.3 (12.7)
ttMeTu	1	$C_{14}H_{21}CuN_3O_4S$	43.2 (43.0)	5.1 (5.4)	10.5 (10.8)
EtTu	1	$C_{12}H_{17}CuN_3O_4S$	39.7 (39.7)	4.7 (4.7)	11.4 (11.6)
diEtTu	0	$C_{14}H_{19}CuN_3O_3S$	45.5 (45.1)	5.2 (5.1)	10.7 (11.3)
ClPhTu	0	$C_{16}H_{14}ClCuN_3O_3S$	44.1 (45.0)	3.7 (3.3)	10.1 (9.8)
diPhTu	1	$C_{22}H_{21}CuN_3O_4S$	54.1 (54.3)	4.4 (4.4)	8.6 (8.6)
etenTu	0	$C_{12}H_{13}CuN_3O_3S$	42.3 (42.0)	3.7 (3.8)	12.0 (12.3)
phenTu[b]	0	$C_{16}H_{13}CuN_3O_3S$	49.2 (49.2)	3.5 (3.4)	10.5 (10.8)
phenTu[c]	0	$C_{16}H_{13}CuN_3O_3S$	49.0 (49.2)	3.7 (3.4)	10.8 (10.8)

[a] Tu = thiourea; Me = N-methyl; ttMe = N,N,N′,N′-tetramethyl; Et = N-ethyl; diEt = N,N′-diethyl; ClPh = N-(2-chlorphenyl); diPh = N,N′-diphenyl; eten = N,N′-ethylene; phen = N,N′-phenylene.

[b] α-phase.

[c] β-phase.

on the Zeiss DMR-21 spectrometer using MgO as a standard.

RESULTS AND DISCUSSION

The remarkable variety of the EPR spectral patterns of the complexes under investigation (Table 2, Figs 1 and 2) reflects significant differences in both cooperative ordering effects and coordination geometries, respectively. Generally, in non-diluted solid state complexes the EPR spectra are influenced by interactions between the paramagnetic centres. The values of g components may be substantially modified by the coupling of g tensors from non-parallel aligned coordination polyhedra. Thus, the experimental spectra carry information as well about the symmetry of the single coordination polyhedron as about the cooperative ordering phenomena in the structure.

The average g value

$$g_{av} = (g_1^c + g_2^c + g_3^c)/3 = (g_z + g_y + g_x)/3 = (g_{\parallel} + 2g_{\perp})/3 \quad (1)$$

is not influenced by the coupling effects in the solid state. The X-ray structural determinations of 16 copper(II) complexes with N-salicylideneglycinate dianions[2-6,11] showed that the geometry in the plane of the chelate ligand remains nearly constant when the additional monodentate ligand is changed. The degree of tetragonality and the cooperative ordering, however, varies dramatically. Cu—L_{ap} distances (L_{ap} = apical ligand) in the range 2.33–3.50 Å were found.

Therefore the shifts in the g_{av} value are mainly influenced by the changes of $g_{\parallel}$, which depend on the tetragonal distortion of the system. The concept of the tetragonality characterized by the parameter $T = R_S/R_L$, where R_S and R_L are the Cu–L lengths in-plane and out-of-plane, respectively, was introduced for characterization of the degree of tetragonal distortion in copper(II) complexes of *tetragonal* symmetry.[12] In our case of complexes of comparatively low symmetry and with coupled g^c tensors, however, we may state that g_{av} reflects sensitively the strength of the axial interaction between copper and the apical fifth donor atom completing the coordination pyramids in N-salicylideneglycinatocopper(II) complexes.[8,9]

According to the results of X-ray structural analysis in Cu(salgly)(Tu), three donor atoms of the Schiff base and the S atom from thiourea are bound in the plane, while the apex of the pyramid is occupied by a phenolic oxygen atom from the adjacent molecule.[4] In this way two molecules are joined to a dimer through Cu—O′ bonds with a length of 278 pm. This relatively long Cu—O′ distance signifies a rather weak axial interaction. In the coordination polyhedron $[CuO_2NS \cdots O']$ such an interaction brings about a g_{av} value of 2.106. It can be assumed that the Cu(salgly)(L_s) compounds, which show g_{av} values in the range 2.104–2.108 (Table 2), form complexes with an axial ligand field comparable to that in Cu(salgly) (Tu).

Table 2. EPR spectral data of N-salicylideneglycinatocopper(II) complexes, Cu(salgly)(L_s)(H_2O)$_x$, arranged in order of increasing axial ligand field strength

Neutral donor ligand (L_s) and crystal water content (x)		EPR parameters				
L_s[a]	x	g_{av}	g_1^c	g_2^c	g_3^c	G[e]
phenTu[b]	0	2.099	2.203	2.049	2.046	4.4
etenTu	0	2.101	2.154	2.116	2.034	—
ClPhTu	0	2.104	2.213	2.063	2.037	4.4
phenTu[c]	0	2.105	2.201	2.069	2.046	—
Tu	0	2.106	2.217[d]	2.066[d]	2.035	4.5
diEtTu	0	2.108	2.221	2.063	2.040	4.4
MeTu	0	2.108	2.178	2.073	= 2.073	—
diPhTu	1	2.111	2.145	= 2.145	2.042	—
EtTu	1	2.113	2.225	2.073	2.041	—
ttMeTu	1	2.116	2.214	2.087	2.048	—

[a] Abbreviations as in Table 1.
[b] α-phase.
[c] β-phase.
[d] According to renewed measurement, slightly deviating from Ref. 7 ($g_1^c = 2.220$, $g_2^c = 2.064$).
[e] So far as molecular g components are observed.

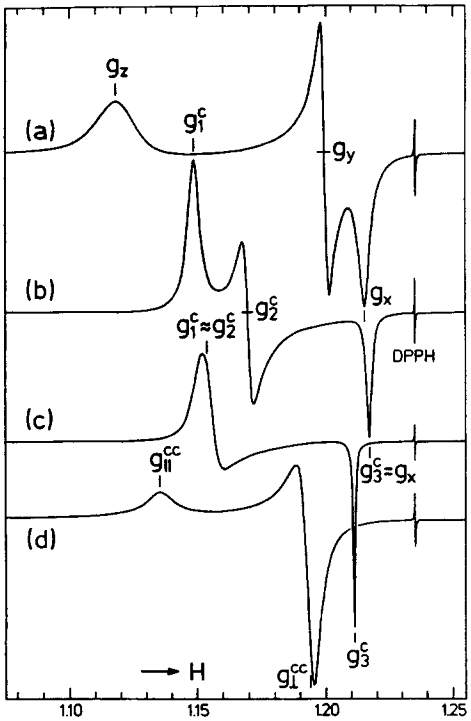


Fig. 1. EPR powder spectra [$\nu = 34.65$ GHz, 295 K] of Cu(salgly)(L_s)(H_2O)$_x$ resulting from coupling of molecular g components (g_z, g_y, g_x): (a) L_s = ClPhTu, $x = 0$ (ferrodistortive pattern); (b) L_s = etenTu, $x = 0$ (disturbed antiferrodistortive); (c) L_s = diPhTu, $x = 1$ (antiferrodistortive); (d) L_s = MeTu, $x = 0$ (four magnetically non-equivalent Cu^{II} sites).

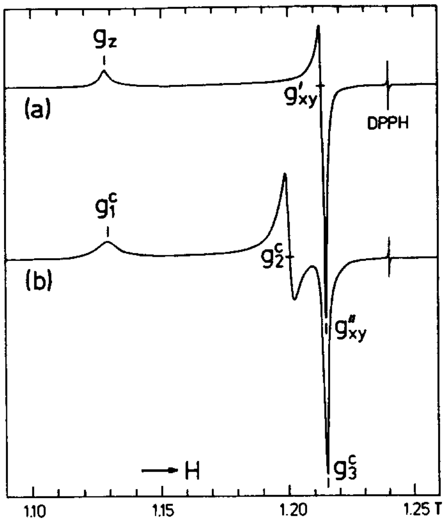
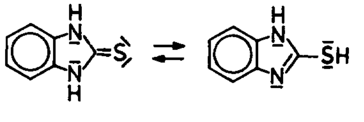


Fig. 2. EPR powder spectra [$\nu = 34.8$ GHz, 295 K] of Cu(salgly)(phenTu): (a) α-phase (quasi-ferrodistortive); (b) β-phase (disturbed ferrodistortive).

The lower g_{av} values lying very near to 2.10 (Table 2) indicate that the Cu^{II} centres in the adduct with ethylenethiourea and in the α-phase of the phenylenethiourea adduct (Fig. 2a) adopt a square-planar coordination without any remarkable axial interaction. In case of the compound Cu(salgly)(phenTu) a second modification (β-phase) with a square-pyramidal coordination around Cu^{II}

($g_{av} = 2.105$) was obtained (Fig. 2b). The g_{av} value, which is remarkably lower than the values usually observed for nitrogen donor ligand adducts,[8] suggests that in both of these phases the neutral ligand (**IIa**) is bound via the S atom, although its tautomeric form benzimidazole-2-thiol (**IIb**) is equipped with a potential N donor atom:



(IIa) **(IIb)**

The coordination via nitrogen in a square-planar complex, however, cannot be completely excluded in the β-phase. In addition to the various degrees of axial interaction, however, these two phases also differ in cooperative ordering effects (see later).

On the other hand, the three complexes under investigation and all the monohydrates show relatively high g_{av} values, which are in the range 2.111–2.116 (Table 2). This indicates a stronger axial ligand field and consequently an apical Cu—O′ distance shorter than 278 pm. The bonding of a carboxyl oxygen from the neighbouring complex molecule in the apex, corresponding to a coordination frequently found in square-pyramidal N-salicylideneglycinatocopper(II) complexes, can be assumed here. As a matter of fact, bonding of an oxygen atom from a water molecule, which is present in these complexes, cannot be excluded.

The ligand field spectra consist of a broad band without clearly resolved structure, which contains all the allowed *d–d* transitions. The maximum of this band shows the expected blue shift with decreasing g_{av} values.[7,8] Band maxima $\bar{\nu}_m$[cm^{-1}] for example are 14,500 [Cu(salgly)(ttMeTu)·H_2O], 16,000 [Cu(salgly)(diEtTu)] and 17,000 [Cu(salgly)(ClPhTu)]. The α- and β-isomers of Cu(salgly)(phenTu) differ not only in their g_{av} values but also in their $\bar{\nu}_m$: 17,500 for the α-phase, 16,500 for the β-phase.

In all complexes under investigation the sharp EPR lines indicate that dipolar coupling operates between the Cu^{2+} ions. For two coupled g tensors of orthorhombic symmetry, which are related with respect to a glide plane, the following equations hold for the crystal g values:[2]

$$g_1^c = \cos^2\gamma g_z + \sin^2\gamma(\cos^2\xi g_y + \sin^2\xi g_x)$$

$$g_2^c = \sin^2\gamma g_z + \cos^2\gamma(\cos^2\xi g_y + \sin^2\xi g_x)$$

$$g_3^c = \sin^2\xi g_y + \cos^2\xi g_x. \qquad (2)$$

Here ξ is the rotation angle around the g_z axis in the g_{xy} plane (Fig. 3b) and γ is the inclination angle of the g_z axis to the (010) glide plane in case of a frequently realized monoclinic unit cell (Fig. 3c). The angles 2ξ and 2γ fully characterize the mutual orientation of two g tensors of orthorhombic symmetry, which are related with respect to a glide plane.

In the particular case of ferrodistortive ordering ($\xi = 0°$, $\gamma = 0°$; Fig. 3a) the crystal g values are equal to the molecular ones ($g_1^c = g_z$, $g_2^c = g_y$, $g_3^c = g_x$). The experimental g factors can be proved, if they are actually molecular, by the parameter G:[13]

$$G = (g_{\parallel} - g_0)/(g_{\perp} - g_0) = (g_z - g_0)/[(g_x + g_y)/2 - g_0] = 4(k_{\parallel}/k_{\perp})^2(\Delta_{\perp}/\Delta_{\parallel}), \qquad (3)$$

where $g_0 = 2.0023$; $k_{\parallel}$ and $k_{\perp}$ are the spin-orbit reduction factors and $\Delta_{\parallel} = \Delta E(d_{x^2-y^2} \leftarrow d_{xy})$, $\Delta_{\perp} = \Delta E(d_{x^2-y^2} \leftarrow d_{xz,yz})$ are the energy splittings in the ligand field. According to measurements on a large number of N-salicylideneglycinatocopper(II) adducts with N and O donor atoms, respectively, the G parameter lies in the range 4.7 ± 0.2.[7,8,14] For the S donor ligand adducts the G value slightly decreases, probably as the consequence of higher covalency of the Cu—S bond. In case of the complex Cu(salgly)(Tu), where according to the results of X-ray structural analysis the order of coordination polyhedra is practically ferrodistortive, a value of $G = 4.5$ is obtained (Table 2). Taking into account the small canting angle $2\gamma = 11°$ between the molecules within the dimer, the adjusted G increases to 4.6. Hence an influence of such a small

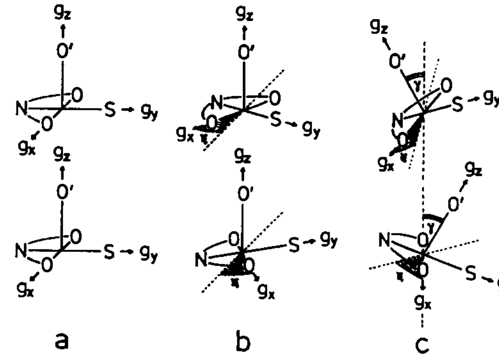


Fig. 3. Successive tilting of two orthorhombic molecular g tensors: (a) all g axes aligned: $\xi = 0°$, $\gamma = 0°$ (ferrodistortive ordering); (b) basal planes of coordination pyramids twisted around z: $0° < \xi < 45°$ (quasi-ferrodistortive ordering); (c) basal planes of coordination pyramids twisted ($\xi \neq 0°$, 45°) and canted against each other: $0° < \gamma \leqslant 45°$ (from disturbed ferrodistortive up to antiferrodistortive ordering).

deviation from ferrodistortive order on G is negligible.[8]

The EPR spectra of adducts with ClPhTu (Fig. 1a) and diEtTu show G values ranging between 4.4 and 4.5, i.e. their g components correspond to molecular ones. The similarity of the EPR spectral parameters of the complexes, where L_s is Tu, ClPhTu and diEtTu, leads to the conclusion that these compounds adopt an analogical structure of dimers, where the complex molecules are weakly bound via the phenolic oxygen atom.

The α-phase of Cu(salgly)(phenTu) delivers an EPR spectrum with very sharp lines and g values yielding $G = 4.4$. Comparing with the remaining complexes under investigation, however, the orthorhombic splitting of the EPR pattern is unreasonably low. This leads us to the conclusion that even though the order of $g_1 \approx g_z \approx g_\parallel$ and $(g_2+g_3)/2 \approx (g_y+g_x)/2 \approx g_\perp$ corresponds to molecular g values, the observed individual components $g_2 \approx g_3$ should result from a coupling. In this case a situation is to be discussed, where the complex molecules are ordered parallel only with respect to their g_z axes ($2\gamma = 0°$). Counter-rotation of neighbouring complex molecules around this axis ($2\xi \approx 90°$) may result in an averaging of the components g_y and g_x feinting tetragonality of a molecular g tensor. Such packing enabled on account of the two phenyl rings might be advantageous for maximizing π–π interactions between the ligand molecules in the structure (Fig. 4). Such a type of structure recently was found in the N,N′-dibutylthiourea adduct of N-salicylideneglycinato-copper(II) by X-ray structure analysis.[11]

The crystal g components for the [Cu(salgly) L$\cdots$O′] complexes with non-parallel aligned molecular axes have been interpreted hitherto in a framework of the simple model of two *axial* g tensors canted by an angle 2γ.[7,8] In such a case the following well-known relations are valid:

$$g_1^{\rm c} = \cos^2\gamma\, g_\parallel + \sin^2\gamma\, g_\perp$$

$$g_2^{\rm c} = \sin^2\gamma\, g_\parallel + \cos^2\gamma\, g_\perp$$

$$g_3^{\rm c} = g_\perp, \qquad (4)$$

resulting from the more general equations (2) for the special case $g_y = g_x$. The mutual orientation of two axial g tensors related by a glide plane is then fully characterized by the canting angle 2γ:

$$2\gamma = \arccos\,[(g_1^{\rm c} - g_2^{\rm c})/(g_1^{\rm c} + g_2^{\rm c} - 2g_3^{\rm c})]. \qquad (5)$$

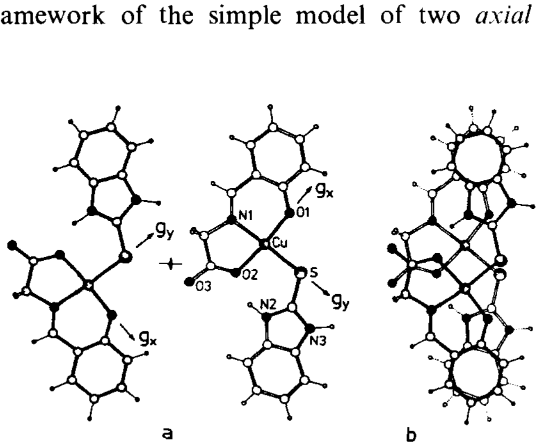


Fig. 4. Proposed orientation of neighbouring complex molecules in α-Cu(salgly) (phenTu) resulting in a crystal g tensor of axial symmetry: (a) molecules placed side by side (just for clearness); (b) molecules arranged one upon the other illustrating π-stacking of phenyl rings.

Since in an exhaustively investigated series of complexes [Cu(salgly)L]$\cdot x$H$_2$O with quite similar [Cu(salgly)L$\cdots$O′] units repeatedly an *orthorhombic* molecular g tensor was observed, replacing the simple equations (4) by more general ones (2) became necessary.[2,9] The correlation of X-ray structural data and single crystal EPR spectra of Cu(salgly)(2-methylimidazole) has shown that in this case $g_\perp$ is equal to $g_3^{\rm c}$ assuming a fictitiously axial molecular g tensor. The corresponding EPR pattern, however, is caused by a twisting of two orthorhombic g tensors by an angle ξ near to 45°.[2] In such a special case the EPR spectrum provides no information about the extent of orthorhombic splitting of the molecular g tensor. For the investigated thiourea adducts with the aid of equations (4) no reasonable molecular g parameters result, i.e. the more general relations (2) have to be used.

The value of the canting angle 2γ derived from equations (2) is

$$2\gamma = \arccos\,[(g_1^{\rm c} - g_2^{\rm c})/(2g_z - g_1^{\rm c} - g_2^{\rm c})]. \qquad (6)$$

Since the g_z values may be estimated rather precisely from the crystal g values according to the procedure described below, the canting angle 2γ may be determined too. In Fig. 5 the dependence of the crystal g values on the canting between the g_{xy} planes of two molecular g tensors is shown for the boundary cases of $2\xi = 0°$ ($g_3^{\rm c} = g_x$) and $2\xi = 90°$ ($g_3^{\rm c} = g_y$), respectively. As one can see, in the case of small canting angles below $\approx 20°$ it is difficult to estimate, whether the orthorhombic splitting of the molecular g tensor or the canting contribute more to the actual experimental EPR pattern. On the other hand the value of 2γ may be determined with an exactness less than 1° at canting angles $2\gamma > \approx 45°$.

From the equation for the twisting angle ξ

$$2\xi = \arccos\,[(g_1^{\rm c} + g_2^{\rm c} - g_3^{\rm c} - g_z)/(g_y - g_x)] \qquad (7)$$

with $g_y \neq g_x$, it follows that contribution of an orthorhombic splitting of the molecular g tensor cannot be divided from the influence of twisting by

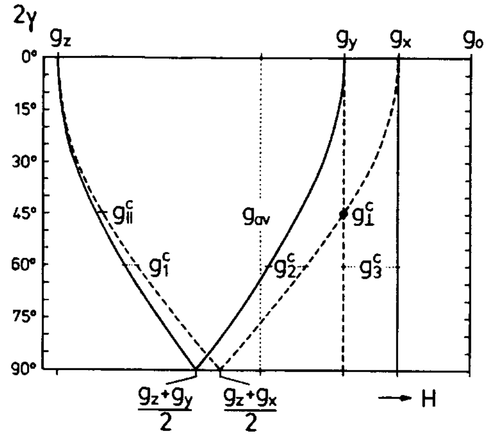


Fig. 5. Dependence of crystal g components on the canting angle 2γ between the g_{xy} planes of orthorhombic molecular g tensors for the boundary cases (a) $\xi = 0°$ (rotation on x axis, full lines) and (b) $\xi = 90°$ (rotation on y axis, broken lines), respectively.

an angle 2ξ. Thus generally, the angle 2ξ cannot be obtained from the EPR pattern alone, and data from X-ray structural investigation are necessary.

Taking into account the consistency of the EPR data in the group of N-salicylideneglycinato-copper(II) complexes, it is possible to limit the range of reliable values for their orthorhombic molecular g parameters. First of all one has to fix pseudo-tetragonal molecular g components from the following expressions, which can be derived from equations (1) and (3):

$$g_{\parallel} = [3g_{av}G - 2g_0(G-1)]/(G+2) \approx g_z$$
$$g_{\perp} = [3g_{av} + g_0(G-1)]/(G+2) \approx (g_y+g_x)/2. \quad (8)$$

The value of g_{av} is known from experiment. The parameter G can be varied in the range 4.4–4.6, which is reasonable for the thiourea adducts under investigation. On such a way from the experimentally known g_{av} and the parameter G, which is varied in a limited range, the field of reliable $g_{\parallel}$ and $g_{\perp}$ values may be calculated.

The ranges for the orthorhombic components g_x and g_y may be obtained on the following way: the upper boundary value for g_x follows from the fact that according to equation (2) $g_x \leqslant g_3^c$. On the other hand, the $g_{\perp}$ value in a system with a ground state wavefunction $d_{x^2-y^2}$ is defined by

$$(g_y+g_x)/2 \approx g_{\perp} = g_0 - 2k_{\perp}^2\lambda_0/\Delta_{\perp}\,; \quad (9)$$

[λ_0 is the spin-orbit coupling constant for a free ion, for Cu^{2+} being -830 cm^{-1}; $k_{\perp}$ and $\Delta_{\perp}$ are explained in equation (3)]. It follows that for physically reasonable values of $k_{\perp}$ and $\Delta_{\perp}$ the lowest g_x cannot be smaller than a fixed boundary value. For complexes with N and O donor atoms this value is assumed to be ≈ 2.04.[13] In the complex Cu(salgly)(3,5-dimethylpyrazole)·H_2O a molecular component $g_x = 2.038$ has been observed.[7] In the case of adducts with one S donor ligand, however, this value becomes slightly lower as a consequence of the larger covalency of the Cu—S bond (lowering of k_x). In the groups of complexes with g_{av} values in the range of 2.100(1) and of 2.106(2) (Table 2) we equate these boundary values with the lowest g^c components observed in each group, i.e. 2.034 and 2.035, respectively. For complexes with square-pyramidal Cu^{II} coordination and consequently little higher g_{av} in the range 2.111–2.116, we fix this boundary value at 2.037. Since g_x and g_y for small differences lie symmetrically with respect to $g_{\perp}$, the range for g_y follows immediately from the ranges for $g_{\perp}$ and g_x.

The dependence of molecular g components on the value of the parameter G is illustrated in Fig. 6 for the complex β-Cu(salgly)(phenTu). As one can see, even for a wide area of G the range of reasonable molecular $g_{\perp}$ and $g_{\parallel}$ values is rather narrow. Less exactly the orthorhombic g_x and g_y components can be estimated. Naturally, the angle 2γ resulting from the experimental crystal g^c parameters and the estimated molecular g components is also a function of G, established by the expression:

$$2\gamma = \arccos\{(g_1^c - g_2^c)(G+2)/[(g_1^c + g_2^c - 2g_0)(G-2) + 2(g_3^c - g_0)G]\}, \quad (10)$$

derived from equations (6) and (8). It should be pronounced that the canting angle 2γ, dependent on the experimental g^c parameters and the chosen

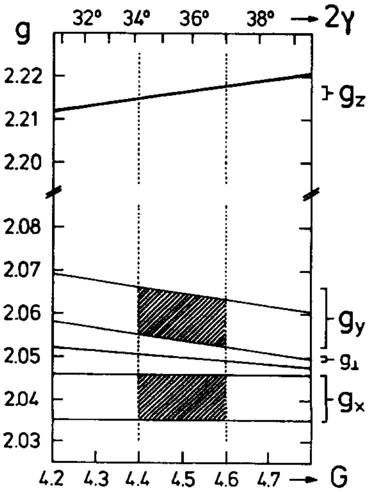


Fig. 6. Dependence of molecular g components and canting angle 2γ on the empirically located parameter G for β-Cu(salgly)(phenTu); ranges of reliable values ($4.4 \leqslant G \leqslant 4.6$) are pronounced by hatching.

G, the range of that is strongly limited, is unaffected by the uncertainty of orthorhombic splitting of $g_{\perp}$. Consequently, the canting angle 2γ, indicated as upper scale in Fig. 6, is well established.

The possible ranges for molecular g parameters and canting angles for all complexes with coupled g values are given in Table 3. The uncertainty in the estimation of orthorhombic g parameters is not greater than 0.015, which is quite reasonable. In correspondence with Fig. 5 the range of acceptable angles 2γ depends on its magnitude. As said above, a reliable estimation of 2γ within a range $\leqslant 1°$ is possible at values $2\gamma > \approx 45°$.

In the β-phase of Cu(salgly)(phenTu) already discussed (Fig. 6), showing square-pyramidal Cu^{II} coordination (Fig. 2b) on the basis of the g_{av} values, we expect the structure of ferrodistortively ordered molecules in a dimer, where the individual complexes are weakly bound. The EPR pattern gives evidence for an additional interdimeric coupling between these dimeric units with a canting angle in the range 34–37°.

In the adduct with etenTu showing square-planar Cu^{II} coordination (Fig. 1b) the g_{xy} planes are canted by a relatively large angle $2\gamma \approx 75°$ in a disturbed-antiferrodistortive ordering. A coupling between aligned single molecules or dimeric complex units, respectively, can be assumed here.

The EPR data (Table 3) for the water-containing adducts with EtTu, ttMeTu, and diPhTu (Fig. 1c) show a large variety of ordering phenomena ranging from an only slightly disturbed-ferrodistortive type ($2\gamma \approx 22$–$28°$) to antiferrodistortive ($2\gamma \approx 90°$). Such ordering phenomena can be realized in a quite different way. A chain-like zigzag structure with oxygen atoms from carboxylate groups acting as bridging atoms is possible. For such a structural type canting angles of 82° and 58°, respectively, have been reported.[2,3] A packing of dimeric species, where the individual molecules within the dimer are bridged by oxygen atoms from carboxylate groups, is also acceptable. In the N-salicylidene-β-alaninato(imidazole)Cu^{II} complex the individual molecules within the dimer are ordered ferrodistortively, but the dimeric units are canted by an angle $2\gamma = 45°$.[15] In the case of K[N-salicylidene-(DL)-α-alaninato)(NCO)Cu^{II}], where every two complex ions are connected via bridging NCO^- groups, however, the canting angle between stacked dimeric units of neighbouring chains has been reported to be 72°,[16,17] and eventually, a coupling of aligned [Cu(salgly)(L_s)(OH_2)] single molecules cannot be excluded.

Finally, the EPR spectrum of the adduct with MeTu presents a particularly interesting coupling pattern (Fig. 1d). The pseudo-*axial* g components cannot be interpreted with reasonable parameters within the framework of the described model of only *two* coupled g tensors. As illustrated in Fig. 5, an axial EPR pattern may also result from the coupling of only two differently orientated orthorhombic g tensors in the special case $\xi \approx 45°$ and $2\gamma \approx 45°$. The observed $g_{\perp} = 2.073$ of the coupled g tensor (Fig. 1d), however, cannot be g_y, because this would require $g_x \approx 2.03$ corresponding to an unreasonably high orthorhombic splitting ($g_y - g_x \geqslant 0.04$!). Therefore in this case the g values seem to result from a coupling of molecular g components of *four* magnetically non-equivalent Cu^{2+} ions in the unit cell. Since the g_{av} value of 2.108 indicates a structure of weakly bound dimers, we assume here a packing of two dimeric units, which are ordered against each other in a disturbed antiferrodistortive way. The individual molecules

Table 3. Ranges of reasonable molecular g values and canting angles 2γ, respectively, for Cu(salgly)(S_L)(H_2O)$_x$ complexes with misaligned coordination polyhedra on the basis of $4.4 \leqslant G < 4.7$

L_s[a]	x	$g_{\perp} = \frac{(g_x+g_y)}{2}$	g_x	g_y	g_z	2γ[°]
Tu	0	2.050	2.035	2.065	2.218	11.1[b]
EtTu	1	2.053(1)	2.037–2.041	2.071–2.063	2.233(2)	25.0 ∓ 3.0
phenTu[c]	0	2.050(1)	2.035–2.046	2.067–2.052	2.216(2)	36.3 ∓ 2.1
ttMeTu	1	2.055(1)	2.037–2.048	2.075–2.060	2.239(2)	44.1 ∓ 1.3
etenTu	0	2.048(1)	2.034	2.064–2.060	2.208(2)	74.9 ∓ 0.4
diPhTu	1	2.052(1)	2.037–2.042	2.069–2.060	2.228(2)	90

[a] Abbreviations as in Table 1.

[b] From X-ray structure determination.[4]

[c] β-phase.

within the dimeric units, however, should be canted disturbed-ferrodistortively. Then, the sum of intra- and interdimer coupling of *four* differently orientated Cu^{II} complex molecules give rise to the above EPR pattern.

Here it is worth mentioning that on preliminary measurements on a monocrystal of the closely related EtTu adduct we have observed *two* angular-dependent EPR lines. This finding obviously gives evidence for the presence of *four* magnetically non-equivalent Cu^{II} sites, because two of them are coupled already corresponding to $2\gamma_1 \approx 25°$ (Table 3). The coupled species are canted by a second canting angle $2\gamma_2 \approx 76°$. Apparently, due to a slight enlargement of $Cu \cdots Cu$ spacings on changing from MeTu to $EtTu + H_2O$, the g^c tensors become prevented from further coupling to g^{cc}. Further investigations on this field are in progress.

CONCLUSIONS

Copper(II) complexes with tridentate Schiff base dianions (TSB^{2-}) of N-salicylideneaminoalkanoate type and additional neutral ligands are characterized by a rather low symmetry of Cu^{II} coordination polyhedra. For investigation of structural details in this kind of complex the Cu(TSB) fragment Cu(salgly) was kept constant and also the donor atom S of the additional ligand of thiourea type. Small changes of the substituents at the thiourea derivatives resulted in striking changes not only of the ordering of complex molecules in the crystalline structure but also of the geometry of the pseudo-tetragonal Cu^{II} coordination pyramids. To characterize the tetragonality, we were forced to take the experimentally established g_{av} values, because conventionally utilized molecular $g_{\parallel}$ components are hidden in all cases of g–g coupling, where the cooperative ordering of complex molecules deviates from ferrodistortive. On the presumption of coupling of no more than two magnetically non-equivalent Cu^{II} centres, a simple concept for calculation of molecular g components from the observed EPR lines was developed and modified including orthorhombic symmetry. On the basis of the used model a very consistent interpretation resulted, giving reliable information on local geometry of Cu^{II}–ligand polyhedra and of the mutual ordering characterized by the angle 2γ between the basal planes of neighbouring coordination pyramids. The canting angle proved to be independent of the extent of orthorhombic distortion. Nevertheless, coupling of more than two magnetically non-equivalent Cu^{II} sites may be detected, because then the application of the concept, leading to unreasonable data, usually fails.

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