

STRUCTURES OF SALICYLALDIMINE COPPER(II) COMPLEXES

by

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The stereochemistry of copper(II) chelates of salicylideneanilines has been discussed on the basis of the spectral, magnetic and dielectric properties. It has been concluded that (a) all complexes containing sterically inactive donor sets are planar and (b) complexes containing sterically active donor sets are either distorted planar or pseudo-tetrahedral.

The copper(II) ion forms complexes with coordination numbers four, five and six, but variation of each structure occurs through bond length or bond angle distortion [1—5].

The copper(II) Schiff base complexes are generally four-coordinated, but six-coordination, and in coordinating solvents five-coordination also occur fairly frequently. Whether or not the four-coordinated Cu(II) complexes are able to bind an additional molecule(s) (*e.g.* pyridine) to form a complex with a coordination number exceeding four is considered to be governed mainly by the (a) electronic and (b) steric factors. When there is no steric hindrance, the stronger ligand field will favour the square-planar configuration; however, the nature of the Cu-L bond (*e.g.* π -character) also plays an important role. Even when the ligand field is not very strong, the complex often favours the square-planar configuration over the octahedral one, if π -bonding is involved in the Cu-L bond.

The modes of splitting of the five-fold degenerate 3d orbitals by crystal-fields of octahedral, tetrahedral, square-planar and bipyramidal symmetries [6—11] and the visible spectra of copper(II) complexes are now well understood, but the effect of lower symmetry is less clear. In the spectra of these Schiff base chelates three types of transitions may be observed: (a) pure d—d transitions, (b) charge-transfer transitions and (c) internal ligand transitions. In this work we discuss only the ligand-field bands which generally appear at around 14—16 kK. Unfortunately, these spectra say nothing about the ground state and the one-electron orbital sequence.

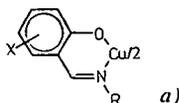
The magnetic properties of octahedral Cu(II) complexes follow the relationship $\mu_{\text{eff}} = \mu_{\text{s.o.}}(1 - 2\lambda/\Delta)$ [12—15]; the moments are independent of temperature and lie in the range 1.9—2.0 B.M. If a planar complex is considered, then the properties will be represented by the equation $\mu_{\text{eff}} = \mu_{\text{s.o.}}(1 - \alpha\lambda/\Delta)$. Δ is the energy separation between the non-degenerate ground term ${}^2B_{1g}$ and the components of the ${}^2T_{2g}$ term; the μ_{eff} values range between 1.8 and 1.9 B. M. [16]. For a tetrahedral arrangement the degenerate ground state 2T_2 is split by spin-orbit interaction; the magnetic moments show a temperature-dependence and lie at about 2.2 B.M. Distortion from

tetrahedral geometry leads to a decrease in the temperature-dependence of the moment and reduces the magnetic moment [e. g. 14—17].

In the present work copper(II) complexes with salicylaldehydes are discussed on the basis of their magnetic, dielectric and spectral properties.

Cu[XSAL-N-alkyl]₂ type complexes

Table I shows the magnetic and dipole moment values of several N-alkyl derivatives (a). The magnetic moments of the N-n-alkyl derivatives undergo practically



no change when the solids are dissolved in benzene or in other inert solvents, which indicates that these copper(II) chelates do not assume a tetrahedral structure when dissolved.

Table I

Magnetic and dipole moments of Cu[XHSAL-NR]₂ type complexes

R =	X =	μ_{eff}	$\mu(D)^{[20]}$	Conf.
CH ₃	H	1.84 ^[16]	1.70	S
C ₂ H ₅	H	1.85 ^[16]	2.16	
<i>n</i> -C ₃ H ₇	H	1.86 ^[16]	1.77	S
<i>i</i> -C ₃ H ₇	H	1.90 ^[20]	2.72	T
<i>n</i> -C ₄ H ₉	H	1.85 ^[16]	1.86	S
<i>s</i> -C ₄ H ₉	H	1.91 ^[20]	2.70	T
<i>t</i> -C ₄ H ₉	H	1.91 ^[20]	3.38	T
<i>n</i> -C ₆ H ₁₁	H	1.85 ^[16]	1.78	S
<i>i</i> -C ₃ H ₇	5-Cl	1.84 ^[20]	3.01	S
<i>t</i> -C ₄ H ₉	3-Cl	1.92 ^[20]	4.24	T
<i>t</i> -C ₄ H ₉	5-Cl	1.91 ^[20]	4.20	T

S: square-planar; T: tetrahedral

The polarity increases in the order *n*-C₃H₇ < *i*-C₃H₇ < *t*-C₄H₉, indicating that the departure from the *trans*-planar configuration increases with increasing bulkiness of the alkyl groups. The dipole moment values are generally higher than those of the corresponding Ni(II) complexes [18], which can be considered as due to the existence of unsymmetrical forms in solution.

The absorption spectra of the Cu[HSAL-N-n-alkyl]₂ type complexes show a single crystal-field band at ca. 16.5 kK, which probably contains several transitions; there is also a shoulder at 22 kK [19—22]. This band can be considered as due to forbidden crystal-field transitions between the 3d levels. These *trans*-planar complexes exhibit almost identical spectra in the crystalline state (Fig. 1) and in inert solvents (Fig. 2), regardless of the number of carbon atoms in the alkyl groups.

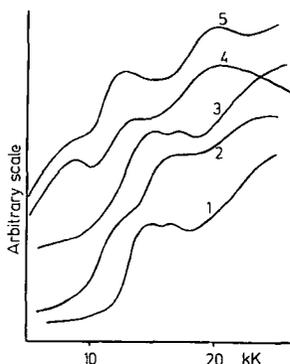


Fig. 1. Reflection spectra of copper(II) chelates.

- 1: $\text{Cu}[\text{HSAL-N-CH}_3]_2$;
- 2: $\text{Cu}[\text{HSAL-N-C}_2\text{H}_5]_2$;
- 3: $\text{Cu}[\text{HSAL-N-}i\text{-C}_3\text{H}_7]_2$;
- 4: $\text{Cu}[\text{HSAL-N-}n\text{-C}_3\text{H}_7]_2$;
- 5: $\text{Cu}[\text{HSAL-N-}t\text{-C}_4\text{H}_9]_2$.

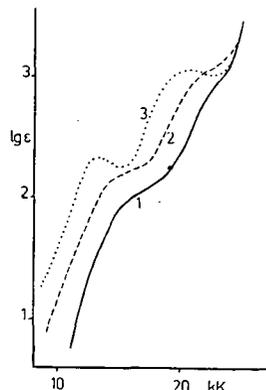


Fig. 2. Electronic spectra of CHCl_3 solutions.

- 1: $\text{Cu}[\text{HSAL-N-CH}_3]_2$;
- 2: $\text{Cu}[\text{HSAL-N-}i\text{-C}_3\text{H}_7]_2$;
- 3: $\text{Cu}[\text{HSAL-N-}t\text{-C}_4\text{H}_9]_2$.

Both as solids and in solution, the pseudo-tetrahedral complexes have bands at 8.5, 13.5 and 21 kK. For a truly tetrahedral Cu(II) complex, the crystal field theory predicts only one transition ${}^2T_2 \leftarrow {}^2E$ [23], but FURLANI and MORPURGO [24] have shown that flattening of the coordination tetrahedron is to be expected in the crystal-field spectral region for Cu(II) complexes. The bands at 8.5 and 13.5 kK can be assigned to d-d transitions of the Cu(II) ion [25].

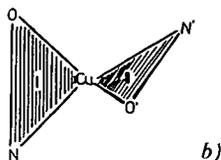
Independently of the nature of the substituent groups in the ring, the *n*-, *i*- and *t*-alkyl complexes exhibit three different types of spectrum [20]. The *n*- C_3H_7 complex has a shoulder at 17 kK and bands at 27.3 and 32.6 kK. The *t*- C_4H_9 complex, on the other hand, has a spectrum with a shoulder at *ca.* 8.6 kK and bands at 13.4, 20.8 and 26.7 kK. Therefore, in solutions of the *t*- C_4H_9 complex, similarly as for the solid, the tetrahedral forms must be present. The *i*- C_3H_7 complexes have spectra intermediate between those of the *n*- C_3H_7 and *t*- C_4H_9 derivatives.*

For the Cu(II) complexes if $\text{R} = \text{CH}_3$ [26], *n*- C_4H_9 or *n*- C_5H_{11} [27], a planar structure has been established by means of X-ray studies. $\text{Cu}[\text{HSAL-NCH}_3]_2$ exists in three modifications. The α -form [28] contains molecules having planar configurations of chelate rings about the metal ion, but stacked one above the other, so that the copper atoms, 3.3 Å apart, form chains running through the crystal. The β -form [29] is isomorphous with the nickel(II) complex and has a chelate ring distorted from planarity, while the γ -form [30] contains dimeric units of the complex with the copper from one molecule bonding to one of the oxygen atoms on the other ring.

It is interesting to note that in the complex $\text{Cu}[\text{HSAL-N-C}_2\text{H}_5]_2$ the copper atoms are four-coordinate, with their coordination squares slightly distorted towards tetrahedral configurations [31].

* Yokoi postulated a configurational equilibrium for the *i*- C_3H_7 complex on the basis of ESR and optical absorption studies [Yokoi, *H.*: Bull. Chem. Soc. Japan, 47, 3037 (1974)].

The degree of distortion from planar towards tetrahedral is given by the dihedral angle θ between the two coordination planes (OCuN and O'CuN') about the metal ion (b). It is interesting that bis(2-OH-acetophenone)trimethylene-diimino-Cu(II)



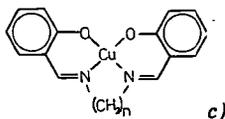
[$\theta = 34.4^\circ$] has a spectrum similar to those of planar Cu(II) complexes, suggesting that only when the degree of distortion has exceeded a threshold value does the spectral pattern change from the planar to the pseudo-tetrahedral [32]. For some *N*-alkyl derivatives the dihedral angles are: Cu[HSAL-NCH₃]₂ 0° [28], Cu[HSAL-N-C₂H₅]₂ 36° [33], Cu[HSAL-N-*i*-C₃H₇]₂ 60° [34], Cu[HSAL-N-*t*-C₄H₉]₂ 54° [35].

It was found that Cu[HSAL-N-*i*-C₃H₇]₂ and the corresponding Co(II) and Zn(II) complexes are isomorphous [36], the latter with a distorted tetrahedral coordination [37]. Thus, a pseudo-tetrahedral structure should also be attributed to the Cu(II) complex. Similarly, a distorted tetrahedral structure can be assigned to Cu[HSAL-N-*s*-C₄H₉]₂. Generally, the *n*-alkyl derivatives in the solid state have planar structures, while the *i*-, *s*- and *t*-alkyl compounds display pseudo-tetrahedral coordination, probably imposed by forces of a steric nature.

Cu[HSAL-polymethylenediamine] type complexes

X-ray diffraction investigations [38, 39] of Cu[HSALen] reveal a dimeric situation involving an intermolecular Cu-O bonding interaction.* The resulting stereochemistry about the copper is approximately square-pyramidal, with an intermolecular Cu-O distance of 2.41 Å [40, 41]. A very similar structure is found for the propylene-bridged analogue; however, in this case the apical position is occupied by an H₂O molecule; the Cu(II)-aquo-oxygen distance is 2.53 Å [42].

The electronic absorption spectra of Cu[HSALen] and similar tetradentate Schiff base complexes have been the subject of a number of investigations [43–50]. Comparison of tetradentate trans-planar and *cis*-planar systems (c) shows spectra



similar in structure, but differing in band intensities. *Trans*-complexes possess absorptions with intensities approximately one order of magnitude less than those of the *cis*-complexes. The higher intensities of absorption of the *cis*-forms are thought

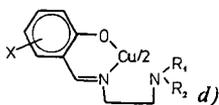
* A structural investigation of the *p*-nitrophenol adduct of Cu[HSALen] demonstrated a H-bonding association; the adduct is monomeric and essentially planar about the metal (Baker, E. N., T. N. Waters: J. Chem. Soc., A, 400 (1970)).

to reflect the electronic contribution to the now electronically allowed transition [49]. For Cu(II) ions, theory predicts that three or four transitions occur between the one-electron 3d energy levels, depending on the symmetry involved [49, 50].

The spectra of square-planar Cu(II) complexes possess only a single broad band in the visible, and the assignment of the transitions is difficult. Circular dichroism [50] indicates the presence of three transitions: (C_2 symmetry) $d_{z^2} \leftarrow d_{xy}$, $d_{x^2-y^2} \leftarrow d_{xy}$ and $d_{xz} \leftarrow d_{xy}$. HOLM [51] found the main band of the trimethylene and tetramethylene derivatives at about 16.6 and 15.7 kK, respectively.

$Cu[XSALen-N(R_1)(R_2)]_2$ type complexes

The compounds (*d*) in which $R_1 = CH_3$ or C_6H_5 and $R_2 = C_6H_5$ give reflec-



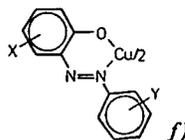
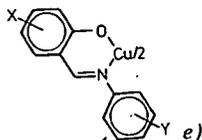
tance spectra with a single absorption band, at ca. 15 kK; these are similar to those of the distorted *trans*-planar $Cu[HSAL-NCH_3]_2$ complexes [16]. The corresponding ligands also act in a bidentate manner with Ni(II) and Co(II), as the β -nitrogen has a very small donor power because of the electronic and steric properties of the phenyl group. The dipole moment in benzene is ~ 2.20 D for both of the Cu(II) complexes [52, 53], which is high with respect to the values of 1.20 D for the analogous Ni(II) complexes and of ca. 1.70 D for the $Cu[HSAL-N-alkyl]_2$ complexes. For the latter compounds it has been suggested that the molecules of the complexes undergo a deformation in solution. X-ray investigation has shown that in the solid state $Cu[XSAL-N-C_6H_5]_2$ has a structure which is intermediate between *trans*-planar and tetrahedral. The dipole moment of 2.20 D probably indicates a distortion from the *trans*-planar configuration. The relatively high intensity of the absorption band at ca. 16.5 kK for these complexes ($\epsilon \sim 120$ and 150 in chloroform) can be interpreted as due to this distortion [48]. The absorption spectra of $Cu[HSALen-N(H)C_6H_5]_2$ and $Cu[5-ClSALen-N(C_2H_5)_2]_2$ are also indicative of a *trans*-planar configuration. It is interesting to note that the ligand 5-Cl-SALen- $N(C_2H_5)_2$ gives rise to five-coordinate structures with Ni(II) and Co(II), the steric hindrance of the two ethyl groups preventing six-coordination.

The reflection spectra of $Cu[5-ClSALen-N(H)CH_3]_2$ and $Cu[HSALen-N(CH_3)_2]_2$ are different from those of the preceding compounds ($\mu(D) = 3.03$). The absorption maximum is shifted to lower energies, from ca. 16.5 to 13.3 kK. These spectra show strong similarities to the spectrum of the N- CH_3 complex, which exhibits a trigonal-bipyramidal configuration [53] when it is a guest in the lattice of the Zn(II) analogue, and to the spectrum of the bis(salicylidene- γ -iminopropyl)amine-Cu(II) complex, which has a distorted trigonal-bipyramidal configuration.

It is interesting to note that there is an approximately linear relationship between ν_{max} and $\log K_1K_2$: the more stable a chelate is, the larger is its ν_{max} value. It can also be seen that the absorption intensities of the alkylated chelates are generally much higher than that of $[Cu(en)_2]^{2+}$ [54].

$$\text{Cu}[\text{HSAL-NXC}_6\text{H}_4]_2 \text{ and } \text{Cu}[\text{XC}_6\text{H}_3\text{O.N=N.XC}_6\text{H}_4]_2 \text{ type complexes}$$

The literature on the azomethines (*e*) is very extensive, but fewer reports have been published on the analogous azo-chelates (*f*) [see e.g. 55—59]. Azomethine che-



lates are structurally very similar to the azo-compounds, of which they are *iso*- π -electronic analogues. Table II contains the dipole and magnetic moments of several azo- and azomethine copper(II) chelates of analogous structure.

Table II shows that all the copper(II) chelates discussed have a magnetic moment between 1.77 and 1.96 B.M. The moments are generally independent of temperature and this precludes a distinction between the different stereochemistries. Much more information about the structural problems is given by the electric dipole moment. If the dihedral angle θ approximates to 90° , the chelate has a tetrahedral configuration. If θ approximates to 0° , the chelate has a trans-planar arrangement; the moments of the O-Cu and O'-Cu, as well as those of the N-Cu and N'-Cu bonds, compensate one another and the observed moment tends to zero.

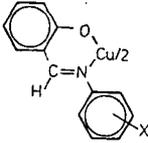
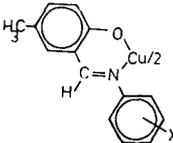
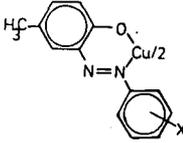
The 5-CH₃ group of the aldehyde ring does not have a considerable effect on the stereochemistry, whereas the substituents on the N-phenyl ring have a very important role. The structures of the 2-CH₃ derivatives, due to the steric hindrance, change from tetrahedral towards square-planar, and the dipole moments decrease. The 2,4,6-(CH₃)₃ derivative has a moment of 0.64 D, the coordination being nearly square-planar. This behaviour may be interpreted in terms of the tetrahedral \leftrightarrow square-planar equilibrium.

It would be expected that the introduction of a large OCH₃ group in the 2-position of the N-phenyl would shift the equilibrium towards a planar configuration and the dipole moment would decrease. Experimentally, the opposite trend is observed. To interpret this anomalous behaviour, it must be supposed that the 2-anisidine derivatives act as tridentate ligands. A weak bond is formed between the Cu(II) and the O atoms of the 2-OCH₃ groups and so a distorted cis-octahedral arrangement with high dipole moment results.

Although the trend of the dipole moments of the three groups in Table II is similar, the azomethines always have higher moments. KOGAN et al. [60] suppose that the dipole moment is not only determined by the stereochemistry, but the polarity of the bonds also plays an important role; the polarity depends on the basicity of the N atom. According to their measurements the pK_a values of azomethines are always higher than those of the corresponding azo derivatives. This shows that the lone-pairs of the N atoms of the azomethines are easily shifted towards the copper(II) atom; the polarity of the N-Cu bonds increases. Thus, for chelates with analogous structures a higher dipole moment may be observed for the azomethine.

The spectral properties are in accordance with the foregoing [25, 61]. The spectra generally show a broad band with medium intensity at around 15 kK (e.g. Fig. 3).

Table II
Magnetic and dipole moment values of some azo- and azomethine copper(II) chelates

								
X=	μ_{eff}	μ (D)	X=	$\mu_{\text{eff}}^{[a]}$	μ (D) ^[a]	X=	$\mu_{\text{eff}}^{[a]}$	μ (D) ^[a]
H	1.96 ^[60]	2.70 ^[60]	H	1.92	2.77	H	1.91	2.25
4-CH ₃	1.94 ^[60]	3.37 ^[60]	4-CH ₃	1.87	3.29	4-CH ₃	1.94	3.05
3-CH ₃	1.95 ^[60]	3.22 ^[60]	3-CH ₃	1.92	3.37	3-CH ₃	1.87	2.65
2-CH ₃	1.89 ^[60]	1.73 ^[60]	2-CH ₃	1.91	1.69	2-CH ₃	1.92	?
2, 4-Me ₂	1.92 ^[60]	2.01 ^[60]	2, 4-Me ₂	1.92	2.06	2, 4-Me ₂	1.88	1.76
2, 4, 6-Me ₃	1.93 ^[60]	0.64 ^[60]	2, 4, 6-Me ₃	1.93	1.27	2, 4, 6-Me ₃	1.94	1.14
2-OCH ₃	1.87	4.98 ^[b]	4-OCH ₃	1.87	3.60	4-OCH ₃	1.92	3.13
3-OCH ₃	1.94	4.58 ^[b]	2-OCH ₃	1.77	4.24	2-OCH ₃	1.92	3.96
4-OCH ₃	1.91	3.83 ^[b]						

^[a] Kogan, A. V. et al.: Zh. Obsch. Khim., **38**, 1607 (1968).

^[b] Kogan, A. V. et al.: Russ. J. Inorg. Chem., **12**, 1630 (1967).

The 2- and/or 2,6-derivatives exhibit this ligand-field band at nearly identical frequencies. It was shown [25, 62] that the ligand-field band was shifted towards lower frequency when the complex was distorted appreciably from the square-planar configuration. On the basis of the spectral changes it may be concluded that the copper(II) chelate molecules take up one pyridine molecule to form five-coordinated complexes.

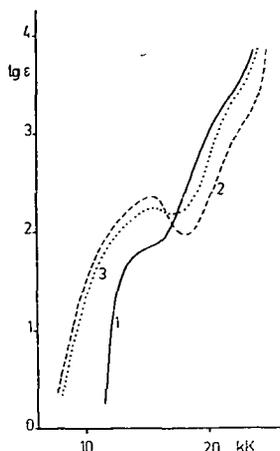


Fig. 3. Visible spectra of copper(II) chelates. 1: $\text{Cu}[\text{HSAL-N-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_2$ in CHCl_3 ; 2: the same in pyridine; 3: $\text{Cu}[\text{HSAL-N-4-CH}_3\text{C}_6\text{H}_4]_2$ in pyridine

The data discussed lead to the following general conclusions:

- (1) all copper(II) chelates containing sterically inactive donor sets are planar;
- (2) all the chelates containing sterically active donor sets are distorted planar or pseudo-tetrahedral;
- (3) complexes which are *trans*-planar in the solid state appear to retain their structure in solution;
- (4) the solution stereochemistry of pseudo-tetrahedral complexes is less clearcut; two distinct possibilities exist:

- (a) the complex in solution involves a planar/tetrahedral equilibrium, and
 - (b) the complexes dissolve without structural change, the dihedral angle not changing appreciably.
- According to our observations version (b) is probable.

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СТРУКТУРА КОМПЛЕКСОВ МЕДИ(II) С САЛИЦИЛАЛЬДАМИНОМ

Ц. Часар

Обсуждена структура хелатов меди(II) с салицилиденеанилинами на основании спектроскопических, магнитных и диэлектрических свойств. Сделано заключение, что а) все комплексы, содержащие стерически неактивные доноры, образуют планарную конфигурацию и б) комплексы, содержащие стерически активные доноры, образуют или деформированные планарные, или псевдо-тетрагональные конфигурации.