X-Ray Structures and Spectral Properties of 4-Coordinate Copper(II) and Palladium(II) Complexes with a Tridentate ONN-Schiff Base Ligand

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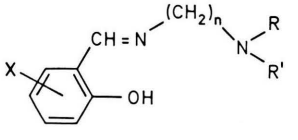
The tridentate mono-basic Schiff base N-(2-diethylaminoethyl)salicylaldimine ≙Hsal-en-NEt_2 forms complexes **1** = [(sal-en-NEt_2)MY] with divalent metals M (Y = halide). The preparation of three copper(II) complexes **1a** (Y = Br), **1b** (Y = Cl), and **1c** (Y = SCN) and one palladium(II) complex **1d** (Y = Cl) is described and the UV/VIS spectra of these complexes in methanol and chloroform are compared and discussed. The crystals of **1a** · $CHCl_3$, **1b** · $CHCl_3$, and **1d** · $CHCl_3$ are all isotypic and crystallize in the orthorhombic space group Pbca, whereas the solvent-free crystals of **1b** (and also **1a**) are monoclinic with the space group $P2_1/c$. The metal is 4-coordinate with an almost planar ONNY donor atom arrangement around the palladium and with a distorted arrangement around the copper. The crystals consist of separate non-bridged complex units and the chloroform is not coordinated.

Introduction

Tridentate mono-basic Schiff base ligands with an ONN set of donor atoms are easily accessible through condensation reactions of enolized 1,3-diketones with N-substituted diamines. In 1965 Sacconi and coworkers [1a–1f] began to report on the results of detailed studies on the complexation behaviour of such tridentate Schiff bases derived from salicylaldehyde and ethylenediamine or propylenediamine:



n = 2,3

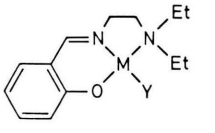
R,R' = alkyl, phenyl

X = Cl, NO_2, alkyl

It turned out that with metals M = Ni(II), Co(II), Cu(II) mostly bis complexes of the type ([X-sal-en-NRR′)$_2$M] ($n = 2$) and [(X-sal-pr-NRR′)$_2$M] ($n = 3$; pr symbolizes a propylene bridge) are formed, although with copper(II) mono complexes such as [(X-sal-en-NRR′)CuY] (Y = anion) were also obtained [1d]. On the basis of mainly spectroscopic, magnetic, and dielectric polarization data it was shown that depending on the nature of M, X, R, and R′ the ligands are either bidentate or tridentate. As a consequence, a variety of modes and geometries of coordination is observed.

Since 1978 Muto and Tokii *et al.* [2a–2c] presented further information on copper and nickel mono complexes such as [(X-sal-en-NRR′)MY] and especially on the tendency to form dimeric structures and to show antiferromagnetic interaction. Structural information based on single crystal X-ray analysis is scarce. The high spin nickel complex [(5-Cl-sal-en-NEt_2)$_2$Ni] was reported [1f] to be monomeric with five-coordinate nickel having an N_3O_2-coordination in a distorted square pyramid. Di Vaira and Orioli [3] determined the crystal structure of [(sal-pr-NMe_2)$_2$Ni] and found a distorted octahedral coordination.

In the course of our kinetic studies on ligand substitution in four-coordinate transition metal complexes [4, 5] we extended the investigations on the lability of bound ligands to the anions Y coordinated by copper(II), platinum(II), or palladium(II) in neutral complexes **1**:



1a: M = Cu(II); Y = Br;
1b: M = Cu(II); Y = Cl;
1c: M = Cu(II); Y = SCN;
1d: M = Pd(II); Y = Cl.

1 ≙ [(sal-en-NEt_2)MY]

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The question of **1** being monomeric or forming bridged dimeric structures [2a, 2c] is of great significance for the kinetic studies mentioned above. Due to the rather low solubilities of **1a–1d** in organic solvents and due to partial dissociation of the dissolved complexes osmometric molecular weight determinations turned out to be of limited value. We decided, therefore, to determine the crystal structures of **1a–1d** by three-dimensional X-ray analysis and use them as a basis for the discussion of the solution spectra of these complexes.

Experimental

Ligand N-(2-diethylaminoethyl)salicylaldimine ≙ Hsal-en-NEt$_2$

A solution of 0.1 mol of N,N-diethylethylenediamine (Ega-Chemie) in 50 ml EtOH is slowly dropped into a stirred solution of 0.1 mol of salicylaldehyde (Bayer AG) in 50 ml EtOH at room temperature. The yellow solution is then heated to boiling and cooled. After evaporation of the solvent the residue is fractionated in vacuo. The yellow oily Schiff base distills at 121 °C/3 mm Hg and is characterized by its ^{1}H NMR spectrum.

Copper complex **1a** *≙ [(sal-en-NEt$_2$)CuBr]*

A solution of 0.01 mol of Hsal-en-NEt$_2$ in 50 ml EtOH is slowly dropped into a solution of 0.01 mol $CuBr_2$ in 100 ml EtOH at room temperature. 2.5 ml of 4 N NaOH (≙0.01 mol) are then added. The solution is heated to boiling and cooled. The solvent is evaporated and the dark green residue treated with hot chloroform. After filtration of the insoluble NaBr formed, hot petroleum ether (50–70 °C) is added to the hot filtrate until crystallization begins. The dark-green crystals (yield: 93%) are filtered off, washed with petroleum ether, and recrystallized from $CHCl_3$/petroleum ether.

Heating of the crystals at 80 °C for 10 h causes a weight loss corresponding to 1 mol of $CHCl_3$ per complex unit. During determination of the melting point $CHCl_3$ evolution at 80 °C is also observed.

Recrystallization from EtOH yields black-green crystals free of solvent.

Copper complex **1b** *≙ [(sal-en-NEt$_2$)CuCl]*

Method A: Preparation as described for **1a**, starting with $CuCl_2 \cdot 2\ H_2O$ (yield: 95%). Final recrystallization from EtOH produces black-green crystals free of solvent.

Method B: 2.9 g NaCl (0.05 mol) are added to a hot aqueous solution of 1.2 g **1a** · $CHCl_3$ (0.0025 mol) with stirring. The solution is heated on a steam bath for 10 min, then cooled and extracted four times with 80 ml $CHCl_3$. The combined chloroform phases are dried with Na_2SO_4. Addition of petroleum ether (50–75 °C) initiates the crystallization of **1b** (yield: > 90%), which is recrystallized from EtOH.

Copper complex **1c** *≙ [(sal-en-NEt$_2$)CuSCN]*

Preparation according to *Method B* as described for **1b**, with a 20-fold molar excess of KSCN being added to a solution of 2.5 mol **1a** in 300 ml water. The aqueous solution, in which darkgreen crystals of **1c** precipitate, is extracted twice with 80 ml $CHCl_3$. Solid **1c** is isolated by addition of petroleum ether to the chloroform solution as described above for **1b** (yield: > 90%). The complex is recrystallized from EtOH.

Palladium complex **1d** *≙ [(sal-en-NEt$_2$)PdCl]*

A solution of 0.67 g Hsal-en-NEt$_2$ (3.05 mmol) in 30 ml EGME (= ethylene glycol mono methyl ether) is added dropwise to a suspension of 0.53 g $PdCl_2$ (3 mmol) in 80 ml EGME at room temperature. The mixture is heated to 90 °C and within 3 h 0.75 ml 4 N NaOH (3 mmol) diluted with 20 ml EGME are added dropwise with stirring. The hot solution is filtered, the filtrate is evaporated to dryness and the residue treated with hot $CHCl_3$. After filtration of the NaCl formed, petroleum ether (50–75 °C) is added to the chloroform solution of the complex and crystallization thus initiated (yield: 75%). By recrystallization from EtOH solvent-free orange crystals are obtained.

UV/VIS spectra

The spectra were taken at room temperature with a Perkin-Elmer spectrophotometer (model 554) in 0.5 cm quartz cells at [complex] = $5 \cdot 10^{-4}$ M, the solvents being $CHCl_3$ and MeOH (reagent grade). The data were collected in the memory of a desk computer for plotting of the spectra.

X-ray structure determinations

Crystals were obtained by slow evaporation of $CHCl_3$ solutions (**1a–1d**) and EtOH solutions (**1b**) of the complexes.

Intensities were measured with a four-circle diffractometer (Siemens-Stoe) using graphite-monochromated Mo–K_α radiation.

Lp and numerical absorption corrections were applied, the structures solved by direct methods, and atomic positions and anisotropic temperature factors refined by least squares to the R-values given in Tab. III*. Hydrogen atoms were positioned geometrically (C–H distance 108 pm) and not refined. All crystallographic calculations were performed with the program SHELX 76, modified for use at a small computer (Data General ECLIPSE S 140). Cell constants were determined by least squares from the 2 θ angles of about 50 reflections.

* Further details of the investigations on crystal structures may be received at: "Fachinformationszentrum Energie, Physik, Mathematik, GmbH, D-7514 Eggenstein-Leopoldshafen 2." The Registry-Nr., CSD 50191, the name of he author, and the reference should be given.

Results and Discussion

Preparation of the complexes

Different synthetic routes have been described for the preparation of the mono complexes [(sal-en-NRR′)MY] and [(sal-pr-NRR′)MY] (M = Cu(II), Ni(II)). One route [2a] is based on bis complexes such as $[(\text{sal-en-NR}_2)_2\text{Cu}]$ and their reaction with copper salts CuY_2. Another approach [1d] is the direct synthesis starting with a Schiff base such as Hsal-en-NRR′ and its reaction with a copper salt CuY_2.

The method applied in this contribution for the preparation of **1a** and also **1b** is the direct synthesis. The acids HBr or HCl generated upon the reaction of Hsal-en-NEt_2 with $CuBr_2$ or $CuCl_2$ were neutralized with sodium hydroxide. Complexes **1c** and also **1b** were obtained through an anion exchange and extraction process:

$$[(\text{sal-en-NEt}_2)\text{CuX}] + \text{H}_2\text{O} \rightleftharpoons [(\text{sal-en-NEt}_2)\text{Cu}(\text{H}_2\text{O})]^+ + \text{X}^- \quad (1)$$

$$[(\text{sal-en-NEt}_2)\text{Cu}(\text{H}_2\text{O})]^+ + \text{Y}^- \rightleftharpoons [(\text{sal-en-NEt}_2)\text{CuY}] + \text{H}_2\text{O} \quad (2)$$

The bromo complex ($X^- = Br^-$) and the chloro complex ($X^- = Cl^-$) dissociate in water according to eq. (1). The addition of an excess of Y^- (*e.g.*, in the form of KSCN) shifts equilibrium (2) to the right and favours the extraction of the complex [(sal-en-NEt_2)CuY] upon addition of chloroform.

The preparation of the palladium complex **1d** from $PdCl_2$ and Hsal-en-NEt_2 was carried out in ethylene glycol mono methyl ether at elevated temperatures because of the slowness of the reaction. It turned out that the addition of the sodium hydroxide has to be slow in order to reduce the formation of palladium black in a side reaction.

The results of elemental analysis as compiled in Table I are in fair agreement with theory. The melting points of the three copper complexes **1a–1c** are not very different, the melting point of **1b** (185–187 °C) agreeing well with the value reported in the literature (186–188 °C [1d]).

Complexes **1a–1d** are reasonably well soluble in polar organic solvents such as MeOH, EtOH, acetonitrile, acetone and chloroform. In weakly polar solvents such as toluene the complexes are much less soluble. In water, the thiocyanato complex **1c** is insoluble whereas **1a** as well as **1b** and – to a lesser extent – also **1d** dissolve slightly (especially upon warming), which is obviously due to dissociation according to (1).

UV/VIS spectra

The spectral properties of mono complexes of the type [(sal-$(CH_2)_n$–NRR′)MY] have been mainly studied for $n = 2, 3$, for R/R′ = H/alkyl, H/phenyl, Me/Me, Ph/Ph, Me/Ph, and for M = Ni(II), Cu(II). So far, the only mono complex with Hsal-en-NEt_2

Table I. Analytical data of the complexes.

Complex	Colour		C[%]	H[%]	N[%]	Anion Y [%][b]	Cu[%]	Mp.[°C]
1a · $CHCl_3$ = [(sal-en-NEt_2)CuBr] · $CHCl_3$	black-green crystals[a]	calcd	34.88	4.18	5.81	16.57	13.18	173–174[d]
		found	35.06	4.24	5.66	16.62	12.89	
1a = [(sal-en-NEt_2)CuBr]	black-green crystals[c]	calcd	43.04	5.28	7.72			175–177
		found	42.82	5.05	7.77			
1b = [(sal-en-NEt_2)CuCl]	black-green crystals[c,g]	calcd	49.06	6.02	8.80	11.14	19.96	185–187[e]
		found	48.93	6.01	8.79	11.07	19.72	
1c = [(sal-en-NEt_2)CuSCN]	dark-green crystals[c]	calcd	49.32	5.62	12.33	17.04	18.64	174–176
		found	48.81	5.38	12.16	16.70	18.19	
1d = [(sal-en-NEt_2)PdCl]	yellow-orange crystals[c,f]	calcd	43.23	5.30	7.76	9.82		212–214
		found	43.33	5.36	7.80	9.69		

[a] Recrystallized from $CHCl_3$/petroleum ether.
[b] Addition of an excess of $AgNO_3$ to the acidic (HNO_3) solutions of **1a–1d** and back titration with NH_4SCN.
[c] Recrystallized from EtOH.
[d] Crystals lose $CHCl_3$ from 80 °C on.
[e] Literature [1d]: 186–188 °C.
[f] Crystallization from $CHCl_3$/petroleum ether yields yellow-orange crystals of **1d** · $CHCl_3$ which lose their chloroform upon heating to > 80 °C.
[g] Crystallization from $CHCl_3$ yields **1b** · $CHCl_3$.

as a ligand was described by Sacconi and Bertini [1d]. It is the copper(II) chloro complex [(sal-en-NEt_2)CuCl] = **1b** for which the diffuse reflectance spectrum was reported to have a maximum at 650 and a shoulder at 740 nm. It follows from Table II that the d–d absorption at 650 nm is also found for solutions of **1b** in chloroform or methanol, although the maximum is slightly blue-shifted.

Table II. Spectrophotometric absorption data for complexes **1a**–**1d** in the wavelength range 300–800 nm.

Complex	Solvent	λ_{max}, nm (ε_{max}, $M^{-1} \cdot cm^{-1}$)
1a	$CHCl_3$	653(268); 374(5110); sh 310(≈5500)
	MeOH	640(157); 373(4800)
1b	$CHCl_3$	644(240); 381(4680); 306(4860)
	MeOH	640(152); 371(4680)
1c	$CHCl_3$	615(346); 378(5380); 306(5050)
	MeOH	630(212); 366(4980)
1d	$CHCl_3$	395(2920); sh 370(≈2300)
	MeOH	382(2770); sh 355(≈2600)

The spectra of the three copper complexes **1a**–**1c** (see Fig. 1 and Table II) are very similar in the sense that a weak and broad d–d band in the range 615–650 nm is observed, and a strong band in the range 365–380 nm, the latter one probably representing a charge transfer excitation of the Cu–O bond [6]. The methanol spectra and the chloroform spectra differ in the following details: (i) the intensity of absorption is higher in $CHCl_3$ than in MeOH, (ii) most of the absorption maxima are slightly red-shifted upon going from MeOH to $CHCl_3$, and (iii) the spectra of the chloro complex and of the bromo complex become identical in MeOH, but not in $CHCl_3$. This finding is explained best by assuming that both **1a** and **1b** (but not **1c**, the thiocyanato complex) dissociate in MeOH according to eq. (1), whereupon the solvento species [(sal-en-NEt_2)CuS]$^+$ is formed (S = MeOH or possibly residual H_2O).

The spectra of **1a**–**1c** have in common a minimum of absorption in the range 520–580 nm (see Fig. 1). The existence of a maximum around 640 nm and the formation of the above minimum are also observed in the solution spectra of planar 4-coordinate *trans*-N_2O_2 copper(II) complexes such as bis(N-ethylsalicylaldiminato)copper(II) upon addition of pyridine [7]. Although this comparison

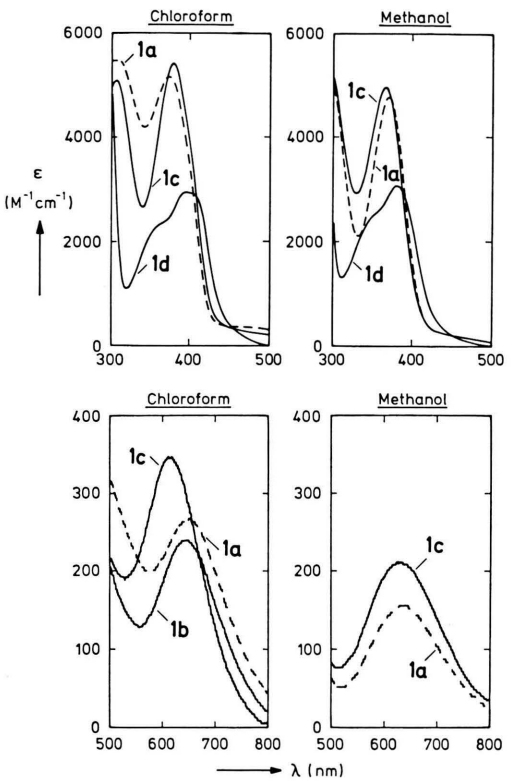

Fig. 1. UV/VIS spectra of complexes
1a = [(sal-en-NEt_2)CuBr], **1b** = [(sal-en-NEt_2)CuCl], **1c** = [(sal-en-NEt_2)CuSCN), and **1d** = [(sal-en-NEt_2)PdCl] in Methanol and Chloroform.

suffers from the fact that there is much less symmetry around the copper in **1a**–**1c** as compared to a *trans*-N_2O_2 coordinate copper, one could conclude, that in methanol and also in chloroform complexes **1a**–**1c** probably coordinate a solvent molecule, which in chloroform is ethanol (added as a stabilizer) or residual water.

The main differences between the spectra of the palladium complex **1d** and the corresponding copper complex **1b** are the following: (i) there is no absorption of **1d** at $\lambda > 500$ nm (ii) the charge transfer band of **1d** at about 390 nm is distinctly less intense than that of **1b** and slightly red-shifted.

Four-coordinate palladium(II) complexes prefer to be square-planar on the one hand and tend to form dinuclear bridged structures on the other hand. Neither for the palladium complex **1d** nor for the copper complexes **1a**–**1c** the absorption spectra alone can rule out convincingly the presence of oxygen or halogen bridged structures.

Table III. Collection of crystallographic data and information on data processing.

Symbol Empirical formula	**1a** · $CHCl_3$ $C_{13}H_{19}BrCuN_2O \cdot CHCl_3$	**1b** · $CHCl_3$ $C_{13}H_{19}ClCuN_2O \cdot CHCl_3$	**1d** · $CHCl_3$ $C_{13}H_{19}ClN_2OPd \cdot CHCl_3$	**1b** $C_{13}H_{19}ClCuN_2O$
Cell constants (pm; °) *a*	1163.8 (.5)	1163.2 (3)	1115.6 (4)	729.4 (3)
b	2816.0 (1.0)	2784.3 (6)	2879.4 (8)	1232.4 (6)
c	1174.6 (.5)	1157.8 (3)	1166.5 (4)	1650.0 (8)
β	–	–	–	108.87 (2)
Space group	Pbca	Pbca	Pbca	$P2_1/c$
Formula units/unit cell	8	8	8	4
Calculated density ($g \cdot cm^{-3}$)	1.66	1.55	1.70	1.51
Number of reflections collected	2819 (θ up to 20°)	4755 (θ up to 22.5°)	3468 (θ up to 22.5°)	1923 (θ up to 22.5°)
Number of symmetry-independent reflections	1794	2453	2466	1840
Reflections with $F > 2\sigma(F)$	1190	2161	2152	–[a]
$R = \frac{\Sigma\lvert F_o - F_c\rvert}{\Sigma\lvert F_o\rvert}$	0.064	0.044	0.037	0.035
$R_w = \frac{\Sigma\sqrt{w}\lvert F_o - F_c\rvert}{\Sigma\sqrt{w}\lvert F_o\rvert}$	0.040	0.042	0.038	0.031
Crystal form	needle along a-axis, ∅ ≈ 0.1 mm	needle along a-axis, ∅ ≈ 0.3 mm	block-like crystal ≈ 0.3 × 0.25 × 0.6 mm^3	prism along a-axis, ≈ 0.6 × 0.2 × 0.15 mm
Linear absorption coefficient (cm^{-1})	35.47	16.83	14.93	17.02
Estimated limits of error for distances and angles	2 pm, 1°	1 pm, 0.5°	1 pm, 0.5°	< 1 pm, 0.4°

[a] All reflections were used for refinement.

X-ray structures

X-ray studies were carried out with crystals of **1a**·$CHCl_3$, **1b**·$CHCl_3$, **1b**, and **1d**·$CHCl_3$. Table III summarizes relevant data.

Evaporation of chloroform solutions of the two copper complexes **1a** (anion = Br^-) and **1b** (anion = Cl^-) and of the palladium complex **1d** (anion = Cl^-) produces crystals containing 1 molecule $CHCl_3$ per metal. These crystals are all isotypic with the orthorhombic space group Pbca. The solvent-free crystals of the copper complex **1b** (anion = Cl^-) obtained from ethanol solutions are monoclinic with the space group $P2_1/c$. It was found that solvent-free crystals of the copper(II) bromo complex **1a** are isotypic with **1b**. Crystals of **1a**·$CHCl_3$, **1b**·$CHCl_3$, and **1d**·$CHCl_3$ easily lose their chloroform upon heating in an oven. The crystallographic analysis proves that the chloroform is not coordinated to the metal in these compounds. As an example Fig. 2 shows a view of the unit cell of the copper bromo complex **1a**·$CHCl_3$ projected along [100], in which the large distance between copper and chloroform becomes apparent (shortest M–$CHCl_3$ distance = 449 pm).

For comparison Fig. 3 presents a view of the unit cell of the solvent-free copper chloro complex **1b** projected along [010]. This view demonstrates very clearly a rather strong tetrahedral distortion of the donor atoms around the copper.

Table IV summarizes details of the inner coordination sphere of the metal. The Cu–O bond length of 190 pm is the shortest Cu-donor atom bond length in all three copper complexes. The Cu–N(1) bond length of 194 pm is remarkably constant, *i.e.*, anion-

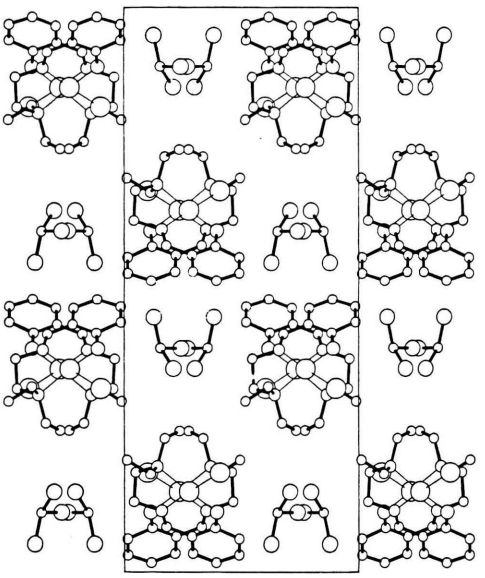

Fig. 2. View of the unit cell of **1a** · $CHCl_3$ projected along [100].

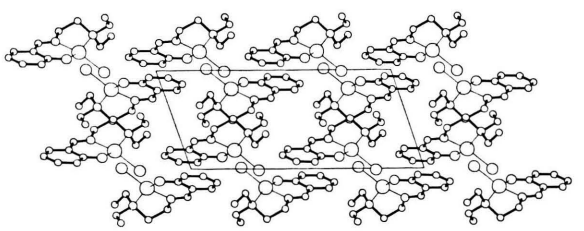

Fig. 3. View of the unit cell of **1b** projected along [010].

independent. Comparing the Cu–O and Cu–N(1) bond lengths of the distorted ($\beta = 17.9°$; see Table IV) complex **1b** [(sal-en-NEt_2)CuCl] with the corresponding Cu–O bond length (average: 189 pm) and Cu–N bond length (average: 194 pm) of the distorted ($\beta = 35.6°$) *trans*-N_2O_2 complex bis (N-ethylsalicylaldiminato)copper(II) [8] one recognizes close agreement. On the other hand the Cu–N(1) bond length (194 pm) is by almost 7% shorter than the Cu–N(2) bond length (208 pm). This is possibly due to the fact that the imino nitrogen atom N(1) is part of the conjugated system while the amino nitrogen atom N(2) is not. It should also be kept in mind that N(1) is a member of a chelate six-membered ring as well as of a chelate five-membered ring, whereas N(2) belongs to the five-membered ring only.

Table IV. Bond lengths (pm) and bond angles (Deg) characterizing the inner coordination sphere of the metal in complexes **1a**·$CHCl_3$, **1b**·$CHCl_3$, **1b**, and **1d**·$CHCl_3$.

Complex	**1a**·$CHCl_3$	**1b**·$CHCl_3$	**1b**	**1d**·$CHCl_3$
Distances[a]				
M–O	189	190	190	199
M–N(1)[b]	194	194	194	196
M–N(2)[b]	209	208	208	208
M–Y[c]	238.2	223.5	223.7	232.6
shortest M–M	584	585	662	560
Angles[a]				
O–M–N(1)	92.1	92.3	92.6	92.9
N(1)–M–N(2)	85.4	84.4	84.6	84.5
N(2)–M–Y	93.8	94.2	95.8	93.9
Y–M–O	90.0	91.0	94.1	88.8
β[d]	12.3	15.0	27.9	1.8

[a] M = Cu(II) or Pd(II);
[b] the numbering N(1) and N(2) refers to $C_6H_4(OH)$–CH=N(1)–$(CH_2)_2$–N(2)Et_2;
[c] represents the anion Cl^- or Br^-;
[d] β is the torsion angle between the Y–M–O plane and the N(1)–M–N(2) plane describing the degree of tetrahedral distortion.

Comparing the palladium chloro complex **1d** · $CHCl_3$ with the corresponding copper chloro complex **1b** · $CHCl_3$ one recognizes distinctly enlarged M–O (190 → 199 pm) and M–Cl bond lengths (223.5 → 232.6 pm) for the palladium complex, whereas the M–N(2) (208 pm) and M–N(1) (196 pm) bond lengths are not significantly different in both complexes. This could well have to do with the "weaker" palladium(II) metal centre coordinating the "hard" donor atoms oxygen and chlorine less strongly than the "weaker" nitrogen atoms. One could also argue that the "bite" of the tridentate ligand is not large enough to allow a strainless planar arrangement around the palladium and that, therefore, the Pd–O bond is slightly stretched from 190 pm in the distorted copper complex to 199 pm in the planar palladium complex. This argument, however, is not supported by a Pd–O bond length of 200 pm in the planar *trans*-N_2O_2 complex bis-(*n*-butylsalicylaldiminato)palladium(II) [9] with two bidentate salicylaldimines serving as ligands. The difference in bond lengths of almost 6% between the "long" Pd–N(2) bond (208 pm) and the "short" Pd–N(1) bond (196 pm) corresponds to that observed for the copper complex **1b** and seems to be an intrinsic property of the ligand. As a matter of fact, the Pd–N(1) distance is slightly smaller and

the Pd–N(2) distance is slightly greater than the "normal" Pd–N distance of 202 pm in the planar complex $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ [10].

The large Cu–Cu distances of 560–662 pm (see Table IV) predict normal paramagnetic behaviour of the copper complexes, *i.e.*, no antiferromagnetic coupling. The shortest Cu–Cl distance between neighbouring complex units was found to be 600 pm in **1b**. This long distance excludes any additional intermolecular Cu–Cl bonding.

Inspection of Fig. 4 shows a more or less planar arrangement of the four donor atoms around the palladium. Table IV confirms that β, the torsion angle between the Y–Pd–O plane and the N(1)–Pd–N(2) plane, is very small, indeed (1.8°). On the other hand it is interesting to note that the salicylaldimine unit is clearly bent off the coordination plane.

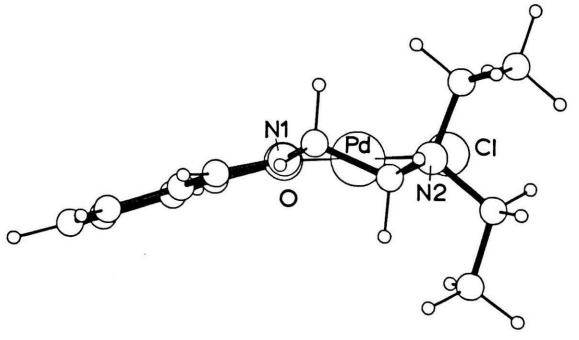

Fig. 4. View of the coordination geometry of the palladium chloro complex **1d** · $CHCl_3$.

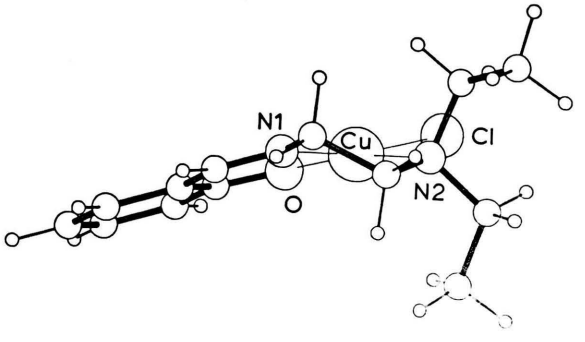

Fig. 5. View of the coordination geometry of the copper chloro complex **1b** · $CHCl_3$.

The torsion angle β observed for the various copper complexes is considerably larger. The degree of distortion is greatest for the solvent-free copper complex **1b** ($\beta = 27.9°$) and almost twice as large as for the complex **1b** · $CHCl_3$ ($\beta = 15°$), although the chloroform is not coordinated. Fig. 5 presents a view of the distorted coordination core of the copper chloro complex **1b** · $CHCl_3$.

The molecular conformation of the thiocyanato complex **1c*** is very similar to that of **1b**. The structure could not be refined to the same accuracy because of the large thermal motion of the terminal ethyl groups. There are strong indications for the anion to be N-bonded to the copper.

As pointed out earlier the question of dinuclear species being present in solutions of complexes **1a–1d** is pertinent to the kinetic studies planned. In this respect the most significant result of the X-ray studies is that in the solid state there is no bridging through oxygen or halogen atoms. The crystals consist of single complex units. This finding and also the UV/VIS spectra discussed earlier can be taken as strong support for the solutions of complexes **1a–1d** to contain separate non-bridged complex units.

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* **1c** = [(sal-en-NEt_2)Cu(NCS)], space group Fdd2, a = 4961(2) pm, b = 1764.8(5) pm, c = 1461.8(5), 32 molecules per unit cell, 2 molecules per asymmetric unit.

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