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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X-ray, UV/VIS Spectra, Tridentate ONN Schiff Base, Copper(II) Complexes, Palladium(II) Complexes

The tridentate mono-basic Schiff base N-(2-diethyaminoethyl)salicylaldimine \( \triangleleft \) sal-en-NEt\(_2\) forms complexes \( 1 = \left[ \text{sal-en-NEt}_2 MY \right] \) 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 \( 1a \cdot \text{CHCl}_3 \) and \( 1b \cdot \text{CHCl}_3 \), and \( 1d \cdot \text{CHCl}_3 \) are all isotypic and crystallize in the orthorhombic space group \( Pbc a \), whereas the solvent-free crystals of \( 1c \) (and also \( 1a \)) are monomeric 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 \( [la-lf] \) 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:

\[
\begin{align*}
X & \quad \text{CH} + \text{N} & \quad \text{(CH}_2\text{)}_n & \quad R, R' = \text{alkyl, phenyl} \\
\text{R, R'} & \quad \text{X = Cl, NO}_2, \text{alkyl} \\
\text{n} & = 2, 3
\end{align*}
\]

It turned out that with metals \( M = \text{Ni}(II), \text{Co}(II), \text{Cu}(II) \) mostly bis complexes of the type \( \left[ \text{X-sal-en-NRR'}_2 M \right] \) (\( n = 2 \)) and \( \left[ \text{X-sal-pr-NRR'}_2 M \right] \) (\( n = 3 \)); \( pr \) symbolizes a propylene bridge) are formed, although with copper(II) mono complexes such as \( \left[ \text{X-sal-en-NRR'} \text{Cu} \right] \) (\( Y = \) 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 \( \left[ \text{X-sal-en-NRR'} \text{Cu} \right] \) 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 \( \left( \text{5-Cl-sal-en-NEt}_2 \text{Ni} \right) \) was reported \( [1f] \) to be monomeric with five-coordinate nickel having an \( N_5\text{O}_2\) coordination in a distorted square pyramid. Di Vaira and Orioli \( [3] \) determined the crystal structure of \( \left[ \text{sal-pr-NMe}_2 \text{Ni} \right] \) 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 \( \mathbf{1} \):

\[
\begin{align*}
al & \quad \text{M} = \text{Cu}(II); \quad Y = Br; \\
b & \quad \text{M} = \text{Cu}(II); \quad Y = Cl; \\
c & \quad \text{M} = \text{Cu}(II); \quad Y = SCN; \\
d & \quad \text{M} = \text{Pd}(II); \quad Y = Cl.
\end{align*}
\]

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The question of 1 being monomeric or forming bridged dimeric structures [2a, 2e] 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 $\cong$ Hsal-en-NEt$_2$

A solution of 0.1 mol of N,N-diethylthelylenediamine (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 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 $\cong$ [(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 ($\cong$ 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 $\cong$ [(sal-en-NEt$_2$)CuCl]**

Method A: Preparation as described for 1a, starting with CuCl$_2$·2 H$_2$O (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$_2$SO$_4$. Addition of petroleum ether (50-75 °C) initiates the crystallization of 1b (yield: > 90%), which is recrystallized from EtOH.

**Copper complex 1c $\cong$ [(sal-en-NEh)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 $\cong$ [(sal-en-NEt$_2$)PdCl$_2$]**

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] = 5·10$^{-4}$ 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$_\alpha$ 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 2θ 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 the 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 ([sal-en-NR2)Cu] and their reaction with copper salts CuY2. Another approach [1d] is the direct synthesis starting with a Schiff base such as Hsal-en-NRR' and its reaction with a copper salt CuY2.

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-NEt2 with CuBr2 or CuCl2 were neutralized with sodium hydroxide. Complexes 1c and also 1b were obtained through an anion exchange and extraction process:

\[
[(\text{sal-en-NEt2})\text{Cu}X] + \text{H}_2\text{O} \rightleftharpoons
[(\text{sal-en-NEt2})\text{Cu}(\text{H}_2\text{O})]^+ + \text{X}^- \tag{1}
\]

\[
[(\text{sal-en-NEt2})\text{Cu}(\text{H}_2\text{O})]^+ + \text{Y}^- \rightleftharpoons
[(\text{sal-en-NEt2})\text{CuY}] + \text{H}_2\text{O} \tag{2}
\]

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-NEt2)CuY] upon addition of chloroform.

Table I. Analytical data of the complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>C[%]</th>
<th>H[%]</th>
<th>N[%]</th>
<th>Anion Y [%]</th>
<th>Cu[%]</th>
<th>Mp.[°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a • CHC13 = [(sal-en-NEt2)CuBr] • CHC13</td>
<td>black-green</td>
<td>34.88</td>
<td>4.18</td>
<td>5.81</td>
<td>16.57</td>
<td>13.18</td>
<td>173–174d</td>
</tr>
<tr>
<td>1a = [(sal-en-NEt2)CuBr]</td>
<td>crystalsa</td>
<td>found</td>
<td>35.06</td>
<td>4.24</td>
<td>5.66</td>
<td>16.62</td>
<td>12.89</td>
</tr>
<tr>
<td>1b = [(sal-en-NEt2)CuCl]</td>
<td>black-green</td>
<td>43.04</td>
<td>5.28</td>
<td>7.72</td>
<td>175–177</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c = [(sal-en-NEt2)CuSCN]</td>
<td>crystalsc</td>
<td>found</td>
<td>42.82</td>
<td>5.05</td>
<td>7.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d = [(sal-en-NEt2)PdCl]</td>
<td>yellow-orange</td>
<td>49.06</td>
<td>6.02</td>
<td>8.80</td>
<td>11.14</td>
<td>19.72</td>
<td>185–187c</td>
</tr>
<tr>
<td>1e = [(sal-en-NEt2)PdCl]</td>
<td>crystalsc,f</td>
<td>found</td>
<td>48.43</td>
<td>6.1</td>
<td>8.79</td>
<td>11.07</td>
<td>17.04</td>
</tr>
<tr>
<td>1f</td>
<td>crystalsc,f</td>
<td>found</td>
<td>48.81</td>
<td>5.38</td>
<td>12.16</td>
<td>16.70</td>
<td>18.19</td>
</tr>
<tr>
<td>1g</td>
<td>crystalsc,f</td>
<td>found</td>
<td>43.25</td>
<td>5.39</td>
<td>7.76</td>
<td>9.82</td>
<td>172–174</td>
</tr>
</tbody>
</table>

a Recrystallized from CHC13/petroleum ether.

b Addition of an excess of Ag2NO3 to the acidic (HNO3) solutions of 1a-1d and back titration with NH4SCN.

c Recrystallized from EtOH.

d Crystals lose CHC13 from 80 °C on.

e Literature [1d]: 186–188 °C.

f Crystallization from CHC13/petroleum ether yields yellow-orange crystals of 1d • CHC13 which lose their chloroform upon heating to ≥ 80 °C.

g Crystallization from CHC13 yields 1b • CHC13.

The preparation of the palladium complex 1d from PdCl2 and Hsal-en-NEt2 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–1e 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 1e 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-(CH2)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-NEt2...
as a ligand was described by Sacconi and Bertini [1d]. It is the copper(II) chloro complex \([\text{sal-en-NEt}_2\text{CuCl}] = 1b\) 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.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>λ &lt;sub&gt;max&lt;/sub&gt;, nm (ε &lt;sub&gt;max&lt;/sub&gt;, M&lt;sup&gt;-1&lt;/sup&gt;·cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>653 (268); 374 (5110); sh 310 (~5500)</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>640 (157); 373 (4800)</td>
</tr>
<tr>
<td>1b</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>644 (240); 381 (4680); 306 (4860)</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>640 (152); 371 (4680)</td>
</tr>
<tr>
<td>1c</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>615 (346); 378 (5380); 306 (5050)</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>630 (212); 366 (4980)</td>
</tr>
<tr>
<td>1d</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>395 (2920); sh 370 (~2300)</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>382 (2770); sh 355 (~2600)</td>
</tr>
</tbody>
</table>

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<sub>3</sub> than in MeOH, (ii) most of the absorption maxima are slightly red-shifted upon going from MeOH to CHCl<sub>3</sub>, and (iii) the spectra of the chloro complex and of the bromo complex become identical in MeOH, but not in CHCl<sub>3</sub>. 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 solvato species \([\text{sal-en-NEt}_2\text{CuS}]^+\) is formed (S = MeOH or possibly residual H<sub>2</sub>O).

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 \(\text{trans-N}_2\text{O}_2\) copper(II) complexes such as bis(N-ethylsalicylaldiminato)copper(II) upon addition of pyridine [7]. Although this comparison suffers from the fact that there is much less symmetry around the copper in 1a–1c as compared to a \(\text{trans-N}_2\text{O}_2\) 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.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Empirical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>1b</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>1d</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>1b'</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>1b (1)</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>1b (2)</td>
<td>CHCl₃</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell constants (pm; °)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1163.8 (0.5)</td>
<td>1163.2 (3)</td>
<td>1155.6 (4)</td>
<td>729.4 (3)</td>
</tr>
<tr>
<td>b</td>
<td>2816.0 (1.0)</td>
<td>2784.3 (6)</td>
<td>2879.4 (8)</td>
<td>1232.4 (6)</td>
</tr>
<tr>
<td>c</td>
<td>1174.6 (0.5)</td>
<td>1157.8 (3)</td>
<td>1166.5 (4)</td>
<td>1650.0 (8)</td>
</tr>
<tr>
<td>β</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>108.87 (2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Space group</th>
<th>Pbca</th>
<th>Pbca</th>
<th>Pbca</th>
<th>P 21/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula units/unit cell</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density (g·cm⁻³)</td>
<td>1.66</td>
<td>1.55</td>
<td>1.70</td>
<td>1.51</td>
</tr>
<tr>
<td>Number of reflections collected</td>
<td>2819 (θ up to 20°)</td>
<td>4755 (θ up to 22.5°)</td>
<td>3468 (θ up to 22.5°)</td>
<td>1923 (θ up to 22.5°)</td>
</tr>
<tr>
<td>Number of symmetry-independent reflections</td>
<td>1794</td>
<td>2453</td>
<td>2466</td>
<td>1840</td>
</tr>
<tr>
<td>Reflections with F &gt; 2σ(F)</td>
<td>1190</td>
<td>2161</td>
<td>2152</td>
<td>–a</td>
</tr>
<tr>
<td>R = Σ</td>
<td>F₀–Fₑ</td>
<td>Σ</td>
<td>F₀</td>
<td></td>
</tr>
<tr>
<td>Rₑ = Σ</td>
<td>w</td>
<td>F₀–Fₑ</td>
<td>Σ</td>
<td>w</td>
</tr>
<tr>
<td>Crystal form</td>
<td>needle along a-axis, δ = 0.1 mm</td>
<td>needle along a-axis, δ = 0.3 mm</td>
<td>block-like crystal</td>
<td>prism along a-axis, (0.3 \times 0.28 \times 0.6 ) mm³</td>
</tr>
<tr>
<td>Linear absorption coefficient (cm⁻¹)</td>
<td>35.47</td>
<td>16.83</td>
<td>14.93</td>
<td>17.02</td>
</tr>
<tr>
<td>Estimated limits of error for distances and angles</td>
<td>2 pm, 1°</td>
<td>1 pm, 0.5°</td>
<td>1 pm, 0.5°</td>
<td>&lt; 1 pm, 0.4°</td>
</tr>
</tbody>
</table>

a  All reflections were used for refinement.

X-ray structures

X-ray studies were carried out with crystals of 1a·CHCl₃, 1b·CHCl₃, 1b', and 1d·CHCl₃. 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 CHCl₃ 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 P 2₁/c. It was found that solvent-free crystals of the copper(II) bromo complex 1a are isotypic with 1b. Crystals of 1a·CHCl₃, 1b·CHCl₃, and 1d·CHCl₃ 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·CHCl₃ projected along [100], in which the large distance between copper and chloroform becomes apparent (shortest M–CHCl₃ 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-
independent. Comparing the Cu–O and Cu–N bond lengths of the distorted (β = 17.9°; see Table IV) complex 1b [(sal-en-NEt₂)CuCl] with the corresponding Cu–O bond length (average: 189 pm) and Cu–N bond length (average: 194 pm) of the distorted (β = 35.6°) trans-N₂O₂ complex bis (N-ethylsalicylaldiminato)copper(II) [8] one recognizes close agreement. On the other hand the Cu–N bond length (194 pm) is by almost 7% shorter than the Cu–N 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.

Comparing the palladium chloro complex 1d · CHCl₃ with the corresponding copper chloro complex 1b · CHCl₃ 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-N₂O₂ 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$_2$O [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 $\beta$, 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.

The torsion angle $\beta$ observed for the various copper complexes is considerably larger. The degree of distortion is greatest for the solvent-free copper complex 1b ($\beta = 27.9^\circ$) and almost twice as large as for the complex 1b $\cdot$ CHCl$_3$ ($\beta = 15^\circ$), although the chloroform is not coordinated. Fig. 5 presents a view of the distorted coordination core of the copper chloro complex 1b $\cdot$ 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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