

Fig. 1. ORTEP (Johnson, 1976) plot showing 50% probability thermal ellipsoids.

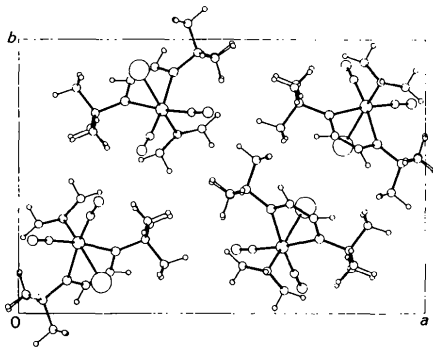


Fig. 2. *c*-axis projection packing diagram (PLUTO, Motherwell, 1978).

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The Structure of Dichloro(2,2':6',2''-terpyridyl)copper(II) Monohydrate, [Cu(C₁₅H₁₁N₃)Cl₂].H₂O

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Abstract. $M_r = 385.7$, monoclinic, space group $C2/c$, $a = 17.254$ (8), $b = 9.594$ (5), $c = 18.779$ (9) Å, $\beta = 96.81$ (9)°, $Z = 8$, $d_m = 1.651$ (9), $d_x = 1.659$ Mg m⁻³, $V = 3086.6$ Å³. The crystal structure of Cu(tpy)Cl₂.H₂O has been determined using three-dimensional single-crystal X-ray data. The material crystallizes as heavy green needles. Least-squares anisotropic refinement led to $R = 6.5\%$ for 2614 reflexions. The crystal consists of discrete monomeric molecules in which the

Cu atom is pentacoordinated. The configuration approaches that of a square pyramid. The various theories concerning pentacoordinated 3d elements are described and the square-pyramidal environment is justified.

Introduction. Cu^{II} is a typical metal ion with respect to the formation of coordination complexes, but is a special one in its reluctance to adopt regular octahedral

or tetrahedral stereochemistry. The subtle asymmetries induced in these geometries are obviously due to its $3d^9$ electronic configuration.

The stereochemistry of the Cu^{II} ion can be formally described as being dominated by a four-coordinate square-planar topology involving four relatively short in-plane bonds, and higher coordination numbers are derived by the presence of further ligands along the axial directions at longer bond lengths. Variations of each possible topology occur through bond-length and/or bond-angle distortions.

As the number of axial copper complexes of known structure increases, the 'effective' coordination number of the local Cu^{II} environment becomes less certain. The axial bond lengths in hexacoordinate complexes (R_L) are frequently 0.6 Å longer than the in-plane bond-lengths (R_S); for pentacoordinate square-pyramidal complexes this difference is about 0.4 Å (Hathaway, 1973). To describe this situation the term 'semi-coordination' has been introduced referring to weakly bonded axial ligands, and the Cu^{II} ion should be considered as having an ellipsoidal distribution of electron density.

Another important factor affecting stereochemistry is the great ability of Cu^{II} coordination polyhedra to undergo distortions leading to several stable configurations which differ by metal-ligand angles and distances. This feature is found frequently in Cu^{II} octahedral complexes and is a special type of non-rigidity called 'plasticity' (Gazo *et al.*, 1976) and the isomers arising from the plasticity of the Cu^{II} metal sphere are named distortion isomers (Gazo, 1974). The preparation of these distortion isomers depends on factors affecting chemical equilibrium.

In a recent theory, Rossi & Hoffmann (1975) using extended Hückel calculations predicted with equal probability either a trigonal-bipyramidal or a tetragonal-pyramidal configuration for a $3d^9$ ion (Cu^{II}). However, in the case where a square-pyramidal environment is adopted, the prediction is for four strong basal bonds corresponding to electron-donor ligands and a weaker apical bond related to an electron-acceptor ligand.

The study of a number of five-coordinate compounds of the type metal(unidentate)₂(tridentate) [$M(E)(D)(ABC)$] has led to the finding that the metal coordination polyhedron is rather irregular and does not correspond to an ideal trigonal bipyramid or to a regular square pyramid. On the contrary, it can be assimilated in most cases to a distorted trigonal bipyramid or square pyramid.

This observation has led Kepert (1974) and Favas & Kepert (1980) to develop a repulsion approach which considers the repulsion between valence-shell electron pairs and/or ligands. In this approach the stereochemical arrangement of the ligands surrounding a central metal atom may be calculated by minimizing the total repulsion energy U obtained by summing over

all individual donor-donor atom repulsions (or valence-shell electron-pair repulsions). In the case of the tridentate ligand ABC and the unidentate ligands D and E the repulsion energy is controlled mainly by the 'bite' $b = 2d_{AB}/(d_{MA} + d_{MB}) = 2d_{BC}/(d_{MB} + d_{MC})$ of the tridentate ligand, the tridentate angle ABC and the unidentate-metal angle DME . A number of important predictions result from the repulsion-energy minima: the angle DME is constant and 100° for $b < 1.4$ and the angle ABC is never equal to 90° . This means that neither the ideal trigonal bipyramid (t.b.p.) nor the ideal square pyramid (s.p.) should exist but, rather, distortions of the two ideal coordinations. For $b = 1.20$, $\angle ABC = 100^\circ$ and $\angle DME = 111^\circ$ an 'ideally' distorted square pyramid (d.s.p.) can be predicted.

The ability of tpy to act as a chelating agent was demonstrated by the work of Morgan & Burstall (1937). Corbridge & Cox (1956) first confirmed the tridentate nature and the virtual planarity of the tpy ligand by determining the crystal structure of $\text{Zn}(\text{tpy})\text{Cl}_2$. These structural results were corroborated by Einstein & Penfold (1966) who carried out a more accurate refinement of the same structure. They found that the Zn atom was surrounded by three N atoms and two Cl atoms in a distorted trigonal-bipyramidal arrangement. In a more recent paper concerning $\text{Co}(2\text{-pyridinecarbaldehyde } 2\text{-pyridylhydrazone})\text{Cl}_2$ [$\text{Co}(\text{paphy})\text{Cl}_2$], Gerlock (1966) interprets the data as indicating a structure close to a square pyramid. In another structural study on $\text{Co}(\text{tpy})\text{Cl}_2$ (Goldschmied & Stephenson, 1970), which is isomorphous with the Zn complex, it was suggested that the Co^{II} atom has a trigonal-bipyramidal coordination.

Recently, many examples of five-coordinate complexes of the first transition series have been reported (Muetterties & Schunn, 1966; Wood, 1972), with special attention given to compounds having the general formula $M(\text{tpy})X_2$, with $M = \text{Mn, Fe, Co, Ni, Cu, Zn, Cd}$, and $X = \text{Cl, Br, I}$ (Harris, Lockyer & Stephenson, 1966; Judge, Reiff, Intille, Ballway & Baker, 1967). In the case of the chlorides they seem to crystallize in three different structures [(I), (II) and (III)] (Table 1). More recently, the structure of

Table 1. Known $M(\text{tpy})\text{Cl}_2$ compounds belonging to the forms (I), (II) or (III), with representative cell parameters given for Zn and Cu

| | Form (I) | Form (II) | Form (III) |
|----------------------|----------------------------------------|-----------------------------------------------------------------------|------------------------------------------------------------------|
| | (1) $\text{Zn}(\text{tpy})\text{Cl}_2$ | (1) $\text{Zn}(\text{tpy})\text{Cl}_2$ | (1) $\text{Cu}(\text{tpy})\text{Cl}_2 \cdot \text{H}_2\text{O}$ |
| a (Å) | 13.95 | 16.21 | 17.254 (8) |
| b (Å) | 9.12 | 8.25 | 9.594 (5) |
| c (Å) | 11.48 | 10.97 | 18.779 (9) |
| β ($^\circ$) | 96 | 93.5 | 96.81 (9) |
| Space group | $I2/a$ | $P2_1/a$ | $C2/c$ |
| | (2) $\text{Cd}(\text{tpy})\text{Cl}_2$ | (2) $M(\text{tpy})\text{Cl}_2$ ($M = \text{Mn, Co, Fe, Cu, Cd}$) | (3) $\text{Cu}(\text{tpy})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ |

$\text{Cu}(\text{tpy})(\text{CN})\text{NO}_3 \cdot \text{H}_2\text{O}$ has been published and seems to belong to form (II) (Anderson, Packard & Wicholas, 1976). Work on the compound $\text{Co}(\text{tpy})(\text{NCO})_2$ reported by Kepert, Kucharski & White (1980) has shown it to be form (I).

The only determinations reported in the literature are those of $M(\text{tpy})\text{Cl}_2$ for $M = \text{Zn}, \text{Co}$ [form (II)] and of $\text{Cu}(\text{tpy})(\text{CN})\text{NO}_3 \cdot \text{H}_2\text{O}$ [form (II)]. No structural information exists for any form (I) or form (III) compound, although all three forms seem to be structurally related, containing a pentacoordinated metal atom.

In order to facilitate the interpretation of the physical-property study undertaken on these compounds and to corroborate the predictions made by the various theories on the pentacoordinated transition-metal complexes, we decided to carry out a structural study of $\text{Cu}(\text{tpy})\text{Cl}_2 \cdot \text{H}_2\text{O}$ [form (III)] isolated for the first time here.

Experimental. Crystals of the compound $\text{Cu}(\text{tpy})\text{Cl}_2 \cdot \text{H}_2\text{O}$ were obtained by crystallization from an aqueous solution saturated with the solid precipitate which was separated from a 1:1 mixture of an aqueous solution of CuCl_2 and an acetone solution of terpyridine.

The Weissenberg and precession photographs revealed monoclinic symmetry with systematic absences (hkl : $h + k = 2n + 1$, $h0l$: $l = 2n + 1$) consistent with space groups Cc or $C2/c$. The unit-cell dimensions have been refined using single-crystal and powder data.

A crystal in the form of a rectangular block ($0.26 \times 0.21 \times 0.25$ mm) was used for data collection. The intensities were measured on a three-circle automatic diffractometer (Enraf-Nonius CAD-3) with $\text{Mo } K\alpha_1$ graphite-monochromated radiation ($\lambda = 0.70929 \text{ \AA}$) and a multiple $\theta/2\theta$ scanning technique up to $\theta_{\text{max}} = 45^\circ$. Three standard reflexions were measured for every batch of 50 reflexions with no significant fluctuation in their intensities. 2614 symmetry-independent reflexions were obtained with $I \geq 3\sigma(I)$, and were corrected for Lorentz and polarization factors, but not for absorption [$\mu(\text{Mo } K\alpha) = 1.8 \text{ mm}^{-1}$].

The positions of the Cu and two Cl atoms were obtained from a three-dimensional Patterson synthesis. Subsequent Fourier and difference syntheses revealed the positions of the C, N and O atoms. Refinement by isotropic then anisotropic full-matrix least squares (Busing, Martin & Levy, 1962) led to a final $R = 0.065$. The space group $C2/c$ was used throughout and confirmed by the refinement. A final difference synthesis shows no significant residual electron density. No attempt was made to locate the H atoms.

Scattering factors were those of McMaster, Kerr del Grande, Mallet & Hubbel (1969), and the anomalous-

dispersion corrections those of Dauben & Templeton (1962).

The final positional and thermal parameters are given in Table 2. Table 3 gives the interatomic distances.*

Discussion. The results of this analysis are shown in a projection on the (010) plane in Fig. 1. The structure consists of monomeric molecules with pentacoordinate stereochemistry around the Cu atom resulting from bonding to a quasi-planar terdentate ligand and to two Cl atoms. The ligand molecules form layers approximately parallel to the (111) or ($\bar{1}\bar{1}1$) planes. Each layer contains molecules related by a center of symmetry. No direct bonding interactions between the different molecules seem to exist in the crystal lattice. The predominant interactions are therefore only hydrogen bonds.

The geometry of the Cu environment may be more closely represented by the distorted square pyramid shown in Fig. 2. It must be remembered that in a pentacoordinate system the two principal stereochemistries are practically of equal energy and the description of the geometry is often a question of preference without any observational basis. However, in the case of $\text{Cu}(\text{tpy})\text{Cl}_2 \cdot \text{H}_2\text{O}$ a number of topological features (a direct result of this analysis) give

* Lists of structure factors, anisotropic thermal parameters and Table 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38078 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final positional and thermal parameters for $\text{Cu}(\text{tpy})\text{Cl}_2 \cdot \text{H}_2\text{O}$

$$B_{\text{eq}} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

| | x | y | z | B_{eq} (\AA^2) |
|-------|---------------|-------------|---------------|------------------------------------|
| Cu | 0.19073 (5) | 0.12101 (9) | 0.42924 (5) | 2.36 (3) |
| Cl(1) | 0.3160 (1) | 0.0732 (2) | 0.4216 (1) | 3.33 (7) |
| Cl(2) | 0.3767 (1) | 0.4422 (2) | 0.1589 (1) | 3.49 (7) |
| N(1) | 0.3217 (3) | 0.4890 (6) | 0.4793 (3) | 2.77 (23) |
| N(2) | 0.0958 (3) | 0.2052 (6) | 0.4566 (3) | 2.42 (21) |
| N(3) | 0.1768 (3) | 0.2836 (6) | 0.3582 (3) | 2.60 (22) |
| C(1) | 0.2255 (4) | 0.0918 (8) | 0.0497 (4) | 3.14 (13) |
| C(2) | 0.2098 (5) | 0.1634 (9) | 0.1104 (5) | 4.04 (26) |
| C(3) | 0.1440 (5) | 0.1282 (10) | 0.1426 (4) | 3.97 (38) |
| C(4) | 0.0953 (4) | 0.0218 (8) | 0.1136 (4) | 3.27 (36) |
| C(5) | 0.3859 (4) | 0.4564 (8) | 0.4480 (6) | 2.67 (34) |
| C(6) | 0.4339 (4) | 0.3433 (7) | 0.4860 (4) | 2.54 (26) |
| C(7) | 0.4970 (4) | 0.2881 (9) | 0.0345 (4) | 3.21 (24) |
| C(8) | 0.0389 (4) | 0.3182 (9) | 0.0080 (4) | 3.32 (30) |
| C(9) | 0.0068 (4) | 0.3707 (9) | 0.0670 (4) | 3.13 (33) |
| C(10) | 0.0627 (4) | 0.3115 (7) | 0.4173 (4) | 2.59 (29) |
| C(11) | 0.1098 (4) | 0.3579 (7) | 0.3607 (4) | 2.62 (26) |
| C(12) | 0.0888 (5) | 0.4670 (9) | 0.3135 (4) | 3.44 (25) |
| C(13) | 0.1380 (5) | 0.4999 (9) | 0.2621 (4) | 3.73 (35) |
| C(14) | 0.2069 (5) | 0.4252 (9) | 0.2608 (4) | 3.62 (34) |
| C(15) | 0.2248 (5) | 0.3180 (9) | 0.3095 (4) | 3.30 (31) |
| O(1) | 0 | 0.1540 (11) | $\frac{1}{2}$ | 6.38 (60) |
| O(2) | $\frac{1}{2}$ | 0.2430 (11) | $\frac{1}{4}$ | 9.93 (68) |

support to the choice of a square-pyramidal interpretation of the Cu environment.

Three important topological results concerning the Cu polyhedron are obtained from the structural data.

(1) The Cu—Cl apical bond is much longer than the Cu—Cl basal bond (Fig. 2), $\Delta d = 0.334 \text{ \AA}$. This is a typical feature of the square-pyramidal configuration.

Table 3. *Interatomic distances (Å) and angles (°) in Cu(tpy)Cl₂·H₂O*

| | | | |
|---------------------------------|-------------|--------------------------------------|-------------|
| Cu—Cl(1) | 2.231 (2) | C(1)—C(2) | 1.385 (11) |
| Cu—Cl(2) | 2.565 (2) | C(2)—C(3) | 1.390 (11) |
| Cu—N(1) | 2.049 (6) | C(3)—C(4) | 1.391 (10) |
| Cu—N(2) | 1.949 (6) | C(4)—C(5) | 1.388 (9) |
| Cu—N(3) | 2.048 (6) | C(5)—C(6) | 1.494 (10) |
| N(1)—C(1) | 1.352 (9) | C(6)—C(7) | 1.400 (10) |
| N(1)—C(5) | 1.351 (9) | C(7)—C(8) | 1.394 (10) |
| N(2)—C(6) | 1.331 (9) | C(8)—C(9) | 1.391 (10) |
| N(2)—C(10) | 1.346 (9) | C(9)—C(10) | 1.390 (10) |
| N(3)—C(11) | 1.364 (9) | C(10)—C(11) | 1.481 (10) |
| N(3)—C(15) | 1.346 (9) | C(11)—C(12) | 1.392 (10) |
| $\langle \text{N—C} \rangle$ | 1.348 | C(12)—C(13) | 1.395 (11) |
| Cl(2)—O(1) | 3.274 (4) | C(13)—C(14) | 1.391 (12) |
| Cl(2)—O(2) | 3.200 (4) | C(14)—C(15) | 1.387 (11) |
| $\langle \text{Cl—O} \rangle$ | 3.237 | $\langle \text{C—C} \rangle$ (intra) | 1.391 |
| | | $\langle \text{C—C} \rangle$ (inter) | 1.488 |
| Important non-bonding distances | | | |
| Cu—C(1) | 3.053 (7) | Cl(1)—N(2) | 3.353 (6) |
| Cu—C(5) | 2.887 (7) | Cl(1)—N(3) | 3.253 (6) |
| Cu—C(6) | 2.844 (7) | Cl(2)—N(1) | 3.457 (6) |
| Cu—C(10) | 2.855 (7) | Cl(2)—N(2) | 3.397 (6) |
| Cu—C(11) | 2.889 (7) | Cl(2)—N(3) | 3.408 (6) |
| Cu—C(15) | 3.047 (8) | N(1)—N(2) | 2.557 (8) |
| Cl(1)—Cl(2) | 3.705 (3) | N(2)—N(3) | 2.559 (8) |
| Cl(1)—N(1) | 3.242 (6) | | |
| Cl(1)—Cu—Cl(2) | 100.94 (6) | Cl(2)—Cu—N(3) | 94.58 (19) |
| Cl(1)—Cu—N(1) | 98.43 (20) | N(1)—Cu—N(2) | 79.50 (22) |
| Cl(1)—Cu—N(2) | 162.39 (24) | N(1)—Cu—N(3) | 157.31 (24) |
| Cl(1)—Cu—N(3) | 98.87 (20) | N(2)—Cu—N(3) | 79.56 (22) |
| Cl(2)—Cu—N(1) | 96.42 (19) | N(1)—N(2)—N(3) | 103.47 (22) |
| Cl(2)—Cu—N(2) | 96.67 (20) | | |

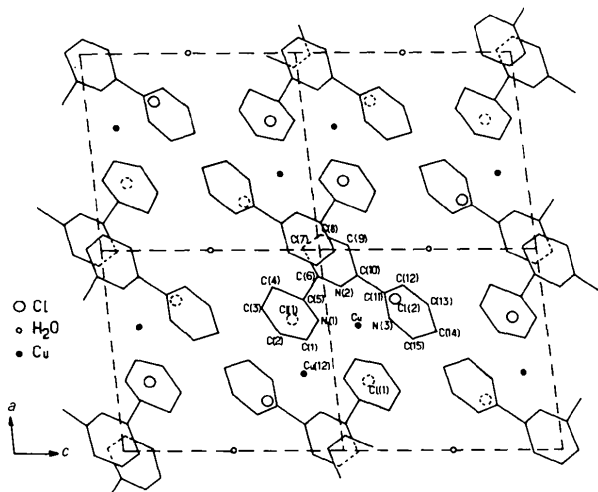


Fig. 1. Projection of the structure on the (010) plane.

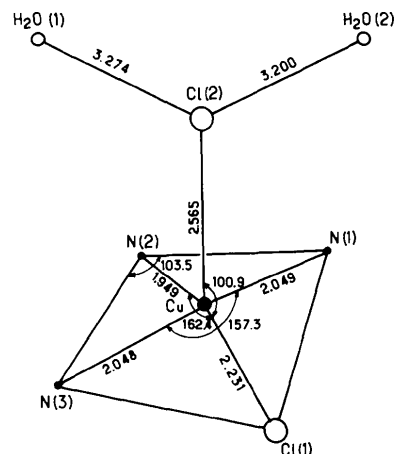


Fig. 2. Tetragonal-pyramidal environment of the Cu^{II} atom in Cu(tpy)Cl₂·H₂O. (Distances are in Å, angles in degrees.)

(2) The Cu atom is found 0.401 Å above the N(1)N(2)N(3)Cl(1) basal plane (Table 4)* and the angles subtended to it by the donor N atoms are less than 90° ($\angle \text{NCuN} = 80^\circ$).

(3) Although the Cu polyhedron is distorted in comparison with the ideal square pyramid, it approaches much closer to this geometry than to the trigonal bipyramid.

In Table 5, we can see the bond-angle sets for five real models and three ideal models. The three ideal models are ideal t.b.p., ideal s.p. and ideal d.s.p. This latter polyhedron is an ideal mixture of the two previous models (66.7% s.p. and 33.3% t.b.p.). The angular deviations from ideality ($\sum \Delta\alpha$) and the per cent d.s.p. character $[(1 - \frac{1}{120} \sum \Delta\alpha)]$ between the actual structures and the ideal polyhedra compared to the maximum deviation ($\sum \Delta\alpha = 120^\circ$) and the per cent d.s.p. character (% d.s.p. = 0 for t.b.p.) show clearly the square-pyramidal nature of the Cu polyhedron and its very close resemblance to an ideally distorted square pyramid.

The main factors which determine the configuration of the cation are: electrostatic repulsion between ligands, nature of the metal—ligand bonds, shape of the molecule, crystal-packing effects and crystal-field stabilization energy. From the electrostatic point of view a distorted square pyramid [apical angle $> 100^\circ$; $\text{Cl}(2)\text{CuCl}(1) = 101^\circ$] is as stable as a trigonal bipyramid (Zeeman, 1963).

However, the work of Kepert (1974) and Favas & Kepert (1980) predicts an 'ideally' distorted square pyramid for an apical angle, $\angle \text{DME} = 111^\circ$, and a tridentate angle, $\angle \text{ABC} = 100^\circ$. Crystal-field stabilization favors the square pyramid for a $3d^9$ ion but when the apical angle is greater than 100° , the

* See deposition footnote.

Table 5. Comparison of five pentacoordinated metal polyhedra to the idealized trigonal-bipyramidal, square-pyramidal and distorted square-pyramidal models

| | Co(tpy)- (NCO) ₂ | Zn(tpy)Cl ₂ | Co(tpy)Cl ₂ | Co(paphy)Cl ₂ | Cu(tpy)- CNNO ₃ .H ₂ O | Cu(tpy)- Cl ₂ .H ₂ O | s.p. | d.s.p. | t.b.p. |
|---------------|--------------------------------|------------------------|------------------------|--------------------------|-------------------------------------------------|-----------------------------------------------|------|--------|--------|
| Cl(1)-M-N(2) | 125°* | 143° | 150° | 157° | 160°* | 162° | 180° | 160° | 120° |
| N(1)-M-N(3) | 152 | 145 | 147 | 146 | 157 | 157 | 180 | 160 | 180 |
| Cl(2)-M-N(1) | 98 | 102 | 102 | 99 | 96 | 96 | 90 | 100 | 90 |
| Cl(2)-M-N(3) | 98 | 98 | 96 | 100 | 93 | 95 | 90 | 100 | 90 |
| Cl(2)-M-N(2) | 125 | 105 | 99 | 94 | 101 | 97 | 90 | 100 | 120 |
| Cl(2)-M-Cl(1) | 111 | 112 | 111 | 110 | 99 | 101 | 90 | 100 | 120 |
| N(1)-M-N(2) | 76 | 74 | 74 | 74 | 78 | 80 | 90 | 90 | 90 |
| N(2)-M-N(3) | 76 | 73 | 76 | 75 | 80 | 80 | 90 | 88 | 90 |
| N(1)-M-Cl(1) | 98 | 97 | 97 | 100 | 98 | 98 | 90 | 88 | 90 |
| N(3)-M-Cl(1) | 98 | 101 | 102 | 102 | 100 | 99 | 90 | 88 | 90 |
| ∑ Δα (s.p.) | 111 | 74 | 60 | 47 | 40 | 36 | | | |
| ∑ Δα (d.s.p.) | 71 | 34 | 22 | 19 | 2 | 6 | | | |
| ∑ Δα (t.b.p.) | 19 | 46 | 60 | 73 | 80 | 84 | | | |
| % d.s.p. | 41 | 72 | 82 | 84 | 99.8 | 99.5 | | | |

* In these compounds the Cl atom is replaced by NCO or CN.

energy difference between the two configurations is very small (Sacconi, 1968). The Rossi & Hoffmann (1975) theory predicts an equal probability for the existence of the two configurations and gives the correct prediction concerning the bond strengths.

It must be mentioned, finally, that in comparison to the Co(tpy)Cl₂ and Zn(tpy)Cl₂ compounds which possess configurations closer to a trigonal bipyramid, the Cu(tpy)Cl₂.H₂O and the Cu(tpy)(CN)NO₃.H₂O complexes containing a non-degenerate pseudo-Jahn-Teller ion (Cu^{II}) should favor a ligand environment having four strong bonds in a square basal plane and a longer apical bond (resembling the tetragonal Jahn-Teller distortion of an octahedral environment).

The comparison of the other well established structures of Zn(tpy)Cl₂ and Co(tpy)Cl₂ with the Cu compounds shows that the Zn configuration is closer to a trigonal bipyramid and the Co configuration is an intermediate case, while the Cu environment is definitely pyramidal (see Table 1). However, even Zn(tpy)Cl₂ can be regarded as having a distorted square-pyramidal coordination (Gerloch, 1966).

There do not seem to be any bonding interactions between molecules in the Cu complex. The metal covalent radii can be calculated using 0.99 Å as the covalent radius for Cl (Pauling, 1960) and leads to basal-in-plane and axial radii for Cu^{II} of 1.24 and 1.58 Å respectively. The basal radius is only slightly shorter than the covalent radius of Cu, 1.27 Å (Pauling, 1960; Tomlinson, Hathaway, Billing & Nichols, 1969). The axial radius is, however, much shorter than the radius calculated from the long-bonded Cu atom in tetragonally distorted octahedral Cu compounds (1.90 Å). This is surely the consequence of the lack of a sixth bond below the square basal plane.

As can be seen from Table 4 (deposited), the individual rings of the ligand are planar; however, the ligand as a whole shows some deviation from planarity. In particular, the three N atoms are significantly

three N atoms are significantly displaced [N(1) displaced [N(1) 0.059 (6), N(2) 0.096 (6), N(3) 0.034 (6) Å] in the same direction as the Cu atom [0.401 (6) Å] in order to create closer contacts with it.

The water molecules which are hydrogen bonded to the Cl(2) atom seem to play an important role in the stabilization of this long-bonded ligand. Loss of crystallinity is observed on X-ray diffraction photographs after heating the crystal at 393 K overnight. On the other hand, the water molecule plays no important role in the compound Cu(tpy)Cl₂.2H₂O which has the same form (II) structure in the anhydrous state (Harris, Lockyer & Stephenson, 1966).

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Bis(*N*-cyclohexylsalicylideneaminato)nickel(II), [Ni(C₁₃H₁₆NO)₂]*

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Abstract. $M_r = 463.3$, triclinic, $P\bar{1}$, $a = 7.939$ (8), $b = 12.261$ (10), $c = 6.578$ (10) Å, $\alpha = 105.2$ (1), $\beta = 74.2$ (1), $\gamma = 102.1$ (1)°, $V = 587.93$ Å³, $D_m = 1.30$, $D_x = 1.308$ Mg m⁻³, $Z = 1$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 1.34$ mm⁻¹, $R = 0.054$ for 1769 observed reflexions [$I > 3\sigma(I)$]. The structure comprises two centrosymmetrically related organic ligands coordinated to Ni through two N and two O atoms arranged in a planar square. The molecular units are discrete with no intermolecular bonding other than van der Waals forces. The cyclohexane group has a stable chair shape and all the bonds and angles are normal.

Introduction. The reaction of salicylaldehyde with cyclohexylamine produces a Schiff's base which is of importance in enzyme reactions (Leussing & Stanfield, 1966). These bases coordinate to various metals such as Cu, Ni, Co and Pd, and this work was undertaken as part of a programme to study the structural changes caused by varying the substituent groups and the metal coordination.

Experimental. Crystals grown from material synthesized according to Sacconi, Paoletti & Ciampolini (1963) and Holm & Swaminathan (1963); cell dimensions determined photographically and refined from measurements of high-angle reflexions on a diffractometer; needle-shaped crystal 0.40 × 0.23 × 0.11 mm

used to obtain intensities on an integrating Weissenberg camera for layers $hk0 \rightarrow hk4$ and $0hl \rightarrow 1kl$, intensities estimated visually, corrections applied for Lp effects but not for absorption or anomalous dispersion, 1837 measured reflexions; structure determined by successive Fourier syntheses (Blount, 1966) using phases calculated for the Ni atom at the origin, all non-hydrogen atoms located and their parameters refined by least squares using the NRC programs (Ahmed, 1970); initially isotropic temperature parameters were refined, and these were changed to anisotropic in the later stages of the refinement; calculated H-atom positions included but not refined; $w = 1/F_o$; final $R = 0.054$, $R_w = 0.075$ (all parameter shifts $< 0.3\sigma$); $F(000) = 246$; scattering factors from *International Tables for X-ray Crystallography* (1962).

Discussion. The final positional and equivalent isotropic thermal parameters are listed in Table 1.† The numbering of the atoms used and the packing of the molecules in the unit cell are shown as a (001) projection in Fig. 1. The thermal-ellipsoid plot of the molecule (Johnson, 1965) is shown in Fig. 2. Bond lengths and bond angles are listed in Table 2.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38218 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Preliminary communication: Kashyap, Bindlish, Bhatia & Jain (1975).