# The Crystal and Molecular Structure of Bis-(2,4,6-trichlorophenolato) diimidazolecopper(II) Monohydrate, Cu(C$_3$H$_4$N$_2$)$_2$(C$_6$H$_2$OCl$_3$)$_2$.H$_2$O

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Bis-(2,4,6-trichlorophenolato)diimidazolecopper(II) monohydrate, Cu(C$_3$H$_4$N$_2$)$_2$(C$_6$H$_2$OCl$_3$)$_2$.H$_2$O, a possible model for the metal-binding site of transferrins, has been synthesized and its structure determined by X-ray crystallography. The crystals are orthorhombic, space group *Pbnb*, with $a = 11\cdot711$ (5) $b = 24\cdot829$ (6) and $c = 8\cdot257$ (4) Å, $D_m = 1\cdot683$ g cm$^{-3}$; $D_x$ for four formula units is $1\cdot688$ g cm$^{-3}$. The structure was solved by conventional Patterson and Fourier methods and refined by use of full-matrix least squares to an $R_1$ value of 0·069. The Cu atom is at a center of symmetry and the six atoms coordinated to Cu form a tetragonally elongated octahedron. Two imidazole N atoms and two phenolic O atoms occupy the corners of an approximate square plane. The observed Cu–N and Cu–O distances are 1·98 Å and 1·97 Å, respectively. The O–chlorine atoms occupy the axial positions at distances of 2·85 Å. The molecules are held together in the crystal by intermolecular hydrogen bonds.

## Introduction

Studies on model systems are needed to extend the interpretation of the resonance Raman spectra of transferrin metal chelates (Tomimatsu, Kint & Scherer, 1973; Carey & Young, 1974; Gaber, Miskowski & Spiro, 1974). Gaber *et al.* (1974) proposed an Fe$^{III}$ complex of ethylenediamine di-(*o*-hydroxyphenylacetate) as a model for Fe$^{III}$ serum transferrin. Since Feeney & Komatsu (1966) implicated the phenoxyl and imidazole moieties of tyrosine and histidine in Cu$^{II}$ binding to transferrins, and there have been no reports of complexes of Cu$^{II}$ with imidazole and phenoxyl (or substituted phenoxyl) groups as mixed ligands (Sundberg & Martin, 1974), we have prepared a model system of this type. In this paper we describe the preparation and crystal structure of bis-(2,4,6-trichlorophenolato)diimidazole Cu$^{II}$.H$_2$O hereinafter TCPI.

## Experimental*

TCPI was prepared by a procedure similar to that described by Harrod (1969) for obtaining complexes of Cu$^{II}$ containing halophenoxyl and amines as mixed ligands. Imidazole (0·2 mol) was dissolved in 25 ml of 0·4*M* CuSO$_4$.5H$_2$O to give a dark blue solution. A second solution, containing 2,4,6-trichlorophenol (0·02 mol) dissolved in 25 ml of 0·8*M* NaOH, was slowly added to the copper–imidazole solution with vigorous stirring. The resulting brown slurry was transferred to a Büchner funnel (SS 576 filter) and washed thoroughly with water. The air-dried precipitate was first extracted

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with benzene to remove any unreacted trichlorophenol, then extracted with ethanol. About 65% of the precipitate was soluble in ethanol; the insoluble fraction was not investigated further. The ethanol extract was filtered through an ultrafine sintered glass filter and allowed to evaporate slowly. The product, which crystallized as yellow-brown plates, was dissolved in ethanol and recrystallized for elemental and X-ray analysis. Analysis for CuC$_{18}$H$_{14}$O$_3$N$_4$Cl$_6$: Calculated Cu = 10·4, C = 35·4, H = 2·3, N = 9·2, Cl = 34·8%; found Cu = 11·3, C = 35·7, H = 2·4, N = 9·2, Cl = 35·5%. Cu content was estimated by an X-ray fluorescence measurement on a single crystal weighing 31·0 µg.

The crystals used for X-ray analysis were yellowish-brown platelets elongated along *c*. Weissenberg and precession photographs were used to determine the space group and preliminary values of unit-cell dimensions. The unit cell is orthorhombic; the systematic extinctions are *h0l* when $h + l$ is odd and 0*kl* and *hk*0 when *k* is odd. The space group is therefore *Pbnb*. Density measurements, by flotation in a mixture of dibromoethane and 1-bromobutane, gave a value of $D_m = 1\cdot683$ g cm$^{-3}$; the calculated value is $D_x = 1\cdot688$ g cm$^{-3}$ for four molecules of Cu(C$_3$H$_4$N$_2$)$_2$(C$_6$H$_2$OCl$_3$)$_2$.H$_2$O per unit cell. The unit-cell dimensions were determined from high-angle $\theta$–2$\theta$ scan data obtained with a 1° take-off angle and Cu $K\alpha_1$ radiation.

### Crystal data

Cu(C$_3$H$_4$N$_2$)$_2$(C$_6$H$_2$OCl$_3$)$_2$.H$_2$O, F.W. 610·59, $a = 11\cdot711$ (5), $b = 24\cdot829$ (6), $c = 8\cdot257$ (4) Å; $\lambda$(Cu $K\alpha_1$) = 1·5405, $\lambda$(Cu $K\alpha_2$) = 1·5443 Å. Orthorhombic, space group *Pbnb*, $Z = 4$, $F(000) = 1220$, $D_m = 1\cdot683$, $D_x = 1\cdot688$ g cm$^{-3}$.

The crystal used for intensity measurements was a

rectangular fragment, cut from a large platelet which measured $0.176 \times 0.074 \times 0.471$ mm (corresponding to the $a$, $b$ and $c$ directions respectively).

Intensity data were collected at room temperature with a G. E. automatic diffractometer equipped with a full-circle goniostat and controlled by an IBM 1800 time-sharing computer. The Ni-filtered copper radiation was detected by a scintillation counter equipped with a single-channel pulse-height analyzer. One quarter of the reciprocal sphere was recorded in the range $0° \leq 2\theta \leq 125°$. The $\theta$–$2\theta$ scan technique was used at a scan rate of $1°$ min$^{-1}$. The scan range varied to include both $\alpha_1$ and $\alpha_2$ peaks. Background counts were obtained $0.5°$ before and after the limits of the scan range. 3746 reflections were measured of which 1931 were unique; of these 26 were measured as zero, and 130 other reflections had $I < \sigma(I)$. These 156 reflections were excluded from the least-squares refinement. The value of $\sigma(I)$ was calculated from the expression $\sigma(I) = [C + (T_c/2T_b)^2(B_1 + B_2)]^{1/2}$ where $C$ is the total count in scan time $T_c$, $B_1$ and $B_2$ are the two background counts taken for $T_b = 10$ s. When a reflection was measured more than once, the intensities were averaged and the standard deviation was set equal to the greater of $(\sum \sigma_i^2)^{1/2}/n$ or $(\sum \Delta_i^2)^{1/2}/(n-1)$ where $\sigma_i$ and $\Delta_i$ are the standard deviations of the $i$th measurement and the deviation of the $i$th measurement from the average respectively, and $n$ is the number of measurements. To reduce the weight given to intense reflections and to compensate for non-random errors an additional term, $(0.03I)^2$, was included in the calculation of $\sigma^2(F^2)$: $\sigma^2(F^2) = [\sigma^2(I) + (0.03I)^2]/(LP)^2$, where LP is the Lorentz–polarization factor. Two standard reflections were measured every 48 reflections; no significant change in their intensities was noted. The data were corrected for absorption. The linear absorption coefficient is 76.22 cm$^{-1}$ for Cu $K\alpha$.

The computer programs used for Lorentz–polarization corrections, Fourier summations, calculation of

distances and angles and least-squares refinement were obtained from Zalkin (1969). Correction for absorption was performed with the program $ABSORB$ (Templeton & Templeton, 1973).

## Structure determination and refinement

The structure was solved by the conventional heavy-atom method. The positions of the Cu atom and the three Cl atoms were determined from a three-dimensional Patterson synthesis. After three cycles of least-squares refinement, the positions of the N, O and C atoms were obtained from a Fourier difference synthesis. The Patterson synthesis indicated that the Cu atom occupies the center of symmetry at (0,0,0). The N atoms were distinguished from the C atoms of the imidazole rings by comparison of their isotropic thermal parameters.

The full-matrix least-squares program minimizes the function $\sum W(\Delta F)^2$ where $\Delta F = |F_o| - |F_c|$; $F_o$ and $F_c$ are the observed and calculated structure factors. The weighting factor $W$ was taken equal to $1/\sigma^2(F)$, where $\sigma(F) = F_o - [F_o^2 - \sigma(F_o^2)]^{1/2}$ when $I > \sigma(I)$ and equal to zero when $I < \sigma(I)$. Scattering factors for all atoms except H were taken from the tables published by Cromer & Waber (1965). The H scattering factors used were those published by Stewart, Davidson & Simpson (1965).

Least-squares refinement of the parameters of the 17 heavy atoms with isotropic temperature factors gave an $R$ index, defined as $\sum ||F_o| - |F_c||/\sum |F_o|$, of 0.19. Additional refinement with anisotropic temperature factors reduced $R$ to 0.09. A difference Fourier synthesis led to the determination of the positional parameters for the seven H atoms in the asymmetric unit. Inclusion of the H atoms in the least-squares refinement, with isotropic temperature factors, and with no restrictions on their positional parameters, reduced the $R$ index to the final value of 0.069. All

Table 1. *Positional and thermal parameters and their standard deviations in* $Cu(C_3H_4N_2)_2(C_6H_2OCl_3)_2 . H_2O$

Estimated standard deviations are indicated in parentheses. The thermal parameters are in Å$^2$. The temperature factor is $\exp(-T)$ where $T = \frac{1}{4}\sum h_i h_j B_{ij} a_i^* a_j^*$ for the anisotropic case and $T = B(\sin \theta/\lambda)^2$ for the isotropic case.

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 0 | 0 | 0 | 3.55 (4) | 2.60 (4) | 2.23 (4) | −0.47 (4) | −0.15 (3) | −0.04 (3) |
| O$W$ | 0.250 | 0.0158 (3) | −0.250 | 4.2 (3) | 3.6 (2) | 3.2 (3) | 0 | 0.3 (2) | 0 |
| Cl(1) | −0.1179 (1) | 0.08847 (6) | 0.1421 (2) | 4.03 (6) | 5.20 (7) | 4.20 (6) | −0.37 (5) | 0.79 (5) | −0.65 (5) |
| Cl(2) | 0.0644 (3) | 0.28513 (7) | 0.2077 (4) | 12.6 (2) | 3.54 (7) | 15.9 (2) | 0.9 (1) | 0.0 (2) | −3.1 (1) |
| Cl(3) | 0.3176 (1) | 0.12644 (6) | −0.0455 (2) | 4.07 (6) | 4.54 (6) | 5.56 (7) | −1.15 (5) | 0.12 (6) | 0.10 (6) |
| O(1) | 0.1101 (3) | 0.0600 (1) | −0.0051 (4) | 4.0 (2) | 2.8 (1) | 3.1 (1) | −0.4 (1) | 0.1 (1) | −0.7 (1) |
| N(1) | −0.0604 (4) | 0.0232 (2) | −0.2130 (5) | 4.0 (2) | 3.2 (2) | 2.5 (2) | −0.4 (2) | −0.4 (1) | 0.0 (1) |
| N(2) | −0.1378 (4) | 0.0217 (2) | −0.4520 (6) | 5.0 (2) | 4.8 (2) | 2.7 (2) | −0.0 (2) | −1.1 (2) | −0.1 (2) |
| C(1) | 0.0980 (4) | 0.1101 (2) | 0.0453 (6) | 3.9 (2) | 3.2 (2) | 2.4 (2) | −0.0 (2) | −0.4 (2) | −0.2 (2) |
| C(2) | −0.0018 (5) | 0.1311 (2) | 0.1155 (6) | 4.3 (2) | 3.6 (2) | 3.2 (2) | −0.0 (2) | −0.3 (2) | −0.1 (2) |
| C(3) | −0.0137 (6) | 0.1845 (2) | 0.1651 (8) | 6.0 (3) | 4.0 (3) | 5.1 (3) | 1.1 (3) | −0.2 (3) | −1.3 (2) |
| C(4) | 0.0772 (7) | 0.2181 (3) | 0.1451 (9) | 7.8 (4) | 3.3 (3) | 6.9 (4) | 0.6 (3) | −0.7 (3) | −1.0 (3) |
| C(5) | 0.1774 (6) | 0.2106 (2) | 0.0784 (8) | 6.1 (3) | 2.9 (2) | 5.7 (3) | −0.6 (2) | −0.9 (3) | −0.4 (2) |
| C(6) | 0.1869 (5) | 0.1480 (2) | 0.0303 (6) | 4.4 (2) | 3.1 (2) | 3.6 (2) | −0.6 (2) | −0.4 (2) | −0.0 (2) |
| C(7) | −0.1097 (5) | −0.0070 (2) | −0.3241 (7) | 4.8 (3) | 3.9 (2) | 3.3 (2) | −0.4 (2) | −0.4 (2) | −0.0 (2) |
| C(8) | −0.1074 (6) | 0.0730 (3) | −0.4246 (9) | 6.5 (4) | 4.3 (3) | 3.6 (3) | −0.1 (3) | −1.1 (3) | 0.6 (2) |
| C(9) | −0.0585 (6) | 0.0737 (2) | −0.2770 (7) | 6.0 (3) | 3.8 (2) | 3.2 (2) | −0.6 (2) | −1.2 (2) | 1.0 (2) |

## Table 1 (cont.)

|        | x            | y          | z           | B        |
|--------|--------------|------------|-------------|----------|
| H(N2)  | −0·167 (6)   | 0·008 (3)  | −0·533 (8)  | 5·2 (17) |
| H(C3)  | −0·081 (5)   | 0·194 (3)  | 0·221 (8)   | 4·9 (15) |
| H(C5)  | 0·246 (5)    | 0·225 (2)  | 0·055 (7)   | 3·9 (12) |
| H(C7)  | −0·128 (6)   | −0·042 (3) | −0·323 (8)  | 6·3 (18) |
| H(C8)  | −0·120 (9)   | 0·088 (4)  | −0·48 (1)   | 9·0 (31) |
| H(C9)  | −0·028 (6)   | 0·103 (3)  | −0·216 (8)  | 5·6 (16) |
| HW     | 0·213 (7)    | 0·027 (3)  | −0·21 (1)   | 6·4 (25) |

parameter shifts in the final cycle were less than $0·1\sigma$. The observed and calculated structure factors for the intense reflections are in good agreement; consequently,
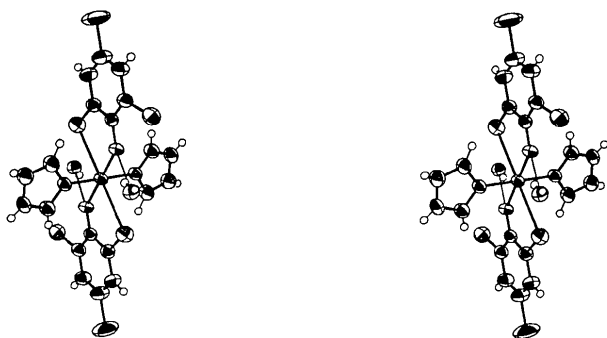


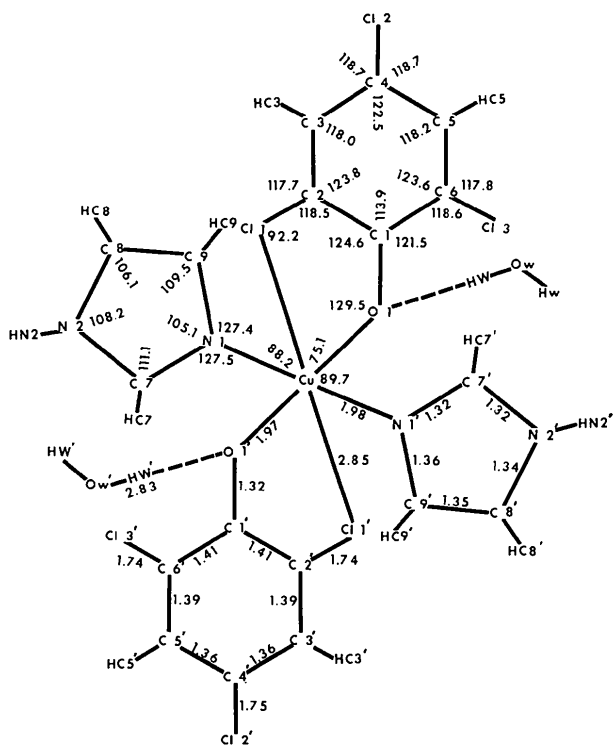Fig. 1 Stereoscopic view of the molecule. The ellipsoids are drawn at the 50% probability level.



Fig. 2. The atom numbering scheme used in this paper and the bond distances and angles between heavy atoms. Estimated standard deviations are 0·01 Å for distances and 0·6° for angles. This view corresponds to that shown in Fig. 1.

a correction for secondary extinction was not made. The final positional and thermal parameters for all atoms and their estimated standard deviations are listed in Table 1. A table listing $F_{obs}$, standard deviations and the difference $(F_{obs}—F_{calc})$ may be obtained upon request.*

## Results and discussion

The crystal structure determination established that the copper complex under investigation is bis-(2,4,6-trichlorophenolato)diimidazolecopper(II) monohydrate. The configuration of the molecule and the thermal motion of the atoms are illustrated in the stereoscopic drawing (Johnson, 1965), Fig. 1. The thermal ellipsoids are drawn at the 50% probability level. A schematic drawing of the molecule with the atom numbering system used in this paper, the interatomic distances and bond angles between the heavy

## Table 2. Distances (Å) involving hydrogen atoms

The e.s.d.'s are 0·1 Å.

| C(3)–H(C3) | 0·9 | C(9)–H(C9) | 1·0 |
|------------|-----|------------|-----|
| C(5)–H(C5) | 1·0 | N(2)–H(N2) | 0·8 |
| C(7)–H(C7) | 0·9 | OW–HW      | 0·6 |
| C(8)–H(C8) | 0·6 |            |     |

## Table 3. Deviation of atoms from least-squares plane and dihedral angles between them

The plane equation is of the form $Ax + By + Cz = D$ where $x, y, z$ and $D$ are in Å relative to the axes $a$, $b$ and $c$.

| Plane (1) |           | Plane (2) |           |
|-----------|-----------|-----------|-----------|
| N(1)      | 0·0005 Å  | C(1)      | −0·0099 Å |
| N(2)      | 0·0044    | C(2)      | 0·0025    |
| C(7)      | −0·0031   | C(3)      | 0·0076    |
| C(8)      | −0·0040   | C(4)      | −0·0105   |
| C(9)      | 0·0022    | C(5)      | 0·0023    |
|           |           | C(6)      | 0·0080    |

| Plane (3) |     | Plane (4) |           |
|-----------|-----|-----------|-----------|
| N(1)      | 0·0 | Cu        | −0·0034   |
| O(1)      | 0·0 | Cl(1)     | 0·0045    |
| N(1')     | 0·0 | C(2)      | −0·0060   |
| O(1')     | 0·0 | C(1)      | 0·0019    |
|           |     | O(1)      | 0·0030    |

Angle (°) between plane normals

| (1)–(2) | −88·45 | (1)–(4) | −89·08 |
|---------|--------|---------|--------|
| (1)–(3) | 26·44  | (2)–(4) | 1·39   |
| (2)–(3) | −86·83 | (3)–(4) | 87·94  |

Coefficients of the equation of the plane (Å)

| Plane | A     | B      | C      | D      |
|-------|-------|--------|--------|--------|
| (1)   | 0·891 | −0·194 | −0·411 | −0·025 |
| (2)   | 0·337 | −0·242 | 0·910  | 0·076  |
| (3)   | 0·664 | −0·588 | −0·463 | 0·000  |
| (4)   | 0·340 | −0·265 | 0·902  | 0·003  |

atoms, is presented in Fig. 2. Distances involving H atoms are in Table 2. A stereoscopic view of the molecular packing in the crystal is shown in Fig. 3. The view is parallel to *c*, with *a* horizontal and *b* vertical. The planarity of the two rings in the asymmetric unit, the out-of-plane distance of atoms making up the plane, and the dihedral angle between the planes are summarized in Table 3.

### The coordination around copper

The Cu atom is at a center of symmetry (0,0,0); the coordination around Cu can be described as a distorted octahedron. The equatorial bonds are to the N atoms of two imidazole rings and to the phenolic O atoms of two trichlorophenolato groups in a *trans* configuration. The angle between the equatorial coordination bonds, N(1)–Cu–O(1), is 90·3°. The axial bonds are to *o*-chlorine atoms of the trichlorophenol molecules. The trichlorophenols are therefore bidentate ligands.

In the TCPI complex the phenolate rings are nearly perpendicular to the equatorial plane [the plane formed by O(1), O(1'), N(1) and N(1')]; the dihedral angle is 86·8°. This orientation is the result of the *o*-chlorine atom forming an axial coordination bond to Cu. The Cu–Cl(1) bond makes an angle of 14·9° with the normal to the equatorial plane. A similar value for the angle between the axial coordination bond and the Cu atom *z*-axis is reported for other Cu$^{II}$ complexes with bidentate O donor ligands (Hobson, Ladd & Povey, 1973; Hathaway, 1972).

The dihedral angles which the imidazole ring makes with the phenolate ring and with the equatorial plane are 88·5° and 26·4°, respectively. This arrangement of the rings permits a compact molecular packing in the crystal.

The observed bond distance for Cu–N(1) of 1·98 Å is in good agreement with other observations as summarized by Ivarsson, Lundberg & Ingri (1972). The Cu–N (imidazole) bond distances all fall in the range of 1·95–2·01 Å. Sundberg & Martin (1974) concluded that in a neutral imidazole molecule the only unshared pair of electrons is on the imino nitrogen, N(1). The $\pi$ electrons of N(2), the amino nitrogen, are part of the aromatic sextet. It is unlikely for a metal ion to coordinate to N(2), since the aromaticity of the ring is thereby compromised. The structure found for the TCPI complex agrees with this conclusion.

The observed Cu–O(1) distance of 1·97 Å is close to the sum of the covalent radii for Cu and O (1·94 Å) (Pauling, 1960) and is in good agreement with the Cu–O distance of 1·94 Å reported for bis-(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) monohydrate (Hobson *et al.*, 1973), and the value of 1·95 Å reported for bis-(2-methoxy-4-nitrophenolato)bis(pyridine)copper(II) (Bullock, Hobson & Povey, 1974).

The observed Cu–Cl(1) bond length of 2·84 Å is close to the average of the Cu–Cl distances found in other complexes where the Cl atom is coordinated to Cu in the axial position. For example, in copper-triazole-chloride complexes, it is 2·77 Å (Jarvis, 1962), Cu(C$_3$H$_4$N$_2$)$_2$Cl$_2$, 2·75 Å (Lundberg, 1972), bisbiuret-copper(II) dichloride, 2·96 Å (Freeman & Smith, 1966), and bissemicarbazidecopper(II) chloride, 2·85 Å (Freeman, 1967). Unlike the situation in TCPI complex, the Cl atoms in all the above mentioned complexes are coordinated to Cu as chloride ions, and the observed Cu–Cl(1) bond lengths reflect the distances of closest approach for the axially coordinated chloride ions. A preliminary report on bis-(2,4,6-trichlorophenolato) (*N*,*N*,*N'N'*-tetramethylethylenediamine)copper(II) (Vogt, La Placa & Bednowitz, 1968) gave no Cu–Cl distance for the *o*-chlorine atoms nearest to Cu, but it was later calculated by Bullock *et al.* (1974) to be 3·07 Å. However, this Cu complex is not comparable to the TCPI complex since in the former, the bidentate diamine ligand imposes a *cis* configuration for the two trichlorophenolato groups, compared to the *trans* configuration in the latter complex.

The Cu–O(1)–C(1) angle of 129·5° is larger than the value of 118° observed for the corresponding angle in the methoxy phenolato ligand (Bullock *et al.*, 1974). The larger value observed for this angle in the TCPI complex is due to the greater size of the Cl atom compared to the O atom.

### The imidazole rings

The interatomic distances and angles in the imidazole ring vary between 1·32–1·36 Å and 105·1–111·1°, respectively. These ranges are in agreement with those reported for other Cu$^{II}$ complexes containing imidazole ligands (Fransson & Lundberg, 1972).

The imidazole ring is planar; the maximum deviation of the ring atoms from the least-squares plane is 0·004 Å. The planarity of the imidazole ring and the
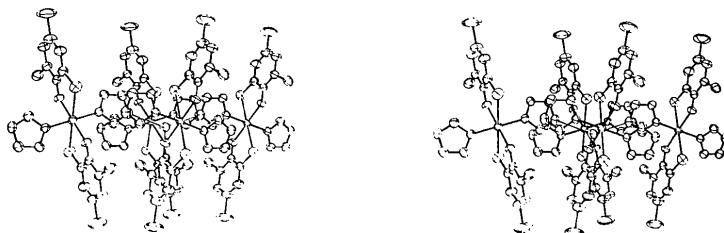
Fig. 3. Stereoscopic view of the molecular packing viewing down *c* with *a* horizontal.

equality of the N(1)–C(7) and N(2)–C(7) bond lengths are consistent with the generally accepted conclusion that the imidazole ring is aromatic (Sundberg & Martin, 1974).

*The phenolate rings*

The C–C bond lengths of the phenolate ring vary between 1·36 and 1·41 Å with a mean of 1·38 Å. There seems to be a systematic decrease in C–C bond length in the phenolate ring with increasing distance from the Cu atom. The three C–Cl bonds average 1·74 Å, a value somewhat larger than usually observed for the C(aromatic)–Cl bond length of 1·70 Å (Sutton, 1965). The bond angles in the phenolate ring range from 113·9° to 123·8° with an average value of 120°. The maximum variation is equal to $16\sigma$ and some, if not all, of this variation can probably be attributed to the non-uniform thermal motion of the atoms in the ring. The phenolate ring is essentially planar, the largest deviation from the mean ring plane is 0·011 Å. The Cl(1), Cl(2), Cl(3) and O(1) atoms are displaced by only 0·004, 0·026, 0·074 and 0·041 Å, respectively, from the mean ring plane.

The thermal parameters of the heavy atoms show an interesting variation which appears to be due to a waggling motion of the rings around their coordination bond. This effect is particularly noticeable for the Cl atoms, as illustrated in Fig. 1 by the larger size of the thermal ellipsoid for Cl(2) compared to Cl(1) and Cl(3), and also by inspection of the thermal parameters listed in Table 1.

*Hydrogen bonds*

The molecules are held together in the crystal by intermolecular hydrogen bonds. Each water molecule forms four hydrogen bonds to four different molecules. Two of the bonds are to phenolic O atoms, O(1), and the other two to N atoms, N(2). The water O atom lies on a twofold axis of symmetry and, consequently, only two of the four bonds are unique. The OW–N(2) distance is 2·94 Å, and the OW–O(1) distance is 2·83 Å which is in excellent agreement with the values reported for bis-(4-formyl-2-methoxyphenolato)bis-(pyridine)copper(II) monohydrate (Hobson *et al.*, 1973). The angles O(1)–OW–N(2) and O(1)–OW–O(1') are 117·6° and 134·2°, respectively. The intermolecular hydrogen bonds are shown in Fig. 3. There are no other intermolecular contacts less than 3·0 Å in the crystal.

The orientation of the imidazole ring around the Cu–N(1) bond would appear to be controlled by the hydrogen bond between N(2), and the water O atom, as well as the tendency to minimize steric hindrance with the phenolato ligand.

Preliminary spectroscopic measurements of bis-(2,4,6-trichlorophenolato) diimidazolecopper(II) monohydrate show that the complex has visible absorption and resonance Raman spectra similar to those for the

Cu$^{II}$ chelates of transferrin and ovotransferrin (Tomimatsu, Kint & Scherer, 1974). This complex thus appears to be a suitable model system for studying the nature of Cu$^{II}$ binding to transferrins.

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