

## Structure of Iodobis(1,10-phenanthroline)copper(II) Iodide Monohydrate

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**Abstract.**  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{I}]\text{I}\cdot\text{H}_2\text{O}$ , (I),  $M_r = 695.52$ , triclinic,  $P\bar{1}$ ,  $a = 12.860$  (3),  $b = 12.049$  (3),  $c = 10.169$  (3) Å,  $\alpha = 114.07$  (3),  $\beta = 120.44$  (4),  $\gamma = 87.57$  (2)°,  $V = 1213.14$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m(\text{floatation}) = 1.92$  (6),  $D_x = 1.89$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 3.261$  mm<sup>-1</sup>,  $F(000) = 666$ , room temperature,  $R = 0.069$  for 2971 observed unique reflections. The local molecular structure involves a square-based, pyramidally distorted trigonal bipyramidal  $\text{CuN}_4\text{I}$  chromophore. The mode of distortion in (I) is the reverse of the form previously found in the five coordinate  $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{Y}$  complexes, associated with the route B (or C) structural pathways of the  $\text{CuN}_4\text{Cl}$  chromophore.

**Introduction.** The distortion pathways between the regular trigonal bipyramidal and the square pyramidal stereochemistries of the  $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$  cation have been previously characterized, Fig. 1 (Harrison, Kennedy, Power, Sheahan & Hathaway, 1981; Hathaway, 1984; Nagle, O'Sullivan, Hathaway & Muller, 1990). Three distortion pathways are available for a five coordinate  $\text{CuN}_4\text{X}$  chromophore, routes A, B and C. Route A is characterized by an elongation of the Cu—X bond length, an opening up of the N(2)—Cu(1)—N(4) back angle and a retention of the  $C_2$  axis of symmetry. Routes B and C are equivalent for a  $[\text{Cu}(\text{bpy})_2\text{X}]^+$  cation and involve the elongation of the in-plane Cu(1)—N(4) [or Cu(1)—N(2)] bond distance, plus the opening up of the opposite N(2)—Cu(1)—X [or N(4)—Cu(1)—X] angle. These distortion routes have been identified in the  $[\text{Cu}(\text{phen})_2(\text{OH}_2)]^{2+}$  cation (phen = 1,10-phenanthroline) (Nakai & Deguchi, 1975; Nakai & Noda, 1978), for the A route and the cation distortion isomers of the  $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$  cation (bpy = 2,2'-bipyridyl) (Harrison *et al.*, 1981) for the B or C routes. Table 1 lists some representative examples, with the relevant bond lengths and bond angles, using the notation of Fig. 1. The B route distortion has been characterized for  $[\text{Cu}(\text{bpy})_2\text{I}][\text{ClO}_4]$  (Hathaway & Murphy, 1980; Nagle *et al.*, 1991), while the structure of  $[\text{Cu}(\text{phen})_2\text{I}]\text{I}\cdot\text{S}_8$  (Hambley, Raston & White, 1977) has a unique  $\text{CuN}_4\text{I}$  chromophore with

$C_2$  symmetry, which is not recognizable as either an A, B or C route distortion, Fig. 1. The crystal structure of (I) has therefore been determined in order to obtain further structural information on the  $[\text{Cu}(\text{phen})_2\text{I}]^+$  cation.

**Experimental.** Single crystals of the title complex were prepared by refluxing 0.20 g of  $[\text{Cu}^{\text{I}}(\text{phen})\text{I}]$  (0.54 mmol) in 50 ml of a 1:1 absolute alcohol/water solution for *ca* 18 h. The dark green crystals obtained were filtered off, washed with the mother liquor and dried in a vacuum. Found: C, 40.71; H, 2.59; N, 7.90%. Calculated:  $\text{C}_{24}\text{H}_{18}\text{CuI}_2\text{N}_4\text{O}$  requires C, 41.41; H, 2.61; N, 8.06%.

Unit-cell data (25 reflections,  $\theta$ , 0–25°) and intensity data were collected on a Philips PW 1100 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Reflections with  $3.0 < \theta < 25^\circ$  in one half of reciprocal space were examined in the  $\omega$ - $2\theta$  scan mode, with a constant scan speed of  $0.05^\circ \text{ s}^{-1}$ , and a variable scan width of  $(0.70 + 0.10 \tan \theta)^\circ$ . 3144 reflections were collected [ $I > 2.5\sigma(I)$ ] ( $h - 13 \rightarrow 13$ ,  $k - 13 \rightarrow 13$ ,  $l 0 \rightarrow 11$ ) and 2971 unique reflections were retained. Lorentz and polarization corrections were applied, but no correction was made for absorption. The structure was solved by the *SHELX76* and *SHELXS86* direct methods (Sheldrick, 1976, 1986), developed by difference Fourier synthesis techniques and refined (290 parameters,  $N/P = 10.2$ ), by blocked-matrix least-squares minimization of  $\sum w(|F_o| - |F_c|)^2$ , with anisotropic temperature factors on all the non-H atoms. H atoms were positioned geometrically and then constrained to ride on the adjacent C or O atoms, assuming C—H and O—H distances of 1.08 Å, and a fixed  $U_{\text{iso}}$  of  $0.07 \text{ \AA}^2$ . Maximum shift/e.s.d. was  $< 0.040$  for all atoms, excluding the O atom of the  $\text{H}_2\text{O}$  molecule, where the max. value was 0.34 on the temperature factors only. A refined weighting scheme was used, with  $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ , with  $k = 1.00$  and  $g = 0.0073$ .  $R = 0.069$  and  $wR = 0.073$ . The max. and min. residual electron densities were 1.90 and  $-2.37 \text{ e \AA}^{-3}$ , on peaks associated with both the coordinated and the ionic I atoms. Complex neutral atomic scattering factors embedded in *SHELX76* (Sheldrick, 1976) were employed, but those for Cu

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Table 1. Relevant bond lengths (Å) and angles (°) of [Cu(chelate)<sub>2</sub>X]Y complexes

	Route	N(2)CuI	N(4)CuI	N(2)CuN(4)	CuN(1)	CuN(2)	CuN(3)	CuN(4)	CuX	References
[Cu(phen) <sub>2</sub> ]I·H <sub>2</sub> O (I)	—	127.4 (2)	115.4 (2)	117.2 (2)	1.946 (7)	2.237 (7)	1.964 (7)	2.089 (7)	2.718 (7)	(a)
[Cu(phen) <sub>2</sub> (OH <sub>2</sub> )](NO <sub>3</sub> ) <sub>2</sub>	A	110.0 (4)	110.0 (4)	139.6 (4)	1.99 (1)	2.03 (1)	1.99 (1)	2.03 (1)	2.18 (1)	(b)
[Cu(bpy) <sub>2</sub> Cl][ClO <sub>4</sub> ]	B	137.1 (1)	126.4 (2)	96.5 (2)	1.993 (4)	2.076 (3)	1.991 (4)	2.136 (5)	2.263 (3)	(c)
[Cu(phen) <sub>2</sub> ]I <sub>2</sub> S <sub>8</sub> (II)	—	125.3 (3)	125.3 (3)	109.4 (4)	2.00 (1)	2.10 (1)	2.00 (1)	2.10 (1)	2.672 (3)	(d)
[Cu(bpy) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub> (III)	B	122.9 (2)	122.8 (2)	114.3 (3)	1.989 (6)	2.090 (8)	1.987 (6)	2.100 (7)	2.675 (4)	(e)

References: (a) Present work; (b) Nakai & Deguchi (1975); (c) Harrison *et al.* (1981); (d) Hambley *et al.* (1977); (e) Hathaway & Murphy (1980).

were taken from Cromer & Waber (1974). All calculations were carried out with *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986), *XANADU* (Roberts & Sheldrick, 1979), *CHEM-X* (Davies, 1980) and *PUBTAB* (Henrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 computers. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 2. Selected bond lengths and angles are given in Table 3. Fig. 2 shows the molecular structure of (I) and the atom-numbering scheme used.\*

**Discussion.** The asymmetric unit of (I) consists of a [Cu(phen)<sub>2</sub>I]<sup>+</sup> cation, an I<sup>-</sup> anion and a water molecule. The cation involves a five coordinate CuN<sub>4</sub>I chromophore with distorted trigonal bipyramidal stereochemistry, Fig. 2. The out-of-plane bond lengths Cu—N(1) and Cu(1)—N(3) are not significantly different: 1.946 (7) and 1.964 (7) Å, respectively [mean Cu—N<sub>ax</sub> = 1.955 (7) Å]. The in-plane Cu(1)—N(2) and Cu(1)—N(4) bond lengths are significantly different: 2.237 (7) and 2.089 (7) Å, respectively [mean Cu—N<sub>eq</sub> = 2.164 (7) Å]. The difference in the mean values, 0.209 Å, is relatively large, compared to the value of *ca* 0.1 Å normally associated with a trigonal bipyramidal Cu<sup>II</sup> stereochemistry (Huq & Skapski, 1971). The Cu(1)—I(2) distance of 2.718 (1) Å is consistent with the sum of the covalent radii for the Cu<sup>II</sup> and I atoms (1.33 + 1.35 = 2.68 Å) (Barclay, Hoskins & Kennard, 1963) and suggests a normal Cu—I bond. The N(1)—Cu(1)—N(3) angle is nearly linear, 178.9 (3)°. The N(1)—Cu(1)—N(2) and N(3)—Cu(1)—N(4) bond angles of 81.7 (3) and 79.4 (3)°, respectively are significantly less than 90° owing to the restricted bite of the phen ligands, as previously observed (Simmons, Alcock, Seff, Fitzgerald & Hathaway, 1985). The in-plane angles, N(2)—Cu(1)—I(2), N(4)—Cu(1)—I(2) and N(2)—Cu(1)—N(4), all deviate significantly from 120°, namely, 127.4 (2), 115.4 (2) and 117.2 (2)°, respectively. The longer equatorial Cu(1)—N(2) bond distance lies opposite the smaller equatorial N(4)—Cu(1)—I(2)

\* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles, mean-plane data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53853 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and thermal parameters (Å<sup>2</sup>) with *e.s.d.*'s in parentheses
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub>
Cu(1)	0.26813 (11)	-0.26001 (10)	0.01523 (14)	0.0419 (6)
I(1)	0.24233 (8)	0.16893 (7)	0.31346 (10)	0.0695 (5)
I(2)	0.22275 (7)	-0.45878 (6)	-0.27484 (9)	0.0582 (4)
N(1)	0.2101 (7)	-0.1597 (6)	-0.1075 (8)	0.045 (1)
C(1)	0.1011 (8)	-0.1916 (8)	-0.2567 (9)	0.045 (1)
C(2)	0.0734 (9)	-0.1161 (9)	-0.3359 (10)	0.062 (1)
C(3)	0.1680 (8)	-0.0041 (8)	-0.2582 (9)	0.059 (1)
C(4)	0.2840 (8)	0.0346 (7)	-0.0959 (9)	0.052 (1)
C(5)	0.3855 (8)	0.1504 (8)	-0.0035 (10)	0.066 (1)
C(6)	0.4979 (8)	0.1837 (8)	0.1522 (10)	0.059 (1)
C(7)	0.5169 (7)	0.1003 (7)	0.2260 (9)	0.041 (1)
C(8)	0.6299 (8)	0.1259 (8)	0.3840 (9)	0.046 (1)
C(9)	0.6425 (8)	0.0410 (8)	0.4476 (10)	0.047 (1)
C(10)	0.5374 (7)	-0.0714 (7)	0.3455 (9)	0.041 (1)
C(11)	0.4194 (7)	-0.0147 (7)	0.1359 (9)	0.042 (1)
C(12)	0.3030 (7)	-0.0468 (7)	-0.0268 (9)	0.042 (1)
N(2)	0.4307 (6)	-0.1006 (6)	0.1940 (7)	0.035 (1)
N(3)	0.3271 (6)	-0.3585 (6)	0.1431 (8)	0.043 (1)
C(13)	0.4222 (8)	-0.4029 (8)	0.1758 (10)	0.061 (1)
C(14)	0.4432 (9)	-0.4846 (8)	0.2493 (11)	0.067 (1)
C(15)	0.3641 (9)	-0.5163 (8)	0.2892 (10)	0.062 (1)
C(16)	0.2652 (8)	-0.4640 (7)	0.2616 (9)	0.040 (1)
C(17)	0.1782 (9)	-0.4875 (8)	0.3036 (9)	0.057 (1)
C(18)	0.0861 (8)	-0.4343 (8)	0.2770 (10)	0.051 (1)
C(19)	0.0669 (8)	-0.3541 (8)	0.1997 (9)	0.041 (1)
C(20)	-0.0277 (8)	-0.2958 (9)	0.1697 (10)	0.055 (1)
C(21)	-0.0383 (9)	-0.2210 (9)	0.0914 (10)	0.057 (1)
C(22)	0.0460 (7)	-0.2061 (8)	0.0467 (9)	0.045 (1)
C(23)	0.1473 (7)	-0.3320 (7)	0.1530 (8)	0.030 (1)
C(24)	0.2486 (7)	-0.3869 (7)	0.1864 (9)	0.041 (1)
N(4)	0.1351 (6)	-0.2589 (6)	0.0758 (8)	0.038 (1)
O(1)	0.2551 (8)	0.2425 (7)	0.6935 (9)	0.084 (1)

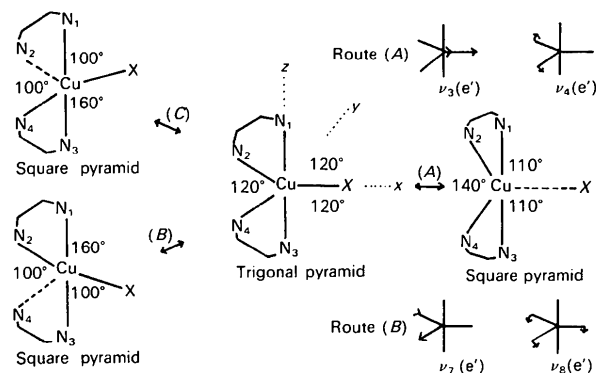


Fig. 1. The structural pathways for the distortion of the CuN<sub>4</sub>Cl chromophore of the [Cu(bpy)<sub>2</sub>Cl]<sup>2+</sup> cations from trigonal bipyramidal to square bipyramidal involving three alternative routes. The effect of the distortion on the X—Cu—N(2), X—Cu—N(4) and N(2)—Cu—N(4) angles is indicated.

Table 3. Selected bond lengths (Å) and bond angles (°) with *e.s.d.'s* in parentheses

Cu(1)—I(2)	2.718 (1)	Cu(1)—N(3)	1.964 (7)
Cu(1)—N(1)	1.946 (7)	Cu(1)—N(4)	2.089 (7)
Cu(1)—N(2)	2.237 (7)		
N(1)—Cu(1)—I(2)	89.8 (2)	N(3)—Cu(1)—N(2)	97.7 (3)
N(2)—Cu(1)—I(2)	127.4 (2)	N(4)—Cu(1)—I(2)	115.4 (2)
N(2)—Cu(1)—N(1)	81.7 (3)	N(4)—Cu(1)—N(1)	100.1 (3)
N(3)—Cu(1)—I(2)	91.3 (2)	N(4)—Cu(1)—N(2)	117.2 (2)
N(3)—Cu(1)—N(1)	178.9 (3)	N(4)—Cu(1)—N(3)	79.4 (3)

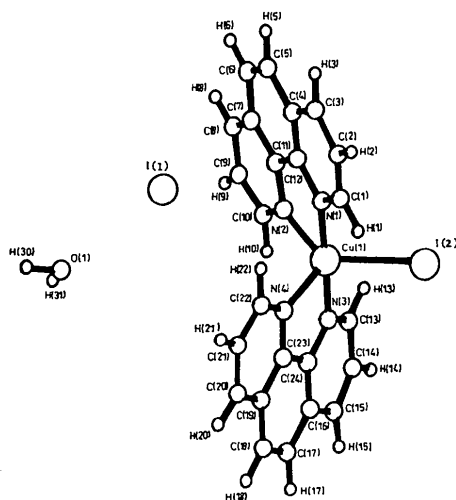


Fig. 2. The molecular structure of  $[\text{Cu}(\text{phen})_2]\text{I}\cdot\text{H}_2\text{O}$  (I) and the atom-numbering scheme used.

angle. There are no unusual bond lengths or bond angles within the phen ligands (Simmons *et al.*, 1985). The individual pyridine rings of the chelating phen ligands are reasonably planar with r.m.s. deviations less than 0.026 Å. The separate pyridine rings within each phen ligand, involve dihedral angles of 0.98 and 3.18°, for the Cu(1)N(1)N(2) and Cu(1)N(3)N(4) phen ligands, respectively, and the mean planes between the two phen ligands are inclined at 58.9° to each other.

The  $\text{CuN}_4\text{I}$  chromophore has been observed previously in  $[\text{Cu}(\text{phen})_2]\text{I}\cdot\text{S}_8$  (II); Hambley *et al.* (1977), Table 1]. It also has a distorted trigonal bipyramidal geometry, but with a crystallographic  $C_2$  axis which coincides with the Cu—I bond. The equatorial Cu—N(2) distance of 2.10 (1) Å is greater than the axial Cu—N(1) distance of 2.00 (1) Å, by 0.1 Å, a value significantly less than the corresponding difference of 0.209 Å in (I). The N(2)—Cu—I angle of 125.3 (3)° in (II) suggests a similar degree of angular distortion to that in (I). However the sense of the distortion in (II) does not conform to any of the route *A*, *B* or *C* structural pathways for a regular trigonal bipyramidal  $\text{CuN}_4\text{X}$  chromophore, Fig. 1. The  $C_2$  symmetry of (II) suggests a route *A* mode of distortion, which would involve an increase in the N(2)—Cu—N(2') angle above 120°, whereas the

N(2)—Cu—N(2') angle of 109.4 (4)° is less than 120°. A route *A* mode of distortion would also lead one to predict an increase in the Cu—I distance whereas the Cu—I distance of 2.672 (3) Å is actually less than that in (I). This suggests that a *negative* route *A* distortion is operative in (II) with respect to the regular trigonal bipyramidal geometry of Fig. 1. In the structure of  $[\text{Cu}(\text{bpy})_2]\text{I}[\text{ClO}_4]$  [(III); Table 1] the  $\text{CuN}_4\text{I}$  chromophore is in a general position with near  $C_2$  symmetry and with an N(2)—Cu—N(4) angle of 114.3 (3)° (also < 120°).

The mode of distortion of (I) is also unusual with respect to the *B* (or *C*) route distortions of Fig. 1. The occurrence of the longer in-plane Cu(1)—N(2) bond length (route *C*), opposite the smaller in-plane N(4)—Cu(1)—I(2) angle is the opposite of the route *B* distortion pathway found in the related structures in the series of cation distortion isomers of the  $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$  cation (Harrison *et al.*, 1981), Table 1. Equally, this sense of distortion of (I) is not accounted for by the  $C_2$  related route *C* distortion of Fig. 1. In this respect the structure of (I) must be described as a 'reversed' square-pyramidal distorted trigonal bipyramidal structure in view of the reversed sense of distortion relative to the structural pathways of Fig. 1.

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## Structure of the Mixed-Valence Salt Bis(*N,N'*-dibenzyl-4,4'-bipyridinium) Aquanonachlorotricuprate(2II, I)

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**Abstract.**  $[\text{C}_{24}\text{H}_{22}\text{N}_2]_2[\text{Cu}_3\text{Cl}_9(\text{H}_2\text{O})]$ ,  $M_r = 1204.64$ , monoclinic,  $C2/c$ ,  $a = 27.78$  (1),  $b = 24.408$  (5),  $c = 18.202$  (5) Å,  $\beta = 125.35$  (2)°,  $V = 10\,065$  (5) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.59$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 17.8$  cm<sup>-1</sup>,  $F(000) = 4879$ ,  $T = 295$  K,  $R = 0.0729$  for 2632 unique observed [ $F \geq 3\sigma(F)$ ] reflections and 278 parameters. The title compound is a mixed-valence salt with a Cu<sup>II</sup>:Cu<sup>I</sup> ratio of 2:1. The structure consists of trimers of loosely associated  $\text{CuCl}_4^{2-}$ ,  $\text{CuCl}_2^-$  and  $(\text{CuCl}_3\text{H}_2\text{O})^-$  anions hydrogen bonded into chains running along the *c* direction of the unit cell. These chains run through stacks of benzyl viologen cations lying in the *ab* plane.

**Introduction.** In recent years this laboratory has been investigating several mixed-valence Cu<sup>II</sup>/Cu<sup>I</sup> systems (Willett, 1987; Willett & Halvorson, 1988; Scott & Willett, 1990). One such compound studied in this laboratory is (paraquat)Cu<sub>2</sub>Cl<sub>4</sub>, a salt reported several years ago (Macfarlane & Williams, 1969; Prout & Murray-Rust, 1969). This compound consists of chains of  $\text{CuCl}_4^{2-}$  tetrahedra sharing edges, co-crystallized parallel to stacks of methyl viologen cations (paraquat). The past studies of this compound allude to a donor-acceptor relationship between the paraquat cations and the  $(\text{Cu}_2\text{Cl}_4)_n$  chains, and powder EPR shows a small Cu<sup>II</sup> signal. Powder conductivity data show semiconductive behavior. An analog of the paraquat salt, employing benzyl viologen in place of the methyl viologen, was synthesized in an effort to enhance these properties. It was postulated that the benzyl viologen dication, which has a more positive reduction potential than that of the methyl viologen, would increase the amount of charge transferred from anion to cation,

and thus the amount of Cu<sup>II</sup> character in the chain. The crystal and molecular structure of the product obtained will be presented in this paper.

**Experimental.** The crystals were prepared using the preparation method developed for (methyl viologen)-Cu<sub>2</sub>Cl<sub>4</sub> (Macfarlane & Williams, 1969). This method produced small brownish-orange needle-shaped crystals. A crystal with dimensions 0.25 × 0.20 × 0.35 mm was selected for data collection on a Syntex P<sub>21</sub> diffractometer, with a graphite monochromator, upgraded to Nicolet R3 specifications (Campana, Shepard & Litchman, 1981). Lattice constants were derived from 25 reflections in the range  $21 < 2\theta < 26^\circ$ . Data were collected with  $\omega$  scans (1.1°); two check reflections monitored every 96 reflections ( $\bar{2}00$  and  $\bar{4}22$ ) show no systematic excursions; 4287 total reflections out to  $2\theta = 45^\circ$ , 2632 unique with  $R(\text{merge}) = 0.024$ ;  $hkl$  ranges,  $0 \leq h \leq 13$ ,  $0 \leq k \leq 26$ ,  $-17 \leq l \leq 17$ . Empirical  $\psi$  scan absorption corrections applied (program XEMP of SHELXTL, Sheldrick, 1985) assuming an ellipsoidally shaped crystal (relative transmission in the range 0.789 to 0.906).

The structure solution was obtained *via* the direct methods routine SOLV in the SHELXTL (version 5.1) crystallographic program package and refinement also utilized that set of programs (Sheldrick, 1985). A difference synthesis based on the Cu and Cl positions yielded the C, N and O atom positions. H atoms, except for phenyl rings, were constrained to ideal positions (C—H and N—H = 0.96 Å) and assigned isotropic thermal parameters 1.2 times larger than the associated atoms. Phenyl ring H atoms were also constrained to ideal positions, but were assigned isotropic thermal parameters of