Structure of Chlorobis(1,10-phenanthroline)copper(II) Nitrate Monohydrate

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Abstract. [CuCl(C$_{12}$H$_8$N$_2$)$_2$]NO$_3$.H$_2$O, $M_r = 539.2$, triclinic, $P\bar{1}$, $a = 11.128$ (1), $b = 12.026$ (4), $c = 9.738$ (2) Å, $\alpha = 108.84$ (2), $\beta = 108.54$ (2), $\gamma = 67.83$ (2)°, $V = 1113.2$ (5) Å^3, $Z = 2$, $D_x = 1.609$, $D_m = 1.616$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.04$ mm^{-1}, $F(000) = 550$, $T = 293$ K, $R = 0.043$ for 4161 unique observed reflections. The bidentate phenanthroline ligands and the chloride ion coordinate to the Cu^{II} atom to form a distorted trigonal bipyramid with equatorial bond lengths Cu—Cl 2.292 (1), Cu—N 2.132 (2) and 2.091 (2) Å, and two equal (within errors) axial Cu—N bond lengths of 1.988 (4) Å.

Introduction. The crystal structure determination of the title compound was undertaken in order to study the bond and angle distortions exhibited by the [Cu(phen)$_2$-Cl]$^+$ cation (phen = 1,10-phenanthroline), a cation distortion isomer of the series [Cu(phen)$_2$Cl]X (X = anion). The stereochemistry of the five-coordinate [CuN$_4$Cl] chromophore can be compared with that of the complex [Cu(phen)$_2$Cl]ClO$_4$ (Boys, Escobar & Martínez-Carrera, 1981) and with that of other related compounds, *e.g.* [Cu(bipy)$_2$Cl]X (bipy = 2,2'-bipyridyl) (Harrison, Kennedy, Power, Sheahan & Hathaway, 1981).

Experimental. Turquoise prismatic-shaped crystals, density measured by flotation in carbon tetrachloride/bromoform. Crystal of average dimensions 0.4 × 0.4 × 0.3 mm used for data collection on a Philips PW 1100 four-circle diffractometer, $\omega/2\theta$ scan mode, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Standard reflections showed statistical variations within 2%. Cell parameters from least-squares fit of 23 reflections with $18 \leq 2\theta \leq 42°$. From 4884 unique reflections with $4.1 \leq 2\theta \leq 54.1°$, 4161 reflections were considered observed with $I > 2\sigma(I)$, Lorentz and polarization corrections applied, absorption ignored. Structure solved using direct-methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on F by block-matrix least squares with anisotropic temperature factors. H atoms of phenthroline molecules calculated geometrically and bonded to parent C atoms with C—H = 0.89 Å with their equivalent iso-

tropic temperature factors; H atoms of water molecule determined from last Fourier difference map. The ten most intense reflections were excluded from the last cycles of refinement, which converged to $R = 0.043$ and $wR = 0.049$ with weighting scheme $w = (F_o/7.5)^2$ if $F_o \leq 7.5$ and $w = (7.5/F_o)^2$ otherwise; $S = 0.91$, $(\Delta/\sigma)_{max} = 0.02$ for coordinates and 0.14 for temperature factors, overall mean $\Delta/\sigma = 0.01$. Highest residuals in difference map were found in the vicinity of Cu and nitrate ions; $(\Delta\rho)_{max} = 0.73$ e Å^{-3}.

Discussion. Atomic parameters, bond distances and angles are listed in Tables 1 and 2.*

Fig. 1 shows the coordination geometry of the complex cation with the atom-numbering scheme. The Cu^{2+} ion is pentacoordinated to the N atoms of the bidentate phenanthroline ligands and the Cl$^-$ ion in a distorted trigonal bipyramidal arrangement. The Cl ion, N(12) and N(22), from phen(1) and phen(2) respectively, occupy equatorial positions in the trigonal base of the bipyramid while the remaining N(11) and N(21) atoms of the phenanthroline molecules occupy axial positions with equal Cu—N bond lengths. The equatorial atoms together with the central Cu^{2+} ion are coplanar, the major deviation from the mean plane of 0.0046 (4) Å being exhibited by the metal ion. The Cu—N in-plane bonds are larger than the Cu—N axial bonds, as previously observed in other trigonal bi-

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Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\mathring{A}^2 \times 10^3)$, *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}*$
Cu	−2238·0 (3)	2646·5 (3)	2908·2 (4)	29
Cl	−2715·8 (10)	4261·0 (7)	4898·0 (9)	62
N(11)	−1738 (3)	3650 (2)	2037 (3)	44
N(12)	−3674 (2)	2588 (2)	846 (3)	42
N(21)	−2726 (2)	1542 (2)	3633 (3)	42
N(22)	−636 (2)	1053 (2)	2522 (3)	38
C(11)	−755 (4)	4162 (3)	2659 (4)	56
C(12)	−556 (4)	4938 (4)	2029 (5)	66
C(13)	−1382 (5)	5206 (3)	728 (5)	68
C(14)	−2413 (4)	4660 (3)	13 (4)	55
C(15)	−3316 (5)	4837 (4)	−1379 (5)	71
C(16)	−4279 (5)	4294 (4)	−1995 (4)	71
C(17)	−4445 (4)	3501 (3)	−1288 (3)	56
C(18)	−5427 (4)	2882 (4)	−1868 (4)	69
C(19)	−5495 (4)	2150 (4)	−1099 (5)	68
C(110)	−4601 (3)	2022 (3)	252 (4)	55
C(111)	−3591 (3)	3318 (3)	84 (3)	43
C(112)	−2554 (3)	3889 (3)	725 (3)	42
C(21)	−3770 (3)	1816 (3)	4200 (4)	54
C(22)	−3993 (4)	957 (4)	4686 (4)	61
C(23)	−3114 (4)	−214 (4)	4596 (4)	57
C(24)	−2010 (3)	−540 (3)	3989 (3)	45
C(25)	−1039 (4)	−1733 (3)	3838 (4)	54
C(26)	−0 (4)	−1982 (3)	3249 (4)	53
C(27)	184 (3)	−1067 (3)	2767 (3)	44
C(28)	1266 (3)	−1271 (3)	2153 (4)	53
C(29)	1363 (4)	−338 (3)	1743 (4)	57
C(210)	393 (3)	817 (3)	1934 (4)	49
C(211)	−738 (3)	118 (2)	2916 (3)	37
C(212)	−1857 (3)	380 (2)	3524 (3)	37
N(1)	2684 (4)	1619 (4)	968 (4)	69
O(11)	1906 (10)	2624 (5)	1086 (9)	216
O(12)	3400 (6)	1271 (6)	2105 (6)	158
O(13)	2749 (6)	861 (5)	−198 (5)	132
O(1)	2505 (4)	3058 (3)	4698 (3)	83

* Equivalent isotropic temperature factor calculated as

$$\bar{U} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$
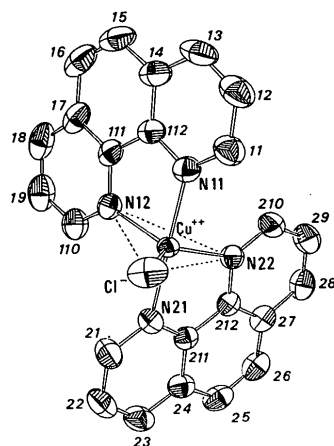

Fig. 1. The complex cation as viewed in the [011] crystallographic direction with atom-numbering scheme. Ellipsoids with 50% probability. H atoms omitted for clarity.

pyramidal Cu^{II} complexes (Huq & Skapski, 1971; Harrison *et al.*, 1981). The in-plane angles differ significantly from the ideal 120° of a regular trigonal bipyramid, the angular distortion being much greater in this complex than that present in the [Cu(phen)$_2$-Cl]ClO$_4$ analogue (Boys, Escobar & Martínez-Carrera, 1981). The larger in-plane angle Cl—Cu—N(22) is

Table 2. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

(a) Metal coordination

Cu—Cl	2·292 (1)	Cu—N(21)	1·988 (4)
Cu—N(11)	1·989 (4)	Cu—N(22)	2·091 (2)
Cu—N(12)	2·132 (2)		

N(11)—Cu—N(12)	80·8 (1)	N(21)—Cu—N(22)	81·4 (1)
N(11)—Cu—N(22)	95·8 (1)	N(21)—Cu—N(12)	96·5 (1)
Cl—Cu—N(11)	91·8 (1)	Cl—Cu—N(21)	92·7 (1)
Cl—Cu—N(12)	119·2 (1)	Cl—Cu—N(22)	135·8 (1)
N(12)—Cu—N(22)	105·0 (1)	N(11)—Cu—N(21)	175·6 (1)

(b) Phenanthroline groups [m = 1,2 for phen (1), (2) respectively]

	$m = 1$	$m = 2$
N(m1)—C(m1)	1·337 (5)	1·328 (5)
N(m1)—C(m12)	1·357 (4)	1·360 (3)
N(m2)—C(m10)	1·327 (5)	1·336 (5)
N(m2)—C(m11)	1·362 (5)	1·352 (5)
C(m1)—C(m2)	1·382 (8)	1·392 (8)
C(m2)—C(m3)	1·361 (6)	1·373 (5)
C(m3)—C(m4)	1·414 (6)	1·400 (6)
C(m4)—C(m5)	1·432 (6)	1·429 (4)
C(m4)—C(m12)	1·400 (6)	1·405 (6)
C(m5)—C(m6)	1·342 (8)	1·344 (6)
C(m6)—C(m7)	1·433 (8)	1·427 (6)
C(m7)—C(m8)	1·419 (6)	1·417 (6)
C(m7)—C(m11)	1·401 (4)	1·401 (4)
C(m8)—C(m9)	1·363 (8)	1·356 (7)
C(m9)—C(m10)	1·388 (5)	1·399 (4)
C(m11)—C(m12)	1·434 (5)	1·432 (5)
C(m1)—N(m1)—C(m12)	118·5 (4)	118·4 (3)
C(m10)—N(m2)—C(m11)	118·3 (3)	117·6 (2)
N(m1)—C(m1)—C(m2)	122·5 (3)	122·2 (3)
C(m1)—C(m2)—C(m3)	119·7 (4)	119·9 (4)
C(m2)—C(m3)—C(m4)	119·6 (5)	119·5 (5)
C(m3)—C(m4)—C(m12)	117·2 (3)	117·0 (3)
C(m5)—C(m4)—C(m12)	118·0 (4)	118·9 (4)
C(m4)—C(m5)—C(m6)	121·8 (5)	120·9 (4)
C(m5)—C(m6)—C(m7)	121·3 (4)	121·5 (3)
C(m6)—C(m7)—C(m11)	118·5 (4)	119·2 (3)
C(m8)—C(m7)—C(m11)	116·6 (4)	116·8 (3)
C(m7)—C(m8)—C(m9)	120·0 (3)	119·7 (3)
C(m8)—C(m9)—C(m10)	119·3 (4)	119·5 (4)
N(m2)—C(m10)—C(m9)	123·0 (5)	122·8 (4)
N(m2)—C(m11)—C(m7)	122·9 (3)	123·6 (3)
C(m7)—C(m11)—C(m12)	119·9 (4)	119·4 (3)
N(m1)—C(m12)—C(m4)	122·4 (3)	123·0 (3)
C(m4)—C(m12)—C(m11)	120·5 (3)	120·1 (2)

(c) Nitrate anion and water molecule

N(1)—O(11)	1·186 (7)	O(1)—H(1)	0·772 (3)
N(1)—O(12)	1·234 (7)	O(2)—H(2)	0·941 (4)
N(1)—O(13)	1·208 (6)		
O(11)—N(1)—O(12)	119·0 (6)	H(1)—O(1)—H(2)	111·2 (5)
O(11)—N(1)—O(13)	124·1 (5)		
O(12)—N(1)—O(13)	116·7 (5)		

opposite to the longest Cu—N(12) bond distance as in the ClO$_4$ analogue and as in the complexes of the series [Cu(bipy)$_2$Cl]X (X = ClO$_4$;NO$_3$.3H$_2$O) reported by Harrison *et al.* (1981).

Chemically equivalent bond lengths and angles in the two phenanthroline ligands are normal and in good agreement with each other. The ligands are essentially planar with maximum deviations of the atoms from their mean planes of 0·029 (3) Å in phen(1) and 0·020 (2) Å in phen(2). The phenanthrolines exhibit normal bite angles of approximately 81° causing the removal of N(11) and N(21) from their ideal axial positions.

Fig. 2 shows the packing of the crystal in projection. The phenanthroline molecules stack over each other: phen(1), in position (x,y,z), presents a separation of
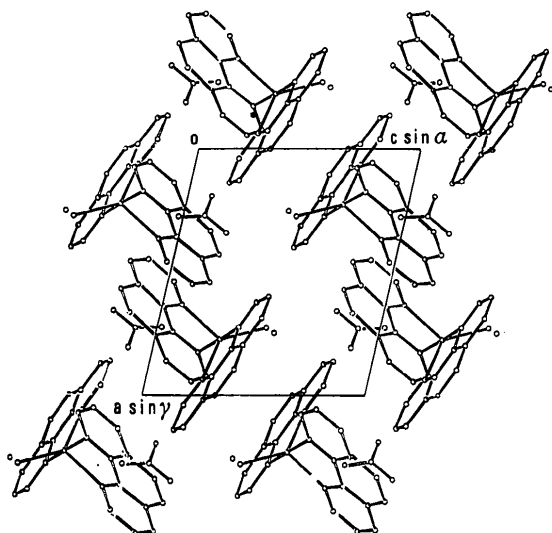
Fig. 2. Projection of the structure, parallel to the crystallographic b axis.

3.41 (2) Å with its corresponding centrosymmetrically related molecule, in position $(-x-1,-y,-z)$, with an overlap estimated as 33%, while phen(2), in position (x,y,z), is at a distance of 3.43 (1) Å from its centrosymmetrically related molecule, in position $(-x,-y,-z+1)$, with an overlap estimated as 47%. The nitrate anion and water molecule are out of the coordination sphere of the metal ion. The water molecule, however, is strongly associated to the complex cation through the coordinated Cl^- ion with a short contact $Cl\cdots H(2)-O(1) = 3.209$ (4), $Cl\cdots H(2)$

$= 2.286$ (1) Å and $Cl-H(2)-O(1) = 166.7$ (3)°. It also exhibits a short contact with the nitrate ion with $O(12)\cdots H(1)-O(1) = 2.909$ (6), $O(12)\cdots H(1) = 2.198$ (6) Å and $O(12)-H(1)-O(1) = 153.5$ (3)°.

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Structure of Triphenyltin(IV) Methoxyethylxanthate

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Abstract. (O-Methoxyethyldithiocarbonato)triphenyltin(IV), $[Sn(S_2COCH_2CH_2OCH_3)(C_6H_5)_3]$, $M_r = 501.24$, triclinic, $P\bar{1}$, $a = 9.400$ (1), $b = 14.277$ (3), $c = 18.506$ (5) Å, $\alpha = 68.14$ (2), $\beta = 83.05$ (1), $\gamma = 75.43$ (1)°, $U = 2229.8$ (9) Å^3, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $T = 295$ (2) K, $D_x = 1.493$ (1), $D_m = 1.47$ (2) g cm^{-3}, $Z = 4$, $F(000) = 1008$, $\mu = 12.32$ cm^{-1}, $R = 0.044$ for 3435 unique reflections $[I \geq 2\sigma(I)]$. There are two independent molecules per asymmetric unit which differ significantly only in their intermolecular contacts. The xanthate $(ROCS_2^-)$ moiety coordinates the tin atom via one S atom $[Sn-S = 2.456$ (3), 2.457 (3) Å] together with a long interaction from the O atom $[Sn-O = 3.107$ (8), 3.094 (8) Å]. A short intermolecular contact between a methylene H and an ether O $[H\cdots O$ 2.47 (2) Å] is observed.

Introduction. The very rare S- and O-xanthate coordination mode has been observed for triphenyltin isopropylxanthate $[Ph_3Sn(iprxa)]$ (Tiekink & Winter, 1986). It was therefore of interest to examine whether