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Chloro(histamine)(1,10-phenanthroline)copper(II) chloride monohydrate

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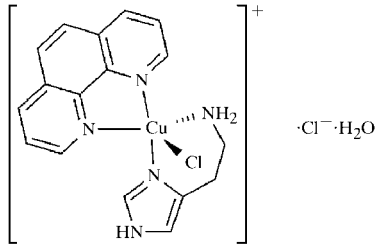
In the cationic complex present in the title compound, chloro[2-(4-imidazolyl-κN^1)ethylamine-κN](1,10-phenanthroline-$\kappa^2 N,N'$)copper(II) chloride monohydrate, $[CuCl(C_5H_9N_3)(C_{12}H_8N_2)]Cl\cdot H_2O$, the metal centre adopts a five-coordinate geometry, ligated by the two phenanthroline N atoms, two amine N atoms of the histamine ligand (one aliphatic and one from the imidazole ring) and a chloro ligand. The geometry around the Cu atom is a distorted compressed trigonal bipyramid, with one phenanthroline N and one imidazole N atom in the axial positions, and the other phenanthroline N atom, the histamine amine N atom and the chloro ligand in the equatorial positions. The structure includes an uncoordinated water molecule, and a Cl^- ion to complete the charge. The water molecule is hydrogen bonded to both Cl^- ions (coordinated and uncoordinated), and exhibits a close Cu···H contact in the equatorial plane of the bipyramid.

Comment

Since Sigman and co-workers reported that 1,10 phenanthroline–copper complexes can function as artificial nucleases (D'Aurora *et al.*, 1978), there has been considerable interest in DNA binding and cleavage by these and other metal–phenanthroline complexes as chemical probes of DNA, because of their potential utility in footprinting techniques. Nucleases are enzymes that catalyse nucleic acid hydrolysis by cleavage of the phosphodiester linkage. Under physiological conditions, this process has a rate constant of the order of 10^{-9} min^{-1}. At this hydrolysis rate, processes such as replication and transcription are not possible. In the presence of metal ions such as copper, the hydrolysis rate for phosphodiesters is increased but is still insignificant on the physiological time scale (Sigman *et al.*, 1993).

Many complexes of the phenanthroline ligand with several metals have been synthesized in order to obtain further insights into their nuclease activity (Sakurai *et al.*, 1995; Ramírez-Ramírez *et al.*, 1998). Some researchers have suggested that the mechanism of action of these artificial nucleases could be explained by a partial intercalation of one phenanthroline ligand between the base pairs of DNA (Veal & Rill, 1991). Moreover, it has been determined that substituents on the phenanthroline clearly influence the way in which copper–phenanthroline complexes bind to DNA (Mahadevan & Palaniandavar, 1998; Meadows *et al.*, 1993). Some natural nucleases contain imidazole groups in their structures. The chemistry of imidazole is of special interest because of its wide occurrence in biological compounds, notably as part of the amino acid histidine and metabolites like histamine. Also, it is well known that copper in living systems is in many cases surrounded by residues of histidine (Baran, 1994).

In this, work we report the synthesis and crystal structure of chlorohistamine(1,10-phenanthroline)copper(II) chloride monohydrate, (I), which contains a mixed-ligand complex with histamine and phenanthroline, and which will be tested as a potential chemical nuclease. Details of the structure of this compound should be helpful in understanding how the chemical nucleases of the copper–phenanthroline system work.



(I)

The molecular structure of (I) is shown in Fig. 1. The Cu^{II} ion displays five-coordinate geometry and can best be described as a compressed trigonal bipyramid (tbp), as can be seen from the distances and angles around the metal (Table 1). Crystal structures of copper(II) complexes with histamine have been reported previously, for example, $[Cu(histamine)Cl_2]$ (Główka *et al.*, 1980) and $[Cu(histamine)(ClO_4)_2]$ (Bonnet & Jeannin, 1970), in which a pseudo-octahedral geometry (or, more properly, a distorted square bipyramidal geometry) is found for copper. In the title complex, the coordination is provided by one phenanthroline ligand, one histamine ligand and one coordinated Cl^- anion. One phenanthroline and one imidazole N atom, *viz*. N9 and N1, are located in the axial positions. The other N atom of the phenanthroline, the aliphatic N atom of histamine and the coordinated Cl^- form the base of the bipyramid. The Cu^{II} ion is located in the middle of the base of the tbp, 0.095 Å out of the mean plane (toward N1) formed by the equatorial ligand atoms (N8, N20 and Cl1). The τ descriptor for five-coordinate complexes, expressed here as the difference between the bond angles N8—Cu—Cl1 and N1—Cu—N9 divided by 60, has a value of 0.62, which can be compared with the ideal values of 1 for a tbp and 0 for a square pyramid (Addison *et al.*, 1984).

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The equatorial angles Cl1—Cu1—N8, Cl1—Cu1—N20 and N8—Cu1—N20 are 133.99 (6), 119.91 (6) and 105.49 (7)°, respectively. The angles involving Cl^- deviate most from the ideal value of 120° for a perfect tbp. The largest equatorial angle gives rise to the cleft in which hydrogen bonding is present, involving the uncoordinated water molecule, the Cl^- anion and the coordinated amine group. The axial N1—Cu1—N9 angle [171.01 (8)°] does not deviate greatly from linearity.

The Cu—Cl1 distance is 2.3380 (7) Å, indicative of a relatively strong bond between copper and the Cl^- ligand. This bond is much shorter than is found for an apically coordinated Cl^- atom in a five-coordinate tetragonal–pyramidal copper(II) complex such as $[Cu(cip)(bipy)Cl](NO_3)\cdot 2H_2O$ (cip is ciprofloxacine and bipy is 2,2′-bipyridine), where the bond distance is 2.549 (2) Å (Wallis *et al.*, 1996). In (I), the axial Cu—N bonds (Cu—N1 and Cu—N9) are shorter than the corresponding equatorial bonds (Cu—N8 and Cu—N20), as expected for a trigonal–bipyramidal structure with four N donors (Masood & Hodgson, 1993). The observed geometry must result primarily from electronic factors, since the conformational flexibility of one of the ligands obviates the influence of steric constraints in the complex (Masood & Hodgson, 1993).

Two-dimensional hydrogen-bond networks are present in the structure of (I). The structure includes an uncoordinated water molecule and a Cl^- anion, which provide stability through a network of hydrogen-bond interactions (Table 2). The water molecule donates atom H1*A* to a hydrogen bond with the coordinated Cl^-. Due to this hydrogen bond, the H atom has a short contact distance to the Cu centre of 2.85 Å [Cu···O1 = 3.577 (3) Å], somewhat smaller than the sum of the van der Waals radii. It is also interesting that this water molecule is located in the plane of the tbp base (0.0822 Å out of the plane formed by the ligand atoms N8, N20 and Cl1) in a position suggestive of the location of an exiting fourth equatorial ligand (Fig. 2).

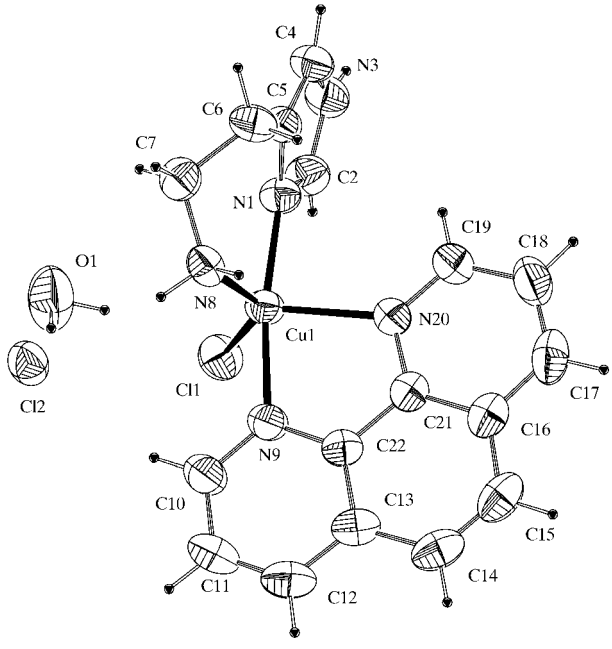

Figure 1
A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

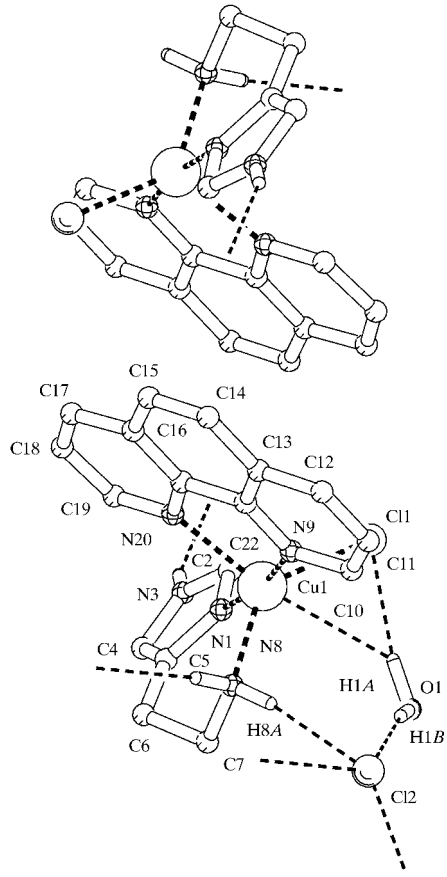

Figure 2
A partial view of the two-dimensional hydrogen-bond network in the structure of (I) and the trigonal–bipyramidal geometry around the Cu atom. The stacking of phenanthroline rings with the adjacent molecule at $(\frac{1}{2}-x, \frac{3}{2}-y, 1-z)$ is shown. The view is along $[\bar{1}00]$, with the *b* axis vertical.

In the extended structure of (I), we observe phenanthroline stacking between molecules related by a centre of symmetry. The stacking distance is 3.468 (5) Å for the contact between the molecule at (x, y, z) and that at $(\frac{1}{2}-x, \frac{3}{2}-y, 1-z)$ (Fig. 2), similar to the distance found in other complexes with this ligand (Mendoza-Díaz *et al.*, 1993). Stacking between the imidazole ring of the coordinated histamine and the phenanthroline ring of the molecule at $(x, 1-y, \frac{1}{2}+z)$ is also observed. However, unlike the stacked phenanthroline groups, which are parallel to each other, the histamine and neighbouring phenanthroline groups form a dihedral angle of 13.48 (13)°, making the stacking less efficient. The perpendicular distance from the centroid of the middle ring of the phenanthroline to the imidazole plane is 3.539 Å. These stacking interactions should favour the stabilization of the tbp geometry over the square pyramid in this case.

Experimental

A solution of 1,10-phenanthroline (1 mmol) in a 1:1 water–ethanol mixture (30 ml) was added slowly to a solution of $CuCl_2·2H_2O$ (1 mmol) in water (10 ml). The resulting solution was warmed and a solution of histamine hydrochloride (1 mmol) in water and containing triethylenediamine (0.4 ml), was added. The reaction mixture was allowed to stand at room temperature overnight and then at 273 K for several days. Blue crystals of (I) suitable for X-ray diffraction formed after several days, and these were filtered off and dried in air.

Compound (I)

Crystal data

$[CuCl(C_5H_9N_3)(C_{12}H_8N_2)]Cl·H_2O$
M_r = 443.81
Monoclinic, $C2/c$
a = 18.2744 (14) Å
b = 12.6490 (11) Å
c = 17.760 (2) Å
β = 111.621 (7)°
V = 3816.3 (6) Å^3
Z = 8
D_x = 1.545 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 83 reflections
θ = 4.8–12.8°
μ = 1.44 mm^{-1}
T = 296 (1) K
Prism, green
0.60 × 0.28 × 0.20 mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
T_{min} = 0.611, T_{max} = 0.749
7754 measured reflections
4402 independent reflections
3424 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°
$h = -23 \rightarrow 23$
$k = -16 \rightarrow 1$
$l = -21 \rightarrow 23$
3 standard reflections
every 97 reflections
intensity decay: 1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.090
S = 1.01
4402 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 2.422P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient: 0.00084 (10)

The H atoms of the water molecule were found in difference maps. The remaining H atoms were placed in idealized positions. In the final cycles of the refinement, all H atoms were constrained to ride on their parent atoms, with methylene C—H distances of 0.97 Å, aryl C—H distances of 0.93 Å, N—H distances of 0.86 Å and NH_2 group N—H distances of 0.90 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(O).

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N1	1.9634 (18)	Cu1—N20	2.1613 (19)
Cu1—N9	2.0241 (18)	Cu1—Cl1	2.3380 (7)
Cu1—N8	2.0593 (19)		
N1—Cu1—N9	171.01 (8)	N8—Cu1—N20	105.49 (7)
N1—Cu1—N8	92.05 (7)	N1—Cu1—Cl1	93.63 (6)
N9—Cu1—N8	90.77 (8)	N9—Cu1—Cl1	90.54 (6)
N1—Cu1—N20	91.67 (7)	N8—Cu1—Cl1	133.99 (6)
N9—Cu1—N20	79.35 (7)	N20—Cu1—Cl1	119.91 (6)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···Cl1	0.98	2.26	3.228 (3)	171
O1—H1B···Cl2	0.94	2.31	3.218 (2)	161
N3—H3A···Cl2^{i}	0.86	2.38	3.169 (2)	154
N8—H8A···Cl2	0.90	2.47	3.3651 (19)	171
N8—H8B···Cl2^{ii}	0.90	2.49	3.379 (2)	170

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* and *PLUTON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1052). Services for accessing these data are described at the back of the journal.

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