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Chlorobis(1,10-phenanthroline-κ^2N,N')copper(II) nitrate 4-nitrobenzoic acid monohydrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.045
wR factor = 0.110
Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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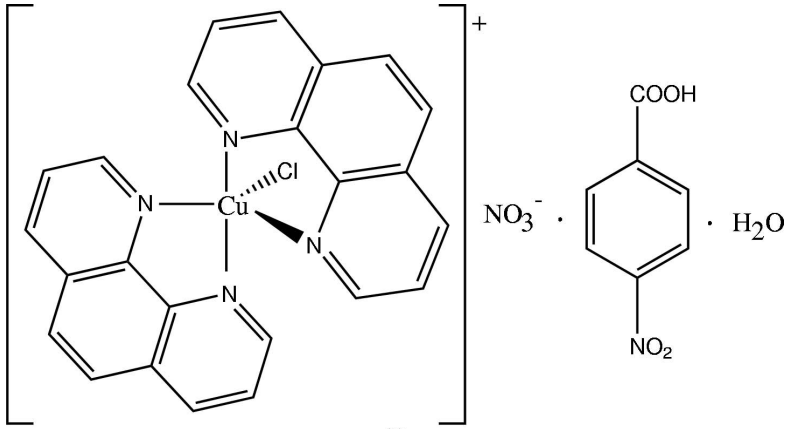
In the crystal structure of the title compound, $[CuCl(C_{12}H_8N_2)_2]NO_3{\cdot}C_7H_5NO_4.H_2O$, the Cu^{II} ion assumes a trigonal–bipyramidal CuN_4Cl coordination geometry arising from two bidentate 1,10-phenanthroline (phen) ligands and one chloride ion, with the chloride ion in an equatorial position. A partially overlapped arrangement between parallel phen rings of neighboring complexes, with face-to-face distances of 3.529 (9) and 3.452 (8) Å, suggests the existence of π–π stacking.

Comment

As π–π stacking between aromatic rings is correlated with the electron-transfer process in some biological systems (Deisenhofer & Michel, 1989), we have been interested in π–π stacking in metal complexes for several years (Nie *et al.*, 2001). The crystal structure of the title copper(II) complex, (I), shows π–π stacking between 1,10-phenanthroline (phen) rings.



(I)

The crystal structure of (I) consists of copper(II) complex cations, nitrate anions, uncoordinated water molecules and nitrobenzoic acid molecules, as shown in Fig. 1. The Cu^{II} atom assumes a CuN_4Cl trigonal–bipyramidal coordination geometry formed by two N,N'-bidentate phen ligands and one equatorial chloride anion (Table 1). The average Cu—N bond distance of 1.987 (3) Å in the axial direction is shorter than the average Cu—N bond distance of 2.095 (3) Å by 0.108 (4) Å (Table 1), which is comparable to the situation found in chlorobis(phen)copper(II) nitrate monohydrate (Boys, 1988).

A partially overlapped arrangement between parallel phen rings of neighboring complex cations is observed (Figs. 2 and 3). The face-to-face distance of 3.529 (9) Å between the N1/N2-phen and $N1^i/N2^i$-phen rings [symmetry code: (i) $2-x$, $-y$, $1-z$] and 3.452 (8) Å between the N3/N4-phen and

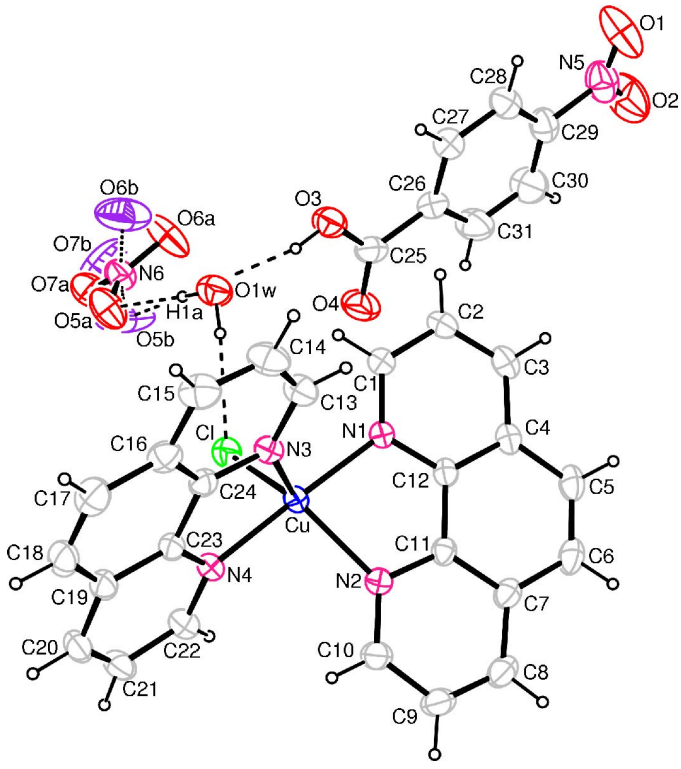


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids (spheres of arbitrary radius for the H atoms). Dashed lines indicate the hydrogen-bonding interactions and dotted lines indicate the minor component of the disordered nitrate anion.

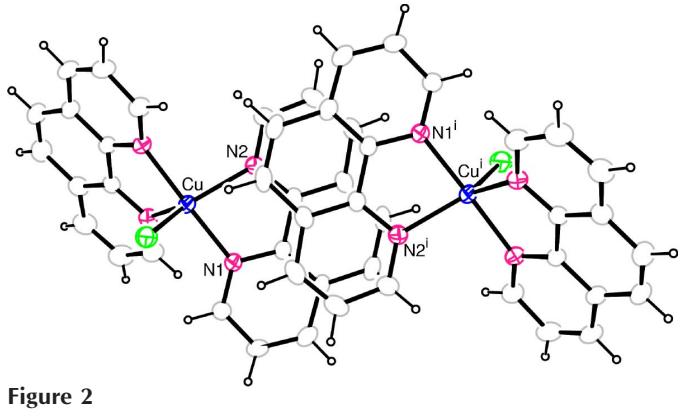


Figure 2
Detail of (I) showing the π–π stacking between the phen rings of neighboring complex cations [symmetry code: (i) $2-x, -y, 1-z$].

N3^{ii}/N4^{ii}-phen rings [symmetry code: (ii) $1-x, -y, 2-z$] suggest the existence of π–π stacking in (I).

The uncoordinated water molecule is hydrogen bonded with the complex cation, nitrate anion and 4-nitrobenzoic acid molecule (Fig. 1 and Table 2). The two disordered components of the nitrate anion display similar hydrogen-bonding modes.

Experimental

An acetonitrile–water (1:1) solution (10 ml) containing 4-nitrobenzoic acid (1.7 g, 1 mmol) and NaOH (0.040 g, 1 mmol) was mixed with an aqueous solution of $CuCl_2{\cdot}2H_2O$ (0.17 g, 1 mmol). The mixture was refluxed for 3 h and a large amount of white precipitate

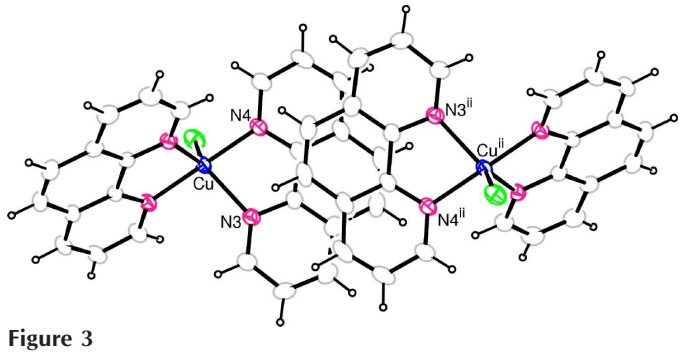


Figure 3
Detail of (I) showing the π–π stacking between the phen rings of neighboring complex cations [symmetry code: (ii) $1-x, -y, 2-z$].

appeared. An acetonitrile solution (5 ml) of phenanthroline (0.20 g, 1 mmol) was added and the mixture was refluxed for a further 1 h, during which time the white precipitate failed to dissolve. A nitric acid solution (5 ml, 65%) was then added and the mixture was refluxed for a further 1 h, after which time the white precipitate had dissolved and the solution color changed to blue. The blue solution was filtered and blue single crystals of (I) were obtained from the filtrate after 10 d.

Crystal data

$[CuCl(C_{12}H_8N_2)_2]NO_3{\cdot}C_7H_5NO_4{\cdot}H_2O$
$M_r = 706.54$
Triclinic, $P\overline{1}$
$a = 9.9326\ (3)$ Å
$b = 11.8986\ (4)$ Å
$c = 13.1517\ (4)$ Å
$\alpha = 82.7790\ (11)^\circ$
$\beta = 84.4600\ (15)^\circ$
$\gamma = 78.7095\ (12)^\circ$
$V = 1508.01\ (8)$ Å^3
$Z = 2$
$D_x = 1.556$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6517 reflections
$\theta = 2.5$–27.4°
$\mu = 0.88$ mm^{-1}
$T = 295\ (2)$ K
Chunk, blue
0.34 × 0.21 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.730$, $T_{max} = 0.888$
14700 measured reflections
6855 independent reflections
5084 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5^\circ$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.110$
$S = 1.01$
6855 reflections
453 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.7183P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—Cl	2.3359 (8)	Cu—N3	2.107 (2)
Cu—N1	1.985 (2)	Cu—N4	1.989 (2)
Cu—N2	2.0823 (19)		
Cl—Cu—N1	91.45 (7)	N1—Cu—N3	98.67 (8)
Cl—Cu—N2	126.90 (6)	N1—Cu—N4	178.01 (9)
Cl—Cu—N3	113.78 (6)	N2—Cu—N3	119.32 (8)
Cl—Cu—N4	90.50 (7)	N2—Cu—N4	97.30 (8)
N1—Cu—N2	81.21 (8)	N3—Cu—N4	80.88 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O1W	0.83	1.74	2.566 (3)	170
O1W—H1A···O5A	0.89	1.85	2.73 (1)	172
O1W—H1A···O5B	0.89	1.96	2.84 (3)	171
O1W—H1B···Cl	0.84	2.31	3.146 (2)	176

The O atoms of the nitrate anion are disordered over two positions. Two site-occupancy factors were initially refined and converged to 0.682 (4) and 0.318 (4); these were fixed as 0.68 and 0.32 in the final cycles of refinement. H atoms attached to O atoms were located in difference Fourier maps and refined as riding in their as-found relative positions, with fixed U_{iso} values of 0.05 Å^2. H atoms on aromatic rings were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and were included in the final cycles of refinement as riding, with the constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) applied.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Boys, D. (1988). *Acta Cryst.* C**44**, 1539–1541.
Deisenhofer, J. & Michel, H. (1989). *EMBO J.* **8**, 2149–2170.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.
Nie, J.-J., Liu, L.-J., Luo, Y. & Xu, D.-J. (2001). *J. Coord. Chem.* **53**, 365–371.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure.* Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.