Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Aquachloro(4-cyanobenzoato-*κO*)(1,10-phenanthroline-κ^2N,N')copper(II) monohydrate

Yi-Li Zhou,[a] Hong-Yin He,[a] Yan Zhang[a] and Long-Guan Zhu[b]*

[a]Department of Chemical Engineering, Jiaxing College, Jiaxing 314001, People's Republic of China, and [b]Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

Correspondence e-mail: chezlg@zju.edu.cn

Received 23 June 2003
Accepted 15 July 2003
Online 24 July 2003

Key indicators

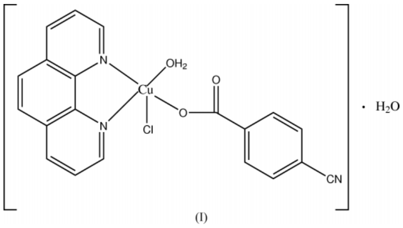
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.088
Data-to-parameter ratio = 11.8

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

The reaction of copper(II) chloride with 4-cyanobenzoic acid and 1,10-phenanthroline in a mixture of dimethylformamide and methanol gives the title complex, $[CuCl(C_8H_4NO_2)(C_{12}H_8N_2)(H_2O)]\cdot H_2O$. The Cu^{II} ion is coordinated by one 1,10-phenanthroline, one water molecule, one Cl atom, and one 4-cyanobenzoate ligand. In the crystal structure, there are O—H···Cl hydrogen bonds and π–π-stacking interactions.

Comment

Complexes with the $[Cu(phen)Cl]^+$ or $[Cu(phen)_2Cl]^+$ chromophore have been extensively investigated due to their interesting electronic properties under pressure or upon heating (Drickamer & Bray, 1990; Murphy *et al.*, 1997; O'Sullivan *et al.*, 1999). Moreover, weak C—H···Cl hydrogen bonding and π–π interactions have been observed in these complexes (Ma *et al.*, 2000). Recently, 4-cyanobenzoic acid (Hcba) has been used to synthesize blue fluorescent complexes (Yuan *et al.*, 2001; He & Zhu, 2003; He *et al.*, 2003). We present here the crystal structure of a copper complex, (I), containing the $[Cu(phen)Cl]^+$ unit and a cba ligand, which provides an interesting example of a mixed-anion quaternary assembly extended *via* hydrogen bonding and π–π interactions.



(I)

Compound (I) is a monomer species, in which the geometry around the Cu^{II} atom is best described as square pyramidal, as shown in Fig. 1. The coordination of the Cu^{II} atom is completed by one chloro ligand, one water O atom, one O atom from a cba ligand, and two N atoms from a 1,10-phenanthroline ligand. The apical position is occupied by the chloro atom at a distance of 2.524 (1) Å, which is longer than the distances in complexes containing a $[Cu(phen)_2Cl]^+$ unit, such as $[Cu(phen)_2Cl](OH)\cdot 6H_2O$, and similar to the distance in $[Cu(bipy)Cl(C_{13}H_8NClFO_3)]\cdot 2H_2O$ (Xie *et al.*, 2003). The cba ligand is coordinated in a monodentate fashion, with a Cu—O(COO$^-$) distance of 1.976 (2) Å, which is longer than in the structure of $[Cu(4,4'\text{-bipy})(cba)_2]_n$ (He & Zhu, 2003). The parameter τ was introduced to describe the distortion of the square pyramidal (Albada *et al.*, 1999). In the case of (I), τ = (164.21−162.57)/60 = 0.0273, which suggests some distortion from ideal square pyramidal.

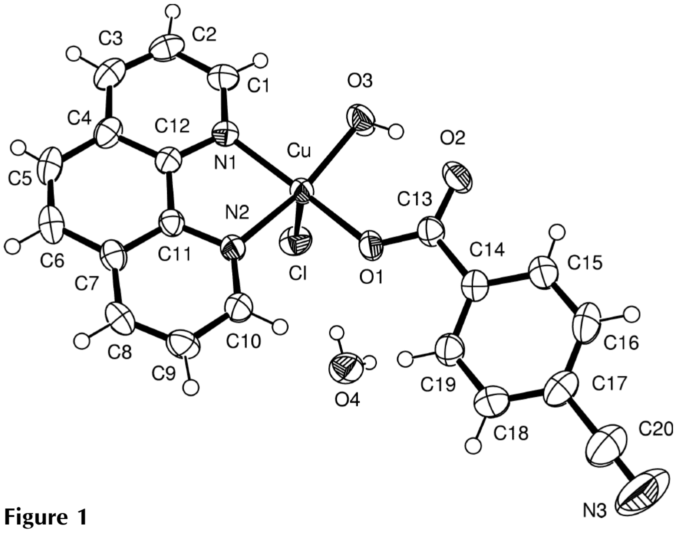


Figure 1
View of the asymmetric unit of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

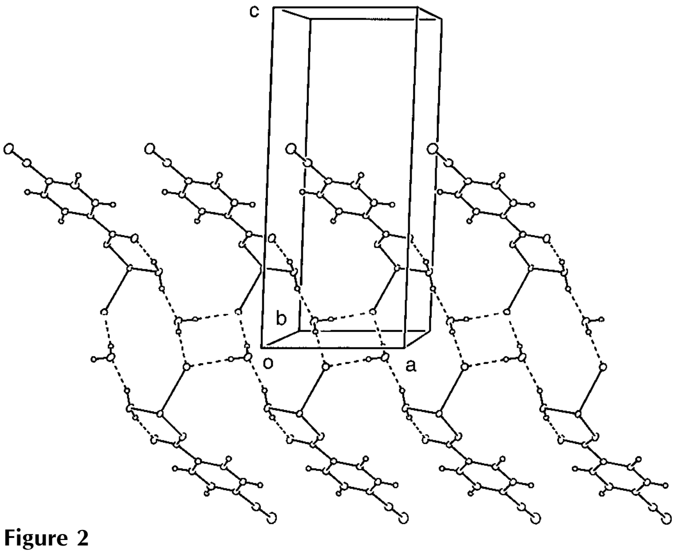


Figure 2
View of the one-dimensional hydrogen-bonding network. The 1,10-phenanthroline ligands have been omitted for clarity. Hydrogen bonding is shown as dotted lines.

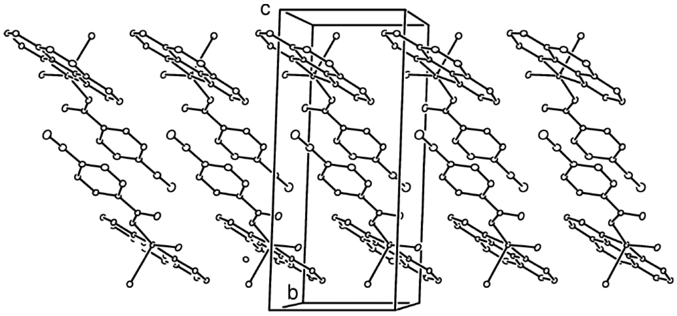


Figure 3
View of the π–π interactions between cba and 1,10-phenanthroline ligands.

A striking feature of this compound is seen in its extended structure, formed through O—H···Cl hydrogen bonding and π–π interactions (Figs. 2 and 3, respectively). The Cl atom forms hydrogen bonds with the uncoordinated water molecule, which is further linked to the Cl and a carboxylate O atom to form hydrogen bonds; thus a one-dimensional hydrogen-bonding network is formed. Stacking between cba ligands is also observed; such interactions result in a dimeric species, as shown in Fig. 3. In addition, stacking is also observed in the phen ligands, to form an extended one-dimensional chain. The interplanar distances for the two π–π interactions are approximately 3.72 and 3.42 Å.

Experimental

$CuCl_2 \cdot 2H_2O$ (0.051 g, 0.3 mmol) and Hcba (0.088 g, 0.6 mmol) were dissolved in *N,N′*-dimethylformamide (20 ml). A solution of 1,10-phenanthroline (0.059 g, 0.3 mmol) in methanol (20 ml) was added to the above solution. After about two weeks, blue crystals suitable for X-ray analysis were obtained and filtered off.

Crystal data

$[CuCl(C_8H_4NO_2)(C_{12}H_8N_2)(H_2O)] \cdot H_2O$
$M_r = 461.35$
Triclinic, $P\bar{1}$
$a = 6.5460$ (6) Å
$b = 9.4402$ (8) Å
$c = 15.6840$ (14) Å
$\alpha = 87.438$ (2)°
$\beta = 88.035$ (2)°
$\gamma = 81.046$ (2)°
$V = 956.07$ (15) Å^3
$Z = 2$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3099 reflections
$\theta = 5.2$–55.6°
$\mu = 1.32$ mm^{-1}
$T = 293$ (2) K
Plate, blue
0.42 × 0.35 × 0.32 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.382$, $T_{max} = 0.655$
5452 measured reflections
3871 independent reflections
3377 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 26.5°$
$h = -8 \rightarrow 7$
$k = -9 \rightarrow 11$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.088$
$S = 1.04$
3871 reflections
327 parameters
All H-atom paramteres refined
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0119 (16)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H13···O4^{i}	0.84 (3)	1.82 (4)	2.645 (3)	164 (3)
O3—H14···O2	0.82 (4)	1.76 (4)	2.559 (3)	163 (4)
O4—H15···Cl	0.849 (18)	2.334 (18)	3.175 (2)	171 (3)
O4—H16···Cl^{ii}	0.823 (18)	2.373 (19)	3.187 (2)	170 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, -z$.

All H atoms were refined; C—H distances are in the range 0.87 (2)–0.95 (3) Å.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

m606 Zhou *et al.* • $[CuCl(C_8H_4NO_2)(C_{12}H_8N_2)(H_2O)] \cdot H_2O$ *Acta Cryst.* (2003). E**59**, m605–m607

References

Albada, G. A. van, Komaei, S. A., Kooijman, H., Spek, A. L. & Reedijk, J. (1999). *Inorg. Chim. Acta*, **287**, 226–231.

Bruker (1997). *SMART* (Version 5.044), *SAINT* (Version 5.01) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Drickamer, H. L. & Bray, H. L. (1990). *Acc. Chem. Res.* **23**, 55–61.

He, H. Y., Ma, A. Q. & Zhu, L. G. (2003). *Acta Cryst.* E**59**, m333–m335.

He, H. Y. & Zhu, L. G. (2003). *Acta Cryst.* E**59**, o174–o176.

Ma, B. Q., Guo, S., Yi, T., Yan, C. H. & Xu, G. X. (2000). *Inorg. Chem. Commun.* **3**, 93–95.

Murphy, G., Nagle, P., Murphy, B. & Hathaway, B. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2645–2652.

O'Sullivan, C., Murphy, G., Murphy, B. & Hathaway, B. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1835–1844.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97, *SHELXS*97. University of Göttingen, Germany.

Xie, L. M., Wang, G. P., He, H. Y. & Zhu, L. G. (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 245–246.

Yuan, R. X., Xiong, R. G., Chen, Z. F., You, X. Z., Peng, S. M. & Lee, G. H. (2001). *Inorg. Chem. Commun.* **4**, 430–433.

Acta Cryst. (2003). E**59**, m605–m607 Zhou *et al.* • $[CuCl(C_8H_4NO_2)(C_{12}H_8N_2)(H_2O)]\cdot H_2O$ **m607**