Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Chloro(pyridine-4-carbonitrile-κN^1)(1,4,7-triazacyclononane-$\kappa^3 N,N',N''$)copper(II) perchlorate

Yu-Hu Wang, Zhao-Dong Wang, Bin Li, Jie Qu, Xin Liu,* Wen Gu and Wen-Zhen Wang

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail:
liuxin64@nankai.edu.cn

Received 6 April 2005
Accepted 22 April 2005
Online 14 May 2005

In the title compound, $[CuCl(C_6H_4N_2)(C_6H_{15}N_3)]ClO_4$, the central copper ion is coordinated by three N atoms from 1,4,7-triazacyclononane, one N atom from the cyanopyridine and one Cl atom, forming a square-pyramidal coordination geometry (τ = 0.31). The crystal packing is stabilized by intermolecular N—H···O and N—H···Cl hydrogen bonds.

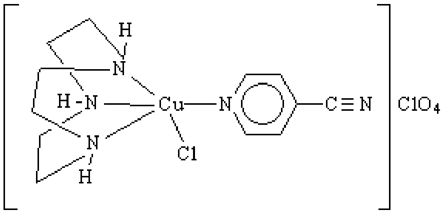
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.033
wR factor = 0.086
Data-to-parameter ratio = 15.9

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

Comment

The small macrocycle ligand 1,4,7-triazacyclononane (tacn) has a rich chemistry (Wieghardt & Chaudhuri, 1988). The interest in such ligands has recently been renewed because of their ability (depending on the nature of the pendant donors) to form metal complexes with tunable physicochemical and functional properties. These complexes have various applications as inorganic medicinal compounds (Swissler *et al.*, 1993), anion or molecular receptors (Wieghardt *et al.*, 1985), catalysts for organic transformations (Hanke *et al.*, 1993; Geilenkirchen *et al.*, 1994), molecular sensors (Xiaoping *et al.*, 1995), and mimics for enzymes catalyzing redox (Diril *et al.*, 1989) and hydrolytic processes (Behle *et al.*, 1995). In this paper, we report the synthesis and crystal structure of the title compound, (I).



(I)

The asymmetric unit of the title compound consists of a $[Cu(tacn)(C_6H_4N_2)Cl]^+$ cation and a ClO_4^- anion. All bond lengths and angles are normal (Table 1). The central copper ion shows a distorted square-pyramidal coordination geometry (Fig. 1) formed by three N atoms from tacn, one N atom from 4-cyanopyridine and one Cl atom. The coordination bond angles deviate from the ideal angles. The Cu^{II} complex has a τ value of 0.31 (Addison *et al.*, 1984; Brophy *et al.* 1999), indicating a substantial distortion towards trigonal bipyramidal geometry. The crystal packing is stabilized by intermolecular N—H···O and N—H···Cl hydrogen bonds (Table 2).

Experimental

To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) in methanol (10 ml), methanol (10 ml) containing tacn·3HCl (0.165 g, 1 mmol;

Searl & Geue, 1984) and NaOH (0.120 g, 3 mmol) was added. 4-Cyanopyridine (0.104 g 1 mmol) was added, with stirring for 3 h, and the mixture was filtered. The filtrate was allowed to evaporate slowly in the open atmosphere. After a few days, dark-blue block crystals suitable for X-ray crystallography were obtained. Yield 75%. Analysis calculated for $C_{12}H_{19}C_{12}CuN_5O_4$: C 33.38, H 4.44, N 16.22%; found: C 34.20, H 4.16, N 15.43%.

Crystal data

$[CuCl(C_6H_4N_2)(C_6H_{15}N_3)]ClO_4$
$M_r = 431.77$
Triclinic, $P\overline{1}$
$a = 7.656$ (3) Å
$b = 10.707$ (5) Å
$c = 10.933$ (5) Å
$\alpha = 73.065$ (6)°
$\beta = 84.573$ (7)°
$\gamma = 86.058$ (7)°
$V = 852.7$ (7) Å^3
$Z = 2$
$D_x = 1.682$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 819 reflections
$\theta = 3.3$–26.3°
$\mu = 1.62$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.24 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.621$, $T_{\max} = 0.771$
4946 measured reflections
3453 independent reflections
2822 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 26.4°$
$h = -8 \rightarrow 9$
$k = -13 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.086$
$S = 1.02$
3453 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.5194P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	2.017 (2)	Cu1—N3	2.195 (2)
Cu1—N4	2.032 (2)	Cu1—Cl1	2.2658 (10)
Cu1—N1	2.101 (2)		
N2—Cu1—N4	174.01 (9)	N3—Cu1—Cl1	120.56 (7)
N2—Cu1—N1	82.99 (9)	C6—N1—Cu1	104.89 (18)
N4—Cu1—N1	92.22 (9)	C1—N1—Cu1	109.61 (17)
N2—Cu1—N3	82.77 (9)	C2—N2—Cu1	105.13 (16)
N4—Cu1—N3	100.23 (9)	C3—N2—Cu1	112.33 (17)
N1—Cu1—N3	82.53 (9)	C5—N3—Cu1	108.40 (17)
N2—Cu1—Cl1	90.25 (7)	C4—N3—Cu1	101.57 (17)
N4—Cu1—Cl1	92.63 (7)	C7—N4—Cu1	120.00 (19)
N1—Cu1—Cl1	155.03 (7)	C11—N4—Cu1	122.15 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.91	2.39	3.234 (3)	154
N2—H2···O1^{ii}	0.91	2.33	3.181 (4)	156
N3—H3···Cl1^{iii}	0.91	2.63	3.420 (3)	146

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y, z-1$; (iii) $-x, -y+2, -z$.

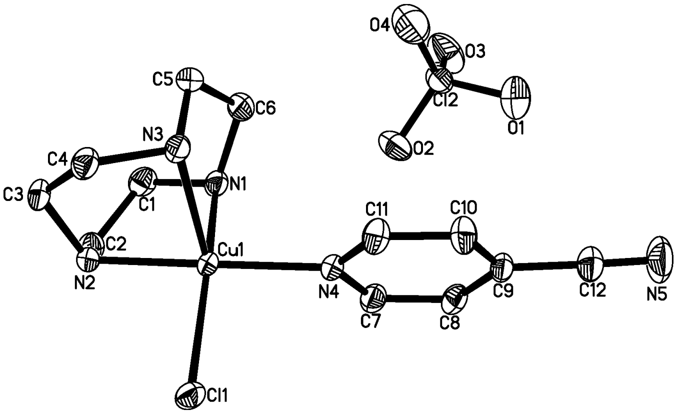


Figure 1
The asymmetric unit of the title compound, with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.2–1.5$U_{\rm eq}$(parent atom).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

This work was supported by the NNSF of China (Nos. 20071020 and 20371027).

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Behle, L., Neuburger, M., Zehnder, M. & Kaden, T. A. (1995). *Helv. Chim. Acta*, **78**, 693–702.

Brophy, M., Murphy, G., Sullivan, C. O., Hathaway, B. & Murphy, B. (1999). *Polyhedron*, **18**, 611–615.

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

Diril, H., Chang, H., Nilges, M. J., Zhang, X., Potenza, J. A., Schugar, H. J., Isied, S. S. & Hendrickson, D. N. (1989). *J. Am. Chem. Soc.* **111**, 5102–5114.

Geilenkirchen, A., Neubold, P., Schneider, R., Wieghardt, K., Flörke, U., Haupt, H. & Nuber, B. (1994). *J. Chem. Soc. Dalton Trans.* pp. 457–464.

Hanke, D., Wieghardt, K., Nuber, B., Lu, R., McMullan, R. K., Koetzle, T. F. & Bau, R. (1993). *Inorg. Chem.* **32**, 4300–4305.

Searl, G. H. & Geue, R. J. (1984). *Aust. J. Chem.* **37**, 959–970.

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

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Swissler, J. L., Sibert, J. W., Burrell, A. K. & Lynch, V. (1993). *Inorg. Chem.* **32**, 4277–4283.

Wieghardt, K. & Chaudhuri, P. (1988). *Progress in Inorganic Chemistry*, edited by S. J. Lippard, pp. 329–330. New York: Wiley.

Wieghardt, K., Tolksdorf, I. & Herrmann, W. (1985). *Inorg. Chem.* **24**, 1230–1235.

Xiaoping, Z., Hsieh, W., Margulis, T. N. & Zompa, L. J. (1995). *Inorg. Chem.* **34**, 2883–2888.

m1102 Wang *et al.* • $[CuCl(C_6H_4N_2)(C_6H_{15}N_3)]ClO_4$ *Acta Cryst.* (2005). E**61**, m1101–m1102