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Di-μ-chloro-bis[(2,2′:6,2″-terpyridine-κ^3N)-copper(II)] diperchlorate: the triclinic polymorph

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The title compound, $[Cu_2Cl_2(C_{15}H_{11}N_3)_2](ClO_4)_2$, crystallized from water as the triclinic polymorph. There are two independent centrosymmetric binuclear dications, $[Cu_2(\text{terpyridine})_2Cl_2]^{2+}$, and four perchlorate anions per unit cell. Each Cu atom has a distorted square-pyramidal geometry. In the crystal structure, the cations are bridged by the perchlorate anions *via* C—H···O hydrogen bonds, thereby forming a three-dimensional network.

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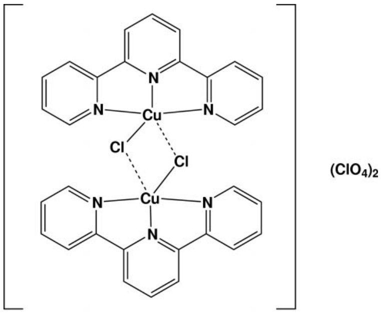
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.015 Å
R factor = 0.068
wR factor = 0.185
Data-to-parameter ratio = 12.9

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

Comment

On addition of $NaClO_4$ to an aqueous solution of $CuCl_2$ and terpyridine, pale blue needle-like crystals appeared after a few hours. Their structure (Fig. 1) was revealed to be the triclinic polymorph of the title compound, (I). There are two independent centrosymmetric binuclear dications per unit cell. Selected bond distances and angles are given in Table 1. The structure analysis of the monoclinic polymorph of (I), obtained from an acteonitrile solution, was recently reported by Valdés-Martínez *et al.* (2002). The overall structures are very similar, but the length of the apical Cu—Cl bond is slightly different. The average distance in the triclinic polymorph is 2.747 (1) Å, compared to 2.698 (2) Å in the monoclinic polymorph. Both Cu atoms have a distorted square-pyramidal geometry, with τ values (Addison *et al.*, 1984) of 0.31 and 0.32 for Cu1 and Cu2, respectively. This is slightly more distorted than in the monoclinic polymorph, where the τ value is 0.27.



(I)

The crystal packing of the triclinic polymorph of (I) is illustrated in Fig. 2. It can be seen that there are no π–π interactions, as were found in the monoclinic polymorph. The cations are bridged by a number of C—H···O(perchlorate) hydrogen bonds; see Table 2. In this way, the molecules are linked to form a three-dimensional network.

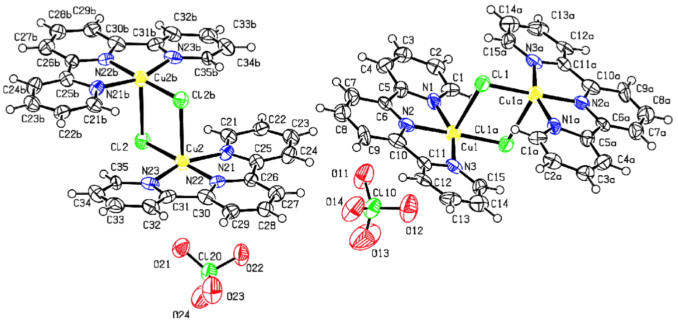


Figure 1

View of the triclinic polymorph of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The two symmetry-related perchlorate anions have been omitted for clarity.

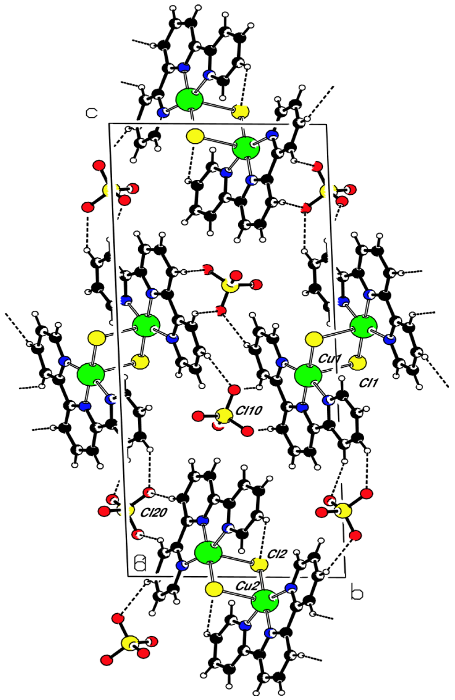


Figure 2

The molecular packing of the triclinic polymorph of (I), viewed down the *a* axis. C—H···O and C—H···Cl hydrogen bonds are shown as dashed lines. Details are given in Table 2.

Experimental

$CuCl_2 \cdot 2H_2O$ (90.7 mg, 0.532 mmol) and 2,2′:6,2″-terpyridine (0.123 g, 0.517 mmol) were dissolved in water (20 ml) and heated to 353 K for 1 h. The terpyridine (terpy) progressively dissolved giving a green solution. After hot filtration $NaClO_4 \cdot H_2O$ (0.25 g, 2.04 mmol) were added to the filtrate at room temperature. Pale-blue needle-like crystals appeared rapidly (more if the mother liquor was kept in the refrigerator). Crystals suitable for X-ray analysis were obtained by recrystallization from hot water. Yield: 93.9 mg (42%). ESI MS *m/z*: 332 ([Cu(terpy)Cl]$^+$), 296 ([Cu(terpy)]$^+$). IR (KBr disc, cm^{-1}): 3435 (*m*), 3080 (*w*), 2963 (*w*), 1630 (*w*), 1600 (*m*), 1578 (*m*), 1499 (*w*), 1475 (*w*), 1447 (*m*), 1408 (*w*), 1384 (*w*), 1329 (*w*), 1303 (*w*), 1290 (*w*), 1262 (*m*), 1185 (*w*), 1167 (*w*), 1099 (*s*), 1083 (*s*), 1050 (*m*), 1020 (*s*), 872 (*w*), 800 (*m*), 787 (*m*), 732 (*w*), 672 (*w*), 649 (*w*), 621 (*m*), 515 (*m*), 439 (*w*), 409 (*w*). Analysis calculated for $C_{30}H_{22}Cl_4Cu_2N_6O_8$ (%): C 41.71, H 257, N 977; found (%): C 41.52, H 254, N 9.69.

Crystal data

$[Cu_2Cl_2(C_{15}H_{11}N_3)_2](ClO_4)_2$
$M_r = 863.42$
Triclinic, $P\bar{1}$
$a = 6.9905$ (8) Å
$b = 9.8696$ (11) Å
$c = 23.782$ (2) Å
$\alpha = 91.431$ (13)°
$\beta = 93.524$ (13)°
$\gamma = 102.678$ (14)°
$V = 1596.6$ (3) Å^3
$Z = 2$
$D_x = 1.796$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6421 reflections
$\theta = 2.2$–25.8°
$\mu = 1.73$ mm^{-1}
$T = 153$ (2) K
Needle, pale blue
0.50 × 0.05 × 0.05 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: refined from ΔF (*DIFABS* in *PLATON*; Spek, 1990)
$T_{min} = 0.250$, $T_{max} = 0.917$
12643 measured reflections
5819 independent reflections
2512 reflections with $I > 2\sigma(I)$
$R_{int} = 0.100$
$\theta_{max} = 26.0°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.185$
$S = 0.97$
5819 reflections
451 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.932 (8)	Cu2—N22	1.944 (8)
Cu1—N3	2.017 (8)	Cu2—N21	2.018 (8)
Cu1—N1	2.033 (8)	Cu2—N23	2.028 (8)
Cu1—Cl1^i	2.218 (3)	Cu2—Cl2	2.226 (3)
Cu1—Cl1	2.751 (3)	Cu2—Cl2^{ii}	2.743 (3)
N2—Cu1—N3	81.3 (4)	N22—Cu2—N21	79.3 (3)
N2—Cu1—N1	79.3 (3)	N22—Cu2—N23	81.2 (3)
N3—Cu1—N1	159.9 (3)	N21—Cu2—N23	159.6 (3)
N2—Cu1—Cl1^i	178.5 (2)	N22—Cu2—Cl2	178.8 (2)
N3—Cu1—Cl1^i	98.9 (3)	N21—Cu2—Cl2	100.5 (2)
N1—Cu1—Cl1^i	100.3 (2)	N23—Cu2—Cl2	98.9 (2)
N2—Cu1—Cl1	92.9 (2)	N22—Cu2—Cl2^{ii}	92.6 (2)
N3—Cu1—Cl1	87.7 (2)	N21—Cu2—Cl2^{ii}	97.1 (2)
N1—Cu1—Cl1	98.9 (2)	N23—Cu2—Cl2^{ii}	89.9 (2)
Cl1^i—Cu1—Cl1	88.55 (9)	Cl2—Cu2—Cl2^{ii}	88.56 (9)
Cu1^i—Cl1—Cu1	91.45 (9)	Cu2—Cl2—Cu2^{ii}	91.44 (9)
N1—C5—C6—N2	0.8 (12)	N21—C25—C26—N22	−2.5 (12)
N2—C10—C11—N3	−4.2 (12)	N22—C30—C31—N23	7.9 (12)

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

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···O22^{iii}	0.95	2.47	3.316 (14)	149
C9—H9*A*···O11^{iv}	0.95	2.37	3.309 (14)	172
C12—H12*A*···O12^{iv}	0.95	2.42	3.172 (14)	137
C13—H13*A*···O12^{v}	0.95	2.37	3.160 (15)	140
C29—H29*A*···O22^{iv}	0.95	2.48	3.421 (13)	170
C32—H32*A*···O21^{iv}	0.95	2.47	3.254 (13)	140
C33—H33*A*···O21^{vi}	0.95	2.46	3.194 (14)	134

Symmetry codes: (iii) $1 + x, 1 + y, z$; (iv) $x - 1, y, z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $-x, -y, -z$.

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All the H atoms, initially located in difference Fourier maps, were included in calculated positions and treated as riding atoms using *SHELXL*97 (Sheldrick, 1997) default parameters. The C—H distances were fixed at 0.95 Å and $U_{\rm iso}$(H) values were fixed at 1.2 times $U_{\rm eq}$(C).

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*99 (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschor. G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Stoe & Cie (2000). *IPDS Software*, Stoe & Cie GmbH, Darmstadt, Germany.
Valdés-Martínez. J., Salazar-Mendoza, D. & Toscano, R. A. (2002). *Acta Cryst.* E**58**, m712–m714.

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