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μ-Terephthalato-bis[aquachloro(1,10-phenanthroline)copper(II)] μ-terephthalato-bis[diaqua(1,10-phenanthroline)cuprate(II)] dichloride dihydrate

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In the title compound, $[Cu_2Cl_2(C_8H_4O_4)(C_{12}H_8N_2)_2(H_2O)_2]\cdot[Cu_2(C_8H_4O_4)(C_{12}H_8N_2)_2(H_2O)_4]Cl_2\cdot 2H_2O$, each Cu atom has a distorted square-pyramidal geometry, but the coordination environments of the two independent Cu centres (Cu1 and Cu2) are very different. Atom Cu1 is surrounded by an O atom from a terephthalate dianion, an aqua O atom, a Cl atom and two N atoms from a 1,10-phenanthroline ligand. Atom Cu2 is surrounded by an O atom from a terephthalate dianion, two aqua O atoms and two N atoms from a 1,10-phenanthroline ligand. The terephthalate dianions, which function as bridges between the cationic and neutral complexes, lie on inversion centres.

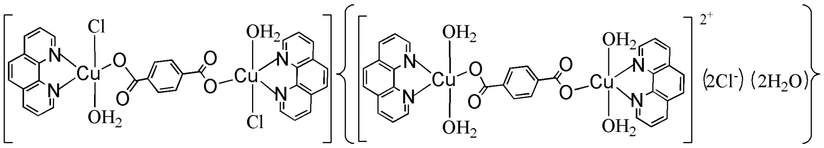
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.069
wR factor = 0.149
Data-to-parameter ratio = 12.2

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

Comment

Among the metal complexes of terephthalic acid (H_2ta) (Cano *et al.*, 1997; Groeneman & Atwood, 1999; Liu *et al.*, 2004; Otto & Wheeler, 2001), the copper–phenanthroline (phen) system has been well studied; the compounds structurally documented include, for example, two dinuclear complexes, *viz.* $[Cu_2(ta)(phen)_4](ClO_4)_2$ and $[Cu_2Cl_2(ta)(phen)_2(H_2O)_2]$, and three polymeric complexes, *viz.* [Cu(ta)(phen)], $[Cu(ta)(phen)(H_2O)]$ and $[Cu(ta)(phen)(H_2O)](H_2O)(DMF)$ (Sun *et al.*, 2000, 2001; Xiao *et al.*, 2004; Zhu *et al.*, 2004). Moreover, it should be pointed out that new complexes are constantly being obtained through different reactions, such as the use of different solvents, synthesis conditions or H-atom acceptors. The title compound, $[Cu_2Cl_2(ta)(phen)_2(H_2O)_2]\cdot[Cu_2(ta)(phen)_2(H_2O)_4]Cl_2\cdot 2H_2O$, (I), is an example that is very different from the previous structures in the Cu^{2+}/phen/H_2ta system.



(I)

The unit cell of (I) contains a $[Cu_2Cl_2(ta)(phen)_2(H_2O)_2]$ neutral molecule, a $[Cu_2(ta)(phen)_2(H_2O)_4]^{2+}$ cation, two Cl^- anions and two water molecules (Fig. 1), with the terephthalate moiety of the two complexes lying on different inversion centres. Each Cu atom has a distorted square-pyramidal geometry, but the coordination environments of the two independent Cu centres (Cu1 and Cu2) are very different. Atom Cu1 is surrounded by an O atom from a terephthalate dianion, an aqua O atom, a Cl atom and two N atoms from a 1,10-phenanthroline ligand, similar to the coordination of the

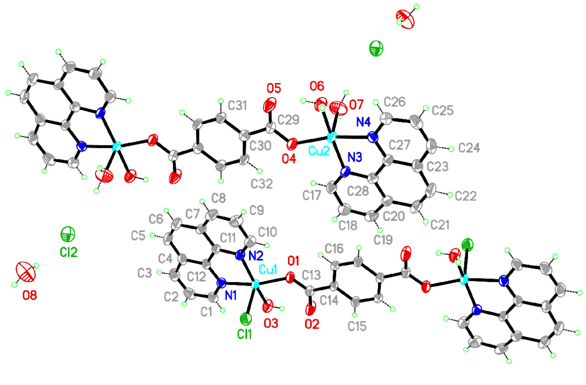


Figure 1

The coordination environment of Cu1 and Cu2 in (I), showing the atomic numbering for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

Cu atom in $[Cu_2Cl_2(ta)(phen)_2(H_2O)_2]$ (Xiao *et al.*, 2004). Atom Cu2 is surrounded by an O atom from a terephthalate dianion, two aqua O atoms and two N atoms from a 1,10-phenanthroline ligand. The terephthalate dianions, which function as bridges between two Cu atoms in the cationic and neutral complexes, lie on inversion centres. If atoms Cl1, Cl2, O7 and O8 are omitted, then there exists an approximate pseudo-inversion plus translational symmetry between the two complexes.

Along the *a* axis, the $[Cu_2Cl_2(ta)(phen)_2(H_2O)_2]$ molecules and $[Cu_2(ta)(phen)_2(H_2O)_4]^{2+}$ cations independently form one-dimensional chain structures through π–π interactions between 1,4-benzenedicarboxylate and 1,10-phenanthroline ligands. The centroid–centroid distance between the benzene rings of 1,4-benzenedicarboxylate and 1,10-phenanthroline moieties is 3.498 (3) Å for the neutral complex and 3.577 (3) Å for the cationic complex. In addition to electrostatic and π–π interactions, O—H···O and O—H···Cl interactions (Table 2) are involved in the formation of a three-dimensional network structure.

Experimental

A solution (10 ml) of dimethylformamide containing $Cu_2Cl_2{\cdot}2H_2O$ (0.5 mol, 0.085 g) and terephthalic acid (0.5 mmol, 0.083 g) was added slowly to a solution (10 ml) of methanol containing 1,10-phenanthroline (0.5 mmol, 0.099 g). The mixture was stirred for a few minutes and left to stand at room temperature for about three weeks, after which blue crystals were obtained.

Crystal data

$[Cu_2Cl_2(C_8H_4O_4)(C_{12}H_8N_2)_2(H_2O)_2]{\cdot}[Cu_2(C_8H_4O_4)(C_{12}H_8N_2)_2(H_2O)_4]Cl_2{\cdot}2H_2O$
$M_r = 1589.13$
Triclinic, $P\overline{1}$
$a = 9.5319\ (8)$ Å
$b = 10.1713\ (9)$ Å
$c = 16.4797\ (14)$ Å
$\alpha = 85.428\ (1)^\circ$
$\beta = 80.718\ (1)^\circ$
$\gamma = 79.379\ (1)^\circ$
$V = 1547.7\ (2)$ Å^3
$Z = 1$
$D_x = 1.705$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3302 reflections
$\theta = 2.4$–25.0°
$\mu = 1.61$ mm^{-1}
$T = 298\ (2)$ K
Prism, blue
0.25 × 0.13 × 0.07 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.689$, $T_{max} = 0.896$
11 533 measured reflections
5573 independent reflections
5088 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.3^\circ$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.149$
$S = 1.24$
5573 reflections
457 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 2.9111P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—O3	1.960 (4)	Cu2—O6	1.942 (4)
Cu1—O1	1.972 (3)	Cu2—O4	1.961 (3)
Cu1—N2	2.009 (4)	Cu2—N3	1.996 (4)
Cu1—N1	2.026 (4)	Cu2—N4	2.016 (4)
Cu1—Cl1	2.5897 (14)	Cu2—O7	2.345 (4)
O3—Cu1—O1	93.31 (14)	O6—Cu2—O4	93.88 (14)
O3—Cu1—N2	163.52 (16)	O6—Cu2—N3	170.93 (16)
O1—Cu1—N2	91.92 (14)	O4—Cu2—N3	91.51 (15)
O3—Cu1—N1	89.47 (15)	O6—Cu2—N4	91.19 (15)
O1—Cu1—N1	165.52 (15)	O4—Cu2—N4	168.80 (15)
N2—Cu1—N1	81.74 (16)	N3—Cu2—N4	82.27 (16)
O3—Cu1—Cl1	101.20 (12)	O6—Cu2—O7	94.65 (16)
O1—Cu1—Cl1	92.35 (11)	O4—Cu2—O7	89.57 (16)
N2—Cu1—Cl1	94.18 (12)	N3—Cu2—O7	92.67 (16)
N1—Cu1—Cl1	101.06 (12)	N4—Cu2—O7	99.97 (17)
C13—O1—Cu1	126.2 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O8^{i}	0.813 (19)	1.88 (3)	2.658 (6)	160 (6)
O3—H3*B*···O2	0.818 (19)	1.70 (2)	2.508 (5)	169 (7)
O6—H6*A*···Cl2^{ii}	0.833 (19)	2.22 (2)	3.034 (4)	166 (6)
O6—H6*B*···O5	0.839 (19)	1.72 (3)	2.523 (5)	160 (6)
O7—H7*A*···Cl2^{iii}	0.837 (19)	2.52 (2)	3.351 (4)	173 (7)
O7—H7*B*···Cl1^{iv}	0.83 (2)	2.624 (19)	3.447 (5)	173 (5)
O8—H8*A*···Cl2	0.83 (2)	2.46 (3)	3.250 (5)	159 (6)
O8—H8*B*···Cl1^{v}	0.83 (2)	2.45 (3)	3.262 (5)	168 (7)

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

The water H atoms were located and refined subject to the restraints O—H = 0.82 (2) Å and H···H 1.39 (1) Å, and with $U_{iso} = 1.5U_{eq}(O)$. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å and with $U_{iso} = 1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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