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catena-Poly[[[di-μ-chloro-bis[(5-nitro-1,10-phenanthroline)copper(II)]]-μ-terephthalato] bis(*N*,*N*′-dimethylformamide)]

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Key indicators

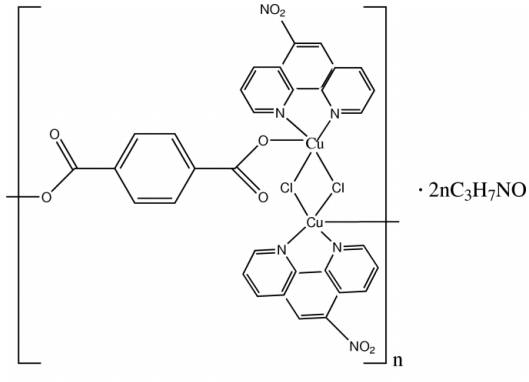
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Some non-H atoms missing
R factor = 0.049
wR factor = 0.124
Data-to-parameter ratio = 13.1

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

In the structure of the title complex, $\{[Cu_2Cl_2(C_8H_4O_4)(C_{12}H_7N_3O_2)_2]\cdot 2C_3H_7NO\}_n$, each copper cation is surrounded by one O atom from a terephthalate (ta) ligand, two bridging Cl atoms, and two N atoms from a 5-nitro-1,10-phenanthroline ligand. Dimeric blocks of $[Cu_2(C_{12}H_7N_3O_2)_2(ta)]$ are held together by two μ-chloro bridges, which create a one-dimensional architecture. There is a center of symmetry halfway between the two Cu atoms and the two Cl atoms and at the center of the phenyl ring of the ta group.

Comment

A study of the structural diversity of coordination polymers is an important strategy for the design and construction of novel networks with functional properties (Dey *et al.*, 2002*a*,*b*; Vaidhlanathan *et al.*, 2001). For example, the Cu^{2+}/1,10-phenanthroline (phen)/terephthalic acid (H_2ta) system has been explored and at least four species have been synthesized, a dimeric complex, $[Cu_2(ta)(phen)_4](ClO_4)_2$, and three polymeric complexes, [Cu(ta)(phen)], Cu(ta)(phen)(H_2O), and Cu(ta)(phen)(H_2O)(DMF) (Sun *et al.*, 2000, 2001). We present here the first crystal structure of a copper(II) complex with both terephthalate and chloro bridges, where phen is replaced by 5-nitro-1,10-phenanthroline (nphen) in the Cu^{2+}/phen/H_2ta system.



(I)

In the title complex, (I), each Cu atom is in a distorted square-pyramidal geometry (Fig. 1). The basal plane (O1, N1, N2 and Cl) consists of two nphen N atoms, one carboxylate O atom from the ta ligand, and one chloro bridge. The apical position is filled by the other Cl atom as a bridge, the corresponding axial bond distance [2.7247 (10) Å] being longer than the equatorial Cu—Cl bond distance [2.2781 (9)°]. The distance for the apical Cu—Cl bridge in (I) is in the range found for di-μ-chloro-dicopper(II) complexes (Molina *et al.*, 1999; Wang *et al.*, 2001; West *et al.*, 2001; Zurowska &

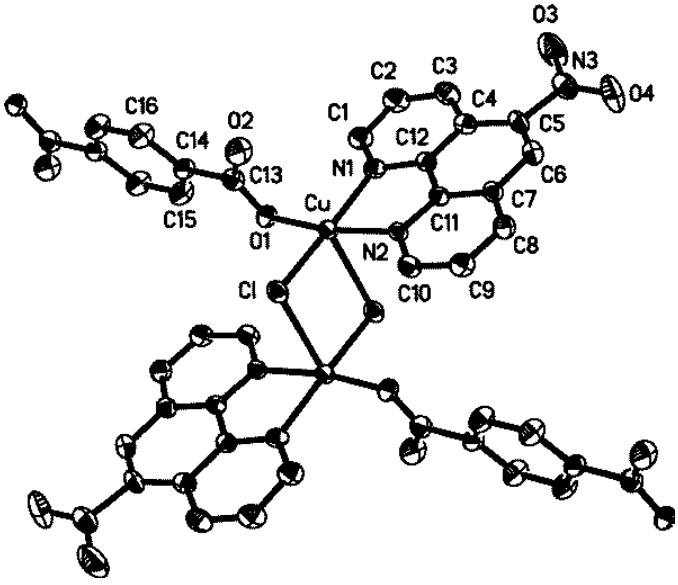


Figure 1
ORTEP-3 diagram (Farrugia, 1997) showing a section of the one-dimensional chain of (I). DMF molecules and H atoms have been omitted. Displacement ellipsoids are drawn at the 30% probability level and only atoms of the asymmetric unit are labeled.

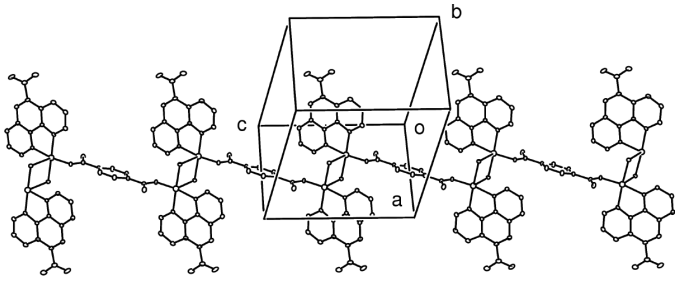


Figure 2
View of the one-dimensional chain of (I).

Mrozinski, 2003). The basal plane is roughly perpendicular to the plane of the phenyl ring of the terephthalate; the dihedral angle is 80.00 (12) Å. The ta dianion binds two copper(II) ions in a bis-monodentate mode. The Cu1—O1 bond length is 1.928 (2) Å and is in agreement with analogous literature distances in copper complexes with a bis-monodentate terephthalate ligand (Li *et al.*, 2001*a*,*b*; Sun *et al.*, 2001; Xanthopoulos *et al.*, 1993; Verdaguer *et al.*, 1984). The dimeric units of $[Cu_2(nphen)_2(ta)]$ in the structure are linked by Cl atoms and the one-dimensional zigzag network is as expected. The intrachain Cu···Cu distances through the chloro bridges and the terephthalate bridge are 3.47 (1) and 10.97 (1) Å, respectively. The shortest interchain Cu···Cu separation is 6.92 (1) Å.

Experimental

The title complex was synthesized, in a narrow tube, by a layered-solution method. The upper layer was 6 ml of a methanol solution of 5-nitro-1,10-phenanthroline (nphen, 0.06 mol l^{-1}). The bottom layer was 6 ml of an *N*,*N*′-dimethylformamide (DMF) solution of $CuCl_2{\cdot}2H_2O$ (0.05 mol l^{-1}) and H_2ta (0.05 mol l^{-1}). The middle layer was 4 ml of of DMF and methanol in a 1:1 volume ratio. After three weeks, green crystals of (I) were obtained by filtration. Elemental analysis for (I): C 47.60, H 3.36, N 11.60%; found: C 47.64, H 3.42, N 11.32%.

Crystal data

$[Cu_2Cl_2(C_8H_4O_4)(C_{12}H_7N_3O_2)_2]{\cdot}2C_3H_7NO$
M_r = 958.7
Triclinic, $P\overline{1}$
a = 9.4185 (11) Å
b = 10.2030 (12) Å
c = 12.3617 (15) Å
α = 106.223 (2)°
β = 93.856 (2)°
γ = 116.698 (2)°
V = 993.0 (2) Å^3
Z = 1
D_x = 1.603 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2222 reflections
θ = 4.8–53.3°
μ = 1.27 mm^{-1}
T = 293 (2) K
Needle, green
0.53 × 0.39 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.04, T_{max} = 0.786
5614 measured reflections
4022 independent reflections
3093 reflections with $I > 2\sigma(I)$
R_{int} = 0.086
θ_{max} = 26.5°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.124
S = 0.96
4022 reflections
308 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.928 (2)	Cu—Cl	2.2781 (9)
Cu—N2	2.031 (3)	Cu—Cl^{i}	2.7248 (11)
Cu—N1	2.042 (3)		
O1—Cu—N2	171.33 (10)	O1—Cu—Cl^{i}	95.33 (8)
O1—Cu—N1	92.19 (11)	N2—Cu—Cl^{i}	88.71 (8)
N2—Cu—N1	79.82 (11)	N1—Cu—Cl^{i}	94.63 (8)
O1—Cu—Cl	93.53 (8)	Cl—Cu—Cl^{i}	92.59 (3)
N2—Cu—Cl	93.95 (8)	Cu—Cl—Cu^{i}	87.41 (3)
N1—Cu—Cl	170.34 (8)		

Symmetry code: (i) $1-x, -y, 1-z$.

H atoms bonded to the C atoms of the terephthalate and 5-nitro-1,10-phenanthroline rings were located from difference Fourier maps and refined isotropically. All H atoms of the DMF molecules were placed in calculated positions using a riding-model approximation, with C—H distances of 0.93 Å for O═C—H and 0.96 Å for methyl H atoms [U_{iso}(H) = 1.2(CH) or 1.5(CH_3) times U_{eq}(parent atom)].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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