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Key indicators

Bis[4-(dimethylamino)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-$\kappa^2 S,S'$)cuprate(II)

In the title salt $(C_7H_{11}N_2)_2[Cu(C_4N_2S_2)_2]$, the Cu^{2+} ion is coordinated by four S atoms of two 1,2-dicyanoethene-1,2-dithiolate (or maleonitriledithiolate, mnt^{2-}) ligands in an approximate square-planar geometry. The Cu atom is located on an inversion centre. Strong hydrogen-bonding interactions between the pyridinium proton and the CN groups of the mnt^{2-} ligand link anions and cations into a one-dimensional chain structure.

Comment

Over the past two decades, studies of intermolecular non-covalent interactions, such as hydrogen-bonding and π–π stacking interactions, in materials science (Saadeh *et al.*, 2000; Lawrence *et al.*, 1999) have yielded materials that exhibit novel properties (Gardner *et al.*, 1995; Venkataraman *et al.*, 1995; Yaghi *et al.*, 1995). Recently, we have been studying supramolecular self-assembly *via* hydrogen-bonding interactions between $[M(mnt)_2]^{n-}$ (M = Ni^{3+} and $n = 1$; M = Zn^{2+} and $n = 2$; mnt is maleonitriledithiolate or 1,2-dicyanoethene-1,2-dithiolate) and pyridinium derivatives (Ren, Chen *et al.*, 2002; Ren, Lu *et al.*, 2002; Ren, Xie *et al.*, 2003) and in this communication we report the crystal structure of [4-Me$_2$NpyH]$_2$[Cu(mnt)$_2$], (I).


(I)
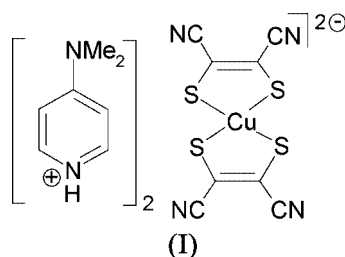
The asymmetric unit of (I) is composed of one 4-Me$_2$NpyH$^+$ monovalent cation and one half-[Cu(mnt)$_2$]$^{2-}$ dianion (Fig. 1). In the anion, the Cu^{2+} ion occupies an inversion centre and is coordinated by four S atoms of two mnt^{2-} ligands, forming a square-planar CuS$_4$ geometry. The Cu—S distances and the internal chelating S—Cu—S angle (Table 1) are in agreement with those observed for other [Cu(mnt)$_2$]$^{2-}$ compounds (Ren, Ma *et al.*, 2003). In the cation, the dimethylamine group is almost coplanar with the pyridine ring, with a dihedral angle between the pyridine ring and the C10/N4/C11 plane of 4.7 (6)°.

The cations and anions are linked by bifurcated hydrogen-bonding interactions to form a one-dimensional chain along the *b* axis of the crystallographic unit cell (Fig. 2). The hydrogen-bonding parameters are listed in Table 2. Within
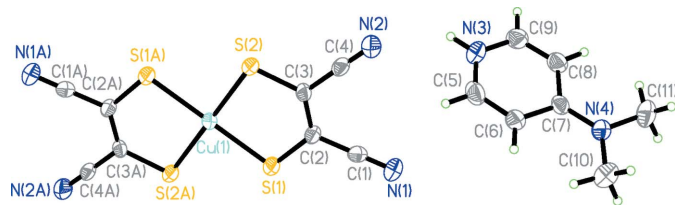
Figure 1
The structure of (I), showing 50% probability displacement ellipsoids for the non-H atoms, with the atom-numbering scheme. [Symmetry code: (A) $2 - x, -y, -z$].
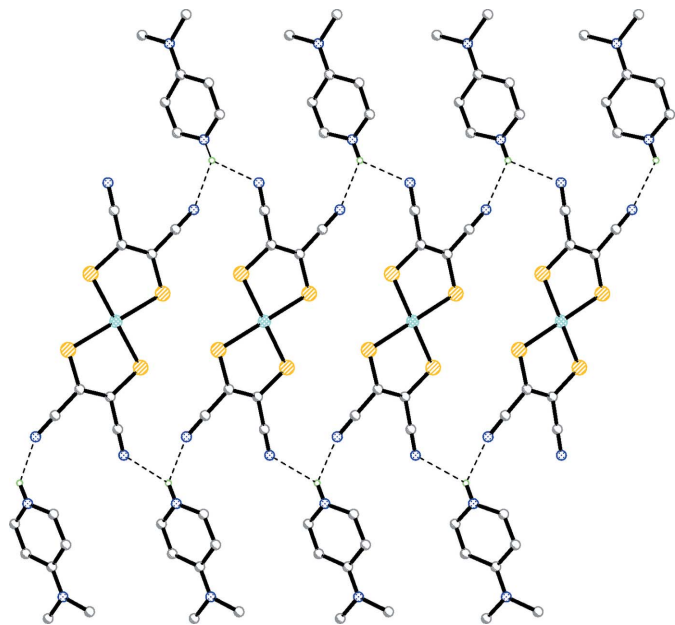
Figure 2
One-dimensional chain of cations and anions formed by hydrogen-bond interactions (dashed lines). H atoms not involved in the interactions shown have been omitted.

each chain, the shortest interatomic distances are 3.793 (2) Å for S1···S2($x, y - 1, z$), 4.4383 (16) Å for Cu1···S2 ($x, y - 1$, z) and 6.0279 (11) Å for Cu1···Cu1($x, y - 1, z$).

Experimental

Disodium maleonitriledithiolate (Na₂mnt) was prepared following the literature procedure (Davison & Holm, 1967). 4-Dimethylaminopyridinium chloride was prepared by the reaction between 4-dimethylaminopyridine and 1 equivalent of dilute hydrochloride acid. A methanol solution (10 ml) of Na₂mnt (374 mg, 2.0 mmol) was mixed with a methanol solution (5 ml) of CuCl₂·2H₂O (171 mg, 1.0 mmol); the mixture was stirred for 10 min at room temperature and filtered. A brown microcrystalline precipitate of (I) formed after addition of a methanol solution (10 ml) containing 4-dimethylaminopyridinium chloride (398 mg, 2.5 mmol) to the filtrate. The solid was filtered off, washed with methanol and then dried in vacuum. Yield 680 mg. Well shaped brown single crystals suitable for X-ray analysis were obtained by diffusing diethyl ether into an acetonitrile solution of the complex for 4 d.

Crystal data

(C₇H₁₁N₂)₂[Cu(C₄N₂S₂)₂]	$Z = 2$
$M_r = 590.26$	$D_x = 1.568$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.271$ (2) Å	$\mu = 1.24$ mm^{-1}
$b = 6.0279$ (11) Å	$T = 293$ (2) K
$c = 17.236$ (3) Å	Thick needle, brown
$\beta = 101.219$ (4)°	$0.20 \times 0.10 \times 0.10$ mm
$V = 1250.5$ (4) Å³	

Data collection

Bruker SMART CCD area-detector diffractometer	5947 measured reflections
φ and ω scans	2196 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	1588 reflections with $I > 2\sigma(I)$
$T_{min} = 0.847$, $T_{max} = 0.901$	$R_{int} = 0.124$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.061$	$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2]$
$wR(F^2) = 0.138$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2196 reflections	$\Delta\rho_{max} = 0.78$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—S2	2.2613 (14)	Cu1—S1	2.2770 (14)
S2—Cu1—S2^i	180	S2^i—Cu1—S1	89.20 (5)
S2—Cu1—S1	90.80 (5)	S1—Cu1—S1^i	180

Symmetry code: (i) $-x + 2, -y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2	0.86	2.29	2.964 (7)	136
N3—H3A···N1^{ii}	0.86	2.54	3.151 (7)	129

Symmetry code: (ii) $x, y + 1, z$.

All H atoms were placed in geometrically calculated positions (C—H = 0.93 and 0.96 Å, and N—H = 0.86 Å), with U_{iso} = $1.2U_{eq}$(C$_{aromatic}$,N) or $1.5U_{eq}$(C$_{methyl}$).

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXTL.

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