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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
Disorder in main residue  
 $R$  factor = 0.041  
 $wR$  factor = 0.088  
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## The bis(maleonitriledithiolato)zincate(II) complex of the monoprotonated 4,4'-bipyridine cation

In the title salt,  $(\text{C}_{10}\text{H}_9\text{N}_2)_2[\text{Zn}(\text{C}_4\text{N}_2\text{S}_2)_2]\cdot\text{C}_2\text{H}_3\text{N}$  or  $[\text{4,4'-bipyH}][\text{Zn}(\text{mnt})_2]\cdot\text{C}_2\text{H}_3\text{N}$ , where  $\text{mnt}^{2-}$  denotes maleonitriledithiolate and 4,4'-bipyH is monoprotonated 4,4'-bipyridine, the  $\text{Zn}^{\text{II}}$  ion is tetrahedrally surrounded by four S atoms of two  $\text{mnt}^{2-}$  ligands. The counter-cations, 4,4'-bipyH<sup>+</sup>, form one-dimensional chains through strong (pyridine)N—H $\cdots$ N(pyridine) hydrogen-bonding interactions. Anions and cations stack in alternating layers which are nearly parallel to the  $bc$  plane of the crystallographic unit cell.

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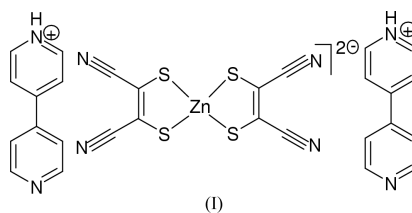
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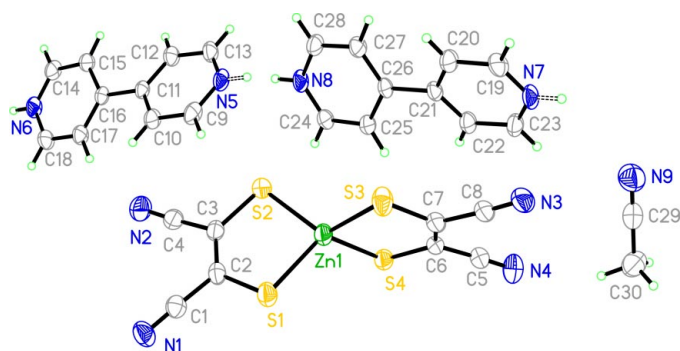
## Comment

In recent years, the principles of supramolecular chemistry, in which a great deal of new concepts concerning intermolecular non-covalent interactions, such as hydrogen-bonding and  $\pi$ - $\pi$ -stacking interactions, have been introduced into the area of materials science (Saadeh *et al.*, 2000; Lawrence *et al.*, 1999). Some of the resulting materials have exhibited novel properties (Gardner *et al.*, 1995; Venkataraman *et al.*, 1995; Fujita *et al.*, 1994; Yaghi *et al.*, 1995).

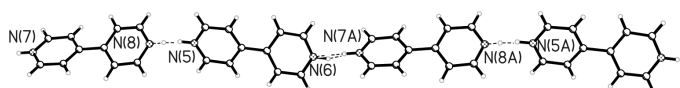
More recently, we have focussed attention on the construction of  $[\text{M}(\text{mnt})_2]^-$  ( $M = \text{Ni}^{\text{III}}$ ,  $\text{Pd}^{\text{III}}$  and  $\text{Pt}^{\text{III}}$ ) with pyridinium derivatives, in which the CN groups of the  $\text{mnt}^{2-}$  ligand and the H—N groups of the pyridinium derivatives may have hydrogen-bonding interactions, and have found that there are strong bifurcated hydrogen-bonding interactions between these molecules (Ren, Chen *et al.*, 2002; Ren, Lu *et al.*, 2002). We have obtained one-dimensional to three-dimensional molecular magnets based on this class of building block. It has been known that a number of salts consisting of pyridinium and some anions with tetrahedral configurations, namely, tetrafluoroborate, perchlorate, periodate, fluoro-sulfonate and perrhenate, appear to be ferroelectric (Czarnecki *et al.*, 1994a,b; Wasicki *et al.*, 1997; Pajak *et al.*, 1998, 2000, 2002; Szafranski *et al.*, 2002). It is also worth noting that there exist bifurcated hydrogen-bonding interactions exist between O or F atoms of anions and the H atom of pyridinium in those ferroelectric materials referred to above.



The molecular geometries of the anions of  $[\text{M}(\text{mnt})_2]^{2-}$ , where  $M$  denotes Zn or Cd, are tetrahedral and similar to the above inorganic anions, so it is expected that new ferroelectric



**Figure 1**  
The structure of complex (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.



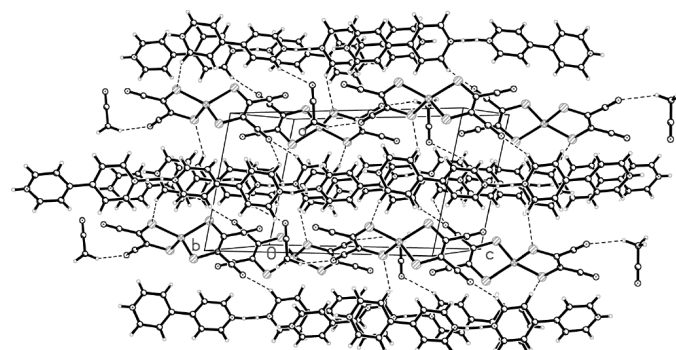
**Figure 2**  
The one-dimensional chain of cations formed by hydrogen-bond interactions.

material families based on ion-pair complexes, which form bipyridinium derivatives and  $[\text{Zn}(\text{mnt})_2]^{2-}$  (or  $[\text{Cd}(\text{mnt})_2]^{2-}$ ) can be obtained. In this communication, we report the crystal structure of  $[4,4'\text{-bipyH}]_2[\text{Zn}(\text{mnt})_2] \cdot \text{C}_2\text{H}_3\text{N}$ , (I).

The structure of (I) is composed of  $4,4'\text{-bipyH}^+$  monovalent cations and  $[\text{Zn}(\text{mnt})_2]^{2-}$ , together with an acetonitrile solvent molecule (Fig. 1). The anion consists of a  $\text{Zn}^{\text{II}}$  ion surrounded by four S atoms of two  $\text{mnt}^{2-}$  ligands, forming a distorted tetrahedron ( $\text{ZnS}_4$ ). The Zn–S distances range from 2.3223 (9) to 2.3373 (9) Å, with internal S–Zn–S chelating angles ranging between 92.22 (3) and 92.95 (3)° (Table 1). The dihedral angle between the  $\text{Zn1/S1/C2/C3/S2}$  and  $\text{Zn1/S3/C6/C7/S4}$  least-squares planes is 87.61 (4)°; thus they are almost perpendicular to each other. These results are in agreement with that of  $[\text{Et}_4\text{N}]_2[\text{Zn}(\text{mnt})_2]$  (Stach *et al.*, 1986). In (I), the cations of the two bipyridyl rings twist away from one another, and the dihedral angles between the two pyridyl rings of  $4,4'\text{-bipyridine}$  is 18.9 (2)° for the molecule containing N5, and 22.2 (2)° for the molecule containing N7. The H atoms bonded to the N atoms of  $4,4'\text{-bipyridine}$  are disordered; this was also found in other compounds containing bipyridine (Lough *et al.*, 2000). The relative occupancies of the H atoms are 0.25/0.75 for H5A/H6A and 0.25/0.75 for H7A/H8A. The adjacent  $4,4'\text{-bipyridinium}$  molecules are linked by strong hydrogen-bonding interactions to form one-dimensional chains along the *c* axis of the unit cell (Fig. 2). The corresponding hydrogen-bonding parameters are listed in Table 2, but there are no hydrogen-bonding interactions between N atoms of CN (mnt) and N atoms of  $4,4'\text{-bipyridinium}$ . The anions and cations form alternating layers, which are nearly parallel to the *bc* plane of the crystallographic unit cell (Fig. 3).

## Experimental

Disodium maleonitriledithiolate ( $\text{Na}_2\text{mnt}$ ) was prepared following the procedure in the literature (Davison & Holm, 1967).  $4,4'\text{-Bipy}$



**Figure 3**  
The layered packing of alternating anions and cations in (I).

ridium chloride was prepared using  $4,4'\text{-bipyridine}$  and one equivalent of dilute hydrochloric acid. A similar method for synthesizing  $[\text{Bu}_4\text{N}]_2[\text{Zn}(\text{mnt})_2]$  (Davison & Holm, 1967) was used to prepare  $[4,4'\text{-bipyH}]_2[\text{Zn}(\text{mnt})_2]$ . Good quality light-red single crystals, suitable for X-ray analysis, were obtained about a week after dispersing ethyl ether into an acetonitrile solution of (I).

### Crystal data

$(\text{C}_{10}\text{H}_9\text{N}_2)_2[\text{Zn}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot \text{C}_2\text{H}_3\text{N}$	$Z = 2$
$M_r = 701.17$	$D_x = 1.485 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.591 (1) \text{ \AA}$	Cell parameters from 120 reflections
$b = 10.086 (1) \text{ \AA}$	$\theta = 2.5\text{--}25.0^\circ$
$c = 16.659 (2) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$\alpha = 88.22 (1)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 76.84 (1)^\circ$	Needle, light red
$\gamma = 88.00 (1)^\circ$	$0.15 \times 0.10 \times 0.10 \text{ mm}$
$V = 1567.8 (3) \text{ \AA}^3$	

### Data collection

Bruker SMART CCD diffractometer	5422 independent reflections
$\omega$ scans	3920 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.062$
$T_{\text{min}} = 0.847$ , $T_{\text{max}} = 0.901$	$\theta_{\text{max}} = 25.0^\circ$
7842 measured reflections	$h = -11 \rightarrow 9$
	$k = -10 \rightarrow 11$
	$l = -19 \rightarrow 19$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5422 reflections	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
398 parameters	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Zn1–S3	2.3223 (9)	Zn1–S1	2.3277 (10)
Zn1–S2	2.3225 (10)	Zn1–S4	2.3373 (9)
S3–Zn1–S2	122.76 (4)	S3–Zn1–S4	92.22 (3)
S3–Zn1–S1	116.27 (4)	S2–Zn1–S4	116.18 (4)
S2–Zn1–S1	92.95 (3)	S1–Zn1–S4	118.89 (3)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N5—H5A $\cdots$ N8	0.86	1.80	2.651 (3)	170
N8—H8A $\cdots$ N5	0.86	1.80	2.651 (3)	173
N6—H6A $\cdots$ N7 <sup>i</sup>	0.86	1.88	2.709 (3)	162
N7—H7A $\cdots$ N6 <sup>ii</sup>	0.86	1.86	2.709 (3)	167

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

All H atoms were placed in geometrically calculated positions ( $C-H = 0.93$  and  $0.97$  Å), with  $U_{iso} = 1.2U_{eq}$  (parent atom).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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