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Tris(ethylenediamine-κ^2N,N')zinc(II) bis(1,2-dicyanoethylenedithiolato-κ^2S,S')cuprate(II)

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The title complex, $[Zn(C_2H_8N_2)_3][Cu(C_4N_2S_2)_2]$, exists as discrete ions. The cation lies on a twofold rotation axis and the anion lies on an inversion centre. The $[Zn(C_2H_8N_2)_3]^{2+}$ cation exhibits a distorted octahedral geometry. In the $[Cu(C_4N_2S_2)_2]^{2-}$ anion, the Cu^{II} atom is in a slightly distorted square-planar environment. The crystal packing is stabilized by hydrogen bonds of the types N—H···N and N—H···S.

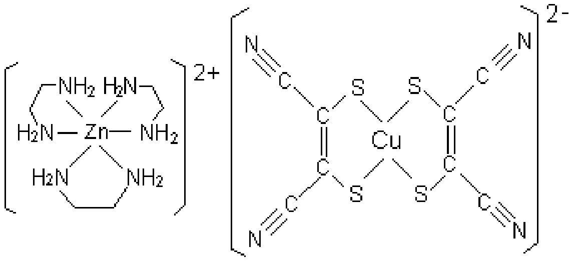
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.065
Data-to-parameter ratio = 15.5

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

Comment

Recently, we have reported a few transition metal ion complexes with 1,2-dicyanoethylenedithiolate ligands (Fu *et al.*, 2004*a*,*b*; Fu *et al.*, 2004; Wang *et al.*, 2004). As an extension of our work on this series of complexes, we report here the crystal structure of the title compound, (I).



(I)

The title compound, (I), consists of discrete $[Zn(en)_3]^{2+}$ cations and $[Cu(mnt)_2]^{2-}$ anions (where en is ethylenediamine and mnt is deprotonated 2,3-dimercaptobutenedinitrile, *viz*. 1,2-dicyanoethylenedithiolate). As shown in Fig. 1, the Zn^{II} atom in the cation has a distorted octahedral geometry formed by six N atoms from three bidentate en ligands. A crystallographic twofold rotation axis in the cation passes through Zn1 and the centre of the C3—C3^{i} bond [symmetry code: (i) $1 - x, y, \frac{3}{2} - z$]. The two symmetry-independent *trans* angles of the ZnN_6 octahedron are 168.83 (10) and 170.18 (8)° (Table 1). The other angles are in the range 78.60 (12)–95.19 (12)°, indicating a distorted octahedral geometry. The average Zn—N bond length of 2.198 (9) Å is comparable to the value of 2.156 (4) Å observed in another $[Zn(en)_3]^{2+}$ cationic complex (Fu *et al.*, 2004*b*).

Atom Cu1 in the centrosymmetric anion has a slightly distorted square-planar environment; atom Cu1 lies on a crystallographic inversion centre. The endocyclic chelate bite angle S1—Cu1—S2 is 90.97 (2)° and the exocyclic angle S1—Cu1—S2^{ii} is 89.03 (2)° [symmetry code: (ii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$]. The Cu—S average bond length of 2.4393 (6) Å is comparable

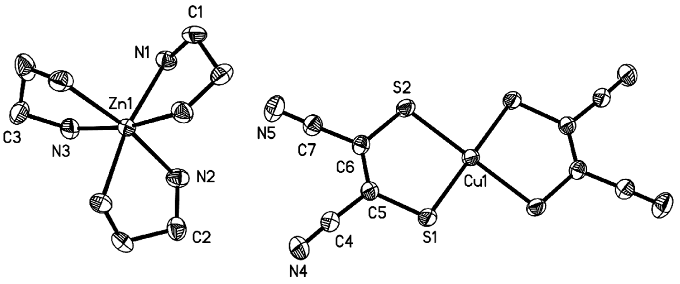


Figure 1
The ions of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. Unlabelled atoms in the cation are related by the symmetry code $(1 - x, y, \frac{3}{2} - z)$. Unlabelled atoms in the anion are related by the symmetry code $(\frac{1}{2} - x, \frac{3}{2} - y, 1 - z)$.

to the value of 2.2576 (12) Å observed in another $[Cu(mnt)_2]^{2-}$ anionic complex (Fu *et al.*, 2004).

The amine N atoms in en and the nitrile N and mercapto S atoms of mnt participate in intermolecular N—H···N and N—H···S hydrogen bonds, forming a three-dimensional hydrogen-bond network (Fig. 2 and Table 2).

Experimental

H_2mnt (1.00 mmol) and NaOH (2.00 mmol) were dissolved in ethanol (20 ml). To this solution, en (1.5 mmol) and an ethanol solution (30 ml) of $ZnSO_4$ (0.5 mmol) and $CuSO_4$ (0.5 mmol) were added dropwise at 313 K. The mixture was stirred for 6 h and part of the solvent was evaporated in a rotary vacuum evaporator. The resulting solution was filtered and left in the air for about 13 d. Large blue block-shaped crystals of (I) were obtained. Elemental analysis found: C 28.45, H 4.01, N 23.57, S 21.66%; calculated for $C_{14}H_{24}N_{10}CuS_4Zn$: 28.52, H 4.10, N 23.76, S 21.76%.

Crystal data

$[Zn(C_2H_8N_2)_3][Cu(C_4N_2S_2)_2]$
M_r = 589.58
Monoclinic, $C2/c$
a = 11.7722 (13) Å
b = 14.4010 (16) Å
c = 14.9053 (17) Å
β = 105.285 (2)°
V = 2437.5 (5) Å^3
Z = 4

D_x = 1.607 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3197 reflections
θ = 2.3–26.3°
μ = 2.22 mm^{-1}
T = 296 (2) K
Block, blue
0.35 × 0.27 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.495, T_{max} = 0.670
6257 measured reflections

2142 independent reflections
1769 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.0°
$h = -14 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.065
S = 1.02
2142 reflections
138 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

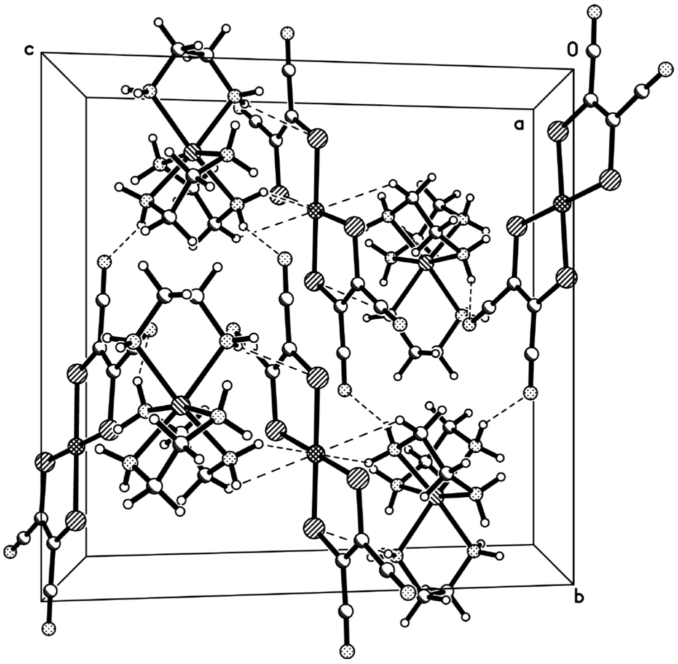


Figure 2
The packing of (I), viewed along the *a* axis. N—H···S and N—H···N hydrogen-bonding interactions are shown as dashed lines.

Table 1
Selected geometric parameters (Å, °).

Cu1—S1	2.2597 (6)	Zn1—N1	2.1958 (18)
Cu1—S2	2.2816 (6)	Zn1—N3	2.211 (2)
Zn1—N2	2.1860 (19)		
S1—Cu1—S2^{ii}	89.03 (2)	N2—Zn1—N3	93.34 (8)
S1—Cu1—S2	90.97 (2)	N1—Zn1—N3	95.03 (8)
N2^{i}—Zn1—N2	95.19 (12)	N2—Zn1—N3^{i}	170.18 (8)
N2—Zn1—N1^{i}	79.75 (7)	N1—Zn1—N3^{i}	93.61 (8)
N2—Zn1—N1	92.68 (8)	N3—Zn1—N3^{i}	78.60 (12)
N1^{i}—Zn1—N1	168.83 (10)		

Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N5	0.90	2.63	3.396 (3)	144
N1—H1*B*···N4^{iii}	0.90	2.48	3.232 (3)	141
N2—H2*A*···S1^{iv}	0.90	3.01	3.702 (2)	135
N2—H2*B*···N5	0.90	2.52	3.348 (3)	153
N3—H3*A*···S2^{v}	0.90	2.77	3.561 (2)	147
N3—H3*B*···S2^{vi}	0.90	2.88	3.655 (2)	145

Symmetry codes: (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (vi) $\frac{1}{2} + x, y - \frac{1}{2}, z$.

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and N—H = 0.90 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics:

m1916 Da-Qi Wang *et al.* • $[Zn(C_2H_8N_2)_3][Cu(C_4N_2S_2)_2]$ *Acta Cryst.* (2004). E**60**, m1915–m1917

SHELXTL (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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