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catena-Poly[[bis(ethylenediamine-κ^2N,N')copper(II)]-μ_3-1,2-dicyanoethylenedithiolato-κ^4N:S,S':N'-[(1,2-dicyanoethylenedithiolato-κ^2S,S')cuprate(II)]]

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Key indicators

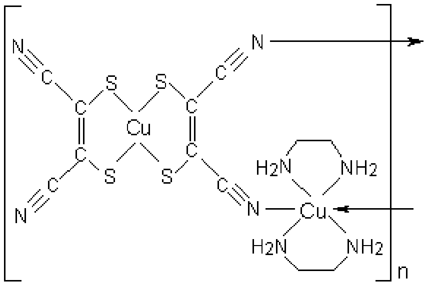
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.036
wR factor = 0.071
Data-to-parameter ratio = 15.2

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

The title complex, $[Cu_2(C_4N_2S_2)_2(C_2H_8N_2)_2]_n$, consists of centrosymmetric $[Cu(C_4N_2S_2)_2]^{2-}$ anions and $[Cu(C_2H_8N_2)_2]^{2+}$ cations. The Cu^{II} atom in each anion shows a slightly distorted square-planar coordination, comprising four S-atom donors from two chelating 2,3-dimercaptobutenedinitrile ligands. The Cu^{II} atom in the cation is six-coordinated by four N-atom donors from two ethylenediamine ligands and two N-atom donors from 2,3-dimercaptobutenedinitrile, and has an elongated octahedral environment. The asymmetric unit contains one cation and two half-anions. The cations and anions are connected by Cu—N (nitrile) bonds to form a one-dimensional chain along the *a* axis. The crystal structure is stabilized by hydrogen bonds of the types N—H···N and N—H···S, forming a three-dimensional network.

Comment

The title compound, (I), is the first structurally characterized complex of a transition metal with both 2,3-dimercaptobutenedinitrile (mnt) and ethylenediamine (en) ligands. It consists of $[Cu(C_4N_2S_2)_2]^{2-}$ anions and $[Cu(C_2H_8N_2)_2]^{2+}$ cations.



(I)

As shown in Fig. 1, atom Cu1 is chelated by two mnt ligands *via* four S atoms. The Cu—S bond lengths are in the range 2.2304 (13)–2.2854 (12) Å (Table 1). The *trans* angles of the CuS_4 square plane are 152.00 (5) and 149.00 (5)°, and the other angles around Cu1 are close to 90°, indicating a distorted square-planar geometry. Atom Cu2 is surrounded by four N atoms from two en ligands and two nitrile N atoms from mnt ligands of different anions (Fig. 2). The three *trans* angles are all exactly 180° by symmetry, as Cu2 lies on an inversion centre. The bonds between Cu2 and nitrile N are longer than those to amine N (Table 1), indicating an elongated octahedral geometry. The coordination geometry of Cu3, also on an inversion centre, is very similar to that of Cu2 (Table 1).

The mnt ligands adopt two forms of coordination; one chelates only *via* two S atoms, and the other also bridges two

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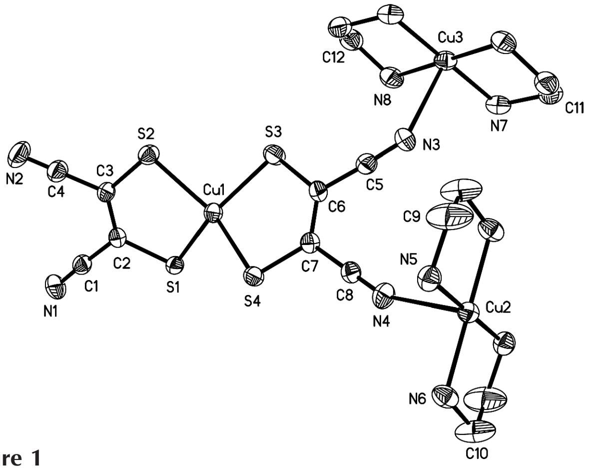

Figure 1
A view of the asymmetric unit of (I), together with additional atoms to complete the en ligands, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

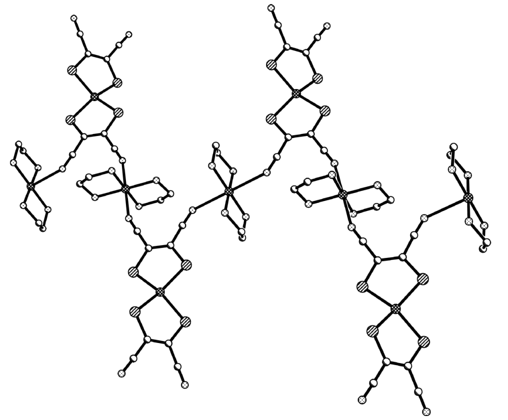

Figure 2
Fragment of the crystal structure of (I), showing the polymeric chain running along the *a* axis. H atoms have been omitted.

adjacent Cu atoms *via* two nitrile N atoms. Through this bridging mode the cations and anions are connected, forming an infinite chain along the *a* axis, as shown in Fig. 2. This situation is very different from the corresponding complex with Cd^{II} replacing Cu^{II} in the cation (Wang *et al.*, 2004), which contains discrete ions. All the amine N atoms of the en ligands, and mercapto S and uncoordinated nitrile N of the mnt ligands participate in intermolecular N—H···N and N—H···S hydrogen bonds, by which adjacent inversion-related chains are interconnected, forming a three-dimensional network (Table 2 and Fig. 3).

Experimental

H_2mnt (1.0 mmol) and NaOH (2.0 mmol) were dissolved in ethanol (20 ml). To this solution were added en (1.0 mmol) and an ethanol solution (30 ml) of $CuSO_4\cdot5H_2O$ (1 mmol) dropwise at 313 K. The mixture was stirred for 4 h and some of the solvent was removed in a rotary vacuum evaporator. The resulting solution was filtered and left in the air for about 6 d. Large blue crystals of (I) were obtained. Elemental analysis found: C 27.25, H 3.00, N 21.11, S 24.25%; calculated for $C_{12}H_{16}Cu_2N_8S_4$: C 27.31, H 3.06, N 21.24, S 24.31%.

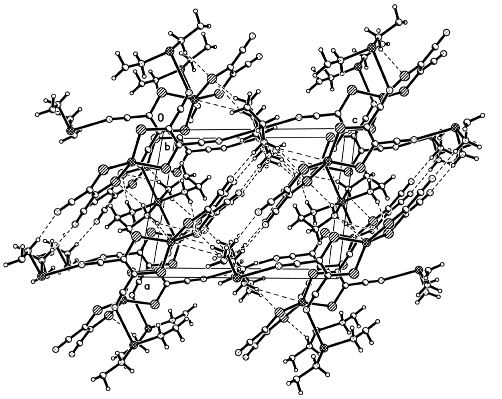

Figure 3
Crystal packing of (I), showing the hydrogen-bonded interactions as dashed lines.

Crystal data

$[Cu_2(C_4N_2S_2)_2(C_2H_8N_2)_2]$
$M_r = 527.65$
Triclinic, $P\overline{1}$
$a = 9.535$ (3) Å
$b = 9.720$ (3) Å
$c = 11.955$ (4) Å
$\alpha = 96.928$ (4)°
$\beta = 95.608$ (4)°
$\gamma = 107.680$ (4)°
$V = 1037.3$ (5) Å^3
$Z = 2$
$D_x = 1.689$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1885 reflections
$\theta = 2.2$–24.8°
$\mu = 2.47$ mm^{-1}
$T = 293$ (2) K
Plate, blue
0.50 × 0.40 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.372$, $T_{\max} = 0.791$
5482 measured reflections
3626 independent reflections
2487 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 11$
$k = -11 \rightarrow 9$
$l = -11 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.071$
$S = 1.00$
3626 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—S3	2.2304 (13)	Cu2—N6	2.013 (3)
Cu1—S1	2.2506 (12)	Cu2—N4	2.576 (3)
Cu1—S4	2.2605 (12)	Cu3—N7	1.984 (3)
Cu1—S2	2.2854 (12)	Cu3—N8	2.010 (3)
Cu2—N5	1.997 (3)	Cu3—N3	2.729 (3)
S3—Cu1—S1	152.00 (5)	N5—Cu2—N4	95.69 (12)
S3—Cu1—S4	92.68 (4)	N6—Cu2—N4	91.94 (12)
S1—Cu1—S4	95.17 (5)	N4^i—Cu2—N4	180
S3—Cu1—S2	95.40 (5)	N7^{ii}—Cu3—N7	180
S1—Cu1—S2	91.57 (5)	N7—Cu3—N8^{ii}	84.67 (14)
S4—Cu1—S2	149.00 (5)	N7—Cu3—N8	95.33 (14)
N5^i—Cu2—N5	180	N8^{ii}—Cu3—N8	180
N5^i—Cu2—N6	83.95 (14)	N7—Cu3—N3^{ii}	85.59 (12)
N5—Cu2—N6	96.05 (14)	N7—Cu3—N3	94.41 (12)
N6^i—Cu2—N6	180	N8^{ii}—Cu3—N3	90.77 (12)
N5—Cu2—N4^i	84.31 (12)	N8—Cu3—N3	89.23 (12)
N6—Cu2—N4^i	88.06 (12)	N3^{ii}—Cu3—N3	180

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N5—H5$A\cdots$N1^{iii}	0.90	2.14	3.039 (5)	176
N5—H5$B\cdots$S1^{iv}	0.90	2.82	3.632 (3)	151
N6—H6$A\cdots$S1^{iv}	0.90	2.70	3.513 (3)	151
N6—H6$B\cdots$N2^{iii}	0.90	2.26	3.098 (5)	155
N7—H7$A\cdots$S1^{v}	0.90	2.54	3.369 (3)	154
N7—H7$B\cdots$S2^{vi}	0.90	2.77	3.621 (4)	158
N8—H8$A\cdots$S2^{vi}	0.90	2.67	3.547 (4)	163

Symmetry codes: (iii) $3-x, 2-y, -z$; (iv) $x, y, 1+z$; (v) $2-x, 2-y, -z$; (vi) $x-1, y, z$.

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), or with N—H = 0.90 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(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: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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