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A coordination polymer with conformationally distinct layers: poly[(μ-1,3-di-4-pyridylpropane-κ^2N:N')bis(μ_3-thiocyanato-κ^3N,S:S)dicopper(**I**)]

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The title compound, $[Cu_2(SCN)_2(C_{13}H_{14}N_2)]_n$, is a two-dimensional coordination polymer containing tetrahedrally coordinated Cu^I atoms bound to one N atom from a 1,3-di-4-pyridylpropane molecule, and one N and two S atoms from three distinct μ_3-thiocyanate anions. The resulting $[Cu_2(SCN)_2]$ staircase motifs align parallel to the *b* crystal axis and link through tethering 1,3-di-4-pyridylpropane ligands into layers parallel to the *bc* crystal plane. Distinct layers with subtly different conformations stack in a $BAA'B'$ pattern, where the BA and $A'B'$ double slabs are related by an inversion center.

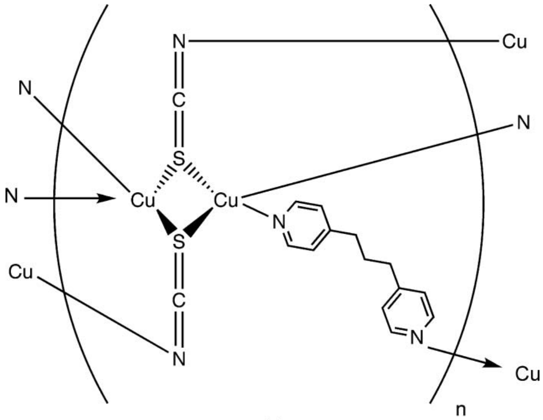
Key indicators

Single-crystal X-ray study
T = 94 K
Mean σ(C–C) = 0.008 Å
R factor = 0.056
wR factor = 0.127
Data-to-parameter ratio = 21.2

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

Comment

A rich chemistry based on copper(I) thiocyanate coordination polymers has been revealed in recent years, with dipodal organodiimine donors being employed to engineer a wide variety of interesting structural motifs. For example, two-dimensional [CuSCN] layers, strutted by 4,4′-bipyridine (4,4′-bpy) ligands, are observed in $[Cu_2(SCN)_2(4,4'\text{-bpy})]_n$ (Blake *et al.*, 1999). Using an ethylene-tethered dipyridyl ligand in this system results in the coordination polymer [Cu(SCN)(1,2-di-4-pyridylethane)]$_n$ which contains one-dimensional [CuSCN] single chains linked into a three-dimensional network with 4^26^38 topology (Wang, Guo *et al.*, 1999).



(I)

We report here the formation of the propylene analog to the above complexes, $[Cu_2(SCN)_2(1,3\text{-di-4-pyridylpropane})]_n$, (I), which was prepared *via* hydrothermal techniques. The structure of (I) is based on $[CuS_2N_2]$ distorted coordination tetrahedra, where the two S donors and one N donor belong to three distinct thiocyanate anions. The fourth coordination site is occupied by an N atom of a 1,3-di-4-pyridylpropane (dpp) molecule. The coordination tetrahedra edge-share through

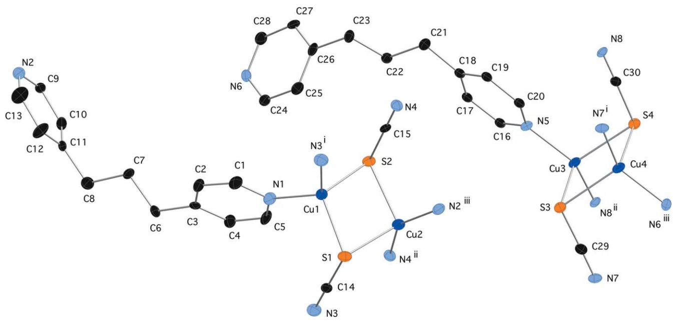


Figure 1
Asymmetric unit of the title compound, with symmetry-equivalent N atoms to complete the Cu coordination, showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. The symmetry codes are as in Table 1.

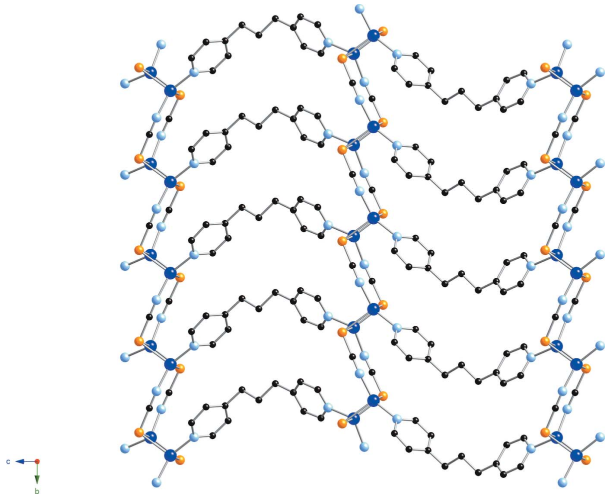


Figure 2
A single polymeric two-dimensional layer motif of type *A* within (I), which lies parallel to the *bc* crystal plane. H atoms have been omitted. Color codes: dark-blue Cu, light-blue N, orange S, black C.

two bridging thiocyanate S atoms to construct [Cu_2S_2] rhomboids. Subtle conformational differences within the dpp molecules and [Cu_2S_2] rhomboids exist in the two crystallographically distinct [$Cu_2(SCN)_2$(dpp)] units (Fig. 1). The Cu1$\cdots$Cu2 and Cu3$\cdots$Cu4 through-space distances are 2.8441 (11) and 2.8390 (13) Å, respectively, falling in the usual range for non-bonding $Cu^I\cdots Cu^I$ cuprophilic interactions (Sundaraman, Zakharov *et al.*, 2005).

The [Cu_2S_2] rhomboids connect to two neighboring [Cu_2S_2] rhomboids in the *b*-axis direction through the N donor atoms of bridging thiocyanate ligands to form [$Cu_2(SCN)_2$] staircases. Neighboring staircases are conjoined *via* tethering dpp ligands to form layers parallel to the *bc* crystal plane. The use of the propylene tether in (I) appears to promote formation of a staircase/tethered layer structure similar to that reported for [$Cu_2(SCN)_2$(*trans*-1,2-di-(4-pyridyl)ethylene)] (Blake *et al.*, 1999). Owing to the dpp conformational differences, two subtly different layers are observed in (I). Layer *A*, formed from Cu1, Cu2 and connected atoms, is shown in Fig. 2. The other half of the asymmetric unit constructs layer *B*, shown in Fig. 3. The [$Cu_2(SCN)_2$] staircases in layer *A* are twisted by ~60° relative to those in layer *B*. Layers *B* and *A* form *BA* double slabs *via* crystal packing forces. These are related through crystallographic inversion centers to afford a *BAA′B′* stacking pattern (Fig. 4), thus building the three-dimensional structure of (I).

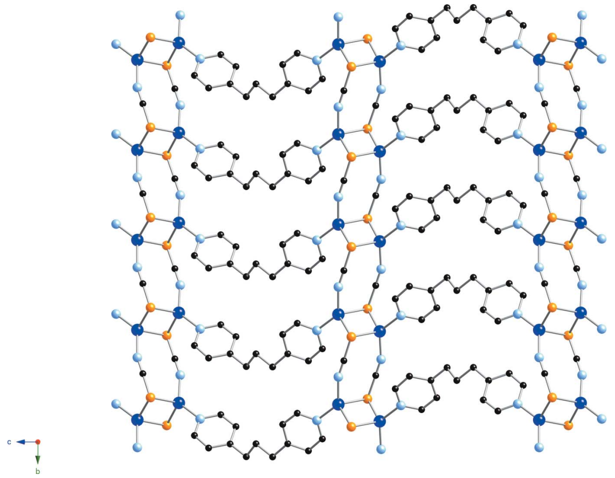


Figure 3
A single polymeric two-dimensional layer motif of type *B* within (I), which lies parallel to the *bc* crystal plane. H atoms have been omitted for clarity. Color codes are as in Fig. 2.

Experimental

All chemicals were obtained commercially. A mixture of copper(I) thiocyanate (40 mg, 0.33 mmol), 1,3-di-4-pyridylpropane (131 mg, 0.66 mmol), aqueous hydrochloric acid (0.4 ml, 1.0 *M*, 0.4 mmol) and water (6.0 g, 330 mmol) was flame-sealed into a borosilicate glass tube, which was then heated under autogenous pressure at 393 K for 42 h. Yellow blocks of the title compound were manually separated from a flocculent brown precipitate.

Crystal data

[$Cu_2(SCN)_2(C_{13}H_{14}N_2)$]
$M_r = 883.00$
Monoclinic, $P2_1/c$
$a = 23.296$ (5) Å
$b = 5.7045$ (11) Å
$c = 30.675$ (6) Å
$\beta = 123.95$ (3)°
$V = 3381.4$ (17) Å^3
$Z = 4$
$D_x = 1.734$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.76$ mm^{-1}
$T = 94$ (2) K
Block, yellow
0.30 × 0.24 × 0.20 mm

Data collection

Bruker *P*4 area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.465$, $T_{max} = 0.575$
21991 measured reflections
8273 independent reflections
4812 reflections with $I > 2\sigma(I)$
$R_{int} = 0.089$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 1.00$
8273 reflections
391 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Cu1—N3^{i}	1.961 (5)	Cu3—N8^{ii}	1.952 (5)
Cu1—N1	2.008 (4)	Cu3—N5	2.008 (4)
Cu1—S1	2.3272 (17)	Cu3—S4	2.4080 (16)
Cu1—S2	2.4142 (18)	Cu3—S3	2.543 (2)
Cu2—N4^{ii}	1.911 (5)	Cu4—N7^{i}	1.931 (4)
Cu2—N2^{iii}	1.977 (4)	Cu4—N6^{iii}	1.999 (4)
Cu2—S2	2.4329 (16)	Cu4—S3	2.3844 (16)
Cu2—S1	2.5630 (18)	Cu4—S4	2.513 (2)
N3^{i}—Cu1—N1	116.35 (19)	N8^{ii}—Cu3—N5	134.07 (18)
N3^{i}—Cu1—S1	104.63 (14)	N8^{ii}—Cu3—S4	101.20 (13)
N1—Cu1—S1	112.68 (14)	N5—Cu3—S4	109.15 (13)
N3^{i}—Cu1—S2	103.68 (14)	N8^{ii}—Cu3—S3	100.54 (14)
N1—Cu1—S2	106.55 (15)	N5—Cu3—S3	101.28 (14)
S1—Cu1—S2	112.77 (6)	S4—Cu3—S3	108.75 (5)
N4^{ii}—Cu2—N2^{iii}	144.51 (19)	N7^{i}—Cu4—N6^{iii}	130.64 (18)
N4^{ii}—Cu2—S2	98.93 (14)	N7^{i}—Cu4—S3	105.26 (14)
N2^{iii}—Cu2—S2	104.87 (14)	N6^{iii}—Cu4—S3	107.87 (13)
N4^{ii}—Cu2—S1	98.99 (14)	N7^{i}—Cu4—S4	101.04 (14)
N2^{iii}—Cu2—S1	100.10 (15)	N6^{iii}—Cu4—S4	100.37 (14)
S2—Cu2—S1	104.42 (6)	S3—Cu4—S4	110.53 (5)
C3—C6—C7—C8	175.6 (5)	C18—C21—C22—C23	−160.9 (5)
C6—C7—C8—C11	177.2 (5)	C21—C22—C23—C26	−179.1 (5)

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

All H atoms were placed in calculated positions, with C—H = 0.93 and 0.97 Å, and refined in riding mode with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (*CrystalMaker*, 2005); software used to prepare material for publication: *SHELXS97*.

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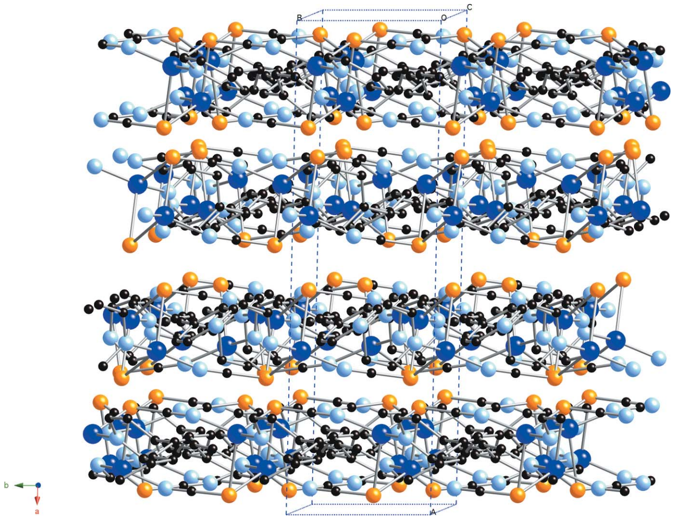

Figure 4
Packing diagram illustrating the stacking of layers in an *BAA'B'* pattern to form the three-dimensional crystal structure of (I).

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