

Tetra- μ_2 -cyano- $\kappa^8C:N$ - μ_2 -2,6-dimethylpyrazine- $\kappa^2N:N'$ -hexakis(2,6-dimethylpyrazine- κN)octa- μ_2 -thiocyanato- $\kappa^{16}N:S$ -decacopper(I,II)

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cnaether@ac.uni-kiel.de**Key indicators**

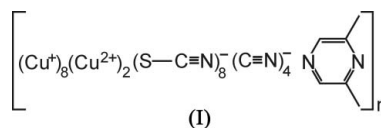
Single-crystal X-ray study
 $T = 220$ K
 Mean $\sigma(C-C) = 0.015$ Å
 Disorder in main residue
 R factor = 0.059
 wR factor = 0.126
 Data-to-parameter ratio = 13.9

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

The asymmetric unit of the title compound $[Cu_8^I Cu_2^{II} (CN)_4 (NCS)_8 (C_6H_8N_2)_7]$, consists of six crystallographically independent Cu atoms, four thiocyanate anions and two cyanide anions, as well as four 2,6-dimethylpyrazine ligands. Two of the six Cu atoms and one of the four 2,6-dimethylpyrazine ligands are located on centres of inversion. The ligand on a special position is therefore disordered due to symmetry. Altogether there are two copper(II) and eight copper(I) cations in the formula unit. The copper(II) cations are each coordinated by four N atoms within a slightly distorted square-planar coordination. The copper(I) cations, on the other hand, are coordinated by four ligands or anions within distorted tetrahedra. From this arrangement, a three-dimensional coordination network is formed.

Comment

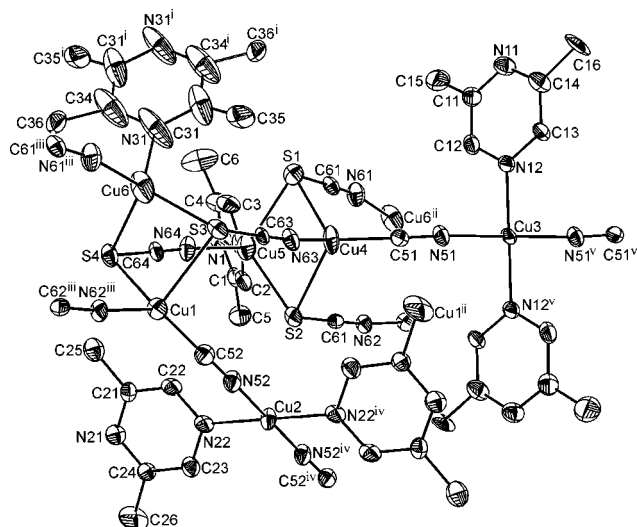
The structure determination of the title compound, (I), was performed within a project on the synthesis, structures and properties of new coordination polymers based on copper(I) halides or pseudo-halides and *N*-donor ligands. Whereas a large number of such coordination polymers with copper(I) halides are known, only a limited number of structures with copper(I) pseudo-halides have been reported. Some examples are given in the reference list (Näther & Jess, 2002; Näther *et al.*, 2003; Teichert & Sheldrick, 1999; Teichert & Sheldrick, 2000). However, the title compound is a mixed copper(I)/copper(II) compound formed serendipitously in the reaction of CuSCN with 2,6-dimethylpyrazine in acetonitrile under solvothermal conditions.



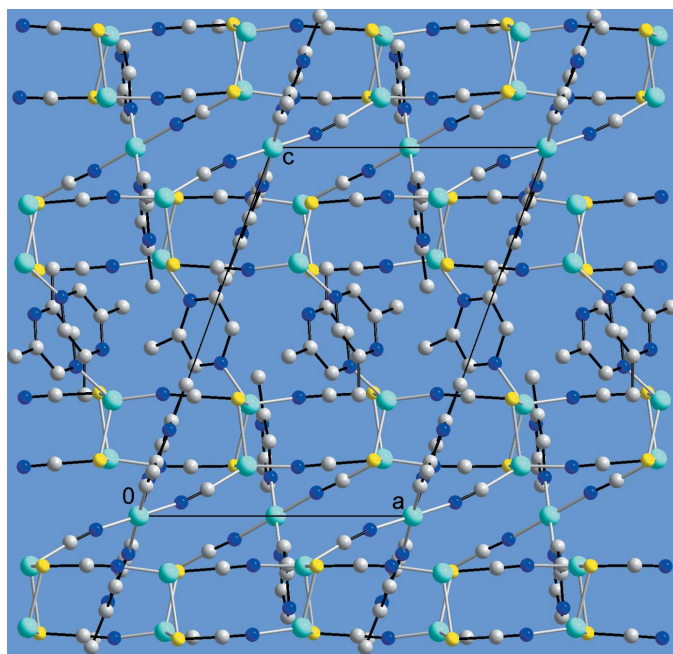
In the crystal structure of (I), six crystallographically independent Cu atoms, four thiocyanate anions, two cyanide anions and four 2,6-dimethylpyrazine ligands are found (Fig. 1). Two Cu atoms and one 2,6-dimethylpyrazine ligand are located on centres of inversion, whereas all other cations, anions and ligands occupy general positions. The two copper(II) cations are connected to two symmetry-related cyanide N atoms and two symmetry-related N atoms of the ligand within a slightly distorted square-planar coordination (Table 1). There are two longer contacts of 3.113 (3) Å (for Cu2) and 3.190 (3) Å (for Cu3) to two symmetry-related S atoms of thiocyanate anions. If these two contacts are considered to participate in the copper coordination, the

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Figure 1

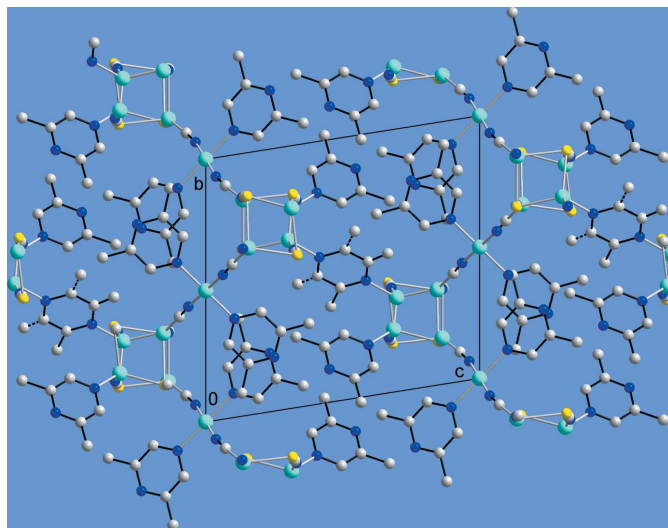
The crystal structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $x - 1, y, z$; (iii) $x + 1, y, z$; (iv) $-x + 2, -y + 2, -z + 2$; (v) $-x + 1, -y + 1, -z + 2$.]


Figure 2

The crystal structure of the title compound, viewed along the *b* axis. H atoms and the disordered methyl groups have been omitted for clarity.

polyhedron around Cu can be described as a strongly distorted tetragonal bipyramid and the distortion can be attributed to the Jahn–Teller effect.

All copper(I) coordination polyhedra show a slightly distorted tetrahedral geometry (Table 1). Atoms Cu1 and Cu4 are each coordinated by one C atom of a cyanide anion, one N atom of a cyanide anion and two S atoms of thiocyanate anions (Fig. 1). Atoms Cu5 and Cu6 are each coordinated by one N atom of a 2,6-dimethylpyrazine ligand, and one N atom and two S atoms of thiocyanate anions (Fig. 1). Pairs of copper(I) cations are connected by S atoms into dimers, which


Figure 3

The crystal structure of the title compound, viewed along the *a* axis. H atoms have been omitted for clarity. The bonds to half of the disordered methyl C atoms are shown as dashed lines.

are linked into chains by the thiocyanate anions (Figs. 2 and 3). These chains extend in the direction of the crystallographic *a* axis. The chains are linked *via* the N atoms of 2,6-dimethylpyrazine ligands, forming layers (Figs. 2 and 3). The layers are connected by the copper(II) cations *via* the cyanide anions into a three-dimensional coordination network (Figs. 2 and 3).

Experimental

The title compound was prepared by the reaction of 1 mmol CuSCN and 1 mmol 2,6-dimethylpyrazine in acetonitrile (2 ml). The reactants were placed in a glass ampoule which was sealed and heated at 413 K for a week. The product consists of very small thin red plates of the title compound as the minor phase and a yellow crystalline powder as the major phase which consists of copper(I)thiocyanate-2,6-dimethylpyrazine. As only CuSCN was used in the synthesis, the Cu²⁺ cations and the cyanide anions must have formed in a complicated redox reaction. The synthesis can be reproduced but in every case only small quantities of the title compound can be isolated.

Crystal data

[Cu₁₀(CN)₄(NCS)₈(C₆H₈N₂)₇]
M_r = 1961.13
 Triclinic, *P* $\bar{1}$
a = 10.2406 (7) Å
b = 13.2211 (12) Å
c = 14.7809 (14) Å
 α = 97.837 (11)°
 β = 109.463 (10)°
 γ = 92.057 (10)°
V = 1862.1 (3) Å³

Z = 1
D_x = 1.749 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 8000 reflections
 θ = 3–50°
 μ = 3.07 mm⁻¹
T = 220 (2) K
 Plate, red
 0.08 × 0.08 × 0.03 mm

Data collection

Stoe IPDS-1 diffractometer
 φ scans
 Absorption correction: none
 11439 measured reflections
 6451 independent reflections
 3143 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.107
 θ_{\max} = 25.0°
h = -12 → 12
k = -15 → 15
l = -17 → 17

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.126$
 $S = 0.89$
 6451 reflections
 463 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.85 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.80 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0015 (3)

Table 1
 Selected geometric parameters (Å, °).

Cu1—C52	1.881 (9)	Cu4—S2	2.636 (3)
Cu1—N62 ⁱ	1.910 (7)	Cu4—Cu5	2.9609 (18)
Cu1—S4	2.542 (3)	Cu5—N64	1.927 (8)
Cu1—S3	2.574 (2)	Cu5—N2	2.035 (8)
Cu2—N52 ⁱⁱ	1.910 (8)	Cu5—S2	2.372 (3)
Cu2—N52	1.910 (8)	Cu5—S1	2.413 (3)
Cu2—N22 ⁱⁱ	2.047 (7)	Cu6—N61 ⁱ	1.945 (8)
Cu2—N22	2.047 (7)	Cu6—N31	2.044 (14)
Cu3—N51 ⁱⁱⁱ	1.912 (7)	Cu6—S4	2.383 (3)
Cu3—N51	1.912 (7)	Cu6—S3	2.414 (3)
Cu3—N12 ⁱⁱⁱ	2.023 (7)	S1—C61	1.659 (9)
Cu3—N12	2.023 (7)	C61—N61	1.145 (11)
Cu4—C51	1.875 (9)	N61—Cu6 ^{iv}	1.945 (8)
Cu4—N63	1.929 (8)	N62—Cu1 ^{iv}	1.910 (7)
Cu4—S1	2.517 (3)		
C52—Cu1—N62 ⁱ	139.8 (4)	S1—Cu4—S2	98.06 (9)
C52—Cu1—S4	108.5 (3)	C51—Cu4—Cu5	129.7 (3)
N62 ⁱ —Cu1—S4	98.3 (2)	N63—Cu4—Cu5	95.3 (2)
C52—Cu1—S3	105.0 (3)	S1—Cu4—Cu5	51.49 (6)
N62 ⁱ —Cu1—S3	101.8 (2)	S2—Cu4—Cu5	49.74 (6)
N52 ⁱⁱ —Cu2—N52	180.0 (5)	N64—Cu5—N2	120.8 (3)
N52 ⁱⁱ —Cu2—N22 ⁱⁱ	89.7 (3)	N64—Cu5—S2	105.9 (3)
N52—Cu2—N22 ⁱⁱ	90.3 (3)	N2—Cu5—S2	110.3 (3)
N52 ⁱⁱ —Cu2—N22	90.3 (3)	N64—Cu5—S1	110.4 (2)
N52—Cu2—N22	89.7 (3)	N2—Cu5—S1	100.2 (2)
N22 ⁱⁱ —Cu2—N22	180.000 (3)	S2—Cu5—S1	108.83 (10)
N51 ⁱⁱⁱ —Cu3—N51	180.000 (2)	N64—Cu5—Cu4	104.7 (2)
N51 ⁱⁱⁱ —Cu3—N12 ⁱⁱⁱ	90.9 (3)	N2—Cu5—Cu4	134.1 (2)
N51—Cu3—N12 ⁱⁱⁱ	89.1 (3)	S2—Cu5—Cu4	57.99 (7)
N51 ⁱⁱⁱ —Cu3—N12	89.1 (3)	S1—Cu5—Cu4	54.71 (8)
N12 ⁱⁱⁱ —Cu3—N12	180.000 (1)	N61 ⁱ —Cu6—N31	106.2 (4)
C51—Cu4—N63	135.0 (4)	N61 ⁱ —Cu6—S4	116.2 (2)
C51—Cu4—S1	104.7 (3)	N31—Cu6—S4	103.4 (3)
N63—Cu4—S1	105.2 (2)	N61 ⁱ —Cu6—S3	106.7 (3)
C51—Cu4—S2	107.5 (3)	N31—Cu6—S3	121.0 (4)
N63—Cu4—S2	100.6 (2)	S4—Cu6—S3	103.97 (10)

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

The aromatic H atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with C—H = 0.94 Å. The methyl H atoms were positioned with idealized geometry, allowed to rotate but not tip, and were refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$] using a riding model with C—H = 0.97 Å. The rather high reliability factors can be attributed to the low scattering power of the small crystal investigated. Even with an extremely long measuring time, the number of observed reflections was very low. Initially, an absorption correction was performed which did not lead to an improvement of the structure model. Therefore, no absorption correction was performed. One of the four crystallographically independent 2,6-dimethylpyrazine ligands is located on a centre of inversion and is therefore disordered over two orientations due to symmetry. The disorder remains if the structure is refined in the non-centrosymmetric space group *P1*. Careful inspection of the reciprocal space gave no hints for superstructure reflections.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB in SHELXTL*.

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