1302 measured reflections
1212 independent reflections

2 standard reflections
every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.059$
$S = 1.114$
1212 reflections
79 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 0.3616P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.289$ e Å^{-3}
$\Delta\rho_{min} = -0.392$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

Cd1—N1	2.274 (2)	N1—C1	1.320 (4)
Cd1—N3^i	2.322 (2)	N1—C3	1.375 (4)
Cd1—S1	2.8510 (13)	N2—C1	1.329 (4)
S1—C4	1.653 (3)	N2—C2	1.347 (5)
C4—N3	1.149 (3)	C2—C3	1.344 (5)
N1—Cd1—N3^i	88.93 (9)	C1—N1—Cd1	125.6 (2)
N1—Cd1—S1	90.04 (7)	C3—N1—Cd1	128.9 (2)
N3^i—Cd1—S1	87.67 (7)	C1—N2—C2	108.7 (3)
C4—S1—Cd1	94.39 (10)	N1—C1—N2	110.3 (3)
N3—C4—S1	178.6 (3)	C3—C2—N2	106.0 (3)
C4—N3—Cd1^{ii}	149.9 (2)	C2—C3—N1	109.5 (3)
C1—N1—C3	105.4 (3)		

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···S1^{iii}	0.90	2.60	3.470 (3)	162

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

Data collection: *SHELXTL-Plus* (Sheldrick, 1990a). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976) in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL97*.

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Copper(I) cyanide–thiomorpholine (3/1)

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Abstract

In the polymeric 3/1 complex of copper(I) cyanide and thiomorpholine, $3CuCN \cdot C_4H_9NS$ or $[Cu_3(CN)_3(C_4H_9NS)]_n$, the CuCN forms two-dimensional sheets, which are held together by the thiomorpholine. Each thiomorpholine molecule bonds to three different sheets.

Comment

In the course of studies of complexes of copper(I) cyanide with thioureas (Stocker *et al.*, 1996), diamines (Stocker, Staeva *et al.*, 1999) and imidazoles (Stocker & Britton, 1999), the title compound, (I), was prepared.

(I)
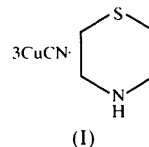
The anisotropic displacement ellipsoids and the labeling are shown in Fig. 1. The atoms in the CN groups were treated as a mixture of C and N atoms at each position, constrained to have the same coordinates and anisotropic displacement parameters, with rationally related occupancies. When the refinement of the occupancies showed that C1—N2 was completely ordered and that C3—N4 was completely disordered within experimental error, the occupancies were fixed at 1.00

and 0.50, respectively. Bond distances (Table 1) are all within the usual ranges for their types. The bonding at Cu1 and Cu3 is tetrahedral, while that at Cu2 is trigonal, very close to planar [Cu2 is 0.032 (6) Å out of the N···N···S plane].
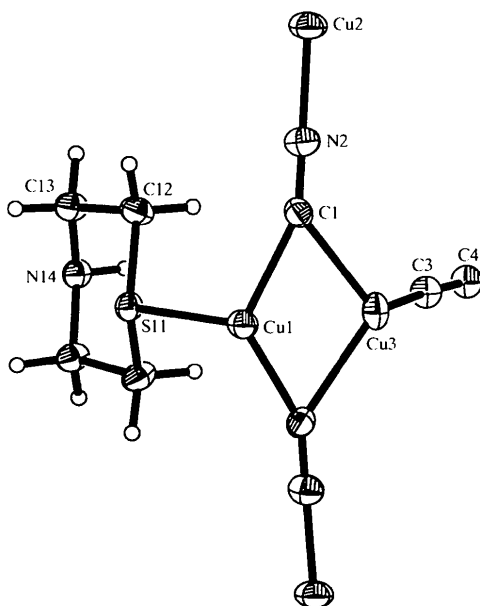

Fig. 1. View of the title compound with displacement ellipsoids shown at the 50% probability level. H atoms are shown with arbitrary size. The view is about 45° away from that in the top view in Fig. 2.
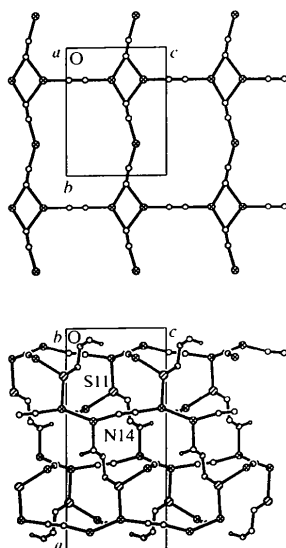

Fig. 2. Top: view along **a**, showing the (CuCN)₃ layer at $y \sim \frac{1}{8}$. The thiomorpholine has been omitted entirely. Bottom: view along **b**, perpendicular to the mirror plane. Only two of the C atoms in each ring can be seen. The H atoms attached to C have been omitted for clarity.

The packing is shown in Fig. 2. All the CuCN moieties occur in layers such as that shown in the upper half of Fig. 2. This particular arrangement for a two-dimensional CuCN polymer has not been found in any of the previously studied CuCN–ligand complexes, but the structural elements in the polymer are familiar. The C3—N4 nitrile forms a disordered ambidentate bridge between Cu3 and Cu1 at $(x, y, 1 + z)$; this type of interaction occurs in the majority of CuCN–ligand complexes. Two C1—N2 nitriles form C-atom bridges between Cu1 and Cu3; this is less common but several examples are known and are discussed by Stocker, Staeva *et al.* (1999). It should be noted that the Cu1···Cu3 distance of 2.4008 (13) Å is shorter than the Cu···Cu distance of 2.556 Å in copper metal; the Cu2C group appears to be held together by a three-center bond. The CuCN layers are then held together by the thiomorpholine as shown in the lower half of Fig. 2. Each thiomorpholine has an S atom bonded to Cu atoms in two adjacent layers, while the N atom is bonded to a Cu in a third layer.

Experimental

The title compound was prepared in a similar fashion to that described by Stocker, Staeva *et al.* (1999). Thiomorpholine (1 mmol) was added to CuCN (3 mmol) dissolved in a solution of sodium thiosulfate (10 mmol) in water (30 ml). The mixture was heated and filtered; crystals of the product appeared on cooling. Data: IR (cm⁻¹): 3450 (*br*, *w*), 3255 (*m*), 2920 (*s*), 2850 (*m*, *sh*), 2127 (*m*), 2085 (*s*), 1640 (*w*, *br*), 1465 (*w*), 1440 (*m*), 1420 (*w*), 1375 (*w*), 1340 (*w*), 1275 (*w*), 1210 (*m*), 1135 (*m*), 1080 (*m*), 1015 (*m*), 975 (*d*, *w*), 925 (*s*), 825 (*s*), 670 (*w*), 600 (*w*), 472 (*w*), 440 (*w*). Analysis calculated for C₇H₉Cu₃N₄S: C 22.61, H 2.44, Cu 51.26, N 15.07, S 8.62%; found: C 22.13, H 2.39, Cu 52.76, N 14.67, S 8.85%.

Crystal data

[Cu₃(CN)₃(C₄H₉NS)]	Mo $K\alpha$ radiation
$M_r = 371.86$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 35
Pnma	reflections
$a = 16.161$ (6) Å	$\theta = 11–20°$
$b = 9.262$ (2) Å	$\mu = 6.08$ mm⁻¹
$c = 7.133$ (3) Å	$T = 297$ (2) K
$V = 1068$ (1) Å³	Prism
$Z = 4$	0.20 × 0.15 × 0.05 mm
$D_x = 2.313$ Mg m⁻³	Light brown
D_m not measured	

Data collection

Enraf–Nonius CAD-4	1104 reflections with
diffractometer	$I > 2\sigma(I)$
ω scans	$R_{int} = 0.047$
Absorption correction:	$\theta_{max} = 30.02°$
ψ scans (North *et al.*,	$h = 0 \rightarrow 22$
1968)	$k = -13 \rightarrow 13$
$T_{min} = 0.38$, $T_{max} = 0.74$	$l = -10 \rightarrow 10$

6333 measured reflections
1640 independent reflections

3 standard reflections
frequency: 80 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.111$
$S = 1.08$
1640 reflections
81 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0590P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.31$ e Å^{-3}
$\Delta\rho_{min} = -1.61$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 1. *Selected bond lengths (Å)*

Cu1—N4^i	1.933 (7)	Cu3—C3	1.916 (7)
Cu1—C1	2.017 (5)	Cu3—N14^{iii}	2.114 (6)
Cu1···Cu3	2.4008 (13)	Cu3—C1	2.176 (5)
Cu1—S11	2.474 (2)	C1—N2	1.140 (7)
Cu2—N2	1.881 (5)	C3—N4	1.151 (9)
Cu2—S11^{ii}	2.377 (2)		

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

The six highest peaks and the four deepest holes in the final difference density map all had magnitudes greater than 1. All of these peaks and holes were between 0.7 and 1.0 Å from one or another of the Cu atoms. The H atoms were placed in idealized positions, except for the amine hydrogen (H14), for which the positional parameters were refined [N—H = 0.89 (8) Å].

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC* and *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1494). Services for accessing these data are described at the back of the journal.

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[Cd(4,4'-bipy)2(NO3)2](2-nitroaniline)2, a novel two-dimensional lattice inclusion compound

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Abstract

In the title complex, poly[[[bis(nitrato-*O*)cadmium(II)]-bis(μ-4,4'-bipyridyl-*N*:*N'*)] bis(2-nitroaniline)], [Cd(NO₃)₂(C₁₀H₈N₂)₂]·2C₆H₆N₂O₂, octahedrally coordinated Cd^{2+} ions are connected by linear rigid 4,4'-bipyridine ligands to form infinite two-dimensional square grids with the nitrate anions occupying the axial positions. The 2-nitroaniline guest molecules fill the space between the grids through π–π stacking interactions. The average Cd—N and Cd—O bond distances are 2.347 (3) and 2.352 (3) Å, respectively.

Comment

Self-assembled metal coordination polymers have emerged as an important class of materials which show potential applications in the fields of host–guest molecular recognition, heterogeneous catalysis and gas adsorption. As part of our continuing studies of organizing non-linear optical chromophores inside metal coordination polymer hosts, we synthesized a novel two-dimensional lattice inclusion compound with a repeat unit of [Cd(4,4'-bipy)₂(NO₃)₂(2-nitroaniline)₂], (I) (4,4'-bipy is 4,4'-bipyridyl).

(I)
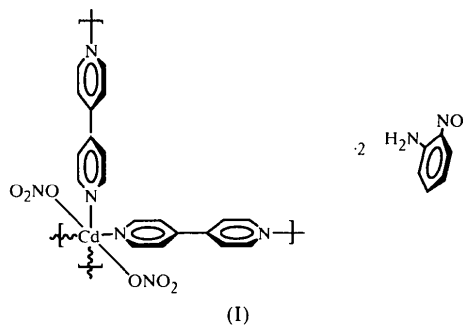
The lattice formed by (I) is shown schematically over and the molecular structure is shown in Fig. 1.