

# Cu<sub>3</sub>(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>Hg(CN)<sub>2</sub>: a novel interpenetrating framework formed from Cu<sup>I</sup>, Cu<sup>II</sup>, Hg<sup>II</sup> and cyanide bridges

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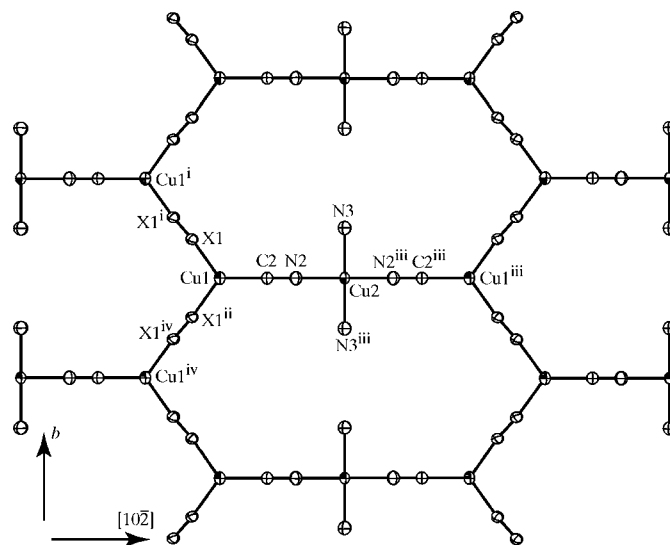
The title compound, poly[diamminehexa- $\mu$ -cyano-dicopper(I)-copper(II)mercury(II)], [Cu<sub>3</sub>Hg(CN)<sub>6</sub>(NH<sub>3</sub>)<sub>2</sub>]<sub>n</sub>, has a novel threefold-interpenetrating structure of three-dimensional frameworks. This three-dimensional framework consists of two-dimensional network Cu<sub>3</sub>(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub> complexes and rod-like Hg(CN)<sub>2</sub> complexes. The two-dimensional network complex contains trigonal-planar Cu<sup>I</sup> (site symmetry *m*) and octahedral Cu<sup>II</sup> (site symmetry 2/*m*) in a 2:1 ratio. Two types of cyanide group form bridges between three coordination sites of Cu<sup>I</sup> and two equatorial sites of Cu<sup>II</sup> to form a two-dimensional structure with large hexagonal windows. One type of CN<sup>-</sup> group is disordered across a center of inversion, while the other resides on the mirror plane. Two NH<sub>3</sub> molecules (site symmetry 2) are located in the hexagonal windows and coordinate to the remaining equatorial sites of Cu<sup>II</sup>. Both N atoms of the rod-like Hg(CN)<sub>2</sub> group (Hg site symmetry 2/*m* and CN<sup>-</sup> site symmetry *m*) coordinate to the axial sites of Cu<sup>II</sup>. This linkage completes the three-dimensional framework and penetrates two hexagonal windows of two two-dimensional network complexes to form the threefold-interpenetrating structure.

## Comment

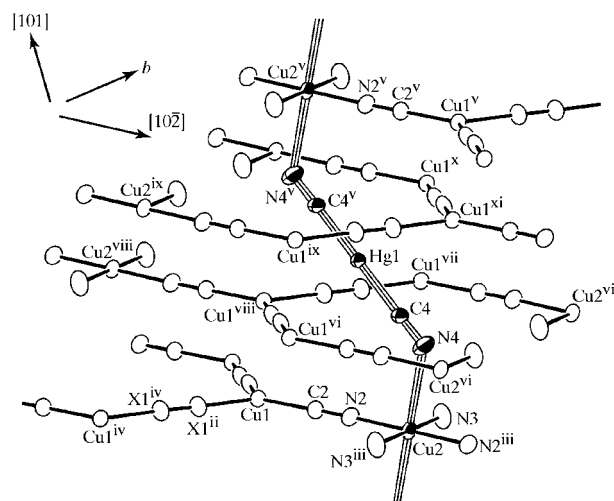
The concept of supramolecular chemistry (Lehn, 1985) has stimulated many chemists to create compounds having a multidimensional and interpenetrating structure. These attempts have typically involved the use of coordination bonds between metal ions and bridging ligands (Robson, 1996; Bowes & Ozin, 1996; Iwamoto, 1996a; Batten & Robson, 1998; Černák *et al.*, 2002). In this method, the bridging ligand is an important key, and many useful bridging ligands have been developed and used so far. Among these ligands, cyanide is a classic example and is one of the most simple; before the birth of supramolecular chemistry, cyanide was often used as a bridging unit for preparing metal complex compounds with a

multidimensional framework structure (Iwamoto, 1984, 1991, 1996b). Although many structural variations of this type of compound have already been reported, more possibilities undoubtedly remain to be discovered. We present here a new simple compound having a novel interpenetrating framework formed by Cu<sup>I</sup>, Cu<sup>II</sup> and Hg<sup>II</sup> atoms and cyanide bridges.

The crystal structure of the title compound, (I), is a threefold-interpenetrating structure of three-dimensional Cu<sub>3</sub>(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>Hg(CN)<sub>2</sub> frameworks. The three-dimensional framework is formed from a two-dimensional network copper–cyanide complex, Cu<sub>3</sub>(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>, and a rod-like Hg(CN)<sub>2</sub> group connecting two Cu<sub>3</sub>(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub> complexes.



**Figure 1**  
 The structure of the two-dimensional network Cu<sub>3</sub>(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub> complex in the (201) plane. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (ii)  $x, -y, z$ ; (iii)  $-x + 1, -y, -z$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$ .]

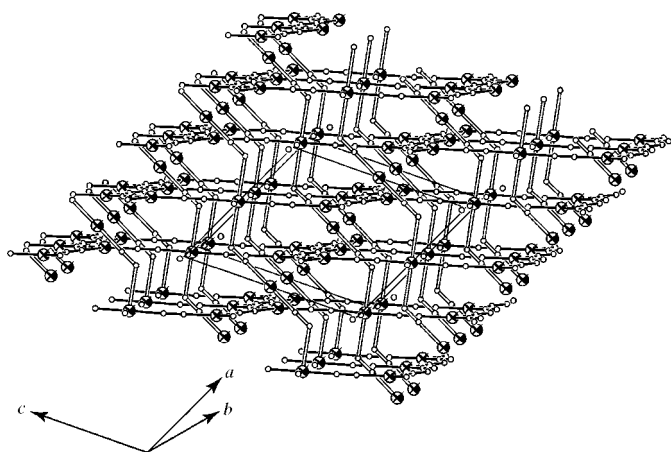


**Figure 2**  
 The structure of the Cu<sub>2</sub>–N<sub>4</sub>–C<sub>4</sub>–Hg<sub>1</sub>–C<sub>4</sub><sup>v</sup>–N<sub>4</sub><sup>v</sup>–Cu<sub>2</sub><sup>v</sup> linkage penetrating two two-dimensional network complexes. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (ii)  $x, -y, z$ ; (iii)  $-x + 1, -y, -z$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$ ; (v)  $-x + 2, y, -z + 1$ ; (vi)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (vii)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (viii)  $-x + 1, y, -z + 1$ ; (ix)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + 1$ ; (x)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + 1$ ; (xi)  $x + 1, y, z$ .]

Figs. 1–3 show the two-dimensional  $\text{Cu}_3(\text{CN})_4(\text{NH}_3)_2$  complex, the rod-like  $\text{Hg}(\text{CN})_2$  as a bridging unit and the resulting interpenetrating structure, respectively.

The two-dimensional network complex contains  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  in a 2:1 ratio, denoted by  $\text{Cu1}$  and  $\text{Cu2}$ , respectively. Atom  $\text{Cu1}$  has a trigonal-planar coordination, with its three coordination sites occupied by cyanide bridges. The cyanide bridges are classified into two groups. One links  $\text{Cu1}$  to a crystallographically equivalent  $\text{Cu1}$  atom. This cyanide ligand, which is denoted by  $X1/X1^{\text{I}}$  here, is in a structurally disordered state because its mid-point sits on an inversion center of the crystal [symmetry code: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ]. The  $\text{Cu1}^{\text{I}}-X1^{\text{I}}-X1-\text{Cu1}$  bridge is repeated along a twofold screw axis parallel to the  $b$  axis to form a zigzag  $\text{Cu1}^{\text{I}}-X1^{\text{I}}-X1-\text{Cu}-X1^{\text{II}}-X1^{\text{IV}}-\text{Cu}^{\text{IV}}$  linkage [symmetry codes: (ii)  $x, -y, z$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$ ]. At the remaining coordination site of  $\text{Cu1}$ , the other type of cyanide group,  $\text{C2/N2}$ , is bound by its  $\text{C}$  atom, while the  $\text{N}$  atom is coordinated to atom  $\text{Cu2}$  to form a  $\text{Cu1}-\text{C2}-\text{N2}-\text{Cu2}$  bridge parallel to the  $[10\bar{2}]$  direction. Atom  $\text{Cu2}$  sits on a  $2/m$  symmetry site, whose twofold rotation axis is parallel to the  $b$  axis, so that another  $\text{C2}^{\text{III}}/\text{N2}^{\text{III}}$  cyanide ligand is coordinated at the *trans* site of  $\text{Cu2}$  to form a  $\text{Cu1}-\text{C2}-\text{N2}-\text{Cu2}-\text{N2}^{\text{III}}-\text{C2}^{\text{III}}-\text{Cu1}^{\text{III}}$  linkage [symmetry code: (iii)  $1 - x, -y, -z$ ]. These two kinds of cyanide linkages form the two-dimensional network structure spreading over the (201) plane. The two-dimensional network has hexagonal windows elongated toward the  $[10\bar{2}]$  direction. The  $\text{NH}_3$  molecules are located in these windows on twofold rotation axes and are coordinated to  $\text{Cu2}$  in a *trans* fashion (Fig. 1).

As shown in Fig. 2, atom  $\text{Hg1}$ , which sits on a  $2/m$  symmetry site, has a linear coordination geometry to give a rod-like  $\text{Hg}(\text{CN})_2$  complex. Both  $\text{N}$  atoms of the  $\text{Hg}(\text{CN})_2$  complex are coordinated to the axial sites of  $\text{Cu2}$  atoms to form a  $\text{Cu2}-\text{N4}-\text{C4}-\text{Hg1}-\text{C4}^{\text{V}}-\text{N4}^{\text{V}}-\text{Cu2}^{\text{V}}$  linkage along the  $[101]$  direction [symmetry code: (v)  $-x + 2, y, -z + 1$ ]. This linkage completes the three-dimensional framework structure of this compound. Moreover, the linkage runs through two hexagonal



**Figure 3**

The  $\text{Cu}_3(\text{CN})_4(\text{NH}_3)_2$  complexes in (I) stacked along the  $[101]$  direction. The  $\text{Cu}-\text{N}-\text{C}-\text{Hg}-\text{C}-\text{N}-\text{Cu}$  linkage runs along the same direction and penetrates two  $\text{Cu}_3(\text{CN})_4(\text{NH}_3)_2$  complexes to form a threefold interpenetrating structure.  $\text{Cu}$  and  $\text{Hg}$  atoms are highlighted with shading.

windows of the two two-dimensional  $\text{Cu}_3(\text{CN})_4(\text{NH}_3)_2$  complexes, which are stacked along the  $[101]$  direction. Therefore, the whole crystal structure is a threefold interpenetrating framework, as shown in Fig. 3.

The  $\text{Cu2}-\text{N4}$  bond length is noticeably longer than the other two  $\text{Cu2}-\text{N}$  bond lengths (Table 1). This large structural deviation from an ideal octahedron arises from the Jahn-Teller effect, which often appears in  $\text{Cu}^{\text{II}}$  complexes, and our case is within the expected range of 2.11–3.28 Å for  $\text{Cu}^{\text{II}}\text{N}_6$ -type complexes in a solid phase (Gažo *et al.*, 1976). An example that is close to our case is an elongated  $\text{Cu}^{\text{II}}-\text{N}$  bond length of 2.583 (13) Å found in a  $\text{Cu}^{\text{II}}-\text{N}-\text{C}-\text{Hg}-\text{C}-\text{N}-\text{Cu}^{\text{II}}$  linkage in the complex  $[(\text{tmeda})\text{Cu}\{\text{Hg}(\text{CN})_2\}_2][\text{HgCl}_4]$  (Draper *et al.*, 2003). The  $\text{Cu2}-\text{N4}-\text{C4}$  bond angle of  $125.0(7)^\circ$  is also far from the ideal value of  $180^\circ$  for such an  $M-\text{N}-\text{C}$  bond angle. This angular distortion is often observed in analogous compounds. In  $[(\text{tmeda})\text{Cu}\{\text{Hg}(\text{CN})_2\}_2][\text{HgCl}_4]$ , a value of  $134.6(7)^\circ$  was reported for the  $\text{Cu}^{\text{II}}-\text{N}-\text{C}$  bond angle at the elongated  $\text{Cu}^{\text{II}}-\text{N}$  bond (Draper *et al.*, 2003). In  $[\text{Cu}(\text{en})_2][\text{Ni}(\text{CN})_4]$ , a value of  $123.6(4)^\circ$  was reported for the corresponding angle (Lokaj *et al.*, 1991). Our case is not far from these examples. However, these geometric parameters and the large displacement parameter of atom  $\text{N4}$  suggest that the connection between atoms  $\text{Cu2}$  and  $\text{N4}$  is considerably weakened. As another view, it might be possible that this compound is a clathrate compound in which the  $\text{Cu}_3(\text{CN})_4(\text{NH}_3)_2$  host includes  $\text{Hg}(\text{CN})_2$  complex guests.

There has been astonishing progress in the structural development of multidimensional structures of complexes using bridging ligands. In those studies, ligands with a large size and a complicated structure are often used. Such approaches are reasonable and important for creating new structures. However, unknown and interesting topology is still buried even in simple systems. Our compound is a good example.

## Experimental

$\text{K}_2[\text{Hg}(\text{CN})_4]$  (1.8 mmol) and an equimolar amount of  $\text{CuCN}$  were dissolved in water (25 ml). The solution was poured into a 50 ml vial and the vial was sealed. The air in the vial was not replaced with inert gas. After 17 months, dark-blue crystals of the title compound were found in the solution, whose color was pale blue at that time. Although the details of its formation reaction are unknown, the crystals contained  $\text{NH}_3$  and  $\text{Cu}^{\text{II}}$  ions, which were not added to the solution at the initial stage. The presence of  $\text{NH}_3$  was supported by elemental analysis and the IR spectrum, and that of  $\text{Cu}^{\text{II}}$  was confirmed from the crystal color and the electric charge balance of the compound. Elemental analysis found: C 12.20, H 1.15, N 19.25%; calculated for  $\text{C}_6\text{H}_6\text{Cu}_3\text{HgN}_8$ : C 12.40, H 1.04, N 19.27%.

### Crystal data

$[\text{Cu}_3\text{Hg}(\text{CN})_6(\text{NH}_3)_2]$   
 $M_r = 581.40$   
 Monoclinic,  $C2/m$   
 $a = 8.915(5) \text{ \AA}$   
 $b = 8.095(4) \text{ \AA}$   
 $c = 10.572(6) \text{ \AA}$   
 $\beta = 116.00(2)^\circ$   
 $V = 685.7(7) \text{ \AA}^3$

$Z = 2$   
 $D_x = 2.814 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 15.73 \text{ mm}^{-1}$   
 $T = 153 \text{ K}$   
 Block, dark blue  
 $0.19 \times 0.16 \times 0.11 \text{ mm}$

## Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer	3830 measured reflections
$\omega$ scans	1071 independent reflections
Absorption correction: numerical (NUMABS; Higashi, 1999)	1071 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.088$ , $T_{\max} = 0.177$	$R_{\text{int}} = 0.052$
	$\theta_{\max} = 30.0^\circ$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 0.6087P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.12$	$\Delta\rho_{\max} = 3.21 \text{ e } \text{Å}^{-3}$
1071 reflections	$\Delta\rho_{\min} = -2.02 \text{ e } \text{Å}^{-3}$
55 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0103 (9)

**Table 1**

Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ).

Hg1—C4	2.049 (7)	Cu2—N4	2.657 (9)
Cu1—X1	1.952 (5)	X1—X1 <sup>i</sup>	1.172 (9)
Cu1—C2	1.919 (8)	N2—C2	1.160 (10)
Cu2—N2	1.975 (7)	N4—C4	1.134 (9)
Cu2—N3	2.034 (7)		
Cu1—X1—X1 <sup>i</sup>	174.8 (6)	N2—Cu2—N3	90.00 (2)
Cu1—C2—N2	179.9 (7)	N2—Cu2—N4	95.0 (3)
X1 <sup>ii</sup> —Cu1—X1	108.3 (2)	N2—Cu2—N4 <sup>iii</sup>	85.0 (3)
X1—Cu1—C2	125.69 (15)	N3—Cu2—N4	90.00 (2)
Cu2—N2—C2	178.3 (7)	Hg1—C4—N4	178.3 (8)
Cu2—N4—C4	125.0 (7)		

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

X1, which is an atom of the disordered X1/X1<sup>i</sup> cyanide group, was treated as a hybrid atom of 50% N and 50% C in the structure refinement. H atoms were placed at idealized positions and refined as riding, with N—H distances of 1.01 Å and  $U_{\text{iso}}(\text{H})$  values of  $1.5U_{\text{eq}}(\text{N3})$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*;

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3012). Services for accessing these data are described at the back of the journal.

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