

## Mercuric cyanide as a receptor of pyrene

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Cocrystallization of pyrene with  $\text{Hg}(\text{CN})_2$  gives a new clathrate, namely bis[dicyanidomercury(II)] pyrene solvate,  $[\text{Hg}(\text{CN})_2]_2 \cdot \text{C}_{16}\text{H}_{10}$ , with molecules of pyrene embedded in cavities of the slightly deformed structure of the mercuric salt; the weak intermolecular  $\text{N} \cdots \text{Hg}$  interactions present in pure  $\text{Hg}(\text{CN})_2$  are maintained in the cocrystal. The X-ray analysis of the resulting compound reveals unusual organic–inorganic interactions. One molecule of  $\text{Hg}(\text{CN})_2$  lies on a crystallographic mirror plane, while in the other, only the Hg atom is on the mirror plane. The molecule of pyrene is cut by a mirror plane perpendicular to the plane of the molecule.

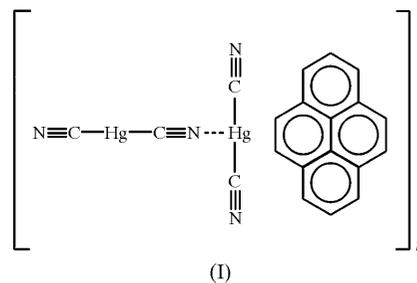
### Comment

The ambidentate cyano group is known as a good connecting unit because it can act as a bridging ligand; it participates in the formation of structures with cavities and channels. These cavities/channels can contain, for example, organic molecules, and  $\text{Hg}(\text{CN})_2$  is a good candidate to form compounds similar to the so-called Werner clathrate (Lipkowski, 1996).

The crystal structure of molecular  $\text{Hg}(\text{CN})_2$ , known for a long time (Hassel, 1926; Hanavolt *et al.*, 1938; Zhdanov & Shugan, 1944; Jones, 1957; Hvoslef, 1958; Seccombe & Kennard, 1969; Reckeweg & Simon, 2002), has interactions between N atoms of one molecule and the Hg atoms of others. These interactions involve  $\text{Hg} \cdots \text{N}$  distances ranging from 2.742 (3) to 3.060 (3) Å (Seccombe & Kennard, 1969) and give rise to a distorted octahedral coordination around the Hg atom.  $\text{Hg}(\text{CN})_2$  crystallizes in the noncentrosymmetric tetragonal space group  $I\bar{4}2d$  (No. 122), and the crystal framework contains cavities and channels propagating along the  $c$  axis and formed by the  $\text{Hg} \cdots \text{N}$  interactions. In order to enable the  $\text{Hg} \cdots \text{N}$  interactions, the molecules of mercuric cyanide are perpendicular to each other (Fig. 1).

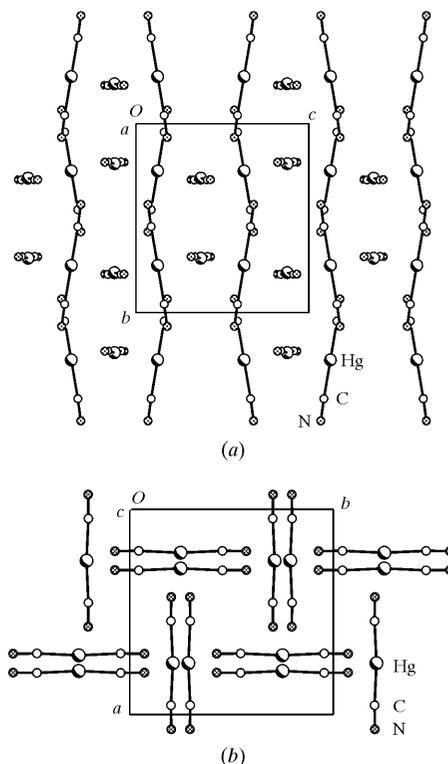
Figs. 1(a) and 1(b) show the structure of  $\text{Hg}(\text{CN})_2$  projected along the  $a$  and  $c$  axes, respectively. The channels have an almost square cross-section with a diagonal length of nearly 6 Å; the cavities/channels are flexible and can be modified in order to contain molecules with suitable dimensions.

In the literature, very few examples exist of cocrystals between  $\text{Hg}(\text{CN})_2$  and an organic molecule. One with tetrahydrofuran has the formula  $[\text{Hg}(\text{CN})_2]_5 \cdot 4\text{C}_4\text{H}_8\text{O}$  (Frey & Ledésert, 1971) and another with methanol is  $\text{Hg}(\text{CN})_2 \cdot \text{CH}_3\text{OH}$  (Ledésert *et al.*, 1969). In both structures, an aggregate of  $\text{Hg}(\text{CN})_2$  molecules, more or less a modification of pure  $\text{Hg}(\text{CN})_2$  and always connected *via*  $\text{Hg} \cdots \text{N}$  interactions, hosts organic molecules of tetrahydrofuran or of methanol.



A cocrystallization was performed between  $\text{Hg}(\text{CN})_2$  and pyrene, and the X-ray analysis of the resulting pink crystals reveals the formula  $[\text{Hg}(\text{CN})_2]_2 \cdot \text{C}_{16}\text{H}_{10}$ , (I) (Fig. 2; Aschero *et al.*, 2004). Tables 1 and 2 list the more significant interactions in the structure. Label *A* refers to atoms related by the crystallographic mirror plane at  $x = \frac{1}{2}$ .

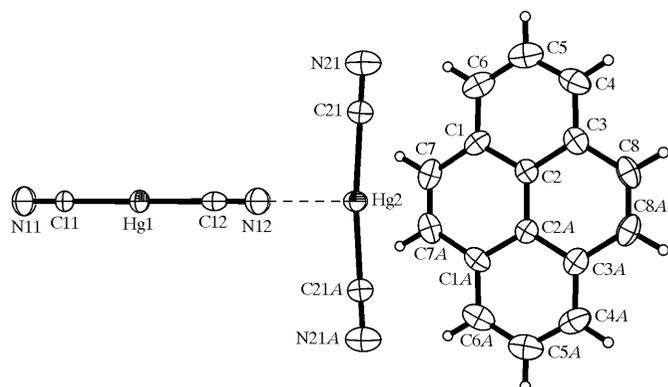
A noncentrosymmetric nonpolar crystal,  $[\text{Hg}(\text{CN})_2]$ , and a centrosymmetric nonpolar one (pyrene,  $P2_1/a$ ) (Hazell *et al.*, 1972) give rise to a noncentrosymmetric polar ([001] axis) cocrystal; the insertion of the organic molecule does not modify the noncentrosymmetric nature of the mercuric



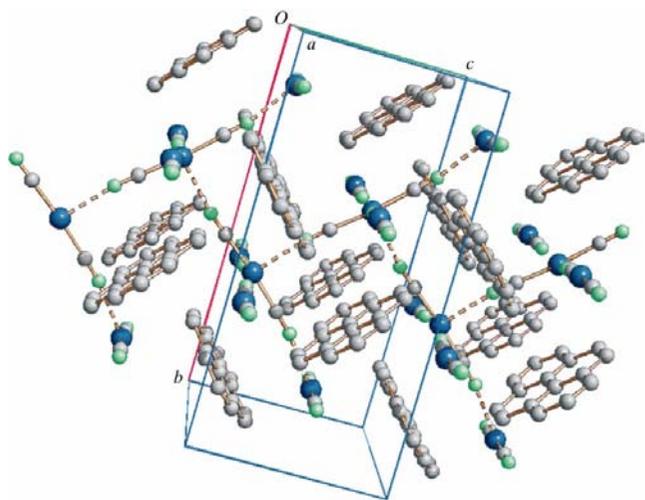
**Figure 1**  
The structure of  $\text{Hg}(\text{CN})_2$ , projected along (a) the  $a$  axis and (b) the  $c$  axis.

cyanide, but polarity is introduced along one axis. The modification of the  $\text{Hg}(\text{CN})_2$  packing in the cocrystal gives rise to  $\text{Hg} \cdots \text{N}$  interactions [2.67 (1) and 2.73 (1) Å] shorter than those in pure  $\text{Hg}(\text{CN})_2$ . The cavities inside the  $\text{Hg}(\text{CN})_2$  framework (with a diagonal size of 8.6 Å), however, are larger than those in pure  $\text{Hg}(\text{CN})_2$ . The molecules of pyrene occupy the cavities, aligning their planes parallel to one side of the nearly square cavity and not along the diagonal, with the consequence of an interaction between the pyrene molecule and the Hg atoms. The perspective view of the unit cell approximately along [100] shows that the planes of the pyrene molecules are mutually perpendicular (Fig. 3), as in pure pyrene crystals.

Figs. 4 and 5 show the bonding and weak intermolecular interactions (Tables 1 and 2). Two types of Hg atoms exist in the unit cell with different surroundings. Atom Hg1, bonded to C11 and C12, lies with its two CN groups on the crystallographic mirror plane and is coordinated by three N atoms of

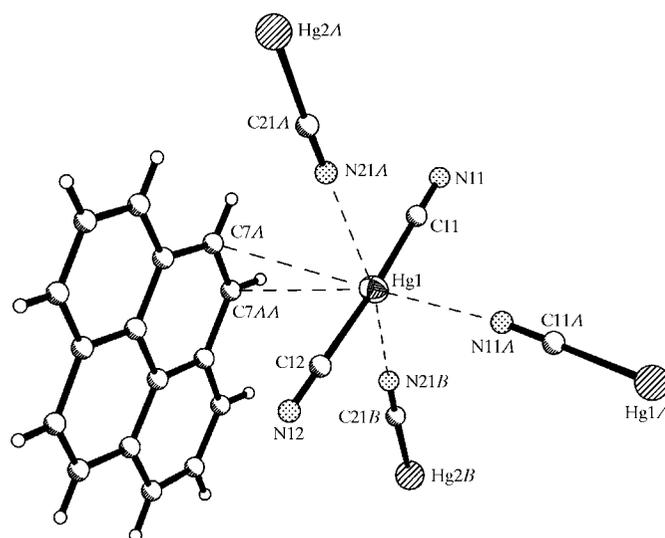


**Figure 2**  
A view of the  $[\text{Hg}(\text{CN})_2]_2 \cdot \text{C}_{16}\text{H}_{10}$  unit, showing the atom labelling and displacement ellipsoids at the 50% probability level; atoms labelled with the suffix *A* are related by the symmetry operation  $(-x + 1, y, z)$ .

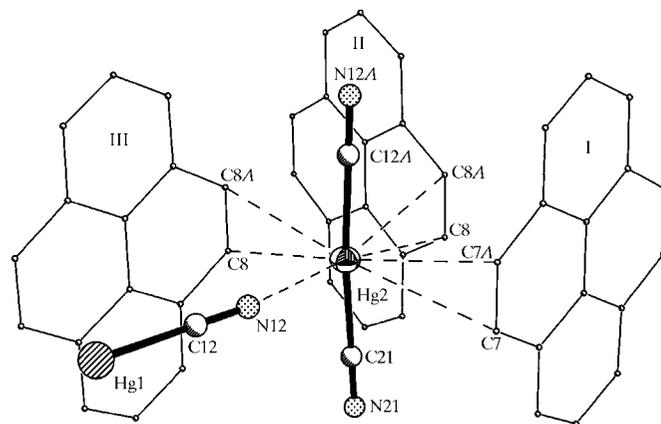


**Figure 3**  
The crystal packing of  $[\text{Hg}(\text{CN})_2]_2 \cdot \text{C}_{16}\text{H}_{10}$ , viewed approximately along the *a* axis. The shortest weak bonds, between mutually perpendicular  $\text{Hg}(\text{CN})_2$  molecules, are shown as dashed bonds.

other molecules and one pyrene molecule, assuming an octahedral coordination (Fig. 4). Atom Hg2, bonded to C21 and with only the Hg atom lying on the mirror plane, is coordinated by atom N12 of another molecule and also by three pyrene molecules *via* C7—C7A and C8—C8A bonds (Fig. 5); the pyrene molecule is cut perpendicularly by the crystallographic mirror plane. Atom Hg2 also has a distorted octahedral coordination. The  $\text{Hg}(\text{CN})_2$  molecules are not linear (Table 1). With respect to the coordination of pyrene to the Hg atoms, the H atoms of atoms C7 and C8, owing to the short  $\text{Hg} \cdots \text{H}$  distances of nearly 3.4 Å and to the orientation of the C—H bonds with respect to Hg, seem to have weak interactions with the metal atom. Therefore, the planar H—C—C—H atom chains seem to interact with Hg atoms.



**Figure 4**  
The coordination around atom Hg1. [Symmetry codes: Hg1A, C11A and N11A:  $x, -y + 1, z + \frac{1}{2}$ ; Hg2A, C21A and N21A:  $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; Hg2B, C21B and N21B:  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; C7A:  $x, y, z - 1$ ; C7AA:  $-x + 1, y, z - 1$ .]



**Figure 5**  
The coordination around atom Hg2. Pyrene molecules I, II and III are at  $(x, y, z)$ ,  $(x, -y, z - \frac{1}{2})$  and  $(x, y, z - 1)$ , respectively. The suffix *A* indicates the symmetry operation  $(-x + 1, y, z)$  for molecule I,  $(-x + 1, -y, z - \frac{1}{2})$  for II and  $(-x + 1, y, z - 1)$  for III.

## Experimental

Hg(CN)<sub>2</sub> was dissolved in acetone and pyrene was added (Aschero *et al.*, 2004).

### Crystal data

[Hg(CN) <sub>2</sub> ] <sub>2</sub> ·C <sub>16</sub> H <sub>10</sub>	$V = 1794.25 (7) \text{ \AA}^3$
$M_r = 707.50$	$Z = 4$
Orthorhombic, $Cmc2_1$	Mo $K\alpha$ radiation
$a = 11.9893 (3) \text{ \AA}$	$\mu = 17.10 \text{ mm}^{-1}$
$b = 17.3480 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 8.6266 (2) \text{ \AA}$	$0.24 \times 0.12 \times 0.10 \text{ mm}$

### Data collection

Siemens P4 APEX diffractometer	10971 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2251 independent reflections
$T_{\min} = 0.072$ , $T_{\max} = 0.181$	2105 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	H-atom parameters constrained
$wR(F^2) = 0.044$	$\Delta\rho_{\text{max}} = 0.69 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\text{min}} = -1.07 \text{ e \AA}^{-3}$
2251 reflections	Absolute structure: Flack (1983),
128 parameters	1016 Friedel pairs
1 restraint	Flack parameter: 0.030 (14)

**Table 1**

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

Hg1—C11	2.032 (9)	C11—N11	1.123 (14)
Hg1—C12	2.033 (10)	C12—N12	1.132 (13)
Hg2—C21	2.038 (5)	C21—N21	1.119 (6)
C11—Hg1—C12	175.4 (4)	N12—C12—Hg1	179.7 (8)
C21—Hg2—C21 <sup>i</sup>	173.6 (3)	N21—C21—Hg2	178.3 (7)
N11—C11—Hg1	179.4 (10)		

Symmetry code: (i)  $-x + 1, y, z$ .

**Table 2**

Intermolecular contact distances ( $\text{\AA}$ ); molecules II and III are defined in Fig. 5.

Hg1...N11A	2.73 (1)
Hg1...N21B	2.87 (1)
Hg1...C7B,C	3.37 (1)
Hg2...C7	3.30 (1)
Hg2...C8 (molecule II)	3.38 (1)
Hg2...C8 (molecule III)	3.24 (1)
Hg2...N12	2.67 (1)

H-atom positions were calculated and were refined as riding on the corresponding C atoms, with  $U_{\text{iso}}(\text{H})$  values constrained to  $1.2U_{\text{eq}}$  of the related C atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990) and *SCHAKAL* (Keller, 1999); software used to prepare material for publication: *SCHAKAL* and *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3083). Services for accessing these data are described at the back of the journal.

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