

# One-dimensional coordination polymers generated from a new triazole bridging ligand and $\text{HgX}_2$ ( $X = \text{Cl}, \text{Br}$ and $\text{I}$ ): characterization and luminescent properties

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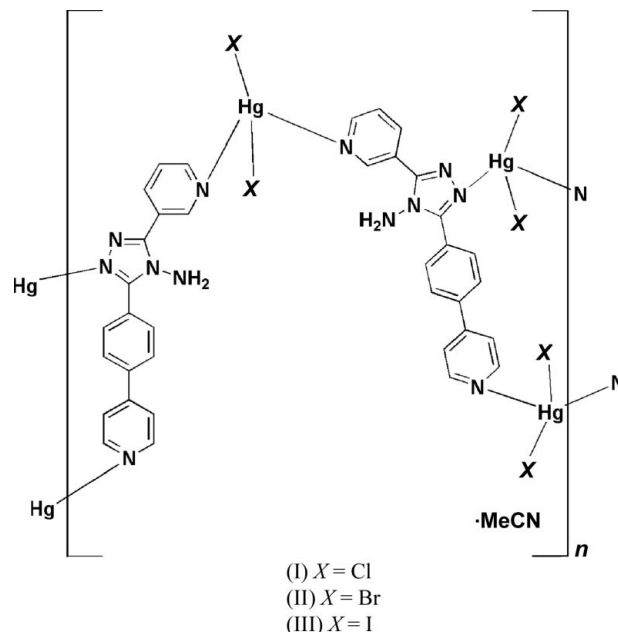
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The new 4-amino-1,2,4-triazole asymmetric bridging ligand 4-amino-5-(pyridin-3-yl)-3-[4-(pyridin-4-yl)phenyl]-4*H*-1,2,4-triazole (*L*) has been used to generate three novel isomorphous one-dimensional coordination polymers, *viz.* *catena*-poly-[[tris[dichloridomercury(II)]-bis[ $\mu_3$ -4-amino-5-(pyridin-3-yl)-3-[4-(pyridin-4-yl)phenyl]-4*H*-1,2,4-triazole]] acetonitrile monosolvate],  $[\text{Hg}_3\text{Cl}_6(\text{C}_{18}\text{H}_{14}\text{N}_6)_2 \cdot \text{CH}_3\text{CN}]_n$ , (I), and the bromido,  $[\text{Hg}_3\text{Br}_6(\text{C}_{18}\text{H}_{14}\text{N}_6)_2 \cdot \text{CH}_3\text{CN}]_n$ , (II), and iodido,  $[\text{Hg}_3\text{I}_6(\text{C}_{18}\text{H}_{14}\text{N}_6)_2 \cdot \text{CH}_3\text{CN}]_n$ , (III), analogs. The asymmetric ligand acts as a tridentate ligand to coordinate the three different  $\text{Hg}^{\text{II}}$  centers (two of which are symmetry-related). Two ligands and two symmetry-related  $\text{Hg}^{\text{II}}$  centers form centrosymmetric rectangular units which are linked into one-dimensional chains *via* the other unique Hg atoms, which sit on mirror planes. The chains are elaborated into a three-dimensional structure *via* interchain hydrogen bonds. The acetonitrile solvent molecules are located in ellipsoidal cavities. The luminescent character of these three coordination complexes was investigated in the solid state.

## Comment

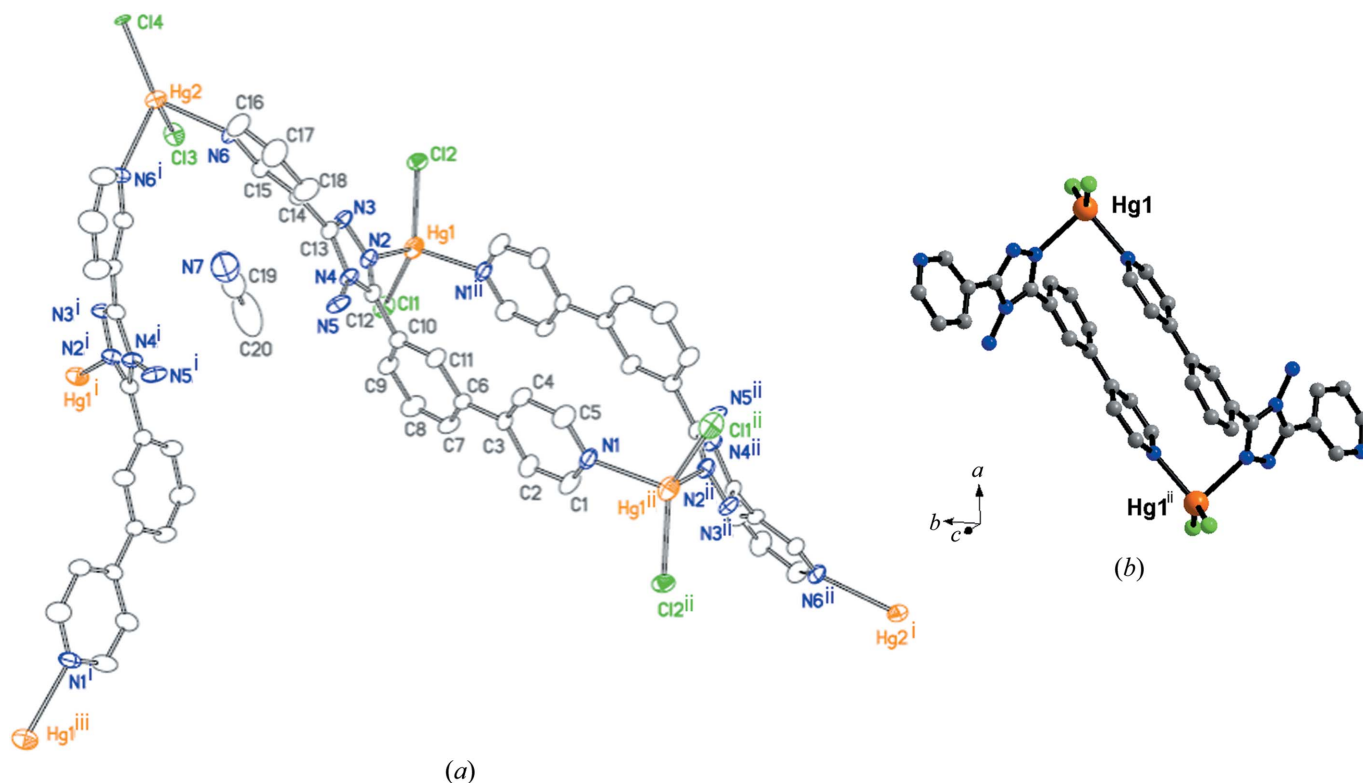
Coordination polymers containing metal nodes and organic ligands have attracted tremendous attention over the past 30 years because of their wide application as functional materials (Long & Yaghi, 2009; Spokoiny *et al.*, 2009). The syntheses of coordination polymers by the judicious choice of organic spacers and metal centers can be an efficient method for obtaining new types of luminescent materials, especially for  $d^{10}$  or  $d^{10}-d^{10}$  systems of metal centers (Morsali & Masoomi, 2009; Tang *et al.*, 2011). The design and construction of coor-

dination polymers based on rigid and bent organic ligands bridged by 4-amino-4*H*-1,2,4-triazole have been pursued because of their specific geometry (Liu *et al.*, 2009; Du *et al.*, 2006). In addition, hydrogen bonds play an important role in constructing high-dimensional supramolecular compounds (Mu *et al.*, 2008).

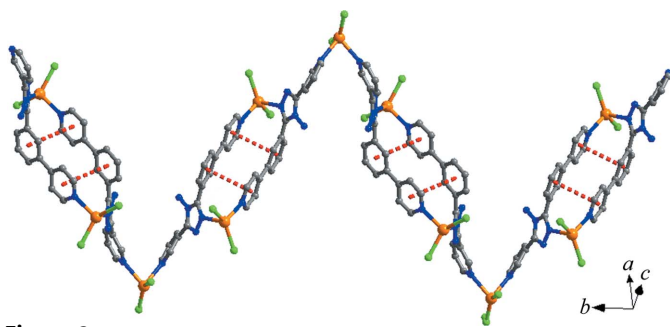


The study of the asymmetric oxadiazole ligand with  $d^{10}$  metal centers has been previously carried out by our group (Song *et al.*, 2010), but the coordination polymers generated by asymmetric 4-amino-4*H*-1,2,4-triazole-based organic ligands are extremely rare. As part of our systematic studies into self-assembly based on asymmetric ligands, we have synthesized a novel asymmetric rigid ligand, *viz.* 4-amino-5-(pyridin-3-yl)-3-[4-(pyridin-4-yl)phenyl]-4*H*-1,2,4-triazole (*L*), which has a short (pyridin-3-yl) and a long arm [4-(pyridin-4-yl)phenyl]. Three novel isomorphous coordination complexes, *viz.*  $[\text{Hg}_3\text{X}_6(\text{L})_2 \cdot \text{CH}_3\text{CN}]_n$ , with  $X = \text{Cl}$ , (I), Br, (II), and I, (III), were obtained and their structures explored.

The isomorphous compounds (I), (II) and (III) crystallized in the orthorhombic space group  $Pnma$ , with one and a half  $\text{Hg}^{\text{II}}$  centers, one *L* ligand, three halide atoms and half an acetonitrile solvent molecule in the asymmetric unit. One of the  $\text{Hg}^{\text{II}}$  centers and the acetonitrile molecule sit on crystallographic mirror planes. The following discussion focuses on the description of the structure of (I), but the comments apply equally well to (II) and (III). Complex (I) contains two crystallographically independent  $\text{Hg}^{\text{II}}$  centers, as shown in Fig. 1(a). The Hg1 center is coordinated by one pyridine N atom from the long arm of one *L* ligand, one N atom of the triazole group of a second *L* ligand and two halide atoms. The Hg2 center, which sits on a mirror plane, is coordinated by two pyridine N atoms from the short arms of two different *L* ligands in addition to two halide atoms. The  $\text{Hg1} \cdots \text{Hg2}$  distance is 8.7286 (18) Å, which is similar to the  $\text{Hg} \cdots \text{Hg}$  distance in our previous report on [2,5-bis(3-pyridyl)-1,3,4-oxadiazole]diiodidomercury (Dong *et al.*, 2003). As shown in

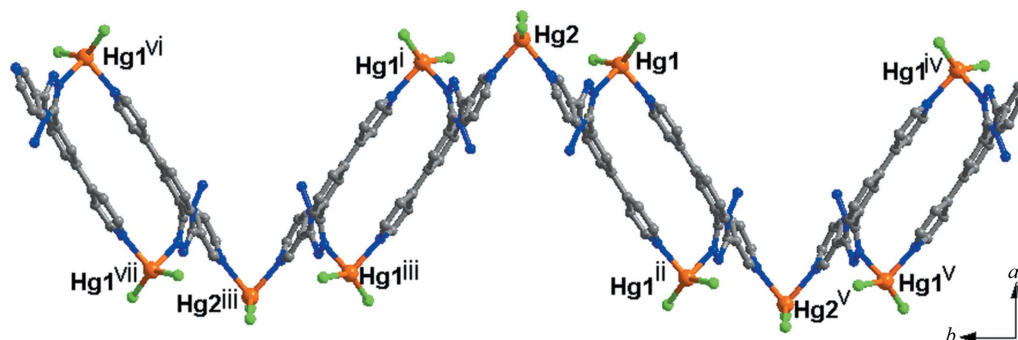


**Figure 1**  
 (a) The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. Only one position of disordered atom Cl4 is shown. (b) The rectangular 20-membered macrocycle formed by two ligands and two Hg<sup>II</sup> centers. [Symmetry codes: (i)  $x, -y + \frac{3}{2}, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + 1, y + \frac{1}{2}, -z + 1$ .]

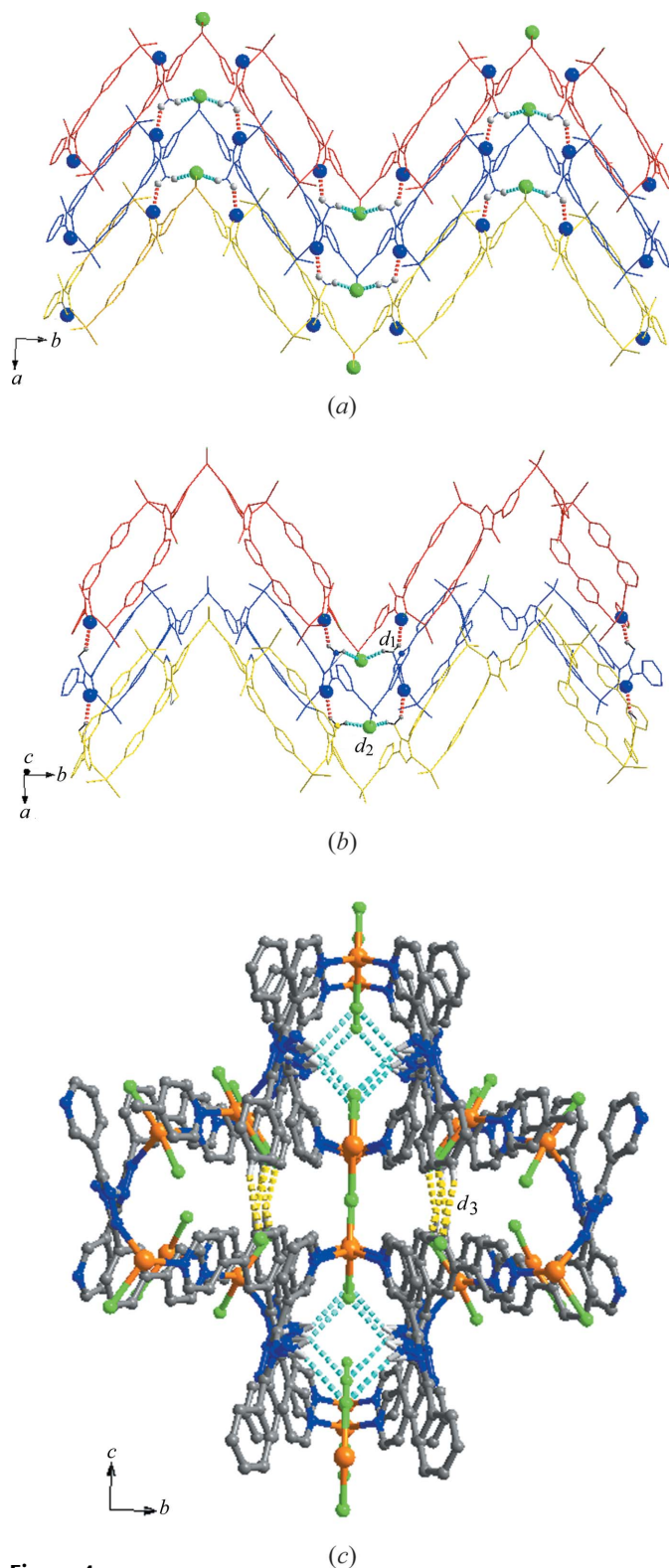


**Figure 2**  
 The  $\pi$ - $\pi$  interactions in the rectangular units of (I) [ $\pi$ - $\pi = 3.799$  (8) Å].

Fig. 1(b), two ligands, two Hg1 centers and four halide atoms form rectangular units, in which the long arms of two ligands and part of the triazole ring with two Hg1 centers form a rectangular 20-membered macrocycle. The pyridine and benzene rings of the long arms of the ligand are almost coplanar, with a dihedral angle of 4.4 (7)° between the planes. In the 'rectangle', there are  $\pi$ - $\pi$  interactions [ $\pi$ - $\pi = 3.799$  (8) Å] between the aromatic groups (Fig. 2), while the two pyridine rings and the two benzene rings in the macrocycle are parallel. As shown in Fig. 3, the nearby Hg2 centers link the rectangles through Hg-N bonds involving the

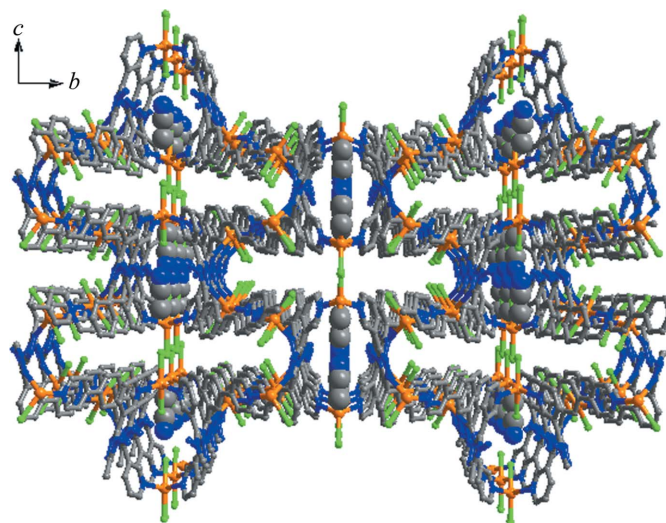


**Figure 3**  
 Extension of the centrosymmetric units of (I) along the [110] direction. [Symmetry codes: (i)  $x, -y + \frac{3}{2}, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + 1, y + \frac{1}{2}, -z + 1$ ; (iv)  $x, -y + \frac{1}{2}, z$ ; (v)  $-x + 1, y - \frac{1}{2}, -z + 1$ ; (vi)  $x, y + 1, z$ ; (vii)  $-x + 1, -y + 2, -z + 1$ .]

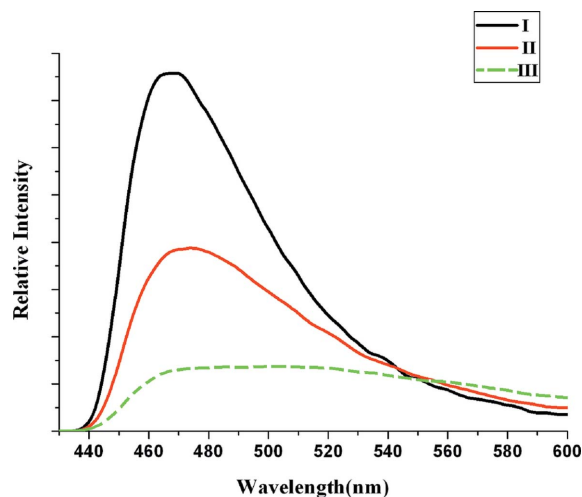


**Figure 4**  
 (a) Hydrogen-bonding interactions extending along the *c* axis of (I), (b) the three-dimensional networks formed *via* the two kinds of hydrogen bonds ( $d_1 = 2.39 \text{ \AA}$  and  $d_2 = 2.70 \text{ \AA}$ ) and (c) the three-dimensional hydrogen-bonded network viewed down the *a* axis ( $d_3 = 2.75 \text{ \AA}$ ).

terminal pyridin-3-yl N atom of the short arm on the ligands to form one-dimensional zigzag chains which run parallel to the [110] direction. The Hg<sub>2</sub> center is located in a distorted



**Figure 5**  
 Ellipsoid cavities containing acetonitrile solvent molecules.



**Figure 6**  
 Solid-state luminescent emission properties of the three novel coordination polymers at room temperature.

tetrahedral environment, similar to our previous report on [2,5-bis(3-pyridyl)-1,3,4-oxadiazole]diiodidomercury (Dong *et al.*, 2003).

As shown in Figs. 4(a) and 4(b), the chains are linked by two types of hydrogen-bonding interactions (N—H...N and N—H...X; X = Cl, Br or I; Tables 1–3) into three-dimensional networks. Weaker hydrogen-bonding interactions, *viz.* C—H...X, extend along the *a* axis (Fig. 4c). In the three-dimensional network, there are ellipsoidal cavities, within which the acetonitrile solvent molecules are arranged regularly (Fig. 5).

The luminescent properties of these three new coordination polymers were investigated in the solid state at room temperature. Upon excitation at  $\lambda = 395 \text{ nm}$ , compounds (I)–(III) showed emission maxima at 469, 474 and 474 nm, respectively. Notably, in the cases of (I), (II) and (III), almost identical emission bands were observed with different intensities (Fig. 6); thus, the different emission luminescent inten-

sities of (I)–(III) might be attributed to the halide-to-ligand charge transfer (XLCT) (Park *et al.*, 2009).

In summary, the asymmetric rigid ligand *L* can be used as a tridentate ligand to coordinate transition metal ions. Three novel one-dimensional coordination polymers have been synthesized based on *L* and  $\text{HgX}_2$  ( $X = \text{Cl, Br and I}$ ), and their luminescent properties investigated in the solid state at room temperature.

## Experimental

For the preparation of 4-amino-5-(3-bromophenyl)-3-(pyridin-3-yl)-4*H*-1,2,4-triazole, a mixture of hydrazine hydrate (6.90 g, 110 mmol), 3-bromobenzonitrile (5.00 g, 27.5 mmol) and pyridine-3-carbonitrile (2.86 g, 27.5 mmol) in ethanediol (10 ml) was stirred at 413 K for 12 h. The reaction was monitored by thin layer chromatography (TLC). Sufficient water was added to the mixture to cause precipitation. The precipitate was purified by silica-gel column chromatography using dichloromethane (DCM) and MeOH (30:1 *v/v*) as eluent to afford 4-amino-5-(3-bromophenyl)-3-(pyridin-3-yl)-4*H*-1,2,4-triazole as a white crystalline solid (yield 2.40 g, 7.6 mmol, 27.6%).  $^1\text{H NMR}$  (300 MHz, DMSO, 298 K, TMS):  $\delta$  9.18 (s, 1H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.73 (d, 1H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.39 (d, 1H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.27 (s, 1H), 8.06 (d, 1H,  $-\text{C}_6\text{H}_4-$ ), 7.75 (d, 1H,  $-\text{C}_6\text{H}_4-$ ), 7.61 (m, 1H,  $-\text{C}_6\text{H}_4-$ ), 7.54 (t, 1H,  $-\text{C}_6\text{H}_4-$ ), 6.42 (s, 2H,  $-\text{NH}_2$ ); IR (KBr pellet,  $\text{cm}^{-1}$ ): 3417 (s), 3355 (s), 1623 (m), 1598 (m), 1567 (m), 1515 (w), 1477 (s), 1447 (m), 1399 (vs), 1331 (w), 1192 (w), 1070 (m), 1030 (w), 1015 (m), 997 (w), 976 (w), 892 (m), 815 (m), 794 (m), 766 (m), 690 (w). Analysis calculated for  $\text{C}_{12}\text{H}_{12}\text{BrN}_5$ : C 22.45, H 1.54, N 8.96%; found: C 22.48, H 1.51, N 9.01%.

For the preparation of 4-amino-5-(pyridin-3-yl)-3-[4-(pyridin-4-yl)phenyl]-4*H*-1,2,4-triazole (*L*), a mixture of 4-amino-5-(3-bromophenyl)-3-(pyridin-3-yl)-4*H*-1,2,4-triazole (2.0 mmol) and pyridine-4-boronic acid (2.4 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.048 mmol), K<sub>2</sub>CO<sub>3</sub> (6 mmol) in an EtOH–H<sub>2</sub>O system was stirred at 348–353 K for 48 h. After removal of the solvent under vacuum, the residue was purified by silica-gel column chromatography using DCM–MeOH (10:1 *v/v*) as eluent to afford *L* as a white crystalline solid (yield 2.40 g, 7.6 mmol, 90.2%).  $^1\text{H NMR}$  (300 MHz, DMSO, 298 K, TMS):  $\delta$  9.22 (s, 1H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.73 (d, 3H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.44 (d, 2H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.13 (d, 1H,  $-\text{C}_5\text{H}_4\text{N}$ ), 8.01 (d, 1H,  $-\text{C}_5\text{H}_4\text{N}$ ), 7.90 (d, 2H,  $-\text{C}_6\text{H}_4-$ ), 7.75 (t, 1H,  $-\text{C}_6\text{H}_4-$ ), 7.63 (m, 1H,  $-\text{C}_6\text{H}_4-$ ), 6.47 (s, 2H,  $-\text{NH}_2$ ); IR (KBr pellet,  $\text{cm}^{-1}$ ): 3406 (s), 3355 (s), 1637 (m), 1593 (m), 1509 (w), 1463 (m), 1400 (vs), 1264 (w), 1193 (w), 1070 (m), 1026 (w), 970 (w), 919 (w), 901 (m), 814 (w), 795 (m), 713 (m), 692 (m), 610 (m). Analysis calculated for  $\text{C}_{18}\text{H}_{14}\text{N}_6$ : C 68.78, H 4.49, N 24.73%; found: C 68.80, H 4.47, N 24.73%.

For the preparation of (I), a solution of  $\text{HgCl}_2$  (10.86 mg, 0.04 mmol) in  $\text{CH}_3\text{CN}$  (7 ml) was layered onto a solution of *L* (6.28 mg, 0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (7 ml). The solution was left for about 5 d at room temperature and colorless crystals of (I) were obtained (yield 80%). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3417 (s), 3330 (s), 2170 (w), 1607 (s), 1518 (w), 1459 (m), 1400 (vs), 1231 (m), 1192 (m), 1122 (m), 1076 (m), 1015 (m), 987 (m), 794 (s), 686 (m), 641 (m), 574 (m). Analysis calculated for  $\text{C}_{38}\text{H}_{31}\text{Cl}_6\text{Hg}_3\text{N}_{13}$ : C 30.75, H 2.11, N 12.27%; found: C 30.78, H 2.06, N 12.28%.

For the preparation of (II), a solution of  $\text{HgBr}_2$  (14.42 mg, 0.04 mmol) in  $\text{CH}_3\text{CN}$  (7 ml) was layered onto a solution of *L* (6.28 mg, 0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (7 ml). The solution was left for about 5 d at room temperature and colorless crystals of (II) were obtained (yield 78%). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3417 (s), 3330 (s), 2170

(w), 1607 (s), 1518 (w), 1459 (m), 1400 (vs), 1231 (m), 1192 (m), 1122 (m), 1076 (m), 1015 (m), 987 (m), 794 (s), 686 (m), 641 (m), 574 (m). Analysis calculated for  $\text{C}_{38}\text{H}_{31}\text{Br}_6\text{Hg}_3\text{N}_{13}$ : C 26.07, H 1.78, N 10.40%; found: C 26.09, H 1.76, N 10.41%.

For the preparation of (III), a solution of  $\text{HgI}_2$  (18.18 mg, 0.04 mmol) in  $\text{CH}_3\text{CN}$  (7 ml) was layered onto a solution of *L* (6.28 mg, 0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (7 ml). The solution was left for about 5 d at room temperature and colorless crystals of (III) were obtained (yield 80%). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3417 (s), 3332 (s), 2170 (w), 1607 (s), 1515 (m), 1458 (m), 1400 (vs), 1230 (m), 1191 (m), 1121 (m), 1074 (m), 1013 (m), 986 (m), 796 (s), 687 (m), 640 (m), 573 (m). Analysis calculated for  $\text{C}_{38}\text{H}_{31}\text{Hg}_3\text{I}_6\text{N}_{13}$ : C 22.45, H 1.54, N 8.96%; found: C 22.46, H 1.52, N 8.98%.

## Compound (I)

### Crystal data

$[\text{Hg}_3\text{Cl}_6(\text{C}_{18}\text{H}_{14}\text{N}_6)_2] \cdot \text{C}_2\text{H}_3\text{N}$	$V = 4506.9$ (14) $\text{\AA}^3$
$M_r = 1484.23$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 12.773$ (2) $\text{\AA}$	$\mu = 10.60$ $\text{mm}^{-1}$
$b = 27.267$ (5) $\text{\AA}$	$T = 298$ K
$c = 12.941$ (2) $\text{\AA}$	$0.32 \times 0.18 \times 0.05$ mm

### Data collection

Bruker SMART CCD area-detector diffractometer	22532 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	4277 independent reflections
$T_{\min} = 0.133$ , $T_{\max} = 0.619$	3278 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.077$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$	12 restraints
$wR(F^2) = 0.188$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\max} = 2.67$ $\text{e \AA}^{-3}$
4277 reflections	$\Delta\rho_{\min} = -1.89$ $\text{e \AA}^{-3}$
287 parameters	

## Compound (II)

### Crystal data

$[\text{Hg}_3\text{Br}_6(\text{C}_{18}\text{H}_{14}\text{N}_6)_2] \cdot \text{C}_2\text{H}_3\text{N}$	$V = 4651.0$ (10) $\text{\AA}^3$
$M_r = 1750.99$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 12.8037$ (16) $\text{\AA}$	$\mu = 15.08$ $\text{mm}^{-1}$
$b = 27.890$ (4) $\text{\AA}$	$T = 298$ K
$c = 13.0245$ (17) $\text{\AA}$	$0.25 \times 0.20 \times 0.03$ mm

### Data collection

Bruker SMART CCD area-detector diffractometer	23320 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	4422 independent reflections
$T_{\min} = 0.117$ , $T_{\max} = 0.661$	3338 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.075$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C7}-\text{H7} \cdots \text{Cl1}^{\text{i}}$	0.93	2.75	3.613 (12)	154
$\text{N5}-\text{H5A} \cdots \text{Cl3}^{\text{ii}}$	0.89	2.70	3.512 (12)	152
$\text{N5}-\text{H5B} \cdots \text{N3}^{\text{ii}}$	0.89	2.39	3.149 (12)	143

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

**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C7—H7...Br1 <sup>i</sup>	0.93	2.85	3.678 (9)	150
N5—H5A...Br3 <sup>ii</sup>	0.91	2.78	3.599 (10)	150
N5—H5B...N3 <sup>ii</sup>	0.90	2.39	3.153 (10)	142

Symmetry codes: (i)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, y, -z + \frac{3}{2}$ .**Table 3**  
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C7—H7...I1 <sup>ii</sup>	0.93	3.02	3.842 (10)	148
N5—H5A...I3 <sup>i</sup>	0.94	2.86	3.706 (10)	150
N5—H5B...N3 <sup>i</sup>	0.92	2.42	3.173 (12)	139

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

$R[F^2 > 2\sigma(F^2)] = 0.049$  281 parameters  
 $wR(F^2) = 0.133$  H-atom parameters constrained  
 $S = 1.03$   $\Delta\rho_{\max} = 2.17 \text{ e } \text{Å}^{-3}$   
 4422 reflections  $\Delta\rho_{\min} = -2.04 \text{ e } \text{Å}^{-3}$

**Compound (III)****Crystal data**

$[\text{Hg}_3\text{I}_6(\text{C}_{18}\text{H}_{14}\text{N}_6)_2] \cdot \text{C}_2\text{H}_3\text{N}$   $V = 4945 (2) \text{ Å}^3$   
 $M_r = 2032.93$   $Z = 4$   
 Orthorhombic,  $Pnma$  Mo  $K\alpha$  radiation  
 $a = 12.822 (3) \text{ Å}$   $\mu = 13.08 \text{ mm}^{-1}$   
 $b = 28.976 (7) \text{ Å}$   $T = 298 \text{ K}$   
 $c = 13.309 (3) \text{ Å}$   $0.50 \times 0.20 \times 0.04 \text{ mm}$

**Data collection**

Bruker SMART CCD area-detector 24554 measured reflections  
 diffractometer 4701 independent reflections  
 Absorption correction: multi-scan 3888 reflections with  $I > 2\sigma(I)$   
 (SADABS; Bruker, 2003)  $R_{\text{int}} = 0.060$   
 $T_{\text{min}} = 0.059, T_{\text{max}} = 0.623$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.050$  18 restraints  
 $wR(F^2) = 0.138$  H-atom parameters constrained  
 $S = 1.04$   $\Delta\rho_{\max} = 2.60 \text{ e } \text{Å}^{-3}$   
 4701 reflections  $\Delta\rho_{\min} = -1.85 \text{ e } \text{Å}^{-3}$   
 280 parameters

For (I), H atoms were placed in geometrically idealized positions and included as riding atoms, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  (aromatic) and C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  (acetonitrile). The NH<sub>2</sub> group was assumed to be NH<sub>3</sub> and three H atoms were added in geometrically idealized positions. One H atom

without an acceptor was then deleted and the remaining H atoms refined as a riding model, with N—H = 0.89 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . One Cl atom (Cl4) is disordered over two positions with refined site-occupation factors in the ratio 0.64 (8):0.36 (8), and the anisotropic displacement parameters (ADPs) of atoms Cl4 and Cl4' were restrained to be pseudo-isotropic within a standard uncertainty of 0.01 Å<sup>2</sup>. The acetonitrile solvent molecule lies on a mirror plane. The highest peak of residual electron density was located at (0.0982, 0.7500, 0.0785), 1.00 Å from atom Hg2.

For (II), H atoms on C and N atoms were treated as for (I). The acetonitrile solvent molecule lies on a mirror plane. The highest peak of residual electron density was located at (0.0488, 0.7500, 0.9981), 0.99 Å from atom Hg2.

For (III), H atoms on C and N atoms were treated as for (I). The acetonitrile solvent molecule lies on a mirror plane. The ADPs of the solvent atoms were restrained to be pseudo-isotropic within a standard uncertainty of 0.01 Å<sup>2</sup>. The highest peak of residual electron density was located at (0.1152, 0.7500, 0.2023), 0.99 Å from atom I4.

For all three compounds, data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: WQ3013). Services for accessing these data are described at the back of the journal.

**References**

- Bruker (2003). SADABS, SAINT and SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dong, Y.-B., Cheng, J.-Y., Ma, J.-P., Wang, H.-Y., Huang, R.-Q., Guo, D.-S. & Smith, M. D. (2003). *Solid State Sci.* **5**, 1177–1186.
- Du, M., Jiang, X.-J. & Zhao, X.-J. (2006). *Inorg. Chem.* **45**, 3998–4006.
- Liu, Q.-K., Mia, J.-P. & Dong, Y.-B. (2009). *Chem. Eur. J.* **15**, 10364–10368.
- Long, J. R. & Yaghi, O. M. (2009). *Chem. Soc. Rev.* **38**, 1213–1215.
- Morsali, A. & Masoomi, M.-Y. (2009). *Coord. Chem. Rev.* **253**, 1882–1905.
- Mu, Z.-C., Shu, L.-J., Fuchs, H., Mayor, M. & Chi, L.-F. (2008). *J. Am. Chem. Soc.* **130**, 10840–10841.
- Park, S.-H., Lee, S.-Y., Jo, M., Lee, J.-Y. & Lee, S.-S. (2009). *CrystEngComm*, **11**, 43–46.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Song, Z.-G., Geng, C.-H., Ma, J.-P. & Dong, Y.-B. (2010). *Inorg. Chem. Commun.* **13**, 809–813.
- Spokoyny, A. M., Kim, D., Sumrein, A. & Mirkin, C. A. (2009). *Chem. Soc. Rev.* **38**, 1218–1227.
- Tang, M., Guo, W., Zhang, S.-Z. & Du, M. (2011). *Inorg. Chem. Commun.* **14**, 1217–1220.