metal-organic compounds

The structures of three Hg$_2$X$_4$L$_2$ macrocycles {X = Cl, Br and I, and L = 1,2-bis[4-(pyridin-3-yl)phenoxy]ethane} assembled from ether-bridged dipyridyl ligands

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The new ether-bridged dipyridyl ligand 1,2-bis[4-(pyridin-3-yl)phenoxy]ethane (L) has been used to synthesize three isostructural centrosymmetric binuclear Hg^{II} macrocycles, namely bis{μ-1,2-bis[4-(pyridin-3-yl)phenoxy]ethane-$\kappa^2 N$:N'}-bis[dichloridomercury(II)], [Hg$_2$Cl$_4$(C$_{24}$H$_{20}$N$_2$O$_2$)$_2$], and the bromido, [Hg$_2$Br$_4$(C$_{24}$H$_{20}$N$_2$O$_2$)$_2$], and iodido, [Hg$_2$I$_4$(C$_{24}$H$_{20}$N$_2$O$_2$)$_2$], analogues. The Hg atoms adopt a highly distorted tetrahedral coordination environment consisting of two halides and two pyridine N-donor atoms from two bridging ligands. In the solid state, the macrocycles form two-dimensional sheets in the bc plane through noncovalent Hg$\cdots X$ and $X\cdots X$ (X = Cl, Br and I) interactions.

Comment

Numerous supramolecular compounds designed and constructed through crystal engineering have attracted significant attention because of their fascinating structural topologies (Chae *et al.*, 2001) and functional applications (Wang *et al.*, 2011). It is well known that the selection of appropriate ligands as building blocks is a key point in the design and synthesis of functional supramolecular compounds. Compared with rigid ligands, flexible ligands can adopt different conformations under varying conditions resulting in potentially novel topologies (Chuang *et al.*, 2010). N-Donor ligands, such as those containing pyridyl groups, are good candidates for the assembly of versatile structures (Fujita *et al.*, 2007). Recently, our group has reported several compounds generated from flexible ether-bridged ligands containing dicyanomethylene groups (Dong *et al.*, 2007), carboxylic acid groups (Jiang *et al.*, 2009), terminal indoline-2,3-dione groups (Fang *et al.*, 2011) and terminal imidazole groups (Yuan *et al.*, 2011). There are

few reports on flexible ether-bridged dipyridyl ligands. In order to investigate further the influence of factors such as the terminal groups of the ligand and the coordinated metal ions on the topologies and properties of supramolecular compounds, we studied the design and synthesis of a new, flexible, ether-bridged dipyridyl ligand, 1,2-bis[4-(pyridin-3-yl)phenoxy]ethane (L). Three new macrocycles have been synthesized based on L and the inorganic salts HgX$_2$ (X = Cl, Br and I), *viz.* [Hg$_2$Cl$_4$L$_2$], (I), [Hg$_2$Br$_4$L$_2$], (II), and [Hg$_2$I$_4$L$_2$], (III). The X-ray crystal structures show that the three compounds are isostructural. We report here the intermolecular interactions in the lattices of the three compounds.


(I) X = Cl
(II) X = Br
(III) X = I
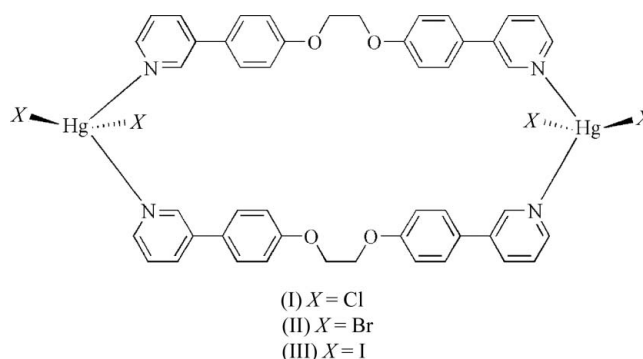
The three isostructural compounds crystallize in the triclinic space group $P\overline{1}$. The unit cells have been chosen in a similar fashion in order to facilitate the structural comparison. The unit cell of (III) became nonstandard (cell setting I, but $b > c > a$). As shown in Fig. 1, each compound contains centrosymmetric macrocycles comprised of two ligands bridging two HgX$_2$ moieties. The Hg^{II} centre lies in a highly distorted tetrahedral coordination environment defined by two N-atom donors from two pyridine rings and two coordinated X^- anions (X = Cl, Br and I). The corresponding metal–ligand interatomic bond lengths and angles exhibit some differences in (I), (II) and (III) (Tables 1–3), but are comparable to the values of reported related Hg^{II} complexes (Masciocchi *et al.*, 2009). The diameters of the cavities in the middle of the macrocycles are 3.269 (7), 3.811 (7) and 2.770 (6) Å for the Cl, Br and I derivatives, respectively.

The flexible L ligand can adopt different conformations under different conditions. In a previous study, a flexible ether-bridged organic ligand with terminal indoline-2,3-dione groups adopts a *trans* conformation about its central core in the free state, but a *gauche* conformation after coordinating to the Ag^I centre (Fang *et al.*, 2011). Here, in (I), the O1—C12—C13—O2 torsion angle of the central ether group is −71.5 (12)° (Fig. 1a). In (II), the torsion angle has changed to −70.1 (9)° (Fig. 1b), and in (III), the corresponding torsion angle is 77.9 (7)° (Fig. 1c). The sign of the torsion angle in (III) is opposite to that in (I) and (II), indicating a difference of some 150° between these torsion angles in the structures, so the ethylene bridge is oriented quite differently in (III) to the corresponding bridges in (I) and (II), as can be seen in Fig. 1.
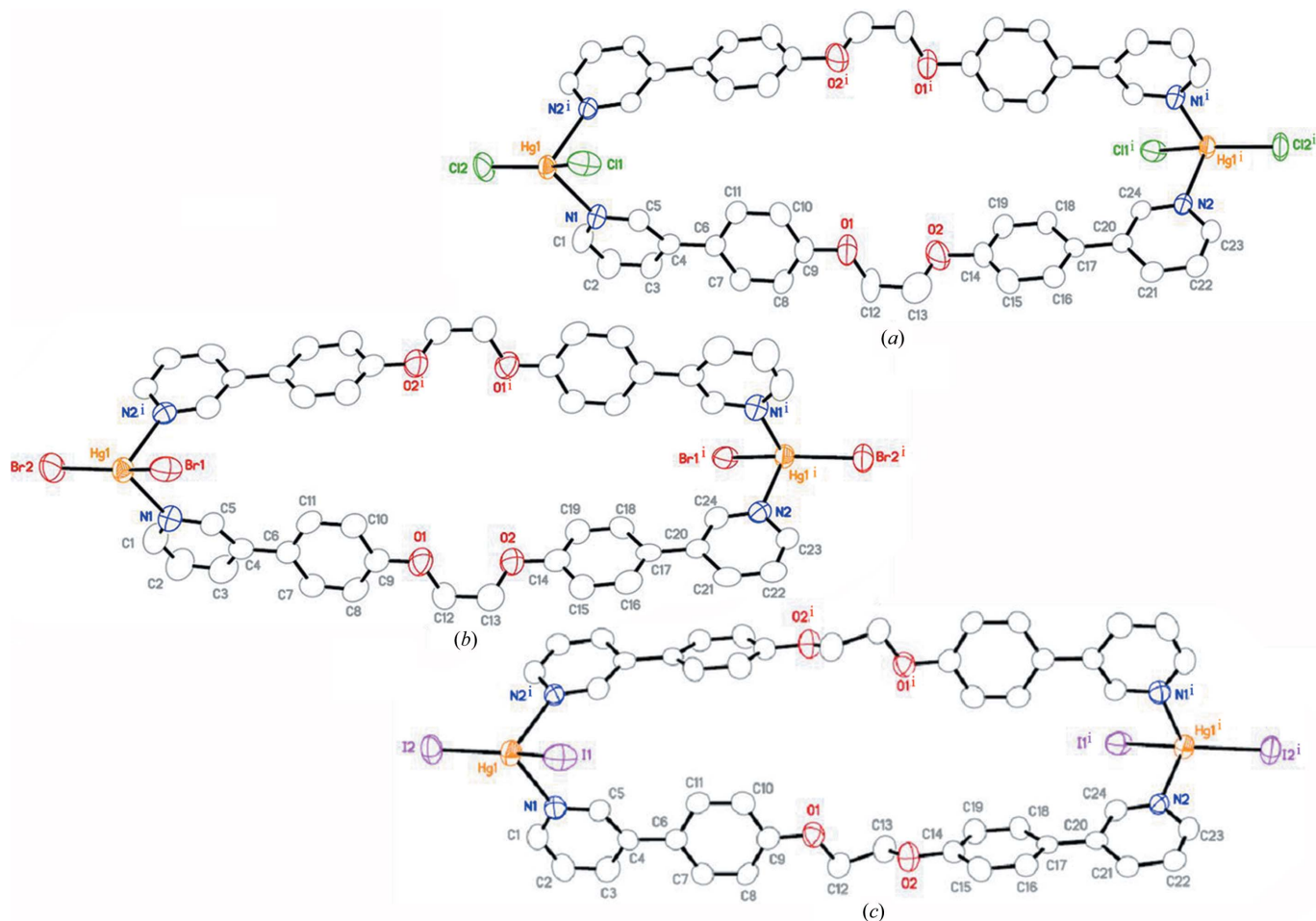
Figure 1
The molecular structure of (*a*) (I), (*b*) (II) and (*c*) (III), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]
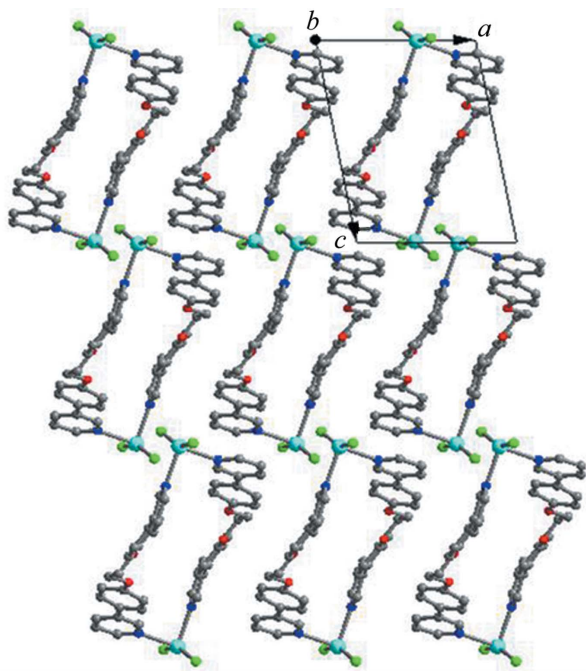
Figure 2
The packing feature of compound (I). H atoms have been omitted for clarity.

Additionally, the dihedral angle between the terminal N1-pyridine plane and the adjacent C6-benzene plane is 24.7 (2)° in (I) and 21.2 (2)° in (II). In contrast, the terminal N2-pyridine plane and the adjacent C17-benzene plane are nearly coplanar, with a dihedral angle of 9.8 (3)° in (I) and 6.8 (2)° in (II). In (III), the dihedral angles between the planes of the relative pyridine rings and benzene rings are 15.0 (2) and 18.5 (2)°.

In the solid state, compounds (I)–(III) have the same packing motif; Fig. 2 shows the packing feature of compound (I). Herein, the representative structure of (I) is described in detail. As shown in Fig. 3, the one-dimensional Hg—Cl chains are formed along the [$0\bar{2}1$] direction through noncovalent Hg···Cl interactions [Hg1···Cl2^{ii}; symmetry code: (ii) $-x + 1$, $-y - 1 -z + 2$]. If three different Cl···Cl interactions [Cl2···Cl1^{ii}, Cl2···Cl2^{ii} and Cl1···Cl1^{iii}; symmetry code: (iii) $-x + 1, -y, -z + 2$] are taken into consideration, a network parallel to the *bc* plane is formed. Fig. 4 shows the chains of Hg—Br moieties in (II) and the chains of Hg—I moieties in (III), with noncovalent interactions emphasized. The important noncovalent interactions in (I)–(III) are compared in Table 4. These two-dimensional sheets driven by noncovalent Hg···*X* and *X*···*X* (*X* = Cl, Br and I) interactions are stacked
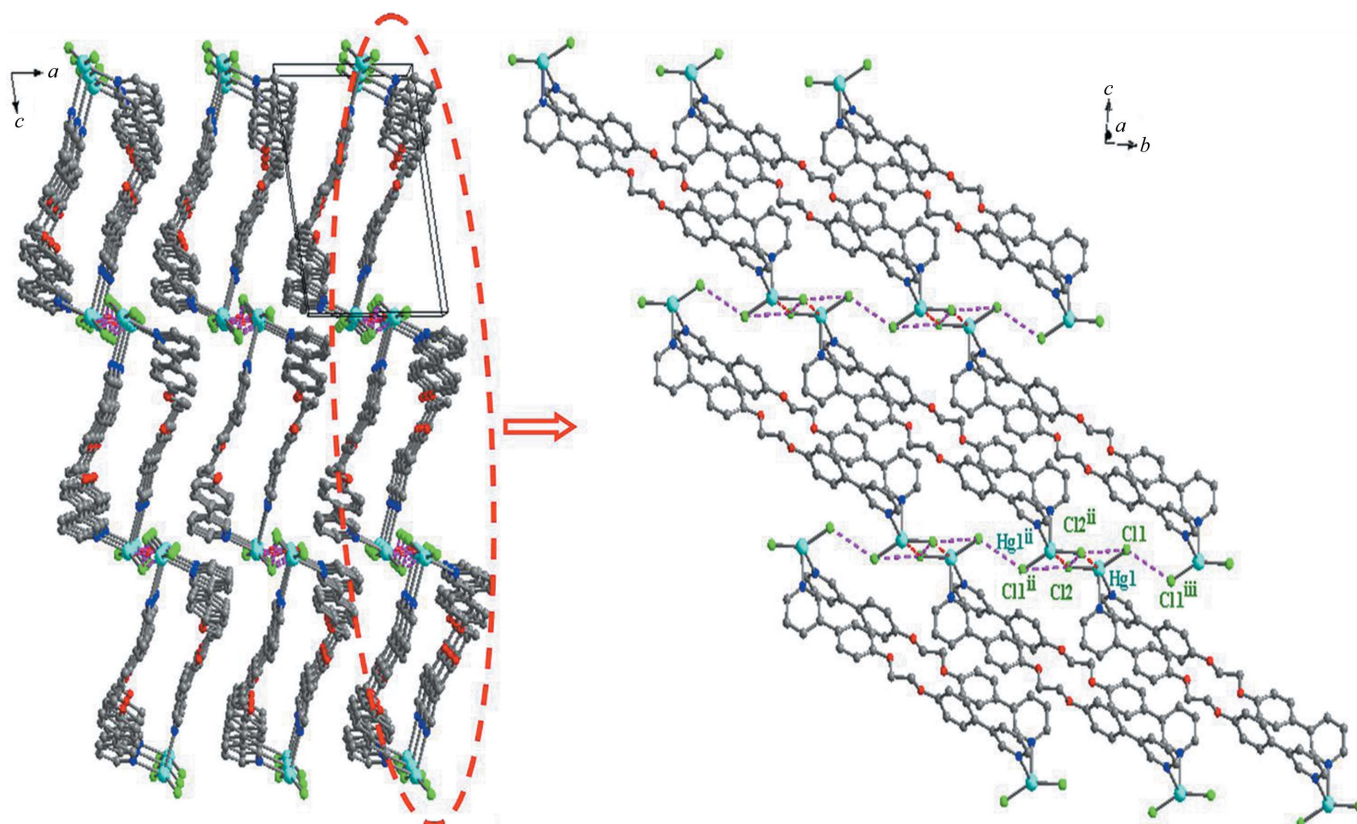
Figure 3
The two-dimensional sheet parallel to the *bc* plane of (I) and the stacking of the sheets along *a*. One-dimensional Hg—Cl chains are formed parallel to [0$\bar{2}$1] through noncovalent Hg$\cdots$Cl interactions (Hg1$\cdots$Cl2^{ii}) and three different Cl$\cdots$Cl interactions (Cl2$\cdots$Cl1^{ii}, Cl2$\cdots$Cl2^{ii} and Cl1$\cdots$Cl1^{iii}). H atoms have been omitted for clarity. [Symmetry codes: (ii) $-x + 1, -y - 1, -z + 2$; (iii) $-x + 1, -y, -z + 2$.]
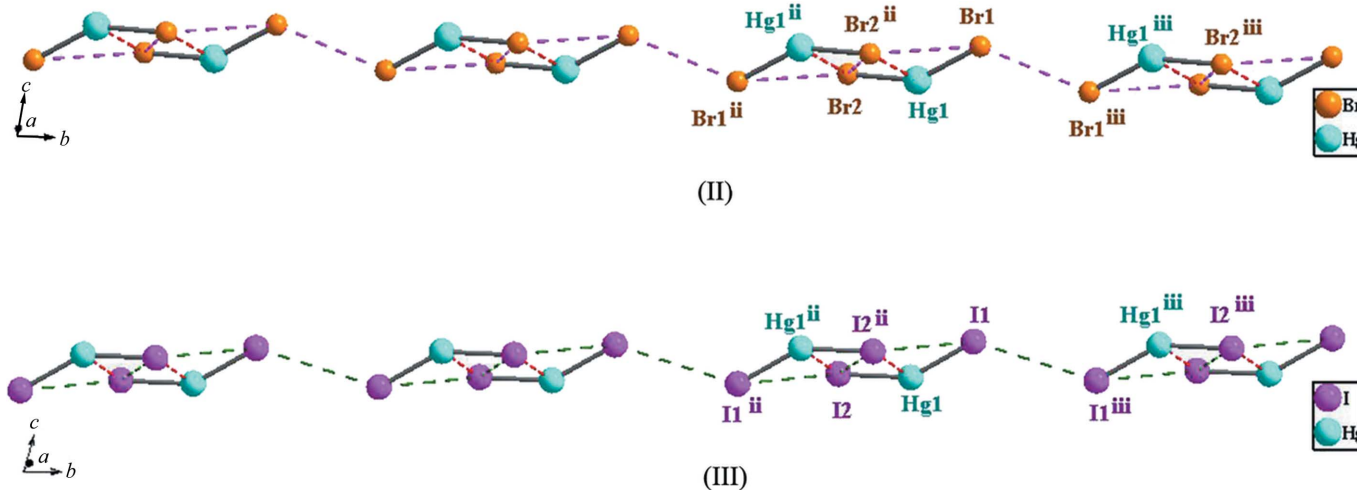

Figure 4
The Hg—*X* fragments and the chains formed by Hg$\cdots$*X* and *X*$\cdots$*X* interactions in (II) and (III) analogous to those shown in Fig. 3. [Symmetry codes: (ii) $-x + 1, -y - 1, -z + 2$; (iii) $-x + 1, -y, -z + 2$.]

along *a* without any offset. The Hg$\cdots$*X* distances, in the range 3.369 (2)–3.9819 (9) Å, are shorter than their van der Waals contact distances. The *X*$\cdots$*X* (*X* = Cl, Br and I) distances in (I), (II) and (III) are a little longer than the sums of the van der Waals radii (van der Waals radii: Hg = 2.15 Å, Cl = 1.80 Å, Br = 1.95 Å and I = 2.15 Å; Batsanov, 2001). Weak Cl$\cdots$Cl interactions as long as 3.72 Å, which is longer than the van der Waals contact of 3.60 Å, have been reported for hexachloro-benzene (Sarma & Desiraju, 1986). The Hg—*X* and the weak *X*$\cdots$*X* interactions are important for assisting in the lattice formation.

In summary, three macrocycles have been synthesized based on the flexible ether-bridged dipyridyl ligand. We anticipate this approach may be useful in constructing novel supramolecular compounds with the flexible ether-bridged dipyridyl ligand.

Experimental

For the preparation of 1,2-bis[4-(pyridin-3-yl)phenoxy]ethane (*L*), sodium hydroxide (0.44 g, 11 mmol) was added with stirring to a solution of 1,2-bis(*p*-tolylsulfonyl)ethane (1.85 g, 5 mmol) and 4-(pyridin-3-yl)phenol (1.71 g, 10 mmol) in anhydrous *N*,*N*-dimethylformamide (50 ml). The mixture was stirred for 24 h at 358 K and monitored by thin-layer chromatography (TLC). After removal of the solvent, the compound was purified by column chromatography using silica gel and CH_2Cl_2–MeOH (20:1 *v*/*v*) to afford *L* as a white crystalline solid (yield 1.54 g, 4.18 mmol, 83.7%). Elemental analysis calculated for $C_{24}H_{20}N_2O_2$: C 78.24, H 5.47, N 7.60%; found: C 78.17, H 5.38, N 7.73%.

For the preparation of (I), a solution of $HgCl_2$ (5.97 mg, 0.022 mmol) in methanol (8 ml) was layered onto a solution of *L* (8.10 mg, 0.022 mmol) in CH_2Cl_2 (8 ml). The system was left for about one week at room temperature and colourless crystals of (I) were obtained (yield 11.11 mg, 79%). IR (KBr pellet, cm^{-1}): 3417 (*m*), 3128 (*m*), 2925 (*w*), 2873 (*w*), 1605 (*s*), 1580 (*w*), 1515 (*s*), 1476 (*s*), 1452 (*m*), 1435 (*m*), 1399 (*s*), 1315 (*w*), 1282 (*s*), 1246 (*s*), 1200 (*w*), 1181 (*s*), 1131 (*w*), 1072 (*m*), 1026 (*w*), 1002 (*w*), 944 (*m*), 840 (*m*), 802 (*s*), 738 (*w*), 698 (*m*), 646 (*w*), 632 (*m*), 556 (*m*), 490 (*w*).

For the preparation of (II), a solution of $HgBr_2$ (7.93 mg, 0.022 mmol) in methanol (8 ml) was layered onto a solution of *L* (8.10 mg, 0.022 mmol) in CH_2Cl_2 (8 ml). The system was left for about one week at room temperature and colourless crystals of (II) were obtained (yield 10.10 mg, 63%). IR (KBr pellet, cm^{-1}): 3415 (*m*), 3128 (*m*), 2925 (*w*), 2873 (*w*), 1605 (*s*), 1516 (*s*), 1476 (*s*), 1452 (*m*), 1436 (*m*), 1400 (*s*), 1282 (*s*), 1246 (*s*), 1181 (*s*), 1130 (*w*), 1072 (*m*), 1026 (*w*), 1001 (*w*), 944 (*m*), 837 (*m*), 802 (*s*), 738 (*w*), 698 (*m*), 646 (*w*), 632 (*m*), 555 (*m*).

For the preparation of (III), a solution of HgI_2 (10.00 mg, 0.022 mmol) in methanol (7 ml) was layered onto a solution of *L* (8.10 mg, 0.022 mmol) in CH_2Cl_2 (7 ml). The system was left for about one week at room temperature and colourless crystals of (III) were obtained (yield 10.67 mg, 59%). IR (KBr pellet, cm^{-1}): 3417 (*m*), 3128 (*m*), 2919 (*w*), 1605 (*s*), 1517 (*s*), 1475 (*s*), 1450 (*m*), 1436 (*m*), 1399 (*s*), 1313 (*w*), 1280 (*s*), 1246 (*s*), 1180 (*s*), 1130 (*w*), 1073 (*m*), 1024 (*w*), 1001 (*w*), 950 (*s*), 836 (*s*), 801 (*s*), 738 (*w*), 700 (*m*), 646 (*w*), 630 (*m*), 553 (*m*).

Compound (I)

Crystal data

$[Hg_2Cl_4(C_{24}H_{20}N_2O_2)_2]$	$\gamma = 84.014 (2)°$
$M_r = 1279.82$	$V = 1102.8 (3)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.7822 (15)$ Å	Mo $K\alpha$ radiation
$b = 10.6904 (18)$ Å	$\mu = 7.25$ mm^{-1}
$c = 12.044 (2)$ Å	$T = 298$ K
$\alpha = 86.662 (2)°$	$0.20 \times 0.15 \times 0.15$ mm
$\beta = 78.930 (2)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	5867 measured reflections
	4066 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	3708 reflections with $I > 2\sigma(I)$
$T_{min} = 0.325$, $T_{max} = 0.410$	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	280 parameters
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{max} = 1.99$ e Å^{-3}
4066 reflections	$\Delta\rho_{min} = -1.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cl1—Hg1	2.337 (2)	Hg1—N2^i	2.463 (5)
Cl2—Hg1	2.338 (2)	N2—Hg1^i	2.463 (5)
Hg1—N1	2.438 (6)		
Cl1—Hg1—Cl2	152.25 (10)	Cl1—Hg1—N2^i	98.41 (14)
Cl1—Hg1—N1	100.05 (16)	Cl2—Hg1—N2^i	98.11 (14)
Cl2—Hg1—N1	103.08 (16)	N1—Hg1—N2^i	86.50 (19)

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

Compound (II)

Crystal data

$[Hg_2Br_4(C_{24}H_{20}N_2O_2)_2]$	$\gamma = 81.635 (5)°$
$M_r = 1457.66$	$V = 1149.1 (8)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.021 (4)$ Å	Mo $K\alpha$ radiation
$b = 11.096 (4)$ Å	$\mu = 10.20$ mm^{-1}
$c = 11.914 (5)$ Å	$T = 298$ K
$\alpha = 81.812 (5)°$	$0.15 \times 0.14 \times 0.13$ mm
$\beta = 78.764 (5)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	6112 measured reflections
	4234 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	3491 reflections with $I > 2\sigma(I)$
$T_{min} = 0.310$, $T_{max} = 0.351$	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	280 parameters
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{max} = 1.19$ e Å^{-3}
4234 reflections	$\Delta\rho_{min} = -1.04$ e Å^{-3}

Compound (III)

Crystal data

$[Hg_2I_4(C_{24}H_{20}N_2O_2)_2]$	$\gamma = 77.620 (2)°$
$M_r = 1645.62$	$V = 1213.3 (4)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.9444 (16)$ Å	Mo $K\alpha$ radiation
$b = 12.352 (2)$ Å	$\mu = 8.91$ mm^{-1}
$c = 12.052 (2)$ Å	$T = 298$ K
$\alpha = 72.641 (2)°$	$0.20 \times 0.15 \times 0.15$ mm
$\beta = 74.882 (2)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	6387 measured reflections
	4426 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	3740 reflections with $I > 2\sigma(I)$
$T_{min} = 0.269$, $T_{max} = 0.348$	$R_{int} = 0.023$

Table 2
Selected geometric parameters (Å, °) for (II).

Br1—Hg1	2.4644 (10)	Hg1—N2^i	2.449 (5)
Br2—Hg1	2.4512 (12)	N2—Hg1^i	2.449 (5)
Hg1—N1	2.443 (6)		
Br1—Hg1—Br2	150.17 (4)	N2^i—Hg1—Br1	97.82 (14)
Br1—Hg1—N1	100.18 (15)	N2^i—Hg1—Br2	100.51 (14)
Br2—Hg1—N1	104.22 (15)	N1—Hg1—N2^i	86.53 (19)

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

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Table 3
Selected geometric parameters (Å, °) for (III).

I1—Hg1	2.6365 (6)	Hg1—N2[i]	2.471 (5)
I2—Hg1	2.6272 (6)	N2—Hg1[i]	2.471 (5)
Hg1—N1	2.482 (5)		
I1—Hg1—I2	149.69 (2)	N2[i]—Hg1—I1	100.74 (11)
I1—Hg1—N1	98.91 (12)	N2[i]—Hg1—I2	100.93 (11)
I2—Hg1—N1	103.46 (12)	N2[i]—Hg1—N1	86.14 (16)

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

Table 4
Comparative geometric parameters (Å) for the important noncovalent interactions in (I), (II) and (III).

	(I) (X = Cl)	(II) (X = Br)	(III) (X = I)
Hg1—X2[ii]	3.369 (2)	3.6254 (19)	3.9819 (9)
X2—X2[ii]	3.935 (3)	4.077 (2)	4.4521 (11)
X2—X1[ii]	3.985 (3)	4.405 (2)	4.7066 (11)
X1—X1[iii]	3.661 (3)	3.914 (2)	4.5354 (12)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	1 restraint
$wR(F^2) = 0.086$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 1.11$ e Å^{-3}
4426 reflections	$\Delta\rho_{min} = -1.10$ e Å^{-3}
280 parameters	

H atoms were placed in geometrically idealized positions and included as riding atoms, with C—H = 0.93 Å and U_{iso}(H) = $1.2U_{eq}$(C) (aromatic), or C—H = 0.97 Å and U_{iso}(H) = $1.2U_{eq}$(C) (methylene). Atoms O1, O2, C12 and C13 in (I) are statistically disordered because of slight rotation about C—O bonds, as evidenced by the elongated atomic displacement ellipsoids for these atoms. Attempts to model the disorder were not successful. The ratio of the disordered part is less than 20%; the minor component is not included in the refinement. In the C6—C11 benzene ring of (III), the bond lengths except for the C6—C11 bond range from 1.358 to 1.378 Å; a restraint of 1.37 (1) Å was applied to the longer C6—C11

bond to keep the rationality of the ring. As a result, the C6—C11 bond length is 1.388 (6) Å.

For all 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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