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Metallosupramolecules of pillar[5]-bis-trithiacrown including a mercury(II) iodide ion-triplet complex

A combination of pillar[5]-bis-trithiacrown and HgI_2 afforded an ion-triplet complex in which the host encapsulates the $(I^- - Hg^{2+} - I^-)$ entity *via* metal- $\cdots\pi$ and C-H- $\cdots I^-$ interactions, reflecting geometrical complementarity.

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A combination of pillar[5]-bis-trithiacrown (L) and mercury(II) halides afforded a monomer complex (Cl⁻-form), a 1-D coordination polymer (Br⁻-form) and a supramolecular ion-triplet complex [(L-Hg²⁺)-L] (I⁻-form). In the ion-triplet complex, the host encapsulates the (I⁻-Hg²⁺-I⁻) entity via Hg²⁺...π and C-H...I⁻ interactions, reflecting geometrical complementarity.

Macrocyclic hosts have played a pivotal role in supramolecular chemistry especially because of their ability to exhibit selective recognition of particular cation (C⁺)^{1,2} or anion (A⁻)^{2,3} guests. The latter recognition is typically more challenging due to the intrinsic nature of many anions including their larger sizes, different shapes and often higher polarizabilities. A number of hetero-di or poly-topic receptors incorporating one or more macrocycle units have been shown to exhibit concurrent cation and anion recognition to form inclusive or endocyclic (guest-in-cavity) ion-pair complexes.⁴ Common motifs of such ion-pair complexes involve, as shown in Fig. 1, (a) contact and (b) solvent-separated arrangement of types [C⁺-A⁻@receptor] and [C⁺-solvent-A⁻@receptor], respectively.³ In principle, the formation of the corresponding ion-triplet complexes exhibiting [A⁻-C²⁺-A⁻@receptor] or [C⁺-A²⁻-C⁺@receptor] arrangements appeared possible under appropriate conditions (Fig. 1c).

Indeed, the Lüning group has shown the formation of a supramolecular ion-triplet complex of calcium(II) ions, [Cl⁻-Ca²⁺-Cl⁻@macrocycle], with a 30-membered [2+2] amide-macrocycle by ESI-mass in solution.⁵ However, no further examples of the formation or isolation of supramolecular ion-triplet complexes of metal ions both in solution and the solid state have been reported so far.

In our experience, endocyclic and exocyclic coordination modes of some thiamacroyclic complexes are known to be

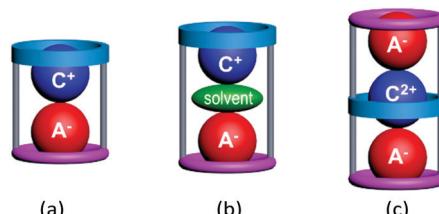


Fig. 1 Schematic representation of (a) a contact ion-pair complex, (b) a solvent-separated ion-pair complex and (c) a contact ion-triplet complex with poly-topic macrocycles.

controlled by several factors that include their anion coordination abilities.^{6,7} Pillar[n]arenes are a relatively new category of macrocyclic receptors and their inclusion complexes with organic guests such as diamines and dinitriles to yield polyrotaxane and *pseudo*-rotaxane structures have been widely studied in recent years.⁸

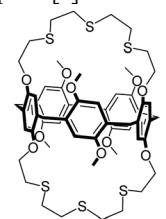
In marked contrast to the big advances in pillar[n]arene chemistry involving organic guests,⁹ their metallosupramolecular derivatives are rare except for studies from our¹⁰ and two other groups.¹¹ In a prior study our modification of a pillar[5]arene to form a *pseudo*[1]catenane-type pillar[5]-monothiacrown showed a chiral inversion upon mercury(II) complexation under anion-coordination control.^{10a} We have also prepared a di-armed pillar[5]arene-based two-dimensional silver(I) poly-*pseudo*-rotaxane in which the same dinitrile guest both threads and crosslinks.^{10b} The Huang group has reported ion-pair recognition of pyridinium iodide¹² and silver trifluoroacetate^{11b} using a peralkylated pillar[5]arene. In this work, we have shown that it is possible to isolate an ion-triplet complex by employing pillar[5]-bis-trithiacrown (L).

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Pillar[5]-bis-trithiacrown (L)

In our results, the coordination modes of the mercury(II) halide complexes of **L** are anion-dependent. For example, **L** forms a mononuclear complex and an infinite type complex *via* an exo-coordination with chloride and bromide, respectively. Surprisingly, mercury(II) iodide led to the formation of an ion-triplet complex (Fig. 1c) as the first example isolated in the solid state to the best of our knowledge. The details are discussed below.

The pillar[5]-bis-trithiacrown **L** was synthesised by bicyclisation employing pillar[5]arene tetrabromide and the required dithiol (yield 30%, Scheme S1 and Fig. S1 and S2, ESI[†]). The tetrabromide precursor was obtained employing a mixture of dibromide, 1,4-dimethoxybenzene, paraformaldehyde and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.^{10b} The crystal structure of **L** was determined and shown to include one *n*-hexane molecule in its central cavity (Fig. S3, S4 and Table S1, ESI[†]). Both trithiacrown loops ($\text{O}-\text{S}-\text{S}-\text{O}$) in **L** show *t-t-t-t* (*t* = *trans*) torsion arrangements reflecting the repulsive interaction between adjacent S donors.

The reaction of **L** with HgCl_2 in dichloromethane/methanol afforded a colourless crystalline product **1**. The X-ray analysis revealed that **1** crystallises in the monoclinic space group *Cc* with $Z = 4$ (Tables S1 and S2, ESI[†]). The structure features an exocyclic mononuclear arrangement of type $[\text{HgCl}_2(\text{CH}_2\text{Cl}_2@\mathbf{L})]$ (Fig. 2 and Fig. S5, ESI[†]). The $\text{Hg}1$ atom, with a distorted tetrahedral geometry [$82.41(12)-126.39(14)$ °], is bonded to two S atoms [$\text{Hg}1-\text{S}2$ 2.611(4), $\text{Hg}1-\text{S}3$ 2.714(3) Å], with its coordination environment completed by two Cl atoms [$\text{Hg}1-\text{Cl}1$ 2.363(4), $\text{Hg}1-\text{Cl}2$ 2.378(4) Å]. Four S donors remain uncoordinated, with a dichloromethane molecule occupying the cavity of **L**.

In **1**, the nonsymmetrical binding of the $\text{Hg}1$ atom induces a large conformational change in the $\text{O}1-\text{S}1-\text{S}2-\text{S}3-\text{O}2$ loop segment from *t-t-t-t* to *g-t-g-g* (*g* = *gauche*, *t* = *trans*) torsion arrangements, with that of the $\text{O}3-\text{S}4-\text{S}5-\text{S}6-\text{O}4$ loop segment (*t-t-t-t*) remaining unchanged. Unlike oxygen-bearing crown ethers, thiamacrocycles so often show a repulsive interaction between adjacent sulfur donors, stabilizing a *trans* torsion arrangement which tends to lead to the adoption of an exo-coordination mode.^{6,7,13}

The reaction of **L** with HgBr_2 in chloroform/acetonitrile yielded the colourless complex **2** which crystallizes in the monoclinic space group *Pc* with $Z = 2$ (Tables S1 and S3, ESI[†]). This product features an exocyclic one-dimensional (1-D) polymeric arrangement of formula $[\text{Hg}_6\text{Br}_{12}(\text{CH}_3\text{CN}@\mathbf{L})_2]_n$ (Fig. 3a). The asymmetric unit contains one formula unit. The crystallographically independent six Hg atoms ($\text{Hg}1-\text{Hg}6$) that lie outside the cavity have

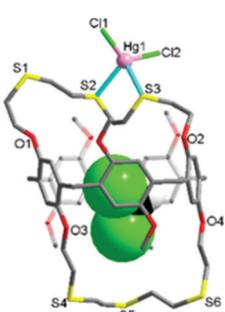


Fig. 2 The exo-coordinated mercury(II) chloride complex $[\text{HgCl}_2(\text{CH}_2\text{Cl}_2@\mathbf{L})]$ (**1**).

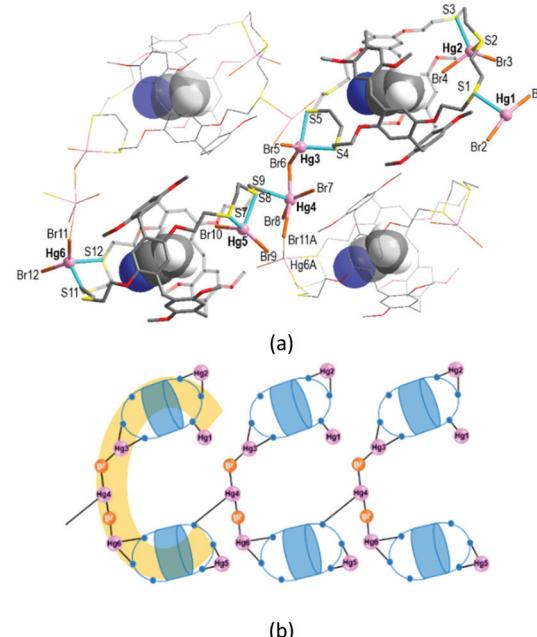


Fig. 3 The exo-coordinated mercury(II) bromide complex $[\text{Hg}_6\text{Br}_{12}(\text{CH}_3\text{CN}@\mathbf{L})_2]$ (**2**): (a) the 1-D polymeric structure (the asymmetric unit is shown with the labelling) and (b) the connectivity pattern showing the linkage of the C-shaped dimers (terminal Br atoms are omitted). Symmetry operation A: $-1 + x, -y, -0.5 + z$.

different coordination environments. First, the terminal $\text{Hg}1$ atom is three-coordinate, being bound to one S atom from one trithiacrown loop and two Br atoms. Second, each of the $\text{Hg}2$, $\text{Hg}3$, $\text{Hg}5$ and $\text{Hg}6\text{A}$ atoms is four-coordinated by two S atoms from one trithiacrown loop and two Br atoms to form a distorted tetrahedral coordination geometry. The $\text{Hg}4$ atom is five-coordinate, being bound to four Br atoms and one S atom to yield a three-way node. An acetonitrile molecule occupies the cavity of each **L**.

In **2**, two $(\text{CH}_3\text{CN}@\mathbf{L})$ units which locate up and down are linked by a linear $\text{Hg}3-\text{Br}-\text{Hg}4-\text{Br}-\text{Hg}6\text{A}$ segment *via* Hg–S bonds [2.577(5)–2.763(5) Å] to form a C-shaped dimer arrangement (Fig. 3b). Individual dimers are further linked *via* a $\text{Hg}4-\text{S}9$ bond [2.734(4) Å] to give a 1-D polymeric structure.

When HgI_2 was reacted with **L** in dichloromethane/methanol, a pale yellow product **3** was isolated. In marked contrast to the chlorido and bromido complexes, **3** is an endocyclic ion-triplet complex with the formula $[\text{I}-\text{Hg}-\text{I}@\mathbf{L}]$ (**3**) which crystallises in the monoclinic space group *P2₁/c* with $Z = 4$ (Fig. 4a and Fig. S6, S7, Tables S1, S4, ESI[†]). In **3**, surprisingly, one $(\text{I}^-\text{Hg}^{2+}\text{I}^-)$ entity locates inside the cavity of **L**. Although some ion-triplet organic cation complexes of types $[(\text{R}_1\text{R}_2\text{NH}_2^+)_2\text{SO}_4^{2-}@\text{bis}(\text{calix}[6]\text{arene})]$ and $[(\text{Cl}^-\text{R}_4\text{N}^+\text{Cl}^-)@\text{bis}(\text{calix}[4]\text{pyrrole})]$ have been reported,¹⁴ no solid ion-triplet metal complexes of such type have been reported so far.

As mentioned above, **L** prefers to form exo-coordinated products with mercury(II) salts. Thus the formation of **3** raises some questions. (i) What is the driving force to stabilize the mercury(II) ion in the centre of the cavity? (ii) How is the iodide ion stabilized inside the crown loop? (iii) How is the linear $(\text{I}^-\text{Hg}^{2+}\text{I}^-)$ entity formed? Each of these aspects is now discussed.

First, some metal ions including K^+ , Cs^+ , Ag^+ and Hg^{2+} interact with aromatic carbons *via* cation- π interactions, with such interactions being well established for calixarenes.^{15,16} With respect to this, the Hg^{2+} centre in 3 is stabilized by five such cation- $\cdot\cdot\pi$ interactions (3.82–4.38 Å, dashed lines in Fig. 4b) to form a pentagonal planar array. Additionally, two I^- ions occupy axial sites to yield an overall pentagonal bipyramidal geometry [$Hg1$ – $I1$ 2.5642(6), $Hg1$ – $I2$ 2.5555(6) Å, $I1$ – $Hg1$ – $I2$ 178.30(2) $^\circ$].

Second, the larger size and softer nature of the I^- ion may play an advantageous role in the confined space. When large numbers of weak H-bonds act cooperatively, quite often they play an important role in stabilizing supramolecular structures. Thus, each I^- ion in 3 is found to interact with five H atoms from different O – CH_2 and O – CH_3 groups *via* C – $H\cdot\cdot I^-$ H-bonds,¹⁷ with the distances and angles being 3.2132(0)–3.5277(0) Å and 133.193(2)–157.987(2) $^\circ$ (Fig. 4c and Table S4, ESI[†]).

Third is the question of how the linear (I^- – Hg^{2+} – I^-) entity might form. Mercury(II) iodide is known to crystallize in several polymorphs including linear, tetrahedral and tetragonal structures depending on the preparation process.¹⁸ In principle, the interaction of solvent-separated ion-pairs is primarily electrostatic, but mercury(II) iodide is quite soluble in common organic solvents including methanol¹⁹ and is present partially as a non-dissociated ion-triplet due to the covalent character.²⁰ As mentioned, each I^- ion is bound to a bridging μ - Hg^{2+} centre to yield a pentagonal pyramidal geometry (Fig. 4c). Since synthetic hosts for halide ions favour two to six binding interactions,^{2,3} each I^- ion in Fig. 4c represents a good example of such a condition being met with six interactions present for each I^- on forming the ion-triplet complex. The linear (I^- – Hg^{2+} – I^-) entity in 3 is intimately associated with the peanut-shaped cavity of L giving rise to an excellent geometric and electronic complementary *via* the multiple cation- π interactions and H-bonds. Thus it is not surprising how the linear arrays of HgI_2 form because the solid structure of the yellow polymorph of HgI_2 , as mentioned, is almost linear (178.3 $^\circ$)^{18b} and the linear

HgI_2 guest from $[I\cdot Hg\cdot I\cdots I\cdot Hg\cdot I]$ columns found in the Cu^{II} / Hg^{II} -MOF (MOF = metal-organic framework) is also stabilised by weak coordination of four iodide ions in the 3-D framework.²¹

Based on the UV-vis titration experiments in chloroform/methanol, the formation constants ($\log K$) for the complexations of L with mercury(II) halides were obtained (Table 1 and Fig. S8–S10, ESI[†]). The $\log K$ values (for 1:1 complexes) tend to be smaller for larger anions because the larger halide ions as a softer base can bind to the mercury(II) centre (soft acid) more tightly and hence reduce the complex stability. The $\log K$ value for the iodide system is, however, larger than expected because the extra stabilization of the ion-triplet *via* the supramolecular interactions probably compensates this effect in part. In the bromide system, the ligand L binds to two mercury(II) ions *via* two steps but the 1:1 (ML) complex is more stable than the 2:1 complex (M_2L) which is formed above the 1 equivalent of $HgBr_2$.

In summary, we report here the isolation of the first solid state example of a supramolecular ion-triplet complex incorporating a hetero-tritopic macrocycle. To achieve this, the pillar[5]-bis-trithiacrown L was synthesised and its anion-dependent mercury(II) halide complexes exhibiting different topological arrangements were isolated. In the chlorido and bromido complexes, exo-coordination *via* Hg – S bonds occurs, with the corresponding anions binding only to the cation (in different mutual configurations). In the iodido complex, however, the mode of interaction of this anion is totally different; it not only interacts with the metal cation but also with the ligand L to form the unique contact ion-triplet complex. Consequently, the formation of the ion-triplet complex reflects that the multiple $Hg^{2+}\cdots\pi$ interactions stabilize the overall structure, with the concerted C – $H\cdot\cdot I^-$ H-bonds being geometrically and electronically well matched to satisfy the mutual complementarity required for binding in the confined central space in L. A further investigation of the potential application of triplet complexes of the present type for the detection and removal of toxic heavy metal species is in progress.

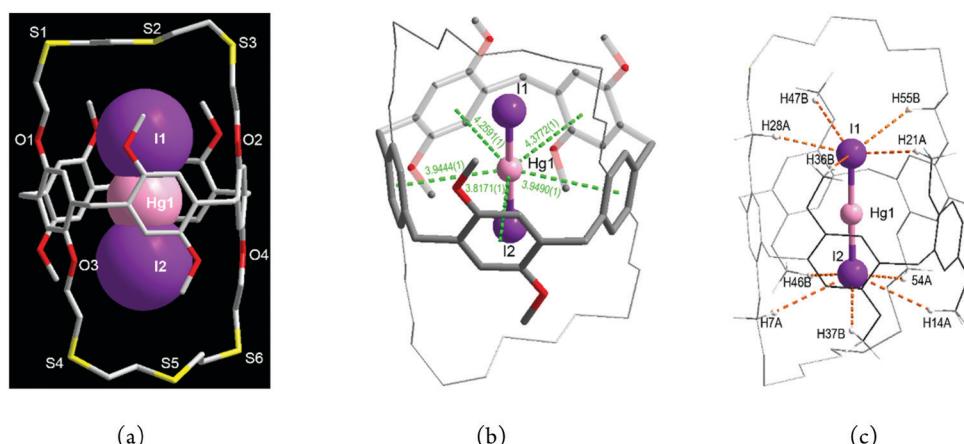


Fig. 4 The contact ion-triplet complex with mercury(II) iodide $[(I\cdot Hg\cdot I)\cdot @L]$ (3): (a) general view showing an $(I^- - Hg^{2+} - I^-)$ entity (space-filling) in the central cavity, (b) a pentagonal bipyramidal geometry with five $Hg^{2+}\cdots\pi$ interactions (green dashed lines) and an I – Hg – I axis and (c) a mercury-shared double pentagonal pyramidal geometry with five C – $H\cdot\cdot I^-$ H-bonds (orange dashed lines) and I – Hg – I axis (only H-bonded H atoms are shown).

Table 1 Formation constants ($\log K$) for the complexations of **L** with mercury(II) halides in chloroform/methanol (1:2.5, v/v) at 298 K^a

Reactions	Products	Formation constants	
$\text{HgCl}_2 + \mathbf{L}$	$\text{Hg}(\mathbf{L})\text{Cl}_2$	$\log K_{11}$	5.94 ± 0.003
$\text{HgBr}_2 + \mathbf{L}$	$\text{Hg}(\mathbf{L})\text{Br}_2$	$\log K_{11}$	4.46 ± 0.006
$2 \text{HgBr}_2 + \mathbf{L}$	$\text{Hg}_2(\mathbf{L})\text{Br}_4$	$\log K_{21}$	8.18 ± 0.002
$\text{HgI}_2 + \mathbf{L}$	$\text{Hg}(\mathbf{L})_2$	$\log K_{11}$	5.10 ± 0.003

^a UV-vis titration method using the HypSpec software.²²

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Conflicts of interest

There are no conflicts to declare.

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