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

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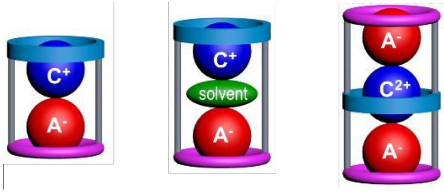
A combination of pillar[5]-*bis*-trithiacrown (L) and mercury(II) halides afforded a monomer complex (Cl$^-$-form), a 1-D coordination polymer (Br$^-$-form) and a supramolecular ion-triplet complex [(I·Hg·I)@L] (I$^-$-form). In the ion-triplet complex, the host encapsulates (I$^-$-Hg^{2+}-I$^-$) entity via Hg^{2+}···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 corresponding *ion-triplet* complexes exhibiting [A$^-$·C^{2+}·A$^-$@receptor] or [C$^+$·A^{2-}·C$^+$@receptor] arrangements appeared possible under appropriate conditions (Fig. 1c).



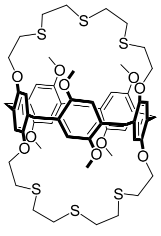
(a) (b) (c)

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.

Indeed, the Lüning group have shown the formation of a supramolecular *ion-triplet* complex of calcium(II) ion, [Cl$^-$·Ca^{2+}·Cl$^-$@macrocycle], with a 30-membered [2+2] amide-macrocycle by ESI-mass in solution.[5b] However no further examples of the formation or isolation on 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 thiamacrocyclic complexes are known to be 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 works from our[10] 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]-*mono*-thiacrown 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 have reported *ion-pair* recognition of pyridinium iodide[12] 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**).



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**

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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, Figs. S1 and S2). The tetrabromide precursor was obtained employing a mixture of dibromide, 1,4-dimethoxybenzene, paraformaldehyde and $BF_3{\cdot}O(C_2H_5)_2$.[10b] The crystal structure of **L** was determined and shown to include one *n*-hexane molecule in its central cavity (Figs. S3, S4 and Table S1). Both trithiacrown loops (O-S-S-S-O) in **L** show *t-t-t-t* (*t* = *trans*) torsion arrangements reflecting the repulsive interaction between adjacent S donors.

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 C*c* with Z = 4 (Tables S1 and S2). The structure features an exocyclic mononuclear arrangement of type [$HgCl_2(CH_2Cl_2$@**L**)] (Fig. 2 and Fig. S5). The Hg1 atom, with a distorted tetrahedral geometry [82.41(12)-126.39(14)°], is bonded to two S atoms [Hg1-S2 2.611(4), Hg1-S3 2.714(3) Å], with its coordination environment completed by two Cl atoms [Hg1-Cl1 2.363(4), Hg1-Cl2 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 Hg1 atom induces the large conformational change of the O1-S1-S2-S3-O2 loop segment from *t-t-t-t* to *g-t-g-g* (*g* = *gauche*, *t* = *trans*) torsion arrangements, remaining that of the O3-S4-S5-S6-O4 loop segment (*t-t-t-t*) 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 adoption of an exo-coordination mode.[6,7,13]

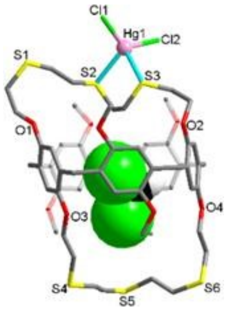
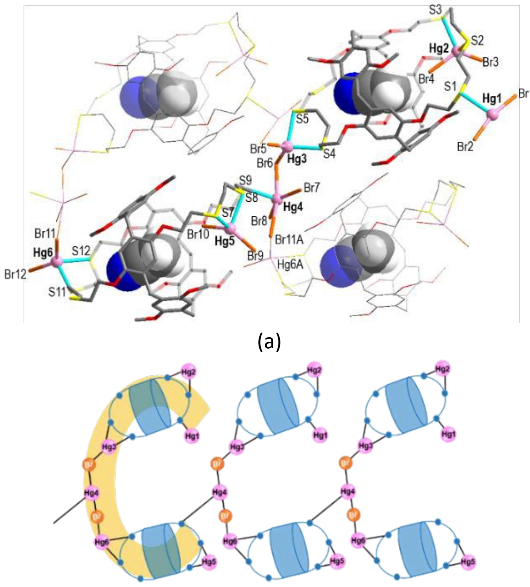


Fig. 2 The exo-coordinated mercury(II) chloride complex [$HgCl_2(CH_2Cl_2$@**L**)] (**1**).

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 (Table S1 and S3). This product features an exocyclic one-dimensional (1-D) polymeric arrangement of formula [$Hg_6Br_{12}(CH_3CN$@**L**$)_2]_n$ (Fig. 3a). The asymmetric unit contains one formula unit. The crystallographically independent six Hg atoms (Hg1-Hg6) that lie outside the cavity have different coordination environments. First, the terminal Hg1 atom is three-coordinate, being bound to one S atom from one trithiacrown loop and two Br atoms. Second, each of Hg2, Hg3, Hg5 and Hg6A atoms is four-coordinated by two S atoms from one trithiacrown loop and two Br atoms to form a distorted tetrahedral coordination geometry. The Hg4 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 (CH_3CN@**L**) units which locate up and down are linked by a linear Hg3-Br-Hg4-Br-Hg6A 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 Hg4-S9 bond [2.734(4) Å] to give a 1-D polymeric structure.



(a)

(b)

Fig. 3 The exo-coordinated mercury(II) bromide complex [$Hg_6Br_{12}(CH_3CN$@**L**$)_2]_n$ (**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.

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 [I·Hg·I@**L**] (**3**) which crystallises in the monoclinic space group $P2_1/c$ with Z = 4 (Fig. 4a, Figs. S6 and S7, Tables S1 and S4). In **3**, surprisingly, one (I^--Hg^{2+}-I^-) entity locates inside the cavity of **L**. Although some *ion-triplets* organic cation complexes of types [$(R_1R_2\text{-}NH_2^+)_2{\cdot}SO_4^{2-}$@bis(calix[6]arene)] and [($Cl^-{\cdot}R_4N^+{\cdot}Cl^-$)@bis(calix[4]pyrrole] have been reported,[14] no solid *ion-triplet* metal complexes of such type have been reported so far.

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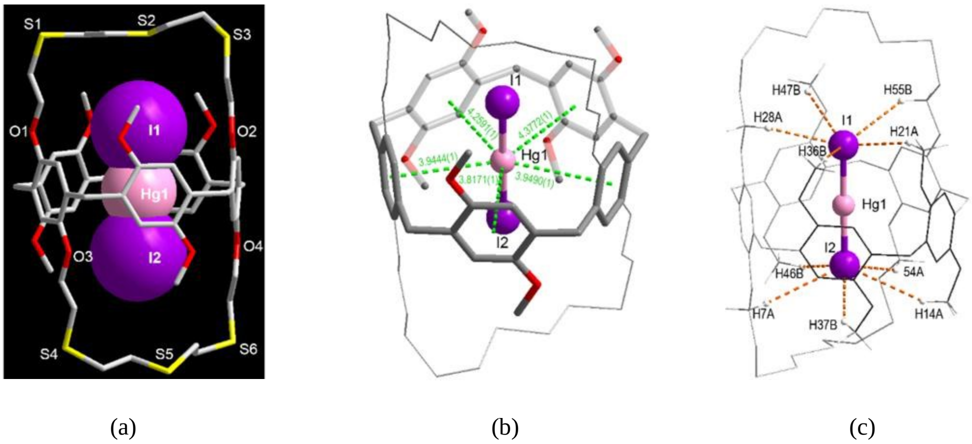

Fig. 4 The contact *ion-triplet* complex with mercury(II) iodide [(I·Hg·I)@**L**] (**3**): (a) general view showing an (I^--Hg^{2+}-I^-) entity (space-filling) in the central cavity, (b) a pentagonal bipyramidal geometry with five $Hg^{2+}\cdots\pi$ interactions (green dashed lines) and an I-Hg-I axis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

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 liner (I^--Hg^{2+}-I^-) entity formed? Each of these aspects are 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···π 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)°].

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 atom from different O-CH_2 and O-CH_3 groups via C-H···I^- H-bonds,[17] with the distances and angles being 3.2132(0)-3.5277(0) Å and 133.193(2)-157.987(2)° (Fig. 4c, Table S4).

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-pair* is primarily electrostatic, but mercury(II) iodide is quite soluble in common organic solvents including methanol[19] and is present partially as 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 represent 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 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°)[18b] and the linear HgI_2 guest from [··I-Hg-I···I-Hg-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 Figs. S8-S10). 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 mercury(II) centre (soft acid) more tightly hence reduce the complex stability. The log *K* value for the iodide system is, however, larger than expected one because the extra stabilization of the ion-triplet via the supramolecular interactions probably compensate such effect in part. In the bromide system, the ligand **L** binds to two mercury(II) ions via two steps but the 1:1 (M**L**) complex is more stable than the 2:1 complex (M_2**L**) which is formed above the 1 equivalent of $HgBr_2$.

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	
$HgCl_2$ + **L**	Hg(**L**)Cl_2	log K_{11}	5.94 ± 0.003
$HgBr_2$ + **L**	Hg(**L**)Br_2	log K_{11}	4.46 ± 0.006
2 $HgBr_2$ + **L**	Hg_2(**L**)Br_4	log K_{21}	8.18 ± 0.002
HgI_2 + **L**	Hg(**L**)I_2	log K_{11}	5.10 ± 0.003

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

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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+}···π interactions stabilize the overall structure, with the concerted C-H···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.

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Conflicts of interest

There are no conflicts to declare.

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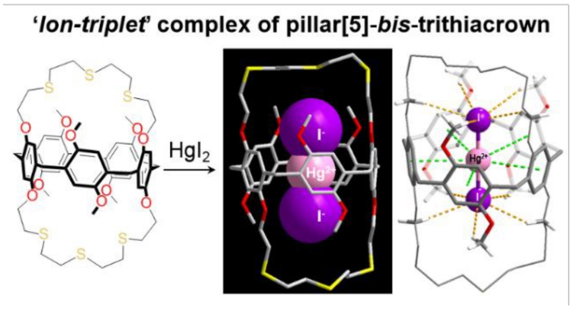
Graphical abstract

In an extension of supramolecular ion-pair complexes, first isolation of a supramolecular *ion-triplet* complex in the solid state is reported. A combination of pillar[5]-*bis*-trithiacrown and HgI_2 afforded a contact *ion-triplet* complex in which the host encapsulates the (I^--Hg^{2+}-I^-) entity with the supramolecular interactions that include $Hg^{2+}\cdots\pi$ and C-H$\cdots I^-$ H-bond interactions, reflecting geometrical complementarity.



'*Ion-triplet*' complex of pillar[5]-*bis*-trithiacrown