

contrast to traditional solution studies, this technique readily affords metal complexes in crystalline form to allow their X-ray structural characterization. Using co-deposition, we have successfully prepared the first metal complexes of corannulene [1], dibenzo[*a,g*]corannulene [2], and hemifullerene [3]. X-ray structural analysis revealed an  $\eta^2$ -rim coordination of the above fullerene fragments in their Rh(II) and Ru(I) complexes. Importantly, multiple metal coordination to a ligand was readily achieved under gas phase conditions to force rare polydentate bridging modes of fullerene fragments. This has resulted in unique complexes ranging from discreet to extended 1D, 2D, and 3D networks. The type of supramolecular architecture is dictated by the geometry and curvature of the fullerene fragment.

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**Keywords:** fullerene fragment, structure, metal coordination

#### P.07.04.1

*Acta Cryst.* (2005). A61, C305

#### Structures of Three 36-azametallacrown-12 Complexes

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Metallacrowns are a new class of metallamacrocycles, which have gained increasing attention over the past decades[1-2]. A novel pentadentate *N*-substituted-salicylhydrazide ligand, pentadentate *N*-substituted-picolyhydrazide ligand and three 36-azametallacrown-12 complexes have been synthesized. A dodonuclear ring of twelve metal atoms linked by twelve N-N groups is an important structural characterization for the one Mn metallacrown and two Ni metallacrowns. Twelve metal ions and twelve ligands construct a 36-membered ring based on the M-N-N-M linkage. The flexibility around the N-N single bond and the conformational adaptability of the pentadentate ligand allow for the formation of the title dodecanuclear complexes and for the propeller configuration of the metal ions. There are some solvent molecules in the 'host' cavity of three azametallacrowns. There are many kinds of intramolecular and intermolecular hydrogen bonds in the title compound.

We are grateful for financial support from the National Natural Science Foundation of China (No. 20431010 and 20171012).

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**Keywords:** supramolecular chemistry, transition metals, complexes

#### P.07.04.2

*Acta Cryst.* (2005). A61, C305

#### A Lower Rim Tert-butyl Calix[4]arene Derivative that Binds Ag(I)

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The X-ray structures of a *tert*-butyl calix[4]arene derivative with  $-O-H$  and  $-O-(CH_2)_2-NH-(P=S)(OCH_2CH_3)_2$  pendant arms (EPS) as molecular complexes with methanol, EPS(MeOH), **1**, with dichloromethane, EPS(Cl<sub>2</sub>CH<sub>2</sub>), **2**, and its complex with silver(I) and acetonitrile, AgEPS(MeCN)K.(ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, **3**, were determined. The structures were solved from 17027 (**1**), 8810 (**2**) and 7729 (**3**) reflections with  $I > 2\sigma(I)$  collected at T=100 K, and refined to R1-factors of 0.054 (**1**), 0.049 (**2**) and 0.090 (**3**). In all compounds, a pair of strong O-H...O(pend) bonds in the lower rim produces relatively open chalice. This, in turn, promotes the hydrophobic interaction with the solvent molecules found included in these cavities. The upper

half of the EPS pendant arms is anchored by N-H...O(ox) intramolecular bonds where now the phenol oxydryl oxygen atoms act as H-bond acceptors. Despite the relative rigidity of the upper half of the hydrophilic cavity, the lower half is pre-organized towards soft metal ion complexation at the thiophosphorous sulphur binding site by unhindered torsion movements, mainly around the N-P  $\sigma$ -bond. The silver(I) complex with EPS, exhibits an approximate C<sub>2</sub> symmetry around the calix axis. The Ag(I) ion is sited on this axis, linearly coordinated to the sulphur atoms of the pendant arms [Ag-S distances of 2.414(2) and 2.422(2) Å,  $\angle(S-Ag-S)=171.99(8)^\circ$ ]. We thank FAPESP (Brazil) and EU (Contract ICA CT 2000-30006) for support.

**Keywords:** calixarene complexes, environmental chemistry, supramacromolecules

#### P.07.04.3

*Acta Cryst.* (2005). A61, C305

#### Two Isomeric Calix(4)arene Complexes with Mercury(II)

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The X-ray structures of two isomeric complexes of partially derivatized 5,11,17,23-tetra-*tert*-butyl[25,27-bis(hydroxy)-26,28-bis(ethylthio ethoxy)]-calix[4]arene (L) with mercury(II) were determined at 120K. The one obtained by slow evaporation from ethanol solvent, LHg(ClO<sub>4</sub>)<sub>2</sub>, crystallizes in the space group Pbc<sub>a</sub> with  $a=15.568(1)$ ,  $b=18.696(1)$ ,  $c=40.322(1)$  Å, and  $Z=8$ . The other one, obtained from an acetonitrile solution, LHg(ClO<sub>4</sub>)<sub>2</sub>.2MeCN, crystallizes in the space group Pccn with  $a=21.794(1)$ ,  $b=45.754(1)$ ,  $c=12.395(1)$  Å, and  $Z=8$ . The structures were solved from 6870 [LHg(ClO<sub>4</sub>)<sub>2</sub>] and 7660 [LHg(ClO<sub>4</sub>)<sub>2</sub>.2MeCN] reflections with  $I > 2\sigma(I)$  and refined to R1-values of 0.053 and 0.073, respectively. The calix[4]arene ligand in both complexes shows hydrophobic cavities with a quite similar squashed cone conformation. In contrast, the hydrophilic cavities exhibit substantial differences in the conformation adopted by the opposite sulfur-containing pendant arms: in LHg(ClO<sub>4</sub>)<sub>2</sub> they are roughly related by a pseudo two-fold axis, while in LHg(ClO<sub>4</sub>)<sub>2</sub>.2MeCN these pendant arms are approximately related through a local mirror plane. Despite these lower rim conformational differences, the Hg(II) ion in both complexes is in a similar environment, *trans* coordinated to the sulfur atoms of the opposite pendant arms, conforming a nearly linear S-Hg-S bond. We thank FAPESP (Brazil) and EU (Contract ICA CT 2000-30006) for support.

**Keywords:** calixarene complexes, environmental chemistry, supramolecules

#### P.07.04.4

*Acta Cryst.* (2005). A61, C305-C306

#### 2D Supramolecular Sheet Generated by $\pi$ Interactions for Cadmium(II) Compounds

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The X-ray structure determinations showed that the coordination polymers [Cd( $\mu$ -Cl)<sub>2</sub>(HPz)<sub>2</sub>]<sub>n</sub> (**1**) and [Cd( $\mu$ -1,3-SCN)<sub>2</sub>(HPz)<sub>2</sub>]<sub>n</sub> (**2**) (HPz = pyrazole) exhibited chain structures made by linear arrays of Cd(II) bridged by chlorine (**1**) (see Fig. 1) or 1,3-SCN (**2**) (see Fig. 2) ions with the pyrazole ligands at the apical sites.

The crystal packing structure of **1** consists of two-dimensional infinite chains along the **b** axis. Hydrogen bonding is the responsible for the self-assembly of linear chains of **1**, yielding a 2D network. Intramolecular hydrogen bonds also occur between N-H and Cl.

