

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 η^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

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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-picolyldiazide 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.

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Keywords: supramolecular chemistry, transition metals, complexes

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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(Cl₂CH₂), **2**, and its complex with silver(I) and acetonitrile, AgEPS(MeCN)K.(ClO₄)₂.H₂O, **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 σ -bond. The silver(I) complex with EPS, exhibits an approximate C₂ 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

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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(ClO₄)₂, crystallizes in the space group Pbc_a 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(ClO₄)₂.2MeCN, 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(ClO₄)₂] and 7660 [LHg(ClO₄)₂.2MeCN] 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(ClO₄)₂ they are roughly related by a pseudo two-fold axis, while in LHg(ClO₄)₂.2MeCN 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

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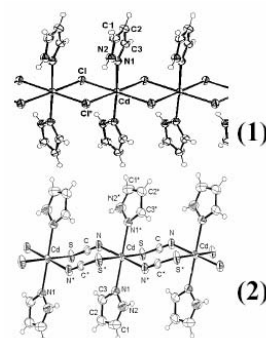
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2D Supramolecular Sheet Generated by π Interactions for Cadmium(II) Compounds

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The X-ray structure determinations showed that the coordination polymers [Cd(μ -Cl)₂(HPz)₂]_n (**1**) and [Cd(μ -1,3-SCN)₂(HPz)₂]_n (**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.



The X-ray single crystal structure of **2** revealed that the closest chains are arranged side by side to facilitate the N-H $\cdots\pi$ and C-H $\cdots\pi$ weak interactions, forming 2D sheets. The 2D sheets are further locked by two weaker $\pi\cdots\pi$ interactions from de pyrazole rings. The N atom of the thiocyanate is found to be intramolecular hydrogen bonded to an N-H pyrazole.

Keywords: supramolecular assemblies, polymers, cadmium

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Connectivity Variation in Coordination Compounds of Isophthalate and Transition Metals

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The coordination of the isophthalate ligand (IPA²⁻) with transition metal cations gives extended networks of variable architecture and dimensionality. The use of different auxiliary ligands and the variation of reaction conditions can provide control over the network dimensionality and/or the assembly of (3-n)-D networks.

Four coordination compounds, prepared by hydrothermal synthesis, are presented and compared to some related examples from the literature.

One structure of Mn(IPA)(Py)₂ is known from the literature [1]: it is made by chains assembled parallel to each other through weak non-bonded interactions. A polymorph of this structure has been prepared, in which there is less symmetry within the network and different packing of the chains.

Three examples of Co-IPA chain-structures are known from the literature [2]: in different reaction conditions one more structure of the same type has been prepared with increased metal-ligand connectivity giving a more robust 1-D network.

The structure of one Ni-IPA 1-D network is known from the literature [2]: two different coordination compounds with Ni²⁺ and IPA²⁻ have been prepared where the connectivity is progressively increased up to obtain a 2-D network.

Hydrothermal conditions were effectively used to investigate the structural variations in closely related coordination compounds structures. The detailed description of the structures, both from the point of view of the metal-ligand connectivity and of the non-bonded connectivity is meant to give some hint about the underlying structure-determining factors.

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Keywords: hydrothermal, connectivity, isophthalate

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A New Organically Templated Vanadium Arsenate

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Materials of open-framework and microporous structures are extensively studied because of their potential applications in catalysis, ionic conductivity, ion-exchange, and magnetic devices. Here we report a compound synthesized under hydrothermal conditions as part of a study of organically templated vanadium arsenates. V₂O₅, Na₂HAsO₄·7H₂O, H₂N(CH₂)₃NH₂ and H₂O in the molar ratio of 2:1:2.4:556 were heated at 180 deg C for 3 days to give black crystals.

The product was characterized by X-ray diffraction, SEM/EDX, FTIR, and TGA. The EDX spectrum indicates presence of vanadium and arsenic in a 3:1 ratio. The IR spectrum has a strong peak at 999 cm⁻¹ that can be assigned to the $\nu(\text{V}=\text{O})$ vibration, strong bands at 973, 800, 634 and 567 cm⁻¹ characteristic of $\nu(\text{M}-\text{O}-\text{M})$ (M = V or As) and $\nu(\text{As}-\text{O})$ [1], and bands in 1623-1383 cm⁻¹ region are due to the NH₂ and CH₂ bending of 1,3-dap. The broad band at 3438 cm⁻¹ can be attributed to O-H stretching.

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Keywords: hydrothermal synthesis, vanadium arsenates, organic template

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Noncovalent Interactions in a Three Component Supramolecular Structure

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Preparation of [(ImH₂)⁺]₂[Co(H₂O)₆]²⁺[Co(TMA)₂(H₂O)₄]⁴⁻ by hydrothermal synthesis, and characterization by single crystal X-ray diffraction is reported. There are distinct cationic and anionic cobalt complex ions. The coordination environment of the cobalt atom in the cationic complex is essentially octahedral, formed by water molecules, while the coordination environment of the cobalt atom in the anionic complex, is distorted octahedral with four water molecules and two trans trianionic trimesate ligands. Two imidazolium monocations complete the structure and provide charge balance. The three moieties interact in the lattice through noncovalent attractions. The carboxylate groups are good hydrogen bond acceptors, while the solvate water molecules and imidazolium cations are good hydrogen bond donors. Thus, it is not surprising to find strong hydrogen bonds between the imidazolium N-H groups and the carboxylate oxygen atoms from the trimesate ligand. The N-H \cdots O hydrogen bonds are in the range 2.693-2.777 Å, and the O-H \cdots O hydrogen bonds are in the range 2.666-2.948 Å. The two imidazolium cations exhibit a pair of N-H $\cdots\pi$ hydrogen bonds (π - π stacking) across an inversion center, and additional π - π interactions to the trimesate ligands.

Crystal Data: *P*-1 *a* = 9.1175(9), *b* = 9.3507(9), *c* = 10.6299(11) Å, α = 79.224(2), β = 87.448(2), γ = 71.995(2)°, *V* = 845.59(15) Å³, *Z* = 1; *T* = 298(2) K; *R*₁ = 0.042, 2688 observed data.

Keywords: crystallography, noncovalent bonding, supramolecular structures

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Preparation and Characterization of NiCl(NO)(PPh₃)₂

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Previous work [1] on the title compound reports an intractable disorder problem; the complex was prepared again following the method of Feltham [2], and purple crystals were prepared by vapour diffusion of hexane into a benzene solution. The compound crystallizes in a C-centered monoclinic space group, with a cell of dimensions: *a* = 17.399(3), *b* = 13.136(3), *c* = 16.954(3) Å, β = 104.74(1)°, *Z* = 4 and *T* = 296 K.

FTIR spectral absorptions attributed to aromatic $\nu(\text{C}-\text{H})$ at 3050 cm⁻¹, $\nu(\text{N}-\text{O})$ at 1716 cm⁻¹, aromatic $\nu(\text{C}-\text{C})$ at 1434 cm⁻¹, and bands for CH in- and out-of-plane bending at 1095 cm⁻¹ and 693 cm⁻¹, respectively. The supramolecular structure contains the expected [3] six-fold phenyl embrace, 6PE, chains linking nickel bis(phosphine) moieties into one-dimensional zigzag chains. However, the lattice also contains a benzene solvate. The benzene molecule is able to form considerably more C-H $\cdots\pi$ interactions than a phenyl ring and becomes the major link, interconnecting three of the 6PE chains via ten C-H $\cdots\pi$ interactions centered about the benzene of crystallization. Additional weak noncovalent interactions supplement these major interactions to form an extensive three-dimensional crystal structure.

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