

ASSEMBLY OF TETRAHEDRAL CLUSTERS OF 12 OCTAHEDRAL METAL IONS AND 18 BIS-BIDENTATE BRIDGING LIGANDSZ.R. Bell¹ J.C. Jeffery M.D. Ward J.A. McCleverty

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A bridging ligand (L) has been prepared containing two bidentate pyrazolopyridine sites separated by a 1,8-naphthyl spacer unit. Coordination of this tetradentate ligand to octahedral metal centers [Co(II), Zn(II)] requires therefore a M2:L3 ratio. In fact reaction of L with these metal ions, followed by precipitation with perchlorate or fluoroborate anions, affords clusters with the stoichiometry M12:L18. These have the topology of a tetra-truncated tetrahedron (below), which has four triangular and four hexagonal faces. The resulting polyhedron has 12 vertices, with a metal ion at each vertex, and 18 edges, with a bridging ligand spanning each edge. Anions are located both at the center of the polyhedral cage, and in the spaces at the centers of the faces. The structure of this cluster is in remarkable contrast to the more well known M2:L3 (triple helicates) and M4:L6 (adamantoid tetrahedral cages) which more usually arise with bridging ligands of this type; the self-assembly requires controlled formation of 72 metal-ligand bonds.

Keywords: TETRAHEDRAL CLUSTERS SELF ASSEMBLY COORDINATION CHEMISTRY

LAYER ASSEMBLY IN ALKALINE-EARTH DERIVATIVES OF UNSATURATED DICARBOXYLIC ACIDSG. Diaz de Delgado¹ A. Briceno² T. Gonzalez²

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Alkaline-earth metal derivatives of unsaturated dicarboxylic acids frequently display layer structures. Extensive hydrogen bonding involving the carboxylate groups, water molecules coordinated to the metal atom, and lattice water provide links within the layers and play an important role in their assembly. For example, tetraaquomesaconate barium(II), [Ba(C₅H₄O₄)(OH₂)_n]_n (1), consists of two-dimensional rectangular grid layers, built up from the self-assembly of zigzag chains of edge sharing {BaO₉} polyhedra linked by bridging, bidentate mesaconate anions. The polymer layers form a three-dimensional network via hydrogen bonds between the coordinated water molecules and the oxygen atoms of the carboxylate groups. A similar assembly is observed in the structure of tetraaquobis(hydrogen maleate) barium(II), [Ba(C₄H₃O₄)(OH₂)₂]₂ (2).

However, in the structure of [Ba₅(C₄H₂O₄)(C₄H₃O₄)(OH₂)₂]₅H₂O (3), a barium maleic acid complex obtained in the same experiment as compound (2), the layers are further apart because they are separated by lattice water molecules and by hydrogen maleate anions. In the Ca and Ba itaconates prepared so far, the interactions between layers are of the Van der Waals type. These and other structures will be discussed in detail.

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Keywords: DICARBOXYLIC ACIDS BA CARBOXYLATES LAYER ASSEMBLY

PRE-ORGANIZATION AND ALLOSTERISM IN COMPLEXES OF Cd(II) AND Pb(II) WITH CALIX[4]ARENE DERIVATIVESE. E. Castellano¹ O. E. Piro² A. F. Danil de Namor³

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The bite ability of ethylester and methylketone pendant arms of butylcalix[4]arene derivatives (L and M) towards binding metal ions and the pre-organization shown by these macrocycles, prompted structural studies of their complexes with the environmentally relevant Cd²⁺ and Pb²⁺ ions. We determined the structures of (MeCN)Cd(L)(ClO₄)_{2.3}MeCN (1), Pb(L)(MeCN)(ClO₄)_{2.5}MeCN₂H₂O (2), (MeCN)Cd(M)(ClO₄)_{2.5}MeCN (3) and Pb(M)(MeCN)(ClO₄)_{2.2}MeCN (4) at 120 K by X-ray diffraction methods from 10517 (1), 10969 (2), 14305 (3) and 10909 (4) reflections with I>2σ(I) and refined them to R1-values of 0.047 (1), 0.077 (2), 0.0361 (3) and 0.0335 (4). All macrocycles adopt a slightly distorted cone conformation with a metal ion in the hydrophilic cavity and an acetonitrile solvent molecule in the calyx. In 1 and 3, at variance with most other calix[4]arene compounds, the MeCN molecule enters the calyx with the cyanide end pointing inward to form a Cd-N bond. There, the Cd²⁺ ion is further coordinated to all eight calixarene oxygen atoms in 1 and all but one carbonyl oxygen in 3. In 1 the ligand-to-cadmium atoms conform the corners of a capped Archimedean square antiprism with the N-atom at the capping site, while in (3) Cd²⁺ is at the center of a distorted triangular dodecahedral. The lead complexes (2) and (4) show a quite similar environment around the metal. The Pb²⁺ ion is coordinated to the eight oxygen atoms, which are at the corners of a tetragonally squashed cube. These results strongly suggest the predominance of ionic interaction in the lower rim during metal complexation in promoting the inclusion of a solvent molecule within the calyx to form a molecular complex (positive allosteric effect).

Keywords: SUPRAMOLECULE, CALYX[4]ARENE, ALLOSTERY

SUPRAMOLECULAR STRUCTURES OF FOUR-COORDINATE NICKEL BIS(TRIPHENYLPHOSPHINE) NITROSYL COMPLEXES

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The multiple phenyl-phenyl edge-to-face (ef) C-H[⋯]η attractive interactions of the concerted sextuple phenyl embrace (SPE) give a sum of interaction energy sufficient to make it a dominant supramolecular motif for triphenylphosphine (TPP) complexes (Dance & Scudder, Chem. Comm. 1995, 1039). The title complexes with the fourth ligand, X = isothiocyanato, azido, or chloro, while closely related have quite different supramolecular structures. The primary extended interactions in the isothiocyanato complex are SPE between adjacent TPP occurring in parallel chains alternating; d[P-P] = 7.087 Å, colinearity = 176.9° and d[P-P] = 7.246 Å, colinearity = 173.0° SPE. Chains are joined by four phenyl ring regions to form layers dominated by ef C-H[⋯]η interactions. Layers are bound by nitrosyl-phenyl and phenyl-phenyl interactions. The chloro complex contains a benzene solvate which has one end inserted into the cleft of an Ni(bis-TPP) fragment located on a pseudo 2-fold axis utilizing one complex-to-benzene ef and one benzene-to-complex ef interaction to each of the TPP ligands. Eight additional ef interactions form the central region of the cavity and the chloro and nitrosyl ligands of another molecule cap the cavity. Thus, the benzene molecule, able to form considerably more C-H[⋯]η interactions, becomes the major supramolecular link in the structure. The shortest intermolecular P-P distances in the azido complex are 7.411 Å and 7.825 Å with colinearities of 86.9° and 117.7°, thus not SPE. The strongest nonbond is a 2.493 Å intramolecular C-H[⋯]N interaction to the lone pair on the N bonded to Ni destroying the pseudo three-fold symmetry of one TPP, while another strong intramolecular C-H[⋯]N interaction to the azido ligand η cloud involves the other TPP, thus disrupting both possibilities to form SPEs. The azido ligand is also involved in intermolecular nonbonded interactions. Thus, as the strongest hydrogen bond acceptor, the azido ligand becomes the most important determiner of the supramolecular structure.

Keywords: SUPRAMOLECULAR STRUCTURE CONCERTED PHENYL EMBRACES HYDROGEN BONDING