

FA4-MS34-T01

Star-burst Prisms and Coordination Polymers.

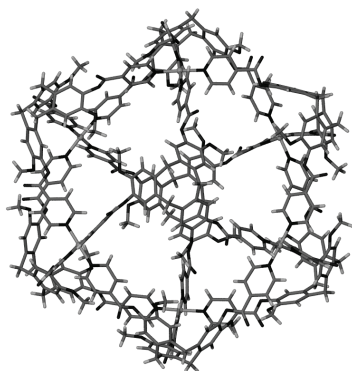
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Pyramidal ligands based on the cyclotrivertatrylene (=CTV) host have rigid molecular cavities. These ligands can form either discrete or polymeric metal-ligand systems, thus creating metallo-supramolecular assemblies or coordination polymers with specific molecular recognition sites. The pyramidal shape of these ligands results in assemblies with distinctive “star-burst” shapes or stellated polyhedra. Discrete metallo-supramolecular assemblies or “star-burst” prisms with these ligands include $[M_nL_2]^{2+}$ capsules;^[2] different types of $[Ag_4L_4]^{4+}$ tetrahedra,^[1,2] and a series of giant $[Pd_6L_8]^{12+}$ stella octangulas (pictured below). A further, and unexpected, trend in this chemistry is the formation of topologically non-trivial assemblies. Capsules forming triply interlocked [2]catenanes have been found with 2,2'-bipyridine or 3-pyridyl derived ligands,^[3] and a $[Pd_4(NO_3)_2(H_2O)_2L_4]^{6+}$ “Solomon’s cube” assembly has a unique molecular topology akin to a self-entangled cube.^[4] The pyramidal shape of the ligands also leads to both known and unusual topologies within coordination polymers,^[2,5] including chains or nets of linked capsules, 2D nets of 4.8² topology, and highly complicated and unusual 3D networks, amongst others. The structural and some solutions chemistry of these supramolecular assemblies and coordination polymers will be presented.



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Structural Chemistry of new Rh and Ir Metallathaboranes – Understanding Cluster Flexibility.

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Metallaboranes and metallaheteroboranes are polyhedral compounds that exhibit M-B and M-H-B bonds, combining structural aspects and chemical reactivity associated with both the metal and borane fragments. As a remarkable feature, they exhibit reversible *nido-to-closo* structural transformations of the metallaborane cluster coupled with hydrogen transfer processes, conferring to these compounds new mechanisms for the functionalization of organic molecules in catalytic cycles [1].

Working in this area, we have recently reported the reversible dihydrogen activation by the 11-vertex rhodathaborane system $[8,8,8-(PPh_3)_2(H)-nido-8,7-RhSB_9H_9-9-(NC_5H_5)]$ and $[1,1-(PPh_3)_2-closo-1,2-RhSB_9H_8-3-(NC_5H_5)]$. This process is the first example of a *closo-to-nido* reductive transformation of a polyhedral cluster, and has showed a remarkable potential towards the catalytic hydrogenation of alkenes and alkynes. The reactivity of these rhodathaboranes is fundamentally a consequence of the molecular redox flexibility of the clusters, and consequently the structural characterization of these species becomes a crucial step to get a detailed understanding of the reactions and catalytic mechanisms [2].

In the present work we will describe the crystallographic structural analysis of a family of new related metallaheteroboranes complexes of the type $[ML_{2/3}-SB_9H_{8/9}L']$, showing hetero-cluster structures related to that of the ideal dodecahedron. These compounds were prepared by different strategies adding metal fragments to the preformed heteroborane anion *arachno-6-SB₉H₁₂*. In most cases the elucidation of the molecular structures was definitively achieved from the single-crystal X-ray analysis. Given the interesting results arising from rhodathaboranes, we are currently exploring the related chemistry of iridium clusters to see if the use of Iridium introduces a mirrored or modified structural chemistry.

In our talk, we will describe the preparation of the complexes, the experimental parameters used in the data collection and in the structural analysis, the detected equilibria between different conformers, and we will discuss in detail the main features of the molecular structures of these new metallathaborane complexes.

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