Guest templated synthesis of tetrahedral $[Pd_{12}L_6]$ cages and their selective encapsulation of o-xylene and mesitylene over other analogues

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Abstract:

Phosphorus centered motifs such as phosphines, phosphine oxides, and phosphonium salts have gained recent attention in the area of functional metal-organic materials as these moieties can offer both rigid and flexible ligand platforms around the central phosphorus atom. In this effort, our group has been focused on the chemistry of amino-P(V) ligands containing central as well as peripheral metal binding groups. Employing phosphoramide ligands of formula, $(RNH)_3PO$ with $Pd(OAc)_2$, a facile route to access the highly basic trianions, $[(RN)_3PO]^{3-}$ $((X)^{3-})$ analogous to PO_4^{3-} ion was developed. The $(X)^{3-}$ ligand, containing a central binding group, acts as a rigid cis-blocking ligand and stabilizes trimeric or prismatic Pd(II) cluster of formula $\{Pd_3X(OAc)_3\}$ [1 or 2].

Further, the utility of the trinuclear $(Pd_3X)^{3+}$ motif as a supramolecular synthon has been explored and interesting examples of neutral cluster cages **1** in tetrahedral topologies were obtained by replacing the acetate bridges in the prismatic cluster with oxalate anion. Herein, we have synthesized two tetrahedral cages **2** and **3** using different linkers chloranilic acid and 2,5-dihydroybenzoquinone respectively, instead of oxalate anion. Cage 2 encapsulates selectively o-xylene whereas 3 encapsulate mesitylene over other analogues. Also, the host-guest chemistry of the tetrahedral cage assemblies was probed by mass spectroscopy, ^1H, 2D-DOSY NMR.

References:

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