Selective solvent capture by molecular assemblies of diosmium sawhorses

Gregory L. Powell and Cynthia B. Powell

Department of Chemistry & Biochemistry, Abilene Christian University, ACU Box 28132, Abilene, Texas 79699-8132, USA, powellg@acu.edu

At high temperatures, Os$_3$(CO)$_{12}$ reacts with monocarboxylic acids to form the diosmium(I) compounds Os$_2$(μ-carboxylate)$_2$(CO)$_6$ known as sawhorse complexes in which four CO ligands form legs that extend from the osmium-osmium vector that represents the top of the sawhorse [1,2]. Dicarboxylic acids have also been used to prepare compounds in which dicarboxylate (DCA) anions bridge several diosmium sawhorses, including tetranuclear [Os$_2$(CO)$_6$(μ-DCA)$_2$(CO)$_6$]$_2$ complexes with two Os$_2$ sawhorse units linked together into a single molecular loop and hexanuclear [Os$_2$(CO)$_6$(μ-DCA)$_3$]$_3$ complexes with three Os$_2$ sawhorse units linked together in a triangular geometry [3].

We have recently been able to use 2,6-naphthalenedicarboxylic acid to provide a larger DCA anion that allowed for the isolation of the first example of an octanuclear osmium complex with four Os$_2$ sawhorse units linked together to form a molecular square of the type [Os$_2$(CO)$_6$(μ-DCA)$_4$]$_4$ (Fig. 1a). Using benzene-1,3,5-tricarboxylic acid (H$_3$BTC), we have also synthesized the first dodecanuclear osmium complex with six Os$_2$ sawhorse units linked together to form a molecular octahedron with the formula [Os$_2$(CO)$_6$(μ-BTC)$_3$]$_3$ (Fig. 1b). The X-ray crystal structures and solvent-capturing propensities of these new MOF-like complexes will be discussed. Dichloromethane molecules occupy the centers of the Os$_{12}$ octahedra, while hexane molecules occupy the large intermolecular voids. Dichloromethane molecules also fill the centers of the Os$_6$ triangles, but not the Os$_8$ squares.

![Fig. 1. The core portions of (a) the [Os$_2$(CO)$_6$(μ-DCA)$_4$] molecular square and (b) the [Os$_2$(CO)$_6$(μ-BTC)$_3$] molecular octahedron.](image)
References