8-2019

Selective solvent capture by molecular assemblies of diosmium sawhorses

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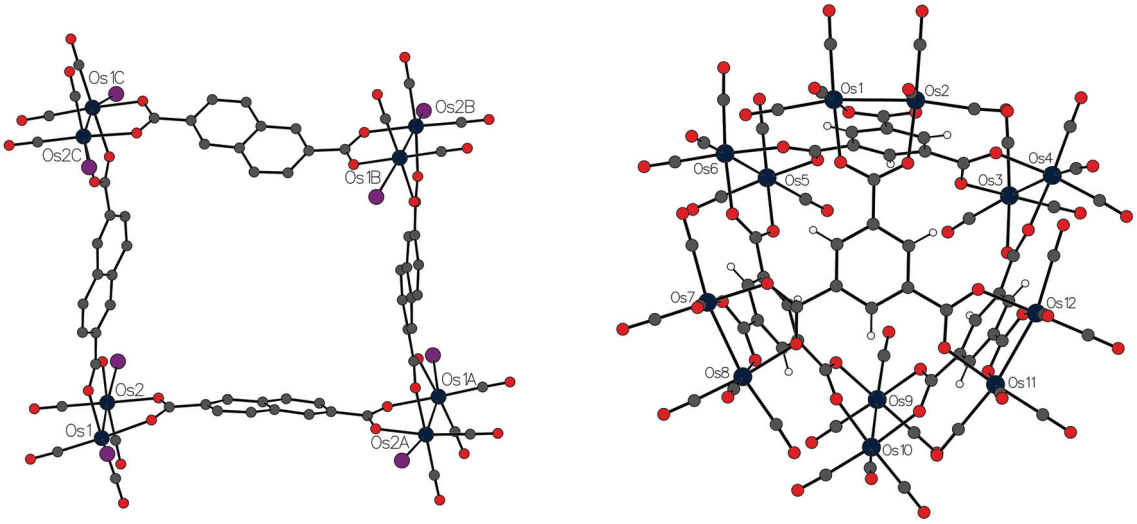
At high temperatures, $Os_3(CO)_{12}$ reacts with monocarboxylic acids to form the diosmium(I) compounds $Os_2(\mu\text{-carboxylate})_2(CO)_6$ known as sawhorse complexes in which four CO ligands form legs that extend from the osmium-osmium vector that represents the top of the sawhorse [1,2]. Dicarboxylic acids have also been used to prepare compounds in which dicarboxylate (DCA) anions bridge several diosmium sawhorses, including tetranuclear $[Os_2(CO)_6]_2(\mu\text{-DCA})_2(CO)_6$ complexes with two Os_2 sawhorse units linked together into a single molecular loop and hexanuclear $[Os_2(CO)_6]_3(\mu\text{-DCA})_3$ 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 $[Os_2(CO)_6]_4(\mu\text{-DCA})_4$ (Fig. 1a). Using benzene-1,3,5-tricarboxylic acid (H_3BTC), 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 $[Os_2(CO)_6]_6(\mu\text{-BTC})_3$ (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.



(a) (b)

Fig. 1. The core portions of (a) the $[Os_2(CO)_6]_4(\mu\text{-DCA})_4$ molecular square and (b) the $[Os_2(CO)_6]_6(\mu\text{-BTC})_3$ molecular octahedron.

References
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