

Selective solvent capture by molecular assemblies of osmium sawhorses

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At high temperatures, $\text{Os}_3(\text{CO})_{12}$ reacts with monocarboxylic acids to form the osmium(I) compounds $\text{Os}_2(\mu\text{-carboxylate})_2(\text{CO})_6$ 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 osmium sawhorses, including tetranuclear $[\text{Os}_2(\text{CO})_6]_2(\mu\text{-DCA})_2(\text{CO})_6$ complexes with two Os_2 sawhorse units linked together into a single molecular loop and hexanuclear $[\text{Os}_2(\text{CO})_6]_3(\mu\text{-DCA})_3$ 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 $[\text{Os}_2(\text{CO})_6]_4(\mu\text{-DCA})_4$ (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 $[\text{Os}_2(\text{CO})_6]_6(\mu\text{-BTC})_3$ (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.

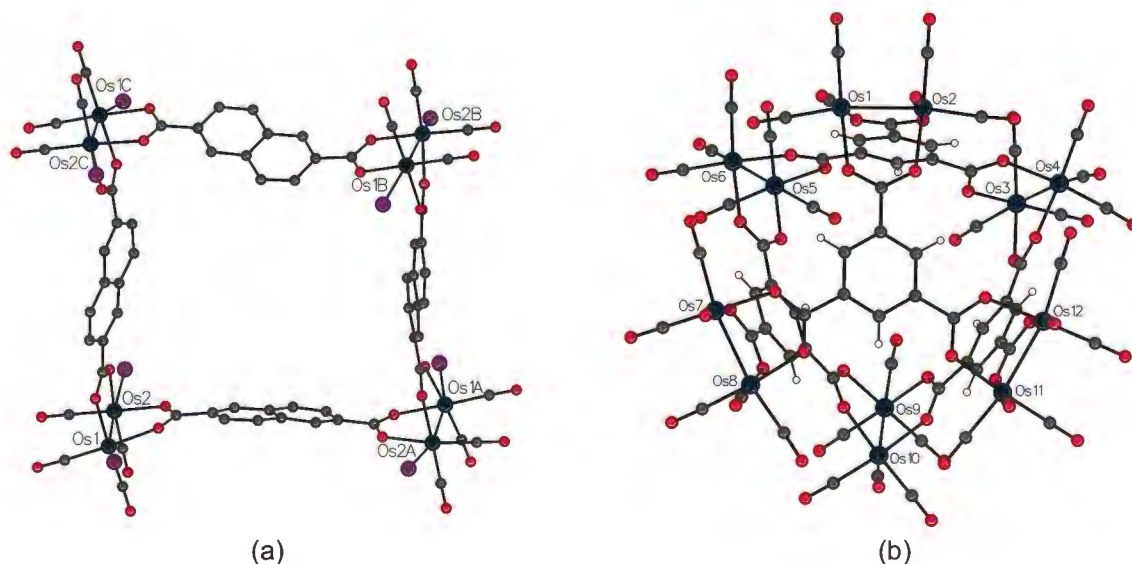


Fig. 1. The core portions of (a) the $[\text{Os}_2(\text{CO})_6]_4(\mu\text{-DCA})_4$ molecular square and (b) the $[\text{Os}_2(\text{CO})_6]_6(\mu\text{-BTC})_3$ molecular octahedron.

References

- [1] Crooks, G. R., Johnson, B. F. G., Lewis, J., Williams, I. G. & Gamlen, G. (1969). *J. Chem. Soc. A*, 2761-2766.
- [2] Pyper, K. J., Jung, J. Y., Newton, B. S., Nesterov, V. N. & Powell, G. L. (2013). *J. Organomet. Chem.* **723**, 103-107.
- [3] Gwini, N., Marolf, D. M., Yoon, S. H., Fikes, A. G., Dugan, A. C., Powell, G. L., Lynch, V. M., Nesterov, V. N. & McCandless, G. T. (2017). *J. Organomet. Chem.* **849-850**, 324-331.