# The Intricate Structural Chemistry of $M^{II}_{2n}L_n$-Type Assemblies
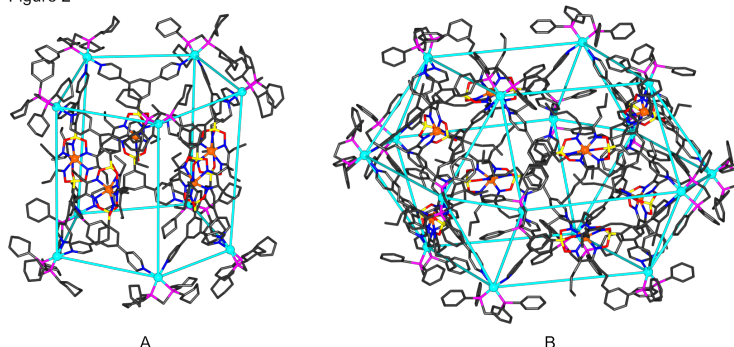
G. Cecot[1], K. Severin[1]*

[1]EPF Lausanne

By choosing an appropriate ligand, it is possible to influence the size, the geometry and the functionality of a metallasupramolecular assembly. Functionalized clathrochelate complexes have recently emerged as a promising new class of metalloligands for applications in supramolecular coordination chemistry. [1] The reaction of *cis*-blocked, square planar M^{II} complexes with tetratopic N-donor ligands is known to give metallasupramolecular assemblies of the formula $M_{2n}L_n$. We recently demonstrate that unusual geometries are accessible like the Pt_8L_4 cage with gyrobifastigium-like geometry. [2] A geometric analysis of the ligands could explain how size and geometry influence the self-assembly process. The metalloligands used gave assemblies of type Pt_8L_4, which adopt barrel- or gyrobifastigium-like structures (Figure 1A and 1B). Larger assemblies are possible, as $Pt_{10}L_5$ complex and a $Pt_{16}L_8$ complex (Figure 1C and 1D). The latter has a molecular weight of more than 23 kDa and a diameter of 4.5 nm, making it the largest, structurally characterized $M_{2n}L_n$ complex described to date.

Figure 1

A   B   C   D
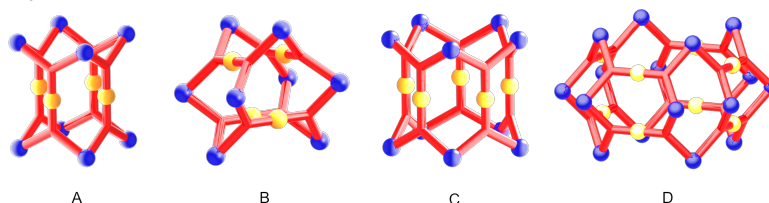
By X-ray crystallography, we characterize both new of $M_{2n}L_n$ complexes, namely a pentagonal $Pt_{10}L_5$ barrel and a $Pt_{16}L_8$ complex (Figure 2A and 2B). The latter assembly displays an unprecedented square orthobicupola geometry. Overall, we think that our study will provide an important foundation for future investigations of coordination barrels.

Figure 2

A   B

[1] G. Cecot, S. M. Jansze, M. D. Wise, K. O. Zhurov, T. K. Ronson, A. M. Castilla, A. Finelli, P. Pattison, E. Solari, R. Scopelliti, G. E. Zelinskii, A. V. Vologzhanina, Y. Z. Voloshin, J. R. Nitschke, K. Severin, *J. Am. Chem. Soc.* **2016**, 138, 2046-2054.
[2] G. Cecot, B. Alameddine, S. Prior, R. De Zorzi, S. Geremia, R. Scopelliti, F. T. Fadaei, E. Solari, K. Severin, *Chem. Commun.* **2016,** 48, 11243-11246.