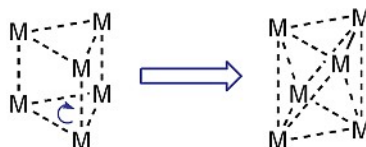


Inducing Helical Chirality by Deforming Hexanuclear Metalloprismatic Structures

Bruno Therrien* and Georg Süss-Fink

Abstract: A comparative structural study of eleven empty and eight filled hexanuclear metalloprismatic cages reveals helical chirality depending on the twist angle between the upper and lower triangles defined by three metal centres.



Keywords: Chirality · Hexanuclear complex · Supramolecular assembly · Triangular prism

Introduction

Self-assembly is a process leading to the formation of discrete nanometer-sized objects or well-defined aggregates in which the overall structure is controlled by the symmetry of the different building blocks.^[1] In the case of metallosupramolecular assemblies, the coordination mode of the metal centre as well as the symmetry of the ligands needs to be controlled in order to allow the formation of the desired aggregates.^[2] If the assembly possesses special properties that are only observed after aggregation, a supramolecular function must be associated

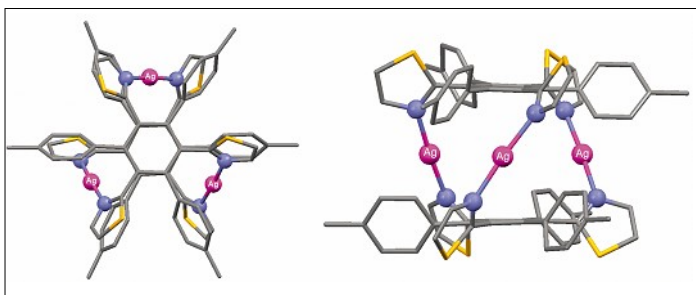


Fig. 1. $[\text{Ag}_3(\text{tris-thiazolyl})]$ double-decker sandwich system^[8a]

with the aggregate. Among such functions, chirality is often found in supramolecular chemistry, the overall structure being chiral, while the individual building blocks are achiral.

Helical chirality is very common in nature.^[3] DNA for example adopts right-handed or left-handed forms, which can undergo molecular motions such as folding^[4] or $P \rightleftharpoons M$ conversion.^[5] The assembly of helicate-type complexes has been extensively studied^[6] since this term was introduced by Lehn in 1987.^[7] Among artificial helical structures, Shionoya and co-workers have developed double-decker sandwich systems connected by three silver centres and two tris(thiazolyl) ligands that shows $P \rightleftharpoons M$ interconversion in solution (Fig. 1).^[8] Similarly, Sherman and co-workers have observed helical chirality of carceplex compounds upon encapsulation of molecules such as (*R*)-2-butanol, pyrazine, or DMSO

in a tetraoxatetrahemicarceplex cage.^[9] The term twistomers was used to describe the phenomena (Fig. 2). A comparative study of structurally characterised capsules of this type revealed that the twist angle can be rather significant, up to 21°.

Recently, we have observed that cationic hexanuclear metalloprisms of the general formula $[(\text{arene})_6\text{M}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{9+}$ ($\text{M} = \text{Ru}$; arene = $p^i\text{PrC}_6\text{H}_4\text{Me}$, C_6Me_6 ; $\text{M} = \text{Rh}$, Ir ; arene = C_5Me_5) containing bridging oxalato ligands (C_2O_4) and 2,4,6-tri(pyridine-4-yl)-1,3,5-triazine (tpt) units display helical chirality as well (Fig. 3).^[10,11] Moreover, a concerted rotation of the aromatic rings of the trigonal tpt subunits creating an additional three-bladed propeller chirality was observed. These two stereogenic phenomena were observed in the solid-state and were shown to persist in solution.

These observations raised the question of generality for chiral conformations of

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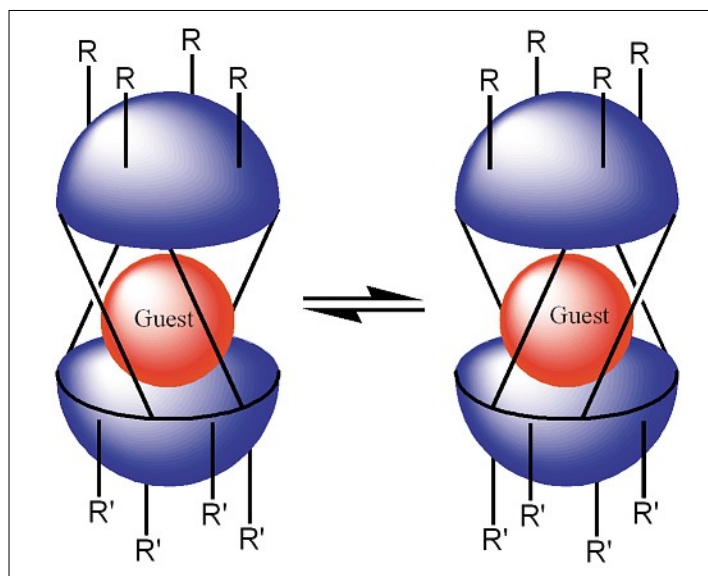


Fig. 2. Schematic representation of carceplex twistomers^[9]

metalloprisms, and whether or not the stereodynamic phenomena observed for these oxalato metalloprisms are unique. In order to address this question, we retrieved all structural data of hexanuclear metalloprisms available and performed a comparative study.

General Remarks

The present study is divided into two sections. The first section is exclusively devoted to empty hexanuclear metalloprisms in which no encapsulated molecule plays a role in the chiral conformation of the metalloprism. The second section deals with hexanuclear metalloprisms in which a molecule is encapsulated within the cavity of the prismatic cage. The inclusion of encapsulated molecule can either enhance or weaken the chirality of the cage, and therefore these filled hexanuclear metalloprisms are discussed separately.

Empty Hexanuclear Metalloprismatic Cages

The general structure of the first series of empty M_6 cage molecules to be discussed here involves the short bridging chloro ligands and 2,4,6-tri(pyridine-4-yl)-1,3,5-triazine (tpt) triangular panels. The cationic arene ruthenium compounds $[(p\text{-}i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2\text{Cl}_6]^{6+}$ and $[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2\text{Cl}_6]^{6+}$ ^[12] as well as the cationic pentamethylcyclopentadienyl rhodium complex, $[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2\text{Cl}_6]^{6+}$ are known.^[13] In Fig. 4, the molecular structures of the three chloro-bridged cages are compared. Due to the proximity of the two tpt units, strong parallel π -stacking interac-

tions between the aromatic rings are observed. Indeed, the centroid–centroid distances between the corresponding triazine rings is slightly shorter than the average metal–metal distances of the chloro bimetallic connectors (Table 1). Therefore, in these systems only a slight deviation from a perfectly eclipsed conformation of the two tpt subunits is observed, while the propeller-like rotation of the pyridyl rings is relatively important.

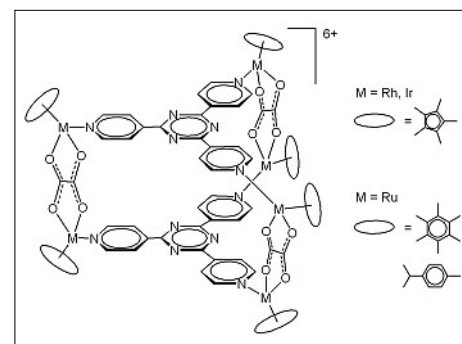


Fig. 3.

Similarly, in the hexanuclear carbonyl rhenium metalloprisms bridged by butyloxy or phenyloxy ligands, $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OC}_4\text{H}_9)_6]$ and $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OC}_2\text{H}_5)_6]$, the centroid–centroid distances between the triazine rings are slightly shorter than the average metal–metal distances of the bimetallic connectors (Fig. 5).^[14] Interestingly, in the analogous carbonyl rhenium metalloprism bridged by 2,2'-bisbenzimidazolato (bbz) ligands, $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{bbz})_3]$,^[15] in which the M–M distances are significantly longer (average Re–Re = 5.5 Å) than those of the alkoxy derivatives $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OC}_4\text{H}_9)_6]$ and $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OC}_2\text{H}_5)_6]$, the centroid–centroid distance of the two triazine rings is even shorter (3.4 Å). The two tpt units curve inward to maximise the π -stacking interactions of the two triazine rings.

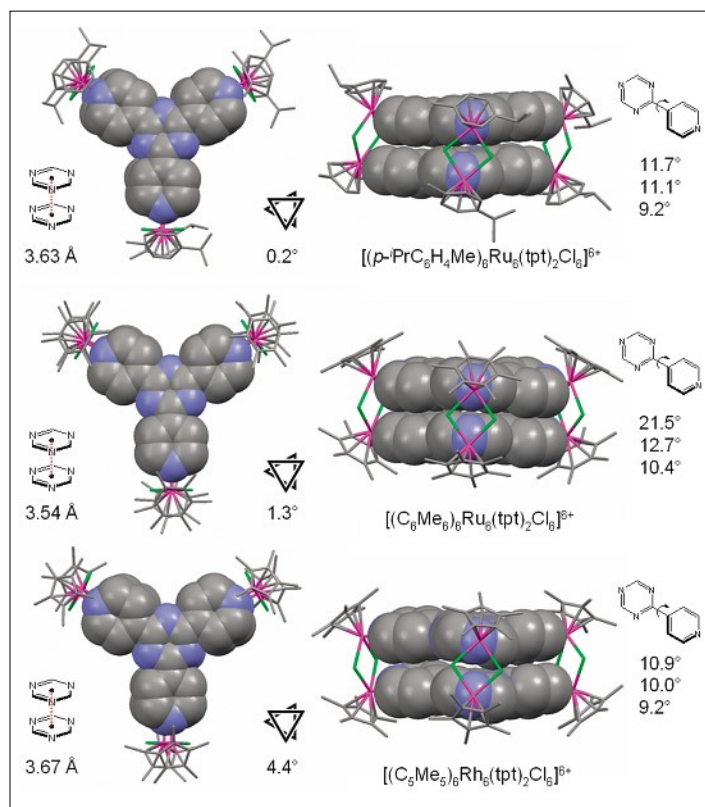


Fig. 4. Structural comparison (top view and side view) of $[(p\text{-}i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2\text{Cl}_6]^{6+}$,^[12] $[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2\text{Cl}_6]^{6+}$,^[12] and $[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2\text{Cl}_6]^{6+}$ ^[13]

Table 1. Chirality and structural parameters for the empty hexanuclear cage molecules

Empty cage complex	Space group	M–M	Δ^a	ref.
$[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2\text{Cl}_6]^{6+}$	$C 2/c$	3.7 Å	0.2°	[12]
$[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2\text{Cl}_6]^{6+}$	$P 2_1/n$	3.7 Å	1.3°	[12]
$[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2\text{Cl}_6]^{6+}$	$P 2_1/c$	3.6 Å	4.4°	[13]
$[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OC}_4\text{H}_9)_6]$	$R 3c$	3.4 Å	1.4°	[14]
$[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OCH}_2\text{Ph})_6]$	$P 1$	3.5 Å	0.2°	[14]
$[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{bbz})_3]$	$C 2/c$	5.7 Å	4.9°	[15]
$[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$	$C 2/c$	5.5 Å	8.5°	[11]
$[(\text{C}_5\text{Me}_5)_6\text{Ir}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$	$F d3c$	5.5 Å	0.0°	[11]
$[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$	$P 3c1$	5.5 Å	2.9°	[10]
$[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$	$C 2/c$	5.5 Å	14.8°	[10]
$[(\text{ant})_3\text{Pt}_6(\text{PEt}_3)_{12}(\text{tpepe})_2]^{6+}$	$R 3c$	5.5 Å	0.0°	[16]

^atwist angle between the two trigonal panels

In the oxalato bridged derivatives, $[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$, $[(\text{C}_5\text{Me}_5)_6\text{Ir}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$, $[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ and $[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$, the metal–metal distances in the dinuclear clips reach 5.5 Å, thus, in theory, giving more conformational freedom to the subunits of the cage molecules. In fact, while the solid-state structure of the triflate salts of the rhodium and ruthenium derivatives show an important deformation of the triangular prismatic arrangement in the solid state, the iridium derivative adopts a per-

fectly eclipsed conformation of the prism (Fig. 6). In $[(\text{C}_5\text{Me}_5)_6\text{Ir}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$, the two tpt panels are strongly curved inward to maximise π -stacking interaction, while the pyridyl rings remain parallel to their triazine core. In contrast, the

cations $[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$, $[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ and $[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ show a distinct distortion, the dimetallic oxalato clips being twisted out of the plane of the tpt units, which give rise to a ‘double-rosette’ type helicity. Furthermore, in these systems, the pyridyl rings are tilted out of the plane of the triazine subunits thus generating a propeller-like chirality. The tilt of the pyridyl ring can be as much as 30°, and the twist of the two tpt units up to 15°.

The large cationic hexanuclear cage molecule, $[(\text{ant})_3\text{Pt}_6(\text{PEt}_3)_{12}(\text{tpepe})_2]^{6+}$ (ant = anthracene), obtained by mixing the molecular clip 1,8- $[\text{Pt}(\text{PEt}_3)_2(\text{NO}_3)]_2(\text{ant})$ and the triangular panels 1,1,1-tris(4-phenyl(4'-ethynylpyridyl)ethane) (tpepe), possesses in the solid state, crystallographically imposed D_{3h} symmetry (space group $R3c$).^[16] Therefore, this system shows no chirality in the solid state.

Filled Hexanuclear Metalloprismatic Cages

The encapsulation of a flat molecule within the cavity of a hexanuclear metalloprism can either enhance or weaken the chi-

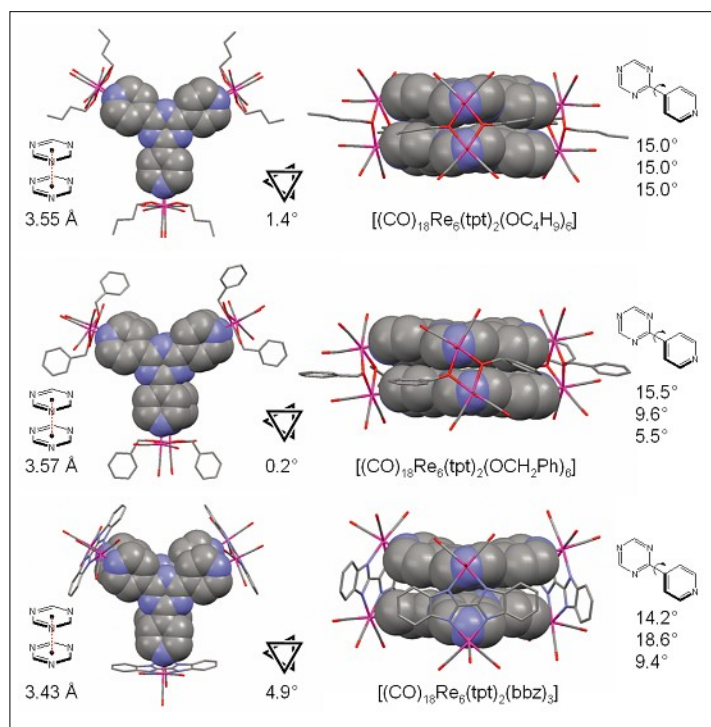


Fig. 5. Structural comparison (top view and side view) of $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OC}_4\text{H}_9)_6]$,^[14] $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{OCH}_2\text{Ph})_6]$,^[14] and $[(\text{CO})_{18}\text{Re}_6(\text{tpt})_2(\text{bbz})_3]$.^[15]

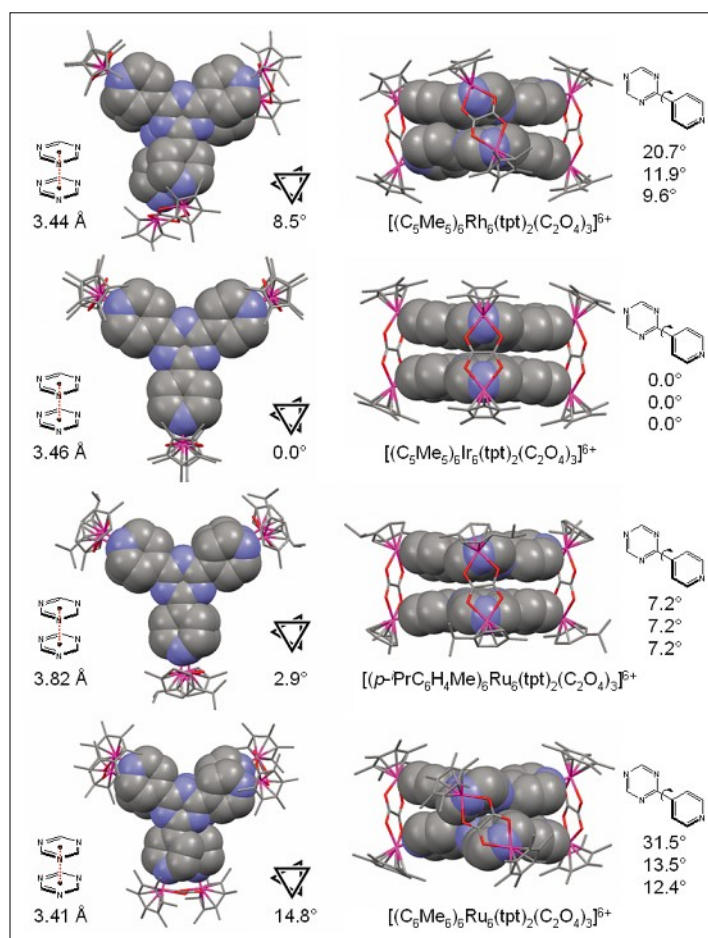
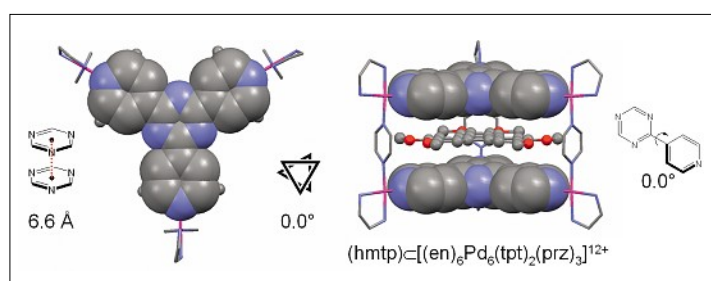
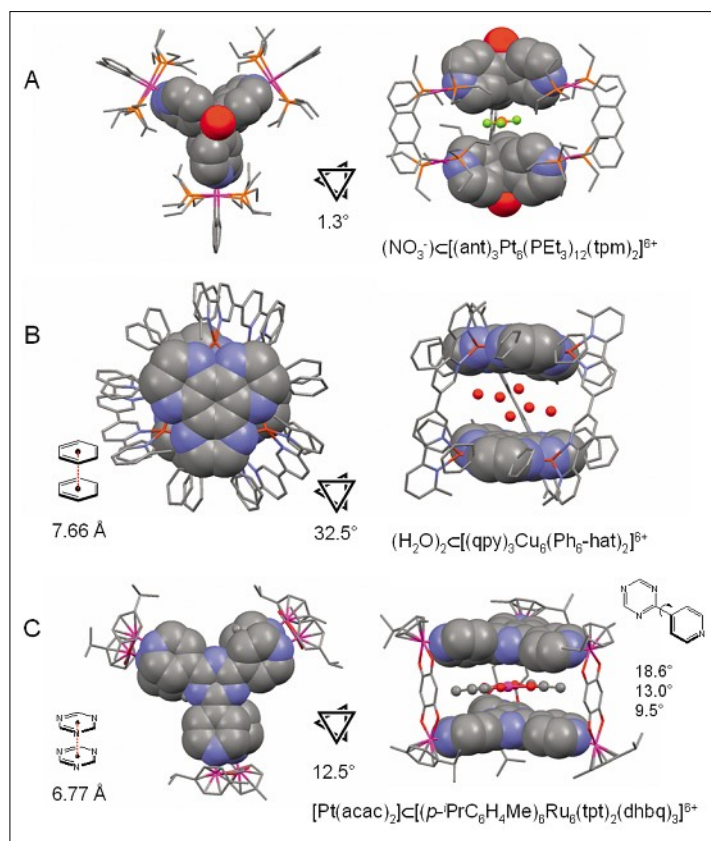


Fig. 6. Structural comparison (top view and side view) of $[(\text{C}_5\text{Me}_5)_6\text{Rh}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$,^[11] $[(\text{C}_5\text{Me}_5)_6\text{Ir}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$,^[11] $[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$,^[10] and $[(\text{C}_6\text{Me}_6)_6\text{Ru}_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$.^[10]

Table 2. Chirality and structural parameters for the filled hexanuclear cage molecules

Filled cage complex	Space group	M–M	Δ a	ref.
$(\text{hntp})\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{prz})_3]^{12+}$	$P 3$	6.6 Å	0.0°	[17]
$(\text{K}^+)\text{C}[\text{Mo}_6(\text{CN})_9(\text{CO})_{18}]^{9-}$	$P 2_1/c$	5.6 Å	0.0°	[18]
$(\text{NO}_3^-)\text{C}[(\text{ant})_3\text{Pt}_6(\text{PEt}_3)_{12}(\text{tpm})_2]^{6+}$	$P 1$	5.7 Å	1.3°	[16]
$(\text{H}_2\text{O})_2\text{C}[(\text{qpy})_3\text{Cu}_6(\text{Ph}_6\text{-hat})_2]^{6+}$	$C 2/c$	7.7 Å	32.5°	[19]
$[\text{Pt}(\text{acac})_2]\text{C}[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{dhbq})_3]^{6+}$	$P 2_1/c$	6.8 Å	12.5°	[20]
$(\text{pyr})_2\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$	$C 222_1$	10.0 Å	33.2°	[21]
$(\text{porph})_2\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$	$P 2_1/n$	9.9 Å	19.6°	[22]
$[\text{Pt}(\text{acac})_2]_2\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$	$P 2_1/c$	10.4 Å	22.5°	[23]

Fig. 7. Structural representations (top view and side view) of hexamethoxytriphenylene in $[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{prz})_3]^{12+}$ [17]Fig. 8. Structural comparison (top view and side view) of the filled systems NO_3^- in $[(\text{ant})_3\text{Pt}_6(\text{PEt}_3)_{12}(\text{tpm})_2]^{6+}$ (A), 16 $2 \text{H}_2\text{O}$ (disordered) in $[(\text{qpy})_3\text{Cu}_6(\text{Ph}_6\text{-hat})_2]^{6+}$ (B) [19] and $[\text{Pt}(\text{acac})_2]$ in $[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{dhbq})_3]^{6+}$ (C) [20]

rality. Moreover, if the encapsulated molecule possesses the proper symmetry and fits perfectly into the cavity, the triangular prismatic conformation can be locked, thus suppressing helical chirality. Table 2 summarises chirality and structural parameters for the filled hexanuclear cage molecules discussed below.

Interestingly, the filled hexanuclear palladoprisim $(\text{hntp})\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{prz})_3]^{12+}$ (prz = pyrazine; hntp = hexamethoxytriphenylene) shows high symmetry ($P3$) with a perfectly eclipsed conformation and a perfectly parallel arrangement of the π -systems. [17] Thus, this system is not chiral (Fig. 7). Similarly, in the idealised D_{3h} anionic cage $[\text{Mo}_6(\text{CN})_9(\text{CO})_{18}]^{9-}$ a potassium sits in the small cavity, 5.6×5.6 Å, thus giving rise to an achiral filled hexanuclear metalloprismatic carceplex. [18]

However, in the slightly more spacious hexanuclear cage molecule $[(\text{ant})_3\text{Pt}_6(\text{PEt}_3)_{12}(\text{tpm})_2]^{6+}$ (tpm = tris(4-pyridyl)methanol), in which a NO_3^- anion is found within the cavity, a deformation of the triangular prismatic conformation is observed, the twist angle between the two tris(4-pyridyl)methanol triangular moieties being 1.3° (Fig. 8A). [16]

Water molecules are encapsulated by a large cationic copper cage, $[(\text{qpy})_3\text{Cu}_6(\text{Ph}_6\text{-hat})_2]^{6+}$, containing hexaphenylhexaazatriphenylene ($\text{Ph}_6\text{-hat}$) triangular panels and quaterpyridine (qpy) connecting ligands (Fig. 8B). [19] The water molecules are disordered within the cavity (six positions with $1/3$ occupation) and therefore play a minor role in the overall geometry of $[(\text{qpy})_3\text{Cu}_6(\text{Ph}_6\text{-hat})_2]^{6+}$. The centroid-centroid distance between the two $\text{Ph}_6\text{-hat}$ panels is 7.7Å with a twist angle of 32.5° .

Recently, we have shown that the cationic cage complex $[(p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\text{tpt})_2(\text{dhbq})_3]^{6+}$ (dhbq = dihydroxybenzoquinonato) is capable of encapsulating $\text{Pt}(\text{acac})_2$ complex (acac = acetylacetonato) within its cavity. [20] To minimise interactions between the methyl groups of the acac moieties and the tpt units, the triangular prism adopts a staggered conformation: The twist angle being 12.5° (Fig. 8C). The platinum atom is stacked midway between the two triazine moieties at 3.4Å from the triazine planes.

In the large palladium cage $[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$ (Me_4bipy = 2,2',6,6'-tetramethyl-4,4'-bipyridine), in which two pyrene (pyr) [21] or porphyrin (porph) [22] or $\text{Pt}(\text{acac})_2$ [23] fit into the cavity, the chirality and distortion of the triangular prism is amplified, the complexes $(\text{pyr})_2\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$, $(\text{porph})_2\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$ and $[\text{Pt}(\text{acac})_2]_2\text{C}[(\text{en})_6\text{Pd}_6(\text{tpt})_2(\text{Me}_4\text{bipy})_3]^{12+}$ were structurally characterised (Fig. 9). In these systems, the deviation from triangular prismatic geometry is quite

significant. The twist of the tpt units varies from 20–33°, while the average rotation of the pyridyl groups with respect to the plane of the triazine core remains low (<8°). This large filled hexanuclear metalloprismatic cage, $[(en)_6Pd_6(tpt)_2(Me_4bipy)_3]^{12+}$, as well as the copper derivative, $[(qpy)_3Cu_6(Ph_6-hat)_2]^{6+}$, show the greatest deformation from the triangular prismatic geometry.

Conclusions

The structural comparison of the nineteen hexanuclear metalloprismatic cage molecules described in this article shows that helical chirality is generated by twisting the two trigonal panels of the cages one against the other. Only for four complexes the X-ray structure analyses reveal a perfectly eclipsed arrangement of the two trigonal panels, so that these cages are not chiral in the solid state. The other fifteen cages show helical chirality in the solid state. The encapsulation of flat molecules in some of the cages may enforce or attenuate the helical chirality by influencing the twist between the trigonal panels. The longer the vertical connectors in these hexanuclear cages are, the greater are the observed twist angles.

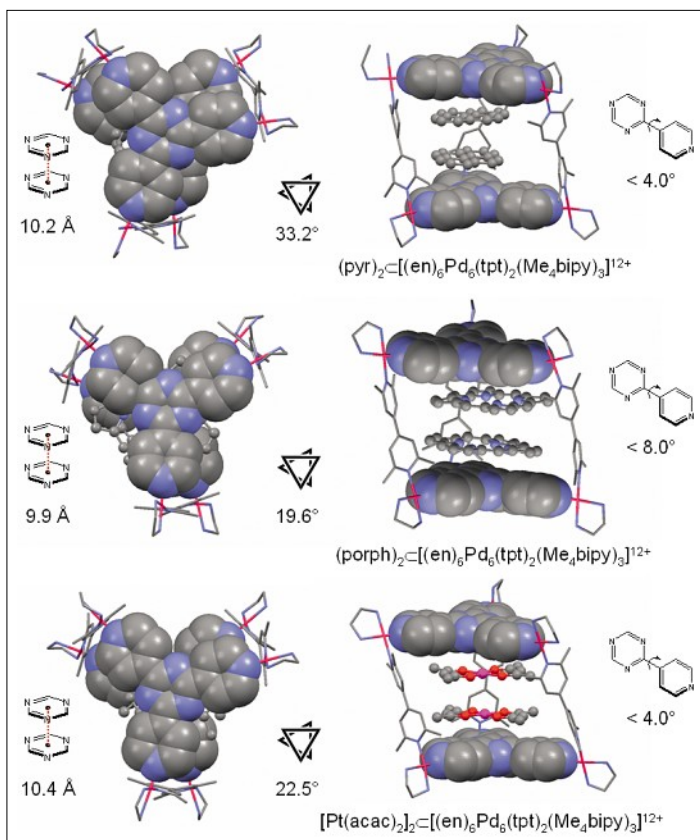


Fig. 9. Structural comparison (top view and side view) of $(pyr)_2$ (top),^[21] $(porph)_2$ (middle)^[22] and $[Pt(acac)_2]_2$ (bottom)^[23] encapsulated in the cationic cage $[(en)_6Pd_6(tpt)_2(Me_4bipy)_3]^{12+}$

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- [1] a) J.-M. Lehn, 'Supramolecular Chemistry – Concepts and Perspectives' Wiley-VCH, Weinheim, **1995**; b) J.-M. Lehn, *Science* **2002**, 295, 2400.
- [2] a) L. Pirondini, F. Bertolini, B. Cantadori, F. Ugozzoli, C. Massera, E. Dalcanale, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 4911 and references therein; b) M. V. Ovchinnikov, B. J. Holliday, C. A. Mirkin, L. N. Zakharov, A. L. Rheingold, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 4927 and references therein; c) Y. K. Kryschenko, S. Russell Seidel, D. C. Muddiman, A. I. Nepomuceno, P. J. Stang, *J. Am. Chem. Soc.* **2003**, 125, 9647; d) J. D. Crowley, A. J. Goshe, B. Bosnich, *Chem. Commun.* **2003**, 2824; e) D. C. Caskey, J. Michl, *J. Org. Chem.* **2005**, 70, 5442; f) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, 38, 369; g) V. Maurizot, M. Yoshizawa, M. Kawano, M. Fujita, *Dalton Trans.* **2006**, 2750; h) M. Albrecht, *Naturwissenschaften* **2007**, 94, 951.
- [3] P. Cintas, *Angew. Chem., Int. Ed.* **2002**, 41, 1139.
- [4] J. C. Nelson, J. G. Saven, J. S. Moore, P. G. Wolynes, *Science* **1997**, 277, 1793.
- [5] C. Mao, W. Sun, Z. Shen, N. C. Seeman, *Nature* **1999**, 397, 144.
- [6] a) R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, 107, 6540; b) A. F. Williams, C. Piguet, G. Bernardinelli, *Angew. Chem., Int. Ed.* **1991**, 30, 1490; c) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem.*

- Rev.* **1997**, 97, 2005; d) M. Albrecht, *Chem. Rev.* **2001**, 101, 3457; e) M. J. Hannon, L. J. Childs, *Supramol. Chem.* **2004**, 16, 7.
- [7] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, 27, 2565.
- [8] a) S. Hiraoka, K. Harano, T. Tanaka, M. Shiro, M. Shionoya, *Angew. Chem., Int. Ed.* **2003**, 42, 5182; b) S. Hiraoka, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2004**, 126, 1214.
- [9] a) R. G. Chapman, J. C. Sherman, *J. Am. Chem. Soc.* **1999**, 121, 1962; b) R. G. Chapman, J. C. Sherman, *J. Org. Chem.* **2000**, 65, 513; c) D. A. Makeiff, J. C. Sherman, *J. Am. Chem. Soc.* **2005**, 127, 12363.
- [10] P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink, B. Therrien, *Chem. Commun.* **2006**, 4691.
- [11] P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink, B. Therrien, *Dalton Trans.* **2007**, 4457. $[(C_5Me_5)_6Ir_6(tpt)_2(C_2O_4)_3][CF_3SO_3]_6$ has been structurally characterised as well by G.-X. Jin, giving exactly the same achiral arrangement of the cage molecule: Y.-F. Han, Y.-J. Lin, W.-G. Jia, L.-H. Weng, G.-X. Jin, *Organometallics* **2007**, 26, 5848.
- [12] P. Govindaswamy, G. Süss-Fink, B. Therrien, *Organometallics* **2007**, 26, 915.
- [13] Y.-F. Han, W.-G. Jia, Y.-J. Lin, G.-X. Jin, *J. Organomet. Chem.* **2008**, 693, 546.
- [14] B. Manimaran, T. Rajendran, Y.-L. Lu, G.-H. Lee, S.-M. Peng, K.-L. Lu, *Eur. J. Inorg. Chem.* **2001**, 633.
- [15] P. H. Dinolfo, V. Coropceanu, J.-L. Brédas, J. T. Hupp, *J. Am. Chem. Soc.* **2006**, 128, 12592.
- [16] C. J. Kuehl, Y. K. Kryschenko, U. Radhakrishnan, S. Russell Seidel, S. D. Huang, P. J. Stang, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 4932.
- [17] K. Kumazawa, K. Biradha, T. Kusukawa, T. Okano, M. Fujita, *Angew. Chem., Int. Ed.* **2003**, 42, 3909.
- [18] S. M. Contakes, T. B. Rauchfuss, *Angew. Chem., Int. Ed.* **2000**, 39, 1984.
- [19] P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem., Int. Ed.* **1993**, 32, 69.
- [20] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. K. Renfrew, P. J. Dyson, *Angew. Chem., Int. Ed.* **2008**, 47, 3773.
- [21] M. Yoshizawa, J. Nakagawa, K. Kumazawa, M. Nagao, M. Kawano, T. Ozeki, M. Fujita, *Angew. Chem., Int. Ed.* **2005**, 44, 1810.
- [22] K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita, *Angew. Chem., Int. Ed.* **2007**, 46, 1803.
- [23] M. Yoshizawa, K. Ono, K. Kumazawa, T. Kato, M. Fujita, *J. Am. Chem. Soc.* **2005**, 127, 10800.