

Probing possible non-covalent interactions on a hexacationic Ag(I)-pillarplex-dodecyldiammonium pseudo-rotaxane as terephthalate salt

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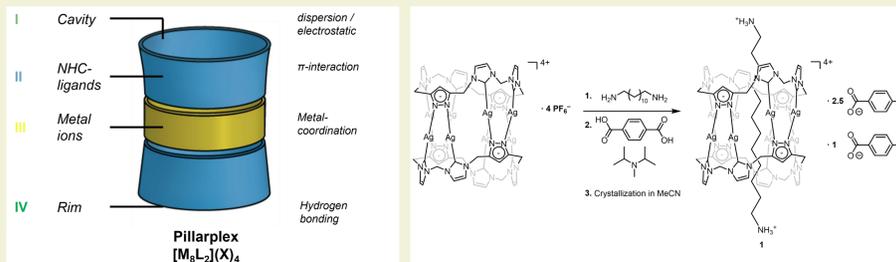
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INTRODUCTION & CONCEPT

The tubular pillarplex complex $[M_6L_2](X)_4$ ($M = Ag, Au$; $L = L^{Me}, L^i$; $X = OTf, OAc, PF_6$) – a supramolecular organometallic complexes (SOCs)^[1] – show exclusive shape selective encapsulation in solution, tuneable solubility by anion exchange reactions, biological activity, shape-adaptability via rim-functionalisation and $[M_6L_2]^{4+}$ can act as ring component to form mechanically-interlocked organometallic rotaxanes.^[2-5] Cation $[M_6L_2]^{4+}$ was conceptually divided into four regions: (I) cavity, (II) aromatic rings, (III) metal ions and (IV) rim (Fig. 1).^[6] Here, structure-specific and highly selective non-covalent interactions are expected.

Fig. 1: Schematic drawing of pillarplex cation $[M_6L_2]^{4+}$ with possible interaction sites: (I) Cavity with dispersion / electrostatic interaction sites, (II) NHC ligands with π -interaction sites, (III) metal ions with metal coordination sites and (IV) rim with H-interaction sites.



To probe aforementioned possible interaction sites (I-IV) via structural characterization, a pillarplex pseudo-rotaxane salt was synthesised, which incorporates necessary components to experimentally probe all possible non-covalent interactions. 1,12-diaminododecane acts as guest molecule for cavity interaction and terephthalate units provide carbonyl groups for hydrogen bonding and their aromatic units for π -interaction sites.^[6]

→ Full Interaction Maps (FIMs) Analysis of $[Ag_6L^{Me}_2]^{4+}$
→ Crystal Structure Analysis of $[Ag_6L^{Me}_2][C_{12}H_{24}(NH_3^+)_2](X)_4$
→ Hirshfeld Surface Analysis of $[Ag_6L^{Me}_2]^{4+}$ and 1,12-diaminododecane

Fig. 2: Reaction mechanism for the synthesis of pseudo-rotaxane $[Ag_6L^{Me}_2][C_{12}H_{24}(NH_3^+)_2](X)_4$ based on SC-XRD structure determination.

FULL INTERACTION MAPS (FIMs)

FIMs analysis^[7-8] was applied to $[Ag_6L^{Me}_2]^{4+}$ to predict the interaction sites of the pillarplex cation with present solvent molecules and/or counter anions and their crystal packing.

The program ISOSTAR^[7-8] divides the pillarplex cation into so-called 3D central groups containing their specific properties. These central groups are converted into a larger molecule by the program SUPERSTAR^[7-8]. The probability of specific interactions for a selected molecule is calculated with the tool FIMs, which is implemented in MERCURY^[9]. Here, standard probes – such as charged/uncharged nitrogen (NH) – with specific interactions are implemented. The central groups of $[Ag_6L^{Me}_2]^{4+}$ are depicted in Fig. 3 and are located only at the NHC ligands and/or the rim.

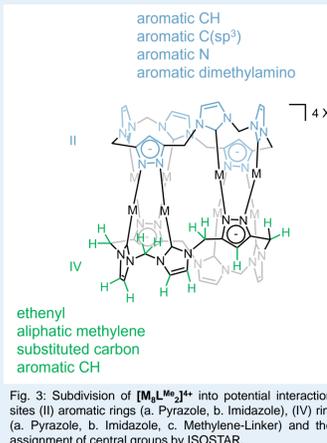


Fig. 3: Subdivision of $[M_6L_2]^{4+}$ into potential interaction sites (I) aromatic rings (a. Pyrazole, b. Imidazole), (IV) rim (a. Pyrazole, b. Imidazole, c. Methylene-Linker) and the assignment of central groups by ISOSTAR.

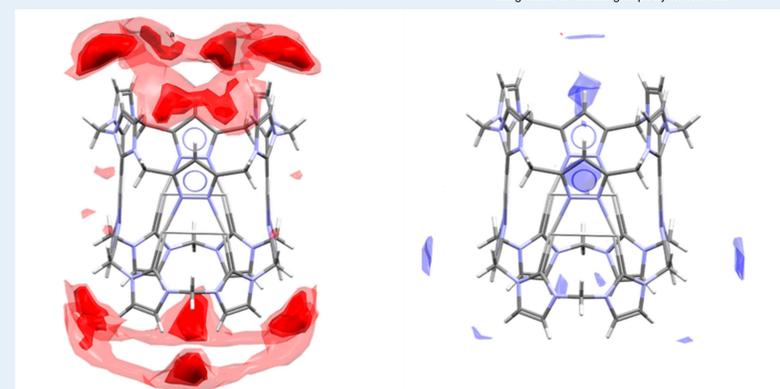


Fig. 4: FIMs analysis of cationic $[Ag_6L^{Me}_2]^{4+}$ towards acceptor probe carbonyl oxygen (left) and donor uncharged NH (right).

Exemplary probes of uncharged NH and carbonyl oxygen were selected as they show possibility to undergo H-bonding, π -interactions and metal coordination. No probability for interactions inside the cavity (I) was observed. At the aromatic rings (II) a high probability was expected for π -interactions, but only slight probability was observed at the imidazolylidene units. Absolutely no interaction close to Ag(I) ions (III) was observed, but especially for probe carbonyl oxygen high probability for H-bonding close to the rim (IV) was observed.^[6]

→ Limited applicability towards metal coordination & encapsulation interaction!

CRYSTAL STRUCTURE ANALYSIS

Suitable single crystals were obtained by slow evaporation of a saturated solution of pseudo-rotaxane 1 in Acetonitrile. The crystal structure was solved and refined in the monoclinic space group $P 2_1/c$ (No. 14) with unit cell dimensions $a = 16.596(14)$ Å, $b = 28.884(2)$ Å, $c = 23.719(2)$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 95.342(4)^\circ$.

The asymmetric unit contains one cationic pillarplex molecule $[Ag_6L^{Me}_2]^{4+}$ with one encapsulated 1,12-diaminododecane, three and a half terephthalate anions and twenty-two co-crystallized water molecules. The terephthalate units 1, 2 and 3 are located on general positions, while terephthalate unit 4 is located on twofold Wyckoff position 2a. $[Ag_6L^{Me}_2]^{4+}$ was analyzed towards intermolecular contacts with solvent, anion, guest and neighbouring cation molecules (Fig. 5).

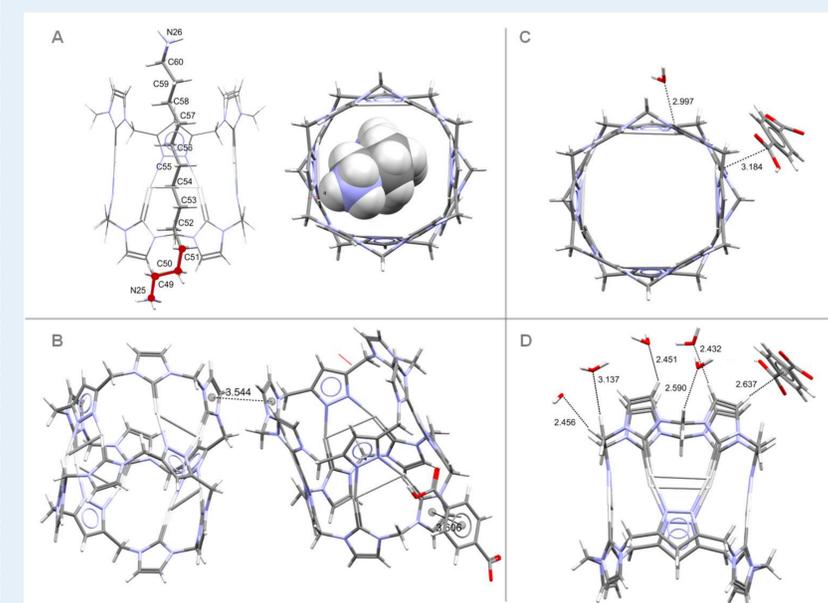


Fig. 5: (A) Hydrophobic interaction inside the cavity (I) and respective gauche formation; (B) π -interactions between aromatic rings (II) of two pillarplex cations and $[Ag_6L^{Me}_2]^{4+}$ and a terephthalate unit; (C) metal ion interactions (III) between Ag(I) ions and water or terephthalate unit; (D) rim interactions (IV) by hydrogen bonding with either water or terephthalate units.

The observed main contributions are based on hydrophobic interaction inside the cavity, hydrogen bonding and π -stacking of macrocyclic ligands and minor contribution based on metal coordination.^[6]

→ High impact of non-covalent interactions on the crystal arrangement!

HIRSHFELD SURFACE ANALYSIS

Non-covalent interactions of Pseudo-Rotaxane 1 were analysed and visualized by Hirshfeld surface analysis (CrystalExplorer^[9-11]) for the cation $[M_6L_2]^{4+}$ and for the guest molecule 1,12-diaminododecane (Fig. 6).

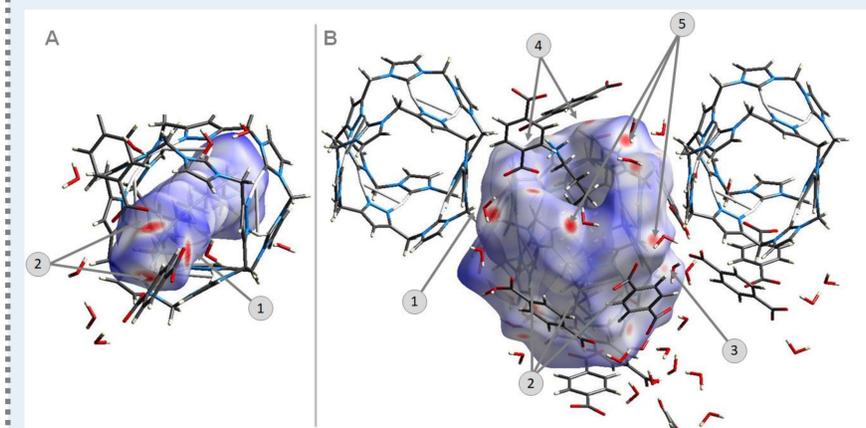


Fig. 6: Overview of the non-covalent interactions calculated by Hirshfeld surface analysis: (A) for guest 1,12-diaminododecane (Volume 318.51 Å³, area 311.21 Å², globularity 0.725 and asphericity 0.613); (B) for $[Ag_6L^{Me}_2]^{4+}$ (Volume 1307.28 Å³, area 920.41 Å², globularity 0.628 and asphericity 0.008).

(A) Surface of guest:

1. N-H...O interaction with O_{H_2O} (1.899 Å / 172.12°)
2. N-H...O interaction with $O_{terephthalate}$ (1.867 Å / 167.58°, 1.898 Å / 170.52°, 2.555 Å / 130.42°)

(B) Surface of cation $[Ag_6L^{Me}_2]^{4+}$:

1. $\pi \cdots \pi$ interaction (3.544 Å / 76.60°) centroid_{py} with neighbouring centroid_{py}
2. $\pi \cdots M$ interaction (3.781 Å / 87.04°, 3.055 Å / 148.51°) centroid_{terephthalate} with Ag(I)
3. $O_{H_2O} \cdots M$ interaction (2.997 Å / 141.41°)
4. $\pi \cdots H$ interaction (2.507 Å / 156.26°, 2.566 Å / 149.97°) centroid_{terephthalate} with H_{Im-C}
5. $H \cdots O_{H_2O}$ interaction (2.589 Å / 163.11°, 2.402 / 165.25°, 3.915 / 138.58°) C-H_{Me}, C-H_{Im}, C-H_{py} with H_2O

By evaluation of the fingerprint plots a quantification towards different contributions (e.g. H-, π -bonding, metal coordination, ...) of non-covalent interactions was performed. For (A) mainly H...X inside the cavity (I) and for (B) mainly H...X bonding (65.2%) but also Ag...X bonding (7.7%) were observed.^[6]

$[Ag_6L^{Me}_2]^{4+}$	1,12-diaminododecane		
	H...all	Ag...all	H...all
H...all	65.2	7.7	100.0
H...Ag	0.3	0.0	10.2
H...N	0.4	0.0	16.3
H...C	8.3	1.2	25.3
H...H	40.8	5.2	31.4
H...O	15.4	1.2	16.8

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