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Heads or Tails? Sandwich-Type Metallocomplexes of Hexakis(2,3-di-O-methyl)- β -cyclodextrin

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Figure 1. (a) Schematic representation of α -CD molecule, its organization, description, and carbon numbering. (b) Possible assemblies of CD molecules organized over metallo-ring (grey spheres represent metal cations) in either typical head-to-head fashion (head-to-head STC), or (c) in hypothetical tail-to-tail fashion (tail-to-tail STC).

Figure 2. Representation of (a) side-view, (b) top-view of RbF-STC; representation of (c) side-view, (d) top-view of AgPF6-STC. Detailed representation of the coordination of (e) rubidium cations in RbF-STC and (f) silver cations in AgPF6-STC. Hydrogen bonds are shown as dashed black lines; Rb⁺, F⁻, and Ag⁺ atoms and water molecules are shown in space-filling model in (a)-(d).

164x111mm (220 x 220 DPI)

Figure 3. (a) Stacking of the RbF-STC and (b) the AgPF6-STC, where the latter is mediated by hydrogen bonding and accommodating PF6[−] anions. (c) Packing of the RbF-STC through Rb⁺⋯F[−] contacts, showing the channels in the structure; (d) packing showing the PF6[−] anions both inside and outside of the AgPF6-STC.

151x91mm (220 x 220 DPI)

Figure 4. (a) Stacking of the AgClO₄-STC, where STCs are mediated by Ag–O–Ag and O–H...O interactions and accommodated with ClO₄[–] anions. (b) Crystal packing showing the ClO₄[–] anions both inside and on the outside of the AgClO₄-STC.

Figure 5. (a) Crystal structure of the 1:1 complex of L and AgBF₄ and (b) detail on the Ag⁺ cation coordination.

Scheme 1. Ligand (L) tail-to-tail coordination with Rb⁺ (RbF-STC) and head-to-head coordination with Ag⁺ (Ag-STC). Anions in Ag-STC were omitted for clarity.

Heads or Tails? Sandwich-Type Metallocomplexes of Hexakis(2,3-di-*O*-methyl)- α -cyclodextrin

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KEYWORDS: cyclodextrin, sandwich-type complex, X-ray crystallography, metal-organic material, rubidium, silver

ABSTRACT

Native and synthetically modified cyclodextrins (CDs) are useful building blocks in construction of large coordination complexes and porous materials with various applications. Sandwich-type complexes (STCs) are one of the important groups in this area. Usually, coordination of secondary hydroxyls or the “head” portal of native CD molecules to a notional multinuclear ring of metal cations leads to formation of head-to-head STCs. Our study introduces a new CD-ligand, hexakis(2,3-di-*O*-methyl)- α -cyclodextrin, which enables formation of intriguing head-to-head, but also novel tail-to-tail STCs. Homometallic silver-based head-to-head STCs, AgPF₆-STC and AgClO₄-STC, were obtained by coordination of ligand methoxy groups to six Ag⁺, while bulky counter-anions are located on the outside but also filling the inner space of infinite linear channels formed. In contrast, unique homometallic tail-to-tail RbF-STC was prepared by complexation of primary hydroxyls, “tails”, to twelve Rb⁺ tightly interconnected by twelve F[−] creating complex structure with accessible pores for potential gas adsorptions.

INTRODUCTION

Cyclodextrins (CDs) are macrocyclic carbohydrate molecules classified based on the number of α -1,4-linked glucose units in their structures. Three most common cyclodextrins are α -CDs (6 glucose units), β -CDs (7 glucose units), and γ -CDs (8 glucose units). In general, the shape of CDs is described as truncated cone with two opposite faces, *i.e.* primary and secondary. The primary narrow face termed as tail, comprises of primary hydroxyl groups whilst secondary

broader face, the head – contain secondary hydroxyl groups (Figure 1a). Because of this arrangement, the molecules of CDs are on the outside hydrophilic and thus to some extent water soluble. In contrary, the interior of the CD torus is considerably less hydrophilic and thus able to include various hydrophobic molecules. Methylation of CD hydroxyl groups improves their solubility not only in organic solvents but also in aqueous solutions by reduction of number of intermolecular hydrogen bonds. Moreover, the methylation slightly extends the hydrophobic cavity which can improve the binding affinities towards hydrophobic guests in comparison with native CDs.¹⁻⁴ For these reasons, in the realm of supramolecular chemistry,⁵ native and methylated CDs have found applications in drug delivery,^{6,7} polymer chemistry,⁸⁻¹² soil decontamination,^{13,14} or in food and cosmetic formulations.^{15,16}

In metallosupramolecular chemistry, CDs are useful building blocks to construct large coordination complexes or porous materials.¹⁷⁻²⁵ Particularly interesting in context of this contribution is the group of sandwich-type complexes (STCs).¹⁹ In general, deprotonation and complexation of the secondary hydroxyl groups with metal ions lead to the formation of head-to-head STCs, where two molecules of CDs are interconnected by coordination to multinuclear metallo-ring (Figure 1b). The metallo-ring can be composed of either one or two different metal salts enabling us to recognize homo- or heterometallic STCs.¹⁹

Figure 1. (a) Schematic representation of α -CD molecule, its organization, description, and carbon numbering. (b) Possible assemblies of CD molecules organized over metallo-ring (grey spheres represent metal cations) in either typical head-to-head fashion (head-to-head STC), or (c) in hypothetical tail-to-tail fashion (tail-to-tail STC).

To date, only two homometallic head-to-head STCs built of Pb^{2+} ions are reported. The earlier one was prepared by Klüfers *et al.* from γ -CD and $\text{Pb}(\text{NO}_3)_2$ in the presence of NaOH yielding hexadecanuclear complex, representing the highest known number of adjacent metal ions per STC.²⁶ The second tetradecanuclear STC was isolated from a bisphasic solvothermal reaction of β -CD with PbCl_2 in water:cyclohexanol mixture.²⁷

Heterometallic head-to-head STCs are generally formed using metal salts and CDs in the presence of auxiliary deprotonating alkali metal hydroxides (Li^+ , Na^+ , K^+ or Rb^+). Cu^{2+} in the presence of alkali-metal hydroxides forms STCs with all, α -, β -, and γ -CDs.²⁸⁻³⁰ α -CD with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in the presence of LiOH and NaOH form corresponding trinuclear STC of the formula $\text{Li}_3[\text{Cu}_3\text{Li}_3(\text{H}_2\text{O})_3(\alpha\text{-CD})_2]$ and $\text{Na}_3[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_3(\alpha\text{-CD})_2]$. Furthermore, it has been shown that α -CD with Fe^{2+} , Mn^{2+} , and Cd^{2+} in the presence of LiOH forms STCs with formulae $\text{Li}_5[\text{Li}_6(\text{H}_2\text{O})_6\text{Fe}_3(\text{H}_2\text{O})_3(\alpha\text{-CD})_2]$,³¹ $\text{Li}_7[\text{Li}_6(\text{H}_2\text{O})_6\text{Mn}_3(\text{H}_2\text{O})_3(\alpha\text{-CD})_2]$,³¹ and $[\text{Li}_6\text{Cd}_3(\text{H}_2\text{O})_9(\alpha\text{-CD})_2]$, respectively.¹⁹ α -CD with Bi^{3+} and VO^{2+} salts in the presence of NaOH forms $[\text{Na}_6(\text{H}_2\text{O})_6\text{Bi}_6(\alpha\text{-CD})_2]$ and $\text{Na}_6[\text{Na}_6(\text{H}_2\text{O})_6(\text{VO})_6(\alpha\text{-CD})_2]$ STCs.³¹ In another report, usage of auxiliary reagents KOH and RbOH with $\text{Cu}(\text{NO}_3)_2$ and α -CD led to dinuclear $\text{K}_4[\text{Cu}_2(\alpha\text{-CD})_2]$ and $\text{Rb}_4[\text{Cu}_2(\alpha\text{-CD})_2]$ hydrated complexes where alkali-metal cations coordinate to primary hydroxyl groups of the CD.²⁸ β -CD in combination with $\text{Cu}(\text{OH})_2$ and LiOH gives head-to-head STC with the formula $\text{Li}_4[\text{Li}_7\text{Cu}_4(\text{H}_2\text{O})_7(\beta\text{-CD})_2]$.²⁹ Vanadium(II) forms $\text{Na}_7[(\text{VO})_7\text{Na}_7(\text{H}_2\text{O})_7(\beta\text{-CD})_2]$ STC with β -CD in the reaction of $\text{VO}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ and NaOH .³² γ -CD-copper STCs were prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and hydroxides of Li^+ , Na^+ , and Rb^+ , where Li^+ plays a key role in formation of tetranuclear $[\text{Li}_4\text{Cu}_4(\text{H}_2\text{O})_4(\gamma\text{-CD})_2]^{4-}$, Na^+ induces complexation into two unsymmetrical STCs $[\text{Na}_4\text{Cu}_4(\gamma\text{-CD})_4(\text{H}_2\text{O})]$, and Rb^+ leads to the formation of an extended structure of two symmetrical STCs with formula $[\text{Rb}_6\text{Cu}_9(\gamma\text{-CD})_2(\text{H}_2\text{O})]$.³⁰ Reaction of γ -CD with CoCl_2 and LiOH resulted in $[\text{Li}_8(\text{H}_2\text{O})_{12}\text{Co}_4(\gamma\text{-CD})_2]$ STC.²⁰ Overall, the organization of CDs in STCs described is always in head-to-head fashion towards the interconnecting metallo-ring,¹⁹ there was no tail-to-tail STC reported till now. It is also noteworthy that the formation of homometallic species is rather exceptional.^{25,26}

Stoddart *et al.* have shown that the use of the *solo* alkali metal ions in combination with native CDs leads to intriguing structures such as polyporous metal-coordination frameworks (reaction of α -CD with RbOH),²⁰ metal-organic frameworks (MOFs; γ -CD with KOH or RbOH yielding CD-MOF-1 or CD-MOF-2, respectively), or other infinite frameworks (γ -CD with NaOH , CsOH , or $\text{Sr}(\text{OH})_2$).^{21,22} The complexing power of CD to K^+ can even be exploited in isolation of gold from gold-bearing raw materials (reaction of α -CD with KAuBr_4).^{23,24}

To further explore the coordination possibilities of CDs *viz.* head-to-head and tail-to-tail binding motifs, we used hexakis(2,3-di-*O*-methyl)- α -cyclodextrin (**L**) for complexation with alkali and transition metals. The methylation at C-2 and C-3 position of the secondary rim was carried out to suppress the coordination of secondary hydroxyls to hard Lewis acid metal ions, by which the participation of the opposing primary hydroxyl rim in metal coordination would be induced. Indeed, by this approach we have introduced a new binding motif of CDs in STCs in tail-to-tail fashion. Coordination of primary hydroxyls of **L** towards the alkali-metal ring was described in the crystal structure of homometallic dodecanuclear rubidium STC prepared in reaction with RbF (RbF -STC, $[(\text{RbF})_{12}(\text{L})_2]$). In comparison, coordination of **L** with Ag^+ proceeds on both faces, primary and secondary, but only the coordination on the secondary face was able to mediate direct contact between two ligands forming STC (Ag -STC, i.e. AgPF_6 -STC, or AgClO_4 -STC, using AgPF_6 or AgClO_4 salts, respectively).

EXPERIMENTAL SECTION

Materials and reagents. α -Cyclodextrin, silver(I) hexafluorophosphate, silver(I) perchlorate, and silver(I) tetrafluoroborate were purchased from TCI Europe. Rubidium(I) fluoride was purchased from Sigma-Aldrich.

Synthesis of hexakis(2,3-di-*O*-methyl)- α -cyclodextrin (L**).** The ligand **L** was prepared according to the slightly modified reported procedure (more details included in Supporting Information).³⁴

Synthesis of RbF-STC complex. The **L** (10 mg, $8.7 \cdot 10^{-6}$ mol) was dissolved in methanol (200 μ L) and the solution was used to dissolve RbF ($6.1 \cdot 10^{-5}$ mol). The final solution was filtered through cotton plug into a small vial, after which diethyl ether as antisolvent was allowed to diffuse into the solution leading to a mixture of three morphologically and crystallographically different crystal species out of which hexagonal single crystals of the complex were easily hand-picked (with the yield of about 30 %) and measured providing the crystal structure of RbF-STC.

Syntheses of Ag-STC complexes. The crystallizations of **L** with AgX salts ($X = \text{PF}_6^-$, ClO_4^- , BF_4^-) have been carried out by preparing separate methanolic solution of the ligand and salts, followed by mixing them, and solvent evaporation at room temperature (see Supporting Information for more details).

X-Ray Crystallography. Single crystal X-ray diffraction data were collected using dual source Rigaku SuperNova Oxford diffractometer equipped with an Atlas detector using mirror-monochromated Cu- K_α radiation ($\lambda = 1.54184$ Å). The data collection and reduction were carried out on the instrument using the program *CrysAlisPro*.³⁵ The intensities were corrected for absorption using the Gaussian face-index absorption correction method.³⁵ Structures were solved with direct methods (SHELXS)^{36,37} and refined by full-matrix least squares on F^2 using the *OLEX2*,³⁸ which utilizes the SHELXL-2017 module.^{36,37} Constraints and restraints are used where appropriate for disordered models (see Supporting Information for more details).

RESULTS AND DISCUSSIONS

Single crystals for X-ray diffraction analysis were obtained using either slow methanol evaporation or slow diffusion of diethyl ether into methanolic solution (For more details, see Experimental section and Supporting Information). The following metal salts were tested for "heads or tails" coordination behavior with ligand **L**: LiOH, NaOH, KOH, RbOH, CsOH, KOAc, RbCl, RbBr, RbI, RbF, ZnBr₂, Zn(OAc)₂, Zn(NO₃)₂, AgPF₆, AgClO₄, AgBF₄, AgOCOCF₃, AgSO₃CF₃, ZrCl₄, ZrOCl₂, TiCl₄, and Y(NO₃)₃. Among all, only RbF, AgPF₆, AgClO₄, AgBF₄, and ZnBr₂ with ligand **L** form the corresponding metal-complexes with generic moiety formulae, [L(Rb)(F)(H₂O)(CH₃OH)], [L(Ag)(H₂O)](PF₆), [L(Ag)(ClO₄)(H₂O)](ClO₄)(H₂O), and [L(Ag)(H₂O)](BF₄)(H₂O), with suitable single-crystals for X-ray diffraction analysis. Here after, these complexes are presented as RbF-STC, AgPF₆-STC, AgClO₄-STC, and AgBF₄-**L**, respectively. Crystal structure of [L(ZnBr₂)(Et₂O)], ZnBr₂-**L**, is shown in the Supporting Information (Figure S4). Three out of four solid-state structures are *pseudo*-isomorphous, viz. RbF-

STC, AgPF₆-STC and AgClO₄-STC, which form intriguing STCs through either primary hydroxyl or secondary methoxy groups coordination (Scheme 1). Crystallization of **L** with RbF provided us with unique tail-to-tail STCs, the primary hydroxyl groups coordinate to Rb⁺ and the metallo-ring is composed of twelve interconnected pairs of Rb⁺ and F⁻. The opposite positioned rims of methoxy groups interact weakly with adjacent STCs and are passive towards metal coordination. In contrary, head-to-head coordination was observed in AgPF₆-STC and AgClO₄-STC. Secondary methoxy groups interact with notional silver-water-ring while counter-anions are distributed equally outside or inside the STC. All STCs presented herein form either hydrogen or coordination bonds which further direct the assemblies into 1D infinite channels in their crystal lattice. The channels of STCs derived from Ag⁺ are filled with bulky anions. In contrast, RbF-STC contains well-incorporated fluoride anions in the rubidium metallo-ring keeping the channels available for possible applications.

Scheme 1. Ligand (**L**) tail-to-tail coordination with Rb⁺ (RbF-STC) and head-to-head coordination with Ag⁺ (Ag-STC). Anions in Ag-STC were omitted for clarity.

RbF-STC: Crystal structure of RbF-STC shows that the two ligands **L** are connected to a tail-to-tail dimer by 12 Rb⁺, with 12 F⁻ as the charge-compensating anions (Figure 2a,b). It crystallizes in a rare space group, *i.e.* *P*6, which follows the molecular symmetry of **L**. The asymmetric unit accordingly comprises two Rb⁺, two F⁻, two monomeric 2,3-di-*O*-methyl- α -D-glucotetrahydropyranoside units (one from each **L**), 4/3 molecules of methanol, and one molecule of water. In RbF-STC, given the tail-to-tail dimerization of **L**, the Rb⁺...O contacts are formed through the tetrahydropyran O atom acting in monodentate mode and the -CH₂OH group acting in bridging mode (Figure 2e). Two symmetrically independent Rb⁺ are chelated by one Rb⁺...O(tetrahydropyran) and one Rb⁺...O(H)(CH₂-) contact to one molecule of **L** and an additional Rb⁺...O(H)(CH₂-) contact to the other molecule of **L**. It is noteworthy that the mode of chelation is slightly different for the two Rb⁺, with the O(tetrahydropyran) and O(H)(CH₂-) moieties coming either from the same 2,3-di-*O*-methyl- α -D-glucotetrahydropyranoside monomer or two neighboring molecules. The seam is reinforced by additional Rb⁺...F⁻ contacts that also participate in short hydrogen bonds with the -CH₂OH groups. Additionally, the RbF-STC is further decorated by molecules of solvent (methanol, water) forming Rb⁺...O contacts. Finally, neighboring RbF-STCs are connected through Rb⁺...F⁻ contacts with neighboring RbF-STCs into layers that stack on top of each other in such a way that the RbF-STCs form continuous channels along the crystallographic axis *c* (Figure 3a,c). No guests could be located inside the RbF-STC.

Crystals of RbF-STC have been submitted for thermogravimetric analysis (TGA). TGA was performed on sample dried at room temperature in the air or activated upon heating at 80 °C under high vacuum. While the former sample showed significant weight loss of volatiles (solvents as methanol and diethyl ether) from the pores up to a decomposition temperature ($T_D = 225$ °C) corresponding to 19 % of its original weight, the activated sample have shown only smaller 6 % weight loss (Figure S3, Supporting Information), both confirming the porosity of the sample. Nevertheless, the sample amount was not satisfactory for thorough experimental gas adsorption studies, therefore, we have performed preliminary computational simulations to evaluate its capacity for adsorption and separation of CO₂ from the flue or natural gas mixtures. RbF-STC structure shows high CO₂ uptake, as well as high working capacity and selectivity, with a significant adsorbent performance score for the flue gas mixture (Section 1.6, Supporting Information).

Figure 2. Representation of (a) side-view, (b) top-view of RbF-STC; representation of (c) side-view, (d) top-view of AgPF₆-STC. Detailed representation of the coordination of e) rubidium cations in RbF-STC and (f) silver cations in AgPF₆-STC. Hydrogen bonds are shown as dashed black lines; Rb⁺, F⁻, and Ag⁺ atoms and water molecules are shown in space-filling model in (a)-(d).

AgPF₆-STC: Unlike in the RbF-STC, in AgPF₆-STC the two ligands **L** are connected into a head-to-head dimer by six Ag⁺ (Figure 2c,d), however, the space group *P6* again follows well the molecular symmetry of **L**. Besides one full occupancy Ag⁺ and two monomeric 2,3-di-*O*-methyl- α -D-glucotetrahydropyranoside units, the asymmetric unit comprises another Ag⁺ modelled with a half-occupancy and one water molecule. The charge is balanced by PF₆[−] which could be found and modelled in 6 discrete positions with the total occupancy of 17/12 which is very close to 1.5 needed to provide charge balance. This is acceptable, given that the precise refinement of the occupancies of partially occupied Ag⁺ and PF₆[−] is difficult due to disorder. The head-to-head dimerization in AgPF₆-STC is driven by Ag⁺⋯O coordination bonds through O atoms of methoxy groups and water molecules (Figure 2f). Interestingly, the coordination by **L** is asymmetric, as one molecule of **L** only coordinates through one methoxy group, while the other one coordinates through two methoxy group of the neighboring 2,3-di-*O*-methyl- α -D-glucotetrahydropyranoside units in a chelating manner. In addition, the Ag cations form an Ag₆(H₂O)₆ crown-like ring with the water molecules as bridging ligands (Figure 2c,d,f). These water molecules seem to be involved in O–H⋯O hydrogen bonds with two methoxy groups and the bridging O atom of the α -cyclodextrin backbone, as well as in O–H⋯F hydrogen bonds with the encapsulated PF₆[−]. Similarly to RbF-STC, individual AgPF₆-STCs form continuous channels along the crystallographic axis *c*. However, unlike the RbF-STC, these channels are formed by O–H⋯O hydrogen bonding between **L** tails and are filled with PF₆[−] (Figure 3b). Finally, AgPF₆-STC stacks pack through weak C–H⋯F interactions with surrounding PF₆[−] (Figure 3d).

Figure 3. (a) Stacking of the RbF-STC and (b) the AgPF₆-STC, where the latter is mediated by hydrogen bonding and accommodating PF₆[−] anions. (c) Packing of the RbF-STC through Rb⁺⋯F[−]

contacts, showing the channels in the structure; (d) packing showing the PF_6^- anions both inside and outside of the $\text{AgPF}_6\text{-STC}$.

$\text{AgClO}_4\text{-STC}$: The asymmetric unit contains four crystallographically independent silver(I) ions, of which one Ag^+ by the space group $P6$ symmetry seam two ligands in head-to-head fashion, similar to $\text{AgPF}_6\text{-STC}$. The two other silvers that are not part of the head-to-head junction are bound to oxygens of primary hydroxyl group of 2,3-di-*O*-methyl- α -D-glucotetrahydropyranoside units, perchlorates, and water molecules displaying complex coordination pattern connecting the tails of the STCs to produce 1D channel like structures as shown in Figure 4a. The 1D channels are filled with highly disordered non-coordinated perchlorate anions. The fourth Ag^+ , that is not part of either head-to-head or tail-to-tail junction, is found between *exo*-1D channels coordinated to perchlorate anions helping the 1D channels to create tight 3D crystal packing as depicted in the Figure 4b. The *exo*-1D-channel perchlorates are unable to coordinate silvers at head-to-head metallo-ring possibly due to steric hindrance by methoxy groups as could be observed from the crystal lattice. The salient coordination features of the 1D channel are (1) circular $-\text{Ag}(\text{H}_2\text{O})-\text{Ag}-$ rim within the head-to-head metallo-ring and (2) $-\text{Ag}(\text{H}_2\text{O})-\text{Ag}-$ bridges between tail-to-tail junctions (Figure 4a) are in the orthogonal direction.

Figure 4. (a) Stacking of the $\text{AgClO}_4\text{-STC}$, where STC are mediated by $\text{Ag}-\text{O}-\text{Ag}$ and $\text{O}-\text{H}\cdots\text{O}$ interactions and accommodated with ClO_4^- anions. (b) Crystal packing showing the ClO_4^- anions both inside and on the outside of the $\text{AgClO}_4\text{-STC}$.

In both cases of Ag-STC , $\text{AgPF}_6\text{-STC}$ and $\text{AgClO}_4\text{-STC}$, there are additional silver cations coordinated to the primary sides. Nevertheless, these cations do not directly connect two adjacent STCs axially, thus do not form similar tail-to-tail connectivity as it had been typically found in STCs and is shown in RbF-STC . Interestingly, in the case of $\text{AgPF}_6\text{-STC}$ only one primary side is decorated by notional silver-ring forming notional silver monolayer between the STCs, while in

the case of AgClO₄-STC both sides are decorated ultimately forming silver-water bilayer in the crystal lattice (Figure S5, Supporting Information).

AgBF₄-L: In an attempt to prepare the silver STC with different anions we have obtained crystals of AgBF₄-L as a 1:1 complex (Figure 5a). In this case, Ag⁺ connect neighboring molecules of L into 2D sheets (Figure 5b). The Ag⁺ is chelated by the tetrahydropyran O atom and the O atom of a -CH₂OH group of one ligand L, further -CH₂OH group of another ligand L (Figure 5a), and three water molecules. It is interesting that the BF₄⁻ are nested within the tail of L, held in place by two O-H...O hydrogen bonds, one with a -CH₂OH group and another one with a water molecule bridging between the BF₄⁻ and another water molecule coordinated to the Ag⁺.

Figure 5. (a) Crystal structure of the 1:1 complex of L and AgBF₄ and (b) detail on the Ag⁺ cation coordination.

CONCLUSIONS

A novel, synthetically easily available ligand for metal coordination, hexakis(2,3-di-*O*-methyl)- α -cyclodextrin (L), was prepared by partial methylation of the parental α -cyclodextrin (CD). The methylation of the head of CD molecule was carried out to suppress the coordination of secondary hydroxyls towards hard Lewis acid metal ions, by which participation of the opposing primary hydroxyl rim in metal coordination could be initiated. Indeed, by this approach we have introduced a novel binding motif of CDs, where unprecedented tail-to-tail organization towards the alkali-metal ring was found in the crystal structure of homometallic dodecanuclear rubidium STC prepared in the reaction of L with RbF (RbF-STC). Yet, the methylated secondary rim is not fully suppressed towards the metal coordination. Use of soft Lewis acid, such as Ag⁺ under neutral conditions, leads to homometallic hexanuclear head-to-head silver STC prepared by the reaction of methoxy groups with AgPF₆ or AgClO₄ forming AgPF₆-STC or AgClO₄-STC, respectively. The STCs presented herein add on to a small library of homometallic species. The choice of metal counter-anion used for STC preparation has a significant impact on final structure and preordains

their possible applicability: i) while small, well-incorporated fluoride anions provide accessibility of pores in RbF-STC crystal structure, the bulky PF_6^- or ClO_4^- in AgPF_6 -STC or AgClO_4 -STC fill the channels which, in contrary, might prevent their further exploitation; ii) fully different crystal packing pattern was observed when Ag^+ counter-anion was exchanged from bulky $\text{PF}_6^-/\text{ClO}_4^-$ to a smaller BF_4^- . The STC was not formed, but, instead, a simple 1:1 metal:L complex has been characterized by single-crystal X-ray diffraction. This study is a pioneering work on use of methylated CDs as ligands for metal coordination, which can certainly provide new possibilities in discoveries of novel porous metal-organic structures derived from renewable natural building blocks.

ASSOCIATED CONTENT

Supporting Information

Synthesis of the ligand, crystallographic and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>

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ABBREVIATIONS

CD = cyclodextrin

STC = sandwich-type complex

DFT = density functional theory

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SAFETY NOTE

Perchlorate salts of metal complexes with organic ligands are potentially explosive. Perchlorate anion was substituted for hexafluorophosphate, nevertheless, this experiment did not lead to the same structure. Please be cautious and handle the perchlorate complexes as highly energetic, potentially hazardous materials and follow the information stated in their safety data sheets.

For Table of Contents Use Only

Heads or Tails? Sandwich-Type Metallocomplexes of Hexakis(2,3-di-*O*-methyl)- α -cyclodextrin

Ondřej Jurček, Rakesh Puttreddy, Filip Topić, Pia Jurček, Pezhman Zarabadi-Poor, Hendrik V. Schröder, Radek Marek, and Kari Rissanen

Methylation of the secondary face of α -cyclodextrin molecule (head) provides a ligand which can be steered by the choice of metal salts into intriguing homometallic sandwich-type complexes (STCs). The CD ligands in the complexes are organized either in head-to-head fashion towards the notional silver metallo-ring (AgPF_6 -STC), or in tail-to-tail mode towards rubidium fluoride ring (RbF -STC). Both STCs are organized into infinite channels, which in case of RbF -STC can lead to novel porous materials.

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