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Maxence Lion, Jérôme Marrot, William Shepard, Nathalie Leclerc, Mohamed Haouas, et al.. Cyclic Oxothiomolybdates: Building Blocks for Cyclodextrin-Based Open Frameworks. ChemPlusChem, 2024, 10.1002/cplu.202400475 . hal-04814351

HAL Id: hal-04814351

<https://hal.science/hal-04814351v1>

Submitted on 2 Dec 2024

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Cyclic Oxothiomolybdates as Chaotropic Scaffold of Cyclodextrin-based Open Framework

Maxence Lion,^[a] Jérôme Marrot,^[a] William Shepard,^[b] Nathalie Leclerc,^[a] Mohamed Haouas,^[a] Emmanuel Cadot^[a] and Clément Falaise*^[a]

[a] Dr. M. Lion, Dr. J. Marrot, Dr. N. Leclerc, Dr. M. Haouas, Prof. Dr. E. Cadot, Dr. C. Falaise
Institut Lavoisier de Versailles, CNRS, UVSQ, Université Paris-Saclay
45 avenue des Etats-Unis, 78035, Versailles (France)
E-mail: emmanuel.cadot@uvsq.fr, clement.falaise@uvsq.fr

[b] Dr. W. Sheppard
Synchrotron SOLEIL
L'orme des merisiers, départementale 129, 91190, Saint-Aubin (France)

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Abstract: Desolvation processes, though common in self-assembled biological structures, are rarely evidenced and utilized in the design of crystalline architectures. In this study, we introduce a novel approach using the $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{guest})]^{2-}$ complex, formed by the self-condensation of four $[\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2]^{2-}$ fragments around a guest unit ($\text{Mo}^{\text{VI}}\text{O}_6\text{H}_4$ or oxalate), as a chaotropic scaffold for crystallizing hybrid organic-inorganic systems with natural cyclodextrins. Our findings reveal that β -cyclodextrin (β -CD) facilitates the formation of various host-guest systems, while α -cyclodextrin (α -CD) induces the formation of a Kagome-type structure with significant voids. These new compounds were thoroughly characterized using X-ray diffraction (both powder and single-crystal), N_2 adsorption, elemental and thermogravimetric analysis. Additionally, solution studies using ^1H NMR titration and small-angle X-ray scattering (SAXS) carried out in liquid state demonstrated pre-association of the building units. These results enhance understanding of the design principles for supramolecular structures composed of inorganic polyanions and cyclodextrins.

Introduction

Natural cyclodextrins are macrocyclic oligosaccharides produced through enzymatic degradation of starch. They comprise six, seven, and eight α -1,4-linked D-glucopyranosyl units for α -, β - and γ -CD, respectively.^[1] These semiflexible hosts feature a hydrophobic cavity, making them ideal for designing host-guest complexes.^[2] In 2010, Stoddart and colleagues demonstrated that γ -CD could serve as a versatile organic building block for constructing hybrid crystalline open frameworks.^[3] These frameworks, known as CD-MOFs (cyclodextrin Metal-Organic Frameworks), are formed by the self-assembly of γ -CD with large alkali metal ions.^[4] The appeal of CD-MOFs extends beyond the beauty of their structural arrangements because they hold significant promises for practical applications, including drug delivery, catalysis, and the separation and purification of liquids and gases, as well as CO_2 capture.^[5-7] The field of CD-based frameworks has seen substantial growth however most of the reported structures exhibit compact hybrid structures with limited void space.^[5]

Water-mediated interactions are crucial in biological systems, playing significant roles in processes such as protein folding, protein-ligand interactions or protein self-assembly.^[8,9] In contrast, water-mediated effects like hydrophobic or chaotropic effects are rarely exploited in the crystal engineering of open frameworks while they can act as predominant contributors within supramolecular recognition processes occurring in aqueous solution. In such context, our group has recently demonstrated that the Anderson-Evans type polyoxometalate $[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ (see Figure 1 A) can specifically interact with the outer walls of cyclodextrins.^[10] This supramolecular interaction has led to the creation of the first open frameworks constructed from α - and β -CDs. The primary driving force behind the formation of these hybrid assemblies lies in the expelling of water molecules in the close vicinity of the inorganic disk-shaped polyanions. The resulting desolvation process known as the chaotropic effect,^[11] presents an appealing strategy for the assembly motif of highly diverse types of supramolecular systems, spanning discrete inclusion complexes and soft matter extended systems resulting from non-covalent associations of non-ionic organic substances, such as surfactants and macrocycles, with chaotropic polyanions, including metal atom clusters, polyoxometalates, or *closo*-borates.^[12-20] For instance, several reports showed that the binding of γ -CD with chaotropic entities leads to robust host-guest complexes in water featuring exceptionally high binding constants (up to 10^6 M^{-1}).^[21]

In the frame of our first report^[10] on CD-POMOFs using Anderson-Evans type polyoxometalate and CDs, we hypothesized that other types of disk-shaped polyanions can be suitable as inorganic scaffolds to enrich the structural diversity of this class of materials. In context, cyclic oxothiomolybdate compounds are an interesting class of inorganic rings because of i) their low charge density in relation with the presence of sulfido groups as soft ligands making them chaotropic entities, ii) their remarkable structural and chemical composition diversity, and iii) their electrocatalytic properties.^[22-25]

Herein, we report that the α and β -CD can self-assemble with two cyclic oxothiomolybdates $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{guest})]^{2-}$ which result from the self-condensation of four $[\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2]^{2+}$ around $\{\text{Mo}^{\text{VI}}\text{O}_6\text{H}_4\}$ or C_2O_4 (see Figure 1 B-E). The supramolecular organizations in the solid-state have been determined from single

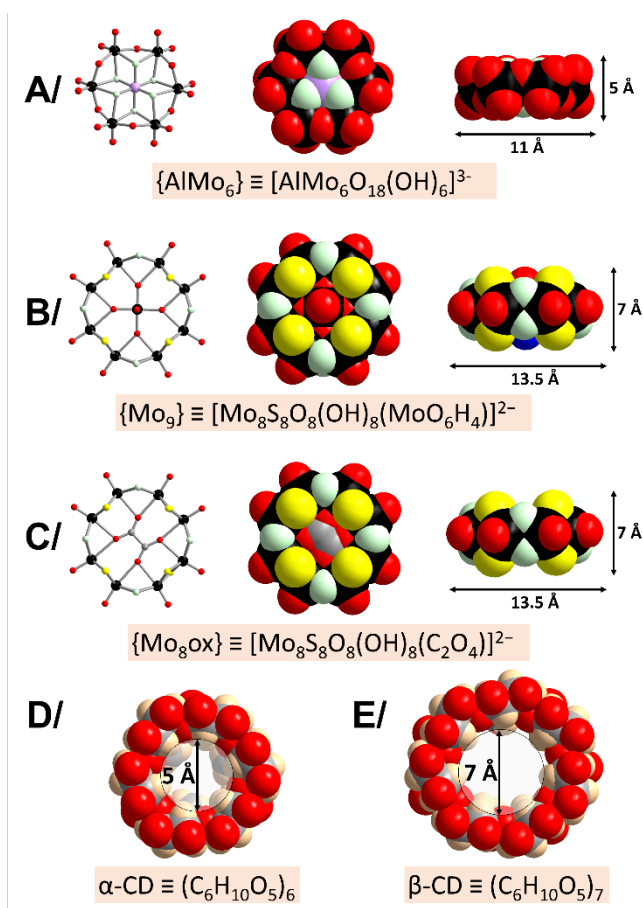


Figure 1. Structural representation of the molecular components used as building blocks. A/ Representation of the Anderson-Evans type polyoxometalate previously used to achieve open CD-based frameworks. B and C/ Representation of the thiooxomolybdate rings built from condensation of four $\{Mo^V_2O_2S_2\}$ units around an hexavalent Mo center ($Mo^VI O_6H_4$) or an oxalate ligand. D/ and E/ Space-filling representation of the native cyclodextrins α - and β -CD. These cyclic polysaccharides are composed of 6 or 7 α -1,4-linked D-glucopyranosyl residues. Color code: black sphere: Mo center; red sphere: oxygen atom; grey sphere: carbon atom; tan sphere: hydrogen atom; light green sphere: hydroxo group of polynuclear entities; blue sphere: aquo group of polynuclear entities.

crystal X-ray analysis, evidencing the formation of 1:1 host-guest complexes with the β -CD while the assembly between oxothiomolybdates and α -CD leads to extended CD-MOFs with Kagome lattice. The resulting compounds have been characterized by X-ray powder diffraction, infrared spectroscopy, elemental analysis, and TGA. Finally, solution studies of reaction solution by 1H NMR and small angle X-ray scattering suggest the existence of pre-associations in solution. This set of results complement nicely our previous report demonstrating disk-shaped polynuclear entities can be used as inorganic scaffolds to enrich the structural diversity of CD-based open frameworks. Furthermore, these overall results highlight also the structural key role of hydroxo groups of polynuclear entities.

Results and Discussion

Synthesis of Supramolecular Hybrid Compounds

Supramolecular compounds formed from oxothiomolybdate rings and α -CD have been successfully isolated through the slow evaporation of aqueous solutions containing α -CD and potassium salts of $[Mo_8S_8O_8(OH)_8(\text{guest})]^{2-}$, where the guest molecule is either octahedral $\{MoO_6H_4\}$ or $\{C_2O_4\}$ oxalate. These crystalline compounds, labeled as $\{Mo_9\}\{\alpha\text{-CD}\}_2$ and $\{Mo_8ox\}\{\alpha\text{-CD}\}_2$, were obtained with a moderate yield ($\sim 40\%$) when the solution had a α -CD to oxothiomolybdate ratio greater than 1.5. Using a lower amount of α -CD (for example, 1 equivalent of α -CD per oxothiomolybdate) resulted in the recrystallization of the inorganic precursors rather than the desired supramolecular structures. Interestingly, we observed that the type of counter-cation significantly influenced the formation of these compounds. Smaller alkali cations (Li^+ and Na^+) did not produce isostructural compounds, unlike the larger alkali cations such as Rb^+ and Cs^+ . This finding suggests that the size of the cation plays a crucial structural role in the aggregation process. This phenomenon parallels the observations of Stoddart and co-workers, who were able to crystallize porous CD-MOFs only in the presence of larger alkali cations.[ref]

Employing similar synthetic approach with β -CD leads to co-crystallization of various compounds. Single crystal X-ray diffraction analysis revealed that the resulting solid product was a mixture of colorless oxothiomolybdate-free β -CD crystals and yellowish crystals of hybrid 1:1 host-guest complexes, namely $\{Mo_9\}@ \beta\text{-CD}$ and $\{Mo_8ox\}@ \beta\text{-CD}$. However, pure 1:1 host-guest complexes can be easily obtained through ethanol vapor diffusion, enabling efficient isolation of the desired compounds. In fact, this approach aligns with previous strategies used to isolate pure phases of host-guest complexes constructed from rhenium clusters and β -CD.

X-ray structural description

$\{Mo_9\}\{\alpha\text{-CD}\}_2$ and $\{Mo_8ox\}\{\alpha\text{-CD}\}_2$. Single-crystal X-ray diffraction analysis showed that both compounds $\{Mo_9\}\{\alpha\text{-CD}\}_2$ and $\{Mo_8ox\}\{\alpha\text{-CD}\}_2$ as potassium salt are isostructural, crystallizing in the non-centrosymmetric space group $P3$. These structures are composed of infinite inorganic chains of oxothiomolybdate rings interconnected by α -CDs. The structural model of $\{Mo_9\}\{\alpha\text{-CD}\}_2$ reveals that the equatorial planes of the α -CDs are aligned parallel to the c axis (Figure 2A). Then, the oxothiomolybdate rings form continuous chains along the c axis with intramolecular parameters consistent with those typically observed in similar compounds.^[26] Potassium cations bridge these rings by interacting with their terminal oxo groups (Figure 2B). Within these one-dimensional chains, the distance between the centers of two crystallographically equivalent oxothiomolybdate rings is approximately 14.2 Å, which corresponds to the c parameter of the unit cell. The supramolecular organization of these frameworks results in a Kagome topology, characterized by large hexagonal rings each surrounded by six smaller triangular rings (Figure 2A). The Kagome structure is well-known in purely inorganic compounds, such as bronze structures, and metal-organic frameworks. In $\{Mo_9\}\{\alpha\text{-CD}\}_2$ and $\{Mo_8ox\}\{\alpha\text{-CD}\}_2$, this arrangement creates two distinct types of channels. The openings of the triangular rings

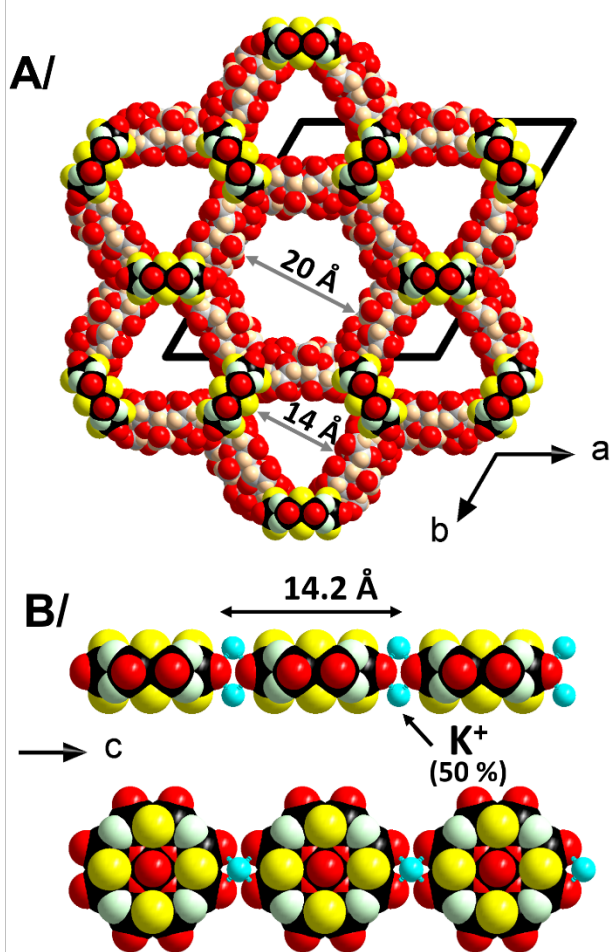
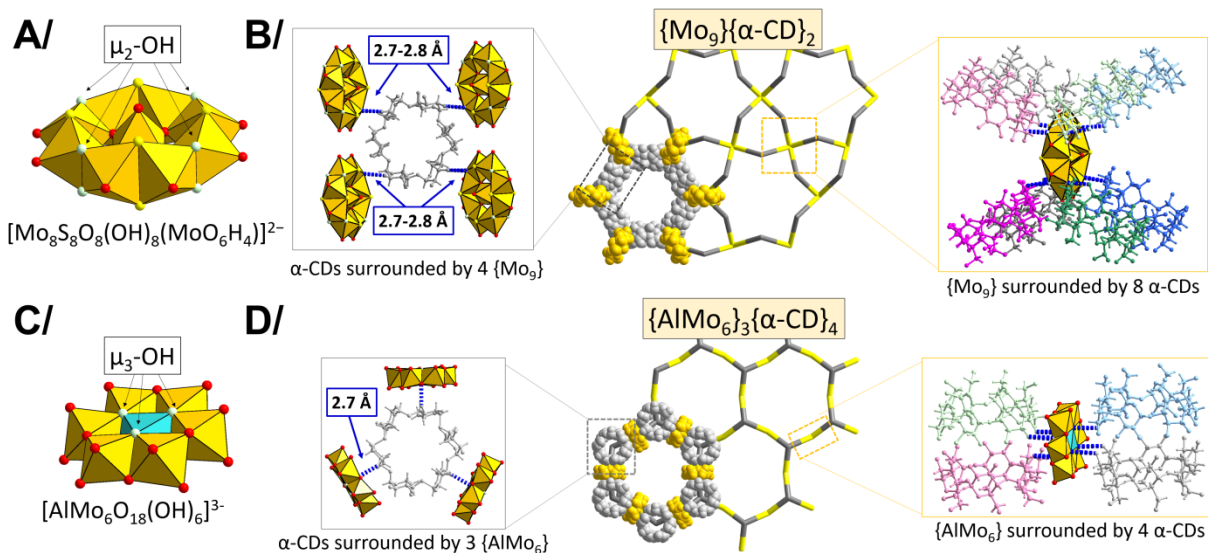


Figure 2. X-ray structural analysis of the supramolecular arrangement of the 1D chain built from oxoanions (occupancy: 50%) and K⁺ cations.



have an estimated diameter of about 14 Å, while the hexagonal rings measure approximately 20 Å in diameter.

In these hybrid frameworks, the secondary face of each $\alpha\text{-CD}$ is oriented towards the triangular tunnels, while the primary face is directed towards the hexagonal channels. This dual orientation contributes to the unique spatial arrangement and stability of the structure.

The structural cohesion of the hybrid frameworks $\{\text{Mo}_9\}\{\alpha\text{-CD}\}_2$ and $\{\text{Mo}_9\text{ox}\}\{\alpha\text{-CD}\}_2$ is primarily maintained by a network of

supramolecular interactions, with hydrogen bonds playing a dominant role. These hydrogen bonds govern the three-dimensional organization of the building blocks in the solid state. Specifically, each oxothiomybdate ring forms hydrogen bonds with eight adjacent $\alpha\text{-CDs}$. These weak interactions involve the bridging hydroxo groups on the inorganic rings and the hydroxo groups on the secondary face of the $\alpha\text{-CDs}$. Simultaneously, each $\alpha\text{-CD}$ engages with four oxothiomybdate rings through hydrogen bonds ($\text{O}\cdots\text{O}$ distances range from 2.7 to 2.8 Å, Figure 3 A-B). Additionally, $\alpha\text{-CDs}$ interact also with each other in multiple ways, further reinforcing the framework's stability. Each $\alpha\text{-CD}$ bonds to two others through four hydrogen bonds involving the hydroxo groups on the larger rim, which strengthens the supramolecular cohesion along the c axis. Moreover, in the (ab) plane, each $\alpha\text{-CD}$ forms a network of hydrogen bonds through its primary face, connecting to two other $\alpha\text{-CDs}$.

RESEARCH ARTICLE

Elemental analysis and thermogravimetric analysis of samples from three different batches consistently show approximately 2.7 α -CDs per oxothiomolybdate unit, despite the X-ray model indicating only two α -CDs per inorganic polyanion. This discrepancy suggests that approximately 0.7 α -CDs per oxothiomolybdate unit reside in the large voids of the structural model. This result indicates that 0.7 α -CD per oxothiomolybdate unit is probably disordered in the large voids of the structural model. The presence of these free cyclodextrins in the cavities may contribute to the framework's stability. For instance, 150°C heating the powder for two hours does not alter the powder X-ray diffraction pattern that aligns well with the calculated Bragg peaks. This result suggests that presence of the additional α -CDs in the voids could contribute to the remarkable stability by preventing the collapse of the supramolecular framework after the departure of crystallization water molecules. However, despite of crystalline structure stability, porosimetry study by nitrogen adsorption did not indicate any significant specific surface area, and various attempts to activate the porous framework using supercritical CO₂ were also unsuccessful.

Interestingly, we observed that using Rb⁺ or Cs⁺ as counter-cations gives structural analogues of K₂{Mo₉}{ α -CD}₂. Single crystal diffraction analysis revealed that the overall structural features remain largely unchanged, as indicated by the unit cell parameters (see supporting information). This behavior contrasts with findings of Khashab and colleagues, who noted that size of alkali cations influence significantly the structural characteristics of supramolecular solids composed of Strandberg-type polyoxomolybdate [P₂Mo₅O₂₃]⁶⁻ and α -CD.^[27] Such a difference in cation size sensitivity likely arises from the crucial role that hydrogen bonds play in determining the topology of hybrid frameworks resulting from recognition processes between inorganic rings [Mo₈S₈O₈(OH)₈(guest)]²⁻ and α -CDs. Interestingly, while both the oxothiomolybdate wheels

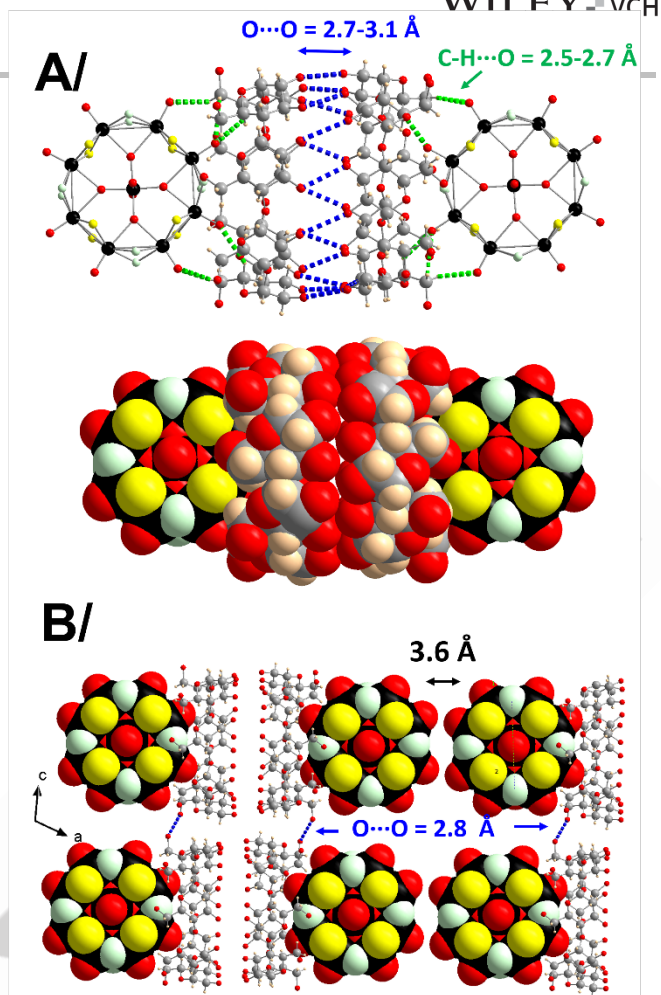


Figure 4. X-ray structural model of {Mo₉}@ β -CD. A/ View of the oxothiomolybdate partially embedded within a β -CD exposing its primary face. The secondary face of this 1:1 complex interacts with another inclusion complex to form a supramolecular 2:2 assembly. B/ View of the bamboo-like arrangement of the 2:2 assemblies forming a layer within the (ac) plane.

Figure 3. Comparison the X-ray structural model of {Mo₉}{ α -CD}₂ with the previously published open framework {AlMo₆}₃{ α -CD}₄ built from the association of α -CD and the Anderson-Evans type polyoxometalate [AlMo₆O₁₈(OH)₆]³⁻. A and C/ View of inorganic polyanions highlighting the location of their hydroxo groups. B and D/ View of the topology of the supramolecular frameworks and highlights on the interactions between the α -CD and the polyanion (the hydrogen bonds are represented in blue dotted lines).

[Mo₈S₈O₈(OH)₈(guest)]²⁻ and [AlMo₆O₁₈(OH)₆]³⁻ share similar size

and shape, their association with α -CDs results in different supramolecular frameworks in the solid-state. In these networks, the packing is primarily governed by hydrogen bonds involving the OH groups of the inorganic entities and those of the secondary face of the macrocyclic sugar. For $[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$, the six hydroxo groups are centrally located and oriented perpendicularly to the equatorial plane of the disk-shaped anion. This allows the polyanion to act as a linear ditopic linker, connecting α -CDs in a head-to-head fashion and maximizing inter-CD hydrogen bonding (see Figure 3 C-D). This generates a honeycomb-like framework where each α -CD is decorated with three polyanions. In contrast, the structural organization of $\{\text{Mo}_9\}\{\alpha\text{-CD}\}_2$ or $\{\text{Mo}_8\text{ox}\}\{\alpha\text{-CD}\}_2$ is significantly different. The eight hydroxo groups on the periphery of $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{guest})]^{2-}$ facilitate interactions with eight α -CDs through the sides of the oxothiomolybdate unit. This results in a dihedral angle of approximately 60° between the plane of the α -CD and the equatorial plane of the inorganic ring (Figure 3 B), while the dihedral angle is about 90° in the case of the compound involving the $[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ anion. This comparison highlights the critical influence of the spatial distribution of the hydroxo groups contributed by the inorganic components in shaping the topology of hydrogen-bonded hybrid frameworks.

$\{\text{Mo}_9\}@ \beta\text{-CD}$ and $\{\text{Mo}_8\text{ox}\}@ \beta\text{-CD}$. The single-crystal X-ray diffraction analysis revealed that the compounds $\{\text{Mo}_9\}@ \beta\text{-CD}$ and $\{\text{Mo}_8\text{ox}\}@ \beta\text{-CD}$ are isostructural and crystallize in the monoclinic space group C2. Each structure features a single crystallographically independent oxothiomolybdate $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{guest})]^{2-}$ partially encapsulated within a β -CD. In this 1:1 host-guest assembly, the primary face of the β -CD interacts closely with the inorganic guest, a phenomenon also observed in previous studies involving β -CD with Keggin-type phosphomolybdates or octahedral rhenium clusters.^[28,29] The dihedral angle between the equatorial plane of the β -CD and those of the oxothiomolybdate is approximately 90° , as shown in Figure 4. This interaction is characterized by short contacts between the terminal oxo groups of the oxothiomolybdate and the H6 and H5 protons of the β -CD, with an average $\text{O}\cdots\text{H}-\text{C}$ distance of about 2.6 Å. The remaining secondary face of this 1:1 complex $\{[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{guest})]@ \beta\text{-CD}\}^{2-}$ engages in a network of 16 hydrogen bonds ($\text{O}\cdots\text{O}$ distances ranging from 2.7 to 3.2 Å) with the secondary face of the neighboring 1:1 inclusion complex, thus featuring a striking supramolecular 2:2 assembly. The shortest distance between the oxothiomolybdate units from two different 2:2 assemblies is approximately 3.6 Å. This discrete bamboo-like arrangement of the 2:2 assemblies forms a layer within the (*ac*) plane, stabilized by hydrogen bonds involving the hydroxo groups of the primary rings ($\text{O}\cdots\text{O}$ distances of about 2.8 Å). These layers are further organized through hydrogen bonding interactions, stacking along the *b* axis with a relative shift of $(a+c)/2$ between adjacent layers, ensuring structural cohesion. Furthermore, potassium ions contribute significantly to the three-dimensional stability of the framework, spanning the β -CDs and oxo groups of the oxothiomolybdate.

Pre-association of $\{\text{Mo}_9\}$ and cyclodextrins in solution

To get more insights into the supramolecular behavior of oxothiomolybdate in the presence of α - or β -CD, solution studies of aqueous mixtures were performed using a set of complementary techniques including ^1H NMR spectroscopy and using small angle X-ray scattering (SAXS). We report herein exclusively the result obtained using the anion $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{MoO}_6\text{H}_4)]^{2-}$.

^1H NMR investigation. The interaction between the lithium salt of $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{MoO}_6\text{H}_4)]^{2-}$ and α - and β -CD was investigated using ^1H NMR titrations with up to 8 equivalents of oxothiomolybdate per cyclodextrin (Figure 6). The lithium salt was specifically employed to prevent precipitation during the experiments. These NMR titrations demonstrate gradual changes in the ^1H resonances as a function of the oxothiomolybdate/CD ratio, indicating the presence of labile host-guest associations that exhibit fast exchange on the NMR time scale. The NMR changes feature interactions that reflects specific behaviors influenced by the host-guest size matching.

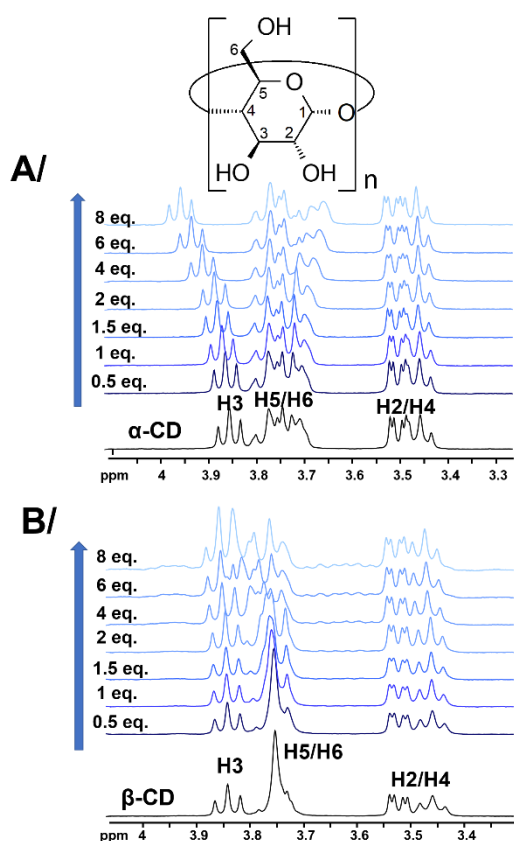


Figure 6. A/ ^1H NMR spectra resulting of the titration of 2 mM aqueous solution of $\alpha\text{-CD}$ by $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{MoO}_6\text{H}_4)]^{2-}$ anion. B/ ^1H NMR spectra resulting of the titration of 3 mM aqueous solution of $\beta\text{-CD}$ by $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{MoO}_6\text{H}_4)]^{2-}$ anion.

As the ratio $\{\text{Mo}_9\}/\alpha\text{-CD}$ increase, the inner protons of $\alpha\text{-CD}$ (H3, H5, and H6) showed progressive signal variations (see Figure 6A). The proton H3 undergoes the most significant downfield shift, while opposite variations were observed for protons H5 and H6. These results suggest that the oxothiomybdate anion interacts with $\alpha\text{-CD}$ in aqueous solution, although the interaction does not appear to be specific to either rim of the $\alpha\text{-CD}$.

In the ^1H NMR spectra of $\beta\text{-CD}$ (Figure 6B), the H6 proton signal is downfield shifted by approximately 0.1 ppm in the presence of 8 equivalents of oxothiomybdate anions. The other proton signals remain unaffected by the addition of the inorganic polyanions. This observation suggests that the oxothiomybdate anion interacts specifically with the primary face of the $\beta\text{-CD}$ torus in solution. This binding mode is further corroborated by the single-crystal X-ray diffraction analysis of the $\{\text{Mo}_9\}@-\beta\text{-CD}$ complex, which reveals a similar interaction in the solid state.

SAXS investigations. SAXS is an effective method for detecting chaotropically-driven aggregation involving nanoions in aqueous solution.^[15,30] We investigated whether $\alpha\text{-CD}$ can aggregate with oxothiomybdates in solution to give assembly reminiscent to those observed in the X-ray diffraction structure of $\{\text{Mo}_9\}(\alpha\text{-CD})_2$, where one $\alpha\text{-CD}$ molecule is surrounded by four oxothiomybdate ions. To explore this, we conducted a SAXS titration experiment using a fixed concentration of $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{MoO}_6\text{H}_4)]^{2-}$ (as Li^+ salt; 20 mM) and varying

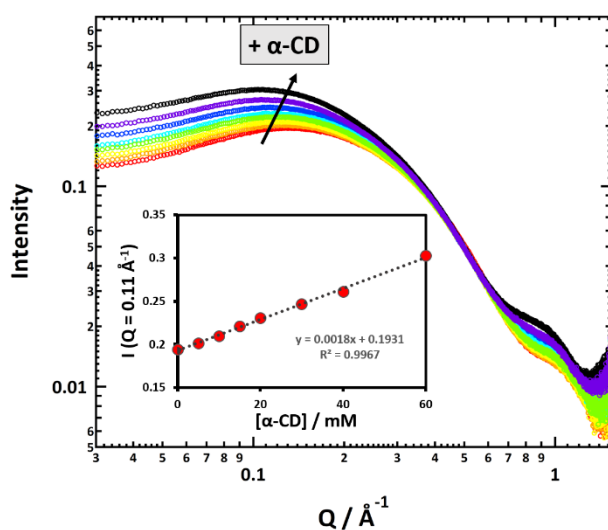


Figure 7. SAXS curves resulting from the titration of 20 mM aqueous solution of $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{MoO}_6\text{H}_4)]^{2-}$ anion with $\alpha\text{-CD}$ (from 0 to 3 eq.). Inset: Plot showing that the evolution of the scattering intensity measured at $Q = 0.11 \text{ \AA}^{-1}$ varies linearly with the concentration of the $\alpha\text{-CD}$ in solution.

concentrations of $\alpha\text{-CD}$ (ranging from 0.25 to 3 equivalents). The results of this SAXS titration are presented in Figure 7.

Firstly, the SAXS curves in the Guinier region show that the overall shape remains unchanged upon the addition of $\alpha\text{-CD}$, indicating that no significant changes in particle size or shape occur upon the titration. Secondly, the scattering intensity increases linearly with the concentration of $\alpha\text{-CD}$. This linear increase suggests that the SAXS curves of the mixtures represent a linear combination of the individual SAXS profiles of the oxothiomybdate ions and $\alpha\text{-CD}$. From these observations, we conclude that the presence of $\alpha\text{-CD}$ does not lead to substantial aggregation of oxothiomybdate ions around the $\alpha\text{-CD}$ molecules in solution.

Conclusion

In the solid state, the supramolecular association of the discoidal oxothiomybdate anions $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{guest})]^{2-}$ with native cyclodextrins leads to hybrid frameworks whose structures vary distinctly based on the size of the organic macrocycles. The use of the smallest cyclodextrin, $\alpha\text{-CD}$, results in unprecedented CD-based frameworks featuring a Kagome lattice that defines large open channels with windows larger than 1.4 nm. Structural analysis reveals that the packing of these building blocks is predominantly controlled by the hydroxo groups of the inorganic polyanions. In contrast, using the larger $\beta\text{-CD}$ allows the isolation of 1:1 host-guest complexes where the inorganic entities interact through their primary faces. This type of recognition was also observed in solutions through NMR investigations. While solution studies indicate that $\alpha\text{-CD}$ interacts with oxothiomybdate, no specific recognition process occurs, unlike with $\beta\text{-CD}$.

These results demonstrate that low-charged oxothiomybdates can interact with non-ionic entities in solution and self-assemble into highly ordered structures in the solid state. Such behavior suggests that the wide diversity of cyclic oxothiomybdate compounds must be considered as chaotropic agents, capable of

constructing a wide variety of supramolecular frameworks or scaffolds, including hierarchical and compartmentalized CD-based frameworks.

Supporting Information

Materials and methods, synthetic procedures, detailed structural descriptions, elemental analyses, infrared spectra, TGA, powder X-ray diffraction patterns under different conditions, and NMR investigations in solution. **The authors have cited additional references within the Supporting Information.**^[30, 31]

Acknowledgments

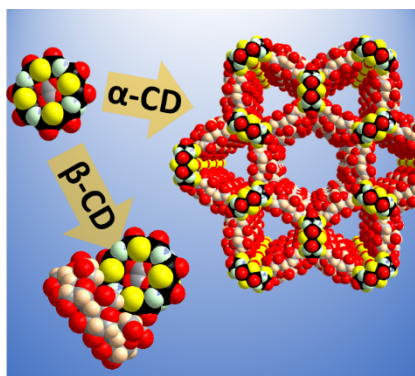
We acknowledge SOLEIL Synchrotron for providing access to beamtime and synchrotron radiation facilities on the PROXIMA-2 and SWING beamline for the single-crystal X-ray diffraction experiments and small-angle X-ray scattering measurements. The authors gratefully acknowledge the CNRS-MOMENTUM program and ANR-PRCI CHAOPOM (grant ANR-22-CE92-0043). This work was also supported by (i) the University of Versailles Saint Quentin, (ii) CNRS, and (iii) Region Ile de France through DIM MaTerRE. Maxence Lion acknowledges Université Paris-Saclay for his PhD grant support.

Keywords: Chaotropic effect • Cyclodextrin • Polyanion • X-ray structure • hybrid framework

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The recognition properties between cyclic oxothiomybdates and cyclodextrin to produce a noteworthy supramolecular organic-inorganic assemblies. This highlight that chaotropic polyanions are promising inorganic building units to construct hybrid architectures with large cavities.

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