Supramolecular Adduct of γ-Cyclodextrin and [Re6Q8(H2O)6]2+ (Q=S, Se)

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Abstract: Slow evaporation of water solution of $[\{Re_6S_8\}(H_2O)_6]^{2+}$ generated *in situ* from $[\{Re_6S_8\}(OH)_6]^{4-}$ in presence of γ-cyclodextrin (CD) leads to crystallization of $\{[\{Re_6S_8\}(H_2O)_6\subset[\gamma\text{-CD}]\}(NO_3)_2 \cdot 12H_2O$ ($1\cdot12H_2O$) supramolecular complex, which was characterized by single-crystal X-ray diffraction crystallography, IR-spectroscopy, thermogravimetric and elemental analyses. X-ray analysis confirms the formation of 1:1 $\{[\{Re_6S_8\}(H_2O)_6]\subset[\gamma\text{-CD}]\}^{2+}$ inclusion compound in the solid state. However, no adduct formation was detected between $[\{Re_6S_8\}(H_2O)_6]^{2+}$ and γ-cyclodextrin in solution, according to ^1H NMR spectroscopy. In the case of *in situ* generated $[\{Re_6Se_8\}(H_2O)_6]^{2+}$ the reaction solution with γ-cyclodextrin is unstable and during the crystallization only amorphous precipitate has been obtained.

Introduction

Metal cluster complexes with general formula $[\{M_6Q_8\}L_6]^n$ (M = Re, Q = S, Se, Te; M = Mo or W, Q = Cl, Br, I; L = organic or inorganic ligands) belong to one of the most general cluster archetypes based on an octahedral metal cluster core with M–M bonding capped with eight μ_3-bridged halide or chalcogenide ligands . Figure 1 (left) shows a representative structure of such cluster.. The main feature of electron precise clusters of this type (24 cluster skeleton electrons) formed by Mo, W and Re is luminescence, which is currently widely explored by different research groups with multiple prospects for practical use.ref
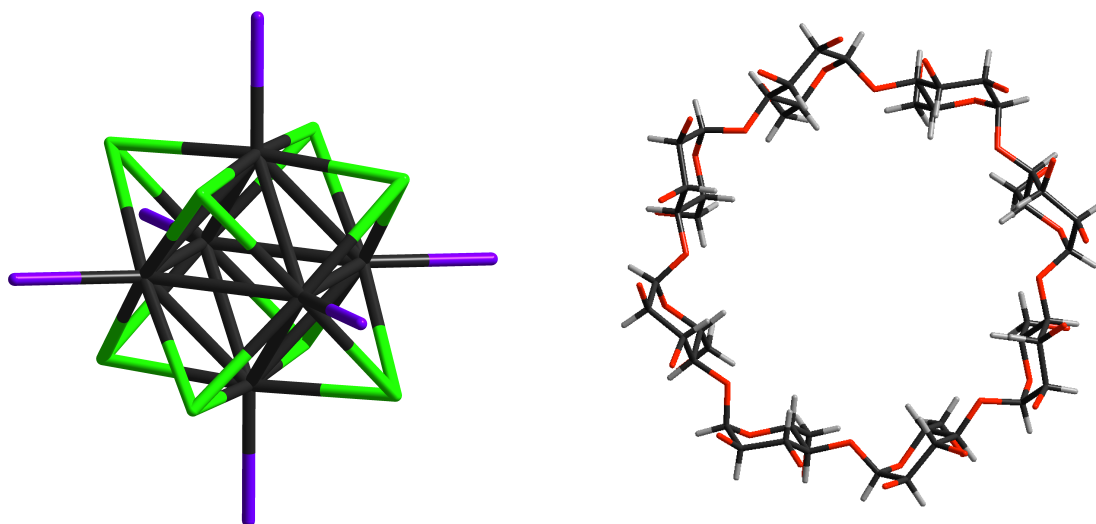

Fig. 1. Structure of octahedral rhenium cluster of type $[\{Re_6Q_8\}L_6]^n$ (left) and γ-cyclodextrin (right).

Octahedral rhenium cluster complexes exhibit luminescence in NIRregion under UV irradiation that can be used for biomedical applications. Moreover, high local concentration of heavy Re atoms in the $\{Re_6Q_8\}^{2+}$ cluster core can be used for design of novel iodine-free X-ray contrast agents. However, these cluster complexes are often insoluble in water at physiological pH (~7.4). To obviate this handicap, a number of strategies aimed at obtaining stable water-soluble clusters with functionalized organic ligands or disperse materials based on them have been proposed. On the other hand, cyclodextrins (CDs) are water-soluble cyclic oligosaccharides made of 6 (α), 7 (β) or 8 (γ) glucopyranose units, which exhibit a hydrophobic internal cavity capable to host a large variety of compounds of appropriate size and

shape. These macrocyclic cavitands can encapsulate active drugs, solubilize poorly soluble compounds, and limit the toxicity of some agents. Thus, a combination of the octahedral Re clusters and CDs can result in a new class of materials for biomedical applications. At first sight, comparison of the cluster size and the size of CDs internal cavity (0.56, 0.70, 0.88 nm respectively for α, β and γ-cyclodextrins) leaves a possibility to form an inclusion compound only with γ-cyclodextrin. Consequently, we have started our research with a study of the interaction between $[\{Re_6S_8\}(H_2O)_6]^{2+}$ and γ-cyclodextrin (Fig. 1, right). In this contribution, we report synthesis and crystal structure of a new inclusion complex $\{[\{Re_6Q_8\}(H_2O)_6]\subset[\gamma\text{-}CD]\}^{2+}$ and its characterization in aqueous solution.

Experiments

The starting material $K_4[\{Re_6S_8\}(OH)_6]\cdot8H_2O$ was prepared according to the literature(REF?). All other reagents were of commercial quality and used as purchased (Sigma Aldrich). IR spectra (4000 – 400 cm^{-1}) were recorded on a Vertex 80 spectrometer. TG experiments were run on a NETZSCH TG 209 F1 device in an Al_2O_3 crucible by heating a sample from 22 to 300°C with 10°C gradient. Energy-dispersive X-ray spectroscopy (EDS) was performed on a Hitachi TM3000 TableTop SEM with Bruker QUANTAX 70 EDS equipment. ^{1}H NMR solution spectra were recorded using 5 mm o.d. tubes with a Bruker Avance 400 MHz spectrometer equipped with a BBI probehead and operated at a magnetic field strength of 9.4 T. D_2O was used as the solvent. Translational diffusion measurements were performed using Bruker's "ledbpgs2s" stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform stabilized by maximum entropy.[25]

Synthesis of $\{[\{Re_6S_8\}(H_2O)_6]\subset[\gamma\text{-}CD]\}(NO_3)_2\cdot12H_2O$ ($1\cdot12H_2O$):

0.485 g (0.27 mmol) of $K_4[\{Re_6S_8\}(OH)_6]\cdot8H_2O$ was dissolved in 20 mL of water, after that 0.5 M HNO_3 was added dropwise under stirring until pH reached 1.5 producing a clear yellow solution. 0.704 g (0.54 mmol) of solid γ-CD was added directly to this solution under stirring. After dissolution of the macrocyclic cavitand the reaction mixture was allowed to slowly evaporate in air to leave a very small volume of a concentrated solution. A crop of yellow crystals was collected by filtration from the very small amount of remaining mother liquor and air dried. Crystals typically contained KNO_3, and were twice recrystallized from water. Yield 50% based on rhenium cluster. Anal. Calcd for $C_{48}H_{116}N_2O_{64}Re_6S_8$: C, 18.5; H, 3.7; N, 0.9; S, 8.2. Found: C, 18.5; H, 3.6; N, 0.9; S, 8.2. IR (KBr, cm^{-1}): ν = 3366 (s), 2926 (s), 2088 (s), 1637 (m), 1383 (m), 1161 (m), 1080 (m), 1053 (m), 1022 (s), 1001 (m), 937 (w), 864 (w), 844 (w), 762 (w), 702 (w), 584 (w), 530 (w), 476 (w), 436 (w), 413 (w). EDS shows Re : S ratio = 6.0 : 7.9 and confirms the absence of K. TGA: weight loss 9.0% between 50 – 150 °C (–12 H_2O); theoretical weight loss: 8.9 %.

Single crystal X-ray diffraction:

The crystal structure of $1\cdot12H_2O$ was determined by X-ray analysis on an Xcalibur (Agilent Technologies) single crystals diffractometer at 130 K, using graphite-monochromated Mo (λ = 0.71073 Å) radiation. The reflections intensities were measured by doing φ-scanning of narrow (0.5º) frames. Empirical absorption correction was applied with SCALE3 ABSPACK program (CrysAlisPro, Agilent Technologies, Version 1.171.37.35). The structure was solved by direct method and refined with full-matrix least-squares treatment anisotropically for non-hydrogen atoms in SHELX 2014/7 using ShelXle program. The structure was solved in $I4$ space group with Flack parameter 0.013(10), but there are no chiral molecules in the complex composition. Solution of the structure in $I4/m$ gives a well-defined cluster cation and disordered γ-CD molecule, with R c.a. 15%. The nitrate anions could not be located from experimental data and were included without refinement. The final formulation of the complex is based on analytical methods and TGA as $\{[\{Re_6S_8\}(H_2O)_6]\subset[\gamma\text{-}CD]\}(NO_3)_2\cdot12H_2O$ vs $\{[\{Re_6S_8\}(H_2O)_6]\subset[\gamma\text{-}CD]\}\cdot12H_2O$ found from XRD.

The hydrogen atoms of water molecules were not localized, while hydrogen atoms of γ-CD molecules were refined in their geometrically calculated positions. Crystal data and refinement details are summarized in Table S1, and main bond distances are listed in Table S2. Further structural information can be found in cif file deposited in CCDC with code....

Results and discussion

This work deals with water soluble rhenium cluster complexes with hydroxo or aqua ligands. $[\{Re_6S_8\}(OH)_6]^{4-}$ exists only in basic media (pH > 8), while $[\{Re_6S_8\}(H_2O)_6]^{2+}$ is stable only in acidic media (pH < 5). At pH ≈ 7, the cluster

however precipitates as $[\{Re_6S_8\}(H_2O)_4(OH)_2]\cdot12H_2O$. Thus search for a Re_6 cluster soluble in water at physiological pH is an important task. We have tried to extend the solubility window of the $[\{Re_6S_8\}(H_2O)_x(OH)_{6-x}]^{(x-4)+}$ species by encapsulation into γ-CD. We have found that reaction of cationic $[\{Re_6S_8\}(H_2O)_6]^{2+}$ cluster at pH 1.4 with γ-CD (pH value was dropped down by 2 M HNO_3) leads to crystallization of 1:1 supramolecular adduct of the composition $\{[\{Re_6S_8\}(H_2O)_6]\subset[\gamma\text{-CD}]\}(NO_3)_2\cdot12H_2O$ (**1**·12H_2O). Typically, it crystallizes together with KNO_3 and must be recrystallized from a small amount of hot water. Yellow-orange prisms of **1**·12H_2O were characterized by XRD. The crystal structure is built from supramolecular aggregates of $\{[\{Re_6S_8\}(H_2O)_6]\subset[\gamma\text{-CD}]\}^{2+}$ (Fig. 2) and water molecules, which fill the free space between the main structural units. The supramolecular unit consists of the octahedral rhenium cluster $[\{Re_6S_8\}(H_2O)_6]^{2+}$ and γ-CD building blocks, which combine together by host-guest interactions without any specific bonding. The closest distance for hydrogen bonding between the cluster-coordinated H_2O molecules positioned in the embedded faces, and OH groups of γ-CD is as large as 3.24 Å. This interaction is a kind of size-specific chemical recognition when the host molecule is γ-CD and the guest entity is the rhenium cluster. The "diameter" of rhenium complex (taken as the distance between a pair of oxygen atoms present on the same central axis) is about 8 Å, which fits to the internal diameter of γ-CD, 8.8 Å. Table 1 summarizes main interatomic bond distances in the rhenium cluster in **1**·12H_2O and in related clusters. As can be seen, incorporation of the cluster into the host cavity does not lead to any compression of the cluster dimensions. Comparison of the Re–O distances in this series of clusters indicates the presence of six coordinated water molecules in **1**. Possibly, the presence of more hydrogen atoms on the ligands (i.e., going from OH^- to H_2O) makes better fitting between the cluster guest and γ-CD host. Moreover, the unique coordinated water molecule located inside the cavity (in the center of the CD) forms strong hydrogen bonds (O…O 2.57 Å) with four disordered water molecules included in the remaining part of the cavity. Hence, the formula of the supramolecular unit is to be written as $\{[[\{Re_6S_8\}(H_2O)_6](H_2O)_4]\subset[\gamma\text{-CD}]\}^{2+}$. Furthermore, the four coordinated water molecules in close distance to the CD periphery form hydrogen bonds with free water molecules (O…O 2.71 Å) and OH groups belonging to γ-CD of *adjacent* supramolecular units (O…O 2.83 – 2.87 Å). In the crystal packing, the main structural units form infinite columns running along [001] crystal direction by means of hydrogen bonding with water molecules (Fig. 3).
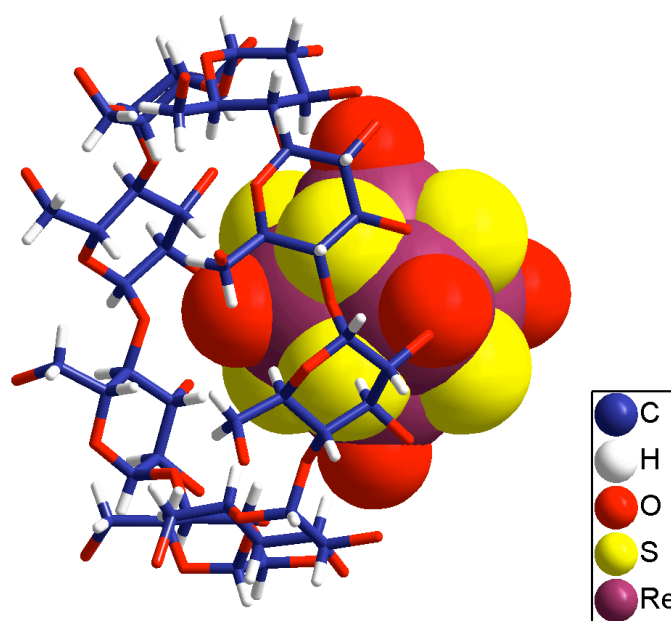

Fig. 2. Structure of the supramolecular association $\{[Re_6S_8(H_2O)_6]\subset[\gamma\text{-CD}]\}^{2+}$ in the solid state.
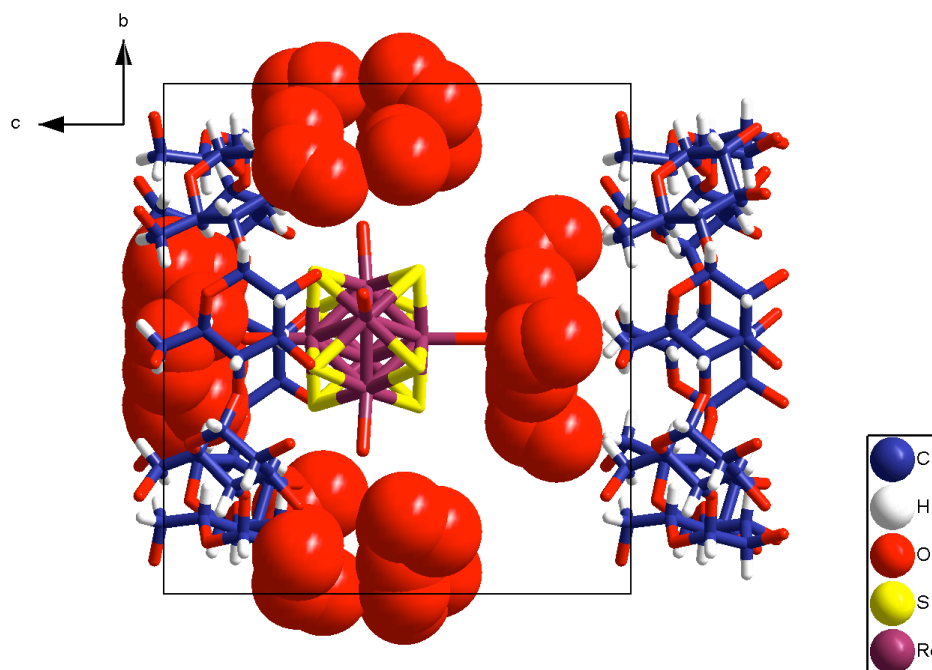
Fig. 3. Fragment of the crystal packing of **1**·12H$_2$O.

Unlike in the solid state, [{Re$_6$S$_8$}(H$_2$O)$_6$]$^{2+}$ appears to not interact, otherwise very weakly, with the γ-CD in solution within a wide concentration range, according to ^{1}H NMR (Figs. S1 and S2). The spectra exhibited the six characteristic resonances of γ-CD where their positions were unvaried within 0.02 ppm whatever the molar ratio and the concentration of the Re cluster added. Also, DOSY NMR showed a too small decrease of the diffusion coefficient of the CD from ca. 250 ± 5 to 240 ± 5 μm^2/s when increasing the amount of the cluster in an 3 mM aqueous solution of γ-CD up to cluster/CD molar ratio of 11. Hence, the formation of **1** seems to be a result of network energy minimization while building the crystal packing by producing multiple hydrogen bonds between the host-guest complex and water molecules, although there is no hydrogen bonding between the host and the guest.

In the case of selenium cluster the interaction between γ-cyclodextrin and cluster aqua complex also was not detected by ^{1}H NMR in the acidic water solution. Moreover this solution is unstable in air and during the crystallization a lot of dark-brown precipitate was found caused by the oxidation of cluster aqua complex.

Table 1. Average atomic bond distances in {Re$_6$S$_8$} rhenium clusters (Å).

Compound	Re–Re	Re–S	Re–O
1·12H$_2$O	2.574(2)	2.420(10)	2.170(60)
K$_2$[Re$_6$S$_8$(H$_2$O)$_2$(OH)$_4$]·2H$_2$O	2.586(6)	2.410(9)	2.105(10)
[Re$_6$S$_8$(H$_2$O)$_4$(OH)$_2$]·12H$_2$O	2.583(3)	2.409(4)	2.116(5)
[Re$_6$S$_8$(H$_2$O)$_6$][Re$_6$S$_8$Br$_6$]·10H$_2$O	2.576(3)	2.409(7)	2.139(7)

K$_4$[{Re$_6$S$_8$}(OH)$_6$] 8H$_2$O   2.587(2)   2.415(4)   2.080(10)

Conclusion

Slow evaporation of acidic water solution of [{Re$_6$S$_8$}(H$_2$O)$_6$]$^{2+}$ generated *in situ* from [{Re$_6$S$_8$}(OH)$_6$]$^{4-}$ and γ-cyclodextrin leads to crystallization of new {[{Re$_6$S$_8$}(H$_2$O)$_6$]⊂[γ-CD]}(NO$_3$)$_2$·12H$_2$O (**1**·12H$_2$O) supramolecular complex. In the crystal structure rhenium cluster and organic cavitand form supramolecular 1:1 complex {[{Re$_6$S$_8$}(H$_2$O)$_6$]⊂[γ-CD]}$^{2+}$. The host-guest interaction is based on the size fit and does not involve specific bonding scheme (coordination or hydrogen bonding). This is the first host-guest inclusion compound for a Re$_6$ cluster with CD reported so far. However, its formation is mostly driven by the crystal packing forces involving multiple hydrogen bonding between the {[{Re$_6$S$_8$}(H$_2$O)$_6$]⊂[γ-CD]}$^{2+}$ aggregates and water molecules. By contrast, no or very weak interaction between the cluster component and γ-CD takes place in solution according to ^{1}H NMR. In the case of selenide cluster [{Re$_6$Se$_8$}(H$_2$O)$_6$]$^{2+}$, its interaction with γ-CD in acidic solution was not detected by ^{1}H NMR technique, and the compound was found to be unstable during the crystallization. Its decomposition prevents any isolation of crystalline product, but leads to the formation of insoluble oxidation products.

Acknowledgments

Supporting Information ?

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Supporting information

Table S1. Experimental details

	1
Chemical formula	$C_{48}H_{56}O_{58}Re_6S_8$
M_r	2934.60
Crystal system, space group	Tetragonal, $I4$
Temperature (K)	130
a, c (Å)	16.8415(4), 15.3787(5)
V (Å^3)	4362.0(3)
Z	2
Radiation type	Mo Ka
μ (mm^{-1})	8.59
Crystal size (mm)	0.15 × 0.10 × 0.08
Diffractometer	New Xcalibur, AtlasS2
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.752, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6544, 3902, 2765
R_{int}	0.026
θ values (°)	$\theta_{max} = 29.4$, $\theta_{min} = 3.4$
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.691
Range of h, k, l	$-16 \leq h \leq 21$, $-14 \leq k \leq 23$, $-14 \leq l \leq 21$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.198, 1.12

No. of reflections, parameters, restraints	3902, 280, 1		
H-atom treatment	H-atom parameters constrained		
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1071P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$		
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.82, -2.31		
Absolute structure	Flack x determined using 756 quotients $[(I+)-(I-)]/[(I+)+(I-)]$ (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).		
Absolute structure parameter	0.013 (10)		

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

Table S2. Selected geometric parameters (Å)

Re1—Re2^i	2.5770(14)	S2—Re2	2.415(8)
Re1—Re2^{ii}	2.5770(14)	S2—Re3	2.399(9)
Re1—Re2^{iii}	2.5770(14)	Re1—S1^{iii}	2.430(6)
Re1—Re2	2.5770(14)	Re1—S1^i	2.430(6)
Re2—Re2^{ii}	2.5704(11)	Re1—S1^{ii}	2.430(6)
Re2—Re2^i	2.5705(11)	Re2—S1^{ii}	2.440(6)
Re2—Re3	2.5720(16)	Re2—S2^{ii}	2.405(8)
Re3—Re2^{ii}	2.5720(16)	Re3—S2^{iii}	2.399(9)
Re3—Re2^{iii}	2.5720(16)	Re3—S2^{ii}	2.399(9)
Re3—Re2^i	2.5720(16)	Re3—S2^i	2.399(9)
S1—Re1	2.430(6)	O1—Re1	2.21(3)
S1—Re2	2.422(6)	O7—Re2	2.137(14)
S1—Re2^i	2.440(6)	O8—Re3	2.14(3)
S2—Re2^i	2.406(8)		

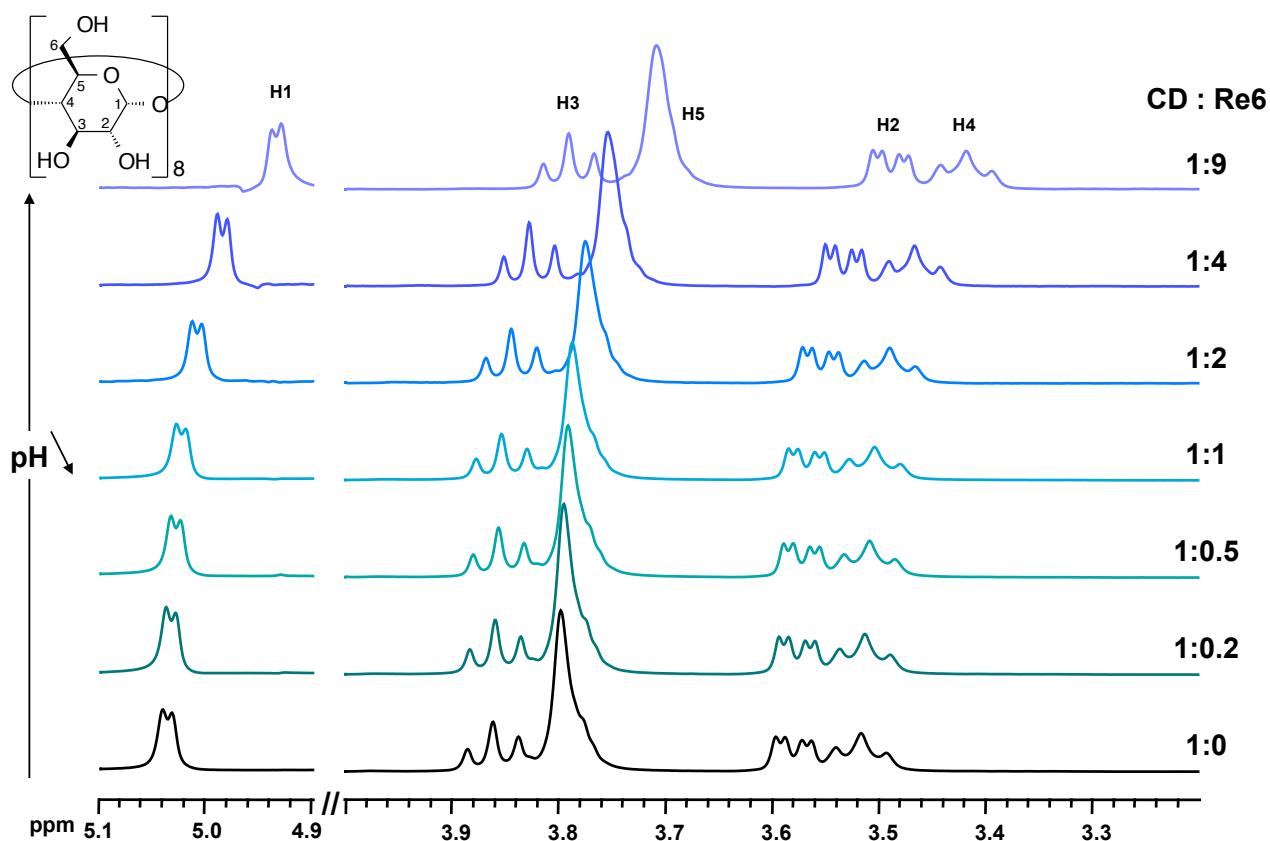Symmetry code(s): (i) y, $-x+1$, z; (ii) $-y+1$, x, z; (iii) $-x+1$, $-y+1$, z.

Figure S1: ^{1}H NMR spectra of γ-CD in presence of various amount of $[\{Re_6S_8\}(H_2O)_6]^{2+}$. The concentration of CD was fixed to 3 mM and that of the Re cluster varied from 0 to 27 mM. The samples are prepared by mixing appropriate amounts of mother solutions of CD (30 mM), Re cluster (30 mM), and D_2O. Because of the difference of pH in these mother solutions (very acidic in cluster solution), the pH in the resulting final sample also varies strongly. As a consequence, a global shift of all resonances happens equally and these effects are attributed to the pH change mainly.
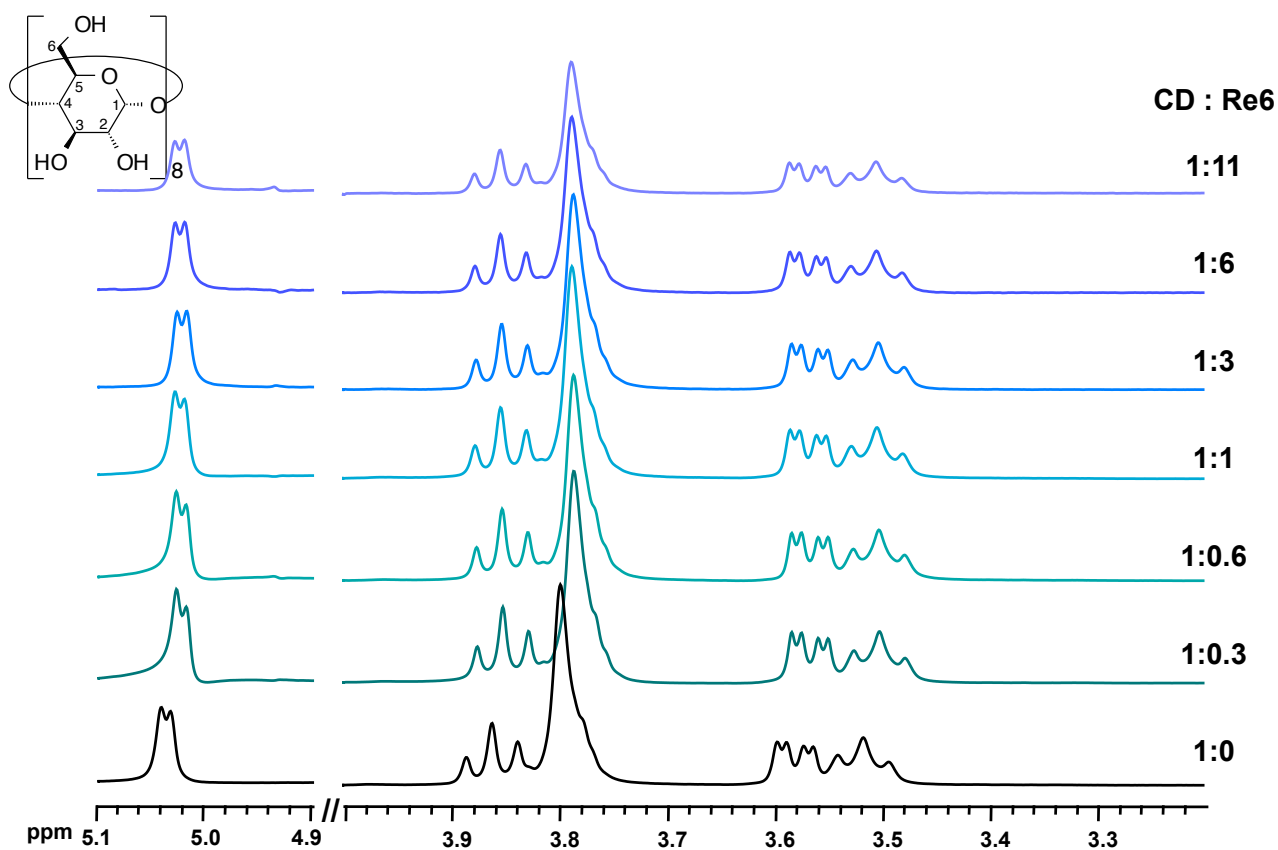
Figure S2: ^{1}H NMR spectra of γ-CD in presence of various amount of $[\{Re_6S_8\}(H_2O)_6]^{2+}$. The concentration of CD was varied 0.27 to 10 mM and that of the Re cluster fixed to 3 mM. The samples are prepared by mixing appropriate amounts of mother solutions of CD (30 mM), Re cluster (30 mM), and D_2O. Note, in this case because of the dilution effect, the pH is not varying anymore within the different samples prepared.