Syntheses and crystal structures of supramolecular compounds of tetranuclear Zr^{IV} and Hf^{IV} aqua hydroxo complexes with macrocyclic cavitand cucurbituril

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Slow evaporation of hydrochloric acid solutions of zirconium(IV) or hafnium(IV) oxochlorides and cucurbituril in air afforded compounds with composition $[M_4(OH)_8(H_2O)_{16}]Cl_8 \cdot (C_{36}H_{36}N_{24}O_{12}) \cdot 16H_2O$, where M = Zr (**1**) or Hf (**2**). According to the X-ray diffraction data, complexes **1** and **2** are isostructural. Their crystal structures can be described as packings of polymer chains consisting of alternating cucurbituril molecules and tetranuclear cations $[M_4(OH)_8(H_2O)_{16}]^{8+}$ linked to each other *via* an extensive network of hydrogen bonds. Compound **2** is the first structurally characterized tetranuclear hafnium aqua complex.

Key words: aqua complexes, zirconium, hafnium, cucurbituril, supramolecular compound, crystal structure, X-ray diffraction analysis.

The formation of polynuclear hydroxo-bridged compounds in aqueous solutions is typical of tetravalent zirconium and hafnium. Polymerization occurs even in strongly acidic ($[H^+]$ = 1—2 mol L^{-1}) and very dilute (10^{-4}—10^{-3} mol L^{-1}) solutions.[1] The published data on their structures are contradictory. Most of complexes are difficult to crystallize, because their kinetic lability and high rates of ligand exchange prevent their isolation from aqueous solutions. Numerous studies[2—11] by physicochemical methods demonstrated that the solutions contain the tetranuclear aqua hydroxo complexes $[M_4(OH)_8(aq)]^{8+}$ (M = Zr or Hf) as the major component along with small amounts of the trinuclear complexes $[M_3(OH)_4(aq)]^{8+}$. According to the results of X-ray diffraction analysis,[2,3] the tetranuclear complex, which is present in aqueous solutions of Zr^{IV} and Hf^{IV} halides as well as of Hf^{IV} perchlorate, is structurally similar to the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ tetramer in $ZrOCl_2 \cdot 8H_2O$. The latter is the only polynuclear zirconium aqua complex, whose structure was established by X-ray diffraction analysis.[12,13] In this cation, four metal atoms form a slightly distorted square and are linked in pairs through two bridging hydroxo groups. Each Zr atom is additionally coordinated by four H_2O molecules. No polynuclear hafnium aqua complexes were structurally characterized.

In the present study, we report the synthesis of tetranuclear zirconium and hafnium aqua complexes from aqueous solutions as supramolecular adducts with organic macrocyclic cavitand cucurbituril. According to the X-ray diffraction data, these compounds are isostructural and have the composition $[M_4(OH)_8(H_2O)_{16}]Cl_8 \cdot (C_{36}H_{36}N_{24}O_{12}) \cdot 16H_2O$ (M = Zr (**1**) or Hf (**2**)).

Results and Discussion

Recently, we have developed a procedure for isolation of metal aqua complexes from aqueous solutions as adducts with cucurbituril. This approach made it possible to prepare in high yields and structurally characterize a series of supramolecular compounds in which aqua complexes of transition and main-group metals are linked to cucurbituril *via* an extensive network of hydrogen bonds.[14—19] The molecule of macrocyclic cavitand cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) consists of six glycoluril fragments linked by methylene bridges.[20] Cucurbituril can form hydrogen bonds with water molecules coordinated to metal atoms due to the presence of 12 polarized carbonyl groups (portals). In multicharged cationic aqua complexes, such as $[M_4(OH)_8(aq)]^{8+}$ (M = Zr or Hf), water molecules possess rather strong acidic properties, which should facilitate hydrogen bonding with the oxygen atoms of the CO groups. For example, after equilibration for one day, pH of a 0.055 *M* solution of zirconium(IV) oxochloride is 1.15.[11] According to the results of ^{17}O and ^{1}H NMR spectroscopic studies of aqueous solutions of $ZrOCl_2 \cdot 8H_2O$, the protons of two of four water molecules coordinated to each Zr atom are very labile, and,

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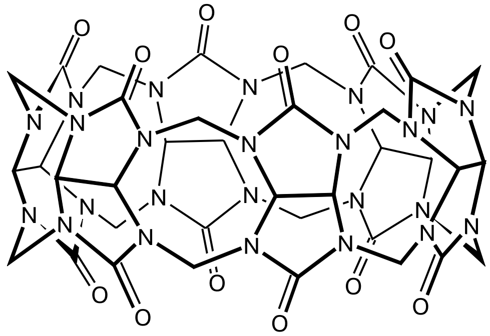
hence, this compound should be considered as a very strong acid.[8]



Cucurbituril

Compounds **1** and **2** were prepared in 62 and 59% yields, respectively, by slow evaporation of solutions of zirconium(IV) or hafnium(IV) oxochlorides ($4 \cdot 10^{-4}$ and $3 \cdot 10^{-4}$ mol L^{-1}, respectively) and cucurbituril in 1—2 *M* HCl in air. Upon storage in air, these compounds partially lose the water molecules of crystallization. Because of this, X-ray diffraction data were collected from crystals embedded in epoxy resin. Powder X-ray diffraction data for **1** and **2** are virtually identical with the theoretically calculated X-ray patterns of these compounds. The IR spectra are insufficiently informative because of the presence of a large number of intense bands belonging to cucurbituril.

According to the X-ray diffraction data, the ratio between cucurbituril and the aqua complex in supramolecular adducts **1** and **2** is 1 : 1. The tetranuclear cation $[M_4(OH)_8(H_2O)_{16}]^{8+}$ in both adducts is structurally similar to the cation in $ZrOCl_2 \cdot 8H_2O$. The metal atoms coordinated by four water molecules form a slightly distorted square and are linked to each other by two bridging hydroxo groups (Fig. 1). In the cation, there are three different metal—metal distances (Table 1) resulting in a trapezoid-like distortion of the square, in contrast to $ZrOCl_2 \cdot 8H_2O$, in which the corresponding distances are equalized (3.558(1) Å).[13] The average metal—metal distances and the average distances between the metal atoms and the oxygen atoms of the bridging OH groups (in **1** and **2**, the average M—OH distances are 2.126(28) and 2.119(27) Å, respectively) agree well with the corresponding average distances in the $M_2(\mu_2\text{-}OH)_2$ structural fragment typical of zirconium and hafnium hydroxy salts. For example, the average Zr—OH distance in $ZrOCl_2 \cdot 8H_2O$ is 2.142(19) Å,[13] the average Zr—OH and Zr...Zr distances in $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$ are 2.123(20) and 3.545(1) Å, respectively,[21] the average Hf—OH and Hf...Hf distances in $Hf(OH)_2SO_4$ are 2.17(5) and 3.562(1) Å, respectively,[22] and the average Hf—OH and Hf...Hf distances in $Hf_4(OH)_6(CrO_4) \cdot 5H_2O$ are 2.125(21) and 3.542(6) Å, respectively.[23] According to the X-ray scattering data, the Hf...Hf distance in the hafnium(IV) cation $[Hf_4(OH)_8(H_2O)_{16}]^{8+}$ present in an aqueous solution is 3.57 Å.[2]

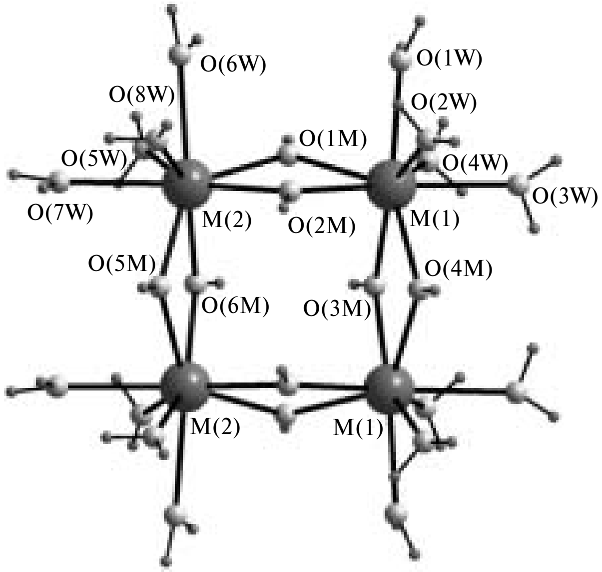


Fig. 1. Structure of the tetranuclear cation $[M_4(OH)_8(H_2O)_{16}]^{8+}$ in compounds **1** (M = Zr) and **2** (M = Hf).

In addition to four oxygen atoms of the OH groups, each metal atom in the $[M_4(OH)_8(H_2O)_{16}]^{8+}$ cation (M = Zr or Hf) is coordinated by four water molecules,

Table 1. Selected bond lengths (*d*) in the tetranuclear cations of compounds **1** and **2**

Bond	*d*/Å	
	$[Zr_4(OH)_8(H_2O)_{16}]^{8+}$	$[Hf_4(OH)_8(H_2O)_{16}]^{8+}$
M(1)—O(1M)	2.138(4)	2.130(4)
M(1)—O(2M)	2.119(5)	2.119(4)
M(1)—O(3M)	2.094(3)	2.087(3)
M(1)—O(4M)	2.173(3)	2.164(3)
M(2)—O(1M)	2.151(5)	2.133(4)
M(2)—O(2M)	2.102(4)	2.091(4)
M(2)—O(5M)	2.134(4)	2.136(3)
M(2)—O(6M)	2.099(4)	2.092(4)
M(1)—O(1W)	2.201(5)	2.176(5)
M(1)—O(2W)	2.269(4)	2.250(5)
M(1)—O(3W)	2.245(5)	2.209(5)
M(1)—O(4W)	2.315(5)	2.293(5)
M(2)—O(5W)	2.325(4)	2.312(5)
M(2)—O(6W)	2.260(5)	2.220(5)
M(2)—O(7W)	2.234(4)	2.201(5)
M(2)—O(8W)	2.289(4)	2.267(4)
M(1)...M(2)	3.5485(9)	3.5357(4)
M(1)...M(1)*	3.5580(13)	3.5551(6)
M(2)...M(2)*	3.5309(12)	3.5272(6)

* The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation $x, -y + 1/2, z$.

two of which are involved in hydrogen bonds with cucurbituril. The M—OH$_2$ bond lengths with these two water molecules (M(1)—O(3W), M(1)—O(4W), M(2)—O(7W), and M(2)—O(8W)) differ only slightly from other analogous bonds (see Table 1), whereas there are two types of M—OH$_2$ distances in the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ cation present in the $ZrOCl_2 \cdot 8H_2O$ compound (2.210(22), 2.224(22) and 2.314(22), 2.338(22) Å).[13] The Zr and Hf atoms in complexes **1** and **2** have a coordination number of eight, and the coordination environment about the metal atoms is a distorted dodecahedron.

The tetranuclear aqua complex is linked to two cucurbituril molecules by a network of hydrogen bonds between four water molecules, which are coordinated to two metal atoms on opposite sides of the tetranuclear aqua complex, and five O atoms of the carbonyl groups of each portal of the cucurbituril molecules (O...O, 2.643(9)—2.946(7) Å) (Fig. 2). The angle between the plane of the quadrangle and the plane of the portals of the cucurbituril molecule is ~40°. The aqua complexes and cucurbituril molecules are linked in infinite chains by hydrogen bonds. The chains are shifted with respect to each other by one-half of the crystallographic translation along the *c* axis, the wide region of one chain fitting the narrow region of another chain (see Fig. 2). In the crystal structure, the chains form a hexagonal packing (Fig. 3). The cavities between the chains are occupied by the water molecules of crystallization and chloride anions. In both structures, there are extensive hydrogen bond networks involving the chloride anions and the O atoms of the cucurbituril and H$_2$O molecules. The formation of such

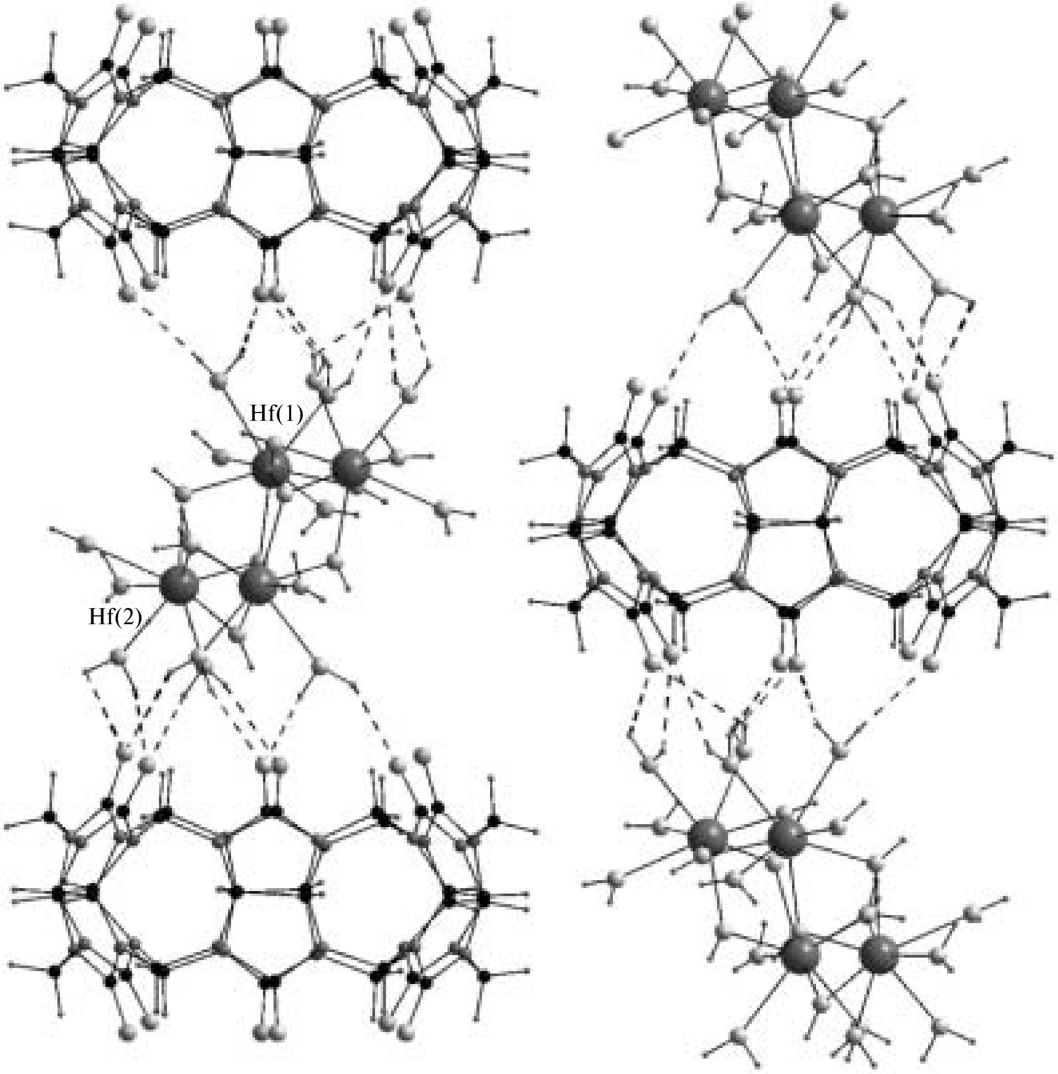


Fig. 2. Fragment of the polymer chains $[\{[M_4(OH)_8(H_2O)_{16}](C_{36}H_{36}N_{24}O_{12})\}^{8+}]_\infty$ in the structure of **2** projected along the *c* axis. Water molecules of solvation and chloride anions are omitted. Hydrogen bonds are indicated by dashed lines.

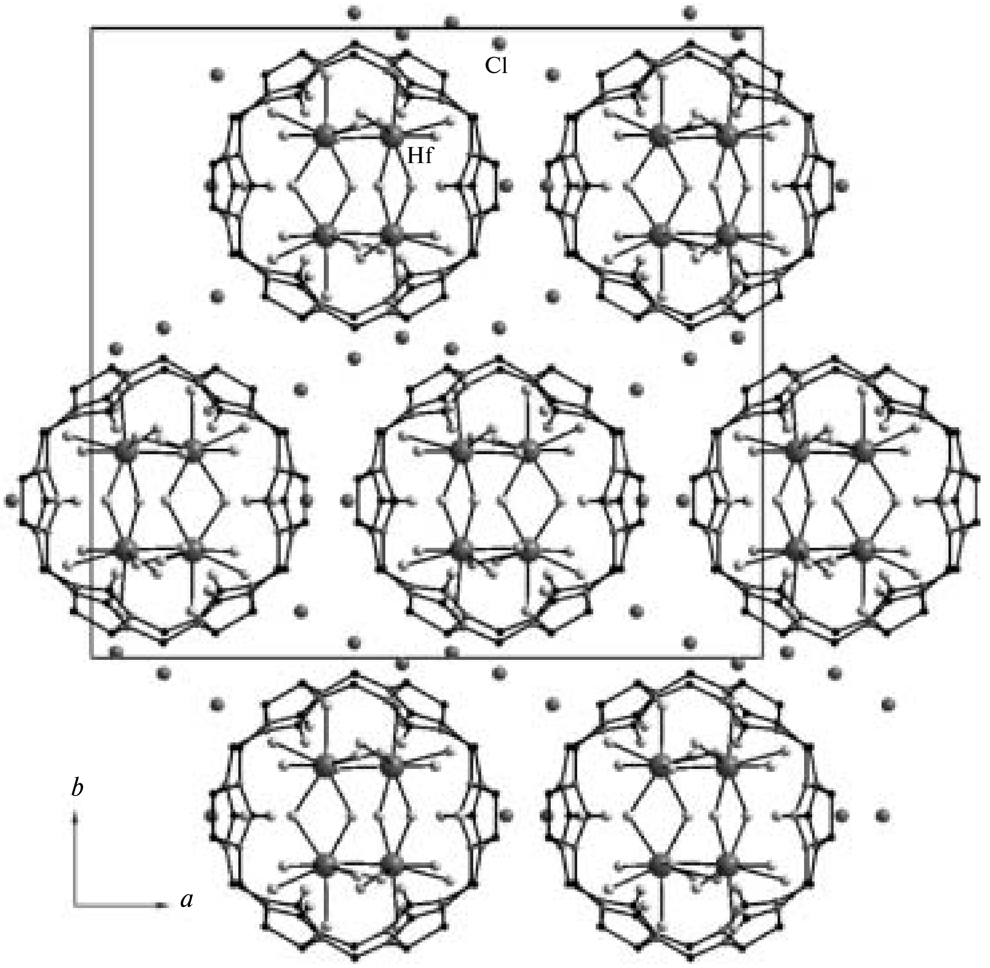


Fig. 3. Packing of the polymer chains in the crystal structure of **2** projected onto the *ab* plane. Water molecules of solvation are omitted.

hydrogen bond networks involving all structural units of the crystal is typical of supramolecular adducts of metal aqua complexes with cucurbituril.[14—19]

To summarize, we demonstrated that macrocyclic cavitand cucurbituril can be used for isolation of polynuclear zirconium and hafnium aqua complexes from aqueous solutions. High charges and rather large sizes of aqua complexes provide good conditions for the preparation of stable supramolecular compounds with cucurbituril due to formation of extensive hydrogen bond networks between the aqua ligands and the O atoms of the portals of the macrocycle. Due to isolation of these compounds as single crystals, we obtained for the first time direct information on the structure of the tetranuclear hafnium aqua complex, which has previously been unknown in the solid state, although the $HfOCl_2 \cdot 8H_2O$ compound isomorphous to $ZrOCl_2 \cdot 8H_2O$ has been described about 80 years ago.[24] According to the X-ray scattering data[3] and results of ^{17}O and ^{1}H NMR spectroscopic study of aqueous solutions of $ZrOCl_2 \cdot 8H_2O$,[8] larger polymeric complexes consisting of the above-described hydroxo-bridged tetranuclear fragments can form in solution. Larger cucurbiturils (composed of more than six glycoluril fragments), which became available in recent years,[25,26] hold promise for isolation of such polymeric aqua complexes from aqueous solutions as supramolecular compounds.

Experimental

Zirconium oxochloride octahydrate $ZrOCl_2 \cdot 8H_2O$ (analytical grade) was used without additional purification.

Hafnium oxochloride octahydrate $HfOCl_2 \cdot 8H_2O$ was prepared from hafnium nitride HfN (high-purity grade) and 12 *M* HCl (reagent grade) according to the following procedure. A mixture of hafnium nitride (10 g) and 12 *M* HCl (40 mL) was placed in a round-bottom flask equipped with a reflux condenser and refluxed for 3 days (reaction of HfN with HCl was described in the literature[27]). The insoluble black precipitate was filtered through a porous glass filter (No. 16). The filtrate was concentrated until a film of white crystals formed and cooled to ~20 °C. The crystals were filtered through a porous glass filter (No. 16) and dried in a desiccator over P_2O_5. The yield was

11.6 g (~50%). The resulting salt was used without additional purification.

Cucurbituril was synthesized according to a modified procedure from glyoxal, carbamide, and paraformaldehyde in an acidic medium followed by recrystallization from HCl.[28,29] Elemental analysis was carried out at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets. Powder X-ray diffraction data were measured on a Philips APD-1700 instrument. Theoretically calculated X-ray diffraction patterns (XPOW program) were fitted to the experimental data on a computer.

Cucurbituril(octa-μ_2-hydroxohexadecaaquatetrazirconium) octachloride hexadecahydrate (1). A mixture of 2 *M* HCl (2 mL) and cucurbituril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$) (0.020 g) was heated until the solid phase was virtually completely dissolved. Simultaneously, a solution of $ZrOCl_2 \cdot 8H_2O$ (0.130 g) in 2 *M* HCl (5 mL) was heated to boiling and added to a hot solution of cucurbituril. The resulting mixture was refluxed until the cucurbituril was completely dissolved (~3 min) and filtered through a paper filter. The hot filtrate was slowly concentrated in air at ~20 °C. Large colorless crystals of complex **1** precipitated after 8—14 days. The crystals were filtered through a paper filter (blue strip) and dried in air. The yield was 0.025 g (62% with respect to cucurbituril). In air, the crystals gradually lost water of crystallization. Found (%): C, 18.65; H, 3.64; N, 13.62. $C_{36}H_{108}Cl_8N_{24}O_{52}Zr_4$. Calculated (%): C, 18.34; H, 4.62; N, 14.26. IR, ν/cm^{-1}: 3296 s, 1725 s, 1635 m, 1480 s, 1405 s, 1365 s, 1315 s, 1285 m, 1250 m, 1230 s, 1190 s, 1145 m, 975 m, 955 s, 805 s, 795 s, 750 m, 660 m, 634 w.

Cucurbituril(octa-μ_2-hydroxohexadecaaquatetrahafnium) octachloride hexadecahydrate (2). A solution of $HfOCl_2 \cdot 8H_2O$ (0.298 g) in 1 *M* HCl (6 mL) was heated to boiling, after which cucurbituril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$) (0.020 g) was added. The resulting mixture was heated until the solid phase was completely dissolved and filtered through a paper filter. The hot filtrate was slowly concentrated in air at ~20 °C. After 8—14 days, large colorless crystals that precipitated were filtered through a paper filter (blue strip) and dried in air. The yield was 0.027 g (59% with respect to cucurbituril). In air, the crystals gradually lost water of crystallization. Found (%): C, 15.79; H, 4.14; Cl, 10.15; N, 11.72. $C_{36}H_{108}Cl_8Hf_4N_{24}O_{52}$. Calculated (%): C, 15.97; H, 4.02; Cl, 10.48; N, 12.42. IR, ν/cm^{-1}: 3296 s,

Table 2. Crystallographic characteristics and details of X-ray diffraction study of compounds **1** and **2**

Parameter	**1**	**2**
Stoichiometric formula	$C_{36}H_{108}Cl_8N_{24}O_{52}Zr_4$	$C_{36}H_{108}Cl_8Hf_4N_{24}O_{52}$
M	2357.94	2707.02
T/K	298(2)	298(2)
λ/Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*
Unit cell parameters		
a/Å	23.8473(15)	23.9509(15)
b/Å	22.4917(15)	22.5300(15)
c/Å	16.5670(11)	16.5640(11)
V/Å^3	8886.0(10)	8938.2(10)
Z	4	4
d_{calc}/g cm^{-3}	1.763	2.012
μ/mm^{-1}	0.808	4.979
Transmission (max/min)	0.8487/0.7878	0.4676/0.2823
F(000)	4816	5328
Crystal dimensions/mm	0.21×0.25×0.31	0.18×0.22×0.34
θ-Scan range/deg	1.71—23.28	1.93—23.29
Ranges of h, k, l	$-26 \le h \le 26$ $-24 \le k \le 19$ $-17 \le l \le 18$	$-26 \le h \le 26$ $-25 \le k \le 24$ $-18 \le l \le 17$
Number of measured reflections	37325	37506
Number of independent reflections	6584 (R_{int} = 0.0949)	6614 (R_{int} = 0.0317)
Completeness of X-ray data up to θ = 23.28° (%)	99.8	99.5
Number of reflections/restrictions/parameters	6584/97/663	6614/79/664
S factor based on F^2	1.092	1.069
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0563$ $wR_2 = 0.0859$	$R_1 = 0.0336$ $wR_2 = 0.0986$
R factors (all reflections)	$R_1 = 0.1091$ $wR_2 = 0.0987$	$R_1 = 0.0388$ $wR_2 = 0.1023$
Extinction coefficient	0	0.00004(2)
Residual electron density (min/max)/e Å^{-3}	0.502/−0.508	1.781/−1.147

1730 s, 1620 m, 1475 s, 1405 s, 1370 s, 1320 s, 1280 m, 1250 m, 1235 s, 1194 s, 1149 m, 980 m, 950 s, 805 m, 795 s, 750 m, 660 m, 634 w.

X-ray diffraction analysis. X-ray diffraction data were collected on an automated Bruker Smart CCD diffractometer equipped with a two-coordinate detector (Mo-Kα radiation, graphite monochromator, ω scanning technique, scan step was 0.3°, frames were exposed for 10 s). The absorption correction was applied based on the intensities of equivalent reflections using the SADABS program.[30] The structure was solved by direct methods using the SHELXS-97 program package[30] and refined anisotropically by the full-matrix least-squares method against F^2_{hkl} using the SHELXL-97 program package.[31] The positions of the H atoms of the cavitand were calculated geometrically and refined in the rigid-body approximation. The H atoms of the coordinated water molecules and the hydroxo groups were revealed from the difference electron density synthesis and included in the refinement. The isotropic thermal parameters of the H atoms were taken equal to $1.5U_{\text{eq}}$ of the nonhydrogen atoms to which these H atoms are bound. The crystallographic characteristics and details of X-ray diffraction studies of compounds **1** and **2** are given in Table 2. The atomic coordinates of compounds **1** and **2** were deposited with the Cambridge Structural Database and can be obtained from the authors.

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