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Supramolecular Assemblies Based on Cucurbituril Adducts of Hydrogen-Bonded Molybdenum and Tungsten Incomplete Cuboidal Aqua Complexes

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Introduction

The designed construction of highly ordered supramolecular architectures with well-defined structures and functions will be greatly facilitated if a diverse set of molecular building blocks leading to highly specific/controlled intermolecular interactions becomes available. Hydrogen bonds have attracted the most attention in mediating the self-assembly of supramolecular structures.[1] If the number of relatively weak hydrogen bonds associated with each molecular building block is small, the interaction usually is not very specific. To increase the strength, directionality, and specificity of hydrogen-bonding interactions, there is currently intense interest in designing arrays of hydrogen bond donor and acceptor sites to control solid-state organization.

Here we report syntheses of examples of a potentially large class of supramolecular architectures based on cucurbituril adducts of hydrogen-bonded incomplete cuboidal aqua cluster complexes. It is now well established that molybdenum and tungsten in oxidation state IV form stable triangular incomplete cuboidal aqua ions $[M_3(\mu_3\text{-E})(\mu_2\text{-E})_3\,(H_2O)_9]^{4+}$ (M = Mo, W; E = O, S, Se) of C_{3v} symmetry with six coordinated H_2O molecules which are cis to the core μ_3-E.[2] Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) is a macrocyclic cavitand with D_{6h} symmetry, having two identical carbonyl-fringed portals.[3] Its capability of holding small guest molecules in the cavity makes cucurbituril very attractive as a synthetic receptor.[4,5]

Table 1. Crystallographic Data for $C_{36}H_{70}Cl_4N_{24}O_{29}S_4W_3$ (**1**) and $C_{41}H_{102}Cl_9Mo_6N_{25}O_{42}S_8$ (**2**)

	1	**2**
formula	$C_{36}H_{70}Cl_4N_{24}O_{29}S_4W_3$	$C_{41}H_{102}Cl_9Mo_6N_{25}O_{42}S_8$
fw	2124.75	2768.65
space group	$P2_1/c$ (No. 14)	P-1 (No. 2)
Z	4	1
a, Å	21.315(4)	12.657(1)
b, Å	14.588(3)	13.072(1)
c, Å	24.486(5)	15.357(2)
α, deg	90	97.802(2)
β, deg	112.70(3)	95.348(2)
γ, deg	90	110.215(2)
V, Å^3	7024(2)	2335.3(4)
D(calcd), g·cm^{-3}	2.009	1.969
temp, °C	20	−113
λ	Mo Kα, 0.71069 Å	Mo Kα, 0.71073 Å
μ, cm^{-1}	52.68	13.17
R1[a]	0.0689	0.0508
wR2[b]	0.1610	0.1350

[a] Conventional R on F_{hkl}: $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Weighted R on $|F_{hkl}|^2$: $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl_2\cdot10H_2O$ (**1**)

Bond Distances

W(1)−W(2)	2.727(2)	W(2)−S(23)	2.268(7)
W(1)−W(3)	2.705(2)	W(2)−Cl(21)	2.509(8)
W(1)−S(1)	2.353(7)	W(2)−O(22M)	2.22(2)
W(1)−S(12)	2.316(7)	W(2)−O(23M)	2.16(2)
W(1)−S(13)	2.285(6)	W(3)−S(1)	2.334(6)
W(1)−Cl(11)	2.481(8)	W(3)−S(13)	2.281(7)
W(1)−O(12M)	2.19(2)	W(3)−S(23)	2.266(8)
W(1)−O(13M)	2.23(2)	W(3)−O(31M)	2.18(2)
W(2)−W(3)	2.714(2)	W(3)−O(32M)	2.16(2)
W(2)−S(1)	2.332(7)	W(3)−O(33M)	2.20(2)
W(2)−S(12)	2.296(7)		

Bond Angles

S(1)−W(1)−Cl(11)	160.0(2)	O(23M)−W(2)−S(12)	90.8(5)
S(12)−W(1)−S(1)	105.7(3)	O(23M)−W(2)−S(23)	164.8(5)
S(12)−W(1)−Cl(11)	87.0(3)	O(23M)−W(2)−Cl(21)	80.9(5)
S(13)−W(1)−S(1)	106.7(2)	O(23M)−W(2)−O(22M)	77.8(6)
S(13)−W(1)−S(12)	97.4(2)	S(13)−W(3)−S(1)	107.4(2)
S(13)−W(1)−Cl(11)	86.4(3)	S(23)−W(3)−S(1)	106.0(3)
O(12M)−W(1)−S(1)	83.9(5)	S(23)−W(3)−S(13)	96.7(3)
O(12M)−W(1)−S(12)	90.4(5)	O(31M)−W(3)−S(1)	158.1(5)
O(12M)−W(1)−S(13)	164.4(5)	O(31M)−W(3)−S(13)	84.5(5)
O(12M)−W(1)−Cl(11)	80.5(5)	O(31M)−W(3)−S(23)	90.3(5)
O(12M)−W(1)−O(13M)	80.1(6)	O(31M)−W(3)−O(33M)	78.7(7)
O(13M)−W(1)−S(1)	84.5(5)	O(32M)−W(3)−S(1)	85.4(4)
O(13M)−W(1)−S(12)	165.4(5)	O(32M)−W(3)−S(13)	92.5(5)
O(13M)−W(1)−S(13)	89.4(5)	O(32M)−W(3)−S(23)	162.4(5)
O(13M)−W(1)−Cl(11)	80.5(5)	O(32M)−W(3)−O(31M)	75.6(7)
O(22M)−W(2)−S(1)	83.8(5)	O(32M)−W(3)−O(33M)	77.7(7)
O(22M)−W(2)−S(12)	163.4(5)	O(33M)−W(3)−S(1)	86.8(5)
O(22M)−W(2)−S(23)	91.2(4)	O(33M)−W(3)−S(13)	162.2(5)
O(22M)−W(2)−Cl(21)	78.0(5)	O(33M)−W(3)−S(23)	89.3(5)
O(23M)−W(2)−S(1)	83.5(5)		

Experimental Section

Syntheses. The starting materials, cucurbituril decahydrate,[3] $[W_3S_4(H_2O)_9]^{4+}$, and $[Mo_3S_4(H_2O)_9]^{4+}$ as solutions in 2 M HCl[6] were prepared by literature methods. All operations were carried out under air.

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Table 3. Selected Bond Distances (Å) and Angles (deg) in $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH)(C_{36}H_{36}N_{24}O_{12})\}Cl_4{\cdot}17H_2O$ (**2**)

Bond Distances

Mo(1)−Mo(2)	2.7448(8)	Mo(2)−S(23)	2.274(2)
Mo(1)−Mo(3)	2.7460(8)	Mo(2)−Cl(21)	2.509(2)
Mo(1)−S(123)	2.339(2)	Mo(2)−O(22M)	2.174(4)
Mo(1)−S(12)	2.274(2)	Mo(2)−O(23M)	2.190(4)
Mo(1)−S(13)	2.285(2)	Mo(3)−S(123)	2.344(2)
Mo(1)−X(11)[a]	2.369(3)	Mo(3)−S(23)	2.272(2)
Mo(1)−O(12M)	2.202(4)	Mo(3)−S(13)	2.275(2)
Mo(1)−O(13M)	2.185(4)	Mo(3)−Cl(31)	2.503(2)
Mo(2)−Mo(3)	2.7394(8)	Mo(3)−O(32M)	2.142(4)
Mo(2)−S(123)	2.345(2)	Mo(3)−O(33M)	2.215(4)
Mo(2)−S(12)	2.277(2)		

Bond Angles

S(123)−Mo(1)−X(11)[a]	160.74(9)	O(22M)−Mo(2)−S(23)	93.3(1)
S(12)−Mo(1)−S(123)	105.89(6)	O(22M)−Mo(2)−Cl(21)	79.7(1)
S(12)−Mo(1)−S(13)	95.38(6)	O(22M)−Mo(2)−O(23M)	79.5(2)
S(12)−Mo(1)−X(11)[a]	86.23(9)	O(23M)−Mo(2)−S(123)	85.7(1)
S(13)−Mo(1)−S(123)	105.68(6)	O(23M)−Mo(2)−S(12)	88.7(1)
S(13)−Mo(1)−X(11)[a]	87.6(1)	O(23M)−Mo(2)−S(23)	166.0(1)
O(12M)−Mo(1)−S(123)	87.0(1)	O(23M)−Mo(2)−Cl(21)	82.0(1)
O(12M)−Mo(1)−S(12)	91.1(1)	S(123)−Mo(3)−Cl(31)	161.57(6)
O(12M)−Mo(1)−S(13)	163.5(1)	S(23)−Mo(3)−S(123)	105.98(6)
O(12M)−Mo(1)−X(11)[a]	77.7(2)	S(23)−Mo(3)−S(13)	95.48(6)
O(13M)−Mo(1)−S(123)	86.9(1)	S(23)−Mo(3)−Cl(31)	86.20(7)
O(13M)−Mo(1)−S(12)	163.1(1)	S(13)−Mo(3)−S(123)	105.84(6)
O(13M)−Mo(1)−S(13)	91.6(1)	S(13)−Mo(3)−Cl(31)	86.23(7)
O(13M)−Mo(1)−X(11)[a]	78.7(1)	O(32M)−Mo(3)−S(123)	85.7(1)
O(13M)−Mo(1)−O(12M)	78.4(2)	O(32M)−Mo(3)−S(23)	161.6(1)
S(123)−Mo(2)−Cl(21)	162.37(6)	O(32M)−Mo(3)−S(13)	94.9(1)
S(12)−Mo(2)−S(123)	105.60(6)	O(32M)−Mo(3)−Cl(31)	79.3(1)
S(12)−Mo(2)−Cl(21)	86.81(6)	O(32M)−Mo(3)−O(33M)	78.3(2)
S(23)−Mo(2)−S(123)	105.93(6)	O(33M)−Mo(3)−S(123)	86.0(1)
S(23)−Mo(2)−S(12)	95.45(6)	O(33M)−Mo(3)−S(23)	88.2(1)
S(23)−Mo(2)−Cl(21)	84.83(6)	O(33M)−Mo(3)−S(13)	166.0(1)
O(22M)−Mo(2)−S(123)	85.6(1)	O(33M)−Mo(3)−Cl(31)	80.5(1)
O(22M)−Mo(2)−S(12)	163.2(1)		

[a] X = 1/2 Cl + 1/2 O.

$\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl_2{\cdot}10H_2O$ (1). To a solution of cucurbituril decahydrate (0.0589 g, 0.050 mmol) in 10 mL of 2.5 M HCl was added 1.00 mL of 50 mM $[W_3S_4(H_2O)_9]^{4+}$ (0.050 mmol) in 2 M HCl. The final solution was mixed thoroughly and allowed to stand at room temperature over 4 days. During this time, blue plate crystals of **1** suitable for crystallography formed and were filtered off and dried in air. Yield: 0.047 g (42%). Anal. Calcd for $C_{36}H_{70}Cl_4N_{24}O_{29}S_4W_3$: C, 20.35; H, 3.32; Cl, 6.67; N, 15.82; S, 6.04. Found: C, 20.55: H, 3.15; Cl, 6.98; N, 15.76; S, 6.00.

$\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH)(C_{36}H_{36}N_{24}O_{12})\}Cl_4{\cdot}17H_2O$ (2). To a solution of cucurbituril decahydrate (0.147 g, 0.125 mmol) in 25 mL of 2.5 M HCl was added 2.00 mL of 125 mM $[Mo_3S_4(H_2O)_9]^{4+}$ (0.250 mmol) in 2 M HCl and pyridine (0.0395 g, 0.500 mmol). The final solution was mixed thoroughly and allowed to stand at room temperature over 2 days. During this time, green plate crystals of **2** suitable for crystallography formed and were filtered off and dried in air. Yield: 0.318 g (91%). Anal. Calcd for $C_{41}H_{102}Cl_9Mo_6N_{25}O_{42}S_8$: C, 17.79; H, 3.71; Cl, 11.52; N, 12.65; S, 9.27. Found: C, 17.63; H, 3.70; Cl, 11.41; N, 12.39; S, 9.38.

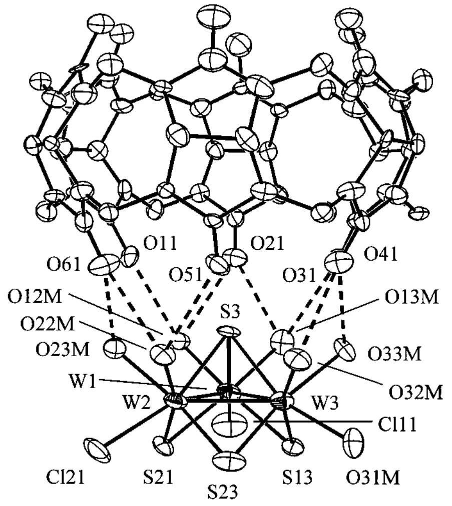

Figure 1. Drawing of $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^{2+}$ in **1**, with partial atom-numbering scheme. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted for clarity. Hydrogen bonding interactions are indicated by dashed lines.

X-ray Crystallography. A dark blue plate (0.028 × 0.30 × 0.40 mm^3) of **1** was mounted at the end of glass fiber. Intensity data were collected at $T = 293$ K on Enraf-Nonius CAD4 diffractometer, Mo Kα ($\lambda = 0.7107$ Å), $\mu = 5.268$ mm^{-1}. Total 12640 reflections were measured up to $\theta_{max} = 25°$, of which 12282 unique, $R_{int} = 0.1050$. The structure was solved by direct method (SHELXS-97) and refined against F^2 in anisotropic approximation (SHELXL-97). Final residuals are: R1 = 0.0689, wR2 = 0.1610 for 3388 $F_{hkl} \geq 4\sigma(F)$, R1 = 0.1777, wR2 = 0.2235, GOF = 0.744 for all unique data.

A dark green plate (0.20 × 0.09 × 0.02 mm^3) of **2** was mounted at the end of glass fiber. Intensity data were collected at $T = 160$ K on Bruker SMART CCD diffractometer, MoKα ($\lambda = 0.71073$ Å), $\mu = 1.317$ mm^{-1}. Total 19815 reflections were measured up to $\theta_{max} = 28.6°$,

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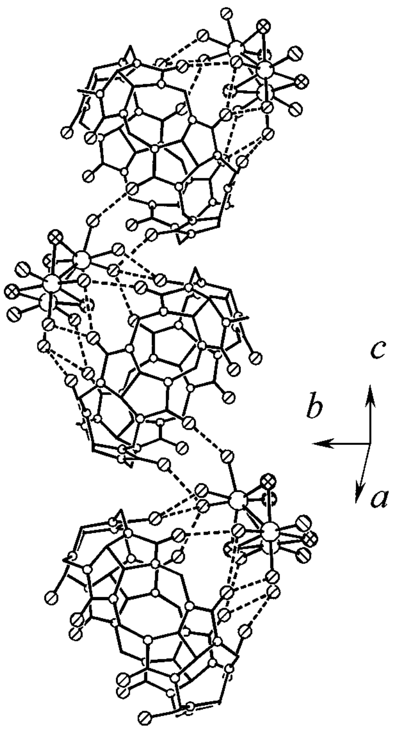

Figure 2. Structure of $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}_n^{2n+}$ polymeric chain in **1**. All hydrogen atoms, chloride ions, and water molecules in the lattice are omitted for clarity. Hydrogen bonding interactions are indicated by dashed lines.

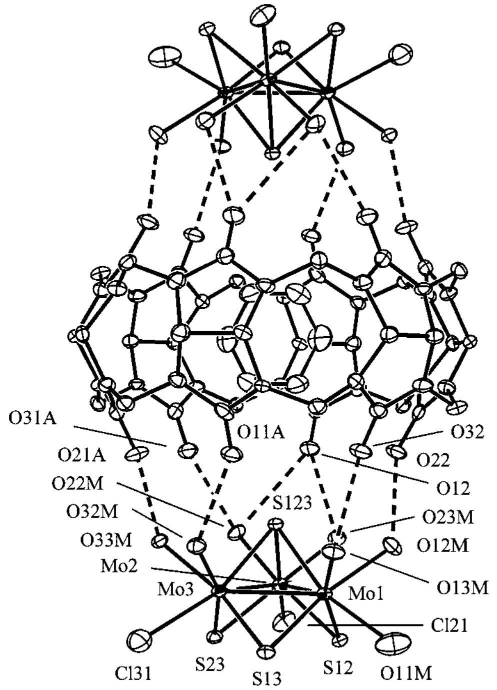

Figure 3. Drawing of $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH)(C_{36}H_{36}N_{24}O_{12})\}^{4+}$ in **2**, with partial atom-numbering scheme. Thermal ellipsoids are given with 50% probability. The cucurbituril molecule has a crystallographically impose inversion center. Disordered position O11M = 1/2Cl + 1/2O. Disordered position of 5/6C + 1/6N in the pyridine molecule are not distinguished. Hydrogen atoms are omitted for clarity. Hydrogen bonding interactions are indicated by dashed lines.

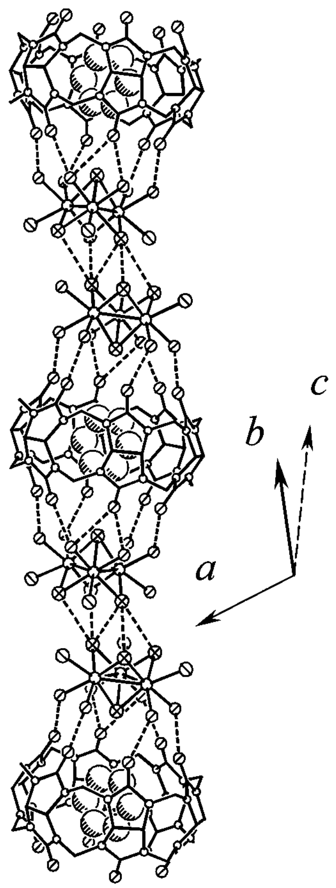

Figure 4. Structure of $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH)(C_{36}H_{36}N_{24}O_{12})\}_n^{4n+}$ polymeric chain in **2**. All hydrogen atoms, chloride ions, and water molecules in the lattice are omitted for clarity. Hydrogen bonding interactions and S···S interactions are indicated by dashed lines.

of which 10584 unique ($R_{\mathrm{int}} = 0.0374$). The structure was solved by direct method and refined against F^2 in anisotropic approximation (SHELXTL). One of the terminal chlorine atoms on Mo appeared to be disordered with H_2O with 1:1 ratio corresponding with coexistence of two cluster cations in the same crystallographic position, $[Mo_3S_4(H_2O)_6Cl_3]^+$ and $[Mo_3S_4(H_2O)_7Cl_2]^{2+}$. The final residuals are: R1 = 0.0508, wR2 = 0.1350 for 6752 $F_{hkl} \geq 4\sigma(F)$, R1 = 0.0936, wR2 = 0.1479, GOF = 1.043 for all unique data.

Crystallographic information for **1** and **2** can be found in Table 1. Bond distances and angles can be found in Tables 2 and 3.

Results and Discussion

The triangular cluster aqua ions $[M_3(\mu_3\text{-E})(\mu_2\text{-E})_3\ (H_2O)_9]^{4+}$ (M = Mo, W; E = O, S, Se) and macrocyclic cavitand cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) can be regarded as promising building blocks in the construction of supramolecular assemblies: six cis to the core μ_3-E coordinated H_2O molecules of $[M_3(\mu_3\text{-E})(\mu_2\text{-E})_3\ (H_2O)_9]^{4+}$ (hydrogen bond donors) complementary to six cucurbituril portal oxygen atoms (acceptors). The shape and symmetry of the building blocks can induce specific crystal structures.

Blue crystals of $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl_2{\cdot}10H_2O$ (**1**) were obtained in 42% yield by reaction of cucurbituril with 1 equiv of $[W_3S_4(H_2O)_9]^{4+}$ in 2.5 M HCl aqueous solution. The X-ray structure of **1** reveals a one-dimensional organic–inorganic hybrid material of alternating cucurbituril molecules and $[W_3S_4(H_2O)_7Cl_2]^{2+}$ cations assembled through hydrogen bonds (Figure 1, 2). There are two coordinated Cl^- on the $[W_3S_4(H_2O)_7Cl_2]^{2+}$ cation which are trans to the core μ_3-S. Each tungsten atom of the cation in **1** is coordinated by two water molecules in cis position to the core μ_3-S. These six cis water molecules form hydrogen bonds with portal oxygen atoms of cucurbituril (O···O, 2.638–2.826 Å) (Figure 1). A trans water molecule (O31M) and cis water molecule (O32M) bound to one of the tungsten atoms (W3) of the triangular cluster form hydrogen bonds to portal oxygen atoms of adjacent cucurbituril (O···O, 2.644 and 2.812 Å) resulting in formation of robust infinite chains running along the *c* axis (Figure 2).

Green crystals of $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH)(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 17H_2O$ (**2**) were obtained in high yield when pyridine was added to the reaction mixture of cucurbituril and 2 equiv of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.5 M HCl aqueous solution. The FT-IR spectrum of **2** clearly shows that the pyridine N atom is protonated (characteristic ν(N−H) bands at 3320 and 3171 cm^{-1}). The X-ray structure analysis reveals a PyH^+ molecule encapsulated in the cucurbituril cavity (Figure 3). The binding of the guest molecule is controlled by effective blocking of two portals of the molecular container.[7] Each portal of cucurbituril in **2** is effectively covered with cluster ions such as a "lid" on a "barrel". Six water molecules in cis position to the core μ_3-S form hydrogen bonds with portal oxygen atoms of cucurbituril (O···O, 2.648−2.731 Å). The cavity of the cluster lidded cucurbituril is large enough to accommodate a pyridine molecule. Furthermore, cucurbituril and triangular aqua complexes form a one-dimensional supramolecular assembly in the solid state in which lidded cucurbituril molecules stack atop one another through noncovalent S···S (2.984−3.330 Å) interactions between two adjacent clusters (Figure 4). The observed S···S distances are substantially shorter than the sum of van der Waals radii (∼3.6 Å) and intramolecular distances of 3.37 Å between pairs of μ_2-S atoms in the same cluster cation. This phenomenon has been already found in the crystal structures of other M_3E_4 complexes.[8] Supramolecular chains form layers in the *yz* plane. The interchain space is filled with chloride anions and water molecules that form a complicated hydrogen-bonding network among themselves. No pyridine molecules are found in the channels.

The supramolecules **1** and **2** are rather stable. They are insoluble in water or hydrochloric acid.

Conclusion

We present two examples of a new family of supramolecular assemblies based on cucurbituril adducts of hydrogen-bonded molybdenum and tungsten incomplete cuboidal aqua complexes. The novel molecular container assemblies are capable of encapsulation of guest molecules in solution. We are continuing to investigate supramolecular assemblies based on cucurbituril adducts of other hydrogen-bonded transition metal cluster aqua complexes (homo- and heterometallic).

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Supporting Information Available: Experimental details of X-ray crystal structure determination, tables of X-ray data collection/refinement parameters, atomic position parameters, and anisotropic displacement parameters for **1**, **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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