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Supramolecular Assemblies Based on Cucurbituril Adducts of Hydrogen-Bonded Cubane-Type Molybdenum−Nickel Sulfide Aqua Complexes

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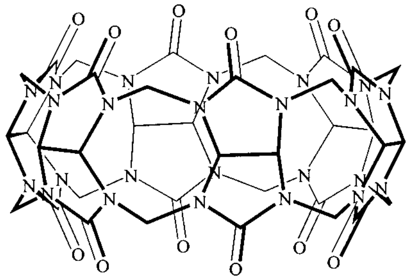
The chemistry of heterometallic sulfide-bridged cuboidal cluster complexes of molybdenum and tungsten is very rich and attracted much attention in the past decade. Compounds of this type are unusually stable and can be used as structural and functional models for bioclusters and transition metal sulfide-based hydroprocessing catalysts. [1,2]

Cubane-type mixed metal cluster complexes $[M_3NiS_4(H_2O)_{10}]^{4+}$ (M = Mo, W) were obtained by incorporating nickel into well-characterized, incomplete cuboidal $[M^{IV}{}_3S_4(H_2O)_9]^{4+}$ cluster cations in a solution of HCl.[3] The complexes are highly reactive toward carbon monoxide, ethylene, and acetylene in aqueous or organic solvents. For instance, the CO uptake on the nickel site of the $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ cluster cation is 1:1 at 25 °C and a CO partial pressure of 1 atm.[4] The cubane-type mixed-metal cluster cation $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ was incorporated into zeolites by ion exchange, which lead to catalysts for benzothiophene hydrodesulfurization [5] as well as to catalysts which are highly selective for the formation of C_2 species from CO and H_2.[6] The isolation of cubane-type mixed metal cluster complexes as hydrolytically stable solid-state materials and their further application to heterogeneous catalysis continues to be a challenging problem.

Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) is a macrocyclic cavitand with D_{6h} symmetry; it has two identical portals decorated by carbonyl groups.[7a]



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Kim and co-workers demonstrated that cucurbituril coordinates alkali metal cations in aqueous solution; they obtained cucurbituril species complexed with Na^+, Rb^+, and Cs^+ cations, which possess unique structures and reactivities.[8] Aliphatic and aromatic ammonium cations also show a high affinity toward cucurbituril due to the strong electrostatic interactions between the ammonium ions and the carbonyl oxygen atoms at the portals of the cucurbituril molecule.[9] The rational design of supramolecular assemblies, based on cucurbituril adducts of hydrogen-bonded incomplete cuboidal and heterometal double cube aqua cluster complexes of molybdenum and tungsten, were recently reported.[10]

We report the synthesis and X-ray single crystal structure analysis of two hydrolytically stable solid-state supramolecular compounds obtained from the $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ cluster cation and the organic cavitand cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) in aqueous solutions of HCl.

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Table 1. Crystallographic Data for $\{[Mo_3S_4Ni(H_2O)_7Cl_3](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 13H_2O$ (**1**) and $\{[Mo_3S_4Ni(H_2O)_8Cl_2][PyH \subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3 \cdot 14.5H_2O$ (**2**)

	1	**2**
formula	$C_{36}H_{76}Cl_4Mo_3N_{24}NiO_{32}S_4$:	$C_{41}H_{87}Cl_5Mo_3N_{25}NiO_{34.5}S_4$:
fw	1973.78	2134.38
space group	*Cc*	$P2_1/n$
Z	4	4
a, Å	20.579(3)	20.819(21)
b, Å	14.405(2)	14.956(9)
c, Å	24.407(4)	24.148(12)
β, deg	103.35(3)	92.53(6)
V, Å^3	7039.9(18)	7511.6(96)
D(calc), g$\cdot$cm^{-3}	1.862	1.887
temp, K	233(2)	293(2)
λ	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
μ, mm^{-1}	1.158	1.13
total number of reflections	7389	5639
observed reflections ($I > 2\sigma(I)$)	5901	2289
R1[a]	0.0803	0.0548
wR2[b]	0.2057	0.1285

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

Experimental Section

Syntheses. The starting materials, i.e., cucurbituril decahydrate[7] and the cluster cation $[Mo_3S_4Ni(H_2O)_9]^{4+}$ in a 3M HCl solution[3a], were prepared according to published methods. All the steps were carried out in air.

$\{[Mo_3S_4Ni(H_2O)_7Cl_3](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 13H_2O$ (1). A total of 2.00 mL of 50 mM $[Mo_3S_4Ni(H_2O)_9]^{4+}$ (0.100 mmol) in 3M HCl was added to a solution of cucurbituril decahydrate (0.0589 g, 0.050 mmol) in 10 mL of 3 M HCl. The final solution was mixed thoroughly and left at room temperature for 7 days. Green plate crystals of **1**, suitable for crystallographic measurements, formed and were filtered off and dried in air for 2 h. Yield: 0.012 g (12%). Anal. Calcd for $C_{36}H_{76}Cl_4Mo_3N_{24}NiO_{32}S_4$: C, 21.91; H, 3.88; Cl, 7.19; N, 17.03; S, 6.50. Found: C, 20.78: H, 3.66; Cl, 7.17; N, 16.97; S, 6.40.

$\{[Mo_3S_4Ni(H_2O)_8Cl_2][PyH \subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3 \cdot 14.5H_2O$ (2). A total of 5.00 mL of 50 mM $[Mo_3S_4Ni(H_2O)_9]^{4+}$ (0.250 mmol) in 3 M HCl and pyridin (0.0395 g, 0.500 mmol) were added to a solution of cucurbituril decahydrate (0.147 g, 0.125 mmol) in 25 mL of 3 M HCl. The final solution was mixed thoroughly and left at room temperature for 2 days. Green plate crystals of **2**, suitable for crystallographic measurements, formed and were filtered off and dried in air for 2 h. Yield: 0.235 g (88%). Anal. Calcd for $C_{41}H_{87}Cl_5Mo_3N_{25}NiO_{34.5}S_4$: C, 23.07; H, 4.11; Cl, 8.31; N, 16.41; S, 6.01. Found: C, 23.37; H, 3.69; Cl, 9.01; N, 16.84; S, 6.17.

X-ray Crystallography. A dark-green plate (0.088 × 0.12 × 0.38 mm^3) of **1** was selected under paraffin oil and mounted at the end of a glass capillary. Intensity data were collected at 233 K on a Siemens SMART CCD diffractometer (Mo Kα ($\lambda = 0.71073$ Å), $\mu = 1.158$ mm^{-1}). A total of 19 703 reflections were measured up to $\theta_{max} = 23.28°$, of which 7389 were unique ($R_{int} = 0.0965$). An empirical absorption correction was performed with SADABS.[11] To solve the structure (direct methods), a refinement with full matrix least squares on F^2 and molecular graphics, the Siemens program package SHELXTL Version 5 was used.[12] The data set of the weakly diffracting crystal did not enable a refinement with anisotropic displacement parameters for all atoms. Therefore, all the atoms, with the exception of Mo, Ni, S, and Cl, were refined with isotropic displacement parameters. All the hydrogen atoms in the cucurbituril molecule were placed at calculated positions and refined (riding model [12]) with different isotropic thermal displacement parameters for each group. Hydrogen atoms in the water molecules could not be found in the difference Fourier map and were not included in the refinement. Several disordered water molecules were described as being partially occupied oxygen atoms. The measured crystal turned out to be twinned and was treated accordingly as an inversion twin (volume ratio of 0.58:0.42).

Table 2. Selected Bond Distances (Å) in $[Mo_3S_4Ni(H_2O)_7Cl_3](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 13H_2O$ (**1**)

bond distances			
Mo(3)−O(2W3)	2.210(15)	Mo(1)−S(1)	2.329(5)
Mo(3)−O(1W3)	2.216(15)	Mo(1)−Cl(3)	2.467(5)
Mo(3)−S(2)	2.322(5)	Mo(1)−Ni(1)	2.645(3)
Mo(3)−S(4)	2.325(5)	Mo(1)−Mo(2)	2.7287(19)
Mo(3)−S(3)	2.348(5)	Mo(2)−O(1W2)	2.180(18)
Mo(3)−Cl(2)	2.509(6)	Mo(2)−O(3W2)	2.205(13)
Mo(3)−Ni(1)	2.647(3)	Mo(2)−O(2W2)	2.239(14)
Mo(3)−Mo(2)	2.742(2)	Mo(2)−S(4)	2.313(6)
Mo(3)−Mo(1)	2.754(2)	Mo(2)−S(1)	2.317(5)
Mo(1)−O(2W1)	2.172(12)	Mo(2)−S(3)	2.339(5)
Mo(1)−O(1W1)	2.245(13)	Mo(2)−Ni(1)	2.651(2)
Mo(1)−S(2)	2.321(6)	Ni(1)−S(1)	2.194(6)
Mo(1)−S(3)	2.328(5)	Ni(1)−S(2)	2.199(6)
Ni(1)−S(4)	2.204(6)	Ni(1)−Cl(1)	2.238(6)

The dark-green crystals of **2** were unstable due to loss of sorbed solvent water; the selected prismatic crystal (0.40 × 0.30 × 0.20 mm^3) was sealed in a glass capillary together with the liquid phase from which it was crystallized. The results of the measurements, made with a Syntex $P2_1$ diffractometer, are summarized in Table 1. The crystal structure was determined with the standard SHELXS program, while refinements were carried out with SHELX-93. Heavy atoms, i.e., Mo, Ni, S, and Cl as well as the solvent molecules (H_2O), were refined anisotropically. All the other atoms were treated isotropically, and hydrogen positions were calculated from stereochemical considerations. No antibumping restraints were necessary for the solvent molecules in the crystal, but only one of the three Cl^- anions, required for charge balance, could be identified unequivocally. The remaining two were distributed over several solvent positions with the lowest displacement parameters, and the occupancy factors were constrained in order to obtain the two required Cl^- anions.

Crystallographic information about compounds **1** and **2** is listed in Table 1 and selected bond distances in Tables 2 and 3.

Results and Discussion

Compounds **1** and **2** are the first examples of hydrolytically stable, supramolecular architectures based on cucurbituril adducts of single-cube Ni−Mo aqua cluster cations. The cuboidal heterometal cluster cations of $[Mo_3(\mu_3\text{-}S)_4Ni(H_2O)_{10}]^{4+}$ have a molecular C_3 axis. Six of the coordinated water molecules (H-donors) are in cis positions with respect to the μ_3-S cap of the

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(11) Sheldrick, G. *SADABS*; Göttingen, 1997.

(12) *SHELXTL* program package, version 5.1; Bruker AXS, Inc.: Madison, WI.

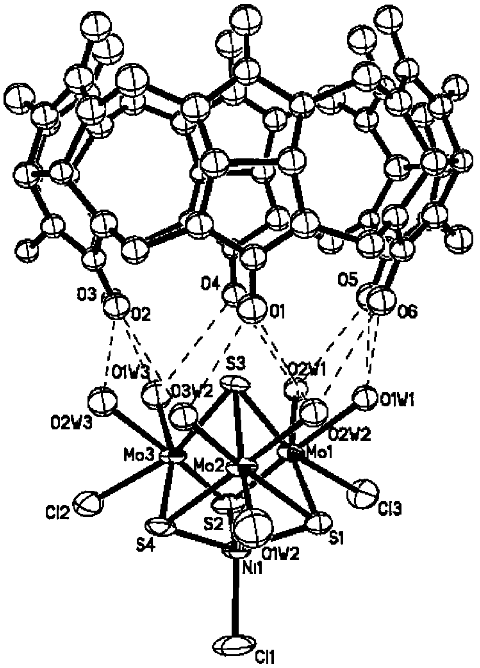

Figure 1. $\{[Mo_3S_4Ni(H_2O)_7Cl_3](C_{36}H_{36}N_{24}O_{12})\}^+$ in **1** with partial atom-numbering scheme. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted for clarity. Hydrogen bonding interactions are indicated by dashed lines.

Mo_3 fragment and are complementary to six portal oxygen atoms (acceptors) of the cucurbituril molecule. Crystallization is thus facilitated by the formation of H-bonded supramolecular aggregates.

Dark-green crystals of $\{[Mo_3S_4Ni(H_2O)_7Cl_3](C_{36}H_{36}N_{24}O_{12})\}Cl\cdot 13H_2O$ (**1**) were obtained in low yield (12%) by the reaction of cucurbituril with $[Mo_3S_4Ni(H_2O)_{10}]^{4+}$ in a 3 M aqueous solution of HCl. The X-ray structure of **1** reveals an organic–inorganic hybrid material of cucurbituril molecules and $[Mo_3S_4Ni(H_2O)_7Cl_3]^+$ cluster cations in a ratio of 1:1, assembled through strong hydrogen bonds (Figure 1). One Cl^- ligand is attached to the Ni center, while the other two Cl^- ligands are coordinated to Mo. The main geometrical parameters of the $\{Mo_3S_4Ni\}$ cluster core in **1** (Table 2) are essentially identical with those of the pure aqua ion $[Mo_3S_4Ni(H_2O)_{10}]^{4+}$ in the *p*-toluenesulfonate salt $[Mo_3S_4Ni(H_2O)_{10}](CH_3C_6H_4SO_3)_4\cdot 7H_2O$[3a]. Each Mo center in **1** is coordinated by two water molecules in the cis position to the μ_3-S(3) cap of the Mo_3 arrangement. These six water molecules form hydrogen bonds with six portal oxygen atoms of cucurbituril ($d(O\cdots O) = 2.616(19) - 2.996(19)$ Å, Figure 1). The Ni–Mo cluster cation and the cucurbituril molecule are held together by complementary H-bonds to form a structure in which only one of the portals of the cucurbituril molecule is effectively covered with the cluster ions to resemble a “lid” on a “barrel”.

Dark-green crystals of $\{[Mo_3S_4Ni(H_2O)_8Cl_2][PyH\subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3\cdot 14.5H_2O$ (**2**) were obtained in very high yield (88%) when pyridine was added to the reaction mixture of cucurbituril and 2 equiv of $[Mo_3S_4Ni(H_2O)_{10}]^{4+}$ in a 3 M aqueous solution of HCl.

First, we studied the interaction of PyH^+ cations with cucurbituril in a 4 M solution of DCl in D_2O (this concentration was selected to increase the solubility of cucurbituril). The formation of the inclusion compound $[PyH\subset C_{36}H_{36}N_{24}O_{12}]^+$ in solution was monitored by ^1H NMR spectroscopy. The addition of 4 equiv of pyridine to a solution of cucurbituril in 4 M DCl/D_2O at 300 K causes very broad signals to appear at $\delta = 8.94$, 9.49, and 9.65 ppm, which shift to low field ($\Delta\delta = 0.7-0.8$ ppm) compared with the signals of the PyD^+ cation in 4 M DCl/D_2O (Figure 2). This suggests that the aromatic ring is encapsulated in the cavity of “nonlidded” cucurbituril and that a fast exchange occurs between free and bound guest species with respect to the NMR time scale.

After adding the $[Mo_3S_4Ni(H_2O)_{10}]^{4+}$ cluster cation, single crystals of **2** were isolated from the solution. The X-ray structure analysis of **2** reveals a PyH^+ cation encapsulated in the cucurbituril cavity (Figure 3).[13] Only one of the portals of the

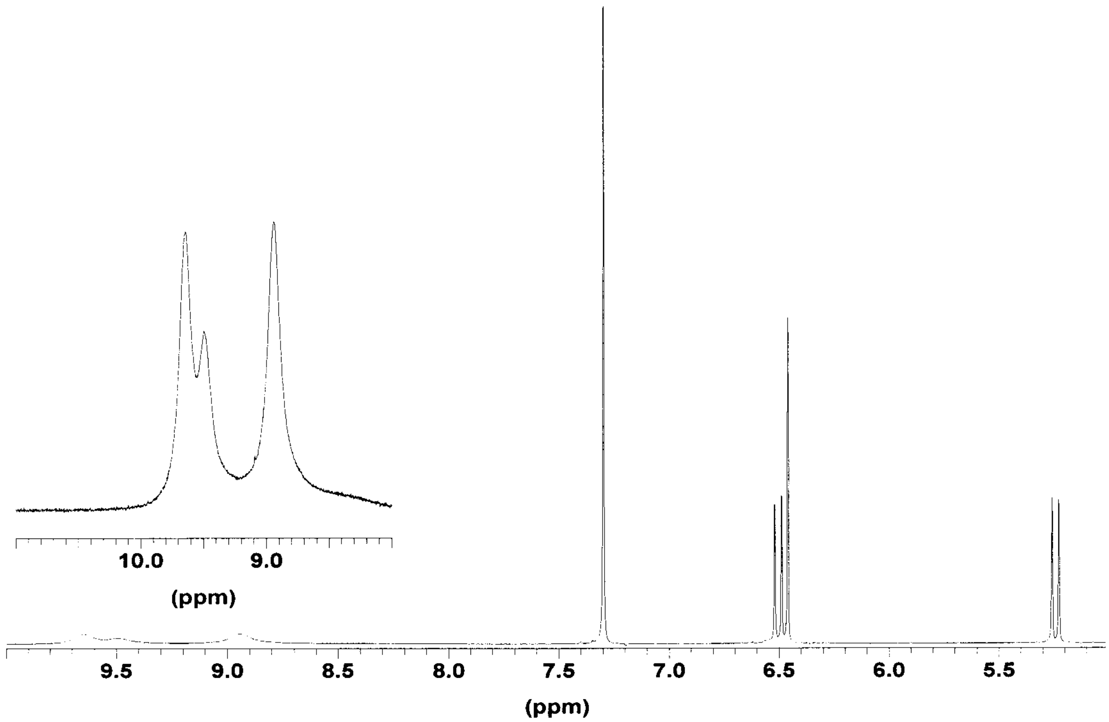

Figure 2. ^1H NMR spectrum of cucurbituril (30mM) and pyridine (130 mM) in 4 M DCl/D_2O at 300 K (Avance 500, Bruker).

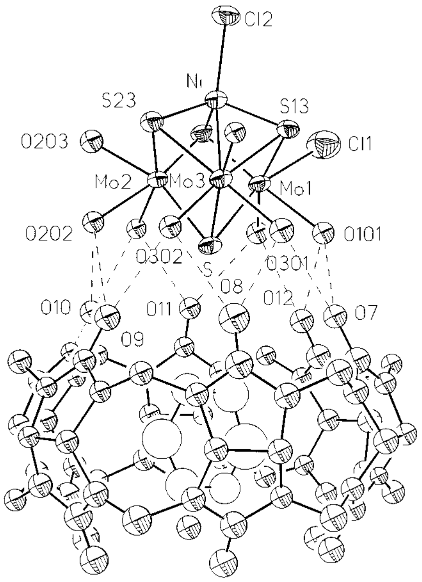

Figure 3. $\{[Mo_3S_4Ni(H_2O)_8Cl_2][PyH\subset C_{36}H_{36}N_{24}O_{12}]\}^{3+}$ in **2**, with partial atom-numbering scheme. Thermal ellipsoids are given with 50% probability. Disordered positions of 5/6C + 1/6N in the pyridine molecule are not distinguished. Hydrogen atoms are omitted for clarity. Hydrogen bonding interactions are indicated by dashed lines.

Table 3. Selected Bond Distances (Å) in $\{[Mo_3S_4Ni(H_2O)_8Cl_2][PyH\subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3{\cdot}14.5H_2O$ (**2**)

bond distances			
Mo(1)−O(101)	2.187(11)	Mo(3)−S	2.323(6)
Mo(1)−O(102)	2.241(11)	Mo(3)−Ni	2.652(3)
Mo(1)−S(13)	2.317(6)	Mo(3)−Mo(2)	2.719(3)
Mo(1)−S(12)	2.320(5)	Mo(2)−O(201)	2.188(11)
Mo(1)−S	2.326(5)	Mo(2)−O(203)	2.202(11)
Mo(1)−Cl(1)	2.448(7)	Mo(2)−O(202)	2.211(11)
Mo(1)−Ni	2.637(3)	Mo(2)−S(23)	2.305(6)
Mo(1)−Mo(2)	2.752(3)	Mo(2)−S	2.317(5)
Mo(1)−Mo(3)	2.752(3)	Mo(2)−S(12)	2.322(6)
Mo(3)−O(302)	2.176(11)	Mo(2)−Ni	2.645(4)
Mo(3)−O(301)	2.212(12)	Ni−S(13)	2.175(6)
Mo(3)−O(303)	2.248(11)	Ni−S(23)	2.185(6)
Mo(3)−S(13)	2.306(6)	Ni−S(12)	2.195(6)
Mo(3)−S(23)	2.317(5)	Ni−Cl(2)	2.222(6)

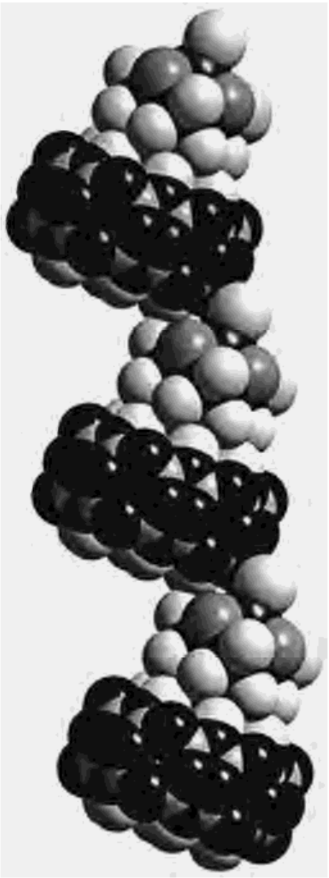

Figure 4. Structure of the $\{[Mo_3S_4Ni(H_2O)_8Cl_2](PyH\subset C_{36}H_{36}N_{24}O_{12})\}_n^{3n+}$ polymeric chain in **2**. All hydrogen atoms, chloride ions, and water molecules in the lattice are omitted for clarity.

cucurbituril molecule in **2** is effectively covered with a cluster cation $[Mo_3S_4Ni(H_2O)_8Cl_2]^{2+}$ in which one Cl^- ligand is attached to the Ni center and the other to Mo (Mo(1) in Figure 3). Again, as in compound **1**, six water molecules in the cis position to the μ_3-S cap of the Mo_3 moiety form hydrogen bonds with the portal oxygen atoms of cucurbituril. The cavity of the cluster-lidded cucurbituril molecule is large enough to accommodate a PyH^+ cation. Furthermore, a water molecule in the trans position (O(203)), bound to one of the Mo centers (Mo(2)) of the cluster, forms a strong hydrogen bond with a portal oxygen atom of an adjacent cucurbituril (d(O(203)···O(1A)) = 2.60(3) Å, symmop for O(1A): x, $1 + y$, z), resulting in the formation of chains in the crystal structure of **2** (Figure 4). 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 interchain space of **2**.

The supramolecules **1** and **2** are hydrolytically stable and are insoluble, even in boiling water or 3 M HCl solution.

Supporting Information Available: An X-ray crystallographic file in CIF format of the structure determinations of $\{[Mo_3S_4Ni(H_2O)_7Cl_3](C_{36}H_{36}N_{24}O_{12})\}Cl{\cdot}13H_2O$ (**1**) and $\{[Mo_3S_4Ni(H_2O)_8Cl_2][PyH\subset C_{36}H_{36}N_{24}O_{12}]\}Cl_3{\cdot}14.5H_2O$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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