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Metal Incorporation into and Dimerization of $\mathrm{M_3E_4}$ Clusters (M = Mo, W; E = S, Se) in Supramolecular Assemblies with Cucurbituril: A Molecular Model of Intercalation[**]

Maxim N. Sokolov, Alexander V. Virovets,
Danil N. Dybtsev, Olga A. Gerasko, Vladimir P. Fedin,[*]
Rita Hernandez-Molina, William Clegg, and
A. Geoffrey Sykes[*]

Incorporation of transition and post transition elements M′ into trinuclear $\mathrm{M_3^{IV}}$ incomplete cuboidal clusters $[\mathrm{M_3E_4(H_2O)_9}]^{4+}$ (M = Mo, W; E = S, Se), first reported in 1986,[1] has developed into a field of considerable research interest.[2, 3] The most fascinating aspect is that the zero oxidation state heteroatom can in many cases be used as the source of M′. Thus with $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$, direct incorporation of Hg, Ga, In, Tl, Sn, Pb, Sb, Bi, Fe, Co, Ni, Cu, and Pd has been achieved.[3] Characterization has, however, remained a serious problem, and in many cases, in particular with the highly charged double cubes (e.g. M′ = Hg, In, Sn, Sb), crystallization has only been possible as the pts⁻ salt of the aqua ion $[\mathrm{Mo_6M'S_8(H_2O)_{18}}](\mathrm{pts})_8 \cdot x\,\mathrm{H_2O}$ (pts⁻ = *p*-toluenesulfonate).[2, 4, 5] This may also be regarded as a supramolecular approach, since the pts⁻ ion is responsible for hydrogen bonding which holds the structure together.

Here we report rational syntheses of examples of a potentially rich and versatile class of supramolecular structures based on cucurbituril adducts. These can be prepared with the trinuclear clusters and heterometal-containing double cubes obtained as derivatives of $[\mathrm{M_3E_4(H_2O)_9}]^{4+}$. Both the trinuclear and double cube products have a molecular C_3 axis. Cucurbituril ($\mathrm{C_{36}H_{36}N_{24}O_{12}}$) is a macrocyclic cavitand with D_{6h} symmetry, having two identical carbonyl-fringed portals.[6] We have identified as potential hydrogen-bond donors six coordinated water molecules, *cis* to the unique μ_3-E group capping the triangle of Mo or W atoms, as complementary to six cucurbituril portal oxygen acceptor atoms. Crystallization should therefore be facilitated by the formation of hydrogen-bonded supramolecular aggregates. Coordination of cucurbituril to Na⁺, Rb⁺, and Cs⁺ has been reported.[7] Also, aliphatic and aromatic ammonium ions show high affinity towards cucurbituril.[8]

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[*] Prof. V. P. Fedin, Dr. M. N. Sokolov, Dr. A. V. Virovets, D. N. Dybtsev, Dr. O. A. Gerasko
Institute of Inorganic Chemistry
Russian Academy of Sciences
pr. Lavrentjeva 3, Novosibirsk 630090 (Russia)
Fax: (+7)3832-344489
E-mail: cluster@che.nsk.su

Prof. A. G. Sykes, Dr. R. Hernandez-Molina, Prof. W. Clegg
Department of Chemistry
The University of Newcastle
Newcastle upon Tyne, NE1 7RU (UK)
Fax: (+44)0191-261-1182
E-mail: A.G.Sykes@newcastle.ac.uk

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Crystals of $[M_6HgE_8(H_2O)_{14}Cl_4](C_{36}H_{36}N_{24}O_{12})Cl_4 \cdot 14\,H_2O$, where the double cube component can be written as $[\{M_3E_4(H_2O)_7Cl_2\}_2Hg]^{4+}$ (M = Mo, E = S (**1**); M = Mo, E = Se (**2**); M = W, E = Se (**3**)), have been prepared by reaction of $[M_3E_4(H_2O)_9]^{4+}$ with metallic Hg in hydrochloric acid and further crystallization in the presence of cucurbituril.[9, 10] X-ray single-crystal analyses have revealed that **1**,[11] **2**,[12] and **3**[13] are isostructural and have cluster cations $[M_6HgE_8(H_2O)_{14}Cl_4]^{4+}$ sandwiched between two cucurbituril units; the cation and cucurbituril are held together by complementary hydrogen bonds (O···O, 2.665–2.768 Å for **1**; O···O, 2.679 Å–2.797 Å for **2**) to form an infinite chain structure (Figure 1 a). The Hg–S distances in **1** are unusually long, with two at 2.768(2) Å and four longer at 2.903(2) Å. This is in good agreement with the value of 2.84(12) Å reported for $[Mo_6HgS_8(H_2O)_{18}](pts)_8 \cdot 20\,H_2O$.[2] In the closest structural analogue of **1**, $[Hg([9]\text{-ane}S_3)_2]^{2+}$,[14] the six Hg–S distances vary between 2.638(3) and 2.728(3) Å, and this seems to be the upper limit for Hg^{II}–S bond lengths ([9]-aneS_3 = 1,4,7-trithiacyclononane). This means that upon formation of the heterometallic double cube Hg retains a large part of its formal Hg^0 oxidation state.[14] The Hg–Se distances in **2** vary between 2.795(1) and 2.9683(9) Å. The chlorides are all *trans* in respect to the unique μ_3-E (capping Mo_3) so that on each Mo_3E_4 unit two chlorides are disordered between the three available positions.

The most striking feature of **1**–**3** is that they are isostructural with the cucurbituril assembly incorporating the incomplete cuboidal dimer adduct, $[\{W_3Se_4(H_2O)_8Cl\}_2](C_{36}H_{36}N_{24}O_{12})Cl_6 \cdot 12\,H_2O$ (**4**).[15] Here dimeric aggregates $(W_3Se_4)_2$, held together by rather short (compared to the sum of the van der Waals radii) Se···Se interactions (3.617–3.740 Å), are embedded between cucurbituril molecules (O···O, 2.719–2.779 Å) in exactly the same way as are heterometallic double cubes **1**–**3**, (Figure 1). Such dimeric aggregates have been reported previously for $[W_3Se_4(NCS)_9]^{5-}$, $[W_3Se_4(CN)_9]^{5-}$, as well as for other M_3E_4 derivatives (M = Mo, W; E = S, Se).[16] Moreover, in binary ME_2 chalcogenides of the early transition metals the chalcogen atoms of the neighboring layers interact with each other in the same way. Metal atoms and small molecules can intercalate between the layers.[17] Thus the structures of **1**–**3**, and of **4**, are formally related as those of a matrix and of an intercalate. This means that the two W_3Se_4 trinuclear units, sandwiched between two cucurbituril molecules in **4**, mimic rather closely two neighboring layers EME···EME in solid ME_2 (in which M_3 units may be regarded as building blocks). This result shows that solid-state chemistry is related to the chemistry of small molecular clusters in a more intimate way than might have been expected. Even secondary effects such as specific noncovalent attractions between chalcogen atoms are important structure-organizing factors, both for solid-state materials like binary chalcogenides, and for packing together of smaller discrete clusters like M_3E_4.

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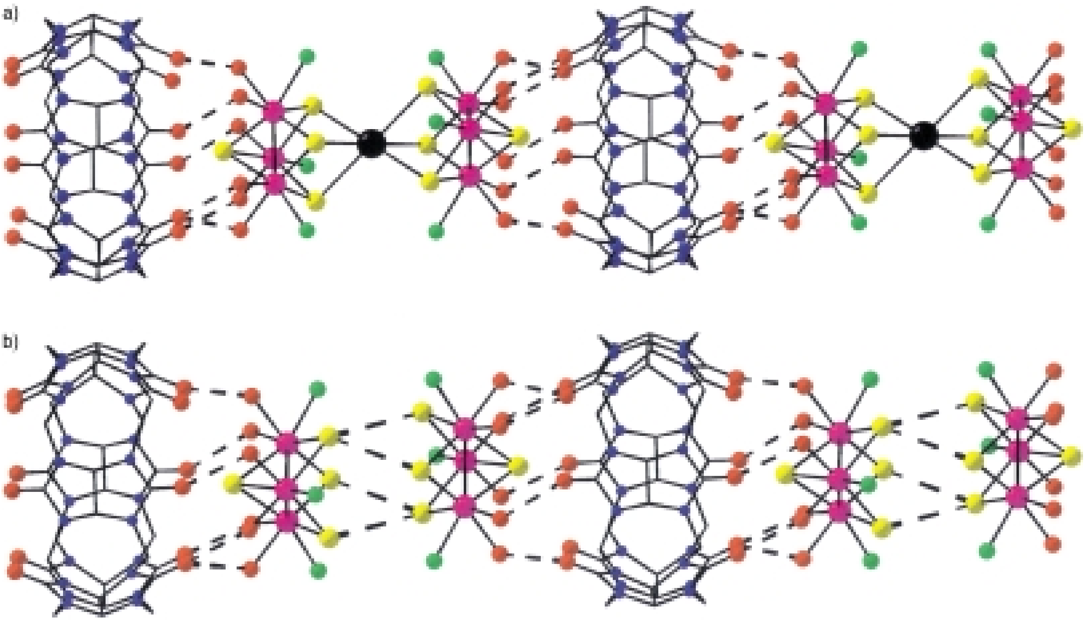

Figure 1. a) Structure of the $[\{[Mo_3Se_4(H_2O)_7Cl_2]_2Hg\}(C_{36}H_{36}N_{24}O_{12})]_n^{4n+}$ polymeric chain in **2**. All hydrogen atoms, chloride ions, and water molecules in the lattice are omitted for clarity. Hydrogen-bonding interactions are indicated by dashed lines; Hg: black; Mo: purple; Se: yellow; O: red; disordered position of ⅔Cl + ⅓O: green; N: blue; C: no spheres. Main bond distances (Å): Mo–Mo, 2.762(1)–2.799(1); Mo–Se, 2.415(1)–2.460(1); Hg–Se, 2.795(1)–2.9683(9). b) Structure of the $[\{W_3Se_4(H_2O)_8Cl\}_2(C_{36}H_{36}N_{24}O_{12})]_n^{6n+}$ polymeric chain in **4**. All hydrogen atoms, chloride ions, and water molecules in the lattice are omitted for clarity. Hydrogen-bonding interactions and Se···Se interactions are indicated by dashed lines; W: purple; Se: yellow; O: red; disordered position of ⅓Cl + ⅔O: green; N: blue; C: no spheres.

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[10] The Se analogues **2** and **3** were prepared similarly. Satisfactory analytical data (C, H, N, Cl) were obtained.

[11] Crystal data for **1**:[18] Crystal dimensions $0.12 \times 0.10 \times 0.06 mm^3$, monoclinic, space group $C2/m$, $a = 16.775(1)$, $b = 18.298(1)$, $c = 15.268(1)$ Å, $\beta = 102.128(1)^\circ$, $V = 4581.9(5)$ Å^3, $\rho_{calcd} = 2.042 g cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 160$ K, total/unique reflections 18445/5645 collected with Bruker SMART CCD diffractometer, $R_{int} = 0.0644$. Final refinement converged with $R_1 = 0.0450$ for 3399 reflections with $F_o \geq 4\sigma(F_o)$ and $wR_2 = 0.1197$ for all reflections.

[12] Crystal data for **2**:[18] Crystal dimensions $0.14 \times 0.08 \times 0.04 mm^3$, monoclinic, space group $C2/m$, $a = 16.832(2)$, $b = 18.340(2)$, $c = 15.287(2)$ Å, $\beta = 101.842(2)^\circ$, $V = 4619(1)$ Å^3, $\rho_{calcd} = 2.296 g cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 160$ K, total/unique reflections 14341/5631 collected with Bruker SMART CCD diffractometer, $R_{int} = 0.0646$. Final refinement converged with $R_1 = 0.0476$ for 3226 reflections with $F_o \geq 4\sigma(F_o)$ and $wR_2 = 0.1218$ for all reflections.

[13] Due to insufficient size of the crystals only cell parameters could be determined for **3**: $a = 16.705(7)$, $b = 18.382(9)$, $c = 15.268(9)$ Å, $\beta = 101.93(4)^\circ$, $V = 4578(6)$ Å^3.

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[15] a) Preparation of **4**: To a saturated (about 5 mM) solution of cucurbituril in 2.5 M HCl (3 ml), a 10 mM solution of $[W_3Se_4(H_2O)_9]^{4+}$ in 2.5 M HCl (3 ml) was added. The mixture was stirred and left for 4 d at room temperature. Dark green crystals suitable for X-ray analysis were obtained (yield 72%). Elemental analysis (%): calcd for $[\{W_3Se_4(H_2O)_8Cl\}_2](C_{36}H_{36}N_{24}O_{12})Cl_6 \cdot 12H_2O$: C 12.29, H 2.63, N 9.55, Cl 8.06; found: C 12.18, H 2.75, N 9.30, Cl 8.10. b) Crystal data for **4**:[18] Crystal dimensions $0.12 \times 0.05 \times 0.03 mm^3$, monoclinic, space group $C2/m$, $a = 16.825(1)$, $b = 8.558(2)$, $c = 15.167(1)$ Å, $\beta = 105.364(2)^\circ$, $V = 4566.5(6)$ Å^3, $\rho_{calcd} = 2.560 g cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 160(1)$ K, total/unique reflections 20050/5663 collected with Bruker SMART CCD diffractometer, $R_{int} = 0.0697$. Final refinement converged with $R_1 = 0.0635$ for 3558 reflections with $F_o \geq 4\sigma(F_o)$ and $wR_2 = 0.1909$ for all reflections.

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Nanoscale Super Clusters of Clusters Assembled around a Dendritic Core[**]

Neil Feeder, Junfeng Geng, Peter G. Goh, Brian F. G. Johnson,* Caroline M. Martin, Douglas S. Shephard,* and Wuzong Zhou

The construction of nanoscale molecular architectures is of considerable current interest.[1–4] The development of dendrimer-based clusters of clusters as quantum dots should provide unique advantages, for example, in the preparation of monodispersed particles with well-defined molecular structures and surface functionalities. In the course of our studies on synthesis, deposition, and ordering of platinum group clusters,[5, 6] we have prepared novel dendrimers based on an "inside-out" approach.

Here we describe the synthesis and characterization of nanoscale super clusters of clusters assembled around a dendritic core. High-resolution transmission electron microscopy (HRTEM) in conjunction with molecular modeling using force-field calculations have been employed to establish the morphology of these nanoparticles. In contrast to the "magic-number" synthesis[7] of colloids wherein metal particles are stabilized by a "passivating" external layer of organic ligands, we have used a large internal organic scaffold, $[DAB\text{-}dendr\text{-}\{N(CH_2PPh_2)_2\}_{16}]$,[8] to construct an array of sixteen clusters, thereby forming a nanoscale self-ordering molecule (DAB = diaminobutane).

Compounds **1** and **2** (Figure 1) were prepared by binding the 16[P-N-P] tridentate terminal functionalities of the organic third-generation dendritic core to cluster units $[Ru_5C(CO)_{12}]$ or $[Au_2Ru_6C(CO)_{16}]$. Both **1** and **2** show a molecular multiple-layer structure (Figure 2). They may be viewed as a sphere consisting of a nonconducting organic core with a sheath of conducting metal particles over the surface, which in turn is covered by a further outer layer of insulating carbonyl ligands. For conduction to occur, an electron introduced into the molecule would first have to tunnel through the carbonyl sheath to the "metallic layer", move through the metallic layer to an exit point, and then tunnel again out of the molecule.

$[DAB\text{-}dendr\text{-}\{N(CH_2PPh_2)_2\}_{16}(\mu_3{:}\eta^1\eta^1\eta^1\text{-}Ru_5C(CO)_{12})_{16}]$ **1**

$[DAB\text{-}dendr\text{-}\{N(CH_2PPh_2)_2\}_{16}(\mu{:}\eta^1\eta^1\text{-}Au_2Ru_6C(CO)_{16})_{16}]$ **2**

In addition to compounds **1** and **2**, we have also prepared and characterized the respective dimeric componds **3** and **4** as

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[*] Prof. B. F. G. Johnson, Dr. D. S. Shephard, N. Feeder, Dr. J. Geng, P. G. Goh, Dr. C. M. Martin, Dr. W. Zhou
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44)1223-336-337
E-mail: bfgj1@cam.ac.uk, dss1001@cam.ac.uk

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