The phase images of the copolymer on HOPG feature a particularly interesting left-handed helical shape (marked by arrows in Figure 3 d).[14] Although we could not distinguish the C_{60} and chiral pendant groups of the copolymer by using AFM, these helical-shaped images may be closely correlated to the macromolecular helical chirality of the polyphenylacetylenes. Scanning tunneling microscopy (STM) may be useful to obtain higher resolution images on HOPG and the results will give us direct information concerning the helicity of the copolymers.[15] The work is now in progress.

In summary, we have prepared and characterized the first example of an optically active helical polymer bearing pendant achiral C_{60} groups which arrange in a helical array with a predominant screw-sense along the polymer backbone. Although such a helical array of the C_{60} units, which exhibits optical activity in the fullerene chromophore region, is presently possible at low temperatures, we believe that the rational design and synthesis of helical polyacetylenes using more bulky chiral pendant groups will afford more stable C_{60}-based helical polymers. This methodology is also useful for constructing a novel helical polymer with the desired pendant in a one-handed helical array.

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Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide Based “Nanosponge”: En Route to Sphere-Surface and Nanoporous-Cluster Chemistry[**]

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Dedicated to Professor Jean-Marie Lehn

A current challenge in nanotechnology is to mimic material constructions and molecular-recognition-type responsive sensing of biological systems. This challenge becomes especially attractive when nanometer-sized objects can be constructed with tailor-made building blocks, this is possible with our unique giant sphere or ring-shaped molybdenum oxide based objects which are made up of {(Mo)Mo$_5$} building blocks and show a huge variety of functionalities, and hence reactivities, comparable to the much smaller fullerenes.[1]

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Herein we refer to the unusual spherical molybdenum oxide based nanoobject **1a** (see ref. [1a]) which has responsive reactivity—like that of a nanosponge. This type of nanoobject may open up new techniques in supramolecular nanotechnology for efficient and specific recognition by a large number of pores/receptor sites, similar to the classical macrocyclic ligands.[2] The maximum pore diameter of a related $\{Mo_nO_m\}$ ring is currently around 0.8 nm. However, the pores sizes are variable since fixed basic pentagonal $\{(Mo)Mo_5\}$ type units (pent) of the cluster object $\{(pent)_{12}(link)_{30}\}$ can be connected with different linkers (link).

$[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(ligand)\}_{30}]^{42-}$ **1a**

Whereas monotopic receptors can only accept one guest, polytopic receptors can bind several (different) substrates/guests simultaneously. This latter type of interaction depends, corresponding to cooperative effects, not only on the type and number of binding sites but also on the overall object symmetry. For the host system **1a** investigations of cooperative, allosteric, and regulatory effects are all, in principle, possible. Additionally in the reported compound, there are quite a large number of different sets of equivalent atoms of the cluster shell which mark out two Platonic and four Archimedean solids, two of which, the rhombitruncated icosidodecahedron and the rhombicosidodecahedron, are the most complex of these solids and are observed now for the first time in chemistry (see Table 1). The results presented herein can be considered as a starting point for *sphere-surface* and *nanoporous-cluster* chemistry with the possibility of use for extended structures and also for interdisciplinary aspects, such as, modeling spherical virus surfaces,[3a] for problems of discrete mathematics regarding spherical-object tilings,[4,5] as well as for catalytic and biomimetic processes because of the presence of large pores providing access to the nanosized cavities. Spherical-object tilings were important for understanding virus structures in connection with Buckminster Fuller's geodesic-dome constructions[3] and even fascinated the artist M. C. Escher.[4c] Additionally, a new type of endohedral clusterization of the associated H_2O molecules is observed upon encapsulation of guest molecules which close the pores, a situation formally comparable to a cell response on extracellular molecules interacting with a cell-surface receptor.

Spherical nanoobjects of the type $\{(pent)_{12}(link)_{30}\}$, with icosahedral symmetry, can be constructed from 12 $\{(Mo)Mo_5\}$ type pentagonal units and 30 (different) linkers,[1] allowing not only overall object sizing but also a sizing of the (because of symmetry reasons) large number of (twenty) tailor-made pores. The construction principle corresponds to that of icosahedral/spherical viruses.[3] If the linker is built up, for example, by a binuclear $\{Mo_2\}$ type unit, that is, two edge-shared $\{MoO_6\}$ octahedra, the pores on the surface of the spherical system correspond to $\{Mo_9O_9\}$ rings with diameters between around 0.6–0.8 nm which are formed by three $\{Mo_2\}$ and three $\{Mo_1\}$ type units[1] (see Figure 1 a,b). In the case of

Table 1. Chemistry creates icosahedral tilings of a sphere: Archimedean and Platonic solids formed by different sets of equivalent atoms of the shell of **2a**.[a]

Atom sets	Platonic/Archimedean solid
12 $Mo(O_7)$	icosahedron (Platonic)
20 C	dodecahedron (Platonic)
30 (P/S)	icosidodecahedron
30 $\{Mo_2\}$	truncated icosahedron
60 N	rhombicosidodecahedron
12×5 $Mo(O_6)$	rhombicosidodecahedron
120 H	rhombitruncated icosidodecahedron

[a] In the text we always refer to idealized polyhedra; see also Figure 5 for H_2O clusters.

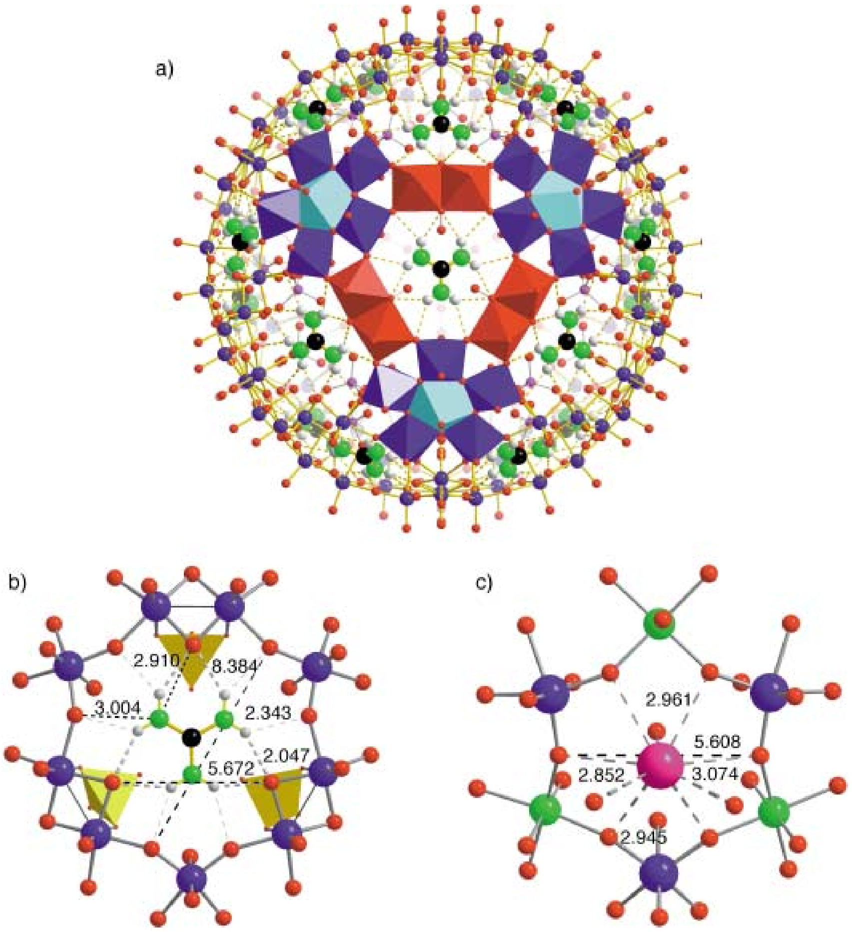

Figure 1. a) Structural details of the spherical cluster anion **2a** in ball and stick representation (diameter approximately 3 nm and cavity diameter around 2 nm), in which three pentagonal $\{(Mo)Mo_5\}$ units (light and dark blue) and three $\{Mo_2\}$ linkers (red) are highlighted in polyhedral representation and form an $\{Mo_9O_9\}$ ring/pore with an encapsulated $[(NH_2)_3C]^+$ ion (C black, N green). b) The interatomic distances for the $\{Mo_9O_9\}$ rings in **2a** reflecting the interaction between the receptors and substrates, these are comparable with those known from related single host–guest systems with classical macrocycles[2d,g,17] (Mo blue, O red, C black, H gray, N green, the $PO_2H_2^-$ and SO_4^{2-} ligands are shown as yellow tetrahedra). c) The interatomic distances of the unpublished cluster with $\{M_6O_6\}$ rings and integrated K^+ ions mentioned in ref. [6c]; K^+ large pink sphere, Mo/V linker atoms green, Mo blue, O red.

mononuclear linkers M^{n+} ($M = Fe^{3+}$,[6a] MoO^{3+},[6b] or $\{VO^{2+}/MoO^{3+}\}$[6c]) the correspondingly smaller $\{Mo_6O_6\}$ rings are formed and are just large enough to "capture" K^+ ions[6c] (Figure 1c). Remarkably, each of the 20 pores/rings has, in principle, receptor properties comparable to those of the classical crown ethers of supramolecular chemistry.[2] It could now be shown that the icosahedral clusters **1a**, known with different ligands[6d] which stabilize the $\{Mo_2O_4\}^{2+}$ linker groups, have, for example, the appropriate pore size to "encapsulate" rather large complementary substrates present in the solution, for example, guanidinium cations (Figure 2).

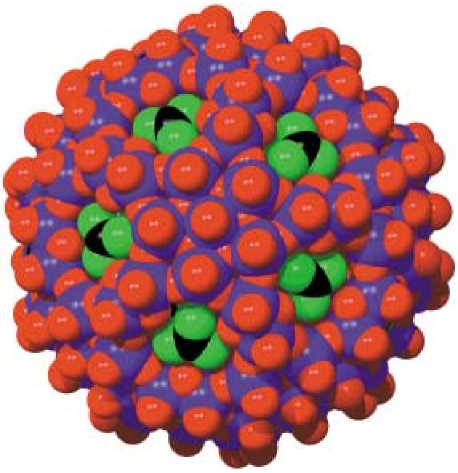

Figure 2. Structure of **2a** (space filling representation) illustrating the "lock and key" type complementarity between the host and its $[(NH_2)_3C]^+$ guests (color code as in Figure 1b).

Correspondingly, by reaction of **1a** (with ligand $= H_2PO_2^-$) with guanidinium sulfate species **2a** is formed and isolated as the crystalline guanidinium salt **2** (space group $R\bar{3}m$) in nearly quantitative yield. As the unit cell of **2** can be approximately reduced to a cubic type we find besides rhombus-shaped crystals also truncated cubes and octahedra. Compound **2** was characterized by elemental analysis, thermogravimetry (to determine the amount of water of crystallization), spectroscopy (IR, Raman), single-crystal X-ray diffraction analysis[7] and bond valence sum (BVS)[8] calculations (to determine the positions of the H_2O ligands and to differentiate between the Mo^{VI} and Mo^{V} centers) as well as with ^{13}C solid-state NMR spectroscopy.

$$[\{[(NH_2)_3C]^+\}_{20} \subset \{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{10}\{Mo_2O_4(H_2PO_2)\}_{20}]^{32-} \quad \mathbf{2a}$$

$$\{[(NH_2)_3C]^+\}_{32}\,\mathbf{2a}\cdot \text{ca. } 200\,H_2O \quad \mathbf{2}$$

In **2** the guanidinium cations $[(NH_2)_3C]^+$, with regard to their shape and symmetry, fit exactly into the pores, that is, the $\{Mo_9O_9\}$ rings (similar to the K^+ ions into the smaller $\{M_6O_6\}$ rings; see Figure 1c and ref. [6c]), and the C_3 axes of the icosahedral point group (I_h) pass through their centers. The interaction between the macrocyclic ring, that is, the bridging oxygen atoms of the binuclear $\{Mo_2\}$ units, and the three H_2N groups of the 20 guanidinum cations is through hydrogen bonding and corresponds to that observed in a monotopic receptor (see Figure 1b).[17]

A fragment of **2a**, based on the 12 pentagonal $\{(Mo)Mo_5\}$ units with altogether 60 $\{MoO_6\}$ octahedra, is an inorganic analogue of the most simple so-called $T = 1$ virus type containing only 12 pentamers ($= 60$ proteins).[3] In both cases the 60 units are packed around the fivefold axes. Noteworthy is the next larger so-called $T = 3$ icosahedral virus type—for instance the tomato bushy stunt virus (TBSV)—in which, besides the 12 pentamers, additionally 20 hexamers, that is, 120 proteins are placed around the local sixfold axes of an icosadeltahedron (Figure 3),[3a] a situation comparable to the positioning of the $20 \times 6 = 120$ H atoms of the guanidinium cations of **2a** on an icosadeltahedron (Figure 3). Reactions of the ball-type cluster with its 20 receptors can be regarded as models for the manipulation of spherical icosahedral viruses.[9a]

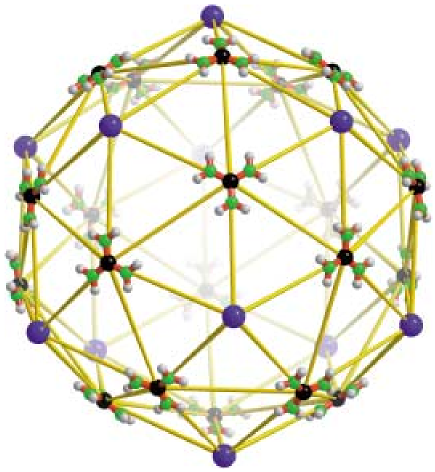

Figure 3. The atoms of the guanidinium cations placed on the icosadeltahedron shown which is obtained by subdividing the surface of the icosahedron (formed by the 12 $\{Mo(O_7)\}$ centers of **2a**) into 60 equilateral triangles (see ref. [3]). The fivefold axes of the icosahedron coincide with those of the icosadeltahedron and correspondingly, the threefold axes of the icosahedron with the "new" local sixfold axes. The icosadeltahedron has local sixfold symmetry elements (relating its subunits/faces) which are not elements of the icosahedral symmetry group.[3] Interestingly, the 120 H atoms pack around the sixfold axes like proteins of the TBSV $T = 3$ spherical virus type.[3] The 12×5 MoO_6 octahedra of the pentagonal $\{(Mo)Mo_5\}$ groups of **2a** are correspondingly packed around the fivefold axes (color code as in Figure 1b).

Chemistry can perform icosahedral tilings of the sphere: Compound **2a** is a remarkable Keplerate[1a] (for a mathematical interpretation see ref. [9b,c]) with an as-yet-unparalleled large number of sets of equivalent atoms forming different types of Platonic and Archimedean solids (Figure 4 and Table 1). A particularly nice sequence of truncation is observed by proceeding from the dodecahedron marked out by the 20 carbon atoms of the guanidinium cation through the distorted rhombicosidodecahedron formed by the related 60 N atoms to the distorted rhombitruncated icosidodecahedron marked out by the 120 H atoms, while it should be noted that the truncation of the rhombitruncated icosidodecahedron leads to the rhombicosidodecahedron (Figure 4). The 120-

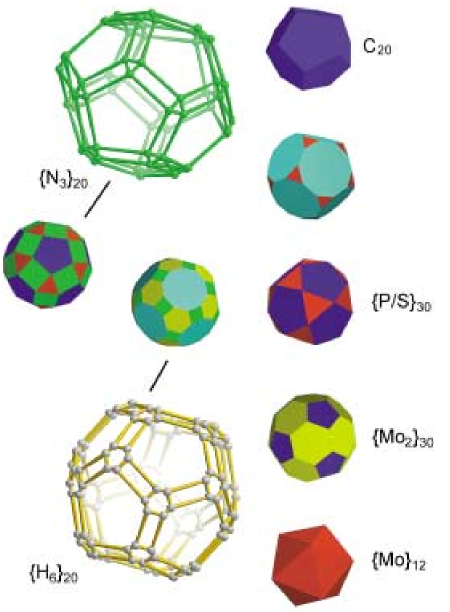

Figure 4. The stepwise truncation of the two Platonic solids, the dodecahedron and icosahedron, gives a series of Archimedean solids, that is, the truncated dodecahedron and the four others given in Table 1. Four of the five shown idealized Archimedean and the two Platonic solids are marked out by equivalent sets of atoms of **2a** (see Table 1). Additionally, the real distorted Archimedean solids $\{N_3\}_{20}$ and $\{H_6\}_{20}$ of **2a** are shown.

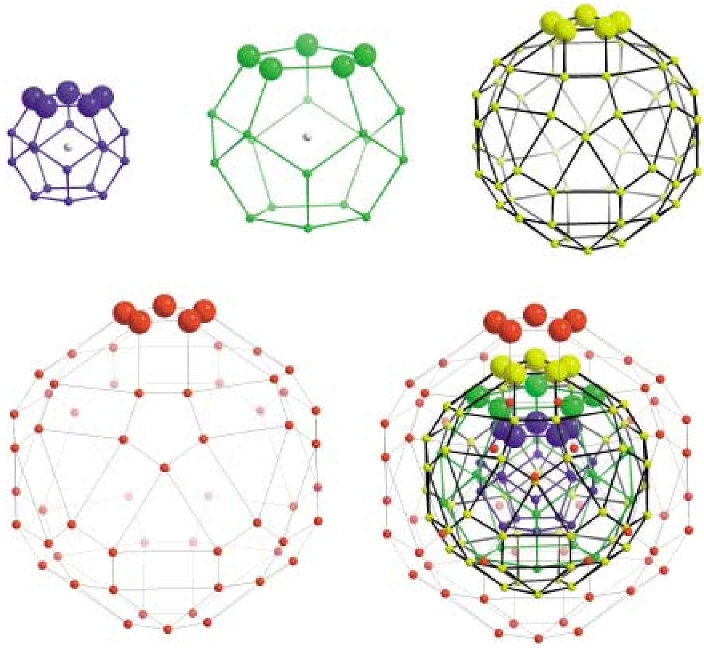

Figure 5. Endohedral hierarchic clusterization of water molecules in the cavity of **2a** resulting in $\{H_2O\}_{20}$ dodecahedra (blue and green) and $\{H_2O\}_{60}$ rhombicosidodecahedra (yellow). The second $\{H_2O\}_{60}$ rhombicosidodecahedron (red) is marked out by the 60 H_2O ligands coordinated to the 12 × 5 Mo atoms of the pentagonal $\{(Mo)Mo_5\}$ units. The set of pentagons marked out by the larger spheres highlights that all the pentagons are parallel with the same orientation of the C_5 axes; all the polyhedra have a common center which is indicated by a white sphere, see note added in proof.

vertex solid represents the most complex Archimedean solid comprising 12 decagons, 20 hexagons, and 30 tetragons. To our knowledge the two polyhedra with 60 and 120 vertices have not been observed in chemistry until now. Additionally, the 30 P/S atoms form an icosidodecahedron, the 12 $Mo(O_7)$ atoms an icosahedron, the 12 × 5 Mo atoms of the $\{(Mo)Mo_5\}$ units a rhombicosidodecahedron, and the 20 $\{Mo^V_2\}$ linkers a distorted truncated icosahedron.

Important aspects in this chemistry are the possibility of closing the giant-ball type structure with the 20 pores which are large enough to allow the passage of small species into the central cavity, and the possibility of a complete removal of substrates from solution, a phenomenon comparable to the effective recognition by a nanosponge. Guanidine plays a central role in many processes of the chemical and pharmaceutical industry[10] and there is an extensive coordination, supramolecular, as well as solid-state chemistry of the cation; it functions as a sterically flexible ligand,[11] anion receptor,[12a] and is used in crystal engineering to lead to host frameworks.[12b] Closing the pores drastically decreases the negative charge of the cluster, stabilizes it, and influences the structure of the remarkable $(H_2O)_n$ cluster,[13] a nanodroplet of water, incarcerated in the open clusters.[1a] This effect is formally comparable with a process (signal transduction) by which a cell converts an extracellular signal into a response.[18] Without the integrated cations the water structure seems to be influenced by the interaction with the crystal water through the pores. This is not the case in **2a** and we observe only highly symmetrical $(H_2O)_n$ polyhedra—hierarchic endohedral clusterization—in the form of dodecahedra and rhombicosidodecahedra (Figure 5). An interesting aspect would also be the self-organization of solvent molecules encapsulated in a closed sphere (the interaction of the water molecules within the polyhedra and between these, will be studied later).

Spherical shell type objects, where the subunits exist in identical environments, are interesting in several aspects: They are easily isolable and often the preferred target of self-assembly processes based on simple units because of their high stability (the surface area is minimum while the strain energy is evenly distributed over the surface). Consequently, these spherical-shell-type objects can be used as adjustable molecular containers, which can be constructed with different building blocks, as in the present situation, while allowing chemical reactions at quite different functional groups which are abundant at the surface. Note: It is impossible to construct a spherical system from one building block only (see, for example ref. [4b]).

Supramolecular chemistry started with selective binding of alkali-metal cations by natural and synthetic macrocyclic ligands, followed later by strong and selective binding of anionic as well as neutral complementary substrates.[2] We could now cross the frontier to a rather large multitude of receptor sites positioned on a stable nanoobject. While it became evident—mainly as a result of the initiative and work of J.-M. Lehn[2]—that a *receptor–substrate supramolecule* is characterized by its geometric (structure/conformation), thermodynamic (stability, entropy, and enthalpy of formation), and kinetic (role of formation and dissociation) features, new categories of receptor–substrate type appear in the present polytopic *super–supramolecule* and offer the chance to study a variety of relevant cooperative effects.

To summarize, the present results highlight that the spherical cluster type under investigation, having a large number of receptor sites, can exist with different linkers, for instance with mononuclear and dinuclear metal centers, and correspondingly with different pore sizes with the consequence that it can act as an effective and specific nanosponge for complementary substrates. The related reactivity should in principle be different from that of monotopic receptors and can be influenced by changing the electronic properties of the host shell.[14] This is a situation comparable to substrates placed on "classical" surfaces, for example, related industrially important metal-oxide surfaces,[15] where the reactivity of the substrates can also be influenced by changing surface properties.[16] The route to "revolutionary" new materials is long but it exists.

Note added in proof (August 26, 2002): The 100 encapsulated water molecules form altogether a novel icosahedral cluster with tetrahedrally coordinated oxygen atoms.

Experimental Section

2: A mixture of $(NH_4)_{42}$**1a**$\cdot 300\,H_2O$ (ligand $= H_2PO_2^-$)[6d] (2.5 g, 0.09 mmol) and $[(NH_2)_2CNH]_2SO_4$ (1.9 g, 8.8 mmol) in H_2O (200 mL) was heated to 90 °C for a short time. The dark-brown solution was kept in an open beaker at room temperature for 1 week (crystallization starts after 1 day). The dark-brown crystals (rhombus type, truncated cubes, and octahedra) which precipitated were collected by filtration over a glass frit, washed with 2-propanol (95 %) and dried in air. Yield: 2.3 g (92 % based on **1a**). Characteristic IR bands (KBr, pellet, 1800–500 cm^{-1}): $\tilde{\nu} = 1655$ (s, δ $(H_2O)/[(H_2N)_3C]^+$), 1180 (w(SO_4)), 1124 (w-m), 1075 (vw), 1038 (w) (H_2PO_2), 976 (m), 945 (sh) (ν(Mo=O)), 851 (m), 793 (s), 725 (s), 631 (w-m), 567 (m) cm^{-1}; characteristic Raman bands (solid; $\lambda_e = 1064$ nm): $\tilde{\nu} = 948$ (w, ν(Mo=O)), 871 (s), ≈845 (sh), 361 (m), ≈315 (w), 296 (w-m) cm^{-1}. Elemental analysis for $C_{52}H_{796}Mo_{132}N_{156}O_{674}P_{20}S_{10}$ (%; calculated with $150\,H_2O$ because the crystals of **2** lose part of the crystal water when removed the mother liquor): C 2.23, H 2.87, N 7.80, P 2.21, S 1.15, found: C 2.5, H 2.9, N 7.1, P 1.9, S 0.9.

The compound type can also be obtained with only one type of ligand coordinated to $\{Mo_2\}$ linkers, for instance by treating **1a** with guanidinium chloride. But as the crystal quality of the related products was too poor for the results to be reported here.

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[7] a) Crystal data for **2**: $C_{52}H_{896}Mo_{132}N_{156}O_{724}P_{20}S_{10}$, $M_r = 28\,901.33\ g\,mol^{-1}$, rhombohedral, space group $R\bar{3}m$, $a = 62.865(2)$, $c = 76.470(4)$ Å, $V = 261\,720(17)$ Å^3, $Z = 12$, $\rho_{calcd} = 2.200\ g\,cm^{-3}$, $\mu = 2.005\ mm^{-1}$, $F(000) = 169\,152$, crystal size $= 0.30 \times 0.20 \times 0.20\ mm^3$. Crystals of **2** were removed from the mother liquor and immediately cooled to 188(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames ($\phi = 0$, 88 and 180°) at a detector distance of 5 cm). A total of 454 502 reflections ($0.65 < \Theta < 25.03°$) were collected of which 52 923 reflections were unique ($R_{int} = 0.0911$). An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined using SHELXL-93 to $R = 0.0820$ for 35 303 reflections with $I > 2\sigma(I)$, $R = 0.1384$ for all reflections; max./min. residual electron density 3.336 and $-2.227\ e\,Å^{-3}$ (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen, **1993/1997/2001**; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, **2001**). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412658; b) Not all of the lattice guanidinium cations could be located because of the disorder problem which as usual affects the location of lattice ingredients in the large cavities between the giant objects. That the intramolecular (H2)N–N(H2) distances (2.3 Å) are not very different from intermolecular (H2)N–O(H2) distances (2.5–2.9 Å) is the additional explanation for why many guanidinium cations could not be found in the crystal structure, as this situation allows the cations to be integrated into the crystal-water lattice in many different ways. But the number of cations is evident from numerous analyses (also after recrystallization of **2**). The presence of only protonated guanidinium units could be demonstrated by ^{13}C solid-state NMR spectroscopy.

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An Inclusion Complex with $[Gd(dmf)_8]^{3+}$ Ions Encapsulated in Pockets of an Anionic Array of $[\{Cu_6(CN)_9\}^{3-}]_\infty$ Units; A Cyanide-Bridged Cu–Gd Layer Structure**

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Lanthanide–transition-metal complexes are attracting increasing attention because of their novel structures and the realization of applications in materials science[1,2] and catalysis.[3] It is of interest to not only continue preparing materials for which applications are known, but also to expand structural and chemical knowledge through the preparation and evaluation of new types of lanthanide–transition-metal complexes. With this goal in mind, we have extended our lanthanide–transition-metal studies from Group 10 transition metals[4] to Group 11 Cu^I complexes. Herein, we report the synthesis and structural characterization of an extended three-dimensional ionic inclusion complex, $[\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2\,DMF]_\infty$,[5] which contains sequestered lanthanide cations, and an extended layered complex, $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$.[6] These complexes constitute new structural classes of lanthanide–transition metal systems.

Although ionic inclusion complexes are known,[7] examples of an encapsulated ion within a charged cage are rare. The new inclusion complex is prepared by a three-component metathesis reaction [Equation (1)]. The anionic three-dimensional host lattice, $[\{Cu_6(CN)_9\}^{3-}]_\infty$, sequesters a cationic guest, $[Gd(dmf)_8]^{3+}$, and two free DMF solvent molecules in each "pocket" (Figure 1). In a slightly modified procedure [Equation (2)], the two-dimensional, infinite, puckered-layer complex $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$ (Figure 2) is formed in which the two Gd^{III} and three Cu^I atoms are bridged by cyanide ligands to form pentagonal rings. Either complex can be prepared in near-quantitative yield.

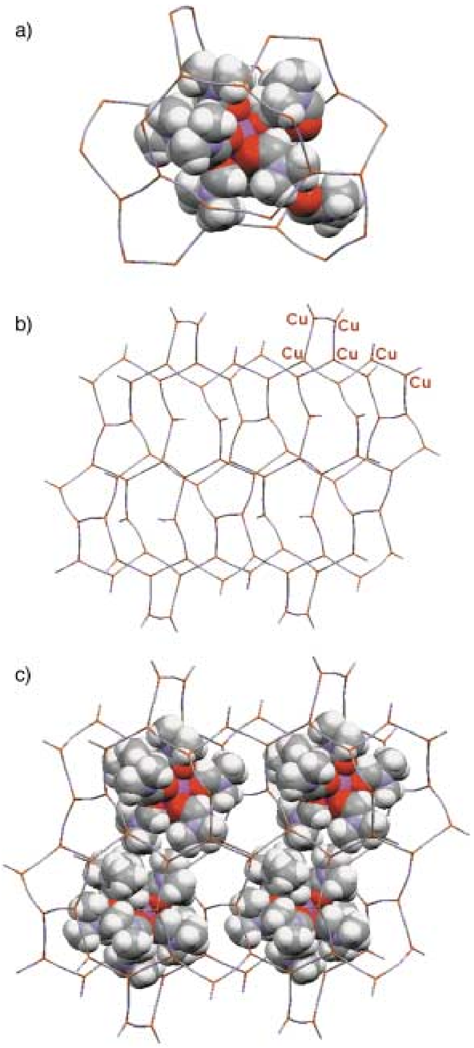

Figure 1. The structure of $[Gd(dmf)_8Cu_6(CN)_9]_\infty$. a) One pocket with an encapsulated $[Gd(dmf)_8]^{3+}$ ion and two DMF molecules. b) The partial structure of the anionic network with four vacant pockets; connections between Cu atoms represent cyanide bridges. c) Four pockets with trapped $[Gd(dmf)_8]^{3+}$ ionic guests.

$$GdCl_3 + 6\,CuCN + 3\,KCN \xrightarrow{DMF} [\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2\,DMF]_\infty + 3\,KCl \tag{1}$$

$$CuCN + KCN \xrightarrow{DMFDMF} K[Cu(CN)_2] \tag{2a}$$

$$2\,GdCl_3 + 6\,K[Cu(CN)_2] \xrightarrow{DMFDMFDMF} [Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty + 6\,KCl + 2\,CuCN \tag{2b}$$

Figure 1 b shows the anionic network $[\{Cu_6(CN)_9\}^{3-}]_\infty$, while Figure 1 a illustrates a pocket that contains a trapped $[Gd(dmf)_8]^{3+}$ ion and two free DMF molecules. All of the

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