Magnetic Properties

DOI: 10.1002/anie.200700795

Extending the $\{(Mo)Mo_5\}_{12}M_{30}$ Capsule Keplerate Sequence: A $\{Cr_{30}\}$ Cluster of $S = 3/2$ Metal Centers with a $\{Na(H_2O)_{12}\}$ Encapsulate**

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In memory of Abhilash Goplan Janardhan

In previous work it was shown that molybdenum oxide based spherical hollow clusters of the type $\{(Mo)Mo_5\}_{12}\{linker\}_{30}$—which, because of their structural features, are also called Keplerates—can be directly synthesized by the addition of linkers, such as $V^{IV}O^{2+}$ and Fe^{III}, to a dynamic library containing (virtual) pentagonal units in solution[1,2] (for general information see also refs. [3–5]). In the $\{linker\}_{30} = \{M_{30}\}$ situation, a network of corner-sharing triangles exists on the sphere surface,[1,2a] and this gives rise, as in the $\{Mo_{72}Fe_{30}\}$ case, to a geometrically frustrated magnetic system which has received a lot of attention.[4d–f,6] In fact, these zero-dimensional materials share topological features with the planar Kagomé lattices which also support geometrical frustration[7] and are of interest for materials science.[7a] The exploration of distinct yet related spin systems, which is an important aspect of the present work, is expected to provide a deeper understanding of basic aspects of geometrical frustration and especially the role played by varying the spin quantum number of the metal centers. Herein we report the synthesis (and new perspectives for the general synthetic principles leading to these types of capsules) of the spherical, hollow $\{(Mo)Mo_5\}_{12}\{Cr^{III}\}_{30}$ type cluster **1a** which contains an interesting encapsulated $\{Na(H_2O)_{12}\}$ type entity. This $\{Mo_{72}Cr_{30}\}$ cluster system exhibits, like the $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}V_{30}\}$ systems, the unique Archimedean solid $\{M_{30}\}$ icosidodecahedron (see below and references [1a,2a]).

If an acidified aqueous solution of sodium molybdate containing a rather high concentration of acetic acid is treated with chromium(III) chloride, green crystals of **1** precipitate after some days (the basic differences to the preparation of the V_{30} and Fe_{30} systems are outlined in the Experimental Section). Compound **1**, which crystallizes in the space group $R\bar{3}$, was characterized by elemental analysis, thermogravimetry (to determine the actual water content based on the release of crystal water), spectroscopy (IR, Raman, UV/Vis), and single-crystal X-ray structure analysis.[8a]

$$[\{Na(H_2O)_{12}\} \subset \{Mo^{VI}{}_{72}Cr^{III}{}_{30}O_{252}(CH_3COO)_{19}(H_2O)_{94}\}]\cdot \text{ca. } 120\,H_2O \equiv \mathbf{1a}\cdot \text{ca. } 120\,H_2O \quad \mathbf{1}$$

The cluster **1a** is of the expected spherical $\{(Mo)Mo_5\}_{12}$-$\{Linker\}_{30}$ ($Linker = Cr^{III}$) type (Figure 1). Correspondingly, the heptacoordinate Mo centers of the 12 pentagonal $\{(Mo)Mo_5\}$ units describe an icosahedron, and the 30 Cr^{III} linkers the quasiregular icosidodecahedron. The latter Archimedean solid is a hybrid of the icosahedron and the dodecahedron and contains 20 triangular and 12 pentagonal faces. It comprises not only equivalent vertices but also equivalent edges and equal dihedral angles (see also refs. [1,2]). The 19 acetate ligands in **1a**, which are mainly disordered, are located inside the cavity and coordinate in a bidentate fashion to the metal centers, preferentially bridging Cr and Mo sites. In the $\{(Mo)Mo_5\}_{12}\{Cr^{III}\}_{30}$ cluster, the 30 Cr^{III} ions have their typical sixfold coordination, that is, with two bonds to the small ligands (either to two H_2O ligands or to one external H_2O and one to an internal acetate) and four bonds of the $Cr\cdots O(Mo)$ type to two pentagonal $\{(Mo)Mo_5\}$ units (Figure 1). This scenario can also be described as 30 Cr^{III} centers trapped in a matrix formed by the 12 pentagonal units/ligands. The Cr^{III} metal ions can be replaced by others, such as Fe^{III} and $V^{IV}O^{2+}$, in the typical way of coordination chemistry; this situation is of special interest for further syntheses and magnetic studies. The solution and solid-state electronic spectrum of **1** shows a band at approximately $15.6 \times 10^3\,cm^{-1}$ which arises from the presence of Cr^{III} and is assigned to the spin-allowed ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition.

One fascinating structural aspect is that a $\{Na(H_2O)_{12}\}$ cluster is encapsulated in the cavity of **1a**. The O atoms of the $\{Na(H_2O)_{12}\}$ cluster form an icosahedron, with its approximate C_5 axes coinciding with the C_5 axes of the metal oxide

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[**] A.M., T.G., M.D., and J.v.S. gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft, A.M. additionally the Fonds der Chemischen Industrie, the German-Israeli Foundation for Scientific Research & Development, the Volkswagenstiftung, and the European Union. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

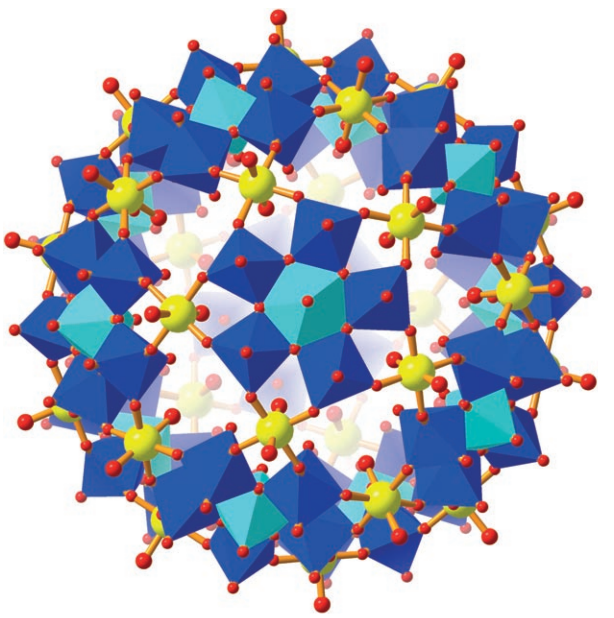

Figure 1. Structure of the spherical capsule $\{(\mathrm{Mo})\mathrm{Mo}_5\}_{12}\{\mathrm{Cr}^{\mathrm{III}}\}_{30}$ highlighting the basic pentagonal units (light and dark blue polyhedral representation; formula in text), which offer five coordination sites, and the 30 $\mathrm{Cr}^{\mathrm{III}}$ linker centers (Cr yellow, O red). The $\mathrm{Cr}^{\mathrm{III}}$ linker centers are in octahedral environments. Internal (disordered) acetate ligands are not shown.

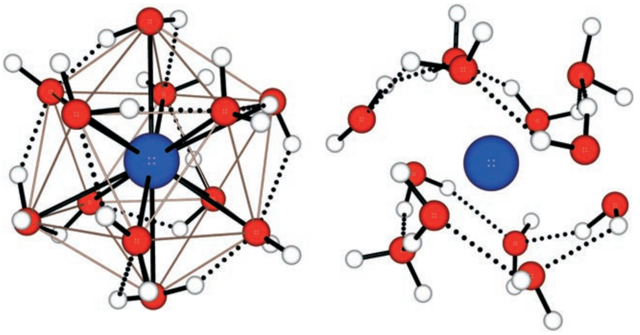

Figure 2. The $\{\mathrm{Na(H_2O)_{12}}\}$ cluster with a central $\mathrm{Na^+}$ ion (blue). Left: H-bond pattern (black dots; H atoms white) and the 12 Na⋯O interactions (black) formally based on the icosahedron of 12 O atoms (red) with the 30 O⋯O edges (light brown), not referred to in right-hand picture. Right: Same H-bond pattern but shown as a sandwich structure with two chair-shaped water rings (average interatomic distances [Å] for the $\bar{3}$ site:[8] O⋯O 2.72, Na⋯O 2.58).

based skeleton (the cluster is found not only at the $\bar{3}$ but also at the $\bar{1}$ site of the crystal lattice). The relatively small water cluster is protected by the hydrophobic shell built up by the acetate ligands and would otherwise not be formed within the cavities of the spherical capsules which have hydrophilic interiors.[2] (Without the acetate ligands the hydrophilic groups would be expected to interact with the relatively small encapsulated water shell preventing the formation of the regular shape; in larger water aggregates, such as $\{\mathrm{H_2O}\}_{100}$, many water molecules interact strongly with each other through hydrogen bonds, which has a stabilizing effect.[8b]) A hydrogen-bond pattern for the icosahedral water cluster[8c] was calculated according to a well established method[8d] by considering electrostatic energy minimization using a combination of simulated thermal annealing and Powell's algorithms (see ref. [8e]). The result obtained corresponds to the minimum-energy structure when the coordinates of the sodium ion and of the 12 oxygen atoms are fixed (in the positions crystallographically determined at −90 °C)[8a] and all O−H bond lengths and H-O-H valence bond angles are fixed at 97 pm and 104.5°, respectively. (It is likely that other hydrogen-bond patterns of similar energy exist, which is in agreement with the comparably large vibrational ellipsoids of the O atoms.) Figure 2 shows the hydrogen-bond pattern, which can be described as a sandwich structure with two chair-shaped $\{\mathrm{H_2O}\}_6$ rings and a sodium ion in between. The average binding energy between water molecules was found to be $-59\ \mathrm{kJ\,mol^{-1}}$, which reflects both the polarization effect by the central sodium cation and hydrogen-bonding interactions. Further details about the structure considering also the influence of the $\mathrm{Na^+}$ ion will be published in a later paper.

Figure 3 shows the magnetic susceptibility temperature product χT and χ^{-1} as functions of temperature. The χT value is $47.17\ \mathrm{cm^3\,K\,mol^{-1}}$ at $T = 300$ K decreasing with decreasing temperature, reaching $3.97\ \mathrm{cm^3\,K\,mol^{-1}}$ at 1.8 K. The Curie–Weiss plot (Figure 3, bottom) is essentially a straight line above $T = 100$ K, and a fit to the Curie–Weiss law yields a Curie constant of $54.8 \pm 0.1\ \mathrm{cm^3\,K\,mol^{-1}}$ and a Weiss temperature of $\theta = -50 \pm 0.1$ K. The magnetization as a function of field at $T = 1.8$ K (not shown) increases rapidly with increasing field slowing down above 2 T, but it does not saturate. Preliminary X-band EPR measurements (not shown) show a broad line at high temperatures, which decreases on lowering the temperature and includes an evolving sharp feature. From these data the value $g = 1.966$ was obtained.

Both the decrease of the χT value with decreasing temperature and the substantial and negative Weiss temperature show that the predominant exchange interactions in **1** are antiferromagnetic which agrees with the fact that the room-temperature χT value is below that for 30 uncoupled spins 3/2 with $g = 1.966$ ($54.35\ \mathrm{cm^3\,K\,mol^{-1}}$). To quantify the magnetic behavior we performed quantum Monte Carlo (QMC) calculations[9,10] of the weak-field susceptibility by adopting a Heisenberg model with isotropic exchange interaction of the form $-J\,\vec{S}_i \cdot \vec{S}_j$ for each pair of spins 3/2 on nearest-neighbor sites i and j of an icosidodecahedron. The values of both J and g were optimized to fit the experimental data. The comparison between experimental and theoretical data was restricted to temperatures $T > 30$ K, because below that temperature the QMC method is not reliable for the icosidodecahedron structure owing to spin-frustration effects.[9] The best fit was achieved for $J/k_{\mathrm{B}} = -8.7 \pm 0.2$ K and $g = 1.96 \pm 0.01$ (Figure 3, bottom). Note that also the weak upturn in χ^{-1} with decreasing T around 50 K is reproduced well by the calculations. In spite of the long superexchange pathway ($\mathrm{Cr^{III}}$-O-$\mathrm{Mo^{VI}}$-O-$\mathrm{Cr^{III}}$) the interaction is quite strong. Literature values for exchange couplings along such a pathway range from about 1 K to about 21 K.[11] The strength of the interaction is determined by the overlap of the Cr d orbitals with the empty d orbitals of the $\mathrm{Mo^{VI}}$ ion.

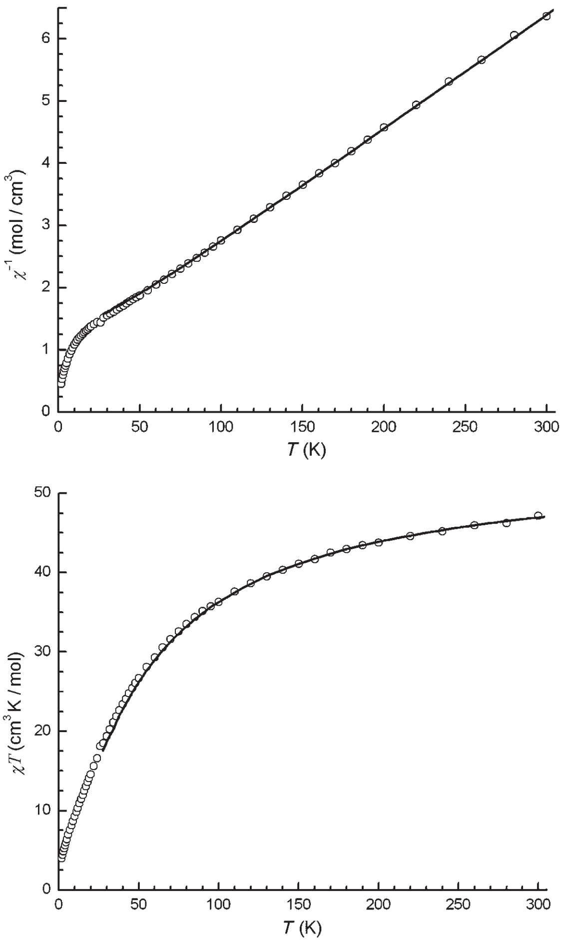

Figure 3. Experimental (symbols) χ^{-1} (top) and χT (bottom) versus temperature and quantum Monte Carlo result (continuous curve) for $J/k_B = -8.7$ K and $g = 1.96$ (see text and Experimental Section).

The moderate J value and the spin quantum number 3/2 for the individual Cr^{III} centers makes compound **1** an interesting and experimentally convenient system for future physical, theoretical, and experimental studies and especially for the comparison of its magnetic properties with those of the corresponding Fe^{III}[2,3,6,12a] and V^{IV}[1] clusters (spins 5/2 and 1/2, respectively) as well as with the spin-related Kagomé systems.[7] Of special interest is the possibility of observing a narrow minimum in the differential susceptibility dM/dH for $H \approx 20$ T (one-third of the saturation field) as has been seen in the Fe^{III} complex.[6c] This minimum in dM/dH is associated with polytopes assembled from corner-sharing triangles and the Kagomé lattice. In addition, because of its convenient spin-state transition energies (see below), **1a** is excellently suited for experimental investigation (by inelastic neutron scattering) of the validity of the rotational band model[6e] which has been developed for these clusters. In contrast, the V system is not suited for such investigations because of its very large exchange constant.

The three, practically isostructural, $\{(Mo)Mo_5\}_{12}\{M\}_{30}$ clusters/skeletons have the sequence of spin values $S = 1/2$ ($M = V^{IV}$), $S = 3/2$ ($M = Cr^{III}$), and $S = 5/2$ ($M = Fe^{III}$) and show quite different magnetic behavior. The capsule/Keplerate with $M = Fe^{III}$ behaves essentially classically because of the large $S = 5/2$ spin centered at 30 different corners of the icosidodecahedron and the weak superexchange interaction.[12a] These factors and the weak exchange interaction are also responsible for the fact that quantum steps in the magnetization versus field have not been observed for accessible temperatures in contrast to other antiferromagnetically coupled systems. For $M = V^{IV}$, where the spin is small and delocalized, the system is called a "Quantum Keplerate".[1a] The electron delocalization creates a very strong spin coupling which has been shown by QMC calculations to be in the range of $J/k_B \approx -245$ K.[1a] This spin coupling causes the excited spin states to be at very high energies, which makes, for example, spin-state crossings inaccessible in conventional laboratory magnetic fields. The spin system of **1a** is in between those of the other two compounds which results in correspondingly intermediate magnetic properties.

It should be possible to synthesize new related compounds with interesting and even new types of magnetic properties. These spherical cluster systems have other unique properties, as well. For example, the $\{Fe_{30}\}$[12b] and $\{Cr_{30}\}$ clusters are "nanoacids" and show an unprecedented type of assembly processes leading to vesicles the size of which can be tuned by changing the pH value, a long-term goal in nanoscience. Future synthetic strategies will be determined by the general characteristics of the spherical clusters which can be compared with "coordination polymers" with spherical periodicity.[13] Coordination polymers are considered as being based on metal ions and (organic) ligand building blocks assembling to infinite one-, two-, and three-dimensional networks, the properties of which depend in a characteristic way on the dimensionality.[13] In our spherical clusters we can refer to metal–ligand interactions between the pentagonal units (the ligands) $\{(Mo)Mo_5O_{21}(H_2O)_6\}^{6-}$ (present in a dynamical library)[1a] and the metal ions. These interactions are comparable to those between lacunary polyoxometalates and metal cations.[4a]

The option of the planned syntheses of molecular spheres based on a careful selection of appropriate pentagonal ligands and metal ions with their specific coordination behavior[14a] allows for the extension of this work to other 3d metal cations which can also lead to mixed-metal as well as mixed-valence clusters with different types of magnetic properties (see for instance ref. [14b]). The preparation of mixed-metal/mixed-valence clusters would correspond to symmetry breaking for the spherical systems which can also be brought about by choosing special cavity-internal ligands attached to the metal centers.[1a] A spherical product is formed preferentially if the following condition is fulfilled: ligand-type pentagonal units with *appropriate* bonding sites are present, as are transition-metal cations which can coordinate to the pentagonal units (that is, assemble around them) maintaining the fivefold symmetry (see Figure 1). In the clusters discussed herein, the repeating unit is $\{(Mo)Mo_5M_{5/2}\}$ ($M = Cr$), in the larger spherical system $\{(Mo^{VI})Mo^{VI}_5\}_{12}\{Mo^{V}_2\}_{30}$ which contains binuclear linkers the repeating unit is $\{(Mo)Mo_5Mo_5\}$.[5b] The repeating units occur 12 times in the spherical clusters corresponding to the icosahedral symmetry.

Experimental Section

$CrCl_3{\cdot}6H_2O$ (8.6 g, 32.27 mmol) was added to a solution of $Na_2MoO_4{\cdot}2H_2O$ (9.0 g, 37.2 mmol) in a H_2O (80 mL)/CH_3COOH (100 %; 35 mL) mixture. After stirring for 5 min it was acidified with 1M HCl (17 mL; resulting pH ≈ 2), and the solution was heated under reflux for 45 min. The resulting green solution was cooled to room temperature and the pale green precipitate (having a similar IR spectrum to the final product) was collected by filtration. Green crystals precipitated from the filtrate after 5 days, were collected by filtration, washed with cold water, and dried in air. Yield: 0.15 g (ca. 1 % based on Cr, see also below); elemental analysis: calcd (%) for $Na_1Mo_{72}Cr_{30}C_{38}O_{516}H_{509}$: C 2.58, H 2.89, Na 0.13; found: C 2.6, H 2.5, Na 0.2 %. (A small error for the number of Na^+ and acetates has to be taken into account.) IR (KBr pellet): $\tilde{\nu} = 1622$ (m, $\delta(H_2O)$), 1547 (m, ν_{as}(COO)), 1423 (w, ν_s(COO)), 953 (m, ν(Mo=O)), 796 (s), 635 (w), 580 (s), 455 cm^{-1} (w); FT-Raman (solid; $\lambda_e = 1064$ nm): $\tilde{\nu} = 948$ (w), 913 (s), ν(Mo=O), 855 cm^{-1} (s); UV/Vis (in H_2O): $\lambda = 642$ nm; UV/Vis (measured against cellulose as white standard) $\lambda = 645$ nm. Note: ratios of MoO_4^{2-}:Cr^{3+} lower than 2:1 led to the formation of the Anderson type cluster $[CrMo_6O_{24}H_6]^{3-}$[15] while a pH value higher than ca. 2.2 led to the formation of a trinuclear Cr^{III} cluster with acetate ligands.[16] The reaction pathway leading to the V_{30} and Fe_{30} clusters is much simpler and the yields are higher. A major difference is that the residence time of H_2O ligands in the Cr^{III} aqua complex used as educt is very long with the consequence that a reactive cation/linker for the pentagonal units is not directly available as for example, in the Fe^{III} case.

Magnetic susceptibility and magnetization measurements were performed on a powder sample of **1** (18.52 mg) using a Quantum Design MPMS XL7 SQUID magnetometer. The data for the molar magnetic susceptibility were corrected for diamagnetic contributions using Pascal's constants ($-7504 \times 10^{-6}\ cm^3\,mol^{-1}$).

Adopting a Heisenberg model of nearest-neighbor exchange interaction between spins $S = 3/2$ on the sites of an icosidodecahedron, quantum Monte Carlo calculations of the susceptibility were performed using the stochastic series expansion[17] of the partition function with directed loops.[18] The detailed balance condition is satisfied by implementing the appropriate "directed-loop equations".[18] The effectiveness of this technique for magnetic molecules has recently been demonstrated for antiferromagnetic Heisenberg spin rings[10] and for a very large variety of finite quantum Heisenberg spin models.[9] It should be noted that though the $\{Mo_{72}Cr_{30}\}$ metal skeleton can be described as icosahedral (this is in fact an (excellent) approximation) the coordination of the internal water and acetate ligands destroys that symmetry to a minor extent as the metal centers (Cr···Cr: 6.32–6.45 Å) do not have the same environment. Thus the assumption of only one exchange coupling constant J is an approximation, but a very good one.

Received: February 21, 2007

Keywords: Kagomé lattice · magnetic properties · polyoxometalates · self-assembly · water cluster

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[8] a) Crystal data for **1**: $C_{38}H_{509}Cr_{30}Mo_{72}NaO_{516}$, $M_r = 17716.12\ g\,mol^{-1}$, space group $R\bar{3}$, $a = 54.4434(14)$, $c = 59.767(2)$ Å, $V = 153420(8)$ Å^3, $Z = 12$, $\rho = 2.301\ g\,cm^{-3}$, $\mu = 2.433\ mm^{-1}$, $F(000) = 103440$, crystal size $= 0.3 \times 0.2 \times 0.1\ mm^3$. A total of 196988 reflections ($1.59 < \Theta < 22.49°$) were collected of which 43996 reflections were unique (R(int) = 0.1807). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.1015$ for 15460 reflections with $I > 2\sigma(I)$, $R = 0.2471$ for all reflections; max./min. residual electron density 1.536 and $-0.714\ e\,Å^{-3}$. Crystals of **1** 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; hemi-

sphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\varphi = 0$, 88 and 180°) at a detector distance of 5 cm). (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen **1997/2001**; structure graphics with DIAMOND 2.1 from K.Brandenburg, Crystal Impact GbR, 2001). CCDC-637150 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The "icosahedral" water cluster appears on crystallographically independent sites $\bar{1}$ and $\bar{3}$, the distortion in the $\bar{1}$ case is more pronounced. b) See for instance M. Henry, H. Bögge, E. Diemann, A. Müller, *J. Mol. Liq.* **2005**, *118*, 155–162 and A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, S. Roy, A. Berkle, *Angew. Chem.* **2002**, *114*, 3756–3761; *Angew. Chem. Int. Ed.* **2002**, *41*, 2805–2808. c) In the present case, a "water cluster" is encapsulated and not a polymolybdate as in ref. [2] where a higher concentration of molybdate was used in the synthesis. d) The method has been shown to be suitable to calculate the neutron diffraction crystallographic H-atom coordinates for water molecules in 13 ice polymorphs (M. Henry, *ChemPhysChem* **2002**, *3*, 607–616) as well as the X-ray diffraction crystallographic H-atom coordinates, for water molecules interacting with polyoxometalate species such as the decavanadate (M. Henry, *J. Cluster Sci.* **2002**, *13*, 437–458); the method is particularly well-suited for studying hydrogen bonding of water molecule assemblies (see for example, D. R. Turner, M. Henry, C. Wilkinson, G. J. McIntyre, S. A. Mason, A. E. Goeta, J. W. Steed, *J. Am. Chem. Soc.* **2005**, *127*, 11063–11074 where the calculation was supported by a single-crystal neutron structure analyses); e) W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in C, the Art of Scientific Computing*, 2nd ed, Cambridge University Press, Cambridge, **1992**, pp. 412–420.

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[12] a) The $S = 5/2$ (Fe^{III}) analogue of complex **1**, $\{Fe_{30}Mo_{72}\}$ has some very intriguing properties which has led to many experimental[6a,c,d] and theoretical[6a–f] studies. Briefly, it is well described by a simple picture of geometrical frustration whereby the $S = 0$ ground state corresponds to a spin topology of three coplanar spin sublattice vectors of length 25, each spin sublattice being associated with ten parallel $S = 5/2$ ion spins, with an angular separation of 120 degrees between the individual sublattice vectors. In the low-temperature regime, with increasing applied magnetic field, H, the three sublattice vectors cant and these may be pictured as a "uniformly folding umbrella"; the projections of the sublattice vectors in the plane normal to the external field maintain a frustration angle of 120 degrees and the magnetization grows linearly with H and ultimately saturates at a field $H_{sat} \approx 17.6$ T. Additionally, at low, nonzero temperatures the differential susceptibility $\partial M/\partial H$ versus H shows a characteristic minimum at $H_{sat}/3$ which has been explained[6c] in terms of the competition between two spin configurations (the canted frustrated phase and a magnetically stiff configuration). Similar behavior can be expected for compound **1**, where, using our result $J/k_B = -8.7$ K, we estimate $H_{sat} \approx 60$ T. A drawback of the Fe^{III} analogue is that owing to the weak superexchange interaction of $J/k_B = -1.57$ K, the energy levels are very closely spaced, and thus the individual spin-state crossings and transitions have not been observed in experiments;[6a,d] b) T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen, A. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 15914–15920 as well as unpublished work by the same authors.

[13] a) R. J. Puddephatt, *Coord. Chem. Rev.* **2001**, *216–217*, 313–332; b) R. Robson, *J. Chem. Soc. Dalton Trans.* **2000**, 3735–3744 in which it was mentioned that in special cases parallels can exist between infinite arrays of coordination polymers and discrete supramolecules, as for example, Fujita's $[M_6(tpt)_4]$ (tpt corresponds to a complex triazine ligand), M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature*, **1995**, *378*, 469–471. Interestingly, the pentagonal units discussed herein also occur in network structures (see refs. [22a,b] of ref. [5b]).

[14] a) The present situation is formally comparable to the "polyassociation" leading, for example, to the impressive helices of J.-M. Lehn. In both cases, polytopic ligands—either preorganized in the form of poly(bipyridine) ligand strands in the helices or existing as pentagonal units in a dynamic library in the spherical systems—interact with a larger number of directing metal cations showing the expected coordination type; in the former cases the copper (I) ions enforce the tetrahedral coordination geometry and in the latter cases the M^{III} ions the octahedral (see J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim, **1995**); b) B. Botar, P. Kögerler, A. Müller, R. Garcia-Serres, C. L. Hill, *Chem. Commun.* **2005**, 5621–5623; see also: A. Müller, B. Botar, H. Bögge, P. Kögerler, A. Berkle, *Chem. Commun.* **2002**, 2944–2945.

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