Supramolecular Chemistry

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Porous Capsules $\{(M)M_5\}_{12}Fe^{III}_{30}$ ($M = Mo^{VI}, W^{VI}$): Sphere Surface Supramolecular Chemistry with 20 Ammonium Ions, Related Solution Properties, and Tuning of Magnetic Exchange Interactions**

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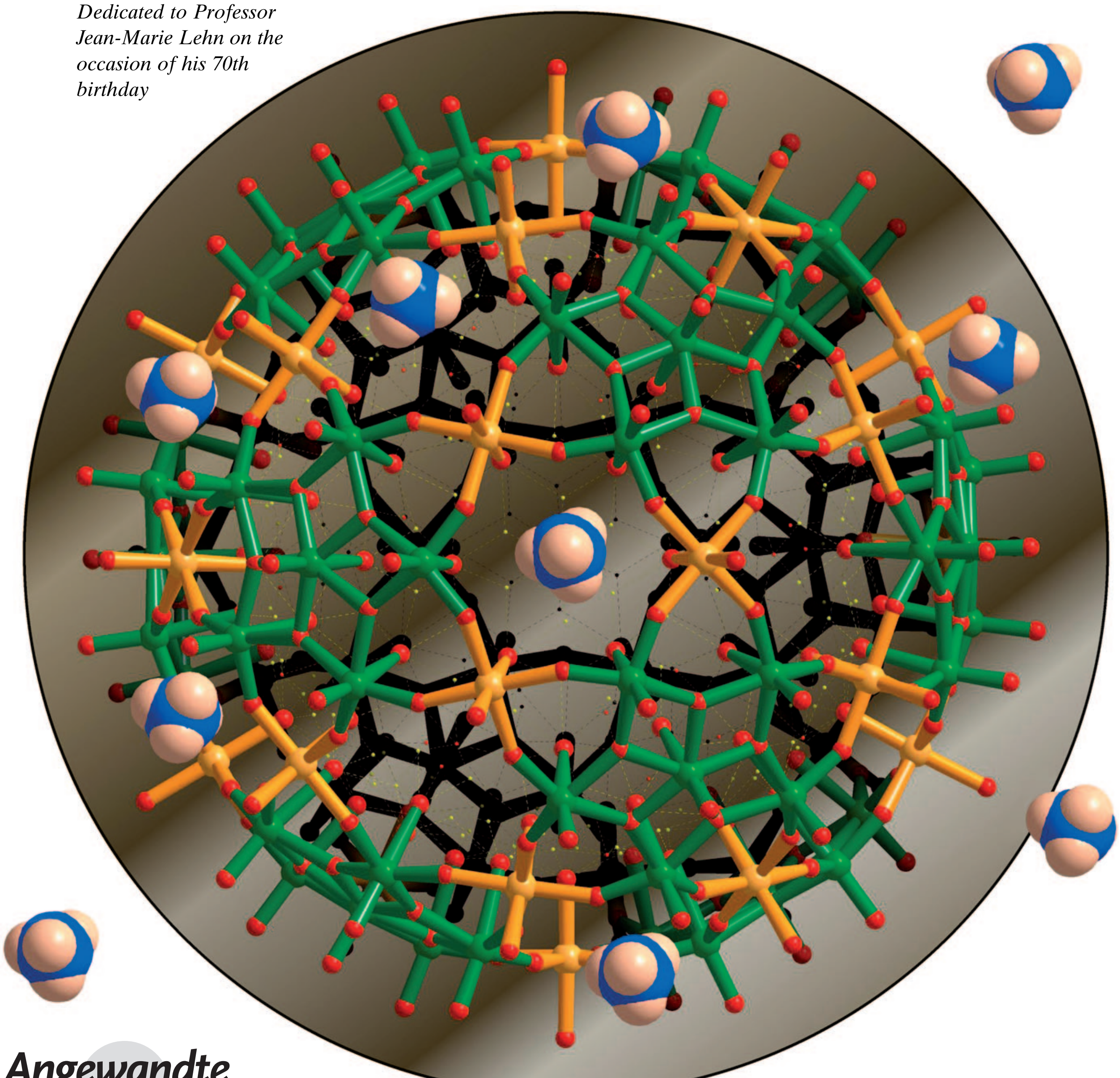
Dedicated to Professor Jean-Marie Lehn on the occasion of his 70th birthday



The variety of properties of soluble, spherical, stable metal oxide based porous nanocapsules of the type $\{(M)M_5\}_{12}$-$(\text{linker})_{30}$ ($M = Mo$, W) with gated pores and well-defined external and tunable internal surfaces—either of the organic/hydrophobic or inorganic/hydrophilic type influencing the different encapsulates' structures—have stimulated groups worldwide to investigate related materials' scientific aspects;[1] for general aspects of the chemistry, see references [1–3d]. In this context, it is noteworthy that chemical studies can be performed at the inner and outer surfaces as well as at the interface between the subunits, as in the case of spherical viruses.[3e] It is important for synthetic aspects that the capsules' basic parts, that is, the 12 metal oxide based pentagonal units, are present in a dynamical library;[4] interestingly, pentagonal units are also the central elements of important spherical structures, such as the C_{60} buckyball, icosahedral viruses, and geodesic domes.[4a] If the linking of the pentagonal units $\{(M)M_5\}$ occurs through mononuclear spacers M′ such as Cr^{3+} and Fe^{3+}, smaller porous capsules are formed;[5,6a] and if binuclear spacers such as $\{Mo_2O_4\}^{2+}$ are used, larger pores are obtained.[1–4a] Importantly, the pentagonal units $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ can act not only as transferable ligands[6a] but can also be transferred from the $\{Mo_{132}\}$ Keplerate into solid-state structures of catalytical interest.[6b] In this context, it is worthwhile to mention that in spite of the existence of more than a thousand polyoxotungstates, the first one containing pentagonal $\{(W)W_5\}$ units was published only quite recently.[4a] Herein we show that $\{(W)W_5\}$ units (for details regarding their formation, see Ref. [4a]) can be linked through Fe^{3+} ions, thus allowing the isolation of the new spherical Keplerate and antiferromagnet **1a**. The obtained results (see title) could be anticipated for the following reasons: First, the presence of the expected 20 crown ether type $\{Fe_3W_3O_6\}$ pores leads (especially because of the high negative cluster charge, and in the context of sphere surface supramolecular chemistry) to the fixation of 20 NH_4^+ ions through hydrogen bonds. Second, the magnetic properties of **1a** showed the expected difference to those of the spherical antiferromagnet $\{Mo_{72}Fe_{30}\}$, exhibiting frustration properties with model character for Kagomé lattices (see below). Preliminary results of the solution properties of **1** were obtained with regard to assembly and pore-based guest uptake–release processes, with an option in the case of appropriate substrates for future investigation of cooperativity, regulation, and allostery phenomena.

Compound **1**, obtained by treating an acidified aqueous solution of sodium tungstate with Fe^{2+} in the presence of oxygen, was characterized by elemental analysis, thermogravimetry (to determine the crystal water content), spectroscopic methods (IR, Raman, UV/Vis), single-crystal X-ray structure analysis (see the Experimental Section), and susceptibility measurements (including related classical Monte Carlo calculations). Solutions of the compound were investigated by light-scattering methods.

The $\{W_{72}Fe_{30}\}$ cluster **1a** (Figure 1, top) belongs to the family of icosahedral porous capsules and polyoxometalates having the general formula $(\text{pentagon})_{12}(\text{linker})_{30}$ mentioned above. The 12 $\{(W)W_5\}$-type pentagonal units are positioned at the vertices of an icosahedron and are linked by 30 Fe^{III} centers spanning an icosidodecahedron. An important result is that 20 NH_4^+ ions are fixed through hydrogen bonds by the 20 $\{Fe_3W_3O_6\}$ pores exhibiting crown ether function (see below and Figure 2).

$$\begin{aligned}&Na_6(NH_4)_{20}(Fe^{III}(H_2O)_6)_2[\{(W^{VI})W^{VI}{}_5O_{21}(SO_4)\}_{12}\text{-}\\&\quad\{(Fe(H_2O))_{30}\}(SO_4)_{13}(H_2O)_{34}]\cdot \text{ca. } 200\,H_2O\\&\quad\equiv Na_6(NH_4)_{20}(Fe^{III}(H_2O)_6)_2\cdot \mathbf{1a}\cdot \text{ca. } 200\,H_2O \qquad \mathbf{1}\end{aligned}$$

Regarding further structural details, there are 25 SO_4^{2-} ligands inside the cavity of the cluster **1a** causing its negative charge, in contrast to the well-known $\{Mo_{72}Fe_{30}\}$ ball, which is practically neutral (it contains acetate instead of sulfate ligands)[6a] and therefore does not show significant pore–NH_4^+ interactions. In the present case we have three different types of sulfate coordination organized in an interesting scenario (Figure 1, bottom). This situation allows investigation of unprecedented types of equilibria inside a cavity in which ligands are weakly coordinated to different positions, which is easily investigable, for example in the case of acetates, with ^1H NMR spectroscopy.[7]

Whereas NH_4^+ ions are preferably recognized by receptors containing tetrahedral recognition sites,[8a,b] they are fixed in the present case by approximately planar $\{Fe_3W_3O_6\}$ pores comparable to the [18]crown-6 scenario, owing to the formation of N−H···O hydrogen bonds (N···O ca. 3.1 Å; Figure 2 bottom). In any case, a tremendous amount of literature exists about the complexation and recognition of the ammonium ion and its derivatives by different hosts. The present situation is comparable to that of substituted ammonium ions, which play a role in biology,[8a] while it is known from the chemical side that macrocyclic polyethers bind

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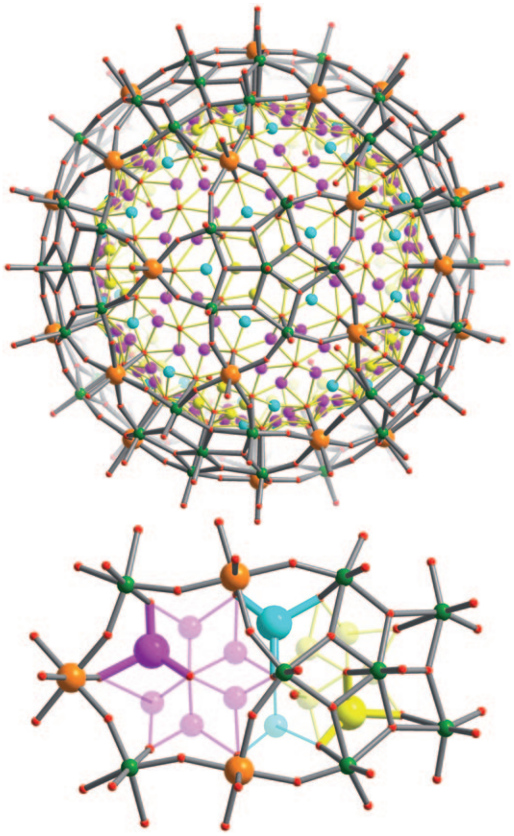

Figure 1. Top: Ball-and-stick representation of the anion **1a** without the NH_4^+ ions but emphasizing the 25 SO_4^{2-} ligands coordinated in three different ways to the inner shell of the cluster and their disorder as a sign of the complexity. 1) 12 SO_4^{2-} ligands coordinate in a tridentate fashion to the 12 $\{(W)W_5\}$-type pentagons, while each ligand is disordered over the five relevant positions (S yellow spheres); 2) five SO_4^{2-} ligands are coordinated in a tridentate fashion to two W atoms of the pentagonal units and one Fe atom, while the ligands are disordered over two positions per Fe^{3+} linker (S turquoise spheres); 3) eight SO_4^{2-} ligands coordinate in a bidentate fashion to one W atom of the pentagonal units and one Fe atom, disordered under each $\{Fe_3W_3O_6\}$-type pore over six positions (S lilac spheres). Bottom: Fragment of the anion **1a** (ball-and-stick representation) showing one $\{Fe_3W_3O_6\}$ pore together with one $\{(W)W_5\}$-type pentagonal unit and the three different coordination types of the SO_4^{2-} ligands. The disordered SO_4^{2-} ligand positions are transparent for clarity. W green, Fe orange, O red.

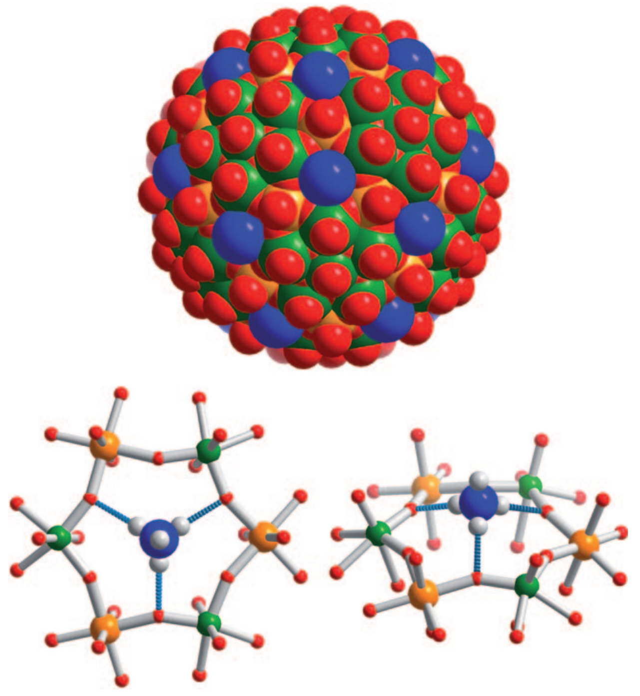

Figure 2. Top: Space-filling representation of **1a** (in the solid state with closed pores) highlighting the affinity of the 20 $\{Fe_3W_3O_6\}$-type pores, acting similarly to [18]crown-6, for the 20 NH_4^+ cations located on the C_3 axes. Bottom: Two views of the pore situation (N blue, H (generated) light gray; other colors as in Figure 1).

primary ammonium ions[8c] by anchoring NH_3^+ groups in their circular cavities through three N−H⋯O hydrogen bonds.[8a] The equilibrium scenarios of solutions of **1** regarding uptake and release of the guests depend on the type of solvent, the concentration, and the temperature (see below). These solutions will be studied in due course by NMR spectroscopy in the case of monosubstituted and diammonium ions, the latter regarding their linker function for the Keplerates.

Regarding the electronic and magnetic structure, the ^{57}Fe Mössbauer spectrum of **1** measured at 80 K shows the presence of Fe^{III} centers in a weakly distorted octahedral environment of O atoms ($\delta = 0.51\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.79\ \mathrm{mm\,s^{-1}}$), and the electronic absorption spectrum in aqueous solution shows a very weak characteristic band at 450 nm caused by an orbital- and spin-forbidden d–d transition (ground state $^6A_{1g}$).

The magnetic properties of Keplerates of the type $\{(Mo)Mo_5\}_{12}M_{30}$ ($M = Fe^{III}, Cr^{III}, V^{IV}$) have received a lot of attention, especially owing to their spherical network based on corner-shared M_3 triangles,[9] which causes geometrical frustrations analogous to those in Kagomé lattices, which play a significant role in materials science.[10] In this context, an interesting problem arose as to whether the exchange interactions between the 30 magnetic centers on the surface of the spherical capsules (i.e., of the mentioned Keplerate type) can be deliberately changed or tuned. According to our knowledge of the geometrical and electronic structures of polyoxomolybdates and -tungstates,[11] such tuning was expected to be possible, as the replacement of the molybdenum oxide based pentagons by those containing tungsten atoms reduces the (anyhow weak) electron delocalization from the 30 3d ions.

Measurements of the weak-field molar susceptibility $\chi = M/H$ were performed using a superconducting quantum interference device magnetometer (Quantum Design) in the temperature range 5–300 K in a fixed applied magnetic field $H = 0.5$ T (Figure 3). The solid curve in Figure 3 is the result of our theoretical modeling, which is based on the following: 1) Nearest-neighbor Fe^{3+} ions within a given cluster are assumed to interact through antiferromagnetic isotropic Heisenberg exchange, and their susceptibility was calculated using the same classical simulational approach, including the value of the spectroscopic splitting factor ($g = 1.974$), as employed previously[9c] for the Keplerate $\{Mo_{72}Fe_{30}\}$. 2) We

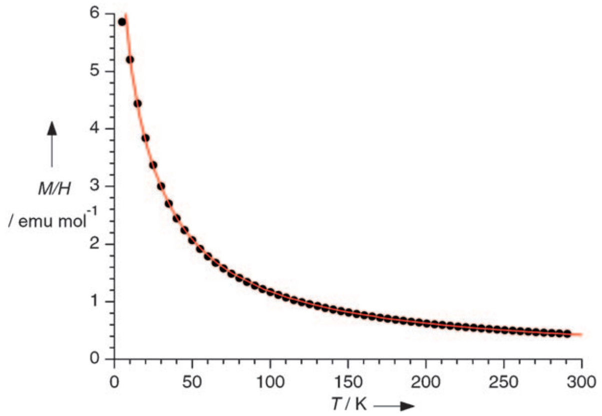

Figure 3. Magnetic susceptibility of **1** versus temperature. Experimental data are filled circles; theory given by the solid curve.

accounted for the presence (identified by a characteristic $1/T$ temperature-dependent contribution) of approximately two uncorrelated Fe^{3+} ions per molecular unit (see formula of **1**) that are magnetically and structurally independent of the cluster skeleton, and we applied a correction for diamagnetism (-10^{-2} emu mol^{-1}). The solid curve is drawn for the choice of the nearest-neighbor classical exchange constant $J_c/k_B = 10.6$ K,[9c] which is compared with the value 13.7 K for $\{Mo_{72}Fe_{30}\}$.[9c] (It should be noted, however, that a fit of comparable quality could be achieved for **1** using values of J_c/k_B differing from the above choice by nearly 10%.) Despite the somewhat provisional nature of our estimate of the exchange constant, the key point is that the replacement of molybdenum by tungsten has led to a significant weakening of the Fe–Fe exchange interaction. Finally, in the near future we will perform susceptibility measurements on **1** down to millikelvin temperatures, with the aim of checking whether quantum corrections to the classical Heisenberg model susceptibility continue to remain ignorable, perhaps in analogy to the fascinating example of the Keplerate $\{Mo_{72}Fe_{30}\}$ (title of the related paper: "Classical and Quantum Magnetism in Giant Keplerate Magnetic Molecules";[9c] see also section titled "Spherical antiferromagnets" in Ref. [9d]).

To get information about the possible release of NH_4^+ ions and the dependent assembly behavior, dilute aqueous solutions of **1** were studied by laser light-scattering techniques.[12a–f] For the case that the NH_4^+ ions of **1** were all released, a self-assembly process leading to blackberry-type structures would not be expected, owing to the electrostatic repulsion caused by the resulting rather high negative charge of the macroion (−32 in total), as in the investigated cases of the Keplerates $\{Mo_{132}\}$[12b] and $\{Mo_{72}V_{30}\}$[12c] with −42 and −31 charges, respectively. The mentioned $\{Mo_{72}V_{30}\}$-type ions can only assemble in water when carrying lower charges arising from incorporation of K^+ cations into the pores, which is the case when the solvent becomes less polar, as for water/acetone mixtures.[12c] However, based on the present light-scattering studies, the formation of supramolecular structures was observed in an aqueous solution of **1** at pH 4.6, while the intensity of the scattered light increased as usual over time, as these types of assembly processes are slow.[12a–f] Preliminary results showed that the scattered intensity is greater than 300 kcps, in connection with an average hydrodynamic radius (R_h) of approximately 31 nm (Figure 4). This finding demonstrates that the present macroion charge in solution is lower than in the scenario characterized by the release of all NH_4^+ ions from the pores of **1a**. Furthermore, after mild heating of the mentioned solution to 40 °C, the total scattered intensity dropped. This result was expected, as the release of the ammonium ions from the pores into the bulk solution is strongly enhanced by increased temperature; the temperature effect on increasing the assembly velocity plays a minor role in this context (for a related effect see, for example, Ref. [12a]). In a preliminary study, after having introduced acetone into the aqueous solution, the assembly process became more pronounced (as detected by an increase of scattered light), and the assemblies increased in size owing to the incorporation of more NH_4^+ ions into the pores.[12g] In light of these first results, the host–guest equilibrium should, in the future, be studied sophisticatedly for alkyl ammonium ions by NMR spectroscopy.[8c]

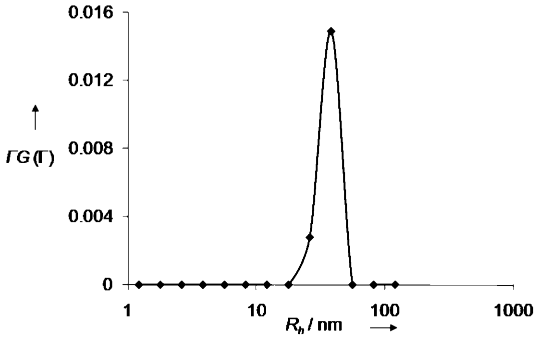

Figure 4. CONTIN analysis[19] of the dynamic light-scattering study on a 0.5 mg mL^{-1} aqueous solution of **1** (pH 4.6; see the Experimental Section). The y axis denotes the relative contribution from particles with different sizes to the total scattered intensity of the solution. R_h is the hydrodynamic radius.

Referring to another topic, the present Keplerates have the potential to considerably advance low-temperature geochemistry research, because they show key functional groups that are present on natural minerals but cannot be studied directly.[13] Regarding an important question concerning the timescales for water-ligand exchange on iron oxide minerals, **1a** is of interest as it exposes H_2O ligands (bound to the Fe^{III} spacers) that are isolated from one another as they are at an oxide mineral surface. The rates of ligand exchange with bulk solution have recently been measured for the $\{Mo_{72}Fe_{30}\}$ cluster[13a] and fall into the microsecond time range, in agreement with the presently obtained preliminary ^{17}O NMR spectroscopy data on solutions of **1**.

Though the principle of the high formation tendency of the present type of spherical Keplerate skeleton has been discussed before[14] (also with respect to the necessary presence of the basic pentagonal units in the reaction medium),[4,5] a useful identification of the pentagonal units integrated into a spherical species through a basic simple physical method has not been described to date. This point is significant as materials science aspects of these compounds are presently being investigated by several groups, but also because wrong spectra were published. Remarkably, the IR spectra between approximately 1000 and 500 cm^{-1} (with bands mostly arising from vibrations of the metal oxide skeleton) observed for the molybdates and tungstates of the same size, that is, those of the type $\{(M)M_5\}_{12}M'_{30}$ (see Figure 5) and of the type $\{(M)M_5\}_{12}(Mo_2O_4)_{30}$ (see Ref. [15]) are practically identical. But there is, of course, a reduced similarity between the differently sized Keplerates, as the larger ones contain 30 $\{Mo_2O_4\}^{2+}$ linkers. To conclude, the IR spectra allow a simple confirmation of the presence of the 12 $\{(M)M_5\}$ units in an icosahedral arrangement.

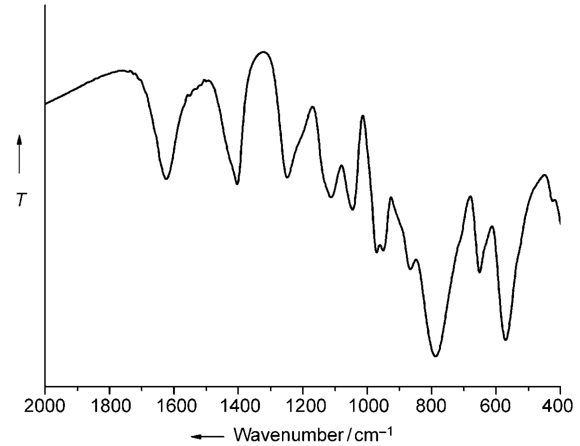

Figure 5. Infrared spectrum of **1** (KBr pellet) showing the characteristic pattern arising from the presence of the 12 icosahedrally arranged pentagonal $\{(W)W_5\}$ units in the region between 1000 and 500 cm^{-1}. Nearly identical patterns are observed for all $\{(M)M_5\}_{12}M'$ (M = Mo, W; M' = V, Cr, Fe) Keplerates; for the typical pictured spectrum for the larger Keplerates of the type $\{(M)M_5\}_{12}\{Mo_2O_4\}_{30}$, see Ref. [15]. For the influence of M in the case of the Raman spectra, see Ref. [4a].

To summarize, there are four interesting results of the present work: 1) the option to perform sphere surface supramolecular inorganic chemistry, 2) the option to tune deliberately the exchange coupling constants of homologous spherical metal oxide based antiferromagnets,[9d] 3) the option to perform in the future unprecedented polyoxotungstate chemistry based on the pentagonal $\{(W)W_5\}$ units, in agreement with Ref. [16], as well as 4) the discovery that, in connection with point (1), the 20 pores with crown ether function of a spherical inorganic nanocluster can fix (recognize) 20 NH_4^+ ions, while the related equilibrium in solution can be tuned. In this context, it should be mentioned that the phenomenon can be correlated with different aspects of counterion effects.[17,18] A challenge is to distinguish between controllable, specific cation coordination and recognition, as in the present case, and types of nonspecific "classical" ion pairing; both, for example, facilitate differently the formation of macroanion-based assemblies. A further challenge will be to study, based on the stepwise fixation of a variety of appropriate substrates in the present type of Keplerates' pores, effects related to allostery, cooperativity, and regulation; in other words, to study interrelated features which result when the occupation of a given site leads to changes in the properties of the other sites (see Ref. [8a]).

Experimental Section

1: $FeSO_4{\cdot}7H_2O$ (3.5 g, 12.6 mmol) was added to a solution of $Na_2WO_4{\cdot}2H_2O$ (4.0 g, 12.1 mmol) in H_2O (25 mL) acidified with H_2SO_4 (0.5 M; 20 mL). After stirring for 8 h in an oil bath at 100 °C and subsequent addition of NH_4Cl (1.25 g, 23.37 mmol) to the orange-yellow solution, the mixture was cooled to room temperature and filtered. The yellow crystals, which precipitated after three weeks, were filtered off, washed with cold water, and dried in air. Yield: 0.55 g. Characteristic IR bands (KBr pellet): $\nu = 1626$ (m, $\delta(H_2O)$), 1402 (m, $\delta_{as}(NH_4^+)$), 1248, 1115, 1047 (all m, $\nu_{as}(SO_4)$ triplet), 970 (m, $\nu(W{=}O)$), 950 (m), 868 (m), 789 (vs), 650 (m), 570 cm^{-1} (s). Raman bands (solid; $\lambda_e = 765$ nm): $\nu = 975$, 903 (s and m, both $\nu(W{=}O)$), 844 (s), 707 (w), 527 (m), 424 (w-m), 358 cm^{-1} (m). UV/Vis (in H_2O): λ(nm) = 312 (O→Fe charge transfer or internal pentagonal unit transitions), 450 (d–d transition observable only in very concentrated solutions). Elemental analysis calcd (%): S 2.98, Fe 6.64, Na 0.51, N 1.04; found: S 2.7, Fe 6.1, Na 0.4, N 1.1. The relatively large amount of Fe^{2+} in the synthesis procedure leads to the presence of $[Fe(H_2O)_6]^{3+}$ in the lattice; see magnetic part and next paragraph.

Crystal data for **1**: $M = 26929.10$ g mol^{-1}, $W_{72}Fe_{32}H_{632}N_{20}Na_6O_{628}S_{25}$, cubic, space group $Fm\bar{3}$, $a = 39.1305(13)$ Å, $V = 59916(3)$ Å^3, $Z = 4$, $\rho = 2.985$ g cm^{-3}, $\mu = 14.728$ mm^{-1}, $F(000) = 49688$, crystal size = $0.5 \times 0.44 \times 0.34$ mm^3. A total of 90167 reflections ($2.27 < \Theta < 26.95°$) were collected, of which 5666 reflections were unique ($R(\text{int}) = 0.0728$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0316$ for 5105 reflections with $I > 2\sigma(I)$, $R = 0.0391$ for all reflections; max/min residual electron density 1.813 and −1.422 e Å^{-3}. Crystals of **1** were removed from the mother liquor and immediately cooled to 183(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). SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1997/2003; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001. The disordered Na^+ and Fe^{III} ions in the large voids of the crystal lattice do not allow, as usual, their positioning. Correspondingly, there is a related error limit in the formula of **1**, also influenced by the found analytical values. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-380386.

Static and dynamic light-scattering experiments were performed on a Brookhaven Instrument laser light-scattering spectrometer equipped with a solid-state laser operating at 532 nm. The data, analyzed by the CONTIN method,[19] can be used to determine the average hydrodynamic radius (R_h) of the assemblies. Detailed descriptions of the SLS and DLS techniques can be found in our earlier publications.[12]

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