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A Small Cavity with Reactive Internal Shell Atoms Spanned by Four $\{As(W/V)_9\}$-Type Building Blocks Allows Host–Guest Chemistry under Confined Conditions

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Abstract: The reaction of $[H_2As^{III}W_{18}O_{60}]^{7-}$ with VO^{2+} and SO_4^{2-} ions in aqueous solution leads to a V^{IV}/V^{V} mixed-valence cluster anion containing the $\{As_4M_{40}O_{140}\}$-type cryptand which has a high formation tendency. An important result is that it exhibits a new type of reactive internal cavity shell. The correspondingly obtained compound $Na(NH_4)_{20}[\{(V^{IV}O(H_2O))(V^{IV}O)_2(SO_4)_2\}\{(As^{III}W_9O_{33})_2(As^{III}W_{7.5}V^{V}{}_{1.5}O_{31})_2(WO_2)_4\}]\cdot 40\,H_2O$ (**1**), which can also be synthesized from a precursor with the preorganized cryptand, was characterized by elemental and thermogravimetric analyses (determination of crystal water content), redox titrations (determination of the number of V^{IV} centers), electronic absorption as well as vibrational spectra, single-crystal X-ray structure analysis (including bond valence sum calculations), and magnetic susceptibility measurements. The relatively small central cavity—formed by the linking of four $\{AsM_9\}$-type lacunary units (M = W/V) by four WO_6 octahedra—allows positioning of a variety of cationic as well as anionic "guests" under confined conditions according to a new approach: replacement of some of the W by V atoms leads to high reactivity of the internal cavity shell as a result of relatively weak VO bonds compared to the WO bonds. This allows an interesting "encapsulation chemistry" with new options. In the present case the cavity contains besides an arrangement of three V^{IV} centers, two sulfate groups that replace O atoms of the $\{AsM_9\}$ units as well as an interesting hydrogen bond situation.

Keywords: cryptand · encapsulation chemistry · magnetism · polyoxometalates · tungsten · vanadium

Introduction

Polyoxometalates constitute—due to their structural variety as well as their relevance to several fields[1–4]—a unique class of inorganic species. Whereas in recent years, a variety of very large polyoxomolybdates have been synthesized and structurally characterized, for example the wheel-shaped anions of the type Mo_{154}, Mo_{176}[5,6] as well as the corresponding derivative Mo_{248},[7] the spherical icosahedral capsule Mo_{132},[8] and the "hedgehog-shaped" Mo_{368}-type cluster species,[9] the chemistry of polyoxotungstates is not so rich regarding nanosized complexes (for reasons see reference [9a]; but note the existence of the W_{148} anion[10]). On the other hand, polyoxotungstates offer other options: special polyoxotungstate(VI) matrices for instance are ideal for embedding "guests", for example, in the form of magnetic centers. In this sense trilacunary-type XW_9 units used as building blocks are of special importance. When three corner-shared octahedra are removed from a Keggin ion, the so-called A-type trilacunary anion is obtained, whereas the loss

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of three edge-shared octahedra results in a B-type trilacunary anion. The latter type, which is obtained if the central atom such as As^{III} has a lone pair of electrons, can be used, for example, as building blocks for the synthesis of sandwich-like mixed- and non-mixed-valence complexes of the type $[(VO)_3(XW_9O_{33})_2]^{n-}$ ($n=11$, 12; X = As^{III}, Sb^{III}) in which two α-B-$[XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}) units are linked by a belt of three VO^{2+} ions[11,12] (see also reference [13]). Quite a variety of encapsulation-type investigations were performed based on the (related) cryptand $\{As_4W_{40}O_{140}\}$, in which four B-type trilacunary units are linked together by four WO_6 octahedra, for example, in clusters with the general formula $[M1M2_mZ_2(H_2O)_2As_4W_{40}O_{140}]^{x-}$, where M1 and M2 ($m=0$ or 1) are alkali and/or alkaline-earth metal cations and Z, first-row transition-metal ions (e.g. Co^{2+}).[14–16] Here we demonstrate the option for a new type of encapsulation chemistry by an unprecedented activation of the $\{As_4W_{40}O_{140}\}$ internal shell cryptand atoms, which is based on the substitution of tungsten atoms of the XW_9 units by vanadium centers with the consequence of an activation of the oxygen atoms at the internal cavity shell. In this context we report here the compound $Na(NH_4)_{20}[\{(V^{IV}O(H_2O))(V^{IV}O)_2(SO_4)_2\}\{(As^{III}W_9O_{33})_2(As^{III}W_{7.5}V^{V}_{1.5}O_{31})_2(WO_2)_4\}]\cdot 40H_2O$ (**1**) ≡ $Na(NH_4)_{20}$-**1a**·$40H_2O$, containing three V^{IV} centers and two sulfate groups in the small anion central cavity which could be made possible due to the replacement of W^{VI} by V^{V} atoms leading to increased reactivity of the O (-V) atoms. The present investigation demonstrates the general option to place a variety of magnetic centers adjacent to *anionic guests* such as sulfate ions under confined conditions in a cryptand, as well as the option to generate interesting hydrogen bonding situations in which water ligands coordinated to the metal centers are involved. Important in this context is the small cavity space which can lead, in principle, to strong exchange interactions.

Results and Discussion

Compound **1** was primarily prepared by heating an aqueous solution of the sodium salt of $[H_2As^{III}W_{18}O_{60}]^{7-}$ (**2a**)[17] and $VOSO_4\cdot 5H_2O$ and was characterized by elemental and thermogravimetric analyses (for determination of crystal water content), electronic absorption as well as vibrational spectra, single-crystal X-ray structure analysis (including bond valence sum calculations), magnetic susceptibility measurements, and redox titrations (for the determination of the number of V^{IV} centers). The mentioned reaction occurs due to the high formation tendency of the anionic $\{As_4M_{40}O_{140}\}$ type cryptand. (Compound **1** can correspondingly also be obtained from the preorganized cryptand abundant in the compound $Na_{27}[Na\{(As^{III}W_9O_{33})_4(WO_2)_4\}]\cdot 60H_2O$ (**3**)[14] (see Experimental Section), but unfortunately the crystal quality is not as good.) Although the basic framework, that is, the cryptand skeleton of **1a**, is formally similar to that of the anions **4a** of $(NH_4)_{21}[\{(NH_4)_3(Co^{II}H_2O)_2\}\{(As^{III}W_9O_{33})_4(WO_2)_4\}]\cdot 19H_2O$ (**4**) ≡ $(NH_4)_{21}$-**4a**·$19H_2O$[15,18] and **5a** of $Na_{23}[\{Na(Na_4)\}\{(As^{III}W_9O_{33})_4(WO_2)_4\}]\cdot 2Cl\cdot nH_2O$ (**5**) ≡ Na_{23}-**5a**·nH_2O (reformulated here),[19] it contains a new type of cavity reactivity and related interesting "encapsulations" (details below).

Each cluster anion of **1a** is "linked" in the crystal lattice to two neighboring anions by disordered $Na(H_2O)_3$ units, leading to the formation of infinite parallel chains (Figure 1a). A characteristic feature of these parallel chains is that they are rotated relative to neighboring chains by 180° parallel to the *c* axis, translated by *c*/2, and are then connected through additional "Na–O bonds" thus forming a layer structure. Interestingly, exactly the same number of Na^+ ions was obtained (one Na^+ ion/formula unit) in spite of varying the NH_4^+ concentration in the reaction medium. This reemphasizes the possible importance of the presence of appropriate countercations for the assembly of (large) polyoxometalate structures.

The cluster anion **1a** (Figure 1b) is, as mentioned above, built up by four trilacunary α-B-$As(W/V)_9$ units connected by four WO_6 octahedra, thereby generating a cyclic arrangement with a small central cavity. Two of the opposite AsM_9 units have two tungsten atoms (mostly) replaced by V^V centers, which corresponds to the related disorder of the anions in the crystal lattice, while the occupancy factor is about 25 % for W and 75 % for V atoms. Each trilacunary unit has six oxygen atoms available for coordination; in Figure 1b the corresponding 4×6 oxygen atoms (red) are marked by a black rectangle. Four of these oxygen atoms are shared with neighboring connecting WO_6 octahedra (see above), that is, two lacunary units share one WO_6 octahedron. The remaining two oxygen atoms participate in two coordination modes: 1) each of the two lacunary units containing only W atoms (these are shown on the left and right in Figure 1b) is linked to an $O{=}V^{IV}O_4$ square pyramid by sharing corners, that is, at the positions marked as S2 in Figure 1c where Co^{2+} is found in **4a**; 2) each of the two lacunary units containing V centers (top and bottom in Figure 1b) is linked to a sulfate group by sharing corners, that is, at the positions marked as S2′ in Figure 1c where NH_4^+ ions are found in **4a**. Referring to the four bridging WO_6 groups: each of these shares one corner with one of the $O{=}V^{IV}O_4$ square pyramids and another corner with a central $V^{IV}O_5(H_2O)$ octahedron, defining the S1 site, which is occupied in **4a** by an NH_4^+ ion. Interestingly, the sulfate groups are stabilized by short hydrogen bonds between the O atoms of the sulfate group and the H_2O ligand of the central $V^{IV}O_5(H_2O)$ octahedron (Figure 2a).

Owing to its small central cavity and the reactive internal cavity shell, the present $\{As_4M_{40}O_{140}\}$-type cryptand (see also references [14,15]) is a remarkable "host" for the incorporation of guest cations and anions, and especially of magnetic centers in presence of anions under confined conditions. The option of making the lacunary fragments more reactive leads to sulfate ligation, which is caused by the partial replacement of W by V atoms, and consequently to weakened metal–oxygen bonds. Under changed reaction conditions by a synthesis similar to that of compound **1**[20] but with a lower

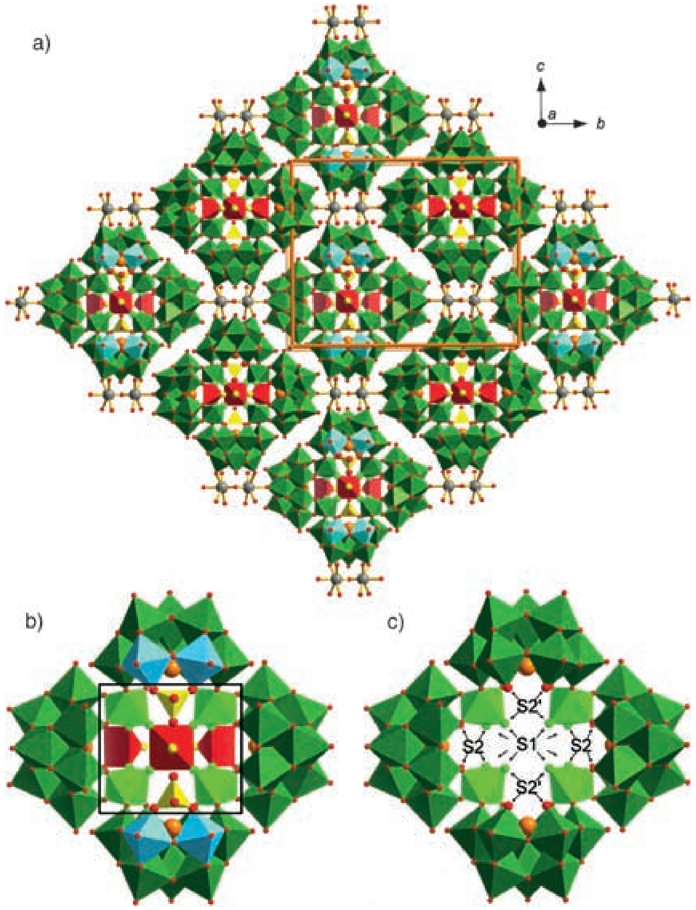

Figure 1. a) Packing of the cluster anions **1a** (see Figure 1b) in the crystal lattice of **1**. Each anion is "connected" to two neighboring anions by disordered $Na(H_2O)_3$ units, leading to the formation of infinite chains parallel to the crystallographic *c* axis (top to bottom). Parallel chains are rotated relative to neighboring chains by 180° parallel to the *c* axis, translated by *c*/2 and then connected through additional "Na–O bonds" forming a layer-type structure (color code as in Figure 1b; Na^+ ions: gray spheres; coordinating H_2O molecules: red spheres). b) and c) Structure of **1a** (b) (in polyhedral representation) and comparison with that of **4a**, **5a** (c; in polyhedral and schematic representation; S1, S2 and S2′ denoted as in reference [15]). All three anions are built up by four AsM_9-type units (green polyhedra; As centers: orange spheres) linked by four WO_6 octahedra (light green polyhedra). In **1a** (b) two tungsten positions in two of the four AsM_9 units (top and bottom) are partially occupied by vanadium atoms (related polyhedra blue). Three additional vanadium centers occupy the sites marked as S1 and S2 in Figure 1c. A $VO_5(H_2O)$ octahedron fills position S1, whereas two OVO_4 square pyramids occupy the S2 positions. The S2′ sites are formally "filled" by SO_4^{2-} tetrahedra, whereas the AsM_9 (i.e. V/W) and SO_4^{2-} units have O atoms in common. (The color code for the polyhedra and the O atoms is chosen to illustrate the *formal* building blocks as given in the formula of **1**: "$V^{IV}O(H_2O)$": red octahedron with two yellow spheres; "$V^{IV}O$": red square pyramids with one yellow sphere; "SO_4": yellow tetrahedra with four red spheres; "WO_2": light green polyhedra with two green spheres). In **4a** (c) the S1 and S2′ positions are occupied by NH_4^+ ions, and both S2 sites by Co^{2+}. In **5a** (c) all S1, S2, and S2′ sites are occupied by Na^+ ions; Cl^- ions bridge the Na^+ ions in the S2 and S2′ sites (see reference [19]).

pH value, the compound $(NH_4)_{20}[\{(V^{IV}O(H_2O)(V^{IV}O)_2)(NH_4)_2\}\{(As^{III}W_9O_{33})_4(WO_2)_4\}]\cdot 40\,H_2O$ (**6**) $\equiv (NH_4)_{20}$-**6a**$\cdot 40\,H_2O$,[20] can be obtained. This is similar to **1** but with

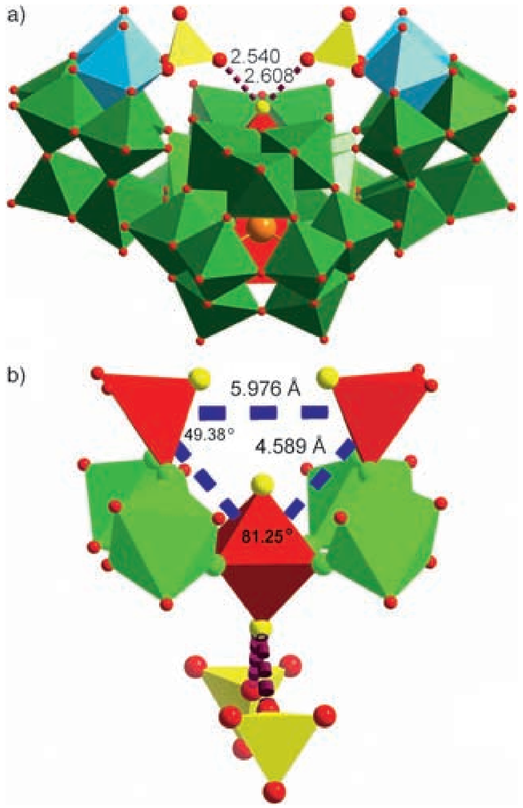

Figure 2. a) Side view of **1a** highlighting the cavity with the interatomic distances [Å] corresponding to short hydrogen bonds between the sulfate groups and the central $V^{IV}O_5(H_2O)$ octahedron. b) The interatomic distances [Å] and angles [°] between the three V^{IV} centers inside the cavity of **1a** defining a triangle (color code as in Figure 1).

the difference that the W atoms are not substituted by V atoms at all and the positions of the sulfate ligands are correspondingly (formally) occupied by NH_4^+ ions. This observation corresponds to the known fact that substitution reactions of the type discussed here, involving a weakening of the WO bonds, are favored at higher pH values (see for example, reference [3]). The complete results of the single-crystal structure analysis of **6a**, which are not of interest in the present context, are not reported here, only the characterization by unit cell dimensions, analytical data, and characteristic magnetic data which show clearly the three encapsulated V^{IV} centers (see below).

Spectroscopic and magnetic properties: The electronic absorption spectrum (Vis/NIR region) of **1** in aqueous solutions shows bands at about 690(sh) and about 860 nm, which arise from d–d (V^{IV}) and/or $V^{IV} \rightarrow W^{VI}$ (IVCT) charge transfer transitions[21] and confirm the presence of the V^{IV} centers.

The magnetic susceptibility of compound **1** was measured as a function of temperature. These data are shown in Figure 3 as the product of molar magnetic susceptibility and temperature against temperature. The χT value at high temperature is $1.08\,emu\,K^{-1}\,mol^{-1}$, which is close to the expected spin-only value for three $S=1/2$ ions ($\chi T = 1.08\,emu\,K$

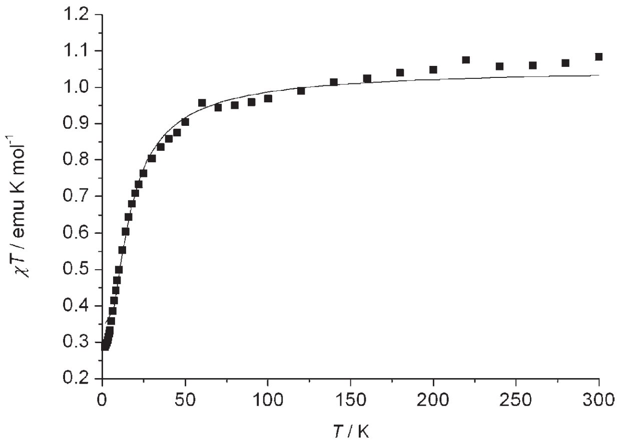

Figure 3. The molar susceptibility temperature product versus temperature for **1**, recorded on a powder sample at an applied field of 0.5 T.

mol^{-1}; the average g value of vanadyl ions was taken to be 1.96[22]). On lowering the temperature the χT product decreases first slightly, then more rapidly. At the lowest temperatures, it seems to be approaching a limiting value. Fitting χ^{-1} versus T to the Curie–Weiss law (35 K $\leq T \leq$ 300 K), yields a Curie constant of 1.12 emu K mol^{-1}, close to the room-temperature χT value, and a Weiss temperature of $\theta = -13.2$ K, indicative of predominantly antiferromagnetic exchange interactions. The χT versus T data can also be fitted to the van Vleck formula for the susceptibility,[23] assuming nearest neighbor exchange interactions only. Although the three vanadyl ions form a triangle in the structure (Figure 2b), there is interestingly no superexchange pathway between vanadyl ions 1 and 3, but only between neighbored vanadyl ions 1 and 2, and 2 and 3. This means that magnetically, the system can be considered formally as a linear trimer. The superexchange pathway is V^{IV}-O-W-O-V^{IV} and the spin Hamiltonian was defined as $\boldsymbol{H} = J(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_2\boldsymbol{S}_3)$. The least-squares fit leads to an exchange interaction constant of $J = 13.2 \pm 0.5$ cm^{-1} and $g = 1.94$. As mentioned above there is no direct superexchange pathway between the outer vanadyl ions and indeed, including a next-nearest neighbor interaction between the two outer vanadyl ions does not improve the fit significantly.

The compound $(NH_4)_{23}[\{(K)(V^{IV}O)_2\}\{(As^{III}W_9O_{33})_4(WO_2)_4\}]\cdot n H_2O$, the anion of which corresponds to **1a** *without* the central V^{IV} atom, has been earlier examined by magnetic susceptibility measurements and ESR spectroscopy.[24] The susceptibility data between 5 and 300 K show no magnetic coupling between the vanadium ions, in agreement with the above given results for **1**. However, based upon single crystal ESR spectra a very weak antiferromagnetic exchange interaction with $J = -0.073$ cm^{-1} could be reliably determined and represents a superexchange pathway through a sequence of even ten W–O bonds.

Compound **6**, in which no substitution of W atoms by V^V has occurred was also studied by magnetic susceptibility measurements. The room-temperature χT value of 1.02 emu K mol^{-1} is consistent with the presence of three $S = 1/2$ ions. The χT product decreases with decreasing temperature, and reaches a small plateau at 5 K ($\chi T \approx 0.4$ emu K mol^{-1}) before decreasing further. The magnetic susceptibility curve was fitted assuming a linear trinuclear cluster without exchange interactions between the outer ions, as for compound **1** (Figure 4). The obtained exchange interaction of $J = 10.7 \pm 0.5$ cm^{-1}, with $g = 1.92$, is slightly smaller than that of **1**; the difference should be due to the presence of the sulfates in **1a**.

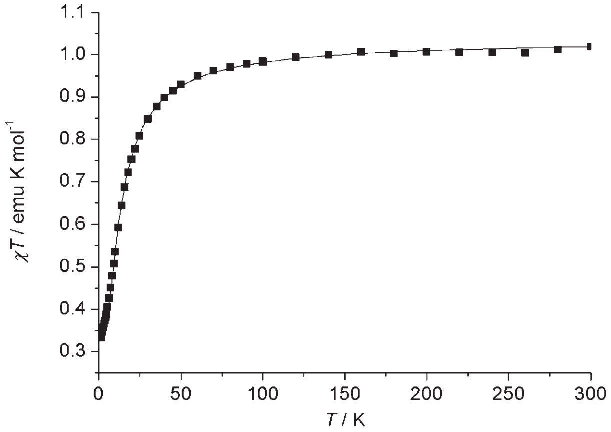

Figure 4. The molar susceptibility temperature product versus temperature for **6** (squares). The drawn line is a fit assuming a linear triangular cluster of three $S = 1/2$ ions, without exchange interactions between the outer ions.

Conclusions and Perspectives

The present discovery shows, in principle, the options of incorporating a variety of (cationic) magnetic centers (see also references [19,25–27]) together with anions in the small cavity of the cryptand. On the other hand, there is the option to investigate interesting related hydrogen bonds situations between oxo anions and H_2O ligands of the metal centers under confined conditions.

The cavity discussed here is much smaller than in some larger polyoxomolybdates that were mentioned in the introduction, for example, in the case of our spherical porous capsules of the type $\{(Mo)Mo_5\}_{12}\{Linkers\}_{30}$[28] which can also encapsulate (cationic) magnetic centers ("*A single-molecule anion made of 132 molybdenum atoms forms a spherical oxide cage that can bind several cations*" was mentioned in a recent highlight referring to that[18] in which the present $\{As_4W_{40}\}$-type cryptand[29] was discussed in that context too). A further option for the future is to study cation inside–outside exchanges by NMR spectroscopy as was done in an interesting earlier study for the present type of cryptand system (see reference [2c]) and which now could be extended to situations in the presence of "encapsulated" anions. Additionally, there is—according to preliminary experiments—the possibility to generate interesting magnetic micelles with cationic surfactants from the cluster anions reported here.[30]

Experimental Section

Preparation of 1: method 1: The sodium salt of **2a** (3 g), which was prepared according to reference [17], was added to an aqueous solution of CH_3COONa/CH_3COOH buffer (pH 4.0) (60 mL) and $VOSO_4{\cdot}5H_2O$ (2 g, 8 mmol). The resulting brown mixture was stirred for 48 h at room temperature, and then heated to 70–80 °C. After addition of NH_4Cl (5 g, 93.4 mmol), the solution was kept at this temperature for 30 min and then filtered while still hot. After six days, dark brown crystals of **1** were filtered. Yield: 1.73 g (54 % based on W).

IR (solid, KBr pellet): $\tilde{\nu}=1616$ (m) [δ (H_2O)], 1402 (s) [δ_{as} (NH_4)], 1209 (w), 1126 (w), 1022 (sh) [all $\nu_{as}(SO_4)$], 956 (s) [ν(W=O)/ν(V=O)], 877 (m), 833 (m), 704 (sh), 621 (m) [ν_{as}(W-O-W)/ν_{as}(W-O-V)] cm^{-1}; Raman (solid, KBr dilution, $\lambda_e=1064$ nm): $\tilde{\nu}=886$ (m), 969 (w) [ν(W=O)/ν(V=O)] cm^{-1}; UV/Vis (in H_2O): λ_{max} (ε) = 862 (208), 694 nm (232 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $H_{162}As_4N_{20}NaO_{188}S_2V_6W_{37}$ (10946.38): N 2.47, Na 0.2, S 0.55, V 2.8, V(IV) 1.5; found: N 2.6, Na 0.2, S 0.3, V 3, V(IV) 1.3.

Method 2: $Na_{27}[Na\{(As^{III}W_9O_{33})_4(WO_2)_4\}]{\cdot}60H_2O$ (**3**; 3 g, 0.26 mmol), which was prepared according to reference [14], was added to an aqueous solution of CH_3COONa/CH_3COOH buffer (pH 4.0) (60 mL) and $VOSO_4{\cdot}5H_2O$ (2 g, 8 mmol). The resulting brown mixture was stirred for 48 h at room temperature, and then heated to 70–80 °C. After addition of NH_4Cl (5 g, 93.4 mmol), the solution was kept at this temperature for 30 min and then filtered while still hot. After five days, the dark brown precipitated crystals of **1** were filtered. Yield: 0.5 g (18 % based on W).

As the quality of the crystals obtained by the alternative preparation method was not as good as those of method 1 the obtained structural data were not given here, though they confirmed the reported structure. Also the analytical, spectroscopic and magnetic data are identical.

Single-crystal X-ray structure determination: Crystals suitable for X-ray crystal structure determination were obtained with the above given synthetic method with the difference that only 1.5 g NH_4Cl was used. This led to better and bigger crystals but also to a longer crystallization time (six weeks). The X-ray crystal structure determination presented here was performed on the crystals obtained primarily.

Crystal data for **1:** $H_{162}As_4N_{20}NaO_{188}S_2V_6W_{37}$, $M_r=10946.38\ g\,mol^{-1}$, orthorhombic, space group *Pnma*, $a=26.201(2)$, $b=28.257(2)$, $c=23.1844(14)$ Å, $V=17165(2)$ Å^3, $Z=4$, $\rho=4.236\ g\,cm^{-3}$, $\mu=25.914\ mm^{-1}$, $F(000)=19428$, crystal size = $0.30\times0.25\times0.15$ mm. 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 ($\theta=0$, 88 and 180°) at a detector distance of 5 cm). A total of 98713 reflections ($1.17<\Theta<27.02°$) were collected of which 19072 reflections were unique ($R(int)=0.0644$). An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined by using SHELXL-93 to $R=0.0447$ for 14594 reflections with $I>2\sigma(I)$, $R=0.0666$ for all reflections; max/min residual electron density 3.798/−3.066 e$Å^{-3}$. (SHELXS/L, SADABS from G.M. Sheldrick, University of Göttingen **1993/97**; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, **2001**.)

Further details of the crystal structure investigation can 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-414216 (**1**).

Magnetic measurements: Magnetic susceptibility measurements were performed on a powder sample using a Quantum Design MPMS XL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions to the molar magnetic susceptibility using Pascal's constants and also for temperature-independent paramagnetism.

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[20] **Preparation of 6:** $VOSO_4{\cdot}5H_2O$ (2 g, 8 mmol) was added to a solution of the sodium salt of **2a** (1.5 g; prepared according to reference [17]) in H_2O (40 mL), which was adjusted to pH 1.9 with 0.5 M H_2SO_4 (2 mL). The solution was stirred at room temperature for 24 h, and then heated to 70–80 °C. After addition of NH_4Cl (3.5 g, 65.38 mmol), the solution was kept at this temperature for 30 min and then filtered hot. After 12 days the precipitated dark brown crystals of **6** were filtered. Yield 0.4 g (24 % based on W). Elemental analysis calcd (%) for $H_{170}As_4N_{22}O_{184}V_3W_{40}$ (11229.5): N 2.7, V 1.3; found: N 2.5, V 1.2. Unit cell parameters for **6**: $a=50.064(3)$, $b=19.8450(10)$, $c=39.185(2)$ Å, $\beta=110.50(1)°$, $V=36465(3)$ Å^3; monoclinic space group $P2_1/c$ (for the magneto-chemical characterization see text).

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[29] According to a nice description in reference [18] the cryptand type can be described as follows: the "[···] polyoxoanion has an annular structure, with a central cation binding site surrounded by four equivalent binding sites arranged on its interior surface. In this arrangement, a "large" central cavity similar to a very distorted cube of eight oxygen atoms is formed, whereas each of the four smaller binding sites has square pyramidal geometry defined by four basal oxygen atoms and an apical arsenic atom [···]".

[30] The treatment of an aqueous solution of **1** with a trichlormethane solution of $\mathrm{DODA^+Br^-}$ leads to a transfer of the complex anion **1a** into the organic phase. Related studies are in progress. For similar encapsulation studies of the giant spherical cluster anions mentioned in the introduction see: a) D. G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M. J. Koop, A. Müller, A. Du Chesne, *Chem. Eur. J.* **2000**, *6*, 385–393; b) D. Volkmer, A. Du Chesne, D. G. Kurth, H. Schnablegger, P. Lehmann, M. J. Koop, A. Müller, *J. Am. Chem. Soc.* **2000**, *122*, 1995–1998; c) D. G. Kurth, D. Volkmer, M. Ruttorf, B. Richter, A. Müller, *Chem. Mater.* **2000**, *12*, 2829–2831; d) D. G. Kurth, P. Lehmann, D. Volkmer, A. Müller, D. Schwahn, *J. Chem. Soc. Dalton Trans.* **2000**, 3989–3998; e) F. Caruso, D. G. Kurth, D. Volkmer, M. J. Koop, A. Müller, *Langmuir* **1998**, *14*, 3462–3465.

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