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Polyoxometalates

Metal-Oxide-Based Nucleation Process under Confined Conditions: Two Mixed-Valence V_6-Type Aggregates Closing the W_{48} Wheel-Type Cluster Cavities**

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Dedicated to Professor C. N. R. Rao

Understanding assembly processes based on the linking of simple XY_n-type polyhedra has been of tremendous interdisciplinary interest since the time of Pauling's original statements referring especially to the silicates.[1a] It seems to be of importance to distinguish between self-assembly and directed-assembly, terms used for elementary processes that probably occurred on the primordial earth.[1b] In bulk solution one can mostly refer to self-assembly, but under confined conditions directed-assembly should be predominant because of the probable influence of the "environment". In nearly all of these cases the elementary processes, especially the first related steps, are not known. The most studied system in this context is that of the polyoxometalates (POMs), in which MO_n-type species appear finally as polyhedra linked (mainly) through corners and edges.[2] Regarding directed-assembly, two reports should be mentioned: a study on a giant wheel-type species in which molecular growth is observed inside the cavity[3] and the discovery of an unprecedented stepwise molecular cascade type growth process based on nucleophilic/electrophilic interactions.[4] Herein we report a process that occurs within the highly negatively charged wheel-shaped $\{P_8W_{48}\}$-type species[5] in which the formation of two mixed-valence $\{V^{V}_4V^{IV}_2O_{12}(H_2O)_2\}^{4+}$ assemblies with linked tetrahedra and octahedra is directed by the internal surface, thereby closing the cluster cavity.[6] This type of process allows generation of a variety of magnetically interesting mixed-valence species by studying systematically the influence of the environment and internal wheel surface under variable redox conditions.

Reaction of a solution of **1** with vanadyl sulfate in aqueous medium yields crystals of **2** after some time. Compound **2**, which crystallizes in the triclinic space group $P\bar{1}$, was characterized by elemental analysis, thermogravimetry to determine the actual crystal water content, spectroscopic methods (IR, resonance Raman, UV/Vis, EPR, MAS-NMR), single-crystal X-ray structure analysis (including bond-valence-sum (BVS) calculations),[7] and susceptibility measurements. A view of the structure of **2** in a mixed polyhedral and ball-and-stick representation is shown in Figure 1.

$$K_{20}Li_5H_7[K_8\subset\{P_8W_{48}O_{184}\}]\cdot x\,H_2O\ (x\approx 92)\quad (\mathbf{1})^{[5]}$$

$$Na_{12}K_8H_4[K_8\subset\{P_8W_{48}O_{184}\}\{V^{V}_4V^{IV}_2O_{12}(H_2O)_2\}_2]\cdot x\,H_2O\ (x\approx 80)\quad (\mathbf{2})$$

The "host" anion, $[K_8\subset P_8W_{48}O_{184}]^{32-}$ (**1a**) with fourfold (D_{4h}) symmetry is derived from the linkage of four $\{P_2W_{12}O_{48}\}$ lacunary fragments of the Wells–Dawson anion $[P_2W_{18}O_{62}]^{6-}$; it encloses eight potassium cations in the positions shown in Figure 2a. The cations at the 3-, 6-, 9-, and 12-o'clock positions in the figure are disordered over two sites above and below the equatorial mirror plane; the remainder lie in that plane. Potassium cations occupy analogous positions within the new host–guest complex **2a** but they are now sandwiched between the two cyclic capping groups

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Supporting information for this article (UV/Vis, IR, and Raman spectra of **2**; ^{31}P MAS-NMR spectra of **1** and **2**; and comments on valence localization/delocalization and the observation of intervalence transitions) is available on the WWW under http://www.angewandte.org or from the author.

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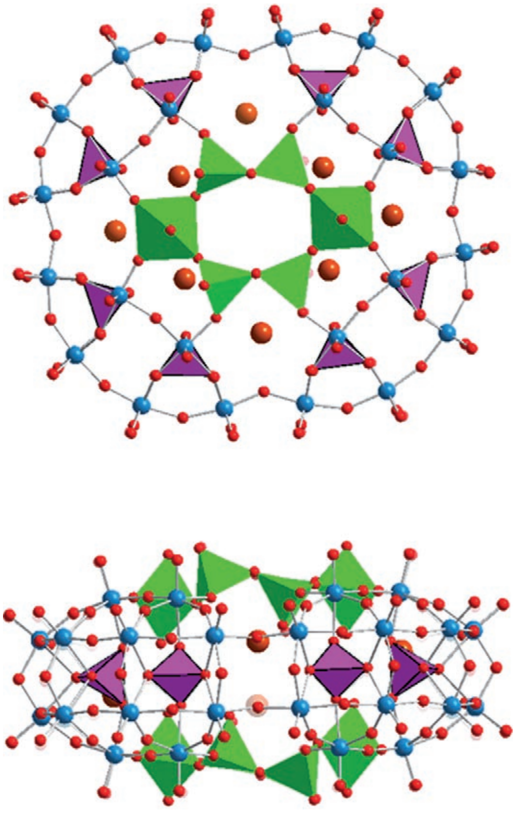

Figure 1. Two views of the structure of **2a** showing the capping V_6 groups and the positions of the K cations within the cavity. Color code: W blue, O small red spheres, K large brown-red spheres, PO_4 pink, VO_n green.

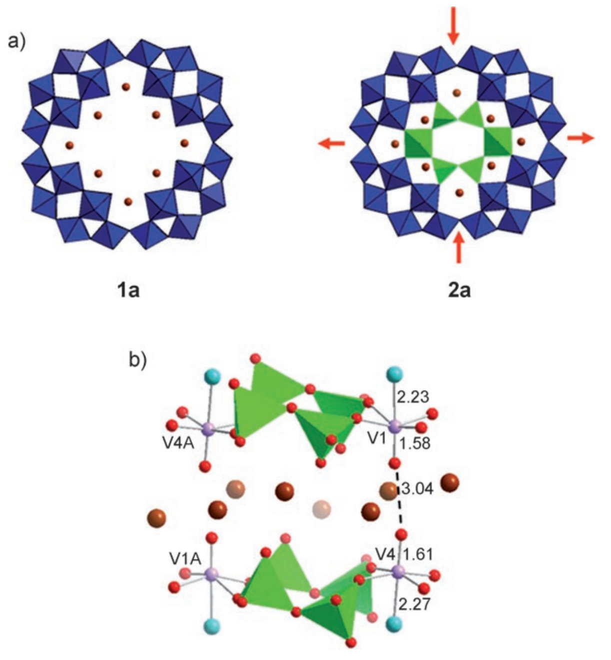

Figure 2. a) Comparison of the structures of **2a** and the host anion **1a** showing the distortion introduced by the $\{V^{V}_{4}V^{IV}_{2}O_{12}(H_2O)_2\}^{4+}$ capping groups **3a**. b) Some metrical details (in Å) of the capping groups **3a**. Color code as in Figure 1 plus V^{IV} lilac, H_2O ligands turquoise.

$\{V^{V}_{4}V^{IV}_{2}O_{12}(H_2O)_2\}^{4+}$ (**3a**), each with two octahedral V^{IV} and four tetrahedral V^{V} centers (Figure 2a). **3a** can be considered formally as an interesting polycation exhibiting two different types of entities, namely, $\{O{=}V(H_2O)\}^{2+}$[8a] and V_2O_5,[8b] which occur under well-defined conditions, the latter in the gas phase, the former in hydrated form in aqueous solution. The formation of **3a** is based on oxidation of V^{IV} by air and does not occur in absence of oxygen. As is evident from the figure the V_6 caps force a rhombic distortion of the square $\{P_8W_{48}\}$ perimeter observed in **1a**.[9] The internal angles of the rhombus in **2a** (of lines extended from the P···P vectors in each $\{P_2W_{12}\}$ unit) are close to 80° and 100°. The overall anion dimensions (measured by the separation between the oxygen atom "hinges" linking the corner-shared $\{WO_6\}$ octahedra at 6- and 12-o'clock positions in Figure 2a versus those at 3- and 9-o'clock positions) are 15.27 and 17.94 Å. As shown in Figure 2b the short terminal V–O bonds of the four VO^{2+} centers are directed towards the interior of the structure and point towards the centroids of groups of three encapsulated potassium cations. The orientation of the VO^{2+} groups places four weakly bound water molecules ($V{-}OH_2 = 2.23$ and 2.27 Å) on the surface of the anion, and this leads to the possibility of attaching (albeit weakly) other ligands at these positions. The structure is a rare example of a polyoxometalate in which $M{-}O_{terminal}$ vectors point towards the interior of the anion.[10] Presumably space limitations (the V···V separation is 6.21 Å) preclude the enclosure of two water molecules.

Magnetic measurements were performed and Figure 3 shows the paramagnetic susceptibility–temperature product and the inverse of the susceptibility recorded on a fresh powder sample of **2** at an applied field of 1 T, both as a function of temperature. The high-temperature χT value of 1.34 $cm^3\,K\,mol^{-1}$ corresponds to the presence of 3.8 V^{IV} centers, which is in good agreement with the four $\{V^{IV}O(H_2O)\}$ units found in the crystallographic studies. From this result it can be immediately concluded that there are no additional $\{V^{IV}O\}^{2+}$ units in the lattice. The Curie–Weiss plot of the inverse of the susceptibility as a function of temperature (Figure 3) gives a Curie constant of 1.35 $cm^3\,K\,mol^{-1}$, which is in excellent agreement with the room-temperature value of χT. The small Weiss temperature of $\theta = -1.8 \pm 0.2$ K shows that the ions are only very weakly interacting, which is

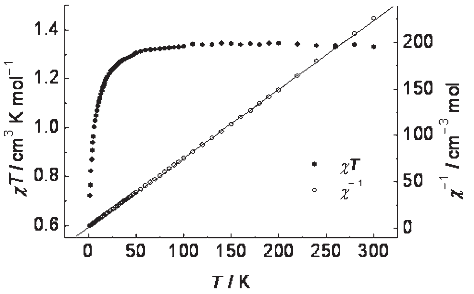

Figure 3. Temperature dependence of χT (filled circles) and χ^{-1} (open circles) recorded at 1 T. The drawn line is a fit to the Curie–Weiss law $\chi^{-1} = T/C - \theta/C$ ($T \geq 15$ K) with the parameters $C = 1.35\ cm^3\,K\,mol^{-1}$ and $\theta = -1.8 \pm 0.2$ K.

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not surprising in view of the orientation and separation of the magnetic ("d_{xy}") orbitals of the V^{IV} centers. The decrease of the value of χT at lower temperatures is not an effect of magnetization saturation because the 0.1 T applied field susceptibility curve does not differ from that measured at an applied field of 1 T. This behavior is probably a consequence of small inter- or intramolecular exchange interactions.

The X-band EPR spectrum recorded on a powder sample exhibits a broad line with $g = 1.95$ at room temperature, but shows a hyperfine splitting from $I = 7/2$ V^{IV} nuclei of the order of $A = 200$ MHz (67×10^{-4} cm^{-1}) at 4.1 K (Figure 4). The magnitude of A and the pattern of hyperfine features are consistent with a triplet state arising from interactions between pairs of V^{IV} centers rather than a single VO^{2+} center, although the "forbidden" half-field line was not observed. Raising the temperature immediately leads to line broadening and disappearance of the hyperfine structure as a result of an increase in spin-lattice relaxation. Owing to the broadness of the spectrum even at 4.1 K it is not possible to obtain an unambiguous set of g and A parameters by simulation. The simulation depicted in Figure 4 corresponds to the parameters shown in Table 1, but these are by no means optimal. Nevertheless, the hyperfine parameters are similar to those reported for the vanadyl tartrate dimers shown in Table 1 and are quite distinct from those of a typical monovanadium(IV)polytungstate, also shown in the Table.

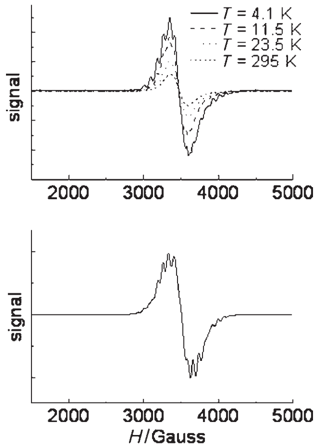

Figure 4. Top: EPR spectrum of **2** at various temperatures (hyperfine splitting only resolved for 4.1 K); bottom: simulation with g and A parameters from Table 1, $D = 0.008$ cm^{-1}, and linewidths of 60 G.

It seems plausible to assume that the "eclipsed" V^{IV} centers (V1 and V4, Figure 2b) account for the triplet state EPR spectrum since the V1···V4A separation is 10.2 Å and would involve an unfavorable V^{IV}(oct.)-O-V^{V}(tet.)-O-V^{V}-(tet.)-V^{IV}(oct.) superexchange pathway. Superexchange between V1 and V4 involves multiple V^{IV}-O-W^{VI}-O-W^{VI}-O-W^{VI}-O-W^{VI}-O-V^{IV} pathways favored by the "mixed-valence" interaction between V^{IV} and W^{VI} (discussed below). Similar exchange involving multiple bond pathways has been demonstrated in $[KAs_4W_{40}(VO)_2O_{140}]^{23-}$.[12] However, the adjacency of the two triplet states within the same anion is almost certainly responsible for the increased spin-lattice relaxation observed. A more detailed single-crystal EPR analysis is warranted for this interesting compound.

Table 1: Selected EPR g and A [10^{-4} cm^{-1}] parameters.

Compound	$V^{IV}\cdots V^{IV}$ [Å]	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	Reference
2	6.21	1.93	1.93	75	30	this work
VO-*dl*-tartrate dimer	4.08	1.953	1.982	72.3	21.3	[11]
VO-*dd*-tartrate dimer	4.35	1.950	1.984	73.2	24.6	[11]
$[PW_{11}V^{IV}O_{40}]^{5-}$		1.915	1.970	167.2	59.7	[14d]

According to the Robin–Day classification[13] **3a** is a Class I mixed-valence fragment/cation since the two valence states are clearly distinguished by their different coordination geometries, while the electron density is predominantly localized on the octahedral site, for which the crystal-field stabilization (here applicable only in a formal sense) is larger than that for the tetrahedral site ($10\,Dq_{tet} = -(4/9)10\,Dq_{oct}$). The electronic spectra of Class I mixed-valence compounds are a combination of the spectra of the individual oxidation states with no additional absorption (intervalence) bands. The situation is a little more complicated when the complete anion **2a** is considered because **3a** is embedded in the polytungstate matrix. In addition to the $V^{IV}V^{V}$ Class I mixed-valence situation, there is also adjacency of V^{IV} with W^{VI}. As has been well established for tungstovanadates(IV) (e.g., $[SiW_{11}V^{IV}O_{40}]^{6-}$), these can be treated as Class II systems with partial electron delocalization from "octahedral" V^{IV} to "octahedral" W^{VI}, which results in intensity-enhanced "d–d transitions" of V^{IV} as well as V^{IV}–W^{VI} "intervalence" charge transfer at around 500 nm (see reference [14]). In contrast to the case of the $V^{IV}V^{V}$ situation, the enhancement of the electron-transfer rate for the $V^{IV}W^{VI}$ case should also be influenced by the vibrations that change the metal–metal distances and therefore modulate the transfer integrals (see the Supporting Information). The UV/Vis spectrum of a freshly prepared solution of **2** (Figure S1 in the Supporting Information) shows just such absorption features.[15]

The slow decomposition of **2** in solution, together with the presence of four paramagnetic centers, precluded the observation of useful multinuclear NMR spectra. However, solid-state spectra could be recorded (see the Supporting Information).

Apart from the points that refer to general aspects of encapsulation chemistry,[16] another interesting phenomenon was discovered. **3a** can be considered to be an interesting mixed-valent polycation that is formed by a nucleation process under confined conditions, and the specific geometric environment influences the type of electron distribution and exchange interactions, which are negligible in the present case. There is no doubt that other nucleation processes can be studied in the $\{P_8W_{48}\}$ cluster cavity under formally similar conditions such as those related to molybdenum oxide based aggregates, which were observed in larger cavities.[3] The interesting aspect is that a variety of magnetically interesting mixed-valence species can be generated by changing the redox potentials.[3]

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Experimental Section

$VOSO_4 \cdot 5\,H_2O$ (0.35 g, 1.38 mmol) was added to a stirred solution of $K_{28}Li_5[H_7P_8W_{48}O_{184}] \cdot 92\,H_2O$ (0.35 g, 0.024 mmol) in freshly prepared 1 M $NaCH_3COO/CH_3COOH$ buffer (30 mL, pH 4.4). The resulting solution was heated to 50 °C for 4 h and then filtered, and the filtrate was allowed to evaporate at room temperature in an open 50-mL Erlenmeyer flask, during which period partial aerial oxidation of vanadium occurred. After 1 week the dark purple crystals were filtered, washed with cold water, and dried in air; yield: 0.2 g (54 %); elemental analysis: calcd for $Na_{12}K_{16}W_{48}P_8V_{12}O_{292}H_{172}$: Na 1.79, K 4.05, V 3.96; found: Na 1.8, K 3.8, V 3.9 %. Characteristic IR bands (KBr pellet): $\tilde{\nu} =$ 1622(m) [$\delta(H_2O)$], 1144(m), 1092(m), 1020(w) [all ν_{as}(P-O)], 956(sh), 935(w), 912(s) [ν(W=O)/ν(V=O)], 791(vs), 708(vs) [ν_{as}(W-O-W)/ν_{as}(W-O-V)], 574(w), 536(w), 467(w) cm^{-1}; characteristic resonance Raman bands (solid/KBr dilution, $\lambda_e = 1064$ nm, cm^{-1}): $\nu = 950$(sh), 923(s) [ν_s(W=O)/ν_s(V=O)]; UV/Vis spectrum (in H_2O, nm): $\lambda = 506$ ($\varepsilon = 7700\,M^{-1}cm^{-1}$) ($V^{IV} \rightarrow W^{VI}$ (IVCT)), 680(sh), 890(w) (d–d (V^{IV})).

Magnetic susceptibility measurements were performed on a powder sample with a Quantum Design MPMS XL7 SQUID magnetometer. The underlying diamagnetic susceptibility was determined by susceptibility measurements on the diamagnetic $\{P_8W_{48}O_{184}\}^{40-}$ host ion, because standard procedures with Pascal's constants give values that are too low. X-band EPR spectra were recorded on a Bruker ESP300 X-band EPR spectrometer equipped with a continuous-flow Helium cryostat. The simulation was performed by using the Bruker WINEPR Simfonia program.

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[7] Crystal data for **2** : $H_{172}K_{16}Na_{12}O_{292}P_8V_{12}W_{48}$, $M = 15\,430.70\ g\,mol^{-1}$, triclinic, space group $P\bar{1}$, $a = 19.7360(14)$, $b = 20.7245(15)$, $c = 21.1487(16)$ Å, $\alpha = 104.134(1)$, $\beta = 117.561(1)$, $\gamma = 104.410(1)°$, $V = 6745.6(9)$ Å^3, $Z = 1$, $\rho = 3.799\ g\,cm^{-3}$, $\mu = 21.203\ mm^{-1}$, $F(000) = 6892$, Crystal size $= 0.45 \times 0.30 \times 0.25\ mm^3$. A total of 39 426 reflections ($1.64 < \theta < 27.02°$) were collected of which 28 343 reflections were unique ($R(\text{int}) = 0.0382$). 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 $R = 0.0589$ for 25 047 reflections with $I > 2\sigma(I)$, $R = 0.0665$ for all reflections; Max/min residual electron density 3.177 and –3.875 e Å^{-3}. Crystals of **2** 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 ($\varphi = 0$, 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**). 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-417620.

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[9] Although the nonrigidity of the $\{P_8W_{48}\}$ assembly should not have been unexpected, the other reported derivatives[6] retain the essentially "square" conformation.

[10] Other examples include equatorial W centers in $[As^{III}{}_2W_{21}O_{69}\text{-}(H_2O)]^{6-}$ (Y. Jeannin, J. Martin-Frère, *J. Am. Chem. Soc.* **1981**, *103*, 1664–1667) and $[P^V{}_2W_{21}O_{71}(H_2O)_3]^{6-}$ (C. M. Tourné, G. F. Tourné, T. J. R. Weakley, *J. Chem. Soc. Dalton Trans.* **1986**, 2237–2242). The problem is of basic importance for larger species such as Mo_{132}, $Mo_{72}Fe_{30}$, and Mo_{154}. In the first two species, the Mo=O bonds are preferably directed outwards (ca. 80 %), but according to a disorder also approximately 20 % $Mo(OH_2)$ groups are directed outwards. In the latter ring-type species, the situation is more complicated because of the presence of more (different) building units. In any case, there is a preference for H_2O ligands on the outer periphery (for compound types, see, for example: A. Müller, S. Roy, *J. Mater. Chem.* **2005**, *15*, 4673–4677 and A. Müller, S. Roy, in *The Chemistry of Nanomaterials: Synthesis, Properties and Applications* (Eds.: C. N. R. Rao, A. Müller, A. K. Cheetham), Wiley-VCH, Weinheim, **2004**, 452-475).

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