Within our study two questions remain. The large length dependence of $-[\theta_H]_{222}$ in the range of 7 to 20 residues has been demonstrated by an independent method,[11] but its cause is unknown. The preliminary two-state model outlined above appears to be inconsistent with experimental $[\theta]_{222}$ values reported for peptides with $N>30$. Experiments to explore these issues are in progress, but their outcomes should not change our most important conclusion. For the class of alanine-rich, lysine-containing peptides with $15>N>27$, the literature equations relating FH to experimental $[\theta]_{222}$ values underestimate $[\theta_H]_{222}$,[12] and the corresponding FH values are overestimated by 25–50%.

Experimental Section

Peptides were prepared as previously described[5d] and purified by repeated reverse-phase high-performance liquid chromatography (RP-HPLC), and characterized by MALDI-MS (matrix-assisted laser desorption ionization mass spectrometry) and amino acid analysis. The purity of all compounds is estimated to be higher than 95%. Solutions were maintained at pH 1–2 for consistency with NMR measurements, and $NaClO_4$ buffers were used for consistency with literature measurements. CD spectra were taken on a thermostated Aviv 62DS circular dichroism spectrometer calibrated according to literature procedures.[13] Concentrations of CD solutions were determined within 5% error both by a quantitative ninhydrin assay[7b] and by amino acid analysis.[14] Solutions of AcHel-$(Ala_4Lys)Ala_2$-NH_2 ($n=4,5$) and selected nontemplated analogues were shown to be monomeric both by CD dilution studies and analytical ultracentrifugation.

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$[M_3V_{18}O_{42}(H_2O)_{12}(XO_4)]\cdot 24H_2O$ (M = Fe, Co; X = V, S): Metal Oxide Based Framework Materials Composed of Polyoxovanadate Clusters**

M. Ishaque Khan,* Elizabeth Yohannes, and Robert J. Doedens

The early transition metal oxide clusters with M=O functionalities constitute a fast emerging class of compounds. Their properties are of both intrinsic and applied interest and envelop such diverse fields as analytical chemistry, biochemical and geochemical processes, catalysis, materials science, and medicine.[1] Metal oxide clusters with molecular weights at par with proteins have been prepared and characterized.[1e] The structure and bonding patterns in these molecular aggregates remarkably resemble the complex transition metal oxide surfaces[1a, 2] employed as catalysts for organic transformations.[2d, 3] Many such catalysts are poorly understood because of their inaccessibility to conventional physicochemical techniques and therefore are not amenable to improvements in their performances. With their proven role in catalysis[4] and in the development of new oxide-supported transition metal catalysts,[4f] metal oxide clusters offer attractive building units with well-defined properties[5, 1b] for the preparation of catalysts and novel surfaces based on metal (and mixed-metal) oxides whose performance could possibly be rationalized in terms of their constituents at the molecular level.[4a]

However, the technique of bringing suitable metal oxide building units together to generate true metal oxide surfaces and framework materials without the incorporation of additional conventional ligands is still in its infancy and has been limited to the synthesis of mainly one-dimensional chains.[6] Here, we report the synthesis and characterization of two

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novel three-dimensional framework materials, **1** and **2**, composed of well-defined vanadium oxide clusters.

$[M_3V_{18}O_{42}(H_2O)_{12}(XO_4)]\cdot 24\,H_2O$ ($M = Fe^{II}$; **1** $M = Co^{II}$; **2** $X = V, S$)

Black prism-shaped crystals of **1** and **2** were isolated in 50–60% yield from the dark colored solution obtained from the reaction of V_2O_5 with $LiOH\cdot H_2O$, hydrazinium sulfate, and $FeCl_2\cdot 4H_2O$ or $CoSO_4\cdot 6H_2O$ in water at 84–86°C. The compounds were characterized by elemental analysis, manganometric titration of the reduced V^{IV} sites, FT-IR spectroscopy, thermal methods, and X-ray single-crystal structure analysis. The IR spectra of these compounds exhibit absorption bands attributable to H_2O, $\nu(SO_4)$, $\nu(VO_4)$, $\nu(V{-}O_{term})$, and $\nu(V{-}(\mu_3\text{-}O))$ groups.

X-ray structure analysis[7] of single crystals of **1** and **2** revealed highly symmetrical isomorphous structures (Figure 1). In each case, the structure consists of $\{V_{18}O_{42}\}$ cages[8]

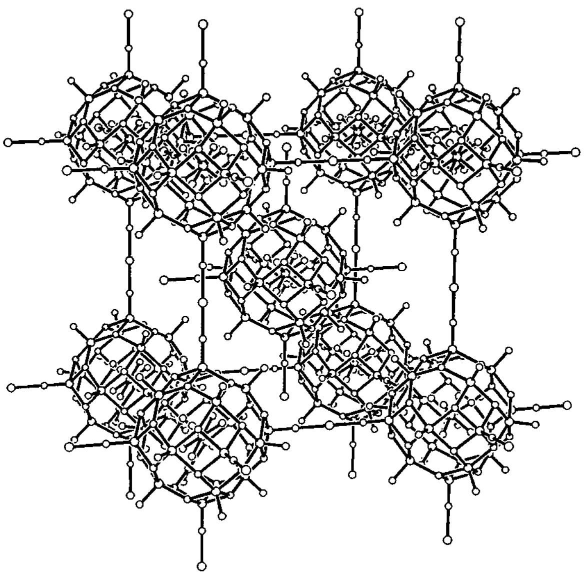

Figure 1. View of the unit cell to show the extended structure of **1** which contains arrays of $\{V_{18}O_{42}(XO_4)\}$ interconnected through $\{Fe(H_2O)_4\}$ bridging units. Water molecules have been omitted for clarity.

with crystallographic $m\bar{3}m$ (O_h) symmetry[7b] linked by bridging $\{M(H_2O)_4\}$ groups into two interpenetrating three-dimensional networks; a consequence of body-centered symmetry.[7c] Each cage hosts a twofold disordered tetrahedral $\{XO_4\}$ group. Based on crystallographic, chemical, and spectroscopic evidence,[9] the final refinement model assumed a disordered distribution of both the VO_4^{3-} and SO_4^{2-} anions for the $\{XO_4\}$ group.

The host $\{V_{18}O_{42}\}$ shell, constructed from 18 $\{VO_5\}$ square pyramids sharing edges through 24 μ_3-oxygen atoms, is known to incorporate VO_4^{3-} and SO_4^{2-} ions[8a] and act as a container for other anions and molecules.[8b] It exists with different electronic populations in two closely related structural forms with different symmetries (T_d and D_{4d}) that are influenced by the stereochemical needs[5a, 10] and the extent of interaction of the encapsulated moiety with the V centers of the shell.[8a–c] For example, in the $Na_6[H_7V^{IV}_{16}V^{V}_2O_{42}(VO_4)]\cdot 21\,H_2O$ cluster,[8a–b] the $\{VO_4^{3-}\}$ group (V–O 1.71 Å) interacts through four μ_4-O atoms with the twelve V centers of the shell to form covalent $(V{-}\mu_4\text{-}O){-}V_{shell}$ ($\mu_4\text{-}O{-}V_{shell}$ 2.39 Å) bonds and confers tetrahedral symmetry to the anion. The cages in **1** and **2** (with O_h symmetry) represent, interestingly, somewhat different situations and illustrate further the structural flexibility of the $\{V_{18}O_{42}\}$ motif.

A view of the $[V_{18}O_{42}(XO_4)]$ cluster in **1** is shown in Figure 2. All bond lengths in the cluster are within normal ranges. The geometry around each V1 atom in twelve of the

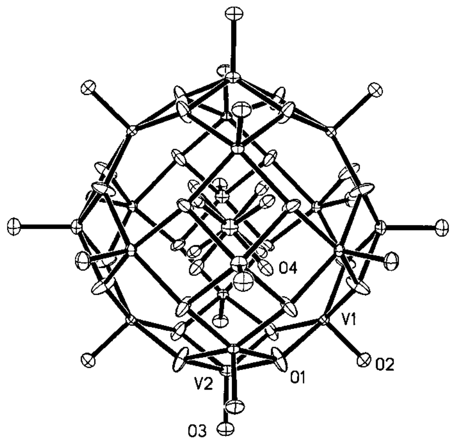

Figure 2. The $[V_{18}O_{42}(XO_4)]$ cluster in the crystal structure of **1**, with the atom labeling scheme in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. The unlabeled central atom, bonded to O4 atoms, represents X. Selected bond lengths [Å] and angles [°]: **1**: V1–O1 1.948(2), V1–O2 1.587(6), V2–O1 1.942(4), V2–O3 1.636(9), Fe1–O3 2.105(9); V1-O1-V2 98.16(14), V1-O1-V1 138.2(3); **2**: V1–O1 1.923(3), V1–O2 1.590(9), V2–O1 1.954(7), V2–O3 1.652(15), Co1–O3 2.118(14); V1-O1-V2 97.3(2), V1-O1-V1 138.7(5).

$\{VO_5\}$ groups is defined by a terminal oxo group (O2) and four μ_3-oxygen atoms (O1). The geometry around V2 in the remaining six $\{VO_5\}$ units is defined by four μ_3-oxo (O1) groups and an apical μ_2-oxygen atom (O3) which is also bonded to the M^{II} center of one of the six $\{M(H_2O)_4\}$ bridges that interlink the $[V_{18}O_{42}(XO_4)]$ clusters. The coordination sphere of M^{II} is completed by four oxygen atoms (O6) from the aqua ligands ($M{-}O(H_2)$ 2.089 Å in **1** and 2.047 Å in **2**), each one exhibiting twofold disorder, and two *trans* μ_2-(O3) groups. The elongated ellipsoid for O1, present in **1** and **2**, is probably a consequence of steric interactions that arise from a short O⋯O contact (2.545(9) Å in **1** and 2.521(13) Å in **2**) between O1 and an O4 site that is only 50% occupied.

The M1–O6 distance and the bond valence sum (BVS)[11a] value (0.39) of the O6 group identify it as H_2O. This conclusion and the result of the manganometric titration of V^{IV} sites (≈9.5 V^{IV} per formula unit)[11b] correspond to the stated formulation of **1** and **2**. The packing in **1** and **2** (Figure 1) generates rectangular tunnels occupied by water of solvation that is readily removed upon heating at about 70°C.

The synthesis and characterization of **1** and **2** represent a step in the direction of the preparation of transition metal oxide based materials composed of suitable metal oxide motifs with controllable properties. In view of the rapidly expanding pool of well-characterized metal oxide clusters, this has potential to provide access to a variety of synthetic materials. The heterometallic centers, such as Fe^{II} and Co^{II}, located in the walls of the tunnels in **1** and **2**, may be incorporated in new solids to fashion materials that may also exhibit properties, such as catalytic activity, which are associated with the heterometallic sites. We are currently evaluating the catalytic and sorptive properties of **1** and **2** and studying other metal oxide based materials containing different heterometallic centers.

Experimental Section

1: An aqueous solution of $LiOH \cdot H_2O$ (3 mL, 5 mmol) was added to a stirred slurry of V_2O_5 (2.5 mmol) in water (10 mL) maintained at 84–86 °C. After the resulting solution was treated with hydrazinium sulfate (2.5 mmol), the reaction mixture was heated for another 10 min. The dark colored solution was diluted to 25 mL (pH = 4.6) and subsequently treated with $FeCl_2 \cdot 4H_2O$ (1.25 mmol) and heated for 3–7 h. The resultant solution was allowed to stand at room temperature in a stoppered flask for 12 h. Dark prism-shaped crystals were filtered from the mother liquor, washed with cold water to remove amorphous impurity, and dried in air at room temperature to give 0.38 g (56% yield based on vanadium) of **1**. FT-IR (KBr; 1200–400 cm^{-1}): $\tilde{\nu}$ = 1131 (m, SO_4), 990 (s, $V-O_{term}$), 807 (m, VO_4), 689 (m, V–(μ_3-O)), 631 (m, V–(μ_3-O)) cm^{-1}. Compound **2** was synthesized in an analogous manner with the equivalent amount of $CoSO_4 \cdot 6H_2O$. FT-IR (KBr): $\tilde{\nu}$ = 1131 (m, SO_4), 990 (s, $V-O_{term}$), 801 (m, VO_4), 680 (m, V–(μ_3-O)), 630 (m, V–(μ_3-O)) cm^{-1}.

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[7] a) Crystal structure analysis: The data were collected at 183 K on a Bruker SMART-CCD diffractometer (graphite monochromated $Mo_{K\alpha}$ radiation; λ = 0.71073 Å) and phi scan frames. The structures were solved by direct methods (SHELXTL Version 5.10) and refined by full-matrix least squares on F^2. Crystal data for $H_{72}O_{82}S_{0.5}Fe_3V_{18.5}$ (**1**): crystal dimensions 0.30 × 0.23 × 0.15 mm, cubic, space group $Im\bar{3}m$ (no. 229), a = 15.4679(4) Å, V = 3700.79(17) Å^3, Z = 2, ρ_{calcd} = 2.253 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 2.926 mm^{-1}. Of the 11888 reflections measured (1.86° ≤ θ ≤ 27.43°), 458 independent reflections were used to solve the structure. Based on all these data and 40 refined parameters, final $R1$ = 0.0445 (all data), w$R2$ = 0.1276, and the goodness-of-fit on F^2 is 1.169. Crystal data for $H_{72}O_{82}S_{0.5}Co_3V_{18.5}$ (**2**): crystal dimensions 0.17 × 0.13 × 0.13 mm, dark green prism, cubic, space group $Im\bar{3}m$ (no. 229), a = 15.4536(5) Å, V = 3690.5(2) Å^3, Z = 2, ρ_{calcd} = 2.268 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 3.019 mm^{-1}. Of the 10552 reflections measured (1.86° ≤ θ ≤ 26.10°), 403 symmetry-independent reflections were used to solve the structure. Based on all these data and 39 refined parameters, $R1$ = 0.0664 (all data), w$R2$ = 0.1870, and the goodness-of-fit on F^2 is 1.213. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata @fiz-karlsruhe.de), on quoting the depository numbers CSD-410238 (**1**) and CSD-410239 (**2**). b) The O_h symmetry refers to the average of the two disordered components. The symmetry, for example, of a $\{V_{19}O_{46}\}$ species composed of a $\{V_{18}O_{42}\}$ cage encapsulating an ordered $\{VO_4\}$ group will be no higher than T_d; c) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460.

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[9] a) The X–O distances (1.538(15) Å in **1** and 1.51(2) Å in **2**) are intermediate between the expected values for SO_4^{2-} and VO_4^{3-}. In the case of **1**, (for which the structural results are most precise), the O displacement ellipsoid is elongated along the X–O bond. The displacement parameter of X was higher than expected when it was refined as 100% V and unrealistically low when only S was included. In the final refinement, the displacement parameter of X was fixed at 0.015 Å^2 and the relative proportions of V and S were allowed to vary. This model converged to approximately equal proportions of V and S (fraction of V: 0.49(5) for **1** and 0.49(8) for **2**). Different displacement parameters would change these proportions, and so the uncertainties are therefore considerably greater than implied by the listed esds; b) IR spectra of **1** and **2** exhibit bands attributable to SO_4^{2-} and VO_4^{3-} ions. Elemental analysis (% S) corresponds to the stated formulation of **1** and **2.** All attempts to prepare **1** and **2** without sulfate were unsuccessful.

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