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Characterization of Novel Vanadium(III)/Acetate Clusters Formed in Aqueous Solution

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We report the first structures of simple acetate complexes of vanadium(III) formed in aqueous solution. Paramagnetic ^{1}H NMR spectroscopy titration experiments indicate the formation of two major V(III)/acetate complexes in acidic aqueous solution for acetate/V(III) ≤ 4, pD 3.50. A novel tetranuclear cluster and a trinuclear cluster have been characterized by X-ray diffraction studies. Mass spectrometry measurements show these clusters retain their integrity in solution.

Vanadium(III) plays an important role in several environmental systems, ranging from redox-active vanadium impurities in crude oils to sulfato−vanadium(III) complexes in ascidians and marine fanworms.[1,2] The aqueous chemistry of vanadium(III) is often complex due to the formation of monomers, dimers, and species of high nuclearities, which can lead to ambiguity on the actual species present. Analysis of the species present in solution is further complicated by the fact that paramagnetic (d^2) vanadium(III) complexes are generally both NMR and EPR silent-EPR spectroscopy signals are typically not observed, since spin−orbit coupling results in a large zero-field splitting and short spin−lattice (T_1) relaxation times.[3] Studies on vanadium(III)/carboxylate complexes isolated from organic solvents and/or neat carboxylic acid solutions have led to the characterization of dinuclear,[4−12] trinuclear,[1,13−18] tetranuclear,[19,20] and octanuclear[18] V(III)/carboxylate clusters with interesting and unusual spectroscopic and magnetic properties. In contrast, very little is known about the formation, structures, and properties of vanadium(III)/carboxylate complexes in aqueous solution.[9,10,21−25] In this communication, mass spectrometry and X-ray structural data are presented as evidence for the formation of trinuclear and tetranuclear vanadium(III)/acetate clusters in acidic aqueous solution. In addition, the formation of the clusters can be monitored by NMR spectroscopy.

Figure 1 gives paramagnetic ^{1}H NMR spectra of equilibrated aqueous solutions of VCl_3 and 7.0×10^{-2} to 4.0 mol equiv acetate at pD 3.50. The chloride ligands of VCl_3 readily dissociate upon dissolution of VCl_3 in water.[26] It is clear from these spectra that at least two distinct V(III)/acetate complexes are formed in solution (labeled Species A (44.3

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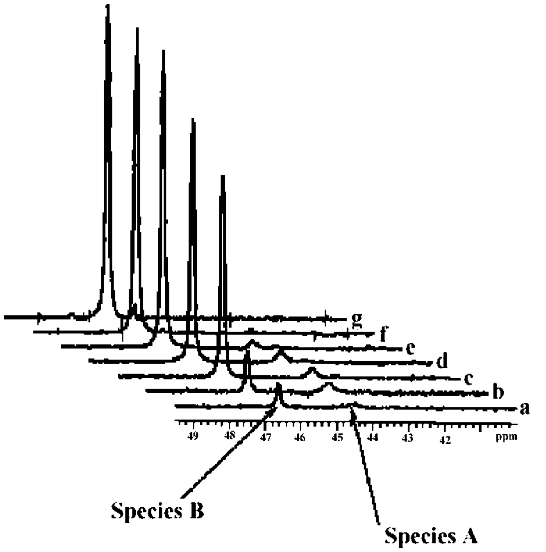

Figure 1. ^1H NMR spectra, showing the 40−50 ppm region, of anaerobic solutions of 0.010 M VCl_3 in D_2O with (a) 0.070, (b) 0.090, (c) 0.50, (d) 0.87, (e) 1.0, (f) 2.0, and (g) 4.0 equiv of CH_3COO^- at pD 3.50 (HEPES buffer) at 25.0 °C. All signals are attributable to acetate's methyl protons in V(III)/acetate complexes. Chemical shifts are referenced against an external sample of TSP.

± 0.2 ppm[27]) and Species B (46.65 ± 0.05 ppm) and both complexes have either one or several chemically equivalent acetate ligands. Extremely small signals are also observed at 43.6, 45.9, and 47.6 ppm in some of these spectra (not shown). Paramagnetic ^1H (methyl) NMR spectroscopy signals have also been observed in the ~40−50 ppm region for V(III)/acetate (and V(III)/propionate) complexes in $CDCl_3$.[1] The observation of signals is a consequence of a direct π-delocalization pathway for the unpaired spin of vanadium(III).[28]

Figure S1 in the Supporting Information gives the corresponding plots of the relative peak areas of Species A and B as a function of the mole equivalent of acetate added. From Figure S1, it can be seen that, while Species A is only found in solutions containing ≤1 equiv of acetate, maximum concentrations of Species B are obtained after ~2 equiv of acetate have been added, after which the concentration of Species B remains unchanged up to 4 equiv of acetate. (Similar conclusions were reached from a UV−visible spectroscopy titration experiment, details of which are given in the Supporting Information.) This suggests that Species B has a V(III)/acetate ratio of ~1:2, whereas Species A has a lower V(III)/acetate ratio.

Two clusters were found to crystallize from deep green aqueous V(III)/acetate solutions at different V(III)/acetate ratios. Blue hexagonal-shaped crystals of $[V_4(\mu\text{-OOCCH}_3)_4(\mu\text{-OH})_4(OH_2)_8]Cl_4\cdot CH_3COOH\cdot 12H_2O$ (**1**) crystallized from a solution of 1:1 V(III)/CH_3COO(H) with the space group *I-42m*. X-ray diffraction studies on cluster **1** revealed a novel, previously unknown tetranuclear vanadium/carboxylate structure. Thermal ellipsoid plots of **1** are given in Figure 2. The core consists of four equivalent distorted octahedral V(III) centers, each center coordinated to two μ-hydroxo ligands, two μ-acetato ligands, and two aqua ligands. The four vanadium(III) centers lie within a plane, with the μ-acetato and μ-hydroxo ligands lying above and below the plane, respectively, in an alternate arrangement around the ring. There are eight disordered chloride positions per tetramer in the asymmetric unit, each with 50% occupancy for a total of four chlorides per tetramer. These positions, when not occupied by a chloride, are filled with disordered solvent water that forms hydrogen bonds to the cluster-bound water. There is additional solvent water present in the cell which is also engaged in hydrogen bonding with the vanadium-bound water. There is also a solvent acetic acid molecule per cluster present in the asymmetric unit, which is disordered over two positions and is engaged in symmetric hydrogen bonding with two bridging hydroxides on the same face of the tetramer. The V−O(OH_2) bond length of 2.038 Å is typical for that found for aqua ligands of V(III) complexes.[29]

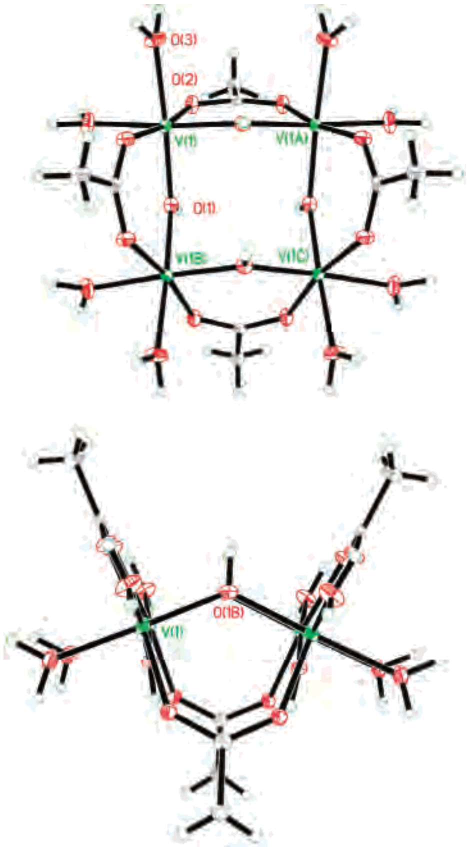

Figure 2. Thermal ellipsoid plots (35%) of the $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCH}_3)_4(OH_2)_8]^{4+}$ core (**1**) showing two different views. The four vanadium(III) atoms are bridged by one μ-hydroxo ligand and one μ-acetato ligand. The remaining coordination sites are occupied by water ligands.

Another crystal form whose core is isostructural to **1**, $[V_4(\mu\text{-OOCCH}_3)_4(\mu\text{-OH})_4(OH_2)_8]Cl_4\cdot 3H_2O$, **1a** (space group *P4-(2)/mnm*), was also structurally characterized. Sufficient **1a** was obtained for elemental analysis, and the oxidation state of the vanadium centers was further confirmed by magnetic susceptibility measurements (see Experimental Section, Supporting Information). Importantly, electrospray mass spectrometry measurements demonstrate that *the V_4 core retains its integrity in solution* (see Supporting Information).

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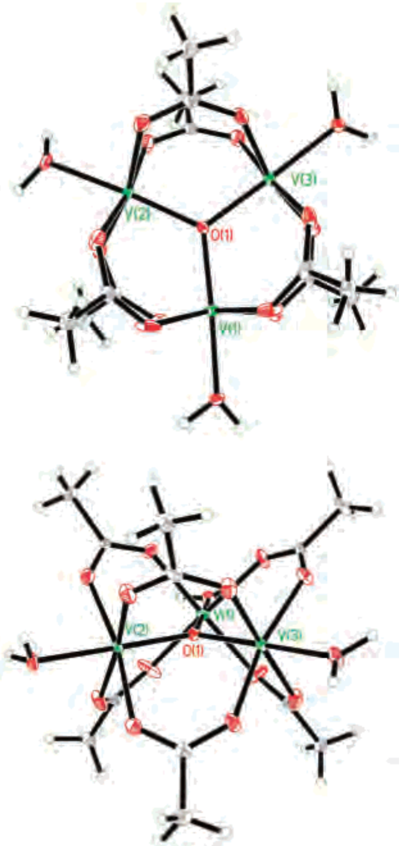

Figure 3. Thermal ellipsoid plots of the $[V_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(OH_2)_3]^+$ core (**2**), showing two different views. **2** has a triangular $V(\mu_3\text{-oxo})$ core, with two μ-acetates bridging the V centers on opposite sides of the V_3 plane.

The structures of **1** and **1a** are significantly different from the other known tetranuclear, butterfly-type V(III)/carboxylate clusters recently isolated by Christou et al. from acetone, in which two of the V(III) centers are bound to a μ_3-oxo ligand, three μ-carboxylate ligands, and a bidentate 2,2′-bipyridine ligand.[19,20] They are also significantly different from reported structures of tetranuclear V(V)/carboxylate clusters with $V_4(\mu\text{-oxo})(\mu\text{-carboxylate})_4$ cores.[30−36]

Deep green block-shaped crystals of a further cluster, $[V_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(OH_2)_3]Cl{\cdot}3.5H_2O$, **2**, were obtained from an aqueous solution of 1:2 V(III)/$CH_3COO(H)$ with the space group *P2(1)2(1)2*. Thermal ellipsoid plots of the core of **2** are given in Figure 3. $[V_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(OH_2)_3]^+$ has a planar triangular arrangement of three equivalent vanadium(III) atoms, with each vanadium center coordinated to a μ_3-oxo ligand, four μ-acetato ligands, and an aqua ligand. The μ_3-oxo ligand lies on the V_3 plane, while the two μ-acetato ligands which bridge to an adjacent V(III) center lie on opposite sides of the V_3 plane. The asymmetric unit is completed by a chloride anion and water molecules. Hydrogen bonding occurs between the one of vanadium-bound water molecules and an acetate oxygen of a neighboring trimer, forming one-dimensional chains of clusters. A range of triangular $[V(III)_3(\mu_3\text{-}O)(\mu\text{-}OOCR)_6L_3]^{n+}$ clusters (including complexes where R = CH_3) have been isolated either from organic solvents or neat carboxylic acid.[13,14,37] Indeed, this structure has also been observed for a wide range of transition metal/carboxylate complexes.[15] There is excellent agreement between the reported V−O bond lengths and V−O−V bond angles for **2** and those reported for $[V(III)_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(CH_3COOH)_2(THF)][VCl_4(CH_3COOH)_2]$ and $[V(III)_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(THF)_3][V_2O_6Cl_6]$.[13,14] Electrospray mass spectrometry measurements of crystals of **2** in anaerobic water demonstrate the presence of **2** in solution.

To summarize, two major V(III)/acetate clusters form in aqueous acidic solution for acetate/V(III) ≤4, pD 3.50, with ^{1}H NMR spectroscopy methyl proton signals at 44.3 ± 0.2 and 46.65 ± 0.05 ppm. Two clusters have been characterized by single-crystal X-ray diffraction studies from acidic aqueous solution. **1** is a new, novel structural type consisting of four coplanar V(III) atoms bridged by μ-hydroxo and μ-acetato ligands. **2** has a triangular $V(III)_3(\mu_3\text{-oxo})$ core with two μ-acetates bridging the V centers. Structurally similar clusters to **2** have been previously isolated from organic solvents or neat acetic acid. We are currently carrying out variable-temperature magnetic susceptibility measurements to investigate single-molecule magnetic properties of these clusters containing the orbitally degenerate V(III), $^3T_{1g}$ ($S = 1$), centers,[20] in addition to probing the nature of the complexes formed between V(III) and carboxylates for a range of other carboxylate ligands.

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Supporting Information Available: Plots of relative peak areas as a function of the mole equiv. of acetate added for the data shown in Figures S1; UV−visible spectral data; Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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