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

Fiona H. Fry,† Brenda A. Dougan,‡ Nichola McCann,† Christopher J. Ziegler,§ and Nicola E. Brasch*‡

Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 0200, Australia, Department of Chemistry, Kent State University, Kent, Ohio 44242, and Department of Chemistry, Knight Chemical Laboratory, University of Akron, Akron, Ohio 44325

Received March 4, 2005

We report the first structures of simple acetate complexes of vanadium(III) formed in aqueous solution. Paramagnetic 1H 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 sulfate–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 (d2) 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 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 octanuclear18 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 1H NMR spectra of equilibrated aqueous solutions of VCl3 and 7.0 × 10−2 to 4.0 mol equiv acetate at pD 3.50. The chloride ligands of VCl3 readily dissociate upon dissolution of VCl3 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

---

*(† To whom correspondence should be addressed. E-mail: nbrasch@kent.edu.
† Australian National University.
‡ Kent State University.
§ University of Akron.)

The observation of signals is a consequence of a 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 $[V_4(\mu_3-OH)_(3)(\mu-OOCCH_3)_4Cl_2(\text{CH}_3\text{COOH})_2\text{H}_2\text{O}(I)]$ crystallized from a solution of 1:1 V(III)/CH_3COOH(H) with the space group I-42m. X-ray diffraction studies on cluster I revealed a novel, previously unknown tetranuclear vanadium/carboxylate structure. Thermal ellipsoid plots of I are given in Figure 2. The

![Figure 1](image1.png)

**Figure 1.** $^1$H 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 pH 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.

$\pm 0.2$ 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 $^1$H (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 $\pi$-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.

Another crystal form whose core is isostructural to I, $[V_4(\mu-OOCCH_3)_4(\mu-OH)_3(\text{OH})_2\text{Cl}_4(\text{H}_2\text{O})](2)$/$\text{mmm}$, 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).
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 µ3-oxo ligand, three µ-carboxylate ligands, and a bidentate 2,2′-bipyridine ligand. They are also significantly different from reported structures of tetranuclear V(V)/carboxylate clusters with V₄(µ-oxo)(µ-carboxylate)₄ cores. Deep green block-shaped crystals of a further cluster, [V(V)(µ-oxo)(µ-OOCCH₃)(OH₂)₃]⁺, have been previously isolated from organic solvents or neat carboxylic acid.

Indeed, this structure has also been observed for a wide range of transition metal/carboxylate complexes. There is excellent agreement between the reported V–O bond lengths and V–O–V bond angles for 2 and those reported for [V(V)(µ-oxo)(µ-OOCCH₃)(CH₃COOH)(THF)][VCl₄(CH₂CO₂H)] and [V(V)(µ-oxo)(µ-OOCCH₃)(THF)][V₂O₂Cl₄].

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 ¹H 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)(µ3-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), ⁳T₁g (S = 1), centers, in addition to probing the nature of the complexes formed between V(III) and carboxylates for a range of other carboxylate ligands.

Acknowledgment. We would like to thank Dr. Boujemaa Moubarak and Professor Keith S. Murray, School of Chemistry, Monash University, Australia, for measuring the magnetic susceptibility of 1 at 300 K. We would also like to acknowledge partial financial support of this work from Kent State University’s Research Council (to N.E.B.) and the NSF-REU program (to B.A.D.). C.J.Z. acknowledges support by the National Science Foundation (CHE-0216371) and a University of Akron Faculty Research Grant (1594).