A novel cationic heteropolyoxovanadium(IV) cluster functionalized with organic species [MnIV{O6{(OCH2CH2)2N(CH2CH2OH)6}]Cl2

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Received (in Purdue, IN, USA) 14th November 2002, Accepted 17th December 2002

First published as an Advance Article on the web 15th January 2003

The solvothermal reaction of (HOCH2CH2)3N with [(n-C4H9)4N][H3V10O28] and MnCl2·4H2O in CH3CN and CH3OH yields a novel cationic heteropolyoxovanadium(IV) cluster, [MnIV{O6{(OCH2CH2)2N(CH2CH2OH)6}Cl2}, containing a fully reduced cyclic [MnV6O18]6− core with the Anderson structure.

Vanadium oxides and their complexes are of current interest due mainly to their relevance to catalysis and biochemical systems, their variable geometries, and their redox properties.1–3 While numerous compounds of molybdenum and tungsten containing hexametallacarbonyl cores exhibiting the Anderson structure4 are known in the polyoxometallate literature,2,3,5 the corresponding structure based on the hexavanadate core is rare. The vast majority of reported polyoxometallate clusters are anionic and a small number of them are neutral.6

During the course of our ongoing investigations7 of the chemistry of vanadium oxide clusters and their derivatives, we have discovered a novel cationic heteropolyoxovanadium(IV) cluster containing a previously unobserved fully reduced metallacyclic core—[MnV6O18]6−—exhibiting the Anderson structure and functionalized with triethanolamine ligands. This report describes the synthesis and characterization by FTIR spectroscopy, elemental analysis, thermogravimetric analysis, manganometric titration, valence sum calculation, and single crystal X-ray diffraction analysis of this new heteropolyoxovanadium(IV) derivative, [MnIV{O6{(OCH2CH2)2N(CH2CH2OH)6}Cl2}].

Dark blue crystals of I were first obtained in ~ 25% yield along with an impurity by the solvothermal reaction of (HOCH2CH2)3N with [(n-C4H9)4N][H3V10O28] and MnCl2·4H2O in the presence of C6H3(COOH)3−·1,3,5 in a mixed solvent (CH3CN–CH3OH) medium at 145 °C for 24 h. We have, however, been able to rationalize the synthesis of I. The compound can now be prepared in pure monophase form and in high yield (~70%) by adopting a slightly different synthetic method that does not require the use of 1,3,5-benzene-tricarboxylic acid.

While the yield is significantly enhanced, the quality of the crystals produced by the modified approach is somewhat poorer. This indicates that although 1,3,5-benzencarboxylic acid is not essential for the synthesis of I, as is expected from the structure and composition of I, the presence of 1,3,5-benzencarboxylic acid in the reaction medium is helpful in obtaining high quality single crystals suitable for X-ray crystallographic work.

The IR spectrum of I exhibits a very strong band at 973 cm−1 which is attributable to ν(V=O), multiple features due to (V–O–V) moieties, and triethanolamine bands in their characteristic regions. The blue color of the crystals of I is indicative of the presence of the reduced vanadium sites in the compound. This was confirmed by the manganometric titration which revealed the presence of 6VIV sites per formula unit. This was further corroborated by room temperature magnetic susceptibility measurement.

The crystal structure of I (Fig. 1) consists of discrete [MnIV{O6{(OCH2CH2)2N(CH2CH2OH)6}]Cl2}2+ cations and chloride anions. A view of the unit cell contents, projected down the a-axis, is given in Fig. 1(a), which clearly shows the relationship between the cations and anions. The cluster cation [MnIV{O6{(OCH2CH2)2N(CH2CH2OH)6}]Cl2}2+ in I contains an unprecedented fully reduced cyclic [MnV6O18]6− framework incorporating six triethanolamine ligands. The [MnV6O18]6− core adopts the Anderson type structure,4 previously observed in polyoxometalates and polyoxotungstates.5,6 The cyclic core of the cation is comprised of a ring of six edge sharing [VO5N] octahedra linked to a central [MnO6] unit. The six vanadium atoms lie alternatively on opposite sides of their mean plane by approximately ±0.17 Å. The Mn(n) ion lies in the V6 plane. The resulting centrosymmetric structure of the cation is shown in Fig. 1(b).

Fig. 1(c) shows the metal atoms and their coordination spheres. Each of the six vanadium atoms is bound to a terminal oxygen atom (V–O 1.593–1.601 Å) as well as to five atoms from the triethanolamine ligands—a nitrogen donor atom (V–N 2.162–2.174 Å), two µ3-O atoms (V–O 1.942–2.035 Å) and two µ2-O atoms (V–O 2.027–2.296 Å). Each adjacent pair of vanadium atoms around the ring is linked by one µ1-O atom and one µ2-O atom; the third bond of each triply bridging oxygen atom is to the central octahedral Mn(n) atom (Mn–µ1-O 2.174–2.205 Å).

As shown in Fig. 1(b), one pendant arm of each of the six triethanolamine ligands projects outward from the hexagonal ring. The oxygen atoms (O19 and O23) of two of these arms are disordered over two positions. The pendant groups are involved in hydrogen bonding with the chloride ions.

Bond valence sum calculations8 show that none of the µ2- and µ1-oxo groups have any hydroxy protons. This result in combination with the number of reduced vanadium(V) sites determined from the redox titration is in agreement with the two units of positive charge on the cluster cation. The charge is balanced by chloride ions.

Thermogravimetric analysis9 of I revealed a two-step weight loss (37.5%) between 250 and 392 °C and a gradual loss of 9.8% between 392 and 700 °C. The observed total weight loss corresponds to the removal of the organic (C, H and N) part of the triethanolamine ligands and the chloride ions which account for ~47.6% of the mass of I. The FT-IR spectrum of the black shining residue left after the heating shows medium intensity bands at 668, 619 and 458 cm−1 indicating it to be a reduced mixed-metal oxide phase.

In conclusion, I constitutes the first example of a reduced hexavanadate based cationic cluster exhibiting the Anderson structure. The structure of the ring in I is similar to the metallacycle observed in the earlier reported compound [Na3V10O41(OCH2CH2)3N(CH2CH2OH)6]·2S2·2CH3OH. The latter contains an oxidized anionic hexavanadate core adopting the Anderson structure.4 The other reported examples of the hexavanadate clusters,12–14 which are functionalized with tris(hydroxymethyl)alkane ligands, contain reduced {V6O18} cores which adopt the Linquist structure.15,16

Published 15 January 2003. Downloaded by University of California - Irvine on 13/08/2015 00:10:35.
C6H3(COOH)3-1,3,5, MnCl2 in the millimolar ratio of 0.05
(a) The unit cell contents of the crystals of [Mn IV VI6O6- Fig. 1
atoms and their coordination environments in the cationic cluster in Å
† Notes and references
§ Selected IR absorption bands for I (KBi pellet, 1600–500 cm-1): 1463s, 140s, 1353, 1300s, 1243m, 1085s, 1050s, 1019m, 973s, 925m, 900m, 751s, 666vs, 640sh, 551m, 507vs cm-1
¶ Crystal data for I: C22H68Cl2MnN6O3V6, M = 1410.52, monoclinic, space group P21, a = 11.2208(5), b = 21.5041(9), c = 11.8126(5), β = 111.2600(10°), V = 2656.2(6) Å3, Z = 2, T = 178(2) K, D = 1.764 Mg m-³, μ = 1.426 mm-1, F(000) = 1450, crystal size = 0.08 x 0.15 x 0.17 mm. A total of 28954 reflections (1.85 < θ < 28.30°) were collected, of which 12675 unique reflections were used for structural elucidation (Rw = 0.0786 (all data). CCDC 196923. See http://www.rsc.org/suppdata/cb2/b21195k/ for crystallographic data in CIF or other electronic format.


8 (a) The room temperature magnetic moment of I indicates the presence of the vanadium(v) sites and high-spin manganese(II). Detailed study of the magnetic properties of I is in progress. The results will be included in a future full paper (b) triethanolamine acts as a tetradentate ligand in the solid state and as tridentate in aqueous solution in a recently reported V triethanol mononuclear complex: D. G. Diller, H. Chen, O. Anderson and M. Miller, J. Am. Chem. Soc., 1993, 115, 6769.


10 The thermogravimetric analysis was performed on Mettler Toledo TGA/SDTA 851E Instrument. A 10.227 mg sample of I was heated in nitrogen atmosphere at a heating rate of 5 °C min-1.


