Title

A novel cationic heteropolyoxovanadium(iv) cluster functionalized with organic ligands : synthesis and characterization of the fully reduced species [Mn II V IV 6 O 6 {(OCH 2 CH 2) 2 N(CH 2 CH 2 OH)} 6]Cl 2

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A novel cationic heteropolyoxovanadium(IV) cluster functionalized with organic ligands: synthesis and characterization of the fully reduced species $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$

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The solvothermal reaction of $(HOCH_2CH_2)_3N$ with $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ and $MnCl_2{\cdot}4H_2O$ in CH_3CN and CH_3OH yields a novel cationic heteropolyoxovanadium(IV) cluster, $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]^{2+}$, containing a fully reduced new cyclic $\{MnV_6N_6O_{18}\}$ 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 hexametalate cores exhibiting the Anderson structure[4] are known in the polyoxometalate literature,[2,3,5] the corresponding structure based on the hexavanadate core is rare. The vast majority of reported polyoxometalate clusters are anionic and a small number of them are neutral.[6]

During the course of our ongoing investigation[7] 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—$\{MnV_6N_6O_{18}\}$—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, $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$ (**1**).

Dark blue crystals of **1** were first obtained in ~25% yield along with an impurity by the solventothermal reaction of $(HOCH_2CH_2)_3N$, $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ and $MnCl_2{\cdot}4H_2O$ in the presence of $C_6H_3(COOH)_3$-1,3,5 in a mixed solvent (CH_3CN–CH_3OH) medium at 145 °C for 24 h.† We have, however, been able to rationalize the synthesis of **1**. The compound can now be prepared in pure monophasic form and in high yield (~70%) by adopting a slightly different synthetic method that does not require the use of 1,3,5-benzenetricarboxylic 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-benzenetricarboxylic acid is not essential for the synthesis of **1**, as is expected from the structure and composition of **1**, the presence of 1,3,5-benzenetricarboxylic acid in the reaction medium is helpful in obtaining high quality single crystals suitable for X-ray crystallographic work.

The IR spectrum§ of **1** 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 **1** 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 $6V^{IV}$ sites per formula unit. This was further corroborated by room temperature magnetic susceptibility measurement.[8a]

The crystal structure¶ of **1** (Fig. 1) consists of discrete $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]^{2+}$ 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 $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]^{2+}$ in **1** contains an unprecedented fully reduced cyclic $\{MnV_6N_6O_{18}\}$ framework incorporating six triethanolamine ligands. The $\{MnV_6N_6O_{18}\}$ core adopts the Anderson type structure,[4] previously observed in polyoxomolybdates and polyoxotungstates.[3a,5] The cyclic core of the cation is comprised of a ring of six edge sharing $\{VO_5N\}$ octahedra linked to a central $\{MnO_6\}$ unit. The six vanadium atoms lie alternatively on opposite sides of their mean plane by approximately ±0.17 Å. The Mn(II) ion lies in the V_6 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 μ_2-O atoms (V–O 1.942–2.035 Å) and two μ_3-O atoms (V–O 2.027–2.296 Å). Each adjacent pair of vanadium atoms around the ring is linked by one μ_2-O atom and one μ_3-O atom; the third bond of each triply bridging oxygen atom is to the central octahedral Mn(II) atom (Mn–μ_3-O 2.174–2.205 Å).

As shown in Fig. 1(b), one pendant arm of each one of the six triethanolamine ligands[8b] 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 valance sum calculations[9] show that none of the μ_2- and μ_3-oxo groups have any hydroxy protons. This result in combination with the number of reduced vanadium(IV) 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 analysis[10] of **1** 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 **1**. 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, **1** constitutes the first example of a reduced hexavanadium based cationic cluster exhibiting the Anderson structure. The structure of the ring in **1** is similar to the metallocycle observed in the earlier reported[11] compound $[NaV_6O_6\{(OCH_2CH_2)_2NCH_2CH_2OH\}_6]_2S_6{\cdot}2CH_3OH$. 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 $\{V_6O_{19}\}$ cores which adopt the Linquist structure.[15,16]

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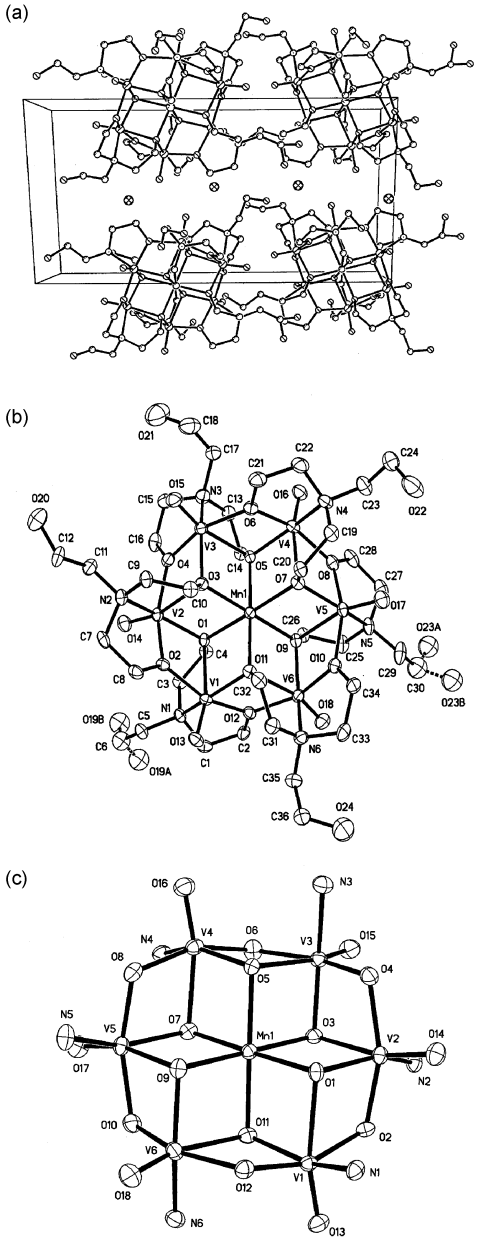

Fig. 1 (a) The unit cell contents of the crystals of $[Mn^{II}V^{IV}{}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$ (**1**), projected down the *a*-axis, showing the relationship between the cluster cations and chloride anions. (b) A view of the cluster cation $[Mn^{II}V^{IV}{}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]^{2+}$ present in the crystals of **1**, showing atom labeling scheme. Disordered oxygen atoms of the pendant arm of the triethanolamine ligand are included. Displacement ellipsoids are drawn at the 50% probability level. (c) The metallocyclic framework $\{MnV_6N_6O_{18}\}$ showing the metal atoms and their coordination environments in the cationic cluster in **1**. Selected bond lengths (Å): Mn1–O 2.174–2.205, V1–O13 1.1593(4), V2–O14 1.593(4), V3–-O15 1.597(4), V4–O16 1.594(4), V5–O17 1.601(4), V6–O18 1.597(4), V–μ_2-O 1.942–2.035, V–μ_3-O 2.027–2.296, V–N 2.162–2.184.

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Notes and references

† Method I: a mixture consisting of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$, $C_6H_3(COOH)_3$-1,3,5, $MnCl_2{\cdot}4H_2O$, CH_3CN, CH_3OH and $(HOCH_2CH_2)_3N$ in the millimolar ratio of 0.05 : 0.25 : 0.15 : 57.42 : 49.4 : 1.9 was placed in a 23 ml Teflon-lined Parr autoclave. The autoclave was heated for 24.5 h in a Thermoline furnace maintained at 145 °C. The furnace was then turned off and the autoclave was left inside the furnace to cool slowly to the room temperature for 12–24 h. The blue crystals were filtered off along with a colorless amorphous impurity from the pale-yellow mother-liquor. The crystals of **1** were washed with methanol, dried in air at room temperature, and mechanically separated from the impurity. Yield ~25% (based on vanadium). The following rationalized modified synthetic method gives **1** in monophasic form and in high yield, albeit at the cost of the crystal quality.

‡ Method II: a mixture of $[(C_4H_9)_4N]_3[H_3V_{10}O_{28}]$, $MnCl_2{\cdot}4H_2O$, CH_3CN, C_2H_5OH and $(HOCH_2CH_2)_3N$ in the millimolar ratio of 0.05 : 0.15 : 57.4 : 34.24 : 1.9 contained in a Teflon-lined Parr autoclave was heated at 145 °C for 24h in a furnace. The furnace was then turned off and the autoclave was left inside the furnace to cool slowly to the room temperature for 24 h. The blue platy crystals of **1** were filtered off from the transparent light green mother-liquor, washed with ethanol, and dried in air at room temperature. Yield ~70% (based on vanadium).

Crystals of **1** are stable in air, insoluble in organic solvents, and soluble in water; these are analyzed satisfactorily for C, H, N, Cl, V and Mn.

§ Selected IR absorption bands for **1** (KBr pellet, 1600–500 cm^{-1}): 1463s, 1440s, 1353m, 1300m, 1243m, 1153w, 1085vs, 1061vs, 1040sh, 1019m, 973vs, 923m, 900m, 751s, 666vs, 640sh, 551m, 507vs cm^{-1}

¶ *Crystal data* for **1**: $C_{36}H_{78}Cl_2MnN_6O_{24}V_6$, M = 1410.52, monoclinic, space group $P2_1$, a = 11.2208(5), b = 21.5041(9), c = 11.8126(5) Å, β = 111.2680(10)°, V = 2656.2(2) A^3, Z = 2, T = 178(2) K, D_c = 1.764 Mg m^{-3}, μ = 1.426 mm^{-1}, $F(000)$ = 1450, crystal size = 0.08 × 0.15 × 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 (R_{int} = 0.0478). The final $R1$ was 0.0786 (all data). CCDC 196923. See http://www.rsc.org/suppdata/cc/b2/b211195k/ for crystallographic data in CIF or other electronic format.

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