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Vanadium(IV) and Mixed-valence Vanadium(IV/V) Oxygen Clusters with Novel Electronic Properties, including the Examples $[V_{12}As_8O_{40}(HCO_2)]^{n-}$ (n = 3 or 5)

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The mixed valence compounds $[NHEt_3]_2[NH_2Me_2][V_{12}As_8O_{40}(HCO_2)]\cdot 2H_2O$ **1** and $Na_5[V_{12}As_8O_{40}(HCO_2)]\cdot 18H_2O$ **2** containing isostructural V–O clusters with encapsulated formate ions and different electron populations, and their characterization are reported; in structurally related V–O clusters spin–spin coupling increases with increasing numbers of V^{IV} centres in a nearly continuous way.

Mixed-valence metal–oxygen and –sulphur clusters that exist with different electron populations are of importance for understanding electron-transfer and electron-storage systems in nature and in materials science. We have isolated the two structurally identical clusters **1** and **2** with different electron populations as well as different types of spin–spin interactions. The cluster **1** contains six practically uncoupled and trapped (down to 20 K) and **2** eight antiferromagnetically coupled V^{IV} (d^1) centres. The cluster **1** was isolated in the form of deep-green crystals of $[NHEt_3]_2[NH_2Me_2][V_{12}As_8O_{40}(HCO_2)]\cdot 2H_2O$ and **2** in the form of deep-blue crystals of $Na_5[V_{12}As_8O_{40}(HCO_2)]\cdot 18H_2O$.*

The compounds were obtained by reduction of aqueous vanadate(V) with hydrazinium monochloride in the presence of As^{III} and *N,N*-dimethylformamide (giving rise to the encapsulated formate ion) and were characterized by elemental analysis (including manganometric titration of the number of V^{IV} centres and thermogravimetric determination of water of crystallization), UV–VIS, near-IR and vibrational spectroscopy,† magnetic measurements, and single-crystal X-ray structure analysis.‡

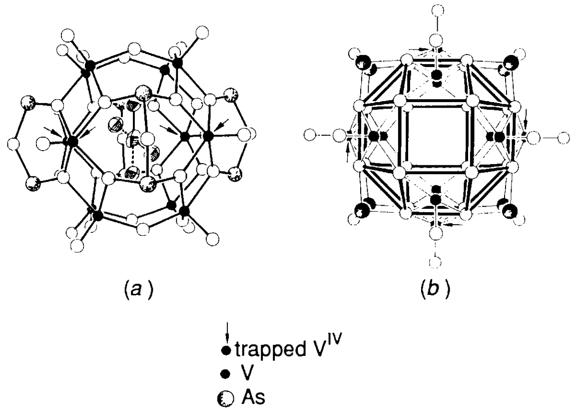

Fig. 1 (*a*) Structure of the cluster shell of **1** and **2** with an encapsulated, disordered formate ion (resolved for one of the two nonequivalent sites of **2**). Average bond distances in **2** (Å): V–O_{term} 1.604, As–O 1.781, V–μ_2–O 1.822, V–μ_3–O 2.016, V('equator')–μ_3–O 1.958, V · · · $O(HCO_2)$ 2.74, O · · · $O(HCO_2)$ > 2.73, V · · · V (in V_4O_4 rings) 3.434, $V(V_4O_4$ rings) · · · V('equator') 3.160. (*b*) Rhombicuboctahedron spanned by 24 O atoms (as in the Keggin structure) of which 16 squares are capped with 12 V=O and 4 As_2O groups.

In both compounds the anion has (idealized) D_{4h} symmetry and consists of twelve (distorted) tetragonal VO_5 pyramids and four handle-like As_2O_5 groups, whereby a hollow sphere is formed (Fig. 1). Within the cluster a disordered formate ion is encapsulated, the disordering of which is resolved in a low temperature X-ray structure analysis of **2**. The twelve VO_5 pyramids can be divided into two classes that differ regarding their position relative to the As_2O_5 groups. The first consists of four pyramids that are bridged through edges by the As_2O_5-groups thus forming the 'equator' of the anion where four V^{IV} centres are trapped (marked in Fig. 1). The other VO_5 pyramids are linked through corners (above and below the 'equator'). Another simple topological description of the structure refers to the rhombicuboctahedron (Fig. 1*b*) spanned by 24 O atoms[1] as in the 'Keggin type basic unit', the

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* Abbreviations for the clusters and corresponding salts are used synonymously.

† Selected IR data (solid; KBr pellet; ν/cm^{-1}) for **1**: $\nu(O_2CH)$ 2800w; $\nu_{as}(CO)$ 1587m, $\nu_s(CO)$ 1340w; $\delta(HCO)$ 1382w; $\pi(HCO_2)$ 1060w; $\nu(V = O)$ 995 s; $\nu_{as}(M–O–M')$; M,M' = As,V) 835m, 797m, 685s, 606m; $\delta(COO)$ 760w (assigned with the help of data for **2**). **2**: $\nu(CH)$ 2800w; $\nu_{as}(CO)$ 1587m, $\nu_s(CO)$ 1346w; $\delta(HCO)$ 1375w; $\nu(V = O)$ 987s; $\nu_{as}(M–O–M'$; M,M' = As,V) 815m, 684s, 595m; $\delta(COO)$ 760w.

UV-VIS–near IR data (KBr pellet, transmission; $10^{-3}\ \nu$/cm^{-1}) for **1**: (IVCT) 9.2, 11.4sh; (d→d) 14.3; [CT(O→V)] 24.1, 28.6; for **2**: (IVCT) 10.9; (d→d) 13.2; [CT(O→V)] 25.3, 30.3 (CT = charge transfer; IVCT = intervalence charge transfer).

‡ *Crystal data* for **1**: $C_{15}H_{45}As_8N_3O_{44}V_{12}$, M = 2182.19, monoclinic, space group $P2_1/c$, a = 11.342(2), b = 18.091(5), c = 13.577(3) Å, β = 92.07(2)°, U = 2784.0 Å^3, μ = 6.67 mm^{-1}, Z = 2, T = 294 K. For **2**: $C_1H_{37}As_8Na_5O_{60}V_{12}$, M = 2334.89, triclinic, space group $P\bar{1}$, a = 12.390(4), b = 15.036(6), c = 15.656(6) Å, α = 104.48(3), β = 90.45(3), γ = 91.18(3)°, U = 2823.0 Å^3, μ = 6.64 mm^{-1}, Z = 2, T = 135 K. Data (Mo-Kα radiation, graphite monochromator) were collected using a Siemens R3m/V diffractometer (ω-scan). The structures were solved by direct methods. The full-matrix least-squares refinement converged to R values of 0.063 {5439 unique reflections [$F_o > 3.92\sigma(F_o)$; 4° < 2θ < 56°]} and 0.059 {7223 unique reflections [$F_o > 3.92\sigma(F_o)$; 4° < 2θ < 50°]} for **1** and **2**, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 Vanadium–oxygen clusters with varying number of V^{IV} (d^1) centres and spin–spin coupling (most of them with the 24 O rhombicuboctahedron of the Keggin structure)

Anion	No. of V^{IV} centres	μ_{eff}/μ_B per/V^{IV}, room temp.	$V^{IV} \cdots V^{IV}$ (trapped) distance/Å	Ref.
$[V_{14}AsO_{40}]^{7-}$ [a]	2	1.77	8.721	2
$[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ [b]	4	1.75	5.649–5.720 [h]	3
$[V_{12}As_8O_{40}(HCO_2)]^{3-}$ **1** [g]	6	1.75	5.254 [i]	—
$[V_{12}As_8O_{40}(HCO_2)]^{5-}$ **2** [g]	8	1.39	*i*	—
$[V_{12}As_8O_{40}(H_2O)]^{4-}$ [c,g]	8	1.38	*i*	3
$[V_{15}O_{36}(Cl)]^{6-}$	8	1.38	*i*	4
$[V_{18}O_{42}(SO_4)]^{8-}$ [d,g]	12	1.14	*i*	5
$[V_{14}As_8O_{42}(SO_3)]^{6-}$ [e,g]	14	1.20	2.813–3.061	3
$[V_{15}As_6O_{42}(H_2O)]^{6-}$ [e,g]	15	1.08	2.870–3.049	6
$[H_4V_{18}O_{42}(I)]^{9-}$ [f,g]	18	1.06	2.795–3.023	7

[a] *Sherwoodite type.*[2] [b] Three-quarters of an AsV_{12} ε-Keggin type species capped with three VO^{3+} and three $AsOH^{4+}$ groups and a K^+ ion. [c] Corresponding to the title compounds (HCO_2^- is replaced by H_2O). [d] 'Extended Keggin' V_{18} species. [e] Derivative of *d*, in which As_2O^{4+} groups have replaced some of the 12 'original' VO groups. [f] Isomeric species of *d*. [g] Basic fragment: rhombicuboctahedron spanned by 24 O atoms [forming (12 + 6) O_4 squares; see Fig. 2]. [h] One V^{IV} centre delocalized (according to the valence bond sum[i]). [i] In the very complicated intermediate region, where the formal number of V^{IV} centres is larger than half of the whole number of V atoms, trapped and delocalized V^{IV} centres may occur (according to valence bond sum calculations; *cf.* I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B*, 1976, **32**, 1957).

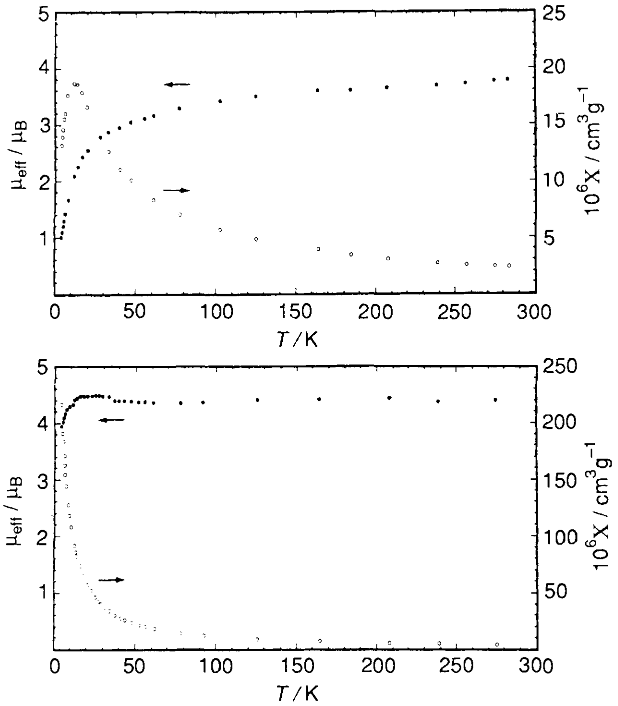

Fig. 2 The magnetic susceptibilities (χ) and effective magnetic moments (μ_{eff}) of **1** and **2** (upper part) in the temperature range 4.2–290 K

(12 + 6) O_4-squares of which are capped by 12 V=O 2+(3+) and 4 As_2O^{4+} groups.

$$[V_{12}As_8O_{40}(HCO_2)]^{3-}$$
1
$$[V_{12}As_8O_{40}(HCO_2)]^{5-}$$
2

Variable-temperature solid-state magnetic susceptibility studies were performed on powdered samples of **1** and **2** in the range 4.2–290 K (see Fig. 2). The effective magnetic moment (μ_{eff}) of **1** is 4.32 μ_B (constant from 20 to 290 K, corresponding to 1.75 μ_B per V^{IV} centre). The effective magnetic moment of **2** varies gradually from 3.94 μ_B at 290 K (1.39 μ_B per V^{IV} centre) to 1.03 μ_B at 4.2 K (0.36 μ_B per V^{IV} centre), with a Néel temperature of 13 K. For all other species of Table 1 the temperature dependence of the susceptibility has been measured between 290 and 80 K. Most of them show, as expected for antiferromagnetically coupled centres, μ_{eff} values which decrease with decreasing temperature.

Nearly all ratios of V^{IV} to V^V can be observed. The situation is demonstrated in Table 1, which shows that V–O clusters with two, four and six (practically uncoupled spins) up to eighteen V^{IV} (d^1) centres (antiferromagnetically coupled without formation of covalent V–V bonds) are possible. In species with a small number of spins [V^{IV} (d^1) centres], the spins are found almost trapped and as far apart as possible resulting in spin-only values for μ_{eff} per V^{IV}. Spin–Spin coupling increases with increasing number of V^{IV} centres (which necessarily come into closer contact) in a nearly continuous way (see μ_{eff} for V^{IV} values in Table 1). A 'pseudo-spin-flip' (crossover from nearly uncoupled centres, from the 2 to the 6 spin system) to antiferromagnetically coupled spin systems [from 8 to 18 V^{IV} (d^1) centres] occurs between **1** and **2**.

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