Pentadecavanadate, $V_{15}O_{42}{}^{9-}$, a New Highly Condensed Fully Oxidized Isopolyvanadate with Kinetic Stability in Water

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The X-ray structure of the new fully oxidized isopolyvanadate, $(TMA)_3H_6V^V{}_{15}O_{42} \cdot 2.5H_2O$ 1 (TMA = tetramethyl-ammonium), prepared by reaction of H_2O_2 with $VOSO_4 \cdot 4H_2O$ shows a bicapped Keggin structure with four-, five- and six-coordinate vanadium atoms; ^{51}V NMR indicates that the same structure has considerable kinetic stability in water at *ca.* pH 3.5 but is thermodynamically unstable with respect to the conventional $V^V{}_{10}O_{28}{}^{6-}$ structure.

Most of the structurally distinct polyvanadates have been reported in the last four years.[1–11] Progress has been particularly marked in the area of partially reduced polyvanadates where complexes with eight or more vanadium atoms with nearly all ratios of $V^{IV} : V^V$ have been recently reported. The potential applications of fully oxidized polyvanadates have attracted our attention and we report here the largest fully oxidized isopolyvanadate to date, pentadecavanadate, $V_{15}O_{42}{}^{9-}$, which extends the known family of such structurally characterized polyvanadates: $V_4O_{12}{}^{4-}$,[1] $V_5O_{14}{}^{3-}$,[2] $V_{10}O_{28}{}^{6-}$,[3] $V_{12}O_{32}{}^{4-}$[4] and $V_{13}O_{34}{}^{3-}$.[5]

The preparation of $V_{15}O_{42}{}^{9-}$ was developed in context with our ongoing research in oxidatively resistant clusters and selective homogeneous catalytical oxidation processes[5,6] and anti-HIV chemotherapy.[12] Pentadecavanadate was prepared by adding an aqueous solution of $VOSO_4 \cdot 4H_2O$ (8.5 mmol, 8 ml) dropwise to rapidly stirred 50% aqueous H_2O_2 (20 ml) at 5 °C over a 10 min period during which time the colour changed from light-yellow to red. The solution was warmed to 25 °C and stirred for another 10 min. TMA chloride (19.5 mmol) in H_2O (6 ml) was then added and the solution was allowed to stand for four days at 25 °C. The lustrous black

crystals produced were filtered, washed with cold water and ethanol and air-dried to give a 36% yield of $(TMA)_3H_6V^V_{15}$-$O_{42}\cdot2.5H_2O$, 1, based on V. The use of different cations in this synthetic procedure leads to different kinetic distributions of polyvanadate products.

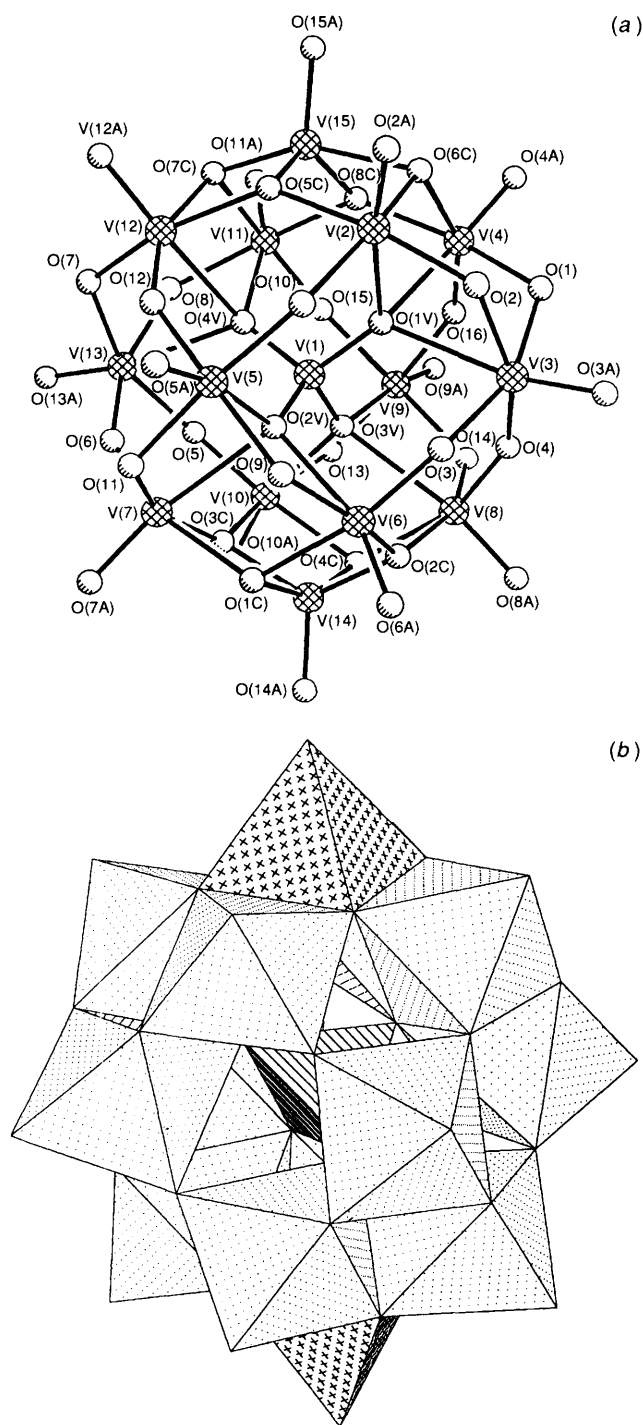The analytical,[†] spectroscopic[†] and X-ray crystallographic

data[‡] are all consistent with the formula given above for 1. The complex is EPR silent (X-band 50 : 50 v/v water : ethylene glycol glass; 20 K) and exhibits an electronic absorption spectrum in H_2O[†] with no absorption maxima in the visible and a long absorption tail extending to 450 nm, both features are consistent with a d^0 electronic configuration. Likewise, the cyclic voltammograms of 1 (25 °C/N_2–0.2 mol dm^{-3} acetate buffer at pH 3.5/glassy carbon working electrode) showed two quasi-reversible (ΔE_p = 100–160 mV) one-electron reduction waves and a third irreversible reduction wave (formal potentials: 0.23, 0.45 and −0.115 V vs. Ag/AgCl, respectively).

Both numbered ball-and-stick and polyhedral diagrams for 1 from the X-ray crystallographic analysis of an exemplary crystal are given in Fig. 1. The structure is that of the Keggin unit common in polyanion chemistry (four internally edge-sharing M_3O_{13} triads tetrahedrally disposed and corner-sharing around an internal T_d 'heteroatom') with two additional five-coordinate terminal VO units capping the pits on either side of Keggin unit that lie on the C_2 axis (see Fig. 1). As the 'heteroatom' is a four-coordinate VO_4 unit and all twelve vanadium atoms of the Keggin unit are distorted (local C_{4v} symmetry) six-coordinate VO_6 units, 1 represents the first polyvanadate with the metal ion exhibiting three different coordination numbers. The structure is disorder-free and similar to the orientationally disordered phosphopolyvanadate, $[PV_{14}O_{42}]^{9-}$, reported by Sasaki and coworkers.[13] The central tetrahedral environment around V is nearly ideal with the O–V–O angles ranging from 108.6(5)–110.0(5)° and the average V–O bond distance is 1.538(10) Å. Only two other polyvanadates contain a central VO_4 unit, the highly reduced complex, $[V^{IV}_{18}O_{42}H_9(V^VO_4)]^{6-14}$ and $[H_{12}V_{13}O_{40}]^{3-}$.[15]

The ^{51}V NMR spectrum (52.6 MHz; δ relative to external neat $VOCl_3$) of 1 indicates the bicapped Keggin structure in Fig. 1 is maintained in both deionized water and aqueous 0.2 mol dm^{-3} acetate buffer at pH 3.5 [δ −507 (1 V, VO_4), −531 (2V, VO_5), −584 (8V, VO_6) and −597 (4V, VO_6)]. Unlike the recently reported isopolyvanadates, $V_{12}O_{32}^{4-}$ and $V_{13}O_{34}^{3-}$, which are not compatible with water, 1, like the long-known complex, $V_{10}O_{28}^{6-}$, is compatible with water. Although kinetically very stable in water and acetate buffer at pH 3.5 (no decomposition for one week at 25 °C or 12 h at 50 °C), two experiments.establish that 1 is not thermodynamically stable under these conditions. First, boiling 1 (2 mmol dm^{-3}) in water for more than 5 min results in its decomposition with the approximate stoichiometry as shown in eqn. (1). Second, gradual acidification of a 2 mmol dm^{-3}

$$V_{15}O_{42}^{9-} + H_2O \rightarrow V_{10}O_{28}^{6-} + 5VO_3^- + 2H^+ \quad (1)$$
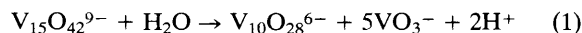
solution of 1 by addition of 0.1 mol dm^{-3} HCl results in gradual loss of the bicapped Keggin structure and the formation of $[VO_2]^+$ ion (^{51}V NMR, δ −543) until at pH ∼0.46 where only $[VO_2]^+$ is present. Neutralization of this solution back to pH 3.5 does not regenerate 1 but $V_{10}O_{28}^{6-}$ with virtually 100% selectivity.

Fig. 1 Molecular structure of **1**: (a) perspective view with the atomic labelling scheme and (b) polyhedral view showing VO_6 units (▨), VO_5 units (⊠) and internal VO_4 unit ▨

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† Satisfactory elemental analyses were obtained IR v/cm^{-1} (KBr, 400–1100 cm^{-1}): 1047w, 949s, 876m, 813w, 592m, 511vw. Electronic spectra, H_2O solvent [λ_{max}/nm (ε, dm^3 mol^{-1} cm^{-1})]: 212 (2.08 × 10^4), 251 (1.73 × 10^4), 327 (4.41 × 10^3).

‡ Crystal data for $C_{12}H_{47}N_3O_{44.5}V_{15}$, **1**, M = 1709.6, monoclinic, space group $P2_1$, a = 11.058(3), b = 19.570(4), c = 11.299(2) Å, β = 93.12(2)°, V = 2441.4(10) Å^3, Z = 2, D_C = 2.326 g cm^{-3}. A black prism crystal (0.11 × 0.30 × 0.39 mm) was mounted on a Siemens P4 diffractometer. Data collection at 173 K using Mo-Kα X-radiation (λ = 0.71073 Å), ω scans gave 5450 reflections (2θ$_{max}$ = 50°), 4679 unique reflections (R_{int} = 0.036), of which 4198 with $F \geqslant 4\sigma(F)$ were used in all calculations. The structure was solved by direct methods (Siemens SHELXTL PLUS) and refined by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-H atoms. At final convergence, R = 0.064, R_w = 0.086, GOF = 1.57 for 597 parameters. 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.

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