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Tridecavanadate, $[H_{12}V_{13}O_{40}]^{3-}$

Lage Pettersson* and Ingegärd Andersson

Department of Inorganic Chemistry, Umeå University, S-901 87, Sweden

Oliver W. Howarth

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

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The chemistry of aqueous vanadates has been considered for some years to be essentially known.[1] However, some questions remain from the earlier work,[2] notably the disputed existence of a linear trimer and the nature of the broad, composite resonance at $\delta_V = -570$ ppm. Also, there was some evidence for a transient species below pH 6, as discussed below. Therefore we are reinvestigating the system by using ^{51}V NMR (131.44 MHz, Umeå) and ^{17}O NMR (54.23 MHz, Warwick) in aqueous solution. In this way we have identified a new transient isopolyvanadate with an unexpectedly symmetrical structure, of either α- or ϵ-Keggin type.

To date, the known aqueous isopolyvanadates have been found to be based either on corner-sharing MO_4 tetrahedra or on arrays of cubically packed, edge-sharing MO_6 octahedra, as in decavanadate.[1,3] The same, or comparable but less complete, cubic arrays are also found in polyoxoanions where Mo(VI)[4] or W(VI)[5] partially or completely replaces V(V). The M(VI) isopolyanions are also known to form $M_{12}O_{40}$ species with α- or β-Keggin structures,[3] having either a tetrahedrally coordinated heteroatom or one or two protons at the center. Vanadium(V) can replace up to four such M(VI) atoms without change of structure. However, despite the possibility of protonation, substitution beyond this point has previously been considered improbable because of the increasing charge of the underlying anion. Three other closely related structures have been reported for heteropolyvanadates(V). Bicapped (PV_{14})[6] and monocapped (PV_{13})[7] vanadophosphate anions have been found, with underlying α-Keggin structures, and also a tricapped dodecavanadotrimanganate with an ϵ-Keggin structure.[8] In each of these cases, the additional metal atoms serve to reduce the overall anionic charge, as do bound protons.

Our solution-state NMR evidence for a transient all-vanadium(V) species having 12 V atoms arranged in a Keggin structure around a central, tetrahedrally coordinated V atom is as follows. When a neutral aqueous vanadate solution, typically 40 mmol dm^{-3} in V and 0.6 M in NaCl, is rapidly acidified at or near room temperature, optimally to pH 1.5, then two new ^{51}V resonances are seen in addition to those arising from the well-known formation of decavanadate. One peak is very narrow (width 7 Hz at 298 K, $\delta_V = -523.3$) and one is much broader (180 Hz, $\delta_V = -538.0$), as shown in Figure 1. The area ratio is 1:12. Figure 2 shows that these resonances decay together, according to first-order kinetics, with a half-life of 80 min at 298 K. There is little effect upon the pH. The diamonds in Figure 2 represent the concentration of the new species measured, by computer deconvolution, from the areas of the very narrow peak, and the almost coincident squares represent the same concentration estimated from the areas of the broad peak, assuming the 1:12 area ratio. We estimate the individual errors in the measurement of areas to be ±12%. A ratio of 1:13 is thus possible, although the overall fit is less good, and the 1:13 ratio does not permit an inert structure (evidenced by the oxygen NMR data below) with full symmetry and just two vanadium resonances. The high symmetry is also confirmed by the extreme narrowness of the central vanadium resonance. In our earlier studies[2] data were obtained only from equilibrated solutions, where the above transients had almost entirely decayed.

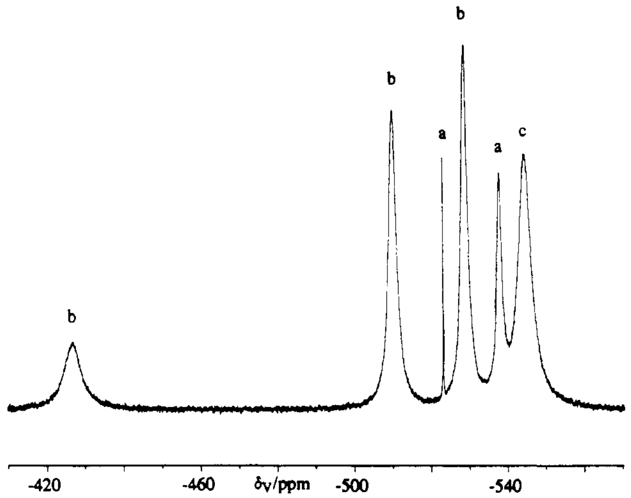

Figure 1. Vanadium-51 NMR spectrum of freshly acidified aqueous vanadate, 40 mmol dm^{-3} in V, 25 °C, 0.6 M NaCl: a = new, transient resonances in 1:12 area ratio; b = decavanadate; c = $[VO_2]^+$.

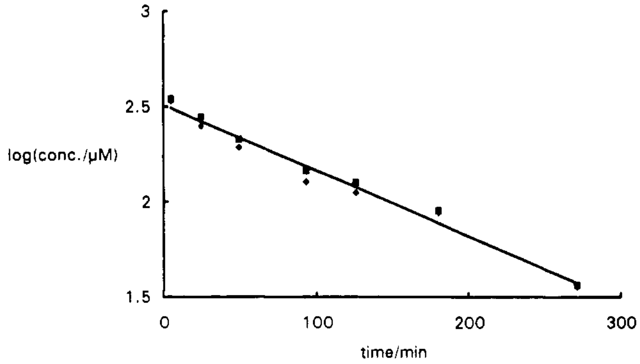

Figure 2. Time decay of new species: ● = log ($\delta_V = -523.3$ peak area); ■ = log ($\delta_V = -538.0$ peak area/12).

Furthermore, a ^{17}O NMR spectrum of a preparation containing [V] = [Na$^+$] = 120 mM and [LiCl] = 480 mM (Figure 3) obtained

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(1) Howarth, O. W. *Prog. Nucl. Magn. Reson. Spectrosc.* **1990**, *22*, 453.

(2) Pettersson, L.; Hedman, B.; Andersson, I.; Ingri, N. *Chem. Scr.* **1983**, *22*, 254. See e.g. Figure 5. Pettersson, L.; Andersson, I.; Hedman, B. *Chem. Scr.* **1985**, *25*, 309.

(3) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer: Berlin, 1983.

(4) Howarth, O. W.; Pettersson, L. P.; Andersson, I. *J. Chem. Soc., Dalton Trans.* **1989**, 1915.

(5) Howarth, O. W.; Hastings, J. J. *Polyhedron* **1990**, *9*, 143.

(6) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1953.

(7) Söderlund, A.; Andersson, I.; Pettersson, L.; Schramm, C. M.; Downey, S. K.; Grate, J. H. Manuscript in preparation.

(8) Ichida, H.; Nagai, K.; Sasaki, Y.; Pope, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 586.

0020-1669/92/1331-4032$03.00/0

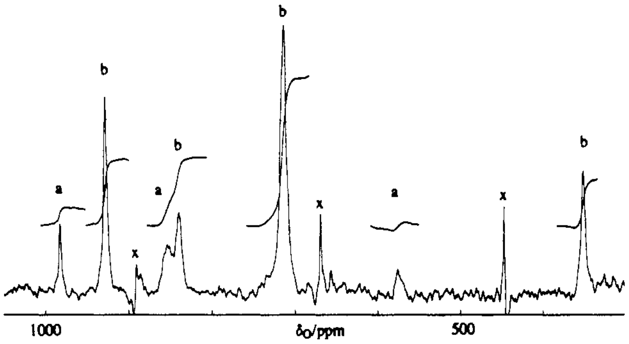

Figure 3. Partial oxygen-17 NMR spectrum of 3% ^{17}O-enriched solution, 25 °C, pH 1.5, 120 mM in V: a = transient resonances; b = decavanadate resonances; x = known spectrometer artifacts.

with modest isotopic enrichment shows three new resonances with the same pattern of decay. (A fourth resonance is also expected between 350 and 400 ppm. It may be concealed by the O_b resonance of decavanadate.) The three new peaks are consistent with the expected area ratios 3:3:1, after allowance for the use of 90° pulses, set to maximize the resonances near 700 ppm and to minimize the solvent resonance. They have shifts of 981, 853, and 575 ppm from solvent O. The new V and O peaks are consistent solely with the symmetrical α- or ϵ-Keggin structures, for all other structures have lower symmetry, and so would give rise to further peaks, and also different area ratios, as found in e.g. β-metatungstate.[9] The very narrow resonance from the central V atom independently points to a symmetrical and probably tetrahedral environment for this atom.

The resolved oxygen resonances are unusual, in that the terminal oxygen shifts are low and one bridging shift is high. They are nevertheless consistent with a Keggin structure protonated at one set of bridging oxygens. Figure 4a shows the protonation sites of an underlying α-Keggin anion, based on data for tetradecavanadophosphate.[6] However, this work could not exclude the alternative possibility of protonation at the edge-sharing oxygens. Figure 4b shows the underlying ϵ-Keggin structure protonated as in dodecavanadotrimanganate(IV), $[H_3V_{12}Mn_3O_{40}]^{5-}$.[8] Extensive protonation at one set of bridging oxygens has the effect of lowering their shifts by up to 250 ppm and of increasing the shift of the other bridging oxygens by approximately the same amount.[6] We assign the resonance at 853 ppm to this second set. The 981 ppm shift is consistent with terminal oxygens in a vanadium-rich species, for it follows the trend observed in molybdovanadate hexametalates[10] and in molybdovanadophosphate dodecametalates.[11] The 575 ppm resonance arises from the central four oxygens. As expected, these are little perturbed from the 565 ppm shift observed in aqueous $[VO_4]^{3-}$.

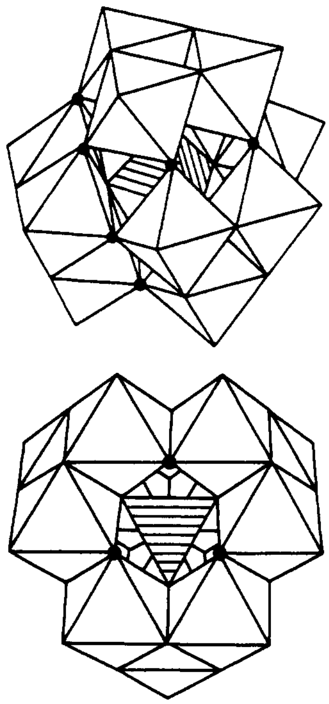

Figure 4. Alternative structures, based on VO_6 polyhedra, where ● = possible bridging oxygen atom set undergoing protonation. The central VO_4 tetrahedron is hatched. Key: (a, top) α-Keggin structure; (b, bottom) ϵ-Keggin structure.

We have not so far been able to identify the precise protonation state of the new anion, but we propose that 12 oxygens are protonated, giving the anionic formula $[H_{12}V_{13}O_{40}]^{3-}$. A 3− charge is commonly found with an aqueous polyoxoanion of this size and at this pH value,[3] an example being $[H_3V_{10}O_{28}]^{3-}$. It is probable that a very symmetrical arrangement of the protons enhances the stability of the anion, for we do not observe any change of shift over the formation range, pH 1–2, in marked contrast to e.g. tetradecavanadophosphate.

Unfortunately, the NMR data cannot distinguish between the α- and the ϵ-Keggin structures (Figure 4a,b). The former is suggested by analogy with tetradecavanadophosphate. On the other hand, the ϵ structure is supported by its having 12 obvious and better-separated sites for protonation, 3 of which are shown in Figure 4b. Such sites seem to be preferred when rings of six edge-shared MO_6 octahedra form part of the structure (ref 8 and also ref 3, p 33). It may prove possible to settle this question, and to create a new range of stable polyanions, by stabilizing the structure via added capping species.

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(9) Hastings, J. J.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1992**, 209.
(10) Howarth, O. W.; Pettersson, L. P.; Andersson, I. *J. Chem. Soc., Dalton Trans.* **1991**, 1799.
(11) Sergienko, V. S.; Porai-Koshits, M. A.; Fedotov, M. A.; Yurchenko, E. N.; Kuznetsova, L. I. *J. Struct. Chem.* **1977**, *18*, 776.
(12) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544.