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- (7) Details will be reported in a full paper.
- (8) Satisfactory analytical and spectral data were obtained for all new compounds.
- (9) Compound 7: yellow crystals; mp 49–51 °C; *m/e* 368 (M⁺, 30%), 246 (CpCoMe₃SiC₂H, 34%); τ (CCl₄) 5.13 (s, 5 H), 7.17 (s, 2 H), 9.70 (s, 18 H); ν_{CCH} 3310 cm⁻¹, $\nu_{\text{C=C}}$ 2090 cm⁻¹. 8: yellow crystals; mp 82.5–84.5 °C; *m/e* 368.0822 (calcd 368.0827, M⁺, 100%), 294 (CpCoMe₃SiC₂SiMe₃, 28%), 246 (CpCoMe₃SiC₂H, 62%), 198 (CpCoC₆H₂, 6%); τ (CCl₄) 5.10 (s, 5 H), 7.00 (s, 2 H), 9.80 (s, 18 H); ν_{CCH} 3310 cm⁻¹, $\nu_{\text{C=C}}$ 2090 cm⁻¹. 9: yellow crystals; mp 62–63 °C; *m/e* 368.0820 (calcd 368.0827, M⁺, 62%), 342 (CpCoMe₃SiC₆SiMe₃, 1%), 294 (CpCoMe₃SiC₂SiMe₃, 2%), 246 (CpCoMe₃SiC₂H, 7%); τ (CCl₄) 5.10 (s, 5 H), 6.03 (s, 2 H), 9.77 (s, 18 H); ¹³C NMR (parts per million from Me₄Si, in C₆D₆) δ 0.7, 59.7, 62.9, 82.3, 98.1, 102.8; $\nu_{\text{C=C}}$ 2140 cm⁻¹. 10: yellow oil; *m/e* 224.0032 (calcd 224.0036, M⁺, 84%), 198 (CpCoC₆H₂, 7%), 165 (M – Co, 100%), 124 (CpCo, 81%); τ (CCl₄) 5.07 (s, 5 H), 6.03 (s, 2 H), 7.07 (s, 2 H); ν_{CCH} 3280 cm⁻¹, $\nu_{\text{C=C}}$ 2095 cm⁻¹. 11: yellow crystals; mp 94–96 °C; *m/e* 224 (M⁺, 59%), 165 (M – Co, 100%), 124 (CpCo, 91%); τ (CCl₄) 5.04 (s, 5 H), 5.55 (s, 2 H), 7.23 (s, 2 H); ν_{CCH} 3300 cm⁻¹, $\nu_{\text{C=C}}$ 2110, 2085 cm⁻¹. 12a: *m/e* 226 (M⁺, 65%), 200 (CpCoC₆H₂, 4%), 175 (CpCoC₄HD, 5%), 167 (M – Co, 95%), 150 (CpCoC₂H₂, 1.5%), 124 (CpCo, 100%); $\nu_{\text{C=C}}$ 2590 cm⁻¹, $\nu_{\text{C=C}}$ 1975 cm⁻¹.
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- (18) Irradiation of this mixture through Pyrex with a medium-pressure Hg lamp gave unchanged starting material.
- (19) In addition to the mechanisms outlined in Schemes I and II, more complicated processes involving metallocyclic intermediates and a series of sigmatropic shifts are conceivable.⁷
- (20) (a) Recipient of a Regents' Predoctoral Fellowship. (b) Fellow of the A. P. Sloan Foundation, 1976–1980.

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Existence and Structure of the Molecular Ion 18-Vanadate(IV)

Sir:

We wish to report the existence of a large spherical oxo anion of vanadium(IV) having the composition V₁₈O₄₂¹²⁻, and to describe briefly its structure as determined by x-ray diffraction

from a crystal of its potassium salt, K₁₂V₁₈O₄₂·16H₂O. Heretofore the only large discrete ion of vanadium identified in a definite structural sense has been the orange decavanadate(V), V₁₀O₂₈⁶⁻.¹ The latter species (with its protonated forms) is known to be the dominant oligomer produced when V₂O₅ is treated with a limited amount of strong base.² On the basis of the work described in this preliminary communication, we now believe that the deep red-brown species V₁₈O₄₂¹²⁻ occupies a position in the aqueous chemistry of vanadium(IV) analogous to that of V₁₀O₂₈⁶⁻ in the chemistry of vanadium(V).

Relatively little has been known of the constitution of the brown solutions obtained by treating VO₂ (or VO²⁺) with hydroxide, even though this reaction was first described by Berzelius in 1831. These solutions are stable in the pH range 9–13(+) in the absence of oxygen, and from them brown to black salts can be crystallized. (The early work is cited in ref 3a.) The sodium and potassium salts were studied carefully ~20 years ago by Weiske⁴ who formulated them as [Na₂V₃O₇·4H₂O]_x and [K₂V₃O₇·2.5H₂O]_x. Several types of measurements made on their solutions convinced him that a very large anion was present in these compounds. The value of x that correctly describes both of these salts is shown below to be 6.

Both the sodium and the potassium salts were prepared by combining solutions of VOSO₄ with the appropriate hydroxide (OH⁻/V, ~5) at 60–70 °C under nitrogen or argon. The resulting deep reddish brown solutions, which were 0.5–0.7 M in vanadium(IV) and near pH 14, were filtered as necessary and chilled for several hours at 0 °C, after which flaky brown crystalline products were separated. The crude products were redissolved to saturation in 0.2 N hydroxide at 70 °C (~6 wt %) under inert gas. Standing for 1–3 days at room temperature produced sharp black tetragonal (Na) or monoclinic (K) prisms, which were recovered in 50–80% overall yields.

Prepared salts were protected against water loss and oxidation. Vanadium was determined by sequential potentiometric titrations with cerium(IV) and iron(II) in 2 N H₂SO₄. The average oxidation state inferred by this means was 4.01 (Na) and 4.00 (K). Potassium was determined as the tetraphenyl borate, sodium by atomic absorption, and water by weight loss in vacuo at 160 and 300 °C.

Calcd for Na₁₂V₁₈O₄₂·24H₂O: V, 39.92; Na, 12.01; H₂O, 18.82. Found: V, 39.6; Na, 13.0; H₂O, 19.43. Calcd for K₁₂V₁₈O₄₂·16H₂O: V, 39.08; K, 20.00; H₂O, 12.29. Found: V, 38.95; K, 20.07; H₂O, 12.48. Several other salts were prepared and analyzed, including those of Ba²⁺, Tl⁺, Cs⁺, Rb⁺, and Na⁺/Cs⁺.

For the sodium salt the dimensions of the tetragonal unit cell, as obtained by the precession method, are $a = 20.83$, $c = 14.40 \text{ \AA}$. The density, as obtained by the flotation method, is 2.45 g/mL. From these and analytical data, the cell was calculated to contain a group of 17.9 V atoms in each asymmetric unit. Preliminary results for the monoclinic potassium salt (refined data given below) implied 17.7 V atoms in each asymmetric unit. This was taken as evidence for the persistence of an 18-vanadate ion in two different space groups, and therefore probably also in the solutions from which the salts crystallized.

A crystal of the potassium salt 0.25 × 0.13 × 0.18 mm was protected in a glass capillary during collection of Mo K α x-ray diffraction data with a Picker four-circle diffractometer. Nineteen hand-centered reflections gave a refined unit cell of dimensions $a = 12.580(1)$, $b = 37.661(4)$, $c = 12.724(1) \text{ \AA}$; $\beta = 97.606(4)^\circ$; $Z = 4$; $D_x = 2.608$, $D_m = 2.58 \text{ g/mL}$.

A total of 3490 symmetry-independent counter data were collected by the θ - 2θ scan method, of which 2984 were considered observed. After all appropriate adjustments of the data, the structure was solved in the uniquely assignable space group

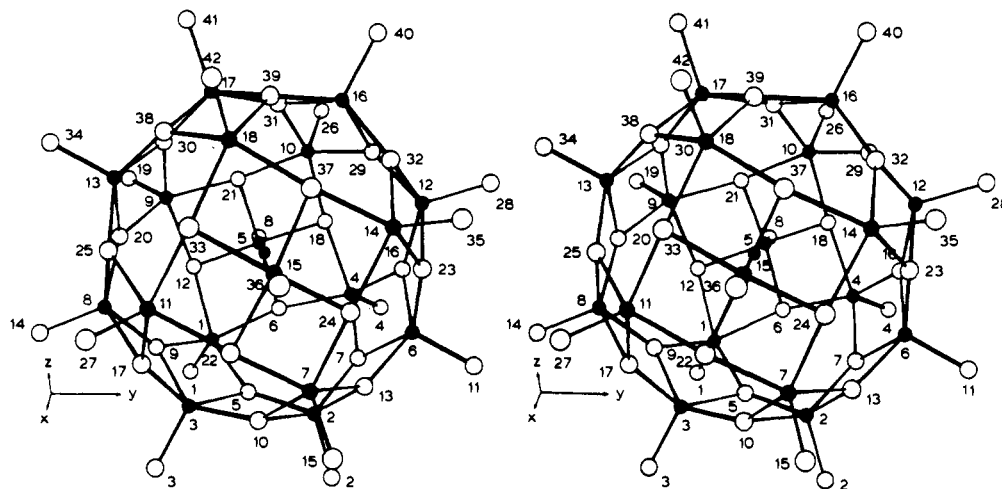


Figure 1. Stereoscopic view of the atomic positions in the ion $V_{18}O_{42}^{12-}$ (V, solid circle; O, open circle). All V-O proximities $< 3 \text{ \AA}$ are shown as bonded; the range of these is 1.54–2.04 \AA . The view is approximately along the virtual S_8 axis.

$P2_1/n$ by direct methods (program MULTAN) and difference Fourier syntheses. Most of the structure was refined to convergence by full-matrix least squares to a final agreement factor $R_F = 0.14$. The present partially anisotropic model of 436 variables does not include 2 K and 5 H_2O known to be present from repeated analysis. Whether this is due to disorder in their positions or to other factors is not known at this time. Several residual peaks ranging up to 3 e/\AA^3 remain in the final difference electron density map.

A stereoscopic projection of the complete vanadate ion, made with the program ORTEP, is shown in Figure 1. The crystallographically asymmetric structure is nearly spherical with a prominent S_8 axis of virtual symmetry; the unconstrained ion probably has the point group symmetry D_{4d} . A cavity in the center is 4.5 \AA in free diameter and appears to be fully occupied by a water molecule. The effective outside diameter of the vanadate unit is 13.5 \AA . Unlike most other known polyoxometallate ions, this structure is not based on close packing of oxygens.

Each of the 18 V atoms is coordinated by five oxygens, one of which is unshared. The distances and angles of the coordination figures $V(O)_5$ are very similar to those already familiar in other oxo compounds of the vanadyl moiety, such as the β -diketonates.⁵ The V-O distances of the outer, unshared oxygens range from 1.54 to 1.67 \AA , averaging 1.61 \AA , and those of the equatorial, shared oxygens range from 1.84 to 2.04 \AA , averaging 1.93 \AA (esd 0.03 \AA for all).

None of the V centers exhibits the octahedral oxygen coordination typical of vanadium(III) ($6 \times 2.0 \text{ \AA}$); therefore all of them are believed to be vanadium(IV). Every vanadium(IV) has at least one neighboring vanadium(IV) within 2.95 \AA of itself, the shortest such distance being 2.88 (1) \AA . These proximities suggest the likelihood of intramolecular antiferromagnetic spin coupling; this has been confirmed by susceptibility measurements using the Gouy method at 22 $^\circ\text{C}$. Corrected values of the paramagnetic component of the susceptibility are the same for the sodium salt (9.3×10^{-3} cgs/mol) and the potassium salt (9.9×10^{-3}). The value expected for 18 free spins of moment 1.73 μ_B each would be 22.9×10^{-3} cgs/mol. Correlation of this data with the details of V-V distances indicates that the threshold proximity for spin pairing of vanadium(IV) in an oxide matrix is 2.92 (1) \AA . This estimate agrees with two other known cases to within the stated error.

The coloration of the ion, which is associated with an absorption band rising continuously from 650 nm into the ul-

traviolet, is too intense to be attributed to the d manifolds localized at vanadium(IV) centers and lies at energies too low to promote vanadium(IV) \leftarrow oxygen charge transfer. Since all vanadium does appear, from structural evidence, to be vanadium(IV) in the ground state, it is possible that the spectrum arises from photodisproportionation to states of the type [vanadium(III)-vanadium(V)]*. Disproportionation of vanadium(IV) is known to be driven chemically in sufficiently concentrated hydroxide.⁴

There are several kinds of evidence that neither $V_{10}O_{28}^{6-}$ nor $V_{18}O_{42}^{12-}$ is stable in very dilute solutions, but that smaller species—perhaps monomeric—are the thermodynamically preferred products near 25 $^\circ\text{C}$ at concentrations less than $\sim 10^{-4}$ M for vanadium(V)² or 2×10^{-3} M for vanadium(IV).^{3,4} In the vanadium(IV) system the equilibrium relationship between monomer and oligomer is not known in detail.

Our further study of the ion 18-vanadate(IV) will include a more precise determination of structure, magnetic measurements at low temperatures, and some investigation of the kinetics of its dissociation and oxygen-exchange reactions in water.

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Supplementary Material Available: A listing of atomic positions, thermal parameters, and structure factors (22 pages). Ordering information is given on any current masthead page.

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