A Hexanuclear Oxovanadium(IV) Anionic Aggregate containing μ_2- and μ_6-Carbonato Groups: Synthesis and Structural Characterization of $(NH_4)_5[(VO)_6(CO)_4(OH)_9]\cdot10H_2O$

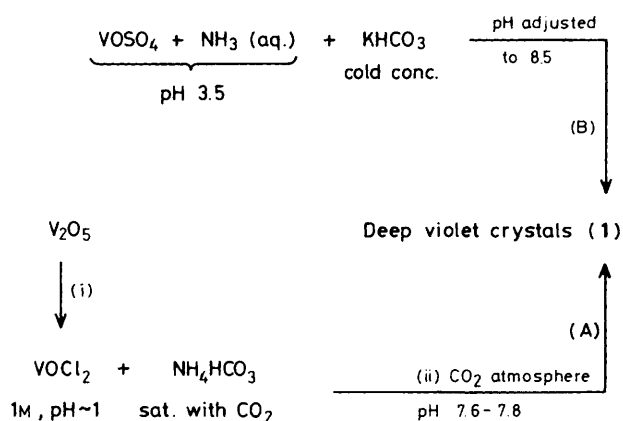**Thomas C. W. Mak,[a]*** **Peng-ju Li,[b]** **Chen-mou Zheng,[b]** and **Kun-yao Huang[b]**

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The reaction of $VOCl_2$ with NH_4HCO_3 under CO_2 afforded the title complex, shown by X-ray crystallography to contain a crown-shaped hexanuclear oxovanadium(IV) anion featuring bridging hydroxo and carbonato groups; the aggregate lies at a site of symmetry m and has approximate $3m$ symmetry, with one carbonato group functioning in a novel μ_6 mode.

Vanadium(IV) oxide, VO_2, is a potentially useful heat-sensitive material as it undergoes a phase transition from a semiconductor to a metallic conductor at 68 °C.[1] A poly-crystalline form of VO_2† exhibiting an abrupt change in electrical resistivity by a factor of about 10^3 at 68 °C has been prepared by low-temperature (350 °C) thermal decomposition and subsequent annealing (414 °C) of an oxovanadium(IV) carbonate complex (1) tentatively formulated as $(NH_4)_2[VO(CO_3)_2]\cdot2VO(OH)_2\cdot6H_2O$.[2] The present paper describes the synthesis of (1) and its structural characterization using spectroscopic and X-ray crystallographic techniques.

Deep violet crystals of (1), synthesized according to Scheme 1(A) in >50% yield, quickly decomposed to a vanadium(v)-containing black mass upon standing in air, but could be preserved for weeks without apparent change under an atmosphere of CO_2. However, elemental analysis results of freshly prepared and preserved samples differed significantly (C 4.53, H 3.96, N 6.62, V 29.7%; C 4.89, H 3.48, N 7.02, V 30.8%; respectively). The electronic spectrum of (1) in 0.6 M NH_4HCO_3 solution showed absorption bands (cm^{-1}, ε in $dm^3\ mol^{-1}\ cm^{-1}$ in parentheses) at 11 960 (22.5), 17 090 (14.4), and 23 640 (8.1), which are attributable to the $^2E \leftarrow$ $^2B_2$, $^2B_1 \leftarrow {}^2B_2$, and $^2A_1 \leftarrow {}^2B_2$ transitions, respectively, of an oxovanadium(IV) complex.[3] The i.r. spectrum (KBr disc) exhibited absorption bands at 3250s,br, 2360w, 1705w,sh, 1641m, 1547s,sh, 1517s,sh, 1410s, 1100m, 1003m,sh, 973s,sh,

948s, 907m,sh, 844m, 686w, 577m,sh, 523s, 447w, and 393w cm^{-1}. With reference to the vibrational frequencies of the carbonate ion in the free[4] and co-ordinated[5—9] states, the i.r. data suggested that the carbonato groups in (1) were involved in at least two different modes of co-ordination. The correct

$$VOSO_4 + NH_3\ (aq.) + KHCO_3 \xrightarrow[\text{to 8.5}]{\text{pH adjusted}}$$

pH 3.5   cold conc.

(B)

V_2O_5 **Deep violet crystals (1)**

(i)   (A)

$VOCl_2 + NH_4HCO_3$ (ii) CO_2 atmosphere

1M, pH~1   sat. with CO_2 pH 7.6—7.8

Scheme 1. (i) To V_2O_5 (10 g) add oxalic acid dihydrate (6.2 g) and a small quantity of water; heat to boiling; gradually add 60 ml conc. $HCl-H_2O$ (1 : 1 v/v) and boil for 20 min; add 2—5 drops of $N_2H_4\cdot H_2O$ to obtain a clear deep blue solution of $VOCl_2$. (ii) Pass CO_2 into 50 ml sat. NH_4HCO_3 for 15 min; under CO_2 atmosphere, add 8 ml $VOCl_2$ (1 M) dropwise and allow solution to crystallize in a stoppered Erlenmeyer flask.

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† For crystalline VO_2, the phase transition at 68 °C is accompanied by an abrupt change in electrical resistivity from 10^{-5} to 1 Ω cm.[1]
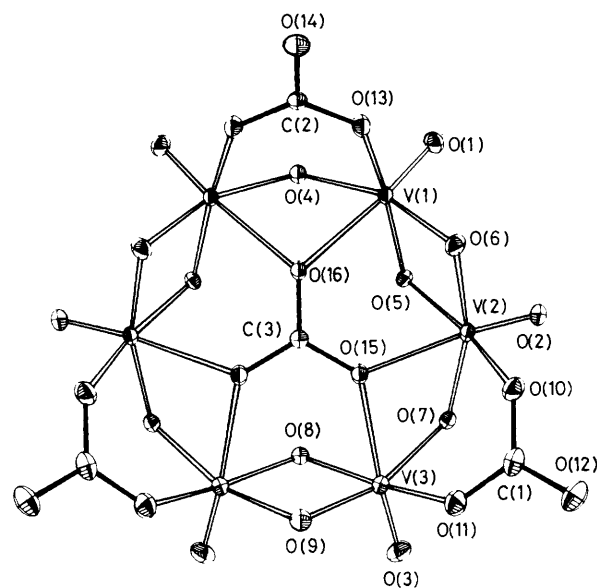
Figure 1. Perspective view of the $[(VO)_6(CO_3)_4(OH)_9]^{5-}$ anion (2) (30% probability ellipsoids). O(1), O(2), and O(3) are vanadyl oxygen atoms. Averaged bond lengths (Å) V=O, 1.616(3); V–O ('*syn*' hydroxo group), 1.956(3); V–O ('*anti*' hydroxo group), 2.012(3); V–O (μ_2-CO$_3$), 2.002(3); V–O (μ_6-CO$_3$), 2.287(3); C–O (μ_2- and μ_6-CO$_3$), 1.291(5); C–O (CO$_3$, *exo*), 1.266(6).

formula $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot10H_2O$‡ was finally established unequivocally by a single-crystal X-ray study.§

The most salient feature in the crystal structure of (1) is the occurrence of the hexanuclear anionic aggregate $[(VO)_6(CO_3)_4(OH)_9]^{5-}$ (2) consolidated by bridging hydroxo and carbonato groups, the latter functioning in an unprecedented μ_6 (3L,6M)¶ mode as well as in the more common μ_2 (2L,2M *syn,syn*)¶ mode (see Figure 1). A crystallographic mirror plane passes through O(14), C(2), O(4), O(16), C(3), O(8), and O(9), and the measured bond lengths and angles are

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‡ Calc. C 4.51, H 4.64, N 6.58, V 28.7%. Agreement with elemental analysis results is only fair, and the stoicheiometry is based on the measured density and X-ray structure determination.

§ *Crystal data* for (1): $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot10H_2O$, $C_4H_{49}N_5O_{37}V_6$, $M = 1065.1$, orthorhombic, space group $Pnam$ (No. 62), $a = 13.273(3)$, $b = 13.504(3)$, $c = 20.142(2)$ Å, $U = 3610(1)$ Å^3, D_m (flotation in CCl$_4$–BrCH$_2$CH$_2$Br) = 1.957, D_c ($Z = 4$) = 1.960 g cm^{-3}, crystal of dimensions $0.32 \times 0.22 \times 0.20$ mm^3 sealed in glass capillary under CO$_2$, Nicolet R3m diffractometer using Mo-K_α (graphite-monochromatized) radiation, $\lambda = 0.71069$ Å, $\mu = 15.64$ cm^{-1}, $T = 295$ K, empirical absorption correction ($\mu r = 0.18$, transmission factors 0.568 to 0.634), 3511 unique reflections ($2\theta_{max} = 54°$), 3056 observed ($|F_o| > 3\sigma|F_o|$). Structure solution was achieved by a combination of direct methods and Fourier techniques. One of the five water molecules in the asymmetric unit exhibited two-fold positional disorder. The non-H atoms were refined anisotropically. All six independent hydroxo H atoms were located, along with fourteen H atoms belonging to the NH$_4$$^+$ and H$_2$O molecules; these were included in structure-factor calculations with assigned isotropic thermal parameters. Refinement for 259 variables converged to $R_F = 0.045$, $R_{wF2} = 0.057$ and $S = 1.413$ with $w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$. Computations were performed on a Data General Nova 3/12 minicomputer using the SHELXTL[10] system. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1, 1986.

¶ The bonding mode is described by the number of donor atoms (L = ligate) that co-ordinate to metal atoms and the number of metal atoms (M = metallic) bonded to the carbonate ion.[11]

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consistent with idealized C_{3v} (3*m*) molecular symmetry. The six metal atoms, each octahedrally co-ordinated, are within ±0.07 Å of their mean plane in a pseudo hexagonal arrangement, with the carbonato groups and '*syn*' hydroxo groups O(6), O(6'), and O(9) lying on one side, and the oxo and remaining six '*anti*' hydroxo groups on the other, such that the whole aggregate (2) takes the shape of an adorned crown. Both independent carbonato groups retain their planarity, and the C–O(*exo*) bonds are significantly shorter than the C–O(bridging) bonds. The metal–oxygen distances in the present complex (see Figure 1 legend) may be compared with those [V=O 1.603(5); V–O(hydroxo) 1.956(5) and 1.969(5) Å] observed for the dinuclear μ-hydroxo-bridged cation in $[(VO)_2(OH)_2(1,4,7\text{-triazacyclononane})_2]Br_2$.[12] It is noteworthy that here a '*syn*' hydroxo group forms much stronger bonds to the vanadium atoms than its '*anti*' partner in the double hydroxo bridge system.

After completion of this work, we noted that Koppel *et al.* had prepared the same compound in 1905 by a different route [Scheme 1(B)] and proposed the stoicheiometry $7VO_2\cdot5CO_2\cdot3(NH_4)_2O\cdot16H_2O$.[13] Recently Labonnette and Taravel revised the formula to $V_{12}O_{28}H_{14}(CO)_8(NH_4)_{10}\cdot23H_2O$,[14] which can be re-written as $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot10\frac{1}{2}H_2O$ to match the present formulation.

The carbonate ion has been known to function as a ligand in the following bonding modes: (1L,1M), (2L,1M), (2L,2M *syn,syn*), (2L,2M *syn,anti*), (3L,2M C_s), (3L,2M C_{2v}), (3L,3M C_{3h}), and (3L,4M).[15] The highest and most symmetric (3L,6M) co-ordination mode is realized in the present example, attesting to the amazing versatility of the seemingly pedestrian carbonate ion in its capacity as a ligand.

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