

# NH<sub>4</sub>V<sub>3</sub>O<sub>8</sub>: a novel sinusoidal layered compound formed by the cation templating effect

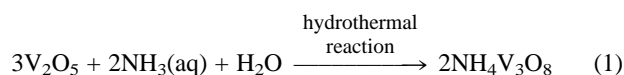
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V<sub>2</sub>O<sub>5</sub> reacts with aqueous NH<sub>3</sub> under hydrothermal conditions to give a novel sinusoidal layered compound NH<sub>4</sub>V<sub>3</sub>O<sub>8</sub>; the structure features weak hydrogen bonds between the V<sub>3</sub>O<sub>8</sub><sup>-</sup> layers and the NH<sub>4</sub><sup>+</sup> cations that occupy the interlayer space.

There has been renewed interest in alkali-metal vanadium oxide bronzes owing to their applications as cathode materials in rechargeable high-energy-density lithium batteries<sup>1</sup> and to their diverse structural chemistry.<sup>2</sup> The common synthetic schemes to produce such compounds include high temperature solid state reactions,<sup>3</sup> redox intercalations<sup>4</sup> or electrochemical methods.<sup>5</sup> Recently, hydrothermal techniques have been demonstrated to facilitate the synthesis and crystal growth of organic-based vanadium oxide bronzes such as α-, β-(H-en)<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub> (en = ethylenediamine)<sup>6</sup> and (DABCOH<sub>2</sub>)V<sub>6</sub>O<sub>14</sub> (DABCO = 1,4-diazabicyclo[2.2.2]octane),<sup>7</sup> to name but a few. To a lesser extent, hydrothermal methods are used in the synthesis of alkali-metal vanadium oxide bronzes.<sup>8</sup> We are interested in the chemistry of metastable layered alkali-metal vanadates that can be used as suitable starting materials for *in situ* hydrothermal intercalation/liquid crystal templating reactions that may produce microporous–mesoporous composite materials.<sup>9</sup> Our entry to this chemistry capitalizes on both the unique chemical properties of V<sub>2</sub>O<sub>5</sub> and the hydrothermal method. Vanadium pentoxide is slightly soluble in water and forms a pale yellow solution containing dispersed V<sub>2</sub>O<sub>5</sub> layers. Such exfoliated layers can react with acids to give the discrete cationic VO<sub>2</sub><sup>+</sup> species as well as react with bases to give a variety of mono-, di- and polyoxometallate anions.<sup>10</sup> By controlling the basicity of the reaction media and by judicious selection of suitable template cations, we have been able to direct the reaction of V<sub>2</sub>O<sub>5</sub> with inorganic bases to form new solid state vanadate compounds rather than discrete isopolyvanadate anions. In this report, we wish to describe the synthesis and structural characterization of a novel layered vanadium oxide compound, NH<sub>4</sub>V<sub>3</sub>O<sub>8</sub> **1**, formed by a mild hydrothermal reaction. Compound **1** is distinct from the many layered compounds in the alkali-metal vanadium oxide family in that it contains highly corrugated layers, and all the vanadium ions in the structure are in the +5 oxidation state.

Pure NH<sub>4</sub>V<sub>3</sub>O<sub>8</sub> can be conveniently prepared from the base-induced polymerization/condensation reaction of V<sub>2</sub>O<sub>5</sub> with aqueous NH<sub>3</sub> under hydrothermal conditions. Thus, when a sealed thick-walled Pyrex tube containing 100 mg (0.55 mmol) V<sub>2</sub>O<sub>5</sub>, 30 mg (0.56 mmol) NH<sub>4</sub>Cl, 0.1 ml (0.37 mmol) 28% aqueous NH<sub>3</sub> and 0.5 ml of a mixed solvent composed of H<sub>2</sub>O–MeOH (1 : 1, v/v) was heated at 110 °C for 4 days, analytically pure orange–brown single crystals of NH<sub>4</sub>V<sub>3</sub>O<sub>8</sub> were obtained in *ca.* 52% yield.‡ It is important to control the molar ratio of V<sub>2</sub>O<sub>5</sub> : NH<sub>3</sub> to *ca.* 3 : 2 as excess NH<sub>3</sub> will lead to the formation of NH<sub>4</sub>VO<sub>3</sub> as a by-product. However, addition of NH<sub>4</sub>Cl to the reaction can increase the yield while suppressing the formation of the by-product. Eqn. (1) is the mass-balanced reaction that describes the formation of **1**:



The structure of **1** was determined by X-ray single crystal analysis.§¶ The asymmetric unit contains one N, three H, two V and five O atoms. Six atoms, including N, H(1), H(2), V(2), O(2) and O(5), are situated on the crystallographic mirror planes perpendicular to the [010] direction. The V<sub>3</sub>O<sub>8</sub><sup>-</sup> layer is formed parallel to the *ab* plane, consisting of highly distorted VO<sub>5</sub> square pyramids around V(1) and VO<sub>6</sub> octahedra around V(2). First, every two square pyramids share a common edge. Such two edge-sharing square pyramid units are then linked with one another to form one-dimensional chains along the *b*-direction. Between these chains reside the VO<sub>6</sub> octahedra which share two edges with two neighboring, edge-sharing square-pyramidal units from one chain and two corners with two different square-pyramidal units from the adjacent chain in an alternating fashion. Fig. 1 shows the interconnection of the VO<sub>5</sub> square pyramids and VO<sub>6</sub> octahedra within one V<sub>3</sub>O<sub>8</sub><sup>-</sup> layer. Five oxygen atoms are engaged in terminal, *i.e.* O(1) and O(2), doubly bridging, *i.e.* O(3) and triply bridging, *i.e.* O(4) and O(5) coordination, respectively. The layers are stacked along the *c*-direction with the NH<sub>4</sub><sup>+</sup> cations occupying the interlayer space. Because of the weak hydrogen bonding between the terminal oxygen atoms in the vanadium oxide layers and the H atoms from the NH<sub>4</sub><sup>+</sup> cations [*i.e.* O(1)–N 3.16 and O(2)–N 2.92 Å], the structure consists of highly corrugated V<sub>3</sub>O<sub>8</sub><sup>-</sup> sheets arranged as if the layers intended to bend over in order to maximize the hydrogen bonding. As a result, each individual layer appears to have the sinusoid shape, shown in Fig. 2, so that two protons from a NH<sub>4</sub><sup>+</sup> cation can each form hydrogen bonds with two terminal O atoms on the same layer. Otherwise, a flat layer can only allow for a single hydrogen bond between the tetrahedral NH<sub>4</sub><sup>+</sup> ion and a terminal O atom from one layer.

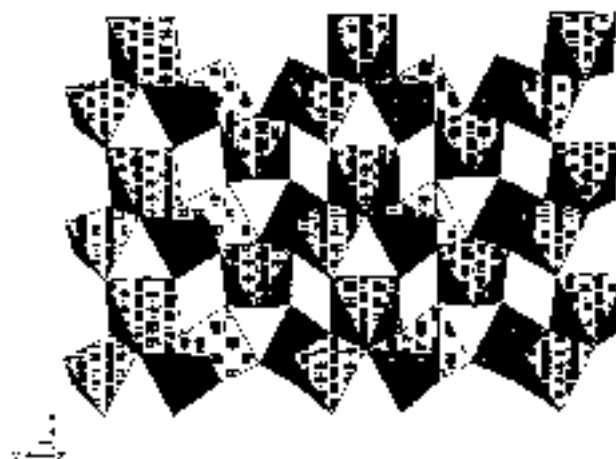


Fig. 1 The structure of one V<sub>3</sub>O<sub>8</sub><sup>-</sup> layer, showing the interconnection of the VO<sub>5</sub> square pyramids and VO<sub>6</sub> octahedra

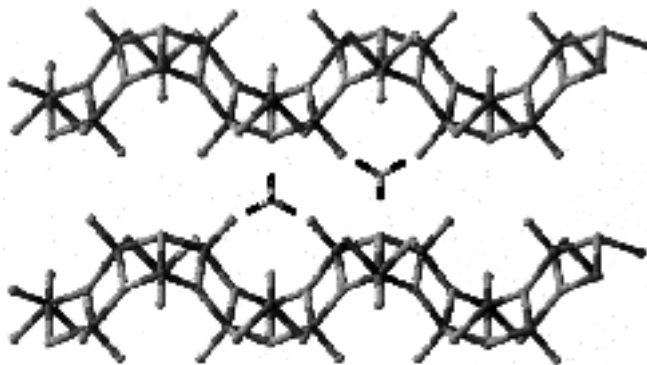


Fig. 2 The structure of layered  $\text{NH}_4\text{V}_3\text{O}_8$ , viewed down the  $a$ -direction

Both vanadium ions are in the +5 formal oxidation state as confirmed by the ESCA study.<sup>||</sup> The V–O bond distances within the layer range from 1.605(4) Å, involving the terminal oxygen atoms, to 2.281(6) Å, involving the triply bridging oxygen atoms.

In conclusion, a novel sinusoidal layered compound  $\text{NH}_4\text{V}_3\text{O}_8$  has been synthesized and structurally characterized. Recently, Whittingham and coworkers showed that  $(\text{NMe}_4)\text{V}_3\text{O}_8$  can be obtained by heating  $(\text{NMe}_4)\text{V}_3\text{O}_7$  in air to ca. 200 °C.<sup>11</sup> However, the structure of  $(\text{NMe}_4)\text{V}_3\text{O}_8$  has remained unknown, and is possibly related to **1**. In the current synthesis, **1** can best be thought of as being formed by reconstructing  $\text{V}_2\text{O}_5$  layers through a base-induced polymerization/condensation reaction in the presence of the  $\text{NH}_4^+$  cation template. To the best of our knowledge, **1** is the first example of a ternary layered vanadium oxide obtained by such a route. This method may open up a new avenue to a potentially large number of novel layered or open-framework materials with the use of other suitable templates.

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## Notes and References

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‡ The product was isolated by water and acetone washing and separated by hand from a small amount of colorless  $\text{NH}_4\text{VO}_3$  (ca. 5–10%) crystals and black  $\text{V}_3\text{O}_{7+\delta}$  (ca. 2%) crystals. The unit cell parameters for  $\text{V}_3\text{O}_{7+\delta}$  are: tetragonal, space group  $P4/mbm$  (no. 127),  $a = 8.9065(6)$ ,  $c = 5.5823(1)$  Å,

$U = 442.82(3)$  Å<sup>3</sup>,  $Z = 2$ . We have not been able to refine the structure satisfactorily because of severe disorder at two oxygen sites.

§ *Crystallographic data for 1*:  $\text{V}_3\text{O}_8\text{H}_4\text{N}$ , monoclinic, space group  $P2_1/m$  (no. 11),  $a = 4.993(7)$ ,  $b = 8.423(1)$ ,  $c = 7.849(1)$  Å,  $\beta = 96.426(3)^\circ$ ,  $U = 328.45(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 3.022$  g cm<sup>-3</sup>,  $\mu = 4.189$  mm<sup>-1</sup>,  $T = 295$  K, structure solution and refinement based on 480 reflections with  $I_o \geq 3.0\sigma(I_o)$  converged at  $R = 0.036$ ,  $R_w = 0.044$  and goodness-of-fit = 1.15. Data were collected on a Siemens SMART diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction based on simulated  $\psi$ -scans was applied to the data set. All hydrogen atoms were located from the difference Fourier maps, and were included in the structure but not refined. Further details of the crystal structure investigations of **1** are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-407899. CCDC 182/829.

¶ The phase identity and homogeneity of **1** were confirmed by comparing the experimental X-ray powder diffraction patterns of the bulk material with those calculated from the single crystal X-ray data.

|| Electron spectroscopy chemical analysis (ESCA) gave two overlapping peaks for  $\text{V}2p_{3/2}$  at 515.37 and 516.68 eV, which is consistent with  $\text{V}^{5+}$  ions in two different coordination environments. In addition, the binding energies for O 1s are 533.77, 531.95 and 530.21 eV, confirming three different bonding modes of the oxygen atoms in  $\text{NH}_4\text{V}_3\text{O}_8$ .

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