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Electrochemical–hydrothermal synthesis and structure of $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$

Xiqu Wang,[a] Lumei Liu,[a] Allan J. Jacobson*[a] and Kent Ross[b]

[a]*Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA. E-mail: ajjacob@uh.edu*
[b]*Texas Center for Superconductivity at the University of Houston, Houston, TX 77204, USA*

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Electrochemical oxidation of a vanadium electrode under hydrothermal conditions in the presence of tetramethylammonium and cobalt ions gives the novel compound $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$.

Open framework structures containing both transition metal and main group elements, for example, vanadium phosphates, have been synthesized hydrothermally by using organic templates.[1–5] Recently, similar hydrothermal synthetic techniques have been used to prepare several vanadium oxides with layered structures.[6–20] These materials have potential applications as heterogeneous oxidation catalysts and as cathodes in secondary lithium batteries. In the vanadium oxide layer structures, templates with different size, charge and hydrogen bonding characteristics are accommodated in the interlayer space by changes in the average vanadium oxidation state, the layer area per vanadium atom, which depends on the degree of condensation (edge, corner or face-sharing) and the relative numbers of vanadium oxygen atom square pyramids (or distorted octahedra) and tetrahedra. Variations in the relative orientations of different polyhedra can lead to changes in the curvature of the vanadium oxygen atom layers providing an additional mechanism to optimize the packing interactions of interlayer templates with different sizes and charge distributions between the layers. For example, the V_3O_7 layers in $[N(CH_3)_4]_2V_6O_{14}$[9] are flattened while those in $(C_6H_{14}N_2)V_6O_{14}\cdot H_2O$[13,14] are highly puckered due to differences in orientations of the VO_4 tetrahedra. The organic templates used in some synthesis reactions, such as in the syntheses of $[(en)_2Cu][V_6O_{14}]$ and $[(en)_2Cu]_2[V_{10}O_{25}]$, result in additional modifications to the layer topology through the formation of interlayer coordination complexes[21] with the ethylenediamine ligands and oxygen atoms in the layers.[15]

Recently, electrocrystallization under hydrothermal conditions has been used successfully for the synthesis of thin films of, for example, $BaTiO_3$,[22] $BaMoO_4$,[23] $LiNiO_2$[24] and $LiCoO_2$.[25] We are investigating the adaptation of this approach to the exploratory synthesis of new phases and for the growth of single crystals. We have reported previously the new barium vanadate $BaV_7O_{16}\cdot nH_2O$[26] and $Zn_2(OH)VO_4$[27] synthesized using this method in the absence of any organic template. Here we report the novel compound $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$ **1** synthesized by hydrothermal electrocrystallization with tetramethylammonium (TMA) as a templating cation.

The synthesis of compound **1** was performed using a Teflon-lined autoclave (inner volume, 100 ml) fitted with feedthroughs for electrical connections between the electrodes inside the reaction chamber and the external circuit. In a typical experiment, 60 mg $CoCO_3$ was dissolved in 50 ml diluted nitric acid solution. 100 mg $N(CH_3)_4OH\cdot 5H_2O$ was then dissolved in this solution and the pH was adjusted to 1.99 with acetic acid. The solution was sealed in the autoclave in air. The anode (working electrode) was a vanadium metal plate (20 × 10 × 0.254 mm). A gold foil was used as cathode (counter electrode). The experiment was conducted with current densities of ≈1 mA generated by using a commercial power source (MacPile, Biologic Scientific Instruments) at 170 ± 2 °C for 90 hours. A sheet of black needles of compound **1** was formed on the vanadium electrode that was covered by a sheet of pale brown lamellae of an unidentified phase. Composition analysis of compound **1** with a JEOL JXA-8600 electron microprobe analysis gave the atomic ratio of $Co:V = 0.95:12$ that is consistent with the title formula derived from the structure refinements. The infrared spectrum measured with a Galaxy FTIR5000 spectrometer showed peaks corresponding to H_2O and TMA at 3391, m; 3256, s; 3180, m; 1614, w; 1481, m; 1413, w cm^{-1}. Other absorption bands were observed at 1103, w; 988, m; 877, s; 772, s; 665, vs; 567, s; 515, w cm^{-1}.

Single crystal X-ray diffraction† revealed that compound **1** crystallized in the triclinic system with unit cell dimensions: $a = 6.6510(1)$ Å, $b = 10.749(1)$ Å, $c = 13.402(1)$ Å, $\alpha = 83.003(2)^\circ$, $\beta = 85.739(2)^\circ$, and $\gamma = 83.971(2)^\circ$. The crystal structure of **1** contains vanadium oxide layers that are cross-linked by CoO_6 octahedra into a framework. The voids in the framework are filled by $N(CH_3)_4$ cations (Fig. 1(a)). Four of the six vanadium sites have square pyramidal coordination by oxygen atoms while the other two are tetrahedrally coordinated. The shortest V–O bond lengths, corresponding to an apical V=O bond in the square pyramids or tetrahedra range

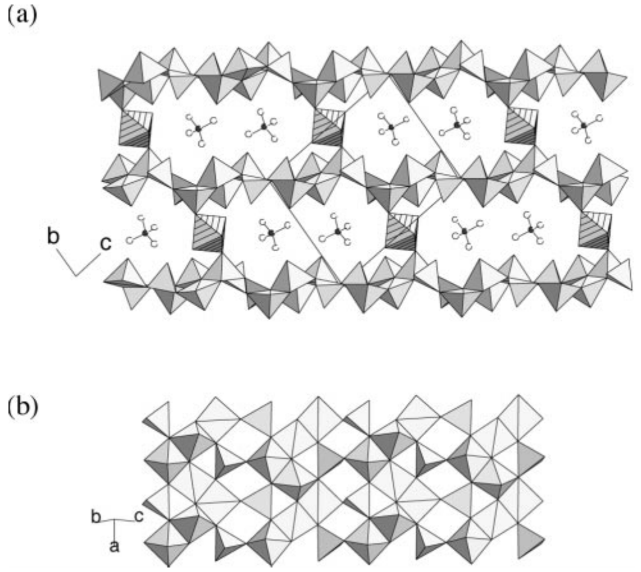

Fig. 1 (a) The structure of $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$ viewed along the *a* axis, CoO_6 octahedra are hatched. (b) A V_3O_7 layer of $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$ viewed perpendicular to the (011) plane.

from 1.591 to 1.619 Å. Other V–O bond lengths are between 1.687 and 1.816 Å in the tetrahedra, and between 1.881 and 2.036 Å in the square pyramids. Bond valence sums (BVS)[28] calculated for the square pyramidal sites range from 4.09 to 4.20 valence units (v.u.) and for the tetrahedral sites are in the range 5.05–5.08 v.u. The VO_5 square pyramids form zigzag chains parallel to [100] by sharing square edges. The apical bonds have an alternating two-up two-down orientation as shown schematically in Fig. 2. The zigzag chains are interconnected by the VO_4 tetrahedra through sharing oxygen atoms into layers parallel to the (011) plane (Fig. 1(b)). Neighboring layers are interconnected by the Co^{2+} cations (BVS = 2.107 v.u.) that have octahedral coordination with four bonds (2.044–2.063 Å) to the interlayer water oxygen atoms forming a square and two apical bonds (2.137 Å) to the V=O oxygen atoms of the VO_5 pyramids. This interconnectedness outlines a [100] channel system with a dumbbell-shaped cross section, the aperture of which is *ca.* 2.7 Å at both dumbbell-ends. The TMA cations are located within the channels (Fig. 1(a)).

The $V_{12}O_{28}$ layers in **1** are closely related to those found in the structures of $[N(CH_3)_4]V_3O_7$,[9] $(C_6H_{14}N_2)V_6O_{14}\cdot H_2O$,[13,14] $[(en)_2M]V_6O_{14}$, M = Cu, Zn[15] and $[NH_3CH_3]V_3O_7$.[17,18] The layers in all of these compounds contain the same type of zigzag pyramidal chains described above. However, the chains are interconnected by the VO_4 tetrahedra in different ways as discussed by Chen *et al.* in ref. 17. As shown in Fig. 2, chain B can be oriented relative to chain A so that the pyramids with apical V=O bonds point up in either of the four positions: (i) 12, (ii) 23, (iii) 34 or (iv) 41. Orientation (i) corresponds to the layers in $[N(CH_3)_4]V_3O_7$ and $(C_6H_{14}N_2)V_6O_{14}\cdot H_2O$ while orientation (iv) corresponds to the layers in $[(en)_2Cu][V_6O_{14}]$, $[NH_3CH_3]V_3O_7$ and the title compound. In the cases of orientations (ii) and (iii) the V=O groups are slightly more crowded and no examples of these or hybrid orientations have been reported to our knowledge. Each of the VO_4 tetrahedra links the zigzag chains though connection with three oxygen atoms. The fourth V=O oxygen atom is not bonded to other V atoms. The orientation of the tetrahedra relative to the zigzag chains has a strong influence on the curvature of the layers. In the structures of $[N(CH_3)_4]V_3O_7$ and $[(en)_2M][V_6O_{14}]$, M = Cu, Zn, the V=O bonds of the tetrahedra are roughly parallel to the apical V = O bonds of the square pyramids of the zigzag chains, and thus the layers are flattened. In the case of $(C_6H_{14}N_2)V_6O_{14}\cdot H_2O$ and $[NH_3CH_3]V_3O_7$ the V=O bonds of the tetrahedra are roughly parallel to the square faces of the pyramids and, therefore, the layers are strongly puckered.

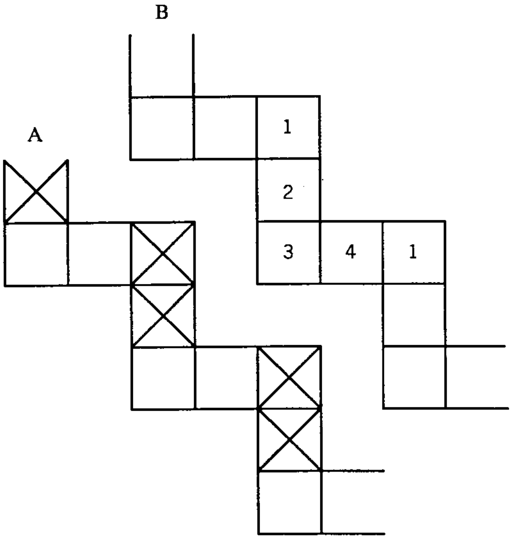

Fig. 2 Relative orientations of two neighboring VO_5 pyramids chains of; see text.

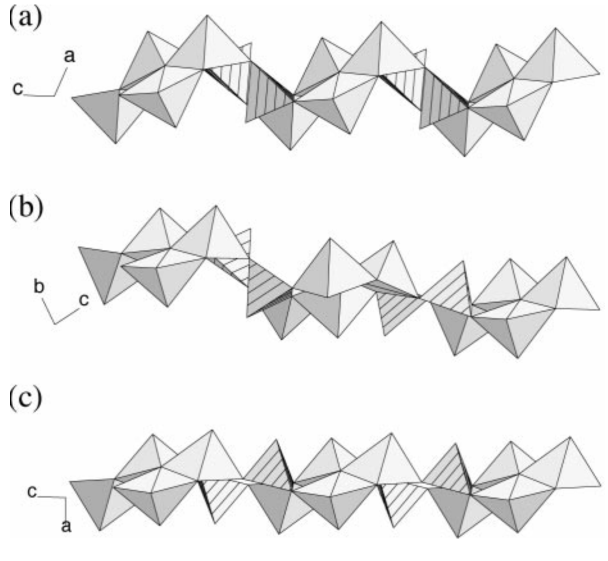

Fig. 3 Side view of the V_3O_7 layers showing the different layer curvatures caused by different orientations of the VO_4 tetrahedra relative to the VO_5 square pyramids. The tetrahedra are shown hatched. (a) $(C_6H_{14}N_2)V_6O_{14}\cdot H_2O$, (b) $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$, (c) $[N(CH_3)_4]V_3O_7$.

In **1**, the Co^{2+} cations are bonded to the V=O oxygen atoms of the VO_5 pyramids in contrast to the $[(en)_2M][V_6O_{14}]$ (M = Cu, Zn) structures where the interlayer M^{2+} cations are bonded to the V=O oxygen atoms of the VO_4 tetrahedra. The linkage between the layers by the interlayer metal cations in **1** (Co–O distance 2.137 Å) is also much stronger than that in the $[(en)_2M][V_6O_{14}]$ compounds (Cu–O, 2.53 Å; Zn–O, 2.45 Å). The structure of **1** differs from any of the previous examples in that both possible orientations of the tetrahedra are present in each layer (Fig. 3). The presence of both tetrahedral orientations arises from a combination of the puckering caused by the cross-linking Co–O bonds between adjacent layers and the flat regions that are required to accommodate the TMA^+ cations in the channels between the layers (Fig. 1(a)).

In summary, crystals of the new compound $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$ have been synthesized by using the electrochemical–hydrothermal method. The $[Co(H_2O)_4V_{12}O_{28}]$ framework contains vanadium oxide layers that represent a new variant of the V_3O_7 layers found in other known compounds. Experimental work is currently in progress to examine the possibility of forming similar compounds with layer-linking cations other than cobalt.

Acknowledgments

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Notes and references

†*Crystallographic data.* Formula: $C_8N_2H_{32}O_{32}CoV_{12}$, M 1338.56. Crystal system: triclinic, space group: $P\bar{1}$. $\mu = 3.348\ mm^{-1}$. $R(F) = 0.0668$, $wR(F^2) = 0.1419$. Unit cell dimensions: $a = 6.6510(1)$, $b = 10.749(1)$, $c = 13.402(1)$ Å, $\alpha = 83.003(2)$, $\beta = 85.739(2)$, $\gamma = 83.971(2)°$. Unit cell volume: 943.9(2) Å^3. $Z = 1$. Temperature of data collection: 293(2) K. Measured reflections: 5593, independent reflections: 3894,

$R(\text{int}) = 0.0440$. Intensities were measured on a SMART platform diffractometer with a 1K CCD detector using Mo-Kα radiation. The structure was solved by direct methods and refined using SHELXTL. CCDC reference number 1145/143.

See http://www.rsc.org/suppdata/jm/1999/859 for crystallographic files in .cif format.

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