# Novel Tungsten, Molybdenum, and Vanadium Oxides Containing Surfactant Ions

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Hydrothermal reaction of tungstic acid, molybdic acid, and vanadium pentoxide with the surfactant template dodecyltrimethylammonium bromide (DTABr) yielded one compound with a Keggin type structure, $[C_{12}H_{25}N(CH_3)_3]_6(H_2W_{12}O_{40})\cdot xH_2O$, and two new layered compounds, $[C_{12}H_{25}N(CH_3)_3]_{0.5}(MoO_{3.25})$ and $[C_{12}H_{25}N(CH_3)_3]_{2/3}V_2O_{5.33}\cdot H_2O$. The tungsten salt produced needlelike crystals of a hexagonal shape while the molybdenum and vanadium salts formed layered structures. FTIR analysis of the tungsten salt was consistent with materials containing Keggin anions. The X-ray powder diffraction data of this material were indexed to a monoclinic cell with $a = 50.56(4)$ Å, $b = 54.41(4)$ Å, $c = 13.12(1)$ Å, and $\beta = 99.21°$. The observed reflections are consistent with space group $C2/m$. Diffraction data obtained from the molybdenum salt showed a between layer d spacing of ca. 22 Å. The vanadium salt was indexed to a triclinic cell with $a = 9.813(3)$ Å, $b = 11.512(3)$ Å, $c = 21.725(5)$ Å, $\alpha = 95.30(1)°$, $\beta = 93.82(6)°$, and $\gamma = 101.12(8)°$, with a layer spacing of 21.6 Å.

## Introduction

An important breakthrough in molecular sieve chemistry was made in 1992 when the synthesis of a new class of molecular sieves, exemplified by MCM-41, was reported by the Mobil group.[1,2] Pore sizes of these mesoporous materials can be engineered to be from 15 Å to greater than 100 Å by using long-chain quarternary ammonium salts, $CH_3(CH_2)_nN(CH_3)_3$ for $9 \le n \le 18$, as the template in the reaction. At the reaction temperature, 100 °C, these molecules aggregate into micelles and it is these micelles that are structure directing. The presence of these liquid-crystal templates is necessary for the formation of MCM-41 type mesoporous materials.[3] At higher temperatures or for $n \le 6$, individual molecules act as the templating agent and more dense microporous materials are formed, such as ZSM-5.

Reis et al.,[4−6] following Günter et al.[7] showed that it is possible to hydrothermally synthesize transition-metal oxides; in their cases hexagonal and pyrochlore tunnel structure tungsten oxides. The discovery of the above mesoporous materials caused the investigation of whether similar large-pore transition-metal oxides could also be synthesized.[8−10] Both hexagonal and layer structures were formed for W, Mo, and V. However, a detailed study of the tungsten compound showed that "despite the superficial similarity of TEM micrographs and powder X-ray patterns of this material to those of mesoporous silicates, the salt contains unconnected Keggin ions $H_2W_{12}O_{40}{}^{6-}$".[10] Attempts to remove the templating ions result in the formation of metal oxides. Stein et al.[10] also showed that when $Nb_xW_{6-x}O_{19}{}^{(2+x)-}$ clusters are formed they can be connected through Nb−O−Si linkages by reaction with tetraethyl orthosilicate.

In recent work, we have found that a number of inorganic transition-metal anions react with cationic surfactant species to form open-channeled structures. Some of the studied transition metals include oxides of vanadium, molybdenum. and tungsten.[11] The salts formed on reaction of molybdenum and vanadium oxides were often found to have platelike structures, while several of the tungsten oxide products were found to have needle like crystal shapes made up of monoclinic cells of Keggin clusters.[12]

In this paper, we report the syntheses and characterization of Keggin cluster tungsten oxide based crystals as well as molybdenum and vanadium layered materials using the surfactant template dodecyltrimethylammonium bromide (DTABr). Analyses and structural determinations are discussed. If the organic surfactant can be removed, then a mesoporous solid might be formed that would allow ionic movement through the now open channels, permitting redox reactions and electrochemical activity.

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## Experimental Section

All syntheses for the materials discussed here are via mild hydrothermal methods.[13] Such techniques have been used extensively in zeolite synthesis[14] and also in more recent work on vanadium and molybdenum phosphates.[15−17] In current work by our group, we have reported on the formation of transition metal oxides, where the oxide is reacted together with an aqueous solution of the desired cationic species, the pH of the resultant solution is adjusted as necessary, and the entire reaction mixture is heated in a Parr reaction vessel at 100−200 °C.[11] As reported previously, pH and temperature are crucial in determining the formation of phase and structure.

**Synthesis of $[C_{12}H_{25}N(CH_3)_3]_6(H_2W_{12}O_{40})\cdot xH_2O$.** The tungsten/DTA structures were synthesized by dissolving dodecyltrimethylammonium bromide in distilled water to make a 30% by weight solution and then adding $H_2WO_4$ to make a 1:1 molar ratio of $WO_3$ to cationic surfactant. The pH was then adjusted from an initial value of 2.3 to 7.6 with sodium hydroxide. The pH adjusted solution was then allowed to react in a covered beaker at room temperature for 3−5 days. During this time period the growth of liquid crystals could be observed. After the liquid crystal formation step the contents of the covered beaker (minus any remaining unreacted $H_2WO_4$) was placed in a Parr bomb and reacted for an additional 72 h at 100 °C. After removal from the bomb, the pH was found to be just over 7 in most cases. Samples were then filtered, washed with distilled water, and air-dried in an oven at 40 °C. Other surfactant-to-metal ratios were also tried, but none yielded a product as crystalline as the 1:1 molar ratio. More dilute starting solutions (10% and 20% by weight of surfactant in solution) yielded the same product as the 30% by weight solution.

**Synthesis of $[C_{12}H_{25}N(CH_3)_3]_{0.5}(MoO_{3.25})$.** In this synthesis, starting materials of either $Na_2MoO_4$ or $H_2MoO_4$ and dodecyltrimethylammonium bromide were mixed in a molar ratio of 1:2 Mo/DTABr in aqueous solution. The gellike solution that resulted at this stage had an initial pH of 6.6 and was acidified with 1 M HCl. The synthesis was attempted at varying pH values and was found to be independent of pH in the range 2.6−6.6. The solution was placed in a Parr bomb and reacted at 155 °C for 2−4 days. The resulting crystals were platelike and yielded powder patterns characteristic of layered materials.[9]

**Synthesis of $[C_{12}H_{25}N(CH_3)_3]_{2/3}\ V_2O_{5.33}\cdot H_2O$.** The $V_2O_5$ starting material was added to 10 or 20% solutions of DTABr in a 1:2 $V_2O_5$/DTA ratio. Initial solution pH's ranged from 2.8 to 2.9 and were adjusted to between pH 6 and 8 with 5 M NaOH. Clumping of the $V_2O_5$ was observed as the pH was raised above 5.5. This clumping was followed by the formation of flat crystals on the surface of the clumps. This mixture was reacted hydrothermally in Parr bombs at temperatures ranging from 85 to 162 °C for 4 days. A light brown gel was produced during the hydrothermal synthesis, which showed only a few broad diffraction lines. The supernatant liquid from this reaction was decanted and over a period of days to weeks layered products crystallized. Crystals ranged from about 1 × 1 to over 5 × 5 mm in size.

**Cation Exchange.** An attempt was made to exchange the cationic surfactant template of the tungsten/surfactant compound with $Na^+$. An ethanol−water mixture saturated with NaCl was made and allowed to react with the tungsten salt. After a week in a covered beaker, the solution and salt was boiled until supersaturation occurred. The product was filtered and washed with large amounts of distilled water to remove all NaCl. X-ray diffraction data showed no difference between the product before and after the reaction.

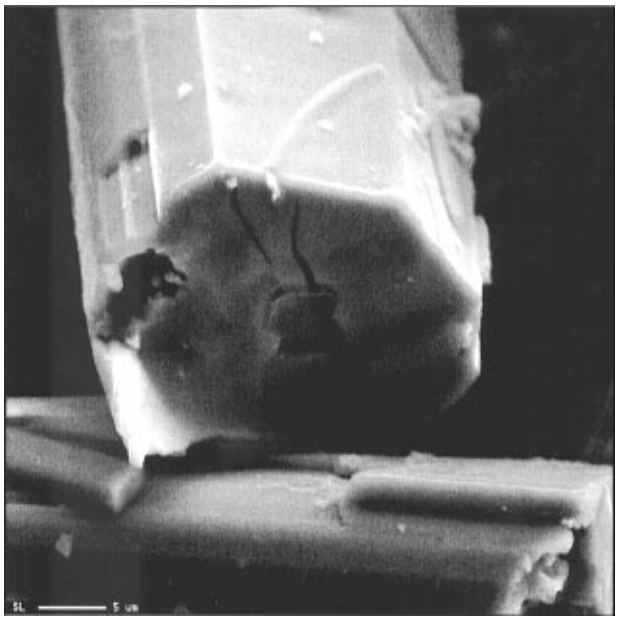

**Figure 1.** Electron micrograph of the hexagonal-shaped cross section of the rodlike crystals of the tungsten compound

**Product Characterization.** Water and surfactant content of the samples were determined using a Perkin-Elmer TGA 7 thermogravimetric analyzer at 5 °C/min in an oxygen or nitrogen environment. In the case of the vanadium compound, the decomposition reaction around 300 °C in oxygen was almost explosive, so very small samples were used. Electron micrographs and chemical analysis was obtained on a JEOL 2000 electron microprobe. Fourier transform infrared spectra were collected on a Perkin-Elmer 2000 FTIR, using KBr pellets. Density measurements were determined by gas displacement or by flotation in chloroform solutions. X-ray powder diffraction measurements were made on a Scintag XDS 2000 powder diffractometer using Cu Kα radiation. Further pattern refinement was done using CSD software.[18] Preliminary single-crystal data on the vanadium oxide samples was collected at room temperature on a four-circle diffractometer Siemens P4 (Ames Lab, Iowa State University) using graphite-monochromatized Mo Kα radiation.

## Results and Discussion

**Tungsten Keggin Cluster/Surfactant.** Figure 1 shows an electron micrograph of the hexagonal-shaped cross section of the needlelike crystals of the tungsten compound. Figure 2 shows the FTIR spectrum collected on a sample of this material. The absorption bands that can be seen at 929.2, 879.6, and 773.6 $cm^{-1}$, are characteristic of the Keggin W−O stretching vibrations[19] and therefore suggest the presence of the $W_{12}O_{40}^{8-}$ ion. Since electron microprobe elemental analysis showed that there was no bromine remaining in this compound, it was possible to determine the surfactant/Keggin cluster ratio from the thermogram shown in Figure 3. The first weight loss is attributed to $H_2O$, the second to loss of the surfactant (DTA), and the remaining weight was assigned to the inorganic residue, confirmed by X-ray analysis to be tungsten trioxide. Calculations indicate 6 DTA chains per Keggin cluster

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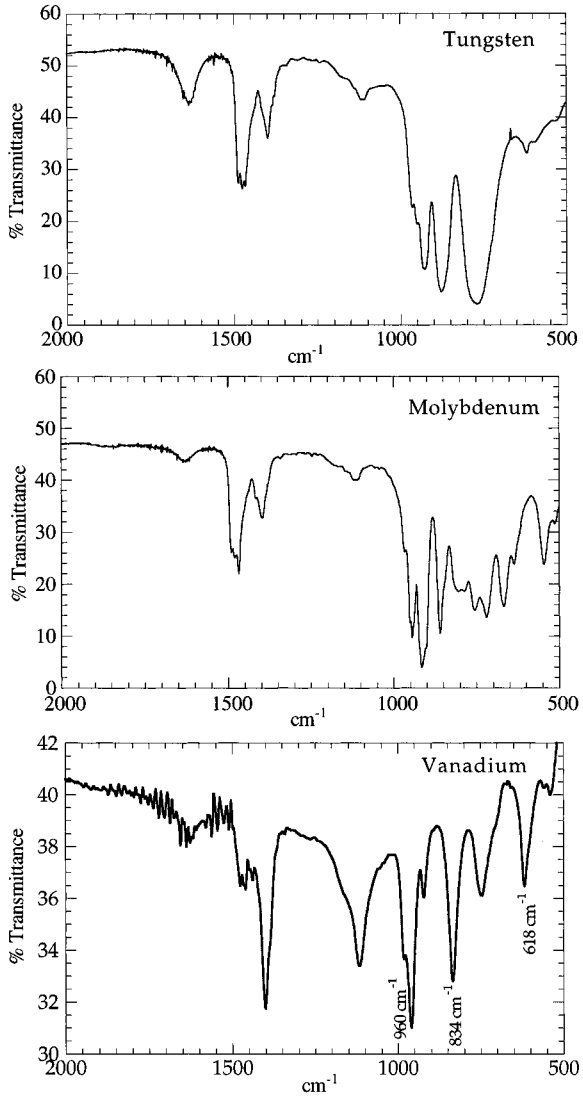


**Figure 2.** FTIR spectra of $C_{12}H_{25}N(CH_3)_3$ tungsten, molybdenum, and vanadium oxide compounds.

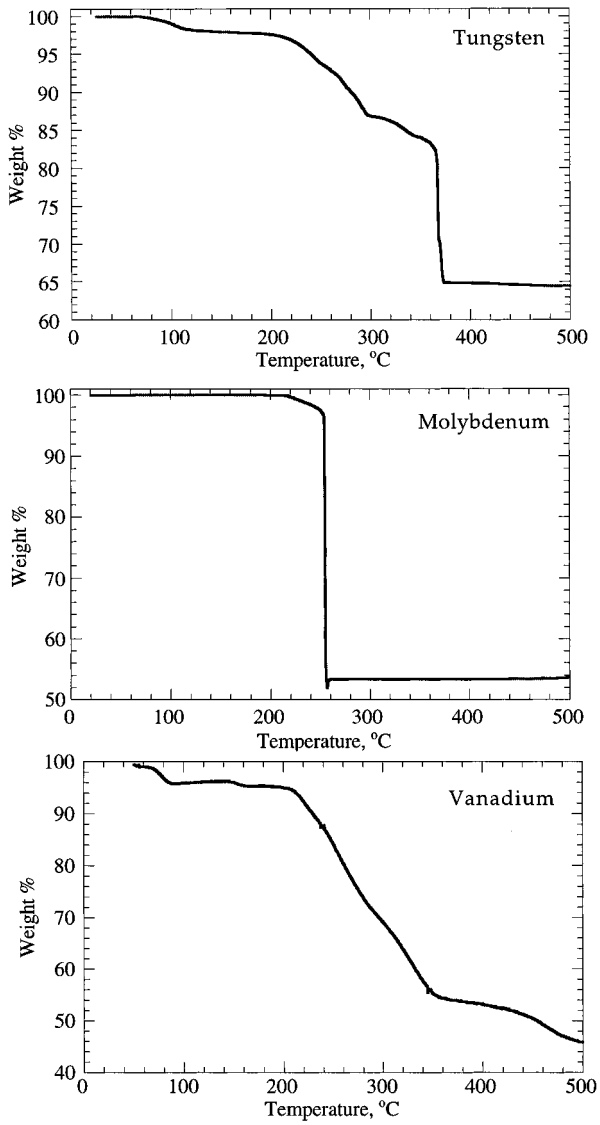


**Figure 3.** TGA curves of $C_{12}H_{25}N(CH_3)_3$ tungsten, molybdenum, and vanadium oxide compounds.

and 4.6 $H_2O$ per $(DTA)_6(H_2W_{12}O_{40})$ unit. Indexing of the X-ray powder pattern (Figure 4) using the ITO method[20] indicates a monoclinic cell with dimensions $a$ = 50.56(4) Å, $b$ = 54.10(4) Å, $c$ = 13.21(1) Å, and $\beta$ = 99.21(2)°. A space group of $C2/m$ was assigned, based on the systematic absences observed. Table 1 shows the X-ray data for the Keggin/DTA sample, and $\Delta 2\theta_{obs-calc}$ is around 0.01° indicating the overall correctness of the indexing. Density via gas displacement was measured as 2.3 g/cm$^3$, which compares well with the value of 2.4 g/cm$^3$ calculated from the lattice parameters and chemical composition. Stein et al.[10] synthesized a Keggin complex using cetyltrimethylammonium bromide as the surfactant. Their measured density was 2.0 g/cm$^3$, with cell dimensions of $a$ = 47.5 Å, $b$ = 30.3 Å, $c$ = 43.6 Å, and $\beta$ = 118° determined from their X-ray powder pattern. The density found for the $C_{12}$-surfactant/Keggin species agrees well with that found by Stein for their $C_{16}$-surfactant/Keggin species, though the cell dimensions of the monoclinic cells for each material are quite different. This is likely due to the chain length and arrangement of the surfactant molecules. The Keggin clusters must be nearly touching in the $c$ direction, as Keggin ions have diameters of around 10−11 Å;[21] they are probably held together by water molecules (hydrogen bonding). Each of these 12 Keggin clusters per unit cell is then surrounded by dodecyltrimethylammonium surfactant chains.

**Lamellar Molybdenum/Surfactant.** The electron micrograph shown in Figure 5 shows the lamellar structure of the molybdenum oxide/DTA product. This flake like micro crystal's layered topology is further evident in the XRD powder pattern in Figure 4, which shows strong preferred orientation along the 001 plane. This sample was prepared as a wet pressed pellet. The $d$ spacing between layers was calculated to be 22.9 Å. Electron diffraction measurements indicated a hexagonal cell with $a$ = 4.76 Å. As with the tungsten compound, qualitative WDS analysis of the molybdenum/DTA sample ruled out the presence of Cl, Br, and Na. TGA data shown in Figure 3 show a single step weight loss, which is the decomposition of the DTA ion leaving pure $MoO_3$, which was verified by X-ray powder analysis on the residual material. Additional weight losses at

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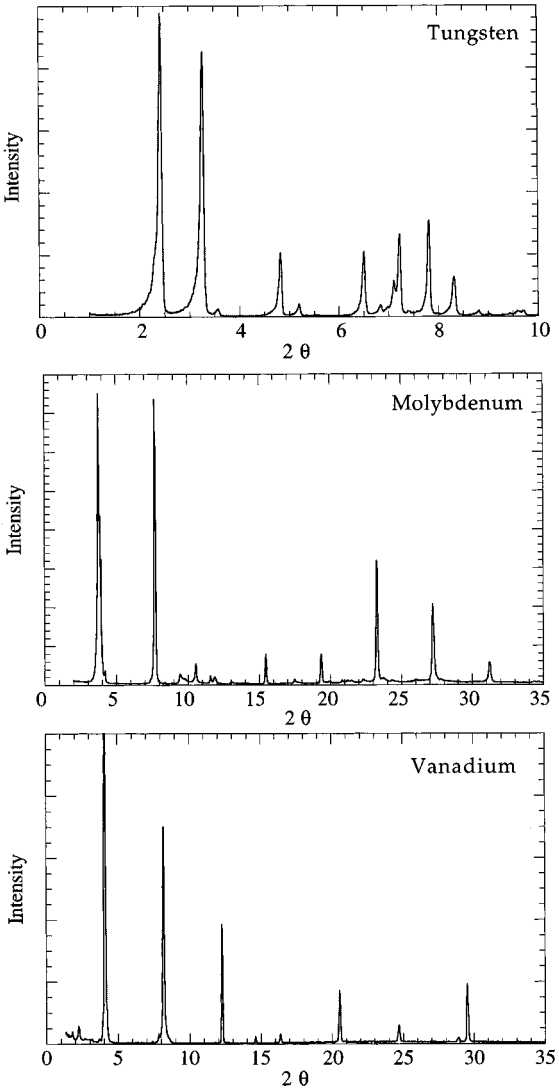


**Figure 4.** X-ray powder patterns of $C_{12}H_{25}N(CH_3)_3$ tungsten, molybdenum, and vanadium oxide compounds.

>650 °C is due to the sublimation of the remaining $MoO_3$ phase. The TGA data leads to the formula $[C_{12}H_{25}N(CH_3)_3]_{0.5}(MoO_{3.25})$. It is of interest to note that it was not possible to remove the surfactant template with anhydrous HCl in diethyl ether and that the entire sample dissolved completely forming a clear yellow solution. Additionally, it was not possible to swell the surfactant portion of the material with mesitylene (known to swell the surfactant micelles in many other similar materials). This may be due to limited accessibility of the surfactant cells between the inorganic oxide layers to the solvent.

**Layered Vanadium Oxide/Surfactant.** The large platelike crystals of this material can be seen in Figure 6. Crystals of the vanadium compound were grown that were nearly a centimeter in length. Crystal thicknesses are on the order of 0.25−0.5 mm. Crystals obtained from the gel prior to hydrothermal reaction were much smaller than those that precipitated from the supernatant liquids after the hydrothermal reactions. The samples recovered from these room temperature syntheses were almost paste or wax like in appearance. These crystals are orange, similar to that of $V_2O_5$ itself indicating that the vanadium is fully oxidized.

The TGA data of Figure 3 are consistent with one surfactant group per 3 vanadium and with the empirical formula $[C_{12}H_{25}N(CH_3)_3]_{2/3}V_2O_{5.33}\cdot H_2O$, which requires a weight loss of 57% compared with the observed one of 54%. The final product of the TGA was predominantly $V_2O_5$ with some $V_2O_3$.

**Table 1. X-ray Data of Keggin Sample**

| *h* | k | l | *I*(obs) | *d*(obs) | *d*(calc) | 2*θ*(obs) | Δ2*θ* |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 862 | 36.64 | 36.81 | 2.409 | 0.011 |
| 0 | 2 | 0 | 1000 | 27.16 | 27.22 | 3.250 | 0.006 |
| 2 | 0 | 0 | 14 | 24.92 | 24.99 | 3.542 | 0.009 |
| 2 | 2 | 0 | 330 | 18.40 | 18.41 | 4.799 | 0.002 |
| 1 | 3 | 0 | 57 | 17.05 | 17.06 | 5.180 | 0.003 |
| 3 | 1 | 0 | 5 | 15.91 | 15.93 | 5.551 | 0.008 |
| 0 | 4 | 0 | 299 | 13.618 | 13.608 | 6.485 | −0.005 |
| 0 | 0 | 1 | 73 | 12.957 | 12.956 | 6.816 | −0.001 |
| 1 | 1 | −1 | 35 | 12.713 | 12.697 | 6.947 | −0.009 |
| 4 | 0 | 0 | 156 | 12.478 | 12.496 | 7.078 | 0.010 |
| 3 | 3 | 0 | 390 | 12.272 | 12.272 | 7.197 | 0.000 |
| 2 | 4 | 0 | 16 | 11.939 | 11.951 | 7.398 | 0.007 |
| 0 | 2 | 1 | 19 | 11.718 | 11.698 | 7.538 | −0.013 |
| 4 | 2 | 0 | 450 | 11.348 | 11.356 | 7.784 | 0.005 |
| 2 | 0 | 1 | 19 | 10.823 | 10.819 | 8.162 | −0.004 |
| 1 | 5 | 0 | 241 | 10.646 | 10.637 | 8.298 | −0.007 |
| 2 | 2 | 1 | 45 | 10.050 | 10.054 | 8.791 | 0.003 |
| 5 | 1 | 0 | 11 | 9.8294 | 9.8321 | 8.989 | 0.002 |
| 3 | 3 | −1 | 4 | 9.4933 | 9.4831 | 9.308 | −0.010 |
| 0 | 4 | 1 | 15 | 9.3826 | 9.3834 | 9.418 | 0.001 |
| 4 | 2 | −1 | 36 | 9.2301 | 9.2285 | 9.574 | −0.002 |
| 3 | 5 | 0 | 28 | 9.1227 | 9.1136 | 9.687 | −0.010 |
| 5 | 3 | 0 | 16 | 8.7506 | 8.7556 | 10.100 | 0.006 |
| 2 | 6 | 0 | 5 | 8.5315 | 8.5277 | 10.360 | −0.005 |
| 3 | 3 | 1 | 13 | 8.4229 | 8.4290 | 10.494 | 0.007 |
| 1 | 5 | −1 | 17 | 8.3578 | 8.3617 | 10.576 | 0.005 |
| 4 | 0 | 1 | | | 8.3531 | | −0.006 |
| 6 | 0 | 0 | 5 | 8.2890 | 8.3303 | 10.664 | 0.053 |
| 1 | 5 | 1 | 1 | 8.0805 | 8.0878 | 10.940 | 0.010 |
| 4 | 2 | 1 | 2 | 7.9737 | 7.9854 | 11.087 | 0.016 |
| 4 | 4 | −1 | | | 7.9576 | | −0.023 |
| 6 | 2 | 0 | | | 7.9656 | | −0.011 |
| 5 | 3 | −1 | 3 | 7.7704 | 7.7757 | 11.378 | 0.008 |
| 1 | 7 | 0 | 1 | 7.6836 | 7.6838 | 11.507 | 0.000 |

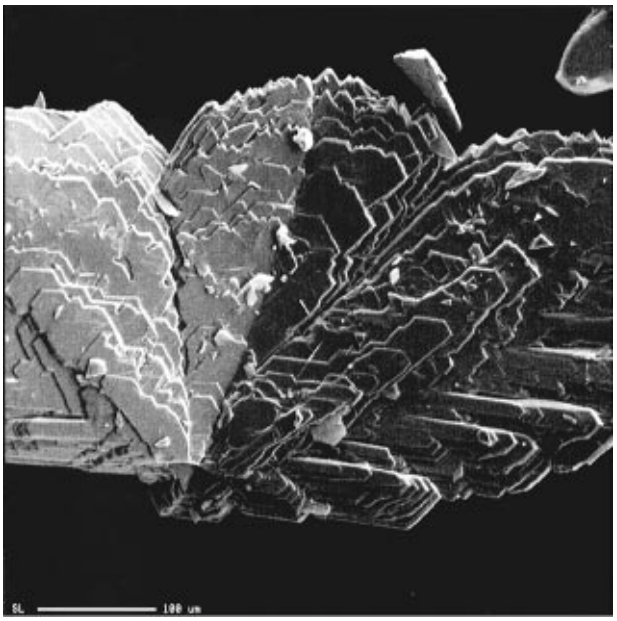

**Figure 5.** Electron microprobe photo of $MoO_3$/DTA compound.

The powder X-ray diffraction pattern of this sample is shown in Figure 4 for a sample showing strong preferred orientation. Figure 7 shows the pattern for a sample where preferred orientation has been minimized. Samples obtained prior to hydrothermal reaction and from the supernatant liquid after reaction were indexed to the same triclinic unit cell with $a = 9.813(3)$ Å, $b = 11.512(3)$ Å, $c = 21.723(1)$ Å, $\alpha = 95.30(1)°$, $\beta =$

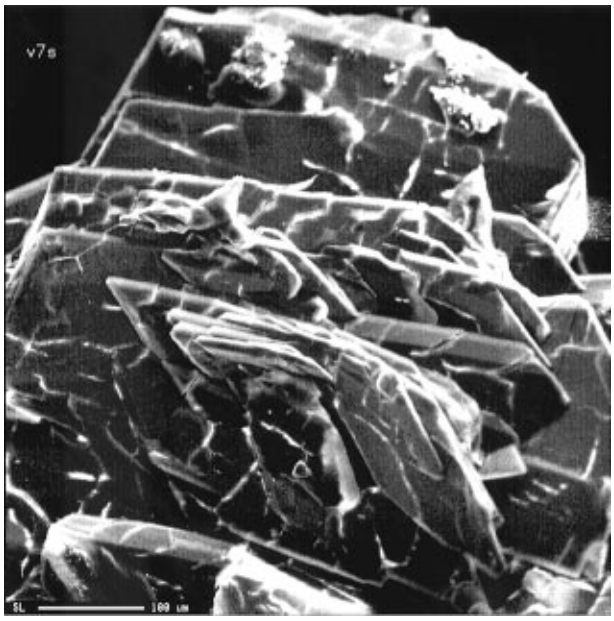

**Figure 6.** Electron microprobe photo of $V_2O_5$/DTA compound.

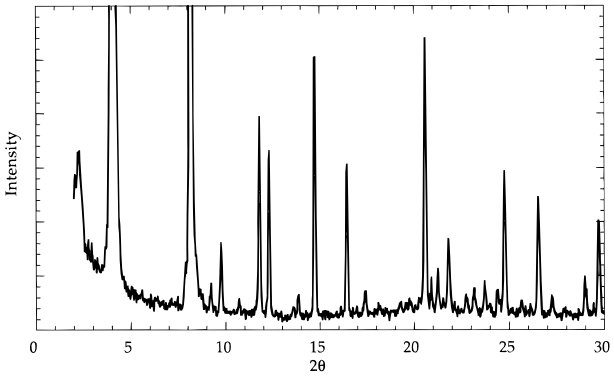


**Figure 7.** X-ray powder diffraction of the $V_2O_5$/DTA compound.

93.82(1)°, and $\gamma$ = 101.12(1)°. Table 2 contains the indexed powder data for one sample. Single-crystal experiments on a posthydrothermal sample did not yield good single-crystal data, as the crystals were twinned. However, the single crystal experiments did allow the unit cell to be indexed to $a$ = 9.793(3) Å, $b$ = 11.495(3) Å, $c$ = 21.687(4) Å, α = 95.35(2)°, $\beta$ = 93.92(2)°, $\gamma$ = 101.10(1)°. The interlayer $d$ spacing for this sample is 21.6 Å. Cracks appeared in these crystals over time, and the $d$ spacings changed. This may be associated with the samples losing water under room conditions after having been removed from the supernatant liquid. The TGA data in Figure 3 shows that the first weight loss occurs around 80 °C, making this a plausible explanation. The $d$ spacing of a sample dried at room temperature over night decreased to 18.9 Å, and the cell parameters were $a$ = 9.93(1) Å, $b$ = 11.86(1) Å, $c$ = 19.19(1) Å, α = 84.72(1)°, $\beta$ = 99.76(1)°, and $\gamma$ = 101.72(1)°. These data are compared in Table 3. Only the $c$ dimension is significantly different (~3 Å) so the two compounds have the same structure except for a 3 Å contraction along the $c$ direction. The volume difference of 210 Å$^3$ is consistent with the loss of around 6 $H_2O$ molecules per unit cell.

The single crystals were found to have the same density as pure chloroform, 1.47 g/cm$^3$. If we assume 12 vanadium atoms per unit cell, then the calculated density is 1.55 g/cm$^3$. This gives the formula of the unit cell as $[C_{12}H_{25}N(CH_3)_3]_4V_{12}O_{32}\cdot 6H_2O$ for the hydrated compound. This volume packing of the DTA is consistent with that in the unit cell of (DTA)Br, listed in

**Table 2. X-ray Data of Vanadium Sample**

| h | k | l | $I$(obs) | $d$(obs) | $d$(calc) | 2$\theta$(obs) | $\Delta 2\theta$ |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 1 | 837 | 21.34 | 21.55 | 4.136 | 0.040 |
| 0 | 0 | 2 | 1000 | 10.759 | 10.776 | 8.211 | 0.013 |
| 0 | 1 | 1 | 13 | 9.5596 | 9.5472 | 9.243 | −0.012 |
| 1 | 0 | −1 | 35 | 9.0359 | 9.0599 | 9.780 | 0.026 |
| 1 | 0 | 1 | 1 | 8.4831 | 8.4953 | 10.419 | 0.015 |
| 0 | 1 | −2 | 9 | 8.2341 | 8.2303 | 10.735 | −0.005 |
| 1 | −1 | 0 | 2 | 8.1478 | 8.1441 | 10.849 | −0.005 |
| 1 | −1 | −1 | 6 | 7.6037 | 7.6069 | 11.629 | 0.005 |
| 1 | 0 | −2 | 155 | 7.4837 | 7.4938 | 11.816 | 0.016 |
| 0 | 0 | 3 | 89 | 7.1804 | 7.1839 | 12.317 | 0.006 |
| 1 | −1 | 2 | 7 | 6.5191 | 6.5119 | 13.572 | −0.015 |
| 1 | −1 | −2 | 5 | 6.4820 | 6.4830 | 13.650 | 0.002 |
| 0 | 1 | −3 | 26 | 6.3760 | 6.3705 | 13.878 | −0.012 |
| 1 | 1 | −2 | 282 | 6.0034 | 6.0111 | 14.744 | 0.019 |
| 1 | 0 | −3 | | | 6.0046 | | 0.003 |
| 0 | 1 | 3 | 3 | 5.7554 | 5.7763 | 15.383 | 0.056 |
| 0 | 0 | 4 | 66 | 5.3844 | 5.3880 | 16.450 | 0.011 |
| 1 | 1 | −3 | 9 | 5.2218 | 5.2187 | 16.966 | −0.010 |
| 0 | 2 | −2 | | | 5.2147 | | −0.023 |
| 0 | 1 | −4 | 42 | 5.0841 | 5.0754 | 17.429 | −0.030 |
| 1 | −2 | 2 | 9 | 4.8874 | 4.8869 | 18.136 | −0.002 |
| 1 | 0 | −4 | | | 4.8813 | | −0.023 |
| 2 | 0 | 0 | 4 | 4.7957 | 4.7964 | 18.486 | 0.003 |
| 0 | 2 | 2 | 7 | 4.7742 | 4.7739 | 18.570 | −0.001 |
| 2 | 0 | −1 | | | 4.7701 | | −0.016 |
| 2 | −1 | 0 | | | 4.7696 | | −0.018 |
| 1 | −2 | −2 | 3 | 4.6773 | 4.6812 | 18.958 | 0.016 |
| 0 | 2 | −3 | | | 4.6749 | | −0.010 |
| 2 | −1 | 1 | 2 | 4.6196 | 4.6179 | 19.197 | −0.007 |
| 2 | 0 | 1 | 14 | 4.5978 | 4.5985 | 19.289 | 0.003 |
| 1 | 0 | 4 | 19 | 4.5345 | 4.5333 | 19.561 | −0.005 |
| 2 | 0 | −2 | | | 4.5299 | | −0.020 |
| 1 | 2 | −1 | 29 | 4.4879 | 4.4919 | 19.766 | 0.018 |
| 1 | −1 | −4 | | | 4.4841 | | −0.017 |
| 0 | 0 | 5 | 266 | 4.3084 | 4.3103 | 20.598 | 0.009 |
| 2 | 0 | 2 | 66 | 4.2448 | 4.2477 | 20.910 | 0.014 |
| 0 | 1 | −5 | 37 | 4.1759 | 4.1771 | 21.259 | 0.006 |
| 1 | −2 | −3 | | | 4.1761 | | 0.001 |
| 2 | 0 | −3 | 10 | 4.1578 | 4.1585 | 21.353 | 0.004 |
| 2 | 1 | 0 | 21 | 4.1193 | 4.1227 | 21.555 | 0.018 |
| 0 | 2 | −4 | | | 4.1151 | | −0.022 |
| 1 | 0 | −5 | 152 | 4.0641 | 4.0652 | 21.851 | 0.006 |
| 2 | −1 | −3 | 21 | 4.0456 | 4.0495 | 21.952 | 0.021 |
| 2 | −1 | 3 | 75 | 3.9077 | 3.9018 | 22.737 | −0.035 |
| 1 | 1 | −5 | 79 | 3.8396 | 3.8428 | 23.146 | 0.020 |
| 2 | 0 | 3 | | | 3.8387 | | −0.005 |
| 1 | −1 | 5 | 30 | 3.8149 | 3.8170 | 23.298 | 0.013 |
| 2 | −2 | 2 | | | 3.8150 | | 0.001 |
| 2 | 0 | −4 | 102 | 3.7478 | 3.7470 | 23.721 | −0.005 |
| 2 | 1 | 2 | 13 | 3.7134 | 3.7121 | 23.944 | −0.008 |
| 0 | 2 | 4 | 9 | 3.6906 | 3.6944 | 24.094 | 0.025 |
| 1 | −2 | −4 | | | 3.6922 | | 0.011 |
| 1 | −3 | −1 | 78 | 3.6465 | 3.6503 | 24.390 | 0.026 |
| 2 | −1 | −4 | | | 3.6450 | | −0.010 |
| 1 | −3 | 2 | 26 | 3.6233 | 3.6270 | 24.548 | 0.025 |
| 0 | 3 | 1 | | | 3.6232 | | −0.001 |
| 0 | 0 | 6 | 193 | 3.5927 | 3.5919 | 24.761 | −0.005 |

**Table 3. Structure Parameters for Vanadium Compounds and $C_{12}H_{25}N(CH_3)_3Br$**

| | V12-wet | V12-dry | C12-Br |
|---|---|---|---|
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 9.813 | 9.936 | 5.661 |
| $b$ (Å) | 11.512 | 11.863 | 7.277 |
| $c$ (Å) | 21.725 | 19.185 | 43.215 |
| α (deg) | 95.303 | 84.720 | 90 |
| $\beta$ (deg) | 93.820 | 99.760 | 92.988 |
| $\gamma$ (deg) | 101.122 | 101.720 | 90 |
| $V$ (Å$^3$) | 2388.8 | 2178.3 | 1777.8 |
| $S(a,b)$ | 110.8 | 115.4 | 41.2 |
| $d$(001) | 21.551 | 18.874 | 43.156 |
| density (calc) | 1.49 | 1.55 | 1.15 |

Table 3 and calculated from the powder pattern of $C_{12}H_{25}N(CH_3)_3Br$.

Bouhaouss et al.[22] reported the formation of intercalation compounds between quarternary ammonium ions, $C_nH_{2n+1}N^+(CH_3)_3$ for $1 \leq n \leq 18$, and vanadium oxide gels. Those compounds contained 0.3−0.4 surfactant species per $V_2O_5$ and for $n = 12$ the lattice repeat distance was 31.4 Å. In contrast the materials reported here and synthesized from crystalline $V_2O_5$ contained 50% more surfactant yet had a repeat distance of only 21.6 Å as prepared and after dehydration 18.9 Å. The much smaller repeat distance observed here might seem to preclude a structure based on a vanadium oxide layer between which lie the surfactant ions, though in the Bouhaouss compounds it was assumed that the alkyl chains were aligned vertically to the oxide layers.

A trimethylammonium C12 cation has a length of about 19 Å, which when combined with the thickness of a continuous vanadium oxide layer, 4.4 Å, appears to lead to a *d* spacing of 23.4 Å for the anhydrous oxide. However, if the chains are tipped to an angle of around 50°, the C12 chain would have an effective length of 14.5 Å giving a repeat distance of 18.9 Å. Although this appears feasible, it is probable that the polar ammonium end of the ion would be adjacent to the oxide layer, which would require an interleaving of the alkyl chains of ions anchored to the faces of opposite oxide layers; this would effectively extend the chain length by around 3 Å.

If the vanadium forms a layer in the *ab* plane, then one can calculate the area per vanadium in the plane. The area of the *ab* plane per unit cell is 111 Å$^2$, giving 9.24 Å$^2$ per vanadium. This is 10% less than that for $V_2O_5$ itself, 10.24 Å$^2$, but greater than that found in $LiV_2O_5$, 8.76 Å$^2$, where the $V_2O_5$ layers are much more puckered. This suggests that the vanadium atoms must reside in at least two planes, possibly intermediate between $V_2O_5$ and $LiV_2O_5$. Alternatively the vanadium oxide layer may not be continuous as in $V_2O_5$ but more like the structure found for the tungsten analogue with disconnected vanadium oxide clusters.

Could this compound contain an ionic cluster such as $V_{12}O_{32}{}^{4-}$? This cluster has an interesting structure, which essentially comprises half a sphere made up of $VO_5$ square pyramids just as in $V_2O_5$ itself. The open center can form inclusion complexes with small molecules such as $CH_3CN$.[23] In this anion four vanadiums are in a plane at the base of the bowl and eight just below the top in another plane. If these were arranged into a sheet, one per unit cell, then the polar end of the ammonium surfactant could interact with the vanadyl groups on the outside of the bowl. However, the unit cell composition would allow only one $V_{12}O_{32}{}^{4-}$ cluster per unit cell, which is inconsistent with the assigned space group.

The FTIR spectrum for this material is shown in Figure 2, and shows that there are shifts in the V−O vibrations, as compared to those in the $V_2O_5$ starting material. $V_2O_5$ shows three major absorption peaks at 617, 827, and 1022 cm$^{-1}$. These three peaks are also present in the DTA·$V_2O_5$ compound being observed at 618, 834, and 960 cm$^{-1}$. The first two associated with vibrations of −V−O−V− and O−$(V)_3$− vanadium oxygen groups are essentially unchanged. However, there is a significant shift in the third peak which is associated with the vanadyl group, −V═O, at the top of the square pyramid. This shift to lower energy indicates a lengthening of the V═O bond, which may be associated with some additional bonding either to the oxygen by for example the trimethylammonium cation or alternatively to the vanadium at the vacant bonding position at the base of the pyramid. This latter could be associated with the additional oxygen in the structure necessary to charge compensate the ammonium cation. Single-crystal X-ray studies will be necessary to clarify the structure and bonding in this layered material.

Very recently a study on cetyltrimethylammonium complexes with $V_2O_5$ was reported.[24] That paper proposes that vanadium oxide forms MCM type compounds, just as suggested earlier by Huo et al.[8] Reaction between ammonium vanadate and CTA chloride led to a white precipate of composition $C_{19.5}H_{46.9}N_{1.0}V_{0.92}O_{4.6}$, indicating one surfactant per vanadium and with a lattice spacing of 27 Å. When this compound, dissolved in ethanol, was acidified to a pH of 2.2, a red-brown precipitate was formed with formula $C_{20.1}H_{48.0}N_{1.0}V_{2.9}O_{11.4}$. This formula can be rearranged to give $[C_{16}H_{33}N(CH_3)_3]V_3O_8{\cdot}3H_2O$, the same ratio of surfactant to vanadium as reported here. However, this material has a strong X-ray reflection at $d = 36$ Å, with two broader and weaker reflections at 18.0 and 9.87 Å. On heating to 200 °C for 2 h the first reflection went to 34 Å, and the pattern was indexed to a hexagonal lattice with $a = 39$ Å very similar to the $WO_3$·CTA compound of Huo.[8] The thermal stability of their vanadium compound is similar to that formed here, not showing weight loss until above 200 °C. The morphology of both compounds is also similar, both having a platy appearance. However, X-ray diffraction shows that the structures are different and further work is needed to determine their precise composition and structure and whether MCM type compounds can indeed be formed with transition metal oxides.

## Conclusion

Three new surfactant/inorganic compounds synthesized via hydrothermal methods were studied and characterized. The $C_{12}H_{25}N(CH_3)_3$ tungsten compound contains Keggin ions, just as reported by Stein et al.[10] for the $C_{16}H_{33}N(CH_3)_3$ tungsten compound, but has a smaller unit cell as expected. The molybdenum and vanadium oxides were found to form layered materials, and the DTA−$V_2O_5$ sample was unique in that it formed both before and after the hydrothermal reaction. We were not able to remove the surfactant template in any of these materials, which might allow the formation of a mesoporous material.

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