Layered tungsten oxide-based organic/inorganic hybrid materials I: Infrared and Raman study

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Tungsten oxide-organic layered hybrid materials have been studied by infrared and Raman spectroscopy, and demonstrate a difference in bonding nature as the length of the interlayer organic ‘spacer’ molecule is increased. Ethylenediamine-tungsten oxide clearly displays a lack of terminal $\text{NH}_3^+$ ammonium groups which appear in hybrids with longer alkane molecules, thus indicating that the longer chains are bound by electrostatic interactions as well as or in place of the hydrogen bonding that must be present in the shorter chain ethylenediamine hybrids. The presence of organic molecules between the tungsten oxide layers, compared with the layered tungstic acid $\text{H}_2\text{WO}_4$, shows a decrease in the apical $\text{W}=\text{O}$ bond strength, as might be expected from the aforementioned electrostatic interaction.

INTRODUCTION

Layered transition metal oxides present a paradigm for strongly correlated electronic systems subject to interesting correlated states and the competition of multiple order parameters. The high temperature oxide superconductors are a much-studied case in point. Moreover the discovery of superconductivity in sodium cobalt oxide $\text{Na}_2\text{CoO}_2$ confirms this general approach of exploring novel layered metal oxides. Here we consider layered tungstates as another new model system capable of displaying a complex phase behaviour dependent upon interlayer coupling and doping state.

Tungsten oxide has been the subject of much research in the past few decades due to its interesting physical and electronic properties and doping capability. Tungsten trioxide can form a variety of stable structures at room temperature, such as pyrochlore, hexagonal, or distorted cubic, all of which are comprised of corner- and/or edge-shared WO$_6$ octahedra. These structures can be doped by inserting mono- or di-valent atomic species into the interstitial vacancy sites within the oxide structure, or by removing oxygen and dramatic colour changes, which has led to tungsten trioxide systems being used in electrochromic applications.

Tungsten trioxide can be hydrated to form layered structures, with a general formula of $\text{WO}_3$-$\text{xH}_2\text{O}$. In the mono-hydrate, $\text{WO}_3$-$\text{H}_2\text{O}$ (or $\text{H}_2\text{WO}_4$), two-dimensional layers of corner-shared WO$_6$ octahedra are formed, with a water molecule (−OH$_2$) substituted for an apical oxygen of the tungsten atom, and a terminal oxygen completing the structure. In the di-hydrate (WO$_3$-2H$_2$O), the second water molecule is inserted between the layers, as in MoO$_3$-2H$_2$O. An increase in the interlayer spacing is observed and it thus follows that one could perhaps substitute organic species between the tungsten oxide layers. Indeed this has proven successful, with various groups succeeding in intercalating organic molecules such as pyrazine, 4,4-bipyridine, pyridine, tert-alkylammonium species, monoaminoalkanes and diamino-alkanes. Such materials provide an interesting template for doping and substitutional (e.g., magnetic ions) studies in low-dimensional systems.

Here we present infrared and Raman results on a selection of WO$_3$-based hybrid materials in order to gain a more extensive understanding of the overall structure; in particular, the bonding nature of the organic to the inorganic layer, and the impact of the organic intercalant on the structure of the inorganic layer.

EXPERIMENTAL

Diaminoalkane-tungsten oxide samples were synthesised as described in Ref. $^{28}$. In brief, $\text{H}_2\text{WO}_4$ was dissolved in hot aqueous ammonia solution (33 wt. %) and then a solution of the organic amines (e.g., $\text{NH}_3$, $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$, hereby abbreviated to DAn; or phenethylamine, $\text{C}_8\text{H}_7(\text{CH}_2)_2\text{NH}_2$, abbreviated to phen) dissolved in ammonia was added in a 2:1 molar ratio. The excess solvent was then evaporated off and the hybrid materials were obtained as white/cream-coloured powders. The entire synthesis was carried out under flowing N$_2$ gas.

Powder X-ray diffraction spectra were recorded using a Philips PW1700 series powder diffractometer with Co Kα radiation. Infrared spectra were collected on a Bomem DA8 FT spectrometer over the mid-IR range (450-4000 cm$^{-1}$) using the KBr disc method with a resolution of 2 cm$^{-1}$. Raman spectra were collected using a Jobin-Yvon LabRam HR spectrometer with an excitation wavelength.
RESULTS AND DISCUSSION

The X-ray diffraction spectra shown in Figure 1 display a strong peak at low 2θ angles. As the length of the intercalated organic molecule is increased, the corresponding d-spacing also increases in a linear fashion (shown in Figure 1b). From the slope and intercept of this line we propose a model by which single molecular layers of 2-dimensional corner-shared WO₆ octahedra are separated by the organic molecules which are aligned almost perpendicular to the tungsten oxide layers. One would expect such a layered compound to display properties approaching those of a purely 2-dimensional system as the distance between the oxide layers is increased (by increasing the length of the organic spacer molecule). The physical properties of this system will be the topic of future publications.

The normalised infrared and Raman spectra of the solid samples studied are shown in Figures 2 and 3 and the peak positions tabulated in Tables I and II. The di-

aminoalkane hybrids WO₄·DAn (hereby abbreviated to W-DAn) with alkyl lengths longer than two carbons have virtually identical spectra and so are summarised in the tables as W-DAn, in comparison with the differing W-DA2.

The infrared spectra of WO₃ and its hydrate, H₂WO₄, have much fewer and broader peaks than their hybrid counterparts. Both the infrared and Raman spectra of these two compounds correspond well with those presented by Daniel et al. These results are summarised in three sections: the effect on the inorganic layer, the effect on the organic species, and the organic-inorganic bonding nature.
TABLE I: Observed peaks in powder samples, 1000-4000 cm\(^{-1}\). \(\nu\) stretching, \(\delta\) deformation/in-plane bending, \textit{sciss}. scissoring, \(\sigma\) bending, \(\omega\) wagging; \(s\) strong, \(m\) medium, \(w\) weak, \(vw\) very weak, \(b\) broad.

| Assignment | WO\(_3\) | H\(_2\)WO\(_4\) | W-DA2 | W-DAn | W-phen |
|------------|---------|----------------|--------|--------|--------|
| \(\nu(O-H)\) | 3410 mb | 3370 w |        |        |        |
|            |         | 3302 s | 3305 vw |        |        |
|            |         | 3244 wb |        | 3242 m | 3247 w |
|            |         | 3212 wb | 3212 m |        |        |
| \(\nu(NH_2,NH_3^+)\) |        | 3134 wb | 3135 s |        |        |
|            |         |        |        | 3061 w | 3063 m |
|            |         |        |        | 3028 w | 3006 w |
| \(\nu(CH_2)\) | 2963 w | 2956 s | 2963 w | 2960 w |        |
|            | 2895 w | 2900 s | 2919 w | 2924 w | 2916 w |
|            | 2910 w | 2883 m | 2868 w | 2870 m | 2861 w |
|            | 2847 w | 2849 w |        |        |        |
| \(\delta(NH_3^+)\) |        |        | 2101 mb | 2090 vw |        |
| Organic    |        |        | 1762 vw | 1760 vw | 1766 w |
|            |        |        | 1700 vw | 1701 vw | 1702 w |
| \(\delta(H_2O)\) |        | 1614 m |        |        |        |
|            |        | 1620 s | 1631 s |        |        |
|            |        | 1597 w | 1602 vw | 1604 w | 1605 mb |
|            |        |        | 1578 s | 1591 mb | 1586 w |
| Sciss. CH\(_2\) | 1471 m | 1472 w | 1495 m |        | 1497” m |
|            | 1467 w | 1469 s | 1465 w | 1445 vw | 1454" m |
|            |        | 1444 w |        | 1446" w |        |
| Sciss. and \(\sigma(CH_2)\) | 1403 vw | 1412 vw | 1393 s | 1384 vw | 1386 vw |
|            | 1382 vw | 1386 vw | 1382 s |        |        |
|            | 1373 w |        |        |        |        |
| \(\sigma(CH_2), \omega(CH_2)\) | 1336 m | 1340 vw | 1310 w | 1333 vw | 1322 vw |
|            | 1299 m | 1296 vw | 1298 w | 1296 w |        |
| \(\sigma(NH_2, NH_3^+)\) |        |        | 1263 w | 1261 vw | 1266 vw |
|            |        |        | 1213 w |        | 1206 m |
|            |        |        | 1189 m | 1197 w |        |
|            |        |        | 1173 m | 1181 vw | 1183 w |
|            |        |        | 1144 m | 1164 vw | 1164 m |
|            |        |        | 1128 vw |        | 1132 vw |
|            |        |        |        |        | 1103 w |
| \(\nu(C-N, C-C)\) |        | 1062 s | 1070 vw | 1083 m | 1066 w |
|            |        |        | 1059 s |        |        |
|            |        | 1030 w | 1030 vw | 1027 m | 1030 m |
|            |        | 1006 w |        | 1001 m |        |
|            |        |        | 962 w | 953 vw | 929 mb |
|            |        |        |        |        | 942 sb |

* Aromatic C=C stretch.
TABLE II: Observed peaks in powder samples, 0-1000 cm$^{-1}$. $\nu$ stretching, $\delta$ deformation/in-plane bending, $\rho$ rocking; $s$ strong, $m$ medium, $w$ weak, $vw$ very weak, $b$ broad.

| Assignment | WO$_3$ | H$_2$WO$_4$ | W-DA2 | W-DAn | W-phen |
|------------|--------|-------------|--------|--------|--------|
| $\nu$(W=O) | IR     | Raman | IR     | Raman | IR     | Raman | IR     | Raman |
|            | 940 mb | 940 vw | 950 s  | 947 s  | 951? m | 900 s  | 1004? s | 888 m |
|            | 885 s  | 888 s  | 905 s  | 890 s  | 902 wb | 888 s  |          |       |
| $\nu$(O–W–O) | 824 sb | 809 s  | 822 mb | 816 mb | 829 m  | 816 mb |          |       |
|            | 756 sb | 774 mb | 760$^b$ sb | 775$^b$ mb | 745 s |          |       |
|            | 714 m  | 740 sb | 724 mb | 732 vw | 678 w  | 679 w  | 697 s  | 668 w  |
|            | 614 w  | 638 sb | 613 sb |          |        |        |        |        |
|            |          |        | 594 vw | 577 sb | 576 vw | 594 vw | 595 w  |       |
| Organic | | | 550 vw | 545 sb | 552 vw | 557 w  | 502 m  | 460 w  |
|           |        |        | 434 vw | 467 vw | 412 w  | 436 vw | 432 w  |       |
| W–OH$_2$ | | | 326 w  | 330 vw | 348 w  | 336 vw | 274 m  | 236 w  |
|          | | | 377 m  | 301 vw | 283 vvv |       |        |       |
| $\delta$(O–W–O) | 252 w  | 236 w  | 222 w  | 226 w  | 254 w  | 238 w  |        |       |
|          | 187 w  | 194 w  | 201 m  | 182 vvv | 187 w  |        |        |       |
| Lattice modes | 136 w  | 144 vvv | 144 vvv | 120 vvv |        |        |        |       |
|            | 94 w   | 106 w  |        |        |        |        |        |       |

$^b$\(\rho$(NH$_3^+$) mode.

I. The effect on the inorganic layer

The presence of co-ordinated water molecules in H$_2$WO$_4$ can be seen by the broad O–H stretching peak at 3410 (3370) cm$^{-1}$ (IR and Raman respectively), the H$_2$O bending peak at 1614 cm$^{-1}$ (IR only), and the W–OH$_2$ co-ordinated water peak in the Raman spectrum at 377 cm$^{-1}$. These peaks do not occur in the WO$_3$ spectra, as expected.

As mentioned earlier, the structure of H$_2$WO$_4$ consists of layers of corner-shared WO$_6$ octahedra with alternate apical arrangements of W–OH$_2$ and W=O. In the Raman spectrum the W=O bonding is shown clearly by a sharp band centred at about 950 cm$^{-1}$. This is also present in the IR spectrum. Surprisingly, the WO$_3$ sample also exhibits a small peak at this position in the Raman and IR spectra. This is not expected as the structure of WO$_3$ consists only of single W–O bonds. However it can be explained by the presence of disorder in the sample and loss of oxygen $^{22}$,$^{41}$, which results in the formation of a small fraction of W=O bonds. There are also W=O terminations on the surfaces of the powder particles.

In the diaminoalkane hybrid compounds the characteristic W=O peak, formerly at 950 cm$^{-1}$ in H$_2$WO$_4$, shifts to a lower frequency of 890-900 cm$^{-1}$. While in several of these compounds there are peaks at 950 cm$^{-1}$ they are not as intense as the W=O peak. It is also of interest to note that the peak at 888 cm$^{-1}$ in the W-DA2 Raman spectrum is a doublet, suggesting perhaps the presence of two different W=O bonds. In W-phen, the peak structure in the range 900-100 cm$^{-1}$ is quite different from the other hybrid spectra. This may be due to the organic molecule being mono-dentate (as IR spectra of other mono-aminoalkane hybrids show that the 950 cm$^{-1}$ W=O peak is virtually unaltered $^{30}$) or more complicated due to the presence of the aromatic ring. In any case, the sharp Raman peak at 1004 cm$^{-1}$ is likely to be a W=O peak due to the similarity in shape between it and the known W=O peak in H$_2$WO$_4$, for example. There may be more than one variation of the W=O bond within the structure, which may also account for the multiple peaks observed in this region, as is the
modes. These bands occur at similar positions in the W−DAn (n− peak centred at 2100 cm−1)

In W2O4 a small peak is observed in the IR spectrum at 1614 cm−1, which corresponds to H2O bending. While the hybrid samples also exhibit peaks near this value (1600-1630 cm−1), these peaks are sharp and well defined, and the vibrational band at 3400 cm−1 (indicative of O−H stretching) is absent. Thus we conclude that most of the co-ordinated water molecules (W−OH2) have been dehydrogenated during the organic intercalation process (a small feature at 377 cm−1 in the Raman spectra may correspond to W−O−H). The peaks in the hybrid spectra in the range 1600-1630 cm−1 correspond instead to NH2 or NH3+ bending.

As only the terminal amino/ammonium group is involved in interactions with the inorganic layer, it is no surprise that the bands corresponding to C−H, C−N and C−C vibrations remain virtually unchanged. The peaks in the hybrid spectra corresponding to these vibrations can be assigned as follows: 2850-2960 cm−1 C−H stretching, 1300-1500 cm−1 CH2 wagging, bending, and scissoring; also C=C aromatic stretching for W-phen (1450-1500 cm−1), 950-1100 cm−1 C−N and C−C stretching. From 460-550 cm−1 there are a small number of unassigned organic bands (including a sharp peak in the IR at 537 cm−1 for W-DA2, corresponding to the bending vibration of the NCCN backbone).

III. The organic−inorganic bonding nature

The most noticeable difference among the hybrid samples is that W-DA2 shows quite a different bonding nature to the hybrids with longer organic chains: there is no evidence for the presence of ammonium (−NH3+) terminal groups in W-DA2. As mentioned previously, W-DA2 lacks a feature at 2100 cm−1 found in the other hybrid spectra that corresponds to deformations of terminal −NH3+. Combined with the presence of the −NH3+ rocking mode found at 770 cm−1, this implies that some of the amine molecules in W-DAn appear as R−NH3+⋯O−W, while all those of W-DA2 appear as neutral −NH2 species. This raises the question of how charge balance is achieved in W-DA2 and also whether hydrogen bonding is the exclusive mechanism of bonding, whereas in the longer organic molecule hybrids there is clearly an electrostatic component as well due to the presence of terminal ammonium groups. There are also differences in the N−H stretch region, suggesting changes in the bonding chemistry as one progresses from DA2 to longer DAn alkyl chains. As mentioned in Section II, the N−H stretching bands for W-DA2 appear at lower wavenumbers than for longer-chain W-DAn species. Hydrogen bonding (which holds the DA2 molecules in place between the layers) will cause these bands to shift to lower frequencies. DA2 is the only case where the inductive effect on the terminal amine groups is known.
to be a perturbing factor to the molecular vibrations due to the shorter alkyl chain length \(32\).

One possible explanation for the observed difference in structure between DA2 and longer DAn molecules intercalated into an acidic metal oxide, arises from examining the trend in basicity of \(\alpha,\omega\)-diamines in solution. Although the trend in basicity only changes slightly with increasing alkyl length for the monoamines (due to combinations of solution effect, steric hindrance to solvation, and number of available H-bonds \(38, 39, 40\)), a substantial increase in basicity is observed in going from DA2 to DA8 (Fig. 5). This increase in base strength for the dianines in aqueous solution.

The formation of alkylammonium as the number of methylene groups (aminoalkanes is due to an increase of the inductive effect \(DA8\) (Fig. 5). This increase in base strength for the dianines is associated with a decrease in the strength of the apical W=O bond of the \(WO_4^{2-}\) layers compared with the layered tungsten oxide monohydrate (tungstic acid), \(H_2WO_4\).
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[41] Commercial WO3 powder is a pale yellow color, which is reduced over 1-2 days in air to a pale green colour. This is indicative of a loss of oxygen but can be regained by storing in an oxygen atmosphere or heating in oxygen for a few hours.