Novel Metastable Structures of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ Obtained by the Deintercalation of Layered Amine Adducts

S. Ayyappan, G. N. Subbanna and C. N. R. Rao*

Abstract: Deintercalation of amines from the layered amine adducts of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ has been employed as a soft chemical route to produce unusual metastable structures of the oxides. After the adducts of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ ($x = 0.25$, 0.5, 0.75) with amines such as triethylamine (TEA), pyridine, n-butylamine and n-octylamine had been characterized, deintercalation was carried out thermally as well as by acid leaching. Thermal deintercalation yielded novel metastable structures of WO_3 and MoO_3 that were significantly different from the stable forms, which contain distorted metal–oxygen octahedra. Thus, ReO_3-type cubic WO_3 was obtained by the thermal deintercalation of $WO_3 \cdot 0.5\,TEA$. Acid leaching of the amines gave metastable phases of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$, which were different from those obtained thermally. All the metastable phases transformed to the corresponding stable forms at higher temperatures.

Keywords
acid leaching · deintercalation · layered oxides · metastable oxides · molybdenum compounds · tungsten compounds

Introduction

Many of the developments in the chemistry of transition metal oxides have originated from the investigations of the oxides of tungsten and molybdenum. Besides forming novel phases such as shear and tunnel structures, both WO_3 and MoO_3 form a variety of bronzes in which the intercalated proton, alkali metal ion and similar species reduce the W and Mo ions, often giving rise to itinerant d electrons. The structures of WO_3 and MoO_3, however, differ significantly: WO_3 has a three-dimensional monoclinic structure and MoO_3 a layered orthorhombic structure,[1–3] although the metal ion occupies a distorted octahedral site in both the cases because of the d^0 configuration. Neither of these oxides is therefore known to exist in the perfectly cubic structure of the ReO_3 type at room temperature. However, both MoO_3 and WO_3 form mono and dihydrates of similar structure without reduction of the metal ions.[2–6] Interestingly, both these oxides form layered (coordinative intercalation) compounds with pyridine derivatives.[6, 7]

We have explored the possibility of preparing cubic (ReO_3 type) and other novel metastable phases of MoO_3 and WO_3 by the deintercalation of the amine adducts. The deintercalation of the alkali metal ions A from intercalation compounds of the type A_xMX_y offers a low-temperature route for the synthesis of novel MX_y phases that are otherwise difficult to prepare.[8, 9] Thus, hexagonal VS_2 can only be prepared by the deintercalation of lithium from $LiVS_2$.[10] There are indications that new forms of WO_3 and MoO_3 result from the dehydration of oxide hydrates.[2, 3, 11, 12] For the purpose of the present study, we have prepared, for the first time, layered adducts of WO_3 and MoO_3 with triethylamine (TEA). After characterization of the adducts by X-ray diffraction, infrared spectra, thermogravimetric analysis and chemical analysis, the amines are deintercalated by thermal treatment in dry air or in dynamic vacuum and by acid leaching. The layered adducts of WO_3 and MoO_3 with pyridine are studied in a similar manner. We then examine the deintercalation of the amines from the adducts of WO_3 with n-butylamine and n-octylamine and also from the TEA adducts of $W_{1-x}Mo_xO_3$ ($x = 0.25$, 0.5, 0.75) solid solutions. The present study reveals not only the unexpected formation of cubic WO_3 of the ReO_3 type, but also of other novel metastable phases of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$, depending on the mode of deintercalation. These unusual phases might well have interesting physical and chemical properties for applications in material sciences.

Results and Discussion

WO_3, $WO_3 \cdot H_2O$, $WO_3 \cdot 2H_2O$, $MoO_3 \cdot 2H_2O$ and $W_{1-x}Mo_xO_3 \cdot H_2O$ all interacted with neat triethylamine (TEA) to form the novel layered adducts of composition $WO_3 \cdot 0.5\,TEA$, $MoO_3 \cdot 0.5\,TEA$ and $W_{1-x}Mo_xO_3 \cdot y\,TEA$. WO_3 also formed such compounds with primary amines such as n-$C_4H_9NH_2$ and n-$C_8H_{17}NH_2$. The molecular volume of TEA is higher than those of pyridine and the primary amines studied here. The structures of the layered adducts were obtained by X-ray diffraction, generally by comparing the calculated and observed patterns. The unit cell dimensions of the various amine adducts of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ are listed in Table 1.

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Table 1. Appearance and unit cell dimensions of the amine intercalates of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$.

Compound	Colour	Structure	*a*/Å	*b*/Å	*c*/Å
$WO_3 \cdot 0.5TEA$	colourless	orthorhombic	9.731(12)	6.885(6)	11.273(8)
$WO_3 \cdot 0.85C_4H_9NH_2$	pale yellow-brown	orthorhombic	11.099(8)	9.890(9)	15.290(20)
$WO_3 \cdot n\text{-}C_8H_{17}NH_2$	colourless	orthorhombic	7.817(5)	11.300(4)	23.244(10)
$WO_3 \cdot pyr$	pale green	tetragonal	5.296(4)	–	11.488(10)
$MoO_3 \cdot pyr$	pale green	tetragonal	5.271(2)	–	11.477(4)
$MoO_3 \cdot 0.5TEA$	pale grey	orthorhombic	9.850(3)	9.411(6)	20.325(9)
$W_{0.75}Mo_{0.25}O_3 \cdot 0.55TEA$	pale grey	orthorhombic	11.513(7)	14.503(7)	17.635(9)
$W_{0.5}Mo_{0.5}O_3 \cdot 0.4TEA$	pale grey	orthorhombic	11.234(6)	14.506(7)	17.476(6)
$W_{0.25}Mo_{0.75}O_3 \cdot 0.5TEA$	pale grey	orthorhombic	10.431(4)	14.287(13)	18.767(8)

The formation of a layered adduct of MoO_3 with TEA is not surprising, since MoO_3 and $MoO_3 \cdot 2H_2O$ both have layered structures themselves. Yet, the layered structures of the starting materials are different to those of the products; this suggests that a structural reorganization takes place when the amine adduct is formed, at least in the case of MoO_3. The situation with WO_3 is somewhat different, since WO_3 does not have the layered structure of its hydrates. It is possible that the high Lewis basicity ($pK_a \approx 10$) of TEA favours adduct formation. With the hydrates of WO_3, TEA adduct formation is straightforward, whereas considerable structural reorganization of the oxide is clearly necessary for the formation of the amine adduct with WO_3. The adducts of WO_3 with TEA, *n*-butylamine and *n*-octylamine possess an orthorhombic structure similar to those of MoO_3 intercalates. It should be noted that the WO_3 hydrates also crystallize in the orthorhombic structure. The amine adducts only decompose to give off the amines at around 650 K. The infrared spectra confirm the presence of metal–amine coordination in the adducts studied: W(Mo)=O and W(Mo)–N stretching bands are observed in the 920–940 and 400–475 cm^{-1} regions. In the following analysis of their behaviour on heating and treatment with acid, the amine adducts are assumed to be intercalated coordination compounds.

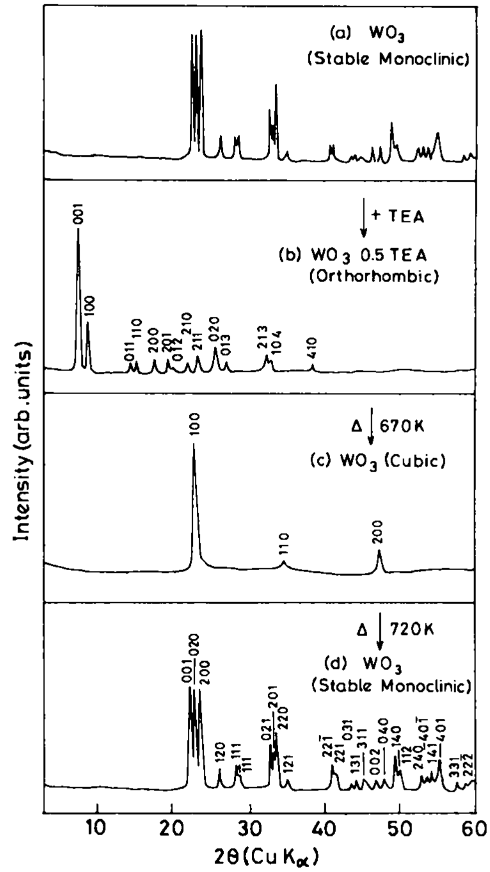

Fig. 1. Powder X-ray diffraction patterns of a) the stable monoclinic phase of WO_3, b) $WO_3 \cdot 0.5TEA$, c) metastable ReO_3-type cubic phase of WO_3 obtained by heating $WO_3 \cdot 0.5TEA$ to 670 K and d) monoclinic WO_3 obtained by heating cubic WO_3 to 720 K.

Thermal deintercalation of TEA adducts of WO_3 and MoO_3: When $WO_3 \cdot 0.5TEA$ was slowly heated, deintercalation of the amine was observed at around 670 K, as measured by thermogravimetry. Figure 1 shows the X-ray powder diffraction patterns of the starting material (monoclinic form of WO_3), the orthorhombic $WO_3 \cdot 0.5TEA$ and the oxide obtained after deintercalation at 670 K. The latter shows no amine bands in the IR spectrum. Its diffraction pattern is very simple and can only be indexed as an undistorted cubic structure similar to that of ReO_3. The cubic cell parameter is (3.812 Å) comparable to that of ReO_3 (3.75 Å). Seguin et al.[11] obtained a cubic phase with $a = 3.71$ Å from the hydrate. Figure 2a shows the bright-field image of the crystallites of the cubic phase along with the electron diffraction pattern. The latter gives a unit cell parameter of 3.80 Å. The lattice image of the cubic phase shows the expected 3.8 Å fringes (Fig. 2b). The crystallites of the cubic phase are small and the morphology is quite different from that of the stable monoclinic phase of WO_3; this suggests that the formation of the cubic phase following deintercalation probably involves lattice reconstruction. The formation of the ReO_3-type

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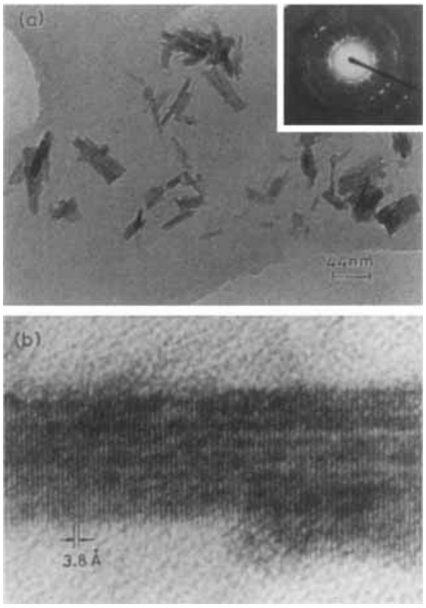

Fig. 2. a) Bright-field image of cubic WO_3 crystals; inset: electron diffraction pattern. b) Lattice image of cubic WO_3.

cubic phase of WO_3 by the thermal deintercalation of $WO_3 \cdot 0.5$TEA has never before been reported. This is also the first definitive report of a perfect cubic structure of a d^0 oxide being formed without any chemical modification. In Figure 3 we compare the cubic and monoclinic structures of WO_3 along the *c* axis. That the cubic phase is metastable is confirmed by the fact that it transforms to the stable monoclinic phase at 720 K (see Fig. 1 d). Accordingly, differential thermal analysis shows an exothermic transition at 720 K.

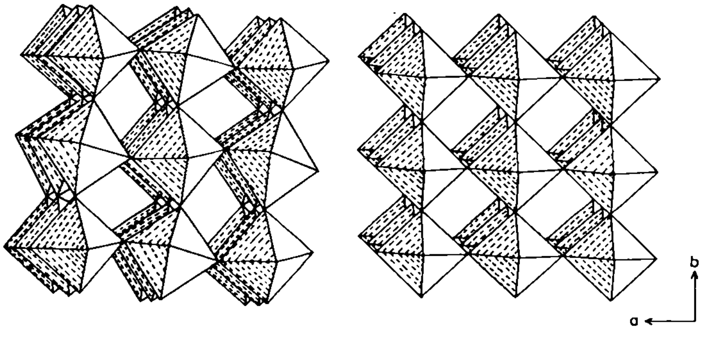

Fig. 3. Structures of monoclinic WO_3 (left) and cubic WO_3 (right).

In Figure 4, the X-ray diffraction patterns of the monoclinic $MoO_3 \cdot 2H_2O$ and of the orthorhombic $MoO_3 \cdot 0.5$TEA are shown. When $MoO_3 \cdot 0.5$TEA was heated to 620 K, deintercalation occurred, as measured by thermogravimetry. The X-ray diffraction pattern of the deintercalation product seems to correspond to a tetragonal structure (Fig. 4c). The unit cell parameters of this phase are $a = 3.430$ and $c = 7.635$ Å. The deintercalated product was partly amorphous, but sufficient crystallites were present to enable us to record an electron diffraction pattern corresponding to the above unit cell. This phase of MoO_3 is metastable and transformed to the stable orthorhombic phase on heating above 670 K. This can be seen from the X-ray diffraction pattern in Figure 4d.

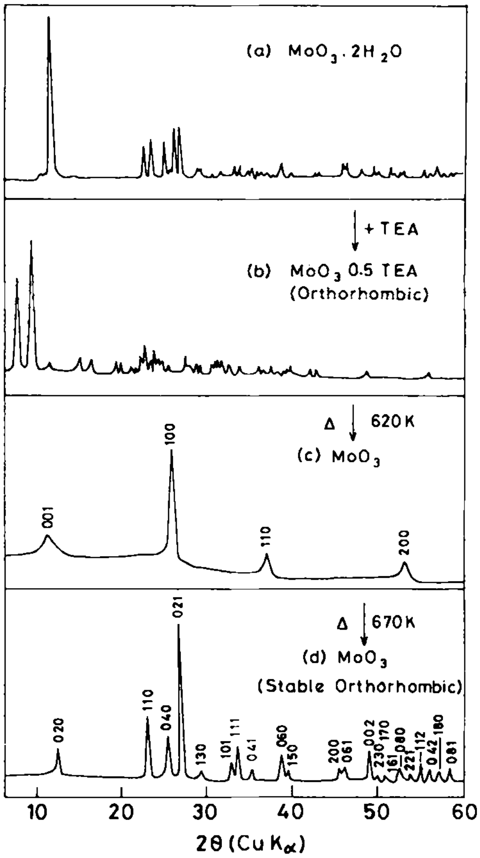

Fig. 4. Powder X-ray diffraction patterns of a) monoclinic $MoO_3 \cdot 2H_2O$, b) $MoO_3 \cdot 0.5$TEA, c) metastable ReO_3-type cubic MoO_3 obtained by heating the amine intercalate to 620 K and d) the stable orthorhombic MoO_3 (layered structure) obtained by heating cubic MoO_3 to 670 K.

The deintercalation of the $WO_3 \cdot$ pyr was achieved by thermal treatment. On heating tetragonal $WO_3 \cdot$ pyr gradually, deintercalation occurred at around 670 K. The product was obtained in a fine particulate form. The structure appears to be tetragonal (just as the intercalation compound), except that the cell parameters differ considerably ($a = 7.501$, $c = 3.324$ Å). These parameters could be confirmed by electron diffraction. This phase transformed to the stable monoclinic form of WO_3 at 720 K. We are not, however, entirely certain of the tetragonal structure of the metastable phase because of the large widths of the X-ray diffraction profiles.

Acid leaching of amine adducts of WO_3 and MoO_3: We examined the deintercalation of $WO_3 \cdot 0.5$TEA and $WO_3 \cdot$ pyr by acid leaching, that is, the amine was washed out as an ammonium salt. Thermogravimetry showed that weight loss (<2%) in the products obtained by acid leaching was negligible. Infrared spectra showed the absence of bands due to the amines. The product obtained by leaching $WO_3 \cdot 0.5$TEA was examined by X-ray powder diffraction (Fig. 5). The pattern could be fitted to an orthorhombic cell with unit cell parameters of $a = 7.793$, $b = 7.931$ and $c = 5.388$ Å. Electron diffraction patterns of this sample confirmed the unit cell parameters. Interestingly, leaching of $WO_3 \cdot$ pyr also gave orthorhombic WO_3 with the same unit cell parameters, as can be seen from the X-ray diffraction pattern (Fig. 6a). Intercalates of *n*-butylamine and *n*-octylamine with WO_3 similarly gave orthorhombic WO_3 of identical unit cell dimensions when leached with acid (Fig. 6b,c). The acid leaching method for deintercalating amines appears to be a

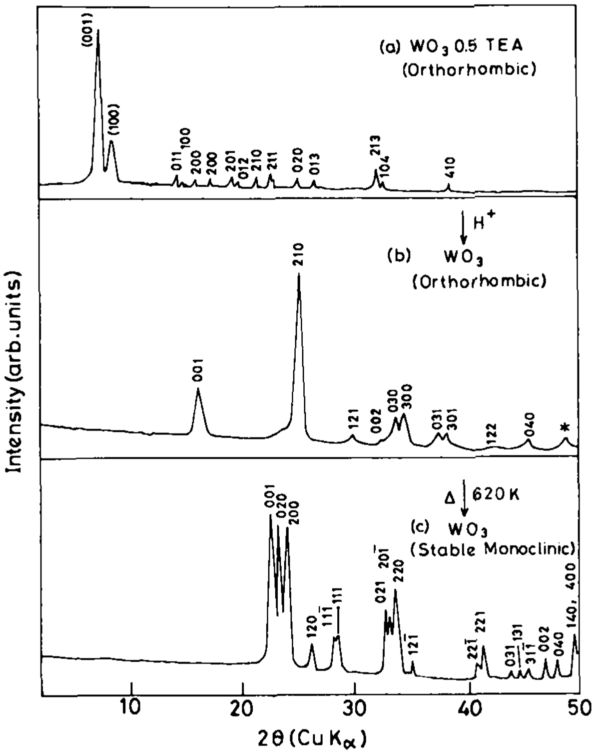

Fig. 5. Powder X-ray diffraction patterns of a) $WO_3 \cdot 0.5TEA$, b) orthorhombic WO_3 obtained by leaching $WO_3 \cdot 0.5TEA$ with acid and c) stable monoclinic WO_3 obtained by heating the orthorhombic WO_3 to 620 K.

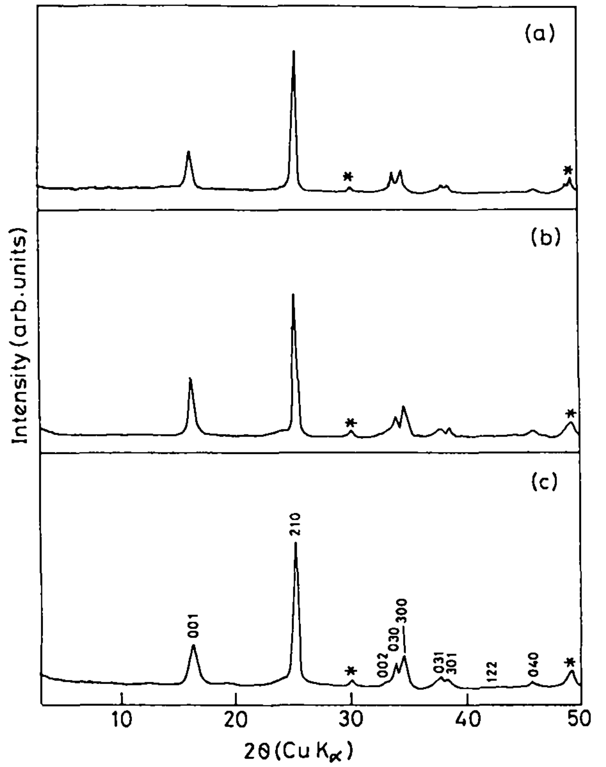

Fig. 6. Powder X-ray diffraction patterns of orthorhombic WO_3 obtained by acid leaching of a) $WO_3 \cdot pyr$, b) $WO_3 \cdot 0.85n\text{-}C_4H_9NH_2$ and c) $WO_3 \cdot n\text{-}C_8H_{17}NH_2$.

delicate process compared to deintercalation by heating. This is shown by the fact that the orthorhombic WO_3 obtained by leaching WO_3–amine intercalates retains the layered structure. There appears to be no real lattice reconstruction here. The orthorhombic form of WO_3 is however metastable and transforms to the stable monoclinic form at 620 K.

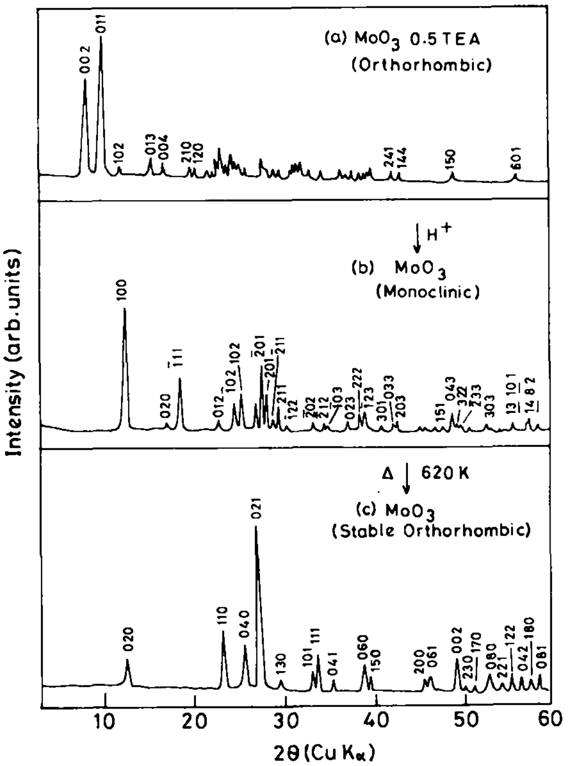

Fig. 7. Powder X-ray diffraction patterns of a) $MoO_3 \cdot 0.5TEA$, b) monoclinic MoO_3 obtained by leaching of $MoO_3 \cdot 0.5TEA$ (or $MoO_3 \cdot pyr$) with acid and c) stable orthorhombic MoO_3. For clarity, only a selection of the *hkl* indices are shown.

Acid leaching of $MoO_3 \cdot pyr$ and $MoO_3 \cdot 0.5TEA$ gave products with similar X-ray diffraction patterns (Fig. 7). The patterns can be indexed to a monoclinic unit cell with $a = 6.824$, $b = 10.126$ and $c = 8.146$ Å and $\beta = 91.85°$. The monoclinic form of MoO_3 is metastable and transforms to the stable orthorhombic MoO_3 at 620 K. The monoclinic form of MoO_3 obtained by leaching amine intercalates was different from β'-MoO_3, a metastable analogue of WO_3, reported by McCarron[2] ($a = 7.12$, $b = 5.37$ and $c = 5.57$ Å and $\beta = 91.9°$) and β-MoO_3 ($a = 7.42$, $b = 7.48$ and $c = 7.69$ Å and $\beta = 90.1°$) reported by Parise et al.[13]

Acid leaching of TEA adducts of $W_{1-x}Mo_xO_3$: Intercalation of $W_{1-x}Mo_xO_3$ ($x = 0.25$, 0.5, 0.75) with TEA gave products in which 0.5, 0.4 and 0.5 moles of the amine had been incorporated. The X-ray powder diffraction patterns can be indexed to orthorhombic cells. The unit cell parameters are given in Table 1. The unit cell volume of the intercalate decreases with increasing molybdenum content in the solid solution. Leaching these intercalates with acid resulted in formation of oxide products of orthorhombic structure, as can be seen from the X-ray powder diffraction patterns shown in Figure 8. The deintercalation process was confirmed by thermogravimetry (weight loss from the oxide product was <2%), and the absence of the amine bands in the infrared spectra. This result is interesting in that acid leaching gives oxide products of the same structure and unit cell dimensions regardless of the molybdenum content in $W_{1-x}Mo_xO_3$, although the unit cell dimensions of the parent oxides are different.

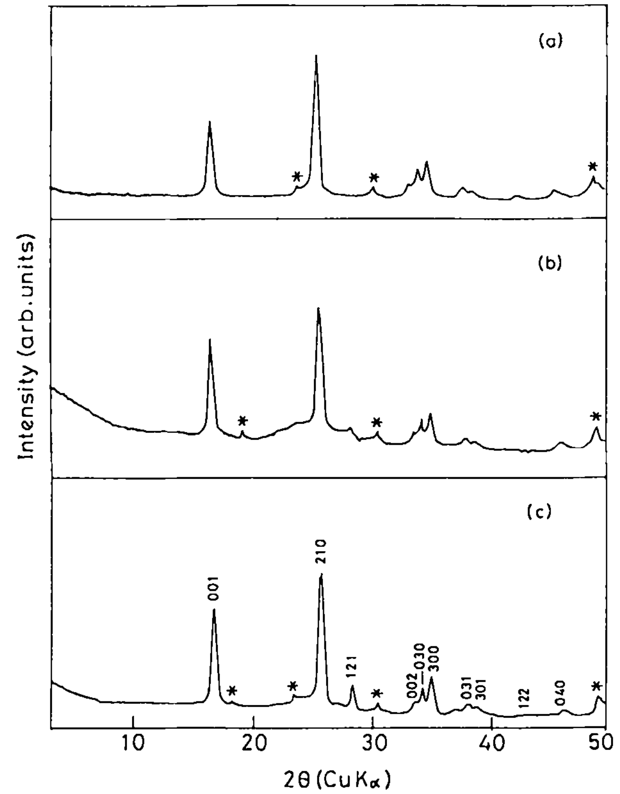

Fig. 8. Powder X-ray diffraction patterns of orthorhombic $W_{0.75}Mo_{0.25}O_3$, $W_{0.5}Mo_{0.5}O_3$ and $W_{0.25}Mo_{0.75}O_3$ obtained by leaching of the TEA intercalates with acid.

Conclusion

The present study demonstrates how the soft chemistry route, involving intercalation of amines in oxides such as WO_3 and MoO_3 followed by deintercalation, can produce novel forms of oxides. The coordination of the amine to the metal atom of the oxide host causes changes in the structure on deintercalation, which depend on the method adopted. In Table 2 we have listed unit cell parameters of the various forms of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ ($x = 0.25$, 0.5, 0.75) phases obtained by the deintercalation thermally or by leaching with acid. It might be thought that the products of deintercalation are the hydrogen bronzes H_xWO_3 and H_xMoO_3. It must, however, be noted that H_xWO_3 is generally blue or dark blue.[14] H_xMoO_3 is blue, green or red.[15] The data in Table 2 shows that the metastable phases of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ do not have the same colour or structure as the hydrogen bronzes. The oxides obtained by thermal decomposition of the intercalates were found to be different to those obtained by leaching with acid. The oxide product obtained by latter method, especially in the case of $WO_3 \cdot$ pyr, possesses a structure closer to that of the parent intercalation compound; this suggests that deintercalation by treatment with acid is milder than the thermal route, which involves lattice reconstruction.

Experimental Procedure

Powder X-ray diffraction patterns were recorded with a STOE X-ray diffractometer employing $Cu_{K\alpha}$ radiation and a position-sensitive detector (PSD). Indexing of the patterns and refinements were carried out with the help of the SADI/P package [16]. Samples of the intercalated and deintercalated WO_3, MoO_3 and $W_{1-x}Mo_xO_3$ for X-ray diffraction were prepared in a glove box. Electron diffraction patterns, high-resolution images and bright field images recorded on several crystals of each sample were obtained with a JEOL-200CX electron microscope operating at 200 kV. Samples for electron microscopy studies were prepared by grinding the powders finely in acetone medium, depositing them on carbon-coated grids. Electron spin resonance measurements were carried out at room temperature with a Varian E-109 X-band spectrometer with DPPH as the reference. Room temperature infrared spectra of samples in dry KBr pellets were recorded on a Bruker-IFS 113 V FT-IR spectrometer. Thermogravimetric analyses were carried out on a Cahn TG-131 system in a dry oxygen atmosphere with a heating rate of 10°min^{-1} from room temperature to 873 K. Elemental analysis for C, H and N was carried out with a Haraeus CHNO rapid analyser.

WO_3 was vacuum-dried before use. MoO_3 was purified by vapour-phase transport at 1070 K in oxygen. $WO_3 \cdot 2H_2O$, $WO_3 \cdot H_2O$ and $MoO_3 \cdot 2H_2O$ were prepared by literature procedures [4,5]. The unit cell dimensions of $WO_3 \cdot H_2O$ and $WO_3 \cdot 2H_2O$ were $a = 5.249$, $b = 10.711$, $c = 5.133$ Å and $a = 7.450$, $b = 6.926$, $c = 3.723$ Å, respectively. The unit cell dimensions of $MoO_3 \cdot 2H_2O$ were $a = 10.476$, $b = 13.822$, $c = 10.606$ Å and $\beta = 91.622°$. $W_{1-x}Mo_xO_3$ ($x = 0.25$, 0.5, 0.75) compositions were prepared by decomposition of the hydrates of corresponding compositions as described in the literature [3]. The unit cell dimensions of these solid solutions obtained from the X-ray powder data were as follows: $x = 0.25$: $a = 7.282$, $b = 7.508$,

Table 2. Novel metastable phases of WO_3, MoO_3 and $W_{1-x}Mo_xO_3$.

Oxide	Description (colour)	a/Å	b/Å	c/Å	Method of preparation
WO_3	stable, monoclinic (greenish yellow)	7.306(1)	7.540(1)	7.692(1) $\beta = 90.881(5)°$	
WO_3	metastable, cubic (pale green)	3.812(7)			$WO_3 \cdot 0.5$TEA heated at 670 K
WO_3	metastable,tetragonal (?) (pale green)	7.501(3)		3.324(4)	$WO_3 \cdot$ pyr heated at 670 K
WO_3	metastable, orthorhombic (greenish yellow)	7.793(3)	7.931(4)	5.388(6)	$WO_3 \cdot 0.5$TEA, $WO_3 \cdot 0.85C_4H_9NH_2$, $WO_3 \cdot$ pyr or $WO_3 \cdot n\text{-}C_8H_{17}NH_2$ leached with acid
MoO_3	stable, orthorhombic (pale green)	3.962(3)	13.858(4)	3.697(1)	
MoO_3	metastable, tetragonal (?) (pale green)	3.430(3)	–	7.635(3)	$MoO_3 \cdot 0.5$TEA heated at 620 K in vacuo
MoO_3	metastable, monoclinic (greenish yellow)	6.824(2)	10.126(5)	8.146(3) $\beta = 91.850(24)°$	$MoO_3 \cdot 0.5$TEA or $MoO_3 \cdot$ pyr leached with acid
$W_{1-x}Mo_xO_3$ [a]	metastable, orthorhombic (greenish yellow)	7.793(3)	7.931(4)	5.388(6)	$W_{1-x}Mo_xO_3 \cdot y$TEA leached with acid

[a] $x = 0.25$, 0.5, 0.75.

$c = 3.811$ Å, $\beta = 90.3°$, $V = 208.357$ Å^3; $x = 0.5$: $a = 7.36$, $b = 7.483$, $c = 3.931$ Å, $\beta = 90.6°$, $V = 215.722$ Å^3; $x = 0.75$: $a = 7.342$, $b = 7.475$, $c = 3.885$ Å, $\beta = 91.3°$, V = 213.160 Å^3. Pyridine was dried by prolonged refluxing over BaO followed by distillation. Reagent grade triethylamine, *n*-butylamine and *n*-octylamine were distilled twice and stored over activated molecular sieves.

$WO_3 \cdot 0.5$TEA was prepared by refluxing $WO_3 \cdot H_2O$ or $WO_3 \cdot 2H_2O$ with excess of TEA in the presence of activated molecular sieves for 4 d. The colourless product was isolated by filtration, washed with TEA and dried in vacuo. The thermogravimetric anyalysis (TGA) of this product (see Fig. 9) showed the composition of the intercalate to be $WO_3 \cdot 0.5$TEA (calcd wt. loss at 620 K, 17.89%; found, 17.7%). Elemental analysis: calcd C 12.5, H 2.70, N 2.11; found C 12.7, H 2.70, N 2.40. The X-ray powder diffraction pattern of $WO_3 \cdot 0.5$TEA can be indexed to an orthorhombic unit cell ($a = 9.731$, $b = 6.885$, $c = 11.273$ Å). Comparison of the observed and calculated spacings supports this structure (Table 3). The infrared spectrum of the intercalate shows the expected bands of the amine, though slightly shifted, in addition to new bands due to W=O and W–N stretching bands around 935 and 400 cm^{-1}, respectively. The ESR spectrum shows only a very weak signal due to W^{5+}, just as $WO_3 \cdot$pyr [6]. $WO_3 \cdot 0.5$TEA could also be prepared by refluxing dry WO_3 with excess TEA for 7 d. The intercalation of amine with the hydrates was, however, much faster than with dry WO_3. Prolonged refluxing of the amine with WO_3, $WO_3 \cdot H_2O$ or $WO_3 \cdot 2H_2O$ did not increase the extent of intercalation.

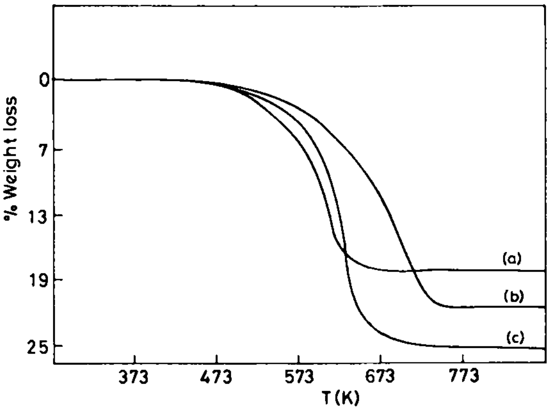

Fig. 9. Typical TGA curves: a) $WO_3 \cdot 0.5$TEA, b) $WO_3 \cdot 0.85n\text{-}C_4H_9NH_2$ and c) $MoO_3 \cdot 0.5$TEA.

Table 3. Observed and calculated X-ray diffraction patterns of $WO_3 \cdot 0.5$TEA.

hkl	d_{obs}	d_{calcd}	*hkl*	d_{obs}	d_{calcd}
001	11.325	11.273	211	3.743	3.747
100	9.764	9.731	020	3.444	3.442
011	5.882	5.876	013	3.294	3.298
110	5.604	5.620	021	3.294	3.292
102	4.884	4.877	104	2.704	2.707
201	4.469	4.467	214	2.299	2.299
112	3.983	3.980			

$MoO_3 \cdot 0.5$TEA was prepared by refluxing $MoO_3 \cdot 2H_2O$ with excess TEA for 5 d. The essentially colourless product was isolated by filtration, washed with TEA and vacuum dried. Thermogravimetric analysis (see Fig. 9) gave a weight loss of 25.65% (Calcd 25.97%) at 650 K. C·H·N analysis: calcd C 15.61, H 3.69, N 3.05; found C 15.56, H 3.86, N 3.60. The X-ray powder diffraction pattern of the intercalate can be indexed to an orthorhombic unit cell. The infrared spectrum of the intercalate shows the shifted bands of the amine in addition to bands due to Mo=O and Mo–N stretching bands around 940 and 400 cm^{-1}, respectively. Refluxing MoO_3 with TEA also resulted in the formation of the intercalate, but the reaction was considerably slower than for the hydrate. Prolonged refluxing of the amine with $MoO_3 \cdot 2H_2O$ did not lead to any increase in the extent of intercalation. The intercalate did not show an ESR signal due to Mo^V.

$WO_3 \cdot$pyr and $MoO_3 \cdot$pyr were prepared by the procedure of Johnson et al. [6,7]. Both $WO_3 \cdot$pyr and $MoO_3 \cdot$pyr were characterized by X-ray powder diffraction, thermogravimetry (observed wt. loss 24.8 and 34.7%, respectively, at around 620 K) and elemental analysis. The unit cell parameters of $WO_3 \cdot$pyr and $MoO_3 \cdot$pyr are $a = 35.296$, $c = 11.488$ Å and $a = 5.271$, $c = 11.477$ Å, respectively, in agreement with Johnson et al [6,7]. The bands in the infrared spectra of these two intercalates are similar to those reported in ref. [6,7]. $WO_3 \cdot$pyr: calcd C 16.36, H 1.58, N 3.89; found C 16.31, H 31.62, N 4.30. $MoO_3 \cdot$pyr: calcd C 26.1, H 2.06, N 6.11; found C 26.9, 3H 2.26, N 6.28.

WO_3 intercalates with $n\text{-}C_4H_9NH_2$ and $n\text{-}C_8H_{17}NH_2$ were prepared by refluxing $WO_3 \cdot H_2O$ or $WO_3 \cdot 2H_2O$ with the amine for 5 d in the presence of molecular sieves. Thermogravimetry and C·H·N analysis gave the compositions as $WO_3 \cdot 0.85n\text{-}C_4H_9NH_2$ and $WO_3 \cdot n\text{-}C_8H_{17}NH_2$. The observed weight losses in the TGA (typical curve in Fig. 9) were 21.3 and 36.0%, respectively, at 745 and 770 K. $WO_3 \cdot 0.85n\text{-}C_4H_9NH_2$: calcd C 16.29, H 3.67, N 4.61; found, C 3 4 g 216.33, H 3.74, N 4.76. $WO_3 \cdot n\text{-}C_8H_{17}NH_2$: calcd C 26.8, H 5.31, N 3.90; found, C 26.6, H 5.27, N 3.88. X-ray powder diffraction patterns of the two amine intercalates can be indexed to an orthorhombic unit cell. The infrared spectra show the characteristic bands of the amines, though shifted, as well as W=O and W–N stretching bands at around 925 and 475 cm^{-1}, respectively.

Intercalation of TEA in $W_{1-x}Mo_xO_3$ (x = 0.25, 0.5, 0.75) was achieved by refluxing the monohydrates of the oxide with the amine for 5 d. The compositions obtained were $W_{0.75}Mo_{0.25}O_3 \cdot 0.5$TEA, $W_{0.5}Mo_{0.5}O_3 \cdot 0.4$TEA and $W_{0.25}Mo_{0.75}O_3 \cdot 0.5$TEA as determined by thermogravimetry and elemental analysis. The observed weight losses in the TGA were 21.3, 15.1 and 23.4%, respectively, at 840, 820 and 770 K. The C·H·N analyses of the three compounds gave C 14.92, H 3.11, N 2.9; C 2.62, H 2.63, N 2.45; and C 16.63, H 3.47, N 3.23, respectively; these results agree with the calculated values. These compounds were characterized by X-ray powder diffraction, and the patterns could be indexed to an orthorhombic unit cell.

Procedure for deintercalation: Intercalates of WO_3 and MoO_3 with TEA and pyridine were heated very slowly to different temperatures in dry air or preferably in a dynamic vacuum, and X-ray powder diffraction patterns recorded at the different stages of heating. These patterns showed marked changes soon after deintercalation (at the minimum temperature for deintercalation as found by TGA), indicating the formation of new phases of WO_3 and MoO_3. Deintercalation at higher temperatures gave X-ray diffraction patterns of the stable phases of the oxides. Deintercalation of the amine intercalates was also carried out by treatment with acid (6 N HNO_3) for periods ranging between 24 h and 7 d at 330 K. The amine is leached out as an ammonium salt, leaving the oxide host in the solid state. It should be noted that WO_3 and MoO_3 themselves do not react with 6 N HNO_3. Infrared spectra of the deintercalated products were recorded to ensure the absence of the amines, and ESR spectra to ensure that there was no reduction of $W(Mo)^{VI}$ to $W(Mo)^V$. Elemental analysis of the deintercalated products did not show the presence of C, H or N.

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