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Thermal behaviour and properties of the $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$ Waugh phase

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Abstract

The thermal degradation of $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$ has been investigated by TG, DTA and TPR methods. The decomposition process in a stream of N_2 takes place in several steps. Only a reversible dehydration process occurs up to 200°C. The subsequent steps show the formation of $[(NH_4)O]_{0.083}MoO_3(H_2O)_{0.25}$ and MoO_3 phases. The reduction of $Mn^{(IV)}$ to $Mn^{(III)}$ can be considered to take place in this inert atmosphere.

Likewise, the TPR process clearly reveals the successive formation of Mo_4O_{11}, MoO_2 and metallic molybdenum. In this treatment the manganese seems to be incoporated in the Mo oxide lattices. Hence, the expansion of the MoO_2 cell volume, observed by XRD with the aid of DRS spectroscopy, presumably leads to the formation of the $Mo^{IV}_{0.9}Mn^{II}_{0.1}O_{1.9}$ solid solution. This last phase also affects the final process, increasing the temperature of molybdenum formation by 111°C, compared to the temperature of molybdenum formation from MoO_2. In this step the manganese segregates as MnO.

The $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$ vibrational spectrum was analysed and discussed on the basis of the different Mo–O bonds in the lattice. The magnetic measurements, together with other spectroscopical information, allow an estimation of the degree of covalence of the Mn–O bond to be made.

INTRODUCTION

Isopoly- and heteropolyanions containing molybdenum and tungsten are an important class of compounds whose structures are built up from sharing MO_6 $(M = W, Mo)$ octahedra [1]. A great number of these compounds have special properties such as high reactivity and structural versatility. They are also important in several fields of chemistry such as catalysis, biology, medicine, geochemistry, materials science and topology [2–4].

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The heteropolymolybdate $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$ and the isomorphous nickel(IV) compounds are the only known Waugh-type phases [1].

The crystal structure of the title compound has been analysed by Waugh et al. [5] and later by Allman and D'Amour [6]. Some spectroscopic studies, such as EPR, electronic spectral and MCD, have been reported [7, 11]. However, neither the thermal nor the magnetic behaviour, not a detailed vibrational analysis, have been performed. For this reason, these aspects are presented and discussed in this work.

EXPERIMENTAL

The $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$ phase was prepared according to Baker and Weakly [7] using a modification of Hall's original method [12].

The purity of the sample was checked by X-ray diffraction analysis using a Philips PW 1714 diffractometer and Cu Kα radiation (nickel filter). For the quantitative analysis, NaCl was used as an external calibration standard. The indexing of the diagram and refinement of the cell parameters were made using a modified form of Werner's PIRUM program [13]. The IR spectra were recorded with a Perkin-Elmer 580 B spectrophotometer using the KBr pellet technique. Raman spectra were obtained with a Spex-Ramalog 1403 double monochromator spectrometer, equipped with a SCAMP data processor. The 514.5 nm line of an Ar-ion laser was used for sample excitation. Because the sample was easily damaged by the laser, depending on the exposure time, the MoO_3 lines were generally observed. The diffuse-reflectance spectra were obtained on a Varian Superscan 3 spectrophotometer using $BaSO_4$ as reference.

The thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Rigaku CN 8002 L2 Thermoanalyser. The measurements were performed in an N_2 stream (0.4 l min^{-1}) and the temperature was raised to 500°C (heating rate 10°C min^{-1}). The specimen was analysed against α-Al_2O_3 as reference. Additional thermal studies were carried out in a crucible furnace using a Pt crucible. These samples were also investigated by XRD, IR and DRS techniques.

The reduction studies were carried out by means of the temperature-programmed reduction technique (TPR) and the reactor was fed with a 10% H_2 reducing agent in an N_2 stream, from 20 to 1000°C at a heating rate of 10°C min^{-1}. The hydrogen consumed was detected by a thermal conductivity cell. The magnetic behaviour was analysed using a DSM-5 pendule magnetometer in the temperature range 4–300 K. $Hg[Co(SCN)_4]$ was used as a standard.

VIBRATIONAL BEHAVIOUR

The $[MnMo_9O_{32}]^{6-}$ heteropolyanion is built up around a manganese atom octahedrally surrounded by oxygen atoms; it is linked by shared edges to three MoO_6 octahedral groups in the same plane. This configuration is related somewhat to the $[MMo_6O_{24}]^{n-}$ Anderson heteropolyanion [14] from which the Waugh anion can be formally derived, if three alternate MoO_6 octahedra are removed from the plane. But unlike Anderson phases, this compound possesses two additional layers: groups of three MoO_6 polyhedra sharing edges and with a common corner, over and under the central plane containing the heteroatom. Thus, there are three types of oxygen atoms in the framework: terminal (unshared); linked to two molybdenum atoms; and linked to three molybdenum atoms and one manganese atom.

For the vibrational analysis, it is convenient to consider the different types of Mo–O bonds, as in the vibrational study of some other isopoly- and heteropolymetalates [15–23]. According to the structure, three types of Mo–O bonds can be clearly distinguished in the $[MnMo_9O_{32}]^{6-}$ framework: $Mo–O_2$ terminal groups ($Mo–O_t$); Mo–O–Mo bridge bonds involving Mo atoms located in the self plane (top or bottom) or interplane (top-middle, bottom-middle); Mo–O–Mn bonds.

Figure 1 shows the vibrational spectrum of $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$. The spectrum can be divided into the following typical regions: 3600–2800 cm^{-1} corresponding to the O–H and N–H stretchings; 1700–1400 cm^{-1} the region of the O–H and N–H bendings; 1000–850 cm^{-1}, assignable to the $Mo–O_2$ terminal stretchings; 700–500 cm^{-1} assignable to the Mo–O–Mo bridge stretchings (the vibrations of the $Mn–O_6$ bonds [24] and the water librations [25, 26] are also located in this last region.) Below 500 cm^{-1} the spectrum is rather difficult to analyse; the Mo–O–Mn bridge stretchings, the deformations of the $Mo–O_2$ terminal groups, the Mo–O–Mo bendings, the NH_4 librations [27], and also the lattice modes, all appear between 500 and 200 cm^{-1}.

An empirical expression that correlates the Mo–O Raman stretching frequencies with their bond distances has been recently developed [28] and allows the assignment to be corroborated knowing the distances: $v\ (cm^{-1}) = 32895 \exp(-2.073R)$, where R is the distance expressed in Å.

The bond length associated with the $Mo–O_t$ stretching is 1.70 Å, while the distances associated with the Mo–O–Mo bridges and Mo–O–Mn bonds are 1.97 and 2.22 Å respectively [6]. These distances are related to the Raman lines located at 955, 550 and 330 cm^{-1} respectively.

Table 1 gives the frequencies and assignment of the $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$ vibrational spectrum.

Finally, it is also possible to calculate the force constants of stretching and stretch–stretch interaction for the $Mo–O_2$ terminal groups by using the Cotton and Wing secular equation [29]. Their values of $k_r = 7.11$ mdyn $Å^{-1}$ and $k_{rr} = 0.45$ mdyn $Å^{-1}$ respectively, are in good agreement with those observed in similar systems, confirming an important Mo–O π-bonding [29].

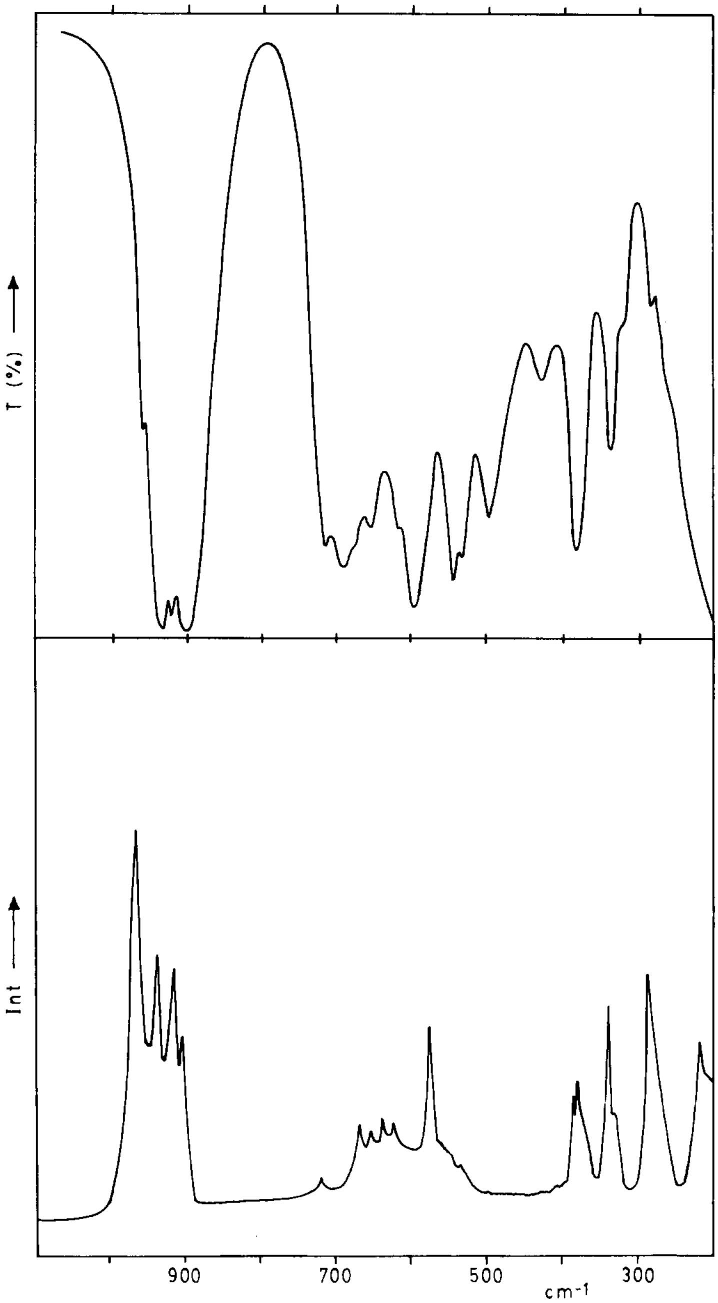

Fig. 1. Vibrational spectrum of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$ (between 1000 and 200 cm^{-1}).

TABLE 1

Assignment of the vibrational spectrum of the typical Waugh phase $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$ (cm^{-1})

IR	Raman	Assignment
3513 s	3490 vw	
3144 vs		ν_1, ν_3H_2O
3019 sh	2985 vw	ν_1, $\nu_3NH_4^+$
2799 sh		
1660 w		$\delta NH_4^+(\nu_2)$
1635 m		$\delta H_2O(\nu_2)$
1620 sh		
1450 sh	1428 w	$\delta NH_4^+(\nu_4)$
1399 vs		
1082 vw		2 Lib. H_2O
955 sh	965 s	
941 sh	938 m	$\nu_sMo–O_t$
933 vs		
920 s	919 m	$\nu_{as}Mo–O_t$
901 vs	902 m	
716 sh	718 vw	
690 s		
679 sh	669 w	
656 m	661 w	νMo–O (bridges)
	650 w	$+\nu$MnO
616 sh	613 w	
595 s	578 m	
	574 sh(br)	
543 m	530 (br)	Lib. H_2O
532 sh		
496 m		
425 w		νMo–O–Mn
379 s	377 w	δMo–O
	371 w	δMn–O
334 m	336 m	
318 sh	329 sh	Lib. NH_4^+
281 sh	284 m	Lattice modes
	214 w	

Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

MAGNETIC BEHAVIOUR

The temperature dependence of the reciprocal magnetic susceptibility of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$ is shown in Fig. 2. The compound obeys the Curie law in the studied range of temperature. The magnetic moment evaluated from the slope of the χ^{-1} versus T plot is 3.84 BM which is

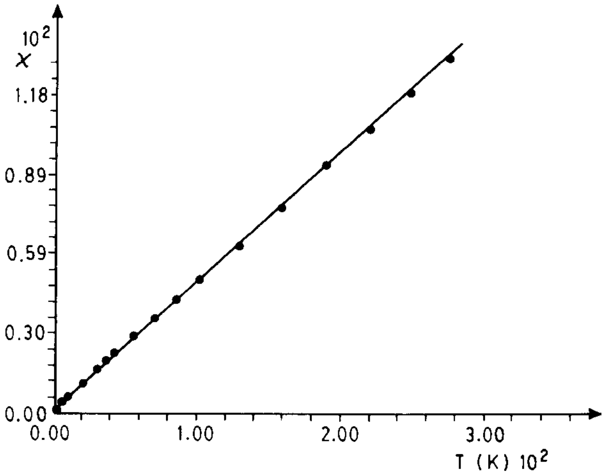

Fig. 2. Reciprocal magnetic susceptibility vs. temperature of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$.

slightly lower than the prediction according to the spin only (3.87 BM).

Employing the "free" ion spin orbit coupling constant $\lambda = 138.3\,cm^{-1}$ [30] and using the electronic and EPR spectroscopic data [7–9, 11], it is possible to estimate the reduction in the delocalization k parameter, which determines the degree of covalence of the Mn–O bond.

An average g value of 1.989 can be calculated from the $g_{\parallel} = 1.992$ and $g_{\perp} = 1.988$ data in the literature [8] for D_3 symmetry. Likewise from the electronic spectra and considering the $^4T_{2g} \leftarrow A_{2g}$ first-allowed spin transition for a d^3 ion in octahedral coordination, which is split in two bands at 20700 and 21400 cm^{-1} [11] due to the axial symmetry, a mean value of 21050 cm^{-1} is obtained for $10Dq$.

Hence, from the expressions [30] $g = 2.0023(1 - 4k^2\lambda_0/10Dq)$ and $\mu = \mu^{so}(1 - 4k^2\lambda_0/10Dq)$, a k value of 0.5 is obtained.

Although the quantitative interpretation of the orbital reduction parameter is problematic and of limited accuracy, there is considerable evidence that it tends to decrease as the covalence of the metal–ligand bond increases [31].

It is evident that the magnetic susceptibility values seem to be affected in a certain way by the covalent contribution; therefore, there is an excellent agreement between the μ value obtained using the above equation and the experimental value.

The k value is an indication that the metal d-electrons are considerably delocalized and partially concentrated on the polymolybdate "ligand". Moreover the high intensity of the bands in the electronic spectrum suggests that the electronic transitions are not pure d–d, involving some charge-transfer character [7].

THERMAL BEHAVIOUR

Thermogravimetric and differential thermal analyses

Figure 3 shows typical TG and DTA curves. It can be observed that eight water molecules are lost in the first step, and $(NH_4)_6[MnMo_9O_{32}]$ anhydrous phase is formed. This process takes place at 158°C and is reversible. In fact the experimental weight loss of 8.60% (theoretical value = 8.56%) is recovered after rehydration by recrystallization. Likewise, the IR spectra of samples heated up to 200°C do not show, in practice, appreciable changes between 1200 and 200 cm^{-1} in comparison with that corresponding to the original compound. However, there is a slight variation in the 500 cm^{-1} region (where the water librations occur).

The second endothermic peak at 230°C is correlated to the loss of 4.5 molecules of NH_3 and the incipient formation of the intermediate $[(NH_4)_2O]_xMoO_3(H_2O)_y$, $x = 0.083$ and $y = 0.25$, the molybdic phase [32]. The XRD pattern reveals poor crystallinity at this temperature, but the experimental weight loss (4.60%) agrees with the theoretical value (4.54%). The third small endothermic peak at 292°C, with a very small weight loss (≈1%), seems to be related to the reduction of Mn(IV), involving the evolution of $0.5O_2$, with probable formation of an Mn(III) compound.

As is known MnO_2 transforms into Mn_2O_3 in air at 530°C, although

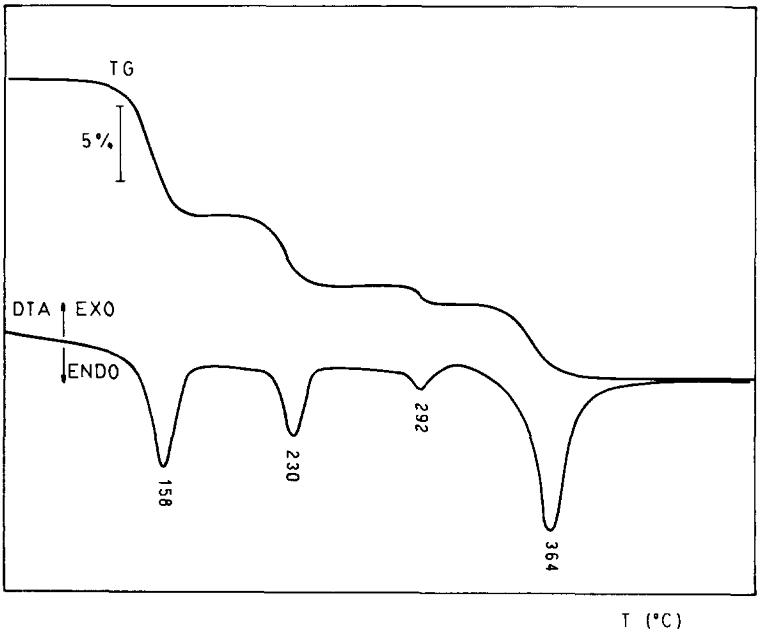

Fig. 3. TG and DTA curves of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$.

the weight loss begins at 350°C [33]. In this case, the reduction process is probably favoured by the presence of NH_3, a situation similar to that observed in the decomposition of Mo(VI) compounds [34]. However, at 300°C, $[(NH_4)_2O]_{0.083}MoO_3(H_2O)_{0.25}$ is a well-crystallized phase and no signal for reduced molybdenum is observed. Nevertheless, the manganese might be mainly present as Mn(III), but no X-ray diffraction lines of any one manganese-compound could be detected at this temperature.

Diffuse reflectance spectroscopy does not suggest the presence of Mn(III) either, because Mn(IV) bands between 400 and 600 nm are present [35]. Therefore unfortunately, the question cannot be clearly resolved. However, from 400°C, a weak band at 590 nm begins to appear.

Finally, the decomposition of $[(NH_4)O]_{0.083}MoO_3(H_2O)_{0.25}$ occurs at 364°C, in agreement with the literature data, with a weight loss of 4.70% and formation of MoO_3 (theoretical weight loss, 4.72%).

According to these results, the following overall decomposition scheme, (total experimental weight loss, 18.88%; theoretical, 18.78%) can be suggested.

$$(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O \xrightarrow{158°C} 8H_2O + (NH_4)_6[MnMo_9O_{32}]$$

$$(NH_4)_6[MnMo_9O_{32}] \xrightarrow{230°C} 9([(NH_4)_2O]_{0.083}MoO_3(H_2O)_{0.25})$$

$$+ 4.5NH_3 + MnO_2?$$

$$Mn(IV) \xrightarrow{292°C} Mn(III), \qquad (MnO_2 \xrightarrow{292°C} 0.5Mn_2O_3 + 0.5H_2O)?$$

$$[(NH_4)_2O]_{0.083}Mo_3(H_2O)_{0.25} \xrightarrow{364°C} 9MoO_3 + 1.5NH_3 + 3H_2O$$

Temperature-programmed reduction measurements

Temperature-programmed reduction (TPR) provides information about the reducibility of the Mo(VI) and Mn(IV) species present in the heteropoly compound. It is well known that the results are usually conditioned by external factors such as the crystal size, heating rate, etc. However, in our working conditions, two discrete reduction steps, which can be attributed to the reduction of molybdenum are clearly observed.

The TPR pattern of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$ is shown in Fig. 4(b), where the reduction behaviour of ammonium heptamolybdate and MnO_2 are also included for comparative purposes. The ammonium heptamolybdate shows two peaks at 721 and 843°C corresponding to the formation of MoO_2 and metallic molybdenum, while MnO_2 presents important signals at 370 and 398°C, attributable to successive reductions to Mn(III) and Mn(II) with the final formation of cubic MnO by the highest temperature reached (1000°C).

The reduction of the Waugh phase was performed using the same procedure as for the TPR measurement, but stopping the reduction at

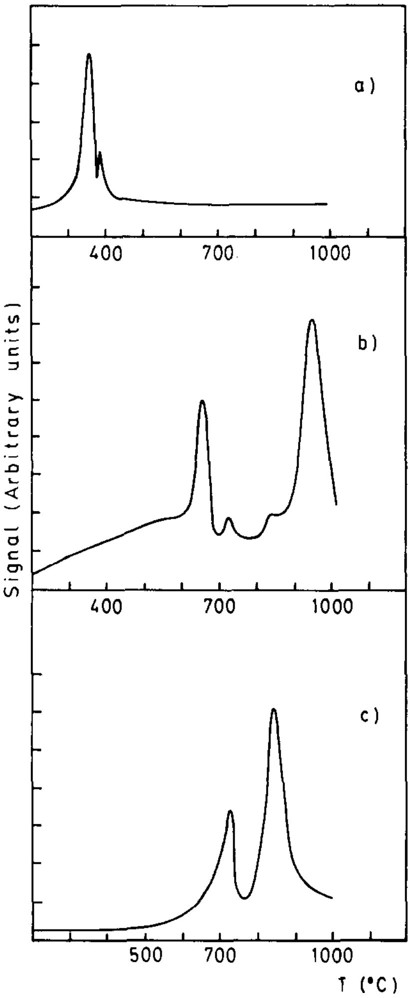

Fig. 4.TPR patterns of (a) MnO_2, (b) $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$, (c) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

pre-determined temperatures. This allows the intermediates to be identified by XRD and other spectroscopic techniques, such as IR and diffuse reflectance spectroscopy.

The reduction sequence for the Mo(VI) species is

$$(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O \xrightarrow{400°C} MoO_3 \xrightarrow{500°C}$$
$$Mo_4O_{11} \xrightarrow{664°C} MoO_2 \xrightarrow{954°C} Mo$$

The subsequent formation of molybdenum nitride can be avoided by manipulation of the time and heating rate [36].

The presence of the Mo_4O_{11} intermediate as a unique phase is observed at 500°C, while MoO_2 appears at 550°C and becomes the unique phase at 664°C. Between this last temperature and 950°C, the XRD patterns are characteristic of the monoclinic MoO_2 oxide, with the diffraction lines at lower angles than for the stoichiometric MoO_2 compound (ASTM file 5-452); the cell volume becomes 9‰ larger, $a = 5.625(2)$ Å, $b = 4.854(5)$ Å, $c = 5.534(2)$ Å, $\beta = 119.73(4)°$.

However, up to 500°C the XRD patterns show very weak additional lines that can be assigned to the manganese compounds. Due to the small manganese content in the lattice, diffuse reflectance spectroscopy seems to be the best technique for detecting this element as well as its oxidation state. Therefore, the following sequence for Mn(IV) can be suggested.

$$\text{Mn(IV) (original compound)} \xrightarrow{300°C} \text{Mn(III)} \xrightarrow{500°C} \text{Mn(II)}$$

The stability range of the trivalent species (as Mn_2O_3) is very narrow, and can be established at approximately 200°C, according to the presence of a weak, broad band centred at 590 nm which is characteristic of the $^5E_g \rightarrow {}^5T_{2g}$ transition of this d^4 ion in an octahedral environment [37–39]. These results are also in agreement with those observed in the study of the incorporation and reducibility of manganese ions in some oxidic systems [40]. In fact, because this band is totally destroyed by heating at 650°C, the Mn(II) is expected to be incorporated into the MoO_2 lattice, forming a mixed oxide with anion vacancies. The solid solution can be formulated as $Mo^{IV}_{0.9}Mn^{II}_{0.1}O_{1.9}$ and correlated to the expansion of the monoclinic MoO_2 unit cell, with the correspondent ionic radius r(Mo(IV)) being 0.65 Å and r(Mn(II) (high-spin)) being 0.83 Å [41].

Finally, the last step in the reduction of molybdenum leading to the formation of metallic Mo phase, is evidently affected by the presence of the manganese in the oxide phase. In fact, the $Mo_{0.9}Mn_{0.1}O_{1.9}$ structure is more resistant to the reduction than the MoO_2 stoichiometric phase, increasing the temperature of this process by 111°C. We believe that manganese segregation occurs in the form of MnO but only two very weak diffraction lines of this oxide ($d = 2.568$ and 1.571) could be detected on the diffraction pattern of samples heated at 1000°C. However, MnO microcrystals can be very well dispersed in a molybdenum matrix, which makes is observation very difficult.

CONCLUSIONS

From the thermal treatment, it can be established that:

(a) In an inert atmosphere (N_2), the process takes place via the formation of $[(NH_4)O]_{0.083}MoO_3(H_2O)_{0.25}$ and MoO_3. Manganese is not incorporated in the MoO_3 lattice.

(b) When the process occurs in a more reduced atmosphere (H_2–N_2), there is evidence for the formation of $Mo_{0.9}Mn_{0.1}O_{1.9}$ solid solution. Likewise, this compound seems to be responsible for the increase in the temperature of the reduction to metallic molybdenum.

(c) The assignment of the vibrational spectrum is confirmed by an empirical expression using the Mo–O bond distances.

(d) The magnetic measurements allow an estimation of the degree of covalence of the Mn–O bond.

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