

IR AND THERMAL STUDIES ON LITHIUM OXOMOLYBDENUM(VI) OXALATE

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A new molybdenum(VI) complex, $\text{Li}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot 2 \text{H}_2\text{O}$ (LMO), was prepared and characterized by chemical analysis and IR spectral studies. Its thermal decomposition was studied by using TG and DTA techniques. LMO loses its two moles of water between 75 and 170° to give the anhydrous product, which decomposes in three stages between 240 and 380°. The first two stages occur in the temperature ranges 240–280° and 280–305°, to give intermediates with the tentative compositions $\text{Li}_6[\text{Mo}_6\text{O}_{19}(\text{C}_2\text{O}_4)_2]$ and $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$, respectively. In the third stage, which extends up to 380°, $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$ decomposes to give the end-product, $\text{Li}_2\text{Mo}_2\text{O}_7$.

Molybdenum(VI) forms a number of oxalato complexes [1]. We recently prepared and studied the thermal decomposition of $\text{Na}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot 4 \text{H}_2\text{O}$ [2] and $\text{A}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)]$, where $\text{A} = \text{K}^+$, NH_4^+ [3]. The present paper deals with the preparation, characterization and thermal decomposition of a new molybdenum(VI) complex, $\text{Li}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot 2 \text{H}_2\text{O}$ (LMO).

Experimental

All the reagents used were BDH products of AnalaR or pro analysi grade. To a hot solution of a mixture containing 1.019 g lithium oxalate and 1.2605 g oxalic acid in about 200 ml distilled water, 4.3185 g MoO_3 (prepared by heating ammonium paramolybdate to about 400° for 2 hr) was added and dissolved in small portions. The solution was filtered to remove any unreacted MoO_3 . A dilute solution of lithium hydroxide was then added and the pH of the solution was adjusted to 3.0. On concentration to about 40 ml and then keeping in the fridge at 5–6° for about 45 days, the solution gave white crystals, which were washed with water and air-dried in a desiccator.

Molybdenum in the LMO was determined gravimetrically as molybdenum oxinate, oxalate by KMnO_4 oxidation, and lithium by atomic absorption spectroscopy. The results of the chemical analysis are: Li^+ 3.23%, Mo 45.01% and $\text{C}_2\text{O}_4^{2-}$ 20.68%; the calculated values for $\text{Li}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot 2 \text{H}_2\text{O}$ are: Li^+ 3.26%,

Mo 45.07% and $C_2O_4^{-2}$ 20.66%. These data confirm that the composition of LMO is $Li_2[Mo_2O_6(C_2O_4)] \cdot 2 H_2O$.

Thermogravimetry (TG) was carried out using a Stanton Redcroft TG 770 thermo-balance. 5–10 mg of sample was used, and the heating rate was 3 deg min^{-1} . DTA curves were taken on a Fischer 260 P differential thermalyser, fitted with an automatic voltage stabilizer, amplifier and recorder. 100–150 mg sample were taken in quartz crucibles, and the heating rate was 10 deg min^{-1} . IR spectra were recorded on a Beckman IR-20 double beam instrument in the range $250\text{--}4000 \text{ cm}^{-1}$, with samples in the form of KBr pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using $Cu\text{--}K_\alpha$ radiation.

Results and discussion

LMO is a white, highly hygroscopic powder, which was kept under anhydrous conditions. The X-ray diffraction pattern of LMO reveals that it is a crystalline compound. The results of the IR studies (Fig. 1A) are summarized in Table 1; the normal bands for the coordinated oxalato group have been assigned on the basis of literature data [4, 5]. The two strong bands at 920 and 900 cm^{-1} suggest the presence of metal–oxygen double bonds, and the bands at 840 and 640 cm^{-1} can be assigned to the asymmetric and symmetric Mo–O stretches, respectively [6–8].

Figure 2 gives the DTA, TG and differential thermogravimetric (DTG) curves for LMO in static air atmosphere. The curves show that the dehydration of LMO takes place in a single step, while the decomposition of oxalate is found to be a multistep process. The various stages are discussed in detail below.

Dehydration

As seen from the TG data, LMO is stable up to 75° . It loses both of its water molecules in a single step between 75 and 170° . This is observed in the DTG plot as a peak at 125° , while the DTA curve shows an endothermic peak at around 120° . The observed weight loss is 8.42%, against the calculated value of 8.45%.

Decomposition of oxalate

Anhydrous LMO is stable up to 240° , and then decomposes in three stages between 240 and 380° , to give the end-product lithium dimolybdate. The first stage extends up to 280° and corresponds to the loss of one mole of carbon monoxide and one mole of carbon dioxide per three moles of anhydrous LMO, to give an intermediate with the tentative composition $Li_6[Mo_6O_{19}(C_2O_4)_2]$. For this reaction the DTG curve shows a maximum at 265° , while the DTA curve shows an endothermic peak at 260° . The observed weight loss is 5.62%, against the calculated value of 5.64%. In the second stage, between 280 and 305° , one more mole each of carbon monoxide and carbon dioxide are lost, to give another intermediate, with the tentative com-

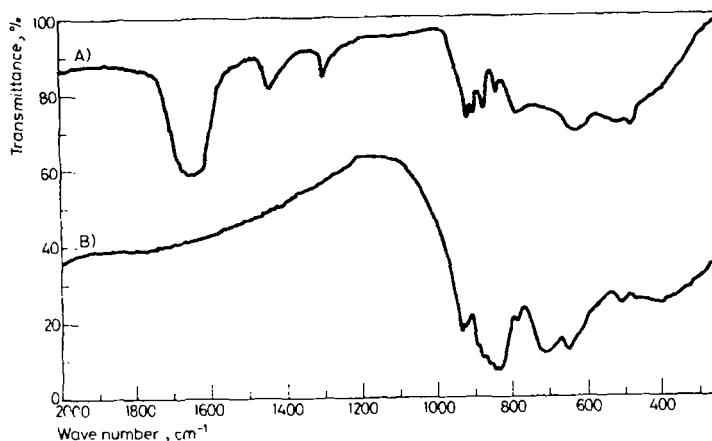


Fig. 1 IR spectra of LMO (A) and LMO heated to 550 °C (B)

Table 1 IR absorption bands of LMO, and their probable assignments

Frequency, cm^{-1} [±]	Probable assignment ^{**}
3500 s, br	$\nu(\text{OH})$ of uncoordinated water
1660 vs	$\nu_{\text{as}}(\text{C}=\text{O})$
1440 s	$\nu_{\text{sym}}(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$
1300 s	$\nu_{\text{sym}}(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
920 s	$\nu_{\text{as}}(\text{Mo}=\text{O})$
900 s	$\nu_{\text{sym}}(\text{Mo}=\text{O})$
880 s	$\nu_{\text{sym}}(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
840 s	$\nu(\text{O}-\text{Mo}-\text{O})$
790 s	$\delta(\text{O}-\text{C}=\text{O}) + \nu(\text{M}-\text{O})$
640 s, br	$\nu(\text{O}-\text{Mo}-\text{O})$
530 w, br	$\nu(\text{M}-\text{O}) + \nu(\text{C}-\text{C})$
485 w	ring deformation + $\delta(\text{O}-\text{C}=\text{O})$

* vs = very strong, s = strong, br = broad, w = weak;

** sym = symmetric, as = asymmetric, δ = bending.

position $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$. This is observed in the DTG and DTA plots as peaks at 290 and 295°, respectively. The observed weight loss is 5.73%, while the calculated value is 5.63%. The third stage occurs between 305 and 380° and corresponds to the decomposition of $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$ with the loss of one more mole each of carbon monoxide and carbon dioxide, to give the end-product $\text{Li}_2\text{Mo}_2\text{O}_7$, the DTG and DTA curves both showing peaks at 350°. The observed weight loss is 5.51%, against the calculated value of 5.62%. The differences between the observed and the calculated values in the second and the third stages may be attributed to the partial overlap

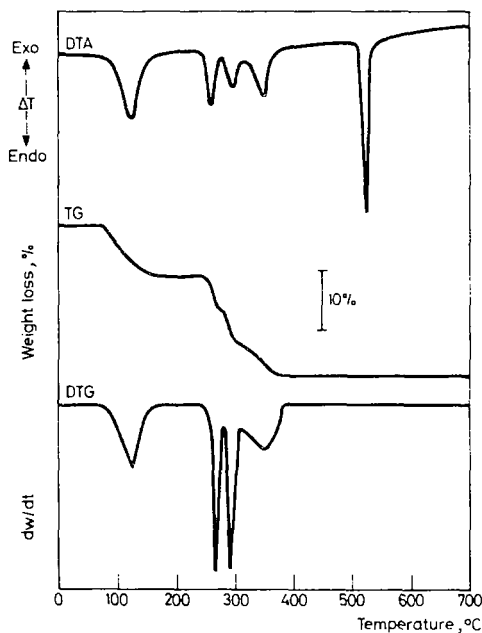
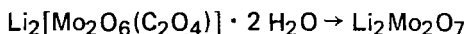


Fig. 2 DTA, TG and DTG curves of LMO in air

of the two steps. The compositions of the two intermediates are well supported by the IR spectra of the samples obtained by heating LMO isothermally at 285 and 315°, respectively. Both spectra indicate the complete absence of carbonate and show the presence of only coordinated oxalate group. The total observed weight loss for the process



is 25.28%, compared to the calculated value of 25.36%.

The absence of any exothermic peak in the DTA plot during oxalate decomposition, that might have appeared due to the oxidation of carbon monoxide to carbon dioxide, is probably due to the geometry of the sample container, which does not permit the free access of air. This makes the chances of oxidation of carbon monoxide to carbon dioxide negligible. Moreover, carbon monoxide is accompanied by the evolution of carbon dioxide. Similar behaviour has been observed during DTA studies on other oxalato compounds on this instrument [9, 10].

Melting

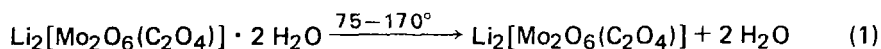
An additional DTA peak is observed at 525°, with no corresponding weight change in the TG curve. This has been attributed to melting of the end-product (melting point of $\text{Li}_2\text{Mo}_2\text{O}_7$ 530°). When LMO is heated isothermally at $535 \pm 5^\circ$, a molten product is obtained which immediately solidifies to a white crystalline compound, confirming that the peak at 525° is due to melting.

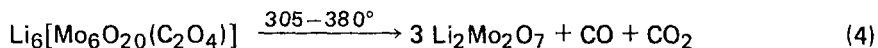
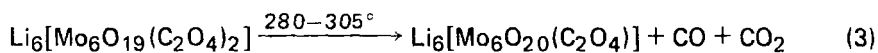
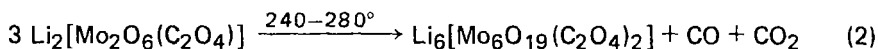
Table 2 d values (Å) for $\text{Li}_2\text{Mo}_2\text{O}_7$ ($\lambda = 1.5405 \text{ \AA}$)

Observed	Reported
7.000	7.02
6.275	6.27
5.574	5.57
5.121	5.12
4.442	4.44
4.269	4.27
4.170	4.17
3.878	3.88
3.789	3.79
3.560	3.56
3.490	3.49
3.409	3.41
3.351	3.35
3.235	3.23
3.167	3.17
3.139	3.14
3.105	3.10
3.018	3.02
2.910	2.91
2.694	2.696
2.645	2.649
2.565	2.561
2.420	2.427
2.378	2.378
2.295	2.296
2.260	2.263
2.190	2.194
2.175	2.174
2.139	2.139
2.012	2.013

The end-product was characterized by chemical analysis, and IR spectral and X-ray diffraction studies on the samples obtained by heating LMO isothermally at 400 and 550°. The two products gave identical chemical analyses, IR spectra and X-ray diffraction patterns. These observations reveal the formation of pure $\text{Li}_2\text{Mo}_2\text{O}_7$ without any other phase. The IR spectrum (Fig. 1B) compares well with those of $\text{K}_2\text{Mo}_2\text{O}_7$ [3] and $\text{Na}_2\text{Mo}_2\text{O}_7$ [2, 11]. The observed d values also closely match the earlier-reported data [12]. A comparison of the observed and reported d values is given in Table 2.

On the basis of all these studies, the following scheme may be proposed for the thermal decomposition of LMO:





Equation (1) represents the dehydration of LMO to give the anhydrous product, which decomposes according to Eqs (2), (3) and (4) to give the end-product, $\text{Li}_2\text{Mo}_2\text{O}_7$. The mechanism proposed here is a tentative one, based on the results obtained from dynamic thermogravimetry and isothermal studies.

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Zusammenfassung – Ein neuer Molybdän(VI)-Komplex der Formel $\text{Li}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot 2 \text{H}_2\text{O}$ (LMO) wurde dargestellt und durch chemische Analyse und IR-spektroskopisch charakterisiert. Die thermische Zersetzung dieses Komplexes wurde mittels TG und DTA untersucht. LMO verliert die zwei Wassermoleküle zwischen 75 und 170° unter Bildung des wasserfreien Produktes, das zwischen 240 und 380° in drei Stufen zersetzt wird. Die in den Temperaturbereich von 240–280° und 280–305° verlaufenden ersten zwei Reaktionsschritte ergeben Intermediäre der tentativen Zusammensetzung $\text{Li}_6[\text{Mo}_6\text{O}_{19}(\text{C}_2\text{O}_4)_2]$ bzw. $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$. In dem sich bis 380° erstreckenden dritten Reaktionsschritt wird $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$ unter Bildung des Endproduktes $\text{Li}_2\text{Mo}_2\text{O}_7$ zersetzt.

Резюме – Получено новое комплексное соединение шестивалентного молибдена с общей формулой $\text{Li}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot 2 \text{H}_2\text{O}$ и идентифицированное химическим анализом и ИК спектроскопией. Термическое разложение комплекса изучено методом ТГ и ДТА. В интервале температур 70–170° соединение теряет две молекулы воды, образуя безводное

соединение, разлагающееся в три стадии в интервале температур 240–380°. Первые две стадии протекают в области температур 240–280° и 280–305° с образованием промежуточных продуктов состава $\text{Li}_6[\text{Mo}_6\text{O}_{19}(\text{C}_2\text{O}_4)_2]$ и $\text{Li}_6[\text{Mo}_6\text{O}_{20}(\text{C}_2\text{O}_4)]$. Последнее соединение разлагается на третьей стадии при температуре до 380° с образованием конечного продукта $\text{Li}_2\text{Mo}_2\text{O}_7$.