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Note

PREPARATION OF LITHIUM TETRA MOLYBDATE BY THE THERMAL DECOMPOSITION OF LITHIUM OXOMOLYBDENUM(VI) OXALATE

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The preparation of mixed oxides by various methods has been of great interest to inorganic chemists and ceramic research workers. Mixed metal oxalates have been used as precursors for the preparation of important materials such as $BaTiO_3$ [1] and $ZnZrO_3$ [2]. Molybdenum(VI) forms a number of oxo compounds, some of which are oxalate complexes [3]. Recently, $Na_2Mo_2O_7$ [4], $K_2Mo_2O_7$ [5], $BaMoO_4$ [6] and Li_2MoO_4 [7] have been prepared by the thermal decomposition of the different mixed metal oxalates. The present paper deals with the preparation, characterization and thermal decomposition of a new molybdenum(VI) oxalato complex, $Li_2[Mo_4O_{12}(C_2O_4)] \cdot 3\ H_2O$ (LMO), which gives $Li_2Mo_4O_{13}$ as end product.

EXPERIMENTAL

All the reagents used were either of Analar or Proanalysi grade. To a hot solution of 1.019 g of lithium oxalate in about 200 ml of distilled water was added 2.879 g of MoO_3 (prepared by heating ammonium paramolybdate at 400 °C for 2 h), and, thus, a saturated solution of MoO_3 in lithium oxalate solution was obtained. The solution was filtered to remove any unreacted MoO_3 and the filtrate was concentrated to about 30 ml. This, on keeping in a fridge at 6–7 °C for about two months, gave white crystals which were filtered, washed with cold water and dried in a vacuum desiccator.

Molybdenum in LMO was determined gravimetrically as molybdenyl oxinate and oxalate by $KMnO_4$ oxidation. Lithium was estimated by atomic absorption spectroscopy. The analysis of the sample gave: Li^+, 1.90; Mo, 52.39; $C_2O_4^{2-}$, 12.00%, while the calculated values for $Li_2[Mo_4O_{12}(C_2O_4)] \cdot 3\ H_2O$ are: Li^+, 1.89; Mo, 52.45; $C_2O_4^{2-}$, 12.02%. These data show that there is no noticeable deviation for LMO with the composition $Li_2[Mo_4O_{12}(C_2O_4)] \cdot 3\ H_2O$.

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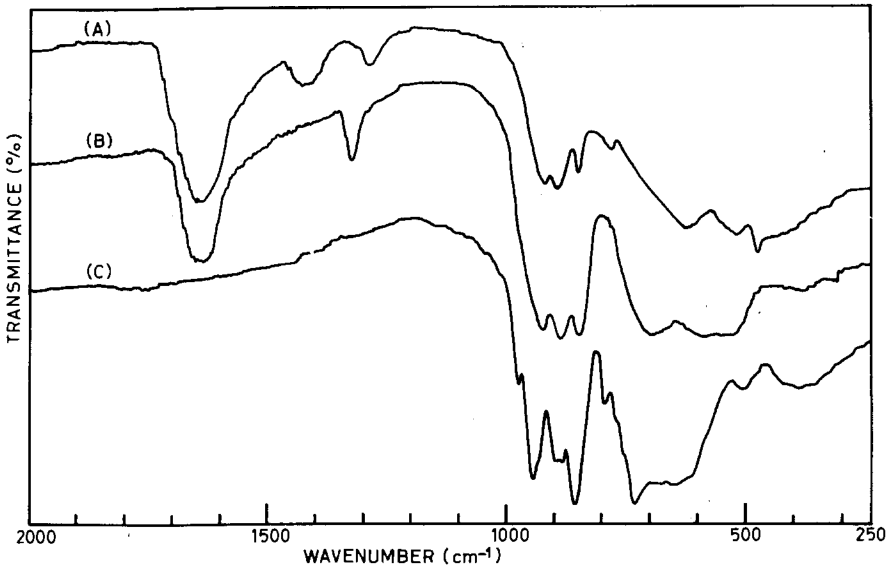

Fig. 1. IR spectra of LMO (A), LMO heated to 305 °C (B), and LMO heated to 400°C (C).

Thermogravimetry (TG) was carried out using a Stanton-Redcroft TG 770 thermobalance. Samples (5–10 mg) were heated at a rate of 3 °C min^{-1}. Differential thermal analysis (DTA) was carried out on a Stanton-Redcroft DTA 673-4, with about 20 mg samples, at a heating rate of 10 °C min^{-1}. Both studies were carried out in an atmosphere of static air. IR spectra were recorded in KBr matrix on a Beckman IR-20 double-beam instrument in the range 250–4000 cm^{-1}. The X-ray diffraction patterns were taken on a Philips diffractometer using Cu K_α radiation.

RESULTS AND DISCUSSION

LMO is a white compound which is highly hygroscopic in nature, and, therefore, kept under anhydrous conditions. The results of the IR studies of LMO (Fig. 1A) are summarized in Table 1 and the normal bands for a coordinated oxalato group have been assigned on the basis of existing data in the literature [8,9]. Besides this, LMO shows two strong bands at 930 and 900 cm^{-1} which suggest the presence of metal–oxygen double bonds while the broad band around 630 cm^{-1} probably results from an O–Mo–O stretch [10].

Figure 2 gives the TG, DTA and differential thermogravimetric (DTG) curves for LMO in a static air atmosphere. The thermogram shows that the dehydration takes place in a single step, followed by the decomposition of anhydrous LMO which takes place in two steps to give the end product $Li_2Mo_4O_{13}$. The various stages are discussed in detail below.

TABLE 1

IR absorption bands of LMO and their probable assignments

Frequency [a]	Probable assignment
3500 VS,br	ν(OH) of uncoordinated water
1650 VS	ν_{as}(C=O)
1440 S	ν_{sym}(C–O)+ ν(C–C)
1300 S	ν_{sym}(C–O)+ δ(O–C=O)
930 S	ν_{as}(Mo=O)
900 S	ν_{sym}(Mo=O)
860 S	ν_{sym}(C–O)+ δ(O–C=O)
630 S,br	ν(O–Mo–O)
515 W	ring def. + δ(O–C=O)
485 W	ν(M–O)+ring def.

[a] VS very strong; S strong; br broad; W weak; sym symmetric; as asymmetric; δ bending.

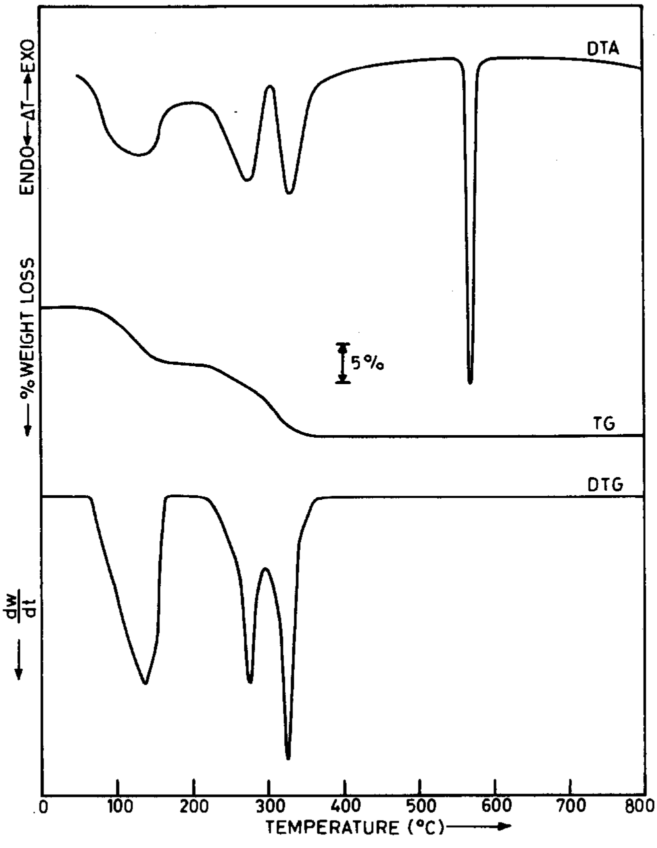

Fig. 2. DTG, TG and DTG curves for LMO in air.

Dehydration

As seen on the TG curve, LMO is stable up to 65 °C and then loses all its three moles of water in a single step between 65 and 170 °C. This is observed in DTA as a broad endothermic peak around 140 °C while DTG shows a peak at 135 °C. The observed weight loss is 7.40% compared to the calculated value of 7.38%.

Decomposition of oxalate

Anhydrous LMO is stable up to 210 °C and thereafter decomposes in two stages. The first stage extends up to 295 °C and corresponds to the loss of one mole of carbon monoxide and one mole of carbon dioxide each per two moles of LMO to give an intermediate with the tentative composition $Li_4[Mo_8O_{25}(C_2O_4)]$. The second stage occurs between 295 and 365 °C and involves the decomposition of $Li_4[Mo_8O_{25}(C_2O_4)]$ to give the end product $Li_2Mo_4O_{13}$. The first stage is observed in DTA and DTG at 270 and 275 °C, respectively, while the peaks at 330 °C in DTA and 325 °C in DTG correspond to the second stage. The observed weight loss for the two stages is 4.86 and 4.98%, respectively, while the calculated value for both the stages is 4.92%. The difference between the observed and the calculated values in the two stages may be attributed to the overlap of the two steps.

The composition assigned to the intermediate is well supported by the IR spectrum of the sample obtained by heating LMO isothermally at 305 ± 5 °C (Fig. 1B) which indicates the complete absence of carbonate and shows the presence of only the oxalato group.

Melting

An additional peak is observed in DTA at 570 °C corresponding to which no weight change is observed on the TG curve. This has been attributed to the melting of the end product. The melting point of $Li_2Mo_4O_{13}$ has been reported to be 568 [11] and 575 °C [12]. Moreover, on heating LMO isothermally at 575 ± 5 °C, a molten product is obtained which, on cooling, immediately solidifies to a white crystalline compound, thus confirming that the peak at 570 °C is due to melting.

The end product was characterized by chemical analysis, IR spectral and X-ray diffraction studies of the samples obtained by heating LMO isothermally for 2 h at 400 and 580 °C. Both these products gave identical chemical analyses, IR spectra (Fig. 1C) and X-ray diffraction patterns. The observed *d* values closely correlate with the earlier reported data by Reau and Fouassier [12] who reported only one X-ray pattern for $Li_2Mo_4O_{13}$. However, Brower et al. [11] reported the so-called low and high polymorphic forms, both having different X-ray patterns and none of them being identical to that reported by Reau and Fouassier. No such polymorphic transition was observed during the present study, probably because the low form is a meta-stable polymorph and, moreover, the formation of both forms has been reported to take place under special experimental conditions, while the present method of preparation is quite different.

The combination of these suggests a three-stage scheme for the thermal decomposition of LMO in air which is as follows

$$\mathrm{Li_2[Mo_4O_{12}(C_2O_4)]\cdot 3\,H_2O \xrightarrow{65-170\,^{\circ}C} Li_2[Mo_4O_{12}(C_2O_4)] + 3\,H_2O} \tag{1}$$

$$\mathrm{2\,Li_2[Mo_4O_{12}(C_2O_4)] \xrightarrow{210-295\,^{\circ}C} Li_4[Mo_8O_{25}(C_2O_4)] + CO + CO_2} \tag{2}$$

$$\mathrm{Li_4[Mo_8O_{25}(C_2O_4)] \xrightarrow{295-365\,^{\circ}C} 2\,Li_2Mo_4O_{13} + CO + CO_2} \tag{3}$$

Equation (1) represents the dehydration of LMO to give the anhydrous product which decomposes according to eqns. (2) and (3) to give the end product. The mechanism proposed here is a tentative one, based on the results obtained from dynamic thermogravimetry and isothermal studies.

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