Preparation, Characterization & Thermal Decomposition of Lithium Oxomolybdenum(VI) Oxalate

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A new diamagnetic Mo(VI) oxalato complex Li₂[MoO₃(C₂O₄)₂].5H₂O (LMO) has been prepared and characterized by chemical analyses and IR spectral data. The TG and DTA studies reveal that dehydration takes place up to 225°C and it is immediately followed by the decomposition of anhydrous oxalate which takes place in three stages. The first two stages occur in the temperature range 225-275 and 275-300°C to form the intermediates with the tentative compositions Li₄[Mo₂O₇(C₂O₄)₂] and Li₃[MoO₃(C₂O₄)] respectively. In the last stage, which extends up to 390°C, Li₂[MoO₃(C₂O₄)] decomposes to give the end product, lithium molybdate. The intermediates and the end product have also been characterized by chemical analyses and IR spectra. The X-ray diffraction patterns of LMO and the intermediate compounds reveal that they are amorphous.

A variety of anionic oxomolybdenum(VI) oxalates have been prepared and characterized. We have prepared yet another Mo(VI) oxalato complex with lithium as the metal cation, Li₂[MoO₃(C₂O₄)₂].15H₂O (LMO). The preparation, characterization and thermal decomposition of this new compound, which appears to be complex and interesting, form the subject of this paper.

Materials and Methods

All the reagents used were either of analar or proanalytical grade. To a hot solution of a mixture containing lithium oxalate (1.019g) and oxalic acid (1.2605g) in doubly distilled water (200 ml) was added MoO₃ (4.3185g, prepared by heating ammonium paramolybdate at about 400°C for 2 hr) in small lots. The solution was filtered to remove any unreacted paramolybdate at about 1400°C (for 2 hr) in small lots. The solution was filtered to remove any unreacted MoO₃. A dilute solution of lithium hydroxide was then added and the pH of the solution adjusted to 3.0 (± 0.2). On adding excess of acetone, white precipitates were obtained, which were washed with acetone and dried in vacuo. The compound thus obtained was then prepared for Ki,Mo₃(C₂O₄)₂].5H₂O(Found: Li, 5.02; Mo, 35.20; C₂O₄²⁻, 32.21. Reqd: Li, 5.08; Mo, 35.16; C₂O₄²⁻, 32.25%). Molybdenum in LMO was determined gravimetrically as molybdenyl oxinate and analysed by atomic absorption spectroscopy. Lithium was estimated by atomic absorption spectroscopy.

Thermogravimetry (TG) was carried out using a Stanton Red Croft TG 770 thermobalance at a heating rate of 3°C min⁻¹ and 5-10 mg of samples were used. The DTA was taken on a Stanton Red Croft DTA 673-4 using ignited alumina as a reference material and the heating rate was 10°C min⁻¹. For DTA, 15-20 mg of the samples were used. Both the studies were carried out in an atmosphere of static air.

IR spectra were recorded in KBr matrix on a Beckman IR-20 double beam spectrophotometer in the range 250-4000 cm⁻¹. The X-ray diffraction patterns were taken on a Philips diffractometer using CuKα radiations. The magnetic measurements were done on a vibrating sample magnetometer model VSM-155 at room temperature (23°C) using a magnetic field of 5500 gauss.

Results and Discussion

LMO is a white powder and is amorphous (X-ray). It is found to be diamagnetic suggesting that LMO is a Mo(VI) complex. The normal bands for coordinated oxalato group have been assigned on the basis of existing data. The IR spectrum of LMO exhibits bands at 3500 (s), 1670 (vs), 1540 (vs), 1450 (vs), 1310 (vs), 935 (s), 850 (s), 690 (s), 580 (s), 485 cm⁻¹ (m, ring deformation + δO–C = O). In oxomolybdenum(VI) compounds containing both bridged and terminal oxygen atoms directly attached to molybdenum, more than one metal-oxygen stretching bands have been observed. Accordingly, the bands at 935 and 890 cm⁻¹ have been assigned to asymmetric and symmetric νMo = O respectively. The two bands at 800 and 730 cm⁻¹ may probably be due to the two nonequivalent O – Mo – O groups. A comparison of the IR spectral data of LMO with those reported in literature suggests that probably LMO also has a similar chain structure.

LMO is stable up to 85°C and loses its 1.5 molecules of water in a single step which extends up to 225°C (Fig.1). This is observed in DTA as a broad endothermic peak around 125°C and in DTG as a
peak around 120°C (Fig. 1). The observed mass loss is 9.88%, as against the calculated value of 9.89%. The X-ray diffraction pattern of the anhydrous product obtained by heating LMO isothermally at 215°C shows it to be an amorphous product.

The decomposition of the anhydrous oxalate occurs between 225 and 390°C and is found to be a multistep process (Fig. 1). Here two molecules of anhydrous LMO lose one molecule of carbon monoxide in the temperature range 225-275°C with a maximum in DTG at 255°C. The observed mass loss is 5.02%, as against the calculated value of 5.13%. An intermediate oxalate carbonate having the tentative composition Li₂[MoO₃(C₂O₄)(CO₃)] is formed.

Next, step, which occurs between 275 and 300°C, with a maximum around 290°C in DTG, corresponds to the loss of one more molecule of carbon monoxide to give an intermediate carbonate with the tentative composition Li₂[MoO₃(CO₃)]. The observed mass loss is 5.36%, where as the calculated value is 5.13%. The difference between the observed and the calculated mass losses may be attributed to the overlap of two steps. The small endothermic peak in DTA around 235°C may correspond to the start of decomposition of oxalate. It is immediately followed by an exothermic peak around 290°C as a result of the dominant oxidation of carbon monoxide liberated during the primary decomposition process. Thus probably this exotherm represents the oxidation of carbon monoxide liberated during both the steps. The third stage which occurs in TG between 300 and 390°C, represents the decomposition of Li₂[MoO₃(CO₃)] to give the end product, lithium molybdate. This stage is observed in DTA and DTG as peaks around 350 and 340°C respectively. The observed mass loss is 16.08%, against the calculated value of 16.13%. The total observed mass loss for the process Li₂[MoO₃(C₂O₄)]1.5H₂O → Li₂MoO₄ is 36.34%, as compared to the calculated value of 36.28%.

An additional endothermic peak is observed in DTA around 700°C corresponding to which no mass change is observed in the TG curve. This peak has been attributed to the melting of the end product. On heating isothermally at 710 ± 5°C, LMO gives a molten product (melting point of Li₂MoO₄ being 705°C) which immediately solidifies to a white crystalline compound, confirming the peak at 700°C to be due to melting.

The X-ray diffraction patterns of the samples obtained by heating LMO isothermally at 275 ± 5°C and at 300 ± 5°C reveal the products to be amorphous. However, their chemical analyses and IR spectra clearly support the assigned compositions. The end products have been characterized by the chemical analyses of the solidified molten product obtained by heating LMO isothermally at 710°C as well as at 400°C. Both these products gave identical chemical analyses, IR spectra and X-ray diffraction patterns. These observations reveal the formation of pure Li₂MoO₄ without any other phase. The IR spectrum compares well with the spectrum of lithium molybdate given in the literature. The observed d values also closely match with the earlier reported data.

On the basis of above observations, a four-stage Scheme 1 is proposed for the thermal decomposition of LMO:

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\begin{align*}
\text{Li}_2[\text{MoO}_3(\text{C}_2\text{O}_4)]0.5\text{H}_2\text{O} & \overset{85-225\,^\circ\mathrm{C}}{\longrightarrow} \\
\text{Li}_2[\text{MoO}_3(\text{C}_2\text{O}_4)] + 1.5\text{H}_2\text{O} & \quad \cdots \quad (1) \\
2\text{Li}_2[\text{MoO}_3(\text{C}_2\text{O}_4)] & \overset{225-275\,^\circ\mathrm{C}}{\longrightarrow} \\
\text{Li}_4[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)(\text{CO}_3)] + \text{CO} & \quad \cdots \quad (2) \\
\text{Li}_2[\text{MoO}_3(\text{C}_2\text{O}_4)(\text{CO}_3)] + \text{CO} & \overset{275-300\,^\circ\mathrm{C}}{\longrightarrow} \\
2\text{Li}_2[\text{MoO}_3(\text{CO}_3)] + \text{CO} & \quad \cdots \quad (3) \\
\text{Li}_2[\text{MoO}_3(\text{CO}_3)] & \overset{300-390\,^\circ\mathrm{C}}{\longrightarrow} \text{Li}_2\text{MoO}_4 + \text{CO}_2 \quad \cdots \quad (4)
\end{align*}
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Scheme 1
The mechanism proposed in Scheme 1 is a tentative one based on the results obtained from dynamic thermogravimetry and isothermal studies.

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References