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PREPARATION OF CAESIUM TETRAMOLYBDATE BY THE THERMAL DECOMPOSITION OF A NEW OXOMOLYBDENUM(VI) OXALATO COMPLEX

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ABSTRACT

The complex $Cs_2(NH_4)_2[Mo_4O_{10}(C_2O_4)_4]$ was prepared and characterised by means of chemical analysis and IR spectral studies. Thermal decomposition studies were carried out using TG, DTA and DTG techniques. The compound is anhydrous and is stable up to 160 ° C. Thereafter it decomposes in four stages. The first and the second stage occur in the temperature ranges 160–210 ° C and 210–270 ° C to give intermediate compounds having the tentative compositions $Cs_4(NH_4)_2[Mo_8O_{20}(C_2O_4)_6(CO_3)]$ and $Cs_4[Mo_8O_{21}(C_2O_4)_4(CO_3)]$ respectively. The third stage occurs in the temperature range 270–330 ° C to give another intermediate compound with the tentative composition $Cs_4[Mo_8O_{24}(C_2O_4)_2]$, which then decomposes in the fourth stage and gives caesium tetramolybdate, $Cs_2Mo_4O_{13}$, at 370 ° C. The end product was characterised by chemical analysis and IR spectral and X-ray studies.

INTRODUCTION

It has been revealed by a literature survey that various mixed metal oxalates have been extensively used for the economic preparation of important materials such as $BaTiO_3$ [1], $ZnZrO_3$ [2], Cs_2MoO_4 and $Cs_2Mo_2O_7$ [3,4] but the preparation of higher molybdates has received scant attention. The present work, which deals with preparation, characterisation and thermal decomposition of a new molybdenum(VI) oxalato complex $Cs_2(NH_4)_2[Mo_4O_{10}(C_2O_4)_4]$, is a continuation of our recent attempt to prepare $K_2Mo_3O_{10}$ [5] and $Na_2Mo_4O_{13}$ [6] by the thermal decomposition of oxomolybdenum(VI) oxalato complexes.

EXPERIMENTAL

All the reagents used were of either AnalaR or proanalysi grade. To a hot solution of 5.042 g of oxalic acid in about 250 ml of distilled water, 5.758 g

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of molybdenum trioxide (prepared by heating ammonium paramolybdate at about 400 °C for 2 h) was added in small lots and the solution was filtered to remove any unreacted molybdenum trioxide. To this 3.3674 g of caesium chloride and 1.07 g of ammonium chloride were added and the solution was concentrated to about 25 ml to obtain the crystals of CAMO, which were washed with distilled water and air dried in a desiccator.

Molybdenum in CAMO was determined gravimetrically as molybdenyl oxinate and oxalate by $KMnO_4$ oxidation. Caesium was estimated by atomic absorption spectroscopy. Ammonia was determined by its liberation with aqueous alkali [7]. The analysis of CAMO gave 3.00% NH_4^+, 22.15% Cs, 32.08% Mo and 29.41% $C_2O_4^{2-}$, the calculated values being 3.01%, 22.19%, 32.04% and 29.39% respectively. These data show that there is no noticeable deviation of CAMO from the composition $Cs_2(NH_4)_2[Mo_4O_{10}(C_2O_4)_4]$.

Thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) were carried out with a Stanton Redcroft thermoanalyser (model STA-780 series) taking 10–20 mg of the samples in platinum crucibles. For DTA, ignited alumina was used as the reference material. The heating rate was 10 °C min^{-1}. IR spectra were recorded on a Perkin–Elmer 1600 series Fourier transform IR instrument in the range 400–4000 cm^{-1} with samples in the form of potassium bromide pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using Cu Kα radiation. The magnetic measurements were performed on a vibrating sample magnetometer (model VSM-155) at room temperature (22 °C) using a magnetic field of 5500 G.

RESULTS AND DISCUSSION

CAMO is a white crystalline compound which is found to be diamagnetic, suggesting that it is a molybdenum(VI) complex. The results of IR studies of CAMO (Fig. 1A) are summarised in Table 1. The normal bands for a coordinated oxalato group have been assigned on the basis of existing data in the literature [8,9]. As well as these, the broad band at 3200 cm^{-1} may result from NH_4^+ asymmetric stretching vibrations and the band at 1400 cm^{-1} is probably due to NH_4^+ bending vibrations [10]. In addition to these, CAMO shows strong bands at 920, 880, 810 and 730 cm^{-1}. The bands at 920 and 880 cm^{-1} suggest the presence of metal–oxygen double bonds and the bands at 810 and 730 cm^{-1} may be assigned to the asymmetric and symmetric Mo–O stretches respectively [11–13].

Figure 2 gives the DTA, TG and DTG curves for CAMO in static air. As seen from the TG curve, CAMO is an anhydrous compound and is stable up to 160 °C. The decomposition is found to be a four-step process. The first step extends up to 210 °C and corresponds to the loss of 2 mol of ammonia, 1 mol of water, 2 mol of carbon monoxide and 1 mol of carbon dioxide per

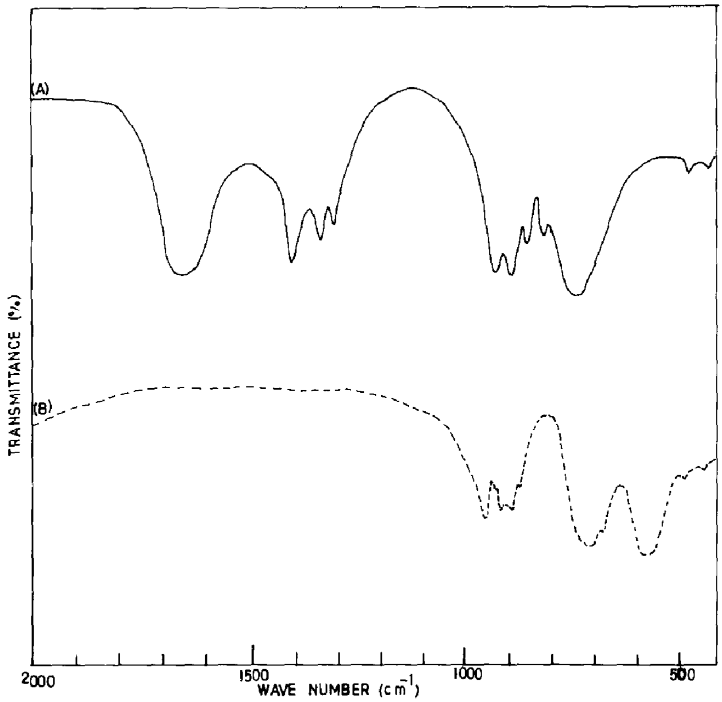

Fig. 1. IR spectra of CAMO (A) and CAMO heated at 380 °C (B).

2 mol of CAMO to give an intermediate with the tentative composition $Cs_4(NH_4)_2[Mo_8O_{20}(C_2O_4)_6(CO_3)]$. This is seen in DTG and DTA as peaks at 190 °C and 200 °C respectively. The observed weight loss is 6.33%

TABLE 1

IR absorption bands of CAMO and their probable assignments

Band		Probable assignments
Frequency (cm^{-1})	Intensity	
3200	s, br	$\nu_{as}(NH_4^+)$
1660	vs, br	$\nu_{as}(C=O)$
1400	vs	$\delta(NH_4^+)$
1340	s	$\nu_{sym}(C-O)+\delta(O-C=O)$
1300	s	
920	s	$\nu_{as}(Mo=O)$
880	s	$\nu_{sym}(Mo=O)$
850	s	$\nu_{sym}(C-O)+\delta(O-C=O)$
810	s	$\nu(O-Mo-O)$
730	s, br	$\nu(O—Mo-O)$
470	m	Ring deformation + $\delta(O-C=O)$
420	m	$\delta(O-C=O)$

vs, Very strong; s, strong; m, medium; br, broad; as, asymmetric; sym, symmetric.

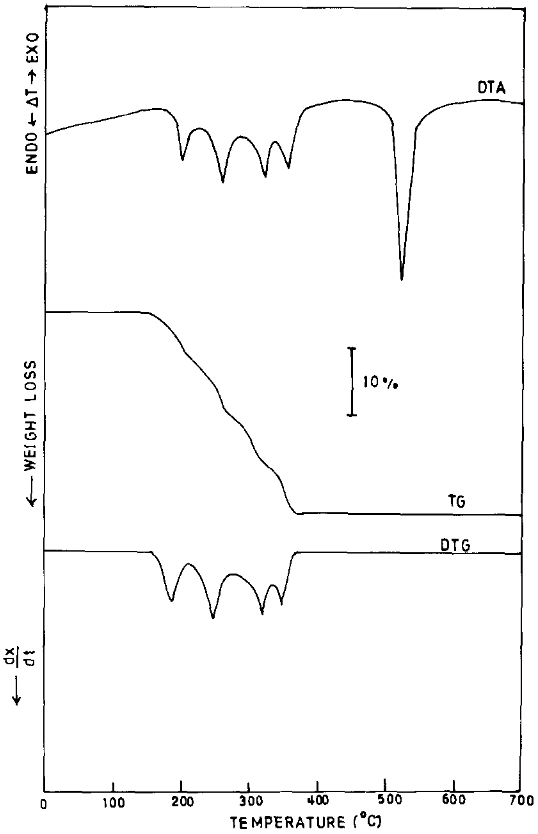

Fig. 2. DTA, TG and DTG curves for CAMO in air.

compared with the calculated value of 6.35%. The second step occurs between 210 and 270 ° C and involves a further loss of 2 mol of ammonia, 1 mol of water and 2 mol of each of carbon monoxide and carbon dioxide to give another intermediate having the tentative composition $Cs_4[Mo_8O_{21}(C_2O_4)_4(CO_3)]$. This is seen in DTG and DTA as peaks at 250 ° C and 260 ° C respectively. The observed weight loss is 8.2% compared with the calculated value of 8.18%. $Cs_4[Mo_8O_{21}(C_2O_4)_4(CO_3)]$ decomposes in a third step that extends up to 330 ° C and loses 2 mol of carbon monoxide and 3 mol of carbon dioxide to give another intermediate compound, $Cs_4[Mo_8O_{24}(C_2O_4)_2]$. This is seen in DTG and DTA as peaks at 320 ° C. The observed weight loss is 7.83% compared with the calculated value of 7.85%. $Cs_4[Mo_8O_{24}(C_2O_4)_2]$ decomposes in the fourth step that extends up to 370 ° C and loses 2 mol of each of carbon monoxide and carbon dioxide to give the end product, $Cs_2Mo_4O_{13}$. This is seen in DTG and DTA as peaks at 350 ° C and 355 ° C respectively. The observed weight loss is 6.00% compared with the calculated value of 6.02%. The total observed weight loss for the process:

$$Cs_2(NH_4)_2[Mo_4O_{10}(C_2O_4)_4] \rightarrow Cs_2Mo_4O_{13}$$

is 28.36% compared with the calculated value of 28.40%.

The composition assigned to the intermediates on the weight loss basis were further confirmed by magnetic measurements and IR spectral studies. CAMO was isothermally heated at $210 \pm 5\,^\circ C$, $270 \pm 5\,^\circ C$ and $330 \pm 5\,^\circ C$ and all these samples were found to be diamagnetic, suggesting that they are molybdenum(VI) compounds [14]. The experimental data were found to agree with the calculated values. All these samples showed the presence of oxalato group [7]. The IR spectra of the former two samples showed the presence of both oxalate and the carbonate groups while that of third indicated the presence of only the oxalato group.

An additional endothermic peak is observed in DTA at 525 °C which does not correspond to any weight change on the TG curve. This has been attributed to the melting of the end product, the reported melting point of $Cs_2Mo_4O_{13}$ being 524 °C [4]. This was further confirmed by heating CAMO isothermally at $530 \pm 5\,^\circ C$ when a molten product was obtained which solidified immediately to give a white crystalline compound.

The end product was obtained by heating CAMO isothermally at 380 °C and 530 °C, the latter giving a molten product which solidified to a crystalline compound. Both of them gave identical analysis results, IR spectra (Fig. 1B) and X-ray diffraction patterns. The IR spectrum is identical to that of $Cs_2Mo_4O_{13}$ reported in the literature [15]. The observed *d* values also agree very closely with previously reported data for $Cs_2Mo_4O_{13}$ [16]. On the basis of all these studies, the following scheme is proposed for the decomposition of CAMO in air:

$$2Cs_2(NH_4)_2[Mo_4O_{10}(C_2O_4)_4] \xrightarrow{160-210\,^\circ C} Cs_4(NH_4)_2[Mo_8O_{20}(C_2O_4)_6(CO_3)] + 2NH_3 + H_2O + 2CO + CO_2 \quad (1)$$

$$Cs_4(NH_4)_2[Mo_8O_{20}(C_2O_4)_6(CO_3)] \xrightarrow{210-270\,^\circ C} Cs_4[Mo_8O_{21}(C_2O_4)_4(CO_3)_2] + 2NH_3 + H_2O + 2CO + 2CO_2 \quad (2)$$

$$Cs_4[Mo_8O_{21}(C_2O_4)_4(CO_3)_2] \xrightarrow{270-330\,^\circ C} Cs_4[Mo_8O_{24}(C_2O_4)_2] + 2CO + 3CO_2 \quad (3)$$

$$Cs_4[Mo_8O_{24}(C_2O_4)_2] \xrightarrow{330-370\,^\circ C} 2Cs_2Mo_4O_{13} + 2CO + 2CO_2 \quad (4)$$

The mechanism proposed here is tentatively based on the results obtained from dynamic thermogravimetry and isothermal studies.

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