

PREPARATION OF CESIUM TRIMOLYBDATE BY THE THERMAL DECOMPOSITION OF A NEW OXOMOLYBDENUM(VI) OXALATO COMPLEX

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A new molybdenum(VI) complex $\text{Cs}_2(\text{NH}_4)_2[\text{Mo}_3\text{O}_8(\text{C}_2\text{O}_4)_3]$ (CAMO) has been prepared and characterized by chemical analysis and IR spectral studies. Thermal decomposition studies have been made using TG, DTA and DTG techniques. The compound is anhydrous and stable up to 160°C . Thereafter it decomposes in three stages. The first and the second stages occur in the temperature ranges $160\text{--}220^\circ\text{C}$ and $220\text{--}280^\circ\text{C}$ to give the intermediate compounds having the tentative compositions $\text{Cs}_4(\text{NH}_4)_2[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_3(\text{CO}_3)_2]$ and $\text{Cs}_4[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_2(\text{CO}_3)_2]$ respectively, the later then decomposing to give the end product $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ at 370°C . The end product was characterized by chemical analysis, IR spectral and X-ray studies.

A literature survey revealed 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 $\text{Cs}_2\text{Mo}_2\text{O}_7$ [3, 4] but the preparation of higher molybdates has received little attention. The present work, which deals with the preparation, characterization and thermal decomposition of a new molybdenum(VI) complex $\text{Cs}_2(\text{NH}_4)_2[\text{Mo}_3\text{O}_8(\text{C}_2\text{O}_4)_3]$, is in continuation of our recent attempt to prepare $\text{K}_2\text{Mo}_3\text{O}_{10}$ which was also prepared by the thermal decomposition a new oxomolybdenum(VI) oxalato complex [5].

Experimental

All the reagents used were either AnalaR or pro-analysi grade. To a hot solution of 3.7815 g of oxalic acid in about 250 ml of distilled water, 4.3185 g

of molybdenum trioxide (prepared by heating ammonium para-molybdate at about 400° 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 cesium chloride and 1.07 g of ammonium chloride were added and the solution was concentrated to about 30 ml to obtain 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. Cesium was estimated by atomic absorption spectroscopy. Ammonia was determined by its liberation with aqueous alkali [6]. The analysis of CAMO gave: NH_4^+ , 3.67 %; Cs, 27.07%; Mo, 29.32% and $\text{C}_2\text{O}_4^{2-}$, 26.89% the calculated values being 3.69%, 27.09%, 29.30% and 26.91% respectively. These data show that there is no noticeable deviation of CAMO from the composition $\text{Cs}_2(\text{NH}_4)_2[\text{Mo}_3\text{O}_8(\text{C}_2\text{O}_4)_3]$.

Thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) were carried out on a Stanton Redcroft thermoanalyzer 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 deg/min. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR 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 Phillips diffractometer using $\text{CuK}\alpha$ radiations. The magnetic measurements were performed on a model VSM-155 vibrating-sample magnetometer at room temperature (22°) using a magnetic field of 5500 Gauss.

Results and discussions

CAMO is a white crystalline compound which is found to be diamagnetic, suggesting that it is a molybdenum(VI) complex. The IR data (Table 1) of CAMO indicate the presence of both the NH_4^+ [7] and the coordinated oxalato group [8, 9]. In addition to these, the presence of metal-oxygen double bonds and that of Mo-O stretches is also indicated by the bands at 910 and 890 cm^{-1} and at 800 and 740 cm^{-1} respectively [10-12].

Figure 1 gives the DTA, TG and DTG curves for CAMO in static air. As seen on the TG curve, CAMO is an anhydrous compound and is stable up to 160°. The decomposition is found to be a three step process. The first step extends up to 220° and corresponds to the loss of two moles of ammonia, one mole of water, three moles of carbon monoxide and one mole of carbon

Table 1 IR absorption bands of CAMO, Intermediate-1, Intermediate-2 and the final product. Frequency, cm^{-1}

CAMO	Intermediate-1		Intermediate-2		Final product
	Frequency	Intensity	Frequency	Intensity	
3200	s, br	1670	1640	vs	840
1660	vs, br	1410	1465	m	910
1400	vs	1360	1380	w	900
1330	s	1320	1080	m	840
1300	s	1060	970	s	710
910	s	910	940	s	690
890	s	900	910	w	660
860	s	820	840	m	610
800	s	720	720	s, br	570
740	s, br	480	640	w	540
470	m	445	475	m	520
420	m		450	w	470

br - broad, vs - very strong, s - strong, m - medium, w - weak

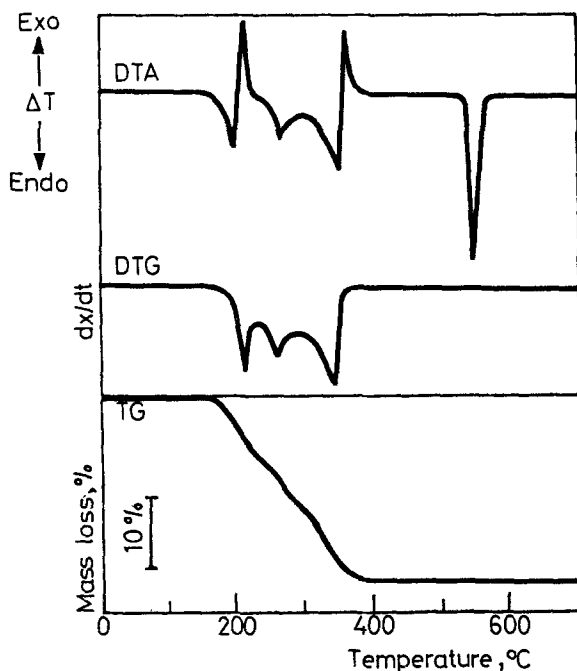
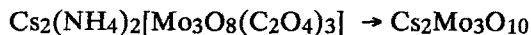


Fig. 1 DTA, TG and DTG curves of CAMO in air

dioxide per two moles of CAMO to give an intermediate with the tentative composition $\text{Cs}_4(\text{NH}_4)_2[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_3(\text{CO}_3)_2]$. This is seen in DTG as peak at 210° . However in DTA, an endothermic peak at 195° is immediately followed by a sharp exothermic peak at 210° which may be due to the dominant oxidation of the evolved carbon monoxide into carbon dioxide. The observed weight loss is 9.19%, against the calculated value of 9.17%. The second step occurs between 220 and 280° and involves a further loss of two moles of ammonia, one mole of water, one mole of carbon monoxide and one mole of carbon dioxide to give another intermediate having the tentative composition $\text{Cs}_4[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_2(\text{CO}_3)_2]$. This step is observed in DTA and DTG as peaks at 265 and 260° respectively. The observed weight loss is 6.13% against the calculated value of 6.32% $\text{Cs}_4[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_2(\text{CO}_3)_2]$ decomposes in the third step that extends up to 370° and loses two moles of carbon monoxide and four moles of carbon dioxide to give the end product $\text{Cs}_2\text{Mo}_3\text{O}_{10}$. This is seen in DTG as peak at 340° . However, in DTA an endothermic peak at 350° is again followed by an exothermic peak at 360° , which may be due to the reason similar to that explained in step first. The

observed weight loss is 11.88 % against the calculated value of 11.82 %. The total observed weight loss for the process:

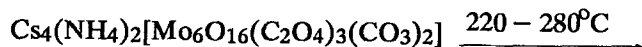
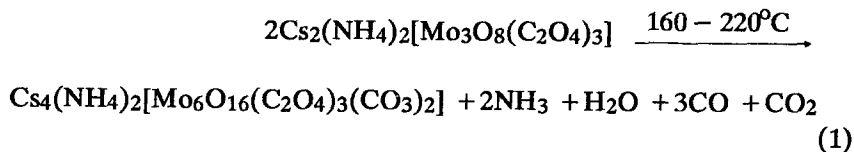


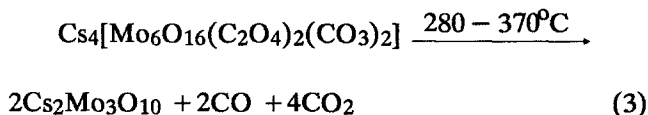
is 27.20% against the calculated value of 27.31%.

The composition assigned to the intermediates on the weight loss basis were further confirmed by chemical analysis, magnetic measurements and IR spectral studies. CAMO was isothermally heated at $220 \pm 5^\circ$ (Intermediate-1) and at $280 \pm 5^\circ$ (Intermediate-2) and both the samples were chemically analysed. The experimental data were found to agree with the calculated values. Both these samples were found to be diamagnetic suggesting that they are molybdenum(VI) complex [13]. The IR data of the two intermediates (Table 1) suggest the presence of both the oxalate and the carbonate groups [8, 14] while the presence of NH_4^+ is indicated only in Intermediate-1.

An additional endothermic peak is observed in DTA at 550° 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 $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ also being the same [4]. This was further confirmed by heating CAMO isothermally at $555 \pm 5^\circ$ 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 385° and at 555° , the later giving a molten product which solidified to a white crystalline compound. Both of them gave identical chemical analysis data, IR spectra and X-ray diffraction patterns. The IR data (Table 1) were found to be identical to those reported for $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ in the literature [15]. The observed 'd' values also match very closely with the earlier reported data for $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ [16]. On the basis of all these studies, the following scheme is proposed for the decomposition of CAMO in air





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References

- 1 P. K. Gallagher and J. Thomson, *J. Am. Ceram. Soc.*, 48 (1965) 644.
- 2 V. B. Reddy, C. R. M. Rao and P. N. Mehrotra, *J. Chem. Tech. Biotechnol.*, 30 (1980) 504.
- 3 S. P. Goel and P. N. Mehrotra, *J. Less Common Metal.*, 106 (1985) 27.
- 4 S. P. Goel and P. N. Mehrotra, *Indian J. Chem.*, 24A (1985) 199.
- 5 S. P. Goel, G. R. Verma, M. P. Sharma and Sanjive Kumar, *Thermochim. Acta*, 141 (1989) 87.
- 6 A. I. Vogel, *A. Text Book of Quantitative Inorganic Analysis*, ELBS, 3rd Edn. 1973, p. 254.
- 7 R. N. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York 1971, p. 3.
- 8 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York 1970, p. 245.
- 9 J. Fujita, A. E. Martel and K. Nakamoto, *J. Chem. Phys.*, 36 (1962) 324.
- 10 C. G. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1959) 3552.
- 11 W. P. Griffith, *J. Chem. Soc.*, (1963) 5345.
- 12 M. Cousins and M. L. H. Green, *J. Chem. Soc.*, (1964) 1567.
- 13 C. M. French and J. H. Garside, *J. Chem. Soc.*, (1962) 2006.
- 14 Reference 7, p. 70.
- 15 B. M. Gatehouse and P. Leverett, *J. Chem. Soc.*, (A), (1971) 2107.
- 16 Salmon and Caillet *Bull. Soc. Chim.*, France (1969) 1569.

Zusammenfassung — Es wurde ein neuer Molybdän(VI)-komplex mit der Formel $\text{Cs}_2(\text{NH}_4)_2[\text{Mo}_3\text{O}_8(\text{C}_2\text{O}_4)_3](\text{CAMO})$ hergestellt und mittels chemischer Analyse und IR-Spektroskopie beschrieben. Die thermische Zersetzung wurde mittels TG, DTA und DTG untersucht. Die Verbindung ist wasserfrei und bis 160°C beständig. Darüber erfolgt eine Zersetzung in drei Schritten. Der erste und zweite Schritt verläuft im Temperaturbereich $160-220^\circ\text{C}$ und $220-280^\circ\text{C}$, wobei Zwischenprodukte mit einer vermutlichen Zusammensetzung von $\text{Cs}_4(\text{NH}_4)_2[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_3(\text{CO}_3)_2]$ bzw. $\text{Cs}_4[\text{Mo}_6\text{O}_{16}(\text{C}_2\text{O}_4)_3(\text{CO}_3)_2]$ entstehen. Letzteres Zwischenprodukt zerfällt bei 370°C , dabei entsteht das Endprodukt $\text{Cs}_2\text{Mo}_3\text{O}_{10}$, welches mittels chemischer Analyse, IR- und Röntgendiffraktionsuntersuchungen charakterisiert wurde.