Thermochimica Acta, 37 (1980) 261—266

Note

THERMAL DECOMPOSITION STUDIES ON MANGANESE(III) SELENITO COMPLEXES

B.L. KHANDELWAL and S.P. MALLELA

Department of Chemistry, Indian Institute of Technology, New Delhi-110029 (India)

(Received 28 September 1979)

In our earlier communication [1] we reported the thermal decomposition studies on some manganese(III) selenites. The present communication describes the preparation and thermal studies of rubidium diselenito manganese(III) sesquihydrate and cesium diselenito manganese(III) trihydrate.

EXPERIMENTAL

Preparation

Rubidium diselenito manganese(III) sesquihydrate, $RbMn(SeO_3)_2 \cdot 1.5\ H_2O$ *(compound 1)*

To a 50 ml solution containing 20 g of selenium dioxide, solid rubidium carbonate was added to raise the pH to 3.5. Carbon dioxide was expelled by heating the solution at low temperature. To this solution, 1.2 g of manganese(III) selenite tetrahydrate was added and stirred vigorously for 2—3 min. The undissolved selenite was separated. The deep brown solution gave dark brown crystals on standing overnight.

Cesium diselenito manganese(III) trihydrate, $CsMn(SeO_3)_2 \cdot 3\ H_2O$ *(compound 2)*

20 g of selenium dioxide was dissolved in 50 ml distilled water and solid cesium carbonate added to raise the pH to 3.5. This solution was treated exactly as described above with manganese(III) selenite tetrahydrate after expelling carbon dioxide. Dark brown crystals were obtained.

Analysis

Selenium was estimated gravimetrically in the elemental form after reduction with sulphurous acid in concentrated HCl. Manganese was estimated spectrophotometrically as permanganate after removal of selenium. Rubidium and cesium were estimated both by flame photometry using filters No. 787 and 852, respectively, and also by the tetraphenylboron method. Analytical data are given in Table 1.

TABLE 1

Analytical and magnetic results

Compound	Manganese (%)		Selenium (%)		Water (%)		Alkali metal (%)		μ_{eff} (BM)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$RbMn(SeO_3)_2 \cdot 1.5H_2O$	13.05	13.73	37.48	37.92	6.40	6.00	20.28	19.97	5.02
$CsMn(SeO_3)_2 \cdot 3H_2O$	11.11	11.21	31.54	31.21	10.88	11.50	26.81	25.23	4.94

Magnetic susceptibilities were determined with a Cahn Faraday Electromagnetic balance using $Hg[Co(NCS)_4]$ as standard. The TGA study was carried out with a Stanton recording thermobalance, model HT-D, and DTA with a Stanton Redcroft DTA 673-4 unit.

RESULTS AND DISCUSSION

The trivalent state of manganese in both the complex selenites is confirmed by the effective magnetic moment value of 4.9 BM at room temperature, the value expected for a high-spin d^4 ion without orbital contribution.

Thermoanalytical curves of the compounds are presented in Figs. 1 and 2. Both compounds lose water of crystallisation, half a mole from compound 1 and one mole from compound 2, in the temperature range 50—150°C. The loss up to around 300°C corresponds to the elimination of one mole of coordinated water from compound 1 and two moles from compound 2. The corresponding endothermic effects were observed in the DTA curves. The infrared spectra of the compounds after being heated to 300°C showed the absence of water vibrations. The exothermic effects for compound 1 at 327°C and for compound 2 at 330°C without any weight loss may be due to some structural change occurring in the compounds on dehydration.

Thermal decomposition transition processes of the anhydrous rubidium compound are rather complex. Several complex reactions occur in the range 360—630°C, as is quite evident from the endothermic peaks at 397, 537 and

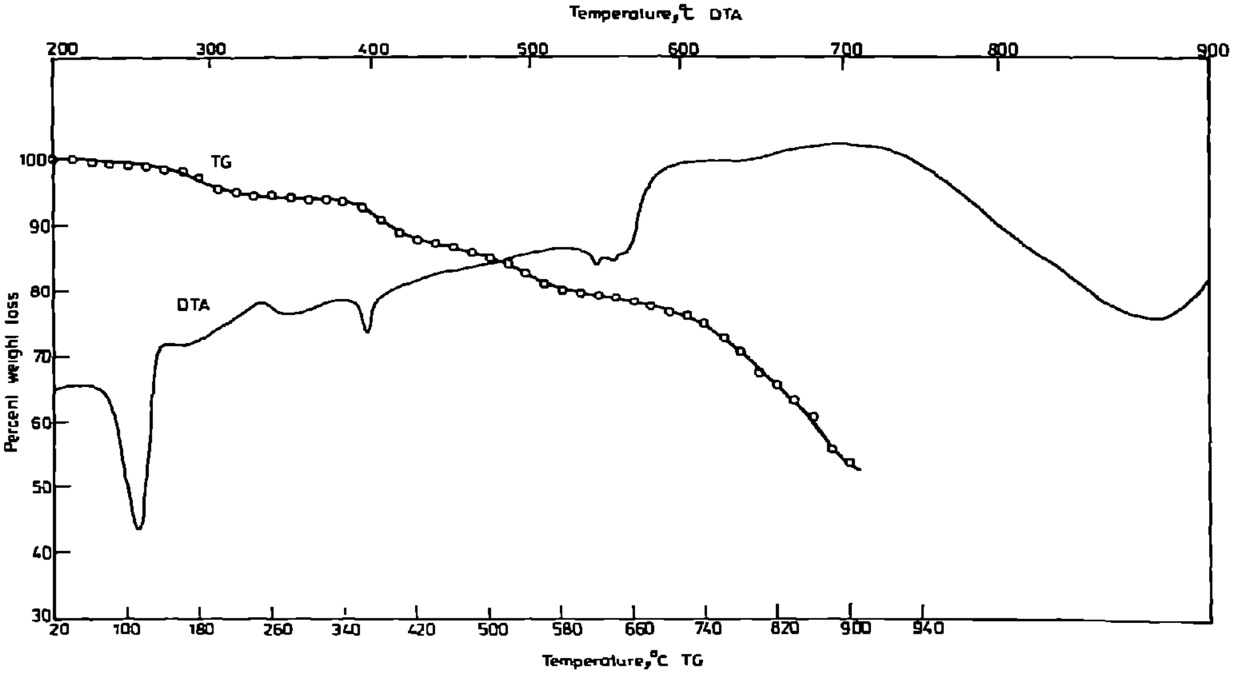

Fig. 1. TG and DTA curves for $RbMn(SeO_3)_2 \cdot 1.5\ H_2O$.

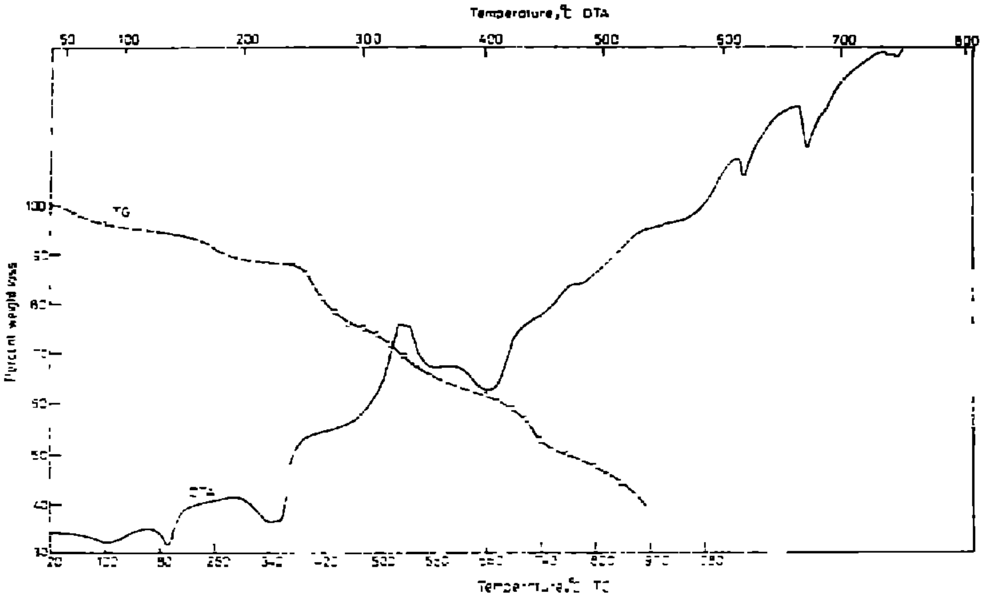

Fig. 2. TG and DTA curves for $CsMn(SeO_3)_2 \cdot 3H_2O$.

547°C. However, the weight change up to 630°C corresponds to the loss of one mole of selenium dioxide and the formation to Rb_2SeO_3 and manganese(III) oxyselenite. The latter finally appears to decompose to Mn_2O_3 via manganese (III) (di)oxyselenite. The formation of Rb_2SeO_3 has been confirmed by treating the heated (630°C) sample with water and analysing the solution obtained for rubidium and selenium. The X-ray diffractogram of the product heated to 900°C showed characteristic *d*-lines for both Rb_2SeO_3 and Mn_2O_3.

The anhydrous cesium compound decomposes to manganese oxyselenite and cesium selenite in the temperature range 360—470°C. The corresponding endothermic effect is observed at 400°C. The transient existence of oxyselenite is evident from the inflexion in the TG curve. The formation of Cs_2SeO_3 at this stage has been ascertained by analysing the aqueous extract of the heated (470°C) compound for cesium and selenium. The manganese oxyselenite finally decomposes to Mn_2O_3 via manganese(III) (di)oxyselenite. The diffractogram of the finally heated (750°C) product showed characteristic *d*-lines for both Cs_2SeO_3 and Mn_2O_3.

In both these compounds, the observed weight losses at higher temperature are more than the theoretically expected values. This is due to slow decomposition of Rb_2SeO_3 and Cs_2SeO_3 as reported earlier [2,3] and is also evident from the continuous loss found in the TG curves. Compound 1 shows an almost continuous loss of weight and it is quite complicated to determine the exact temperature range in which a particular transition occurs. Thus it showed a rather higher temperature range for the formation of oxy- and (di)oxyselenites compared with those of potassium [1] and cesium complex selenites.

Thermoanalytical results and proposed thermal decomposition processes of these selenites are given in Table 2.

TABLE 2

Thermoanalytical results

Dehydration/decomposition transition			Temp (°C)		Loss (%)	
			TG	DTA	Calc.	Found
$RbMn(SeO_3)_2 \cdot 1.5\ H_2$						
$2\ RbMn(SeO_3)_2 \cdot 1.5\ H_2O$	→	$2\ RbMn(SeO_3)_2H_2O$	50—150		2.1	2.0
$2\ RbMn(SeO_3)_3H_2O$	→	$2\ RbMn(SeO_3)_2$	150—300	256endo 327exo	6.4	6.0
$2\ RbMn(SeO_3)_2$	→	$Rb_2SeO_3 + Mn_2O(SeO_3)_2$	360—630	397endo 537endo 547endo	19.0	20.0
$Rb_2SeO_3 + Mn_2O(SeO_3)_2$	→	$Rb_2SeO_3 + Mn_2O_2(SeO_3)$	640—810	637endo	30.6	31.0
$Rb_2SeO_3 + Mn_2O_2(SeO_3)$	→	$Rb_2SeO_3 + Mn_2O_3$	820—920	877endo	42.6	51.0
$CsMn(SeO_3)_2 \cdot 3\ H_2O$						
$2\ CsMn(SeO_3)_2 \cdot 3\ H_2O$	→	$2\ CsMn(SeO_3)_2 \cdot 2\ H_2O$	50—160	81endo 134endo	3.62	5.2
$2\ CsMn(SeO_3)_2 \cdot 2\ H_2O$	→	$2\ CsMn(SeO_3)_2$	160—320	220endo 330exo	10.86	11.5
$2\ CsMn(SeO_3)_2$	→	$Cs_2SeO_3 + Mn_2O(SeO_3)_2$	360—470	400endo	22.07	25.0
$Cs_2SeO_3 + Mn_2O(SeO_3)_2$	→	$Cs_2SeO_3 + Mn_2O_2(SeO_3)$	500—600	614endo	33.26	36.0
$Cs_2SeO_3 + Mn_2O_2(SeO_3)$	→	$Cs_2SeO_3 + Mn_2O_3$	600—780	670endo 736endo 745endo	44.45	50.0

REFERENCES

1 B.L. Khandelwal and S.P. Mallela, Thermochim. Acta, 33 (1979) 355.
2 T.V. Klushina, O.N. Evstafeva, N.M. Selivanova, V.V. Lapin, Y M. Khozhainev and G.E. Kalenchunk, Russ. J. Inorg, Chem., 19 (1974) 163.
3 T.V. Klushina, O.N. Evstafeva, N.M. Selivanova, Y M. Khozhainov and A.Y. Manosova, Russ. J. Inorg. Chem., 20 (1975) 160.