

THERMAL AND OTHER STUDIES ON BIVALENT METAL SELENITES

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$\text{BaSeO}_3 \cdot 2.5\text{H}_2\text{O}$ (I), $\text{PbSeO}_3 \cdot 2\text{H}_2\text{O}$ (II) and $\text{CdSeO}_3 \cdot 3.5\text{H}_2\text{O}$ (III) were prepared and analysed. Their hygroscopicity and solubility was investigated. These compounds have high thermal stability, as shown by their TG and DTA data. IR spectra show multi-dentate coordination of selenite to cations, due to considerable splitting of the asymmetric ν_3 and ν_4 bands of SeO_3^{2-} in the $780\text{--}730\text{ cm}^{-1}$ and $420\text{--}325\text{ cm}^{-1}$ region.

Tentative structures have been proposed involving bridging oxygen atoms.

Verma [1] investigated the extraction of uranium(VI) by selenite. Qureshi [2] and Rawat et al. [3] employed a stannic selenite column to separate La from Y, Eu or Lu, etc. Ebert and Havelicek [4] reported that certain selenites have ferroelectric properties. All this prompted us to prepare and study $\text{BaSeO}_3 \cdot 2.5\text{H}_2\text{O}$ (I), $\text{PbSeO}_3 \cdot 2\text{H}_2\text{O}$ (II) and $\text{CdSeO}_3 \cdot 3.5\text{H}_2\text{O}$. Based on thermal, IR, solubility and hygroscopicity studies tentative structures have been proposed.

Experimental

The compounds were synthesized by adding a solution of 1.0 M acetates (BDH) of Ba, Pb or Cd to 0.944 M selenous acid. Selenous acid solution was prepared by dissolving selenium dioxide (BDH) in distilled water. The solution was filtered and its selenium content determined gravimetrically [5]. On addition of an acetate solution slowly with constant stirring to the selenous acid solution, a white precipitate was formed. The pH of supernatant liquid was (I) 8.34, (II) 7.09 and (III) 7.02. It was measured by means of a Global Digital pH meter/DPH 500. The yields for I and II were 78 to 84%, whereas for III it was 54.68%.

All three cations were estimated gravimetrically [5], barium as sulphate, lead as molybdate and cadmium as thiocyanate. The selenium content was determined [5] by sulphur dioxide and conc. HCl. Water was obtained by difference and thermal analysis. The analysis results are given in Table 1. A Graphic Controls RL 1/273/1001 TG and DTA instrument was employed for thermal studies. The

Table 1 Analysis results

		Obs%	Calculated, %
BaSeO ₃ · 2.5H ₂ O	Ba	44.16	44.34
	Se	25.32	25.56
	H ₂ O	15.14	14.56
PbSeO ₃ · 2H ₂ O	Pb	55.65	55.94
	Se	21.12	21.35
	H ₂ O	10.40	9.72
CdSeO ₃ · 3.5H ₂ O	Cd	36.98	37.16
	Se	26.05	26.12
	H ₂ O	21.15	20.83

heating rate was 10 deg/min in static air with Al₂O₃ as reference material. The instrument had a temperature range up to 1273 K. IR spectra were recorded on a Perkin-Elmer (No. 021-6326) instrument, in the region 4000-200 cm⁻¹, using KBr technique.

Results and discussion

Effect of moisture

Weighed quantities of barium, lead and cadmium selenites were kept in open, humid environment for 48 h. In case of barium selenite there was no change in weight. Lead and cadmium selenites showed 1.10 and 2.00% increase, respectively. Sathianandan et al. [6] also observed a strong affinity of cadmium selenite for water.

Solubility

The three selenites did not show any sign of solubility at room (298 K) and higher temperature (333-343 K). The solvents tried were water, acetone, ethanol, methanol, dimethylsulfoxide and dimethyl formamide. However, the selenites dissolved in HCl and HNO₃.

Cadmium selenite was soluble in glacial acetic acid. Well formed and transparent crystals of cadmium selenite were grown from glacial acetic acid. The largest crystal was 6 × 4 × 5 mm³. The crystals may have semiconducting nature.

Thermal studies

Compound (I) starts losing weight at 698 K (Fig. 1). This loss goes on until at 745 K, it becomes slow. This loss may be due to the elimination of 2.5 moles of water. The calculated weight loss corresponding to 2.5 moles of water is 13.4% (obs. 14.50%). It is also accompanied by an endothermic peak at 733 K. This appears to be due to the following decomposition:

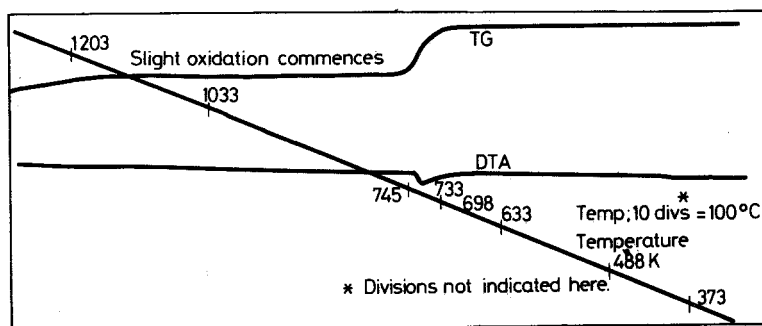
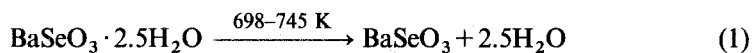
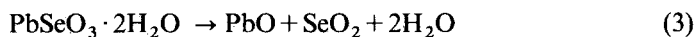


Fig. 1 TG and DTA curves of BaSeO₃ · 2.5H₂O. Sample weight (DTA): 9.10 mg

No further change is observed up to 1033 K, then slight oxidation is noticed which continues till 1203 K. Losoi and Valkonen [7] observed that BaSeO₃ and SrSeO₃ do not decompose below 1273 K, but undergo a slight oxidation to selenate above 973 K. The sample does show a mass loss of about 3% from 1203 to 1273 K with a trend to continue. This may be attributed to the reaction:



However, it was not possible to confirm this change as the temperature could not be raised beyond 1273 K. Compound (II) starts decomposing at a relatively high temperature (Fig. 2). The change is fast up to a loss of about 9% mass which is equivalent to the loss of two moles of water (calc. 9.72%) and is accompanied by an endothermic peak at 925 K. After this loss, the change becomes relatively slow and continues up to 1153 K, 30.0% mass loss. This appears to be due to the following partial decomposition reaction:



After loss of 30% mass, the reaction rate increases (Fig. 2) up to the temperature of 1273 K. The mass loss expected for reaction (3) is 39.73%, which is observed up to 1203 K. But the compound continues to decrease in mass even beyond 1203 K. This additional loss may be attributed to the evaporation of PbO which fuses [8] at 1153 K and evaporates at higher temperatures. Compound (III) starts losing weight at 603 K. This loss goes on steadily with increases in temperature and at

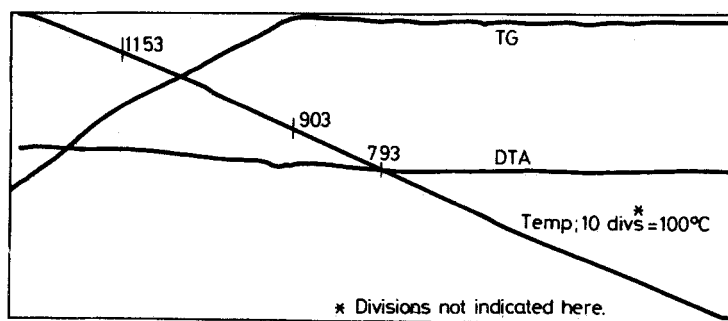


Fig. 2 TG and DTA curves of $\text{PbSeO}_3 \cdot 2\text{H}_2\text{O}$. Sample weight (DTA): 8.24 mg

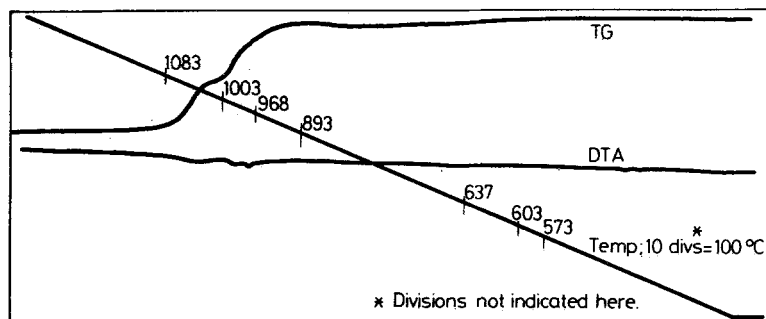


Fig. 3 TG and DTA curves of $\text{CdSeO}_3 \cdot 3.5\text{H}_2\text{O}$. Sample weight (DTA): 6.49 mg

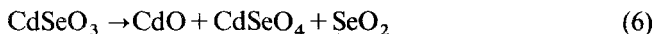
about 893 K it becomes very fast until at 1003 K a small plateau appears (Fig. 3). The loss corresponds to 21.0% by weight of the compound, attributable to the elimination of 3.5 moles of water (calc. 20.83%). It is accompanied by an endotherm at 968 K. The temperature range of the mass loss is unusually wide and high. This may be due to the presence of different types of water molecules like coordinated and/or bridged.

The decrease in mass from 1008 to 1083 K is 16%. This loss does not correspond to the elimination of selenium dioxide according to either of the following reactions:



Table 2 IR frequencies, cm^{-1} . Relative intensities are in parentheses. VW = Very Weak

Compound I	Compound II	Compound III	Assignments
BaSeO ₃ ·2.5H ₂ O	PbSeO ₃ ·2H ₂ O	CdSeO ₃ ·3.5H ₂ O	
	242(5)		
250(8)	251(3)		
	270(2)		
275(5)			
285(3)	290(1)		
298(3)			
325(5)	325(4)		
	360(4)		
378(4)		375(1)	
390(5)		400(2)	$\nu_4(\text{O-Se-O})\text{SeO}_3^{2-}$
405(6)	407(7)		
420(4)	421(8)		
458(6)		435(3)	$\nu_2(\text{O-Se-O})\text{SeO}_3^{2-}$
515(6)	470(1)	510(8)	M-O-Se
540(6)			
580(5)			
	640(9)		
	670(10)		
	690(9)		
730(9)		725(8)	
735(10)		750(10)	$\nu_3(\text{O-Se-O})\text{SeO}_3^{2-}$
755(9)	758(7)		
780(4)			
800(2)	800(4)	800(4)	$\nu_1(\text{O-Se-O})\text{SeO}_3^{2-}$
825(7)			
855(3)			M-O-Se
		900(1)	
945(VW)	958(2)		
	970(2)		
	990(2)	1035(3)	
	1085(3)	1065(4)	
		1100(3)	
		1120(3)	
1382(7)	1350(5)	1390(3)	$\text{CO}_3^{2-}/\text{NO}_3^-$ traces
		1550(1)	
		1580(1)	$\delta\text{H}_2\text{O}$
		1635(2)	
1630(1)	1620(6)		
	2295(w)		$\nu(\text{OH}) (\text{H}_2\text{O})$
2350(2)			
2925(5)	2800(VW)	2940(1)	Hydrogen bonding
3450(6)		3440(8) (Vb)	$\nu(\text{O-H}) (\text{H}_2\text{O})$



as the expected loss for SeO_2 elimination would be 36.70%. Harrison et al. [9], Lutz and coworkers [10] while studying the alkaline earth metal sulphites, Zn, Cd and Pb sulphites observed that the decomposition product consisted of oxides, sulphates and basic sulphates as well. This is further supported by the observation of Lossoi and Valkonen [7] that similar selenites oxidise slightly to selenate above 973 K. The difference between the observed and expected mass loss is due to the partial oxidation of selenite and also formation of CdO as represented by reaction (6).

Infrared studies

In accordance with the high thermal stability and low solubility of selenites there is considerable splitting of the asymmetric (O-Se-O) (SeO_3^{2-}) ν_3 and ν_4 bands (Table 2), in the region $780\text{--}730\text{ cm}^{-1}$ and $420\text{--}325\text{ cm}^{-1}$, respectively. This

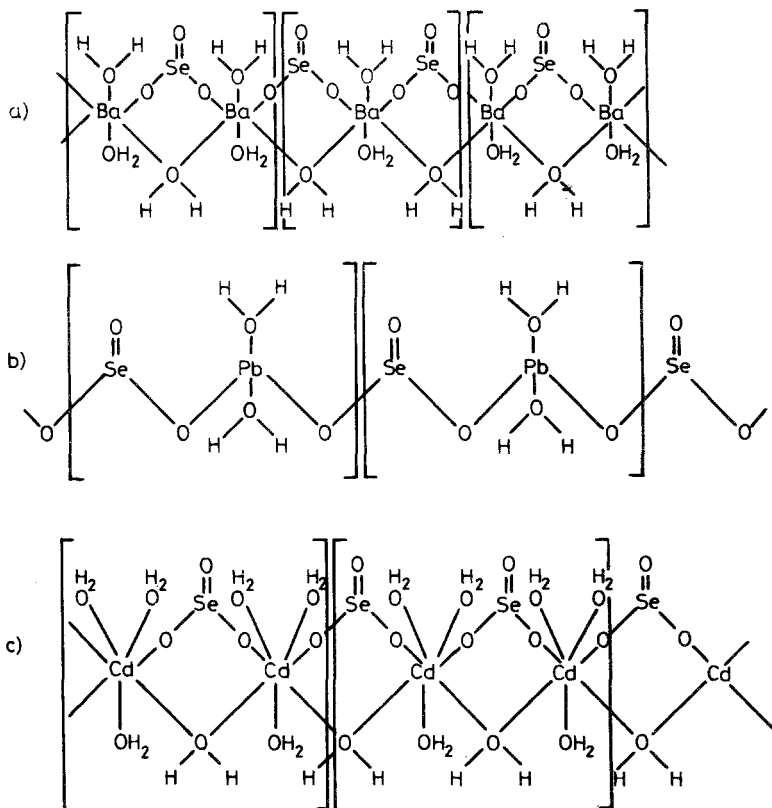


Fig. 4 Tentative structures. a) $\text{BaSeO}_3 \cdot 2.5\text{H}_2\text{O}$; b) $\text{PbSeO}_3 \cdot 2\text{H}_2\text{O}$; c) $\text{CdSeO}_3 \cdot 3.5\text{H}_2\text{O}$. Hydrogen bonding not shown for clarity

suggests [11, 12] a lowering of the ligand symmetry from C_{3v} to C_s and multidentate coordination of the selenite through oxygen. And M–O–Se bands at and around 515 and 958 cm^{-1} also support [6] the coordination through oxygen. Bands around 1620, 2300, 2900 and 3400 cm^{-1} have been assigned [6, 13, 14] to $\delta\text{H}_2\text{O}$, $\nu(\text{O}-\text{H})$ (H_2O), hydrogen bonding and $\nu(\text{O}-\text{H})$ (H_2O); respectively. However, there are many other bands (Table 2), which could not be assigned.

On the basis of thermal, IR and solubility studies, tentative structures, involving bridging oxygen atoms, have been suggested (Fig. 4).

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Zusammenfassung — $\text{BaSeO}_3 \cdot 2.5\text{H}_2\text{O}$ (I), $\text{PbSeO}_3 \cdot 2\text{H}_2\text{O}$ (II) und $\text{CdSeO}_3 \cdot 3.5\text{H}_2\text{O}$ (III) wurden hergestellt, analysiert sowie deren Hygroskopizität und Löslichkeit untersucht. TG- und DTA-Untersuchungen erweisen die hohe thermische Stabilität dieser Verbindungen. Die IR-Spektren zeigen mehrzählige Koordination von Selenit zu Kationen, was aus einer beträchtlichen Aufspaltung der antisymmetrischen ν_3 und ν_4 Banden von SeO_3^{2-} im Bereich 780–730 cm^{-1} bzw. 420–325 cm^{-1} hervorgeht. Es wurden versuchsweise Strukturen mit überbrückenden Sauerstoffatomen vorgeschlagen.

Резюме — Вновь полученные соединения $\text{BaSeO}_3 \cdot 2.5\text{H}_2\text{O}$, $\text{PbSeO}_3 \cdot 2\text{H}_2\text{O}$ и $\text{CdSeO}_3 \cdot 3.5\text{H}_2\text{O}$ охарактеризованы элементарным анализом и изучена их гигроскопичность и растворимость. Согласно данным ТГ и ДТА соединения обладают высокой термостойкостью. ИК спектры показали полидентатную координацию селенит-аниона по отношению к катионам, вызывая значительное расщепление симметричных ν_3 и ν_4 полос SeO_3^{2-} в области 780–730 и 420–325 cm^{-1} . Для всех соединений предложены пробные структуры, включающие мостиковые атомы кислорода.