CALCIUM SELENITES

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The following selenites were studied by the solubility method, thermal analysis, powder X-ray diagrams, and IR molecular spectroscopy: $CaSeO_3.H_2O$, $CaSeO_3$ (two crystalline modifications), $Ca(HSeO_3)_2.H_2O$, $CaSe_2O_5$, and $Ca_2S_3O_8$ (hitherto unknown). Exact conditions for the preparation of the selenites and their bonding relations are given.

An increased attention has been paid in recent years to the study of selenites in connection with their ferroelectric properties, which were observed with some of them. For this reason, we started a systematic study of these compounds, calcium selenites forming the subject of the present work.

Some authors[1-5] were concerned with the preparation and properties of the compounds $CaSeO_3.H_2O$ and $CaSeO_3$ while a lesser attention has been paid[1,2,4,6] to compounds with a ratio of Ca : Se = 1 : 2. Paetzold and Simon[11-13] derived from IR spectra of alkaline selenites the constitution and symmetry of the anions SeO_3^{2-}, $HSeO_3^-$, and $S_2O_5^{2-}$, and calculated the force constants of the Se–O bonds. They proposed the point group of symmetry C_{3v} for the anion SeO_3^{2-}, C_s for $HSeO_3^-$ with the OH group bound to SeO_2, C_{2v} for $Se_2O_5^{2-}$ with two SeO_2 groups bound with an oxygen bridge.

Our aim was to prepare all selenites in the $CaSeO_3$–SeO_2–H_2O system at 298 K and to study their bonding relations.

EXPERIMENTAL

The compound $CaSeO_3.H_2O$ was prepared by precipitation of an aqueous solution of 0·2 mol/dm^3 sodium selenite (Lachema, pure) with 0·2 mol/dm^3 aqueous $Ca(ClO_4)_2$ prepared by dissolving $CaCO_3$ (Lachema, pure) in perchloric acid (Laborchemie, pure). The deuterate, $CaSeO_3.D_2O$, for IR spectroscopy was prepared from anhydrous $CaSeO_3$ by shaking with heavy water for several hours. The compound $Ca(DSeO_3)_2.D_2O$ for IR spectroscopy was prepared from $CaSeO_3.D_2O$, SeO_2 and D_2O according to the solubility diagram. SeO_2 was supplied by Lachema as pure. The starting compounds and products were analysed gravimetrically. Se was determined by reduction with SO_2 to Se according to the method of Bode[7,15] modified by us, calcium was determined as CaO after thermal decomposition of the oxalate[8] (for $CaSeO_3.H_2O$ calculated: 21·6% Ca and 42·6% Se, found: 21·6% Ca and 42·8% Se; for $Ca(HSeO_3)_2.H_2O$ calculated: 12·8% Ca and 50·3% Se, found: 12·6% Ca and 50·1% Se). Solubilities were determined from volumetric analyses. Se(IV) was determined iodometrically[9], Ca complexometrically after addition of NaOH with the use of kalkonalide as indicator[10].

Thermal decompositions at increasing temperature were done with the use of a Derivatograph (MOM, Budapest) in the range 293—873 K at a rate of 5 K/min. Powder X-ray diagrams were obtained on an apparatus of the firm Chirana in cells of Siemens or Chirana with a diameter of 57·3 mm. The samples were placed on a rod or (with anhydrous compounds) in a capillary of Lindenmann glass with a diameter of 0·3—0·5 mm. The time of exposition was on the average 45 min at a voltage of 35 kV and current of 20 mA. Difractograms were recorded on a difractograph (Chirana) at 35 kV and 16—18 mA. IR spectra were recorded on a UR 20 type apparatus (Carl Zeiss, Jena) in the range 400—4 000 cm^{-1}; a nujol suspension was placed in KBr cuvettes. The region of stretching vibrations of the OH group was measured also in a tripene suspension.

RESULTS

Solubility in the System $CaSeO_3$–SeO_2–H_2O at 298 K

The solubility was studied by the Schreinemakers' method; the time of equilibration did not exceed several days. The solubility diagram according to Gibbs and Roozeboom is shown in Fig. 1. It is seen that the incongruently soluble compound $Ca.(HSeO_3)_2.H_2O$ is formed in the crystallization field III, while the crystallization fields I and V correspond to the starting compounds. The equilibrium between two solid phases and a solution of a composition given by the peritonic, *P*, or eutonic point, *E*, is illustrated by the fields II and IV, respectively. The composition in the peritonic point *P* is 6·7% $CaSeO_3$, 4·3% SeO_2, and 89·0% H_2O, in the eutonic point *E* 8·5% $CaSeO_3$, 63·7% SeO_2, and 27·8% H_2O. The phase reaction $CaSeO_3 + SeO_2 + 2\,H_2O \rightleftharpoons Ca(HSeO_3)_2.H_2O$ takes place in the field II at a composition of the liquid phase corresponding to point *P*.

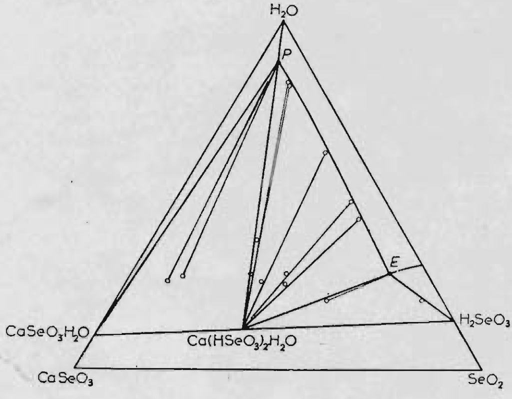

FIG. 1

Solubility diagram for $CaSeO_3$–SeO_2–H_2O system at 298 K. From left to right: I, II, III, IV, V

Based on the mentioned solubility diagram, the compound $Ca(HSeO_3)_2.H_2O$ was prepared by mixing 20 parts (by weight) $CaSeO_3$, 30 parts SeO_2 and 50 parts H_2O, waiting till the equilibrium was attained, filtering off the crystalline substance on an S3 glass frit, washing with ethanol and ether, and drying on the air at room temperature. The product is colourless, finely crystalline, and stable on the air at room temperature.

Thermal Analysis, Powder X-Ray Diagrams, and IR *Spectroscopy*

The results of thermal decomposition of $CaSeO_3.H_2O$ are given in Table I. The starting compounds and products were studied roentgenographically. The interlayer distances are given below in pm, numbers in parentheses are relative intensities (from 1 to 10) observed visually.

TABLE I
Thermal decomposition of selenites

Temperature, K	GTA	DTA	Notes
		$CaSeO_3.H_2O$	
408–488	decrease	*endo*	dehydration
533–833	−9·59% delay	—	$CaSeO_3$ anhyd. cryst. *I*
833–843	—	*endo*	recrystallization
843 and more	—	—	$CaSeO_3$ anhyd. cryst. *II*
		$Ca(HSeO_3)_2.H_2O$	
353–363	decrease	*endo*	partial dehydration
373–403	−8·86% delay	—	? (see Discussion)
418–513	decrease	double *endo*	total dehydration
528–593	−12·0% delay	—	$CaSe_2O_5$
603–638	decrease	*endo*	partial loss of SeO_2
653	−29·9% delay	—	$Ca_2Se_3O_8$
688–733	decrease	*endo*	loss of rest of SeO_2
773 and more	−46·9% delay	—	$CaSeO_3$ anhyd. cryst. *II*

$CaSeO_3.H_2O$:

730(6), 490(8), 373(5), 369(6), 335(2), 325(1), 318(8), 299(9), 271(10), 252 (2), 228(5), 202(3), 193(1), 189(5), 183(2), 178(8), 168·0(4), 164·7(1), 159·0(1), 154·6(1), 149·2(5), 145·8(1), 141·5(2), 138·2(2), 132·7(1), 128·9(2), 127·5(1), 125·4(1), 123·2(2), 121·1(1), 118·2(3), 108·2(1).

TABLE II

IR Spectra of selenites, hydrogenselenites, their hydrates and deuterates (cm^{-1})

$\tilde{\nu}CaSeO_3.H_2O$	$\tilde{\nu}CaSeO_3.D_2O$	$\frac{\tilde{\nu}CaSeO_3.H_2O}{\tilde{\nu}CaSeO_3.D_2O}$	Assignment
420 m	424 m	0·99	δSeO_3
433 m	450 m	0·96	
463 m	485 m	0·95	
636 m	510 sh	1·25	ϱH_2O
705 s	705 s	1·00	$\nu_s SeO_3$
756 s	749 s	1·01	
784 s	782 s	1·00	$\nu_{as} SeO_3$
846 s	836 s	1·01	
1 680 m	1 229 m	1·37	δH_2O
3 200 s	2 393 m	1·34	νH_2O
—	2 460 sh	1·35	
3 317 m	2 493 m	1·33	

$\tilde{\nu}Ca(HSeO_3)_2.H_2O$	$\tilde{\nu}Ca(DSeO_3)_2.D_2O$	$\frac{\tilde{\nu}Ca(HSeO_3)_2.H_2O}{\tilde{\nu}Ca(DSeO_3)_2.D_2O}$	Assignment
455 sh	450 m	1·01	δSeO_2
474 s	472 m	1·00	
635 sh	620 sh	1·02	νSeO(SeOH)
656 s	640 s	1·03	
760 sh	774 s	0·98	$\nu_{as} SeO_2$
813 s	817 s	1·00	
835 s	838 sh	1·00	$\nu_s SeO_2$
870 s	871 s	1·00	
950 sh	—	—	γOH(SeOH)?
1 205 w	overlapped	—	δOH(SeOH)
1 264 m	924 m	1·37	
1 682 wb	1 230 w	1·37	$\delta OH(H_2O)$
1 850 vwb	—	—	?
2 390 mb	1 775 mb	1·35	νOH(SeOH)
2 750 mb	2 050 mg	1·34	
3 225 mb	2 400 mb	1·34	$\nu OH(H_2O)$
3 520 w	2 615 m	1·35	

$CaSeO_3$ anhydrous, crystalline, *I*:

400(3), 342(1), 307(4), 295(10), 236(6), 225(1). 193(3), 186(1), 183(4), 175(2), 170·9(2), 169·2(2), 162·0(1), 159·0(1), 154·1(1), 149·6(2), 147·3(2), 135·7(1), 127·2(1), 125·2(1).

$CaSeO_3$ anhydrous, crystalline, *II*:

407(3), 383(3), 350(3), 318(6), 294(10), 274(1), 265(6), 225(1), 213(1), 193(3), 190(3), 177(1), 172(1), 165·2(1), 161·5(1), 155·1(1), 142·6(2), 134·7(1).
The differences between both modifications were substantiated also difractographically.

The data about thermal decomposition of calcium hydrogenselenite monohydrate are given in Table I. The starting substance and the products of the reaction were studied roentgenographically.

$Ca(HSeO_3)_2.H_2O$:

680(4), 490(3), 440(3), 430(5), 361(7), 350(5), 332(3), 327(5), 314(1), 301(10), 284(4), 276(1), 212(2), 203(3), 190(2), 182(3), 176(2), 172(1), 169·8(3), 159·0(2), 152·3(2), 148·8(1), 145·0(1), 142·6(1), 137·8(1), 134·7(1), 131·1(1), 111·1(1), 107·5(2).

$CaSe_2O_5$:

374(1), 330(10), 306(3), 288(2), 261(1), 225(1), 217(2), 197(3), 175(2), 166·3(1), 160·0(1), 155·1(1), 145·8(1), 121·1(1), 116·1(1).

TABLE III

IR Spectra of Crystalline $CaSeO_3$ (*I*), $CaSe_2O_5$, and $Ca_2Se_3O_8$ (cm^{-1})

ν_s Symmetric stretching, ν_{as} antisymmetric stretching, δ bending in-plane, γ bending out-of-plane (torsion), ϱ rocking, w weak, vw very weak, m medium, s strong, b broad, sh shoulder.

$\tilde{\nu}CaSeO_3$(I)	Assignment	$\nu CaSe_2O_5$	Assignment	$\tilde{\nu}Ca_2Se_3O_8$	Assignment
435 m	δSeO_3	426 w	δSeO_2	435 w	$\delta SeO_2 + \delta SeO_3$
458 m		462 sh		497 m	
480 m		515 m	$\nu Se—O—Se$	593 s	$\nu Se—O—Se$
713 s	$\nu_s SeO_3$	563 s		715 s	$\nu SeO_2 + \nu SeO_3$
755 sh		580 sh		767 s	
783 s	$\nu_{as} SeO_3$	798 s	$\nu_{as} SeO_2$	855 m	
840 s		811 sh		810 s	
		852 s	$\nu_s SeO_2$	825 sh	
		871 s		888 sh	
		890 s		920 m	

$Ca_2Se_3O_8$:

430(6), 375(3), 353(1), 323(10), 305(5), 279(5), 268(5), 254(2), 249(2), 227(1), 205(2), 195(1), 180(4), 171(1), 165·2(1), 161·0(4), 153·7(1), 151·4(2), 131·5(2), 113·4(1).

IR spectra of $CaSeO_3.H_2O$, $Ca(HSeO_3)_2.H_2O$, $CaSeO_3$ anhydrous crystalline *I* $CaSe_2O_5$, $Ca_2Se_3O_8$, and their deuterates are given in Tables II – III. The assigning of spectral bands was done according to Paetzold[11–13].

DISCUSSION

A selenite of the composition Ca : Se : H_2O = 1 : 2 : 2 was found in the system $CaSeO_3$–SeO_2–H_2O at 298 K. Other authors[1,2,4,6] could not decide whether this

TABLE IV

Force constants of Se–O bonds

Substance	ν_s, cm^{-1}	ν_{as}, cm^{-1}	k_{SeO}, Nm^{-1}
$CaSeO_3.H_2O$	731	815	487
for SeO_2 group	853	787	528
$Ca(HSeO_3)_2.H_2O$			
for SeOH group	656	—	337
$CaSeO_3$ anhyd. cryst. *I*	734	816	485
for SeO_2 group	881	820	567
$CaSe_2O_5$			
for Se–O–Se bonds	540	—	229
$Ca_2Se_3O_8$ for Se–O–Se bonds	593	—	276

TABLE V

Energies and lengths of hydrogen bonds

Substance	E, kJ mol^{-1}	Distance O···O, pm
$CaSeO_3.H_2O$	29	279
	36	274
$Ca(HSeO_3)_2.H_2O$	35	275
	—	263
	—	256

is a monohydrate of hydrogenselenite or a dihydrate of diselenite of calcium. A study of similar systems containing alkaline metals (M^I) revealed hydrogenselenites[14,15] of the composition $M^I : Se = 1 : 1, 1 : 2, 1 : 4$, and $5 : 4$, in the case of magnesium[16] the compound $Mg(HSeO_3)_2.4\,H_2O$, and with barium no acidic salt was found but only anhydrous barium diselenite[17]. The presence of the vibration bands νOH(SeOH) and δOH(SeOH) in the IR spectrum (Table II) is an evidence that the compound formed in the system is a monohydrate of calcium hydrogenselenite.

Thermal analysis of $CaSeO_3$ (Table I) and powder X-ray diagrams suggest that anhydrous crystalline calcium selenite *I* is formed at 408–488 K, which recrystallizes at 833–843 K to form another crystalline modification of anhydrous calcium selenite (II); and this phase change is endothermic.

Thermal decomposition of calcium hydrogenselenite at 353–513 K leads to the diselenite, $CaSe_2O_5$. The compound looses first 1·5 mol of water at 353–363 K and then the remaining 0·5 mol H_2O at 418–513 K in two waves. Further decomposition of the diselenite leads at 603–638 K to triselenite, $Ca_2Se_3O_8$, which at 688 to 733 K changes to the second modification of anhydrous selenite, $CaSeO_3$ anhydrous crystalline *II*. The only possible explanation of this complicated thermal decomposition is based on the assumption of unequality of the positions occupied by the $HSeO_3^-$ ion in the crystal structure of the hydrogenselenite. The water of constitution and hydration is set free under formation of diselenite ions more readily from one half of these positions than from the other half. The conversion of diselenite to selenite proceeds analogously: SeO_2 is set free more readily from one half of the positions than from the other, therefore the intermediate product, $Ca_2Se_3O_8$, can be isolated. Its IR spectrum (Table III) suggests that Se–O–Se bonds are present in the structure of $Ca_2Se_3O_8$; and it is probable with respect to the width of the interval of stretching vibrations of the Se–O bond that the mentioned structure contains both SeO_2 and SeO_3 groups in accord with the concept mentioned above.

Force constants of Se–O bonds for the selenites under study calculated from the wave numbers of IR spectral bands are given in Table IV. They were calculated from equations derived from a diatomic model with the use of the Lehman's equation[18] for averaging of wave numbers by the method described earlier[16] with magnesium selenites. It follows from Table IV that the force constants are somewhat higher for SeO_2 groups in the hydrogenselenite and diselenite ions than for SeO_3 groups; and for SeOH and Se–O–Se they are, on the contrary, much lower than for SeO_3. The situation is analogous with alkaline selenites according to Paetzold's data and also with magnesium selenites according to our data[16].

The energies and lengths of hydrogen bonds for the studied compounds derived from IR wave numbers of stretching vibrations of the OH group are given in Table V. The energies were calculated (in kJ) according to Sokolov[19] as

$$E = (\nu_0 - \nu)/4{\cdot}0611\,.\,10^{-3}\nu_0\,.$$

The wave number, ν_0, of the stretching vibration of the free water molecule was set equal to 3750 cm^{-1}. The hydrogen bond lengths were determined from correlation diagrams[20-24] of ν_{OH} against $R_{O...O}$ and besides they were calculated from the empirical equation of Falk and Knop[25]. Averages from the obtained values were taken. The hydrogen bonds in the studied selenites can be classified as weak or moderately strong.

REFERENCES

1. Muspratt J. S.: J. Chem. Soc. *2*, 52 (1849).
2. Nilson L. F.: Bull. Soc. Chim. Fr. *21*, 253 (1874).
3. Chukhlantsev V. G.: Zh. Neorg. Khim. *1*, 2300 (1956).
4. Rocchiccioli C.: C. R. Acad. Sci. *247*, 1108 (1958).
5. Lenher V., Wechter E. J.: J. Amer. Chem. Soc. *47*, 1253 (1925).
6. Berzelius J. J.: Ann. Chim. Phys. *9*, 225 (1818).
7. Bode H.: Z. Anal. Chem. *153*, 335 (1956).
8. Tomíček O.: *Kvantitativní analysa*, p. 95. Published by Státní zdravotnické nakladatelství, Prague 1958.
9. Ganitskii M. Zh., Zhelinokraite V. I.: Zh. Neorg. Khim. *2*, 1341 (1957).
10. Přibil R.: *Komplexometrie*, p. 256. Published by SNTL, Prague 1977.
11. Simon A., Paetzold R.: Z. Anorg. Allg. Chem. *303*, 39 (1960).
12. Paetzold R., Simon A.: Z. Anorg. Allg. Chem. *301*, 246 (1959).
13. Simon A., Paetzold R.: Z. Elektrochem. Ber. Bunsenges. Phys. Chem. *64*, 209 (1960).
14. Sabbah R., Périnet G.: J. Chem. Phys. *62*, 929 (1965); *63*, 322 (1966).
15. Janitzki J.: Z. Anorg. Allg. Chem. *205*, 49 (1932).
16. Ebert M., Havlíček D.: Chem. Zvesti *34*, 441 (1980).
17. Neal L., McCrosky C. R.: J. Amer. Chem. Soc. *60*, 911 (1938).
18. Lehman W. J.: J. Mol. Spectrosc. *7*, 261 (1961).
19. Sokolov N. D.: Usp. Fiz. Nauk *57*, 205 (1955).
20. Naberukhin I. I., Efimov I. I.: Zh. Strukt. Khim. *12*, 591 (1971).
21. Pirrene J.: Physica (Utrecht) *21*, 971 (1955).
22. Novak A.: Structure and Bonding *18*, 177 (1974).
23. Ratajczak H., Orville-Thomas W. J.: J. Mol. Struct. *1*, 449 (1967—8).
24. Nakamoto K., Marghoshes M., Rundle R. E.: J. Amer. Chem. Soc. *77*, 6480 (1955).
25. Falk M., Knop O. in the book: *Water in Stoichiometric Hydrates* (*A Comprehensive Treatise*) (F. Franks, Ed.), Vol. 2, p. 55. Plenum Press, New York, London 1973.

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