Lithium and sodium antimonates

[a]M. DRÁTOVSKÝ and [b]J. KARLÍČEK

[a]*Department of Inorganic Chemistry, Faculty of Natural Sciences,*
Charles University, 128 40 Prague

[b]*Department of Chemistry, Pedagogical Faculty,*
306 19 Plzeň

Received 3 December 1980

Dedicated to Professor Stanislav Škramovský,
in honour of his 80th birthday

The existence of the compounds Li[Sb(OH)$_6$] and Na[Sb(OH)$_6$] was verified and new compounds with the overall composition $Li_3SbO_4 \cdot 4H_2O$ and $Na_4Sb_2O_7 \cdot 7H_2O$ were discovered by studying the solubility in the ternary systems, LiOH—$LiSbO_3$—H_2O and NaOH—$NaSbO_3$—H_2O. Both newly isolated substances and the products of their thermal decomposition were successfully indexed. Their constitution was characterized on the basis of their i.r. spectra.

Проверено существование соединений Li[Sb(OH)$_6$] и Na[Sb(OH)$_6$] и обнаружены новые соединения общего состава $Li_3SbO_4 \cdot 4H_2O$ и $Na_4Sb_2O_7 \cdot 7H_2O$ с помощью изучения растворимости третичных систем, LiOH—$LiSbO_3$—H_2O и NaOH—$NaSbO_3$—H_2O. Новоизолированные вещества и продукты их термического разложения были успешно снабжены показателями. Охарактеризован их состав на основании ИК спектров.

Hydrated lithium and sodium antimonates precipitate from potassium antimonate solutions in the form of crystalline hexahydroxoantimonates [1—10]. Hydrated antimonates with an alkali metal-to-antimony ratio greater than 1 : 1 have not been described in the literature, except for our work on potassium antimonates [11] and the work of *Urazov et al.* [12], who, in a study of the Na_2O—Sb_2O_5—H_2O system, described several hydrates with Na : Sb ratios of 1 : 1 and 3 : 1, in addition to the already known hexahydroxoantimonate. The final products of the thermal decomposition of the Li[Sb(OH)$_6$] and Na[Sb(OH)$_6$] compounds are crystalline trioxoantimonates, $MSbO_3$ [4, 13—15]. The anhydrous sodium salt $NaSbO_3$ crystallizes in the rhombohedral system [4, 16] and the partially dehydrated product, $NaSbO_3 \cdot 0.5H_2O$, in the cubic system [4, 14, 16, 17]. No crystallographic data are given in the literature for the anhydrous lithium salt prepared by thermal decomposition of the hydrate, Li[Sb(OH)$_6$], but the product of the same composition, obtained by ignition of antimony(III) oxide with lithium chloride and bromide in an oxygen atmosphere [10], has been described as rhombohedral. By ignition of a mixture of sodium or lithium nitrate with anhydrous potassium antimonate, the products $LiSbO_3$ and $NaSbO_3$ were obtained, crystallizing in the cubic system [18]; the cubic structure of this sodium trioxoantimonate differs from that of the $NaSbO_3 \cdot 0.5H_2O$ product. Tetraoxoantimonates M_3SbO_4 were also prepared; tetrahedral Li_3SbO_4 [19] by igniting antimony(III) oxide with lithium carbonate in an oxygen atmosphere and monoclinic Na_3SbO_4 by igniting antimony(III) oxide with sodium peroxide and sulfate [20—22].

This work on lithium and sodium antimonates continues a similar study of potassium antimonates [11] and their common purpose is to study the conditions for the existence of antimonates with a $M^I : Sb$ ratio of one.

Experimental

Chemicals

The initial compounds, Li[Sb(OH)$_6$] and Na[Sb(OH)$_6$], were prepared by precipitating potassium antimonate solutions with a small excess of lithium or sodium chloride [23]. Potassium antimonate was prepared by reaction of antimony(III) oxide with hydrogen peroxide in a potassium hydroxide medium [23], or an anal. grade Merck preparation with the composition $KSbO_3 \cdot 2.5H_2O$ was used. The other chemicals used were of anal. grade purity (Lachema, Brno).

Analytical methods

Lithium and sodium were determined as the sulfates after prior separation of antimony in the form of antimony(III) sulfide. The deviation of the determinations from the mean value did not exceed 0.8% rel. Antimony was determined iodometrically in a tartrate medium, after reduction of Sb(V) to Sb(III) [24], with a maximum deviation of the results from the mean of 1.3% rel. No Sb(III) was detected in the preparations and thus the Sb(V) content equalled the total antimony content. Water was determined from the difference of the result from 100% and from the weight loss during thermal decomposition.

Solubility study

The solubility in the $LiOH-LiSbO_3-H_2O$ and $NaOH-NaSbO_3-H_2O$ systems was studied at a temperature of 298 ± 1 K in a nitrogen atmosphere. For each system, a series of samples with alkali hydroxide concentration varying from a saturated to a very dilute solution was prepared. The corresponding antimonates were added to these solutions. Equilibration took 2 to 3 months and was followed by analyses of part of the solid phase, because analyses of the liquid phase were not decisive for equilibrium establishment.

Thermography

Thermal study of solid samples was carried out with a Derivatograph type OD 2 instrument (Hungary). The samples were heated at a rate of 5 K per min up to a temperature of 900 or 1200 K.

X-Ray patterns

The pulverized samples were studied using a Mikrometa 2 instrument (Chirana) with CuK_α-radiation at a voltage of 35 kV and a current of 20 mA. The patterns were obtained either in Lindenmann glass capillaries on a film with an exposure time of 90 min and the diffraction lines were measured with a precision of 0.05 mm on a Hilger ruler (Great Britain), or the diffractions were recorded on an NRX X-ray diffraction evaluation unit (Tesla) and the band positions were read with a precision of 0.5 mm. The line intensities were determined visually on a ten-point scale. The *hkl* symbols were assigned to the diffraction lines obtained. Theoretical values of the diffraction angles and interplanar distances were computed on a Hewlett—Packard 9830 A calculator using the DTEOROB and DTEORSPEC programs [25].

Infrared spectroscopy

The infrared spectra were obtained from 400 to 4000 cm^{-1} on a UR-20 spectrophotometer (Zeiss, Jena) in nujol mulls.

Results

The results of the solubility studies in the $LiOH—LiSbO_3—H_2O$ and $NaOH—NaSbO_3—H_2O$ systems at a temperature of 298 K are given in Tables 1 and 2, from which it follows that in the first system a product with the summary composition $LiSbO_3 \cdot 3.6H_2O$ is formed in contact with less concentrated lithium hydroxide solutions and the product $Li_3SbO_4 \cdot 4H_2O$ in contact with more concentrated ones. In the other system, a product with the summary composition $NaSbO_3 \cdot 3.6H_2O$ is formed in contact with less concentrated NaOH solutions and $Na_4Sb_2O_7 \cdot 7H_2O$ in contact with more concentrated ones. These solid phase compositions are obtained from the intercept of the lines connecting the image points of the liquid and separated, undried solid phase for each sample in an isothermal diagram of the ternary system $Li(Na)_2O—Sb_2O_5—H_2O$. Moreover, the compounds formed were separated from the mother liquor, washed with ethyl

Table 1

Analyses of the Li_2O—Sb_2O_5—H_2O system at a temperature of 298 K

No.	Liquid phase mass %			Mixture of liquid and solid phase, mass %			Solid phase
	Li_2O	Sb_2O_5	H_2O	Li_2O	Sb_2O_5	H_2O	
1	0.01	0.01	99.98	3.42	36.95	59.63	$LiSbO_3\cdot3.6H_2O$
2	1.74	0.01	98.25	3.57	28.01	68.42	
3	2.01	0.01	97.98	3.98	30.97	65.05	
4	3.15	0.01	96.84	5.10	45.19	49.71	
5	3.89	0.01	96.10	5.23	40.84	53.93	
6	4.66	0.01	95.33	5.54	32.90	61.56	
7	5.37	0.01	94.62	11.24	32.60	56.16	$Li_3SbO_4\cdot4H_2O$
8	5.40	0.01	94.59	13.23	43.48	43.29	
9	6.16	0.01	93.83	12.53	36.70	50.77	
10	6.45	0.01	93.54	9.86	19.79	70.35	

alcohol and acetone and dried in a vacuum dessicator over silica gel at laboratory temperature. The water content of these preparations was slightly lower than that in the analyzed, undried substances and varied between $LiSbO_3\cdot(3.2—3.6)H_2O$ and $Li_3SbO_4\cdot(3.5—3.8)H_2O$ for the lithium salts and $NaSbO_3\cdot(3.3—3.5)H_2O$ and $Na_4Sb_2O_7\cdot(6.2—6.8)H_2O$ for the sodium salts.

The thermal decomposition of the $LiSbO_3\cdot xH_2O$ and $NaSbO_3\cdot xH_2O$ hydrates leads to gradual loss of water with increasing temperature and finally to the anhydrous substances $MSbO_3$ at a temperature of 850—900 K. The decomposition of the hydrates $Li_3SbO_4\cdot xH_2O$ and $Na_4Sb_2O_7\cdot xH_2O$ involved two steps: the hydrate $Li_3SbO_4\cdot3.5H_2O$ was formed from the lithium salt around 400 K and dehydration to the product Li_3SbO_4 was complete at 1000 K; with the sodium salt, the lower hydrate $Na_4Sb_2O_7\cdot2.3H_2O$ was formed at a temperature of 800 K and decomposition to the anhydrous product $Na_4Sb_2O_7$ was complete at 1050 K.

The X-ray study was carried out with all the substances obtained during the solubility study in the heterogeneous systems and with all the products of their final thermal decomposition.

The comparison of the diffraction angles and interplanar distances of the anhydrous product $NaSbO_3$ with the literature data [4, 14—17] verified that the rhombohedral modification of $NaSbO_3$ is formed by thermal decomposition of the $NaSbO_3\cdot xH_2O$ hydrate. An X-ray study of the $LiSbO_3$ product obtained by thermal decomposition of the $LiSbO_3\cdot xH_2O$ hydrate was performed for the first time; however, it was found when comparing the observed diffraction angles and

Table 2

Analyses of the Na_2O—Sb_2O_5—H_2O system at a temperature of 298 K

No.	Liquid phase mass %			Mixture of liquid and solid phase, mass %			Solid phase
	Na_2O	Sb_2O_5	H_2O	Na_2O	Sb_2O_5	H_2O	
1	0.04	0.19	99.77	2.99	14.03	82.98	$NaSbO_3 \cdot 3.6H_2O$
2	4.53	0.03	95.44	5.66	11.92	82.42	
3	9.18	0.01	90.81	10.07	9.91	80.02	
4	12.38	0.01	87.61	12.12	11.00	76.88	
5	14.33	0.01	85.66	13.89	15.62	70.49	
6	14.88	0.01	85.11	13.78	10.46	75.76	
7	15.95	0.01	84.04	14.94	18.02	67.04	
8	17.99	0.02	81.99	15.90	19.35	64.75	
9	20.10	0.01	79.89	18.42	13.01	68.57	
10	27.45	0.02	72.53	20.90	26.07	53.03	
11	28.30	0.02	71.68	19.41	34.26	46.33	
12	28.51	0.02	71.47	18.73	38.08	43.19	
13	30.12	0.02	69.86	24.78	19.00	56.22	
14	30.77	0.04	69.19	28.98	12.08	58.94	$Na_4Sb_2O_7 \cdot 7H_2O$
15	31.41	0.04	68.55	27.91	22.99	49.10	
16	32.75	0.05	67.20	30.86	18.00	51.14	
17	33.79	0.04	66.17	29.95	17.92	52.13	
18	34.17	0.04	65.79	29.92	20.60	49.48	
19	34.35	0.05	65.60	30.65	18.26	51.09	
20	34.65	0.05	65.30	26.63	34.51	38.86	
21	35.56	0.04	64.40	28.67	27.72	43.61	
22	36.19	0.04	63.77	31.04	21.82	47.14	

interplanar distances with the data calculated from the published lattice constants [10] that the product has the same rhombic structure as the $LiSbO_3$ antimonate present in the product from another method (see p. 630). The diffraction lines of the other substances were indexed and the lattice parameters were calculated (Table 3). The lattice data for the substances $Li[Sb(OH)_6] \cdot 0.6H_2O$, Li_3SbO_4, and $Na[Sb(OH)_6] \cdot 0.5H_2O$ agree with the published data [4, 5, 8, 19]; the anhydrous product Li_3SbO_4 was prepared for the first time by decomposition and has the same structure as the product of the same composition prepared by ignition of antimony(III) oxide and lithium carbonate in an oxygen atmosphere [19]. The lattice data were calculated for the first time for the other substances. The diffraction lines of the anhydrous product $Na_4Sb_2O_7$ could only be indexed with relatively large lattice constant values.

The results of the X-ray studies of lithium and sodium antimonates are summarized in Tables 3—6.

Table 3

Crystal systems and lattice parameters of the lithium and sodium antimonates

No.	Substance	Crystal system	Lattice parameter[a]	
1	$Li[Sb(OH)_6]\cdot 0.6H_2O$	Hexagonal	$a = 533$ (4)	$c = 489$ (4)
2	$Li_3SbO_4\cdot 3.8H_2O$	Hexagonal	$a = 928$ (3)	$c = 980$ (3)
3	$LiSbO_3$	Rhombohedral	$a = 489.3$ $b = 849.1$	$c = 518.3$
4	Li_3SbO_4	Tetragonal	$a = 596$ (5)	$c = 837$ (6)
5	$Na[Sb(OH)_6]\cdot 0.5H_2O$	Tetragonal	$a = 798$ (5)	$c = 782$ (5)
6	$Na_4Sb_2O_7\cdot 6.8H_2O$	Tetragonal	$a = 1097$ (9)	$c = 1355$ (10)
7	$NaSbO_3$	Rhombohedral	$a = 612.5$	$\alpha = 51.05°$
8	$Na_4Sb_2O_7$	Tetragonal	$a = 1686$ (12)	$c = 1552$ (11)

a) Lattice parameters in pm, standard deviations in brackets.

Table 4

X-ray data for $Li_3SbO_4\cdot 3.8H_2O$[a]

I_0	d_0	*h*	*k*	*l*	I_0	d_0	*h*	*k*	*l*
8	470.0	1	1	0	3	147.8	3	3	2
10	420.0	1	0	2	3	140.3	4	0	5
7	330.0	0	0	3	2	138.4	1	5	2
1	265.0	1	1	3	3	134.8	5	0	4
9	257.0	1	2	2	8*d*	128.8	2	5	0
7	232.0	2	2	0	2	123.6	6	0	3
8	208.0	3	0	3	5	119.6	1	4	6
5	204.0	1	3	2	4	116.9	2	0	8
6*d*	173.2	1	4	1	2	116.0	4	4	0
7	164.6	1	2	5	1	113.8	2	5	4
7*d*	152.9	3	3	1	3	112.5	3	3	6

a) Interplanar distances in pm; I_0 — relative intensity, d_0 — observed interplanar distance.

The infrared spectra of the hydrates $Na[Sb(OH)_6]\cdot 0.5H_2O$, $Na_4Sb_2O_7\cdot 6.8H_2O$, $Li[Sb(OH)_6]\cdot 0.6H_2O$, and $Li_3SbO_4\cdot 3.8H_2O$ (Table 7) exhibit absorption bands for vibrations of the SbO, SbOH, OH, and H_2O bonds. The i.r. spectra of the lower hydrate, $Li_3SbO_4\cdot 3.5H_2O$ have the same shape as those of the hydrate

Table 5

X-ray data for $Na_4Sb_2O_7 \cdot 6.8H_2O$

I_0	d_0	h	k	l	I_0	d_0	h	k	l
5	850.0	1	0	1	4	176.7	6	0	2
9	510.0	2	0	1	1	175.4	5	2	4
10	460.0	1	2	1	1	170.5	4	5	0
8	400.0	1	2	2	3	162.9	6	3	1
4	392.0	1	1	3	4	153.9	6	3	3
2	350.0	2	0	3	2	152.3	6	4	0
2	342.0	0	0	4	1	147.5	4	4	6
2	334.0	1	2	3	1	147.1	5 7	5 1	3 3
1	295.0	2	2	3	2	145.8	4	3	7
4	281.0	1	2	4	2	126.6	6	4	6
2	246.0	2	4	0	2	120.6	9	1	1
3	241.0	2	4	1	1	119.2	7	2	7
1	238.0	1	2	5	4	115.6	7	5	5
7	230.0	2	4	2	3	115.3	9	3	1
3	200.0	2	4	4	3	114.9	8	2	6
1	186.7	3	5	0	3	114.7	8	5	2
3*d*	183.0	6	0	0	2	113.9	0	0	12
6	178.7	6	1	1					

Table 6

X-ray data for $Na_4Sb_2O_7$

I_0	d_0	h	k	l	I_0	d_0	h	k	l
2	650.0	1	1	2	2*d*	170.1	4	9	1
10	530.0	1	3	0	2	166.4	7	7	2
2	440.0	1	3	2	3	161.4	9	3	4
3	400.0	1	4	1	4	159.9	6	0	8
2	380.0	2	4	0	3	158.3	8	7	1
3	299.0	4	4	0	4	153.0	2	0	10
1	289.0	5	3	0	3	150.6	7	1	8
1	273.0	1	6	1	6	146.9	3	9	6
9	264.0	6	0	2	3	140.6	1	0	11
5	237.0	2	2	6	3	137.9	5	7	8
6	229.0	2	7	1	1	136.1	6	0	10
1	219.0	7	0	3	4	132.3	9	9	0
1	213.0	2	4	6	1	130.7	4	11	5
3	203.0	1	7	4	2*d*	128.2	7	9	6
3	198.1	2	8	2	5	118.6	11 4	9 4	0 12
7	187.0	9	1	0					

Table 7

Infrared spectra of hydrated lithium and sodium antimonates [a]

$\mathrm{Li[Sb(OH)_6]\cdot 0.6H_2O}$	$\mathrm{Li_3SbO_4\cdot 3.8H_2O}$	$\mathrm{Na[Sb(OH)_6]\cdot 0.5H_2O}$	$\mathrm{Na_4Sb_2O_7\cdot 6.8H_2O}$	$\mathrm{Na_4Sb_2O_7\cdot 2.3H_2O}$	Assignment
420 m	417 m				ν(LiO)
	470 m				
510 w	505 m				
535 w		630 vs	633 s		$\nu_L(\mathrm{H_2O})$
				405 m	ν(SbO)
				440 m	
				465 w	
				485 m	
580 s	576 m	530 m	529 m	524 s	
610 s	600 m	591 vs	570 s	575 vs	
625 vs	625 vs	602 vs	587 vs	655 s	
675 vs	675 vs		685 vs	680 m	
		700 s	705 vs		γ(SbOH)
		740 s	745 s		
810 m		790 m			
1045 s	1035 s	1040 m	1038 m	1040 vw	δ(SbOH)
1075 s	1072 m	1082 m	1090 s		
1130 m		1112 s	1115 s		
1190 w	1165 w	1125 s	1130 s	1139 vw	
1675 vw	1675 vw	1640 vw	1650 vw		$\delta(\mathrm{H_2O})$

Table 7 (Continued)

$Li[Sb(OH)_6]\cdot 0.6H_2O$	$Li_3SbO_4\cdot 3.8H_2O$	$Na[Sb(OH)_6]\cdot 0.5H_2O$	$Na_4Sb_2O_7\cdot 6.8H_2O$	$Na_4Sb_2O_7\cdot 2.3H_2O$	Assignment
2070 vw	2070 vw				
2220 w		2165 w	2160 w		$2\delta(H_2O)$
3210 vs	3250 vs	3190 vs	3190 vs	3180 w	$\nu(OH)$ in SbOH
3270 vs	3280 vs	3220 vs	3240 vs	3210 w	
	3325 vs	3280 vs			
3360 vs	3400 vs		3350 s		
3440 vs	3440 s	3430 vs	3430 s		$\nu(OH)$ in H_2O

a) Band wavenumber in cm^{-1}; ν — stretching vibration, δ — deformation planar vibration, γ — deformation out-of-plane vibration, $\nu_L(H_2O)$ — libration vibration of water; vs — very strong, s — strong, m — medium, w — weak, vw — very weak.

Table 8

Infrared spectra of anhydrous lithium and sodium antimonates

$LiSbO_3$	Li_3SbO_4	$NaSbO_3$	$Na_4Sb_2O_7$
			408 m
	430 s		435 m
	455 s		465 w
473 s	480 s		485 w
506 m			
		530 s	527 s
563 s			
575 s	580 s	582 vs	585 vs
630 vs	640 vs	645 s	650 s
		680 m	680 m
720 s	720 s		
765 s	770 m		

$Li_3SbO_4 \cdot 3.8H_2O$ and the lower hydrate $Na_4Sb_2O_7 \cdot 2.3H_2O$ has weak bands corresponding to deformation vibrations of SbOH groups and stretching vibrations of OH groups. The deformation vibration bands of water are not perceptible. The absorption bands in the infrared spectra of the anhydrous compounds $LiSbO_3$, Li_3SbO_4, $NaSbO_3$, and $Na_4Sb_2O_7$ are given in Table 8.

Discussion

The solubility study in the $LiOH$—$LiSbO_3$—H_2O system was performed for the first time and, in addition to the hydrate $LiSbO_3 \cdot 3.6H_2O$ described earlier [4, 26, 27], the existence of the compound $Li_3SbO_4 \cdot 4H_2O$ was verified. In the study of the solubility in the $NaOH$—$NaSbO_3$—H_2O system, the existence of hydrated antimonates with a Na:Sb ratio of 3:1, described earlier in the literature [12], was not verified, but only two substances were found in the system, the compound $NaSbO_3 \cdot 3.6H_2O$ described earlier [4, 5, 8, 26] and a newly isolated compound, $Na_4Sb_2O_7 \cdot 7H_2O$. During isolation of these substances from the mother liquor, the amount of water of crystallization decreases somewhat. This is characteristic of alkali metal antimonates, together with fluctuating and nonstoichiometric content of water of crystallization, and is in agreement with the other literature data [9, 11, 27, 28]. The individuality of the new substances, $Li_3SbO_4 \cdot 4H_2O$ and $Na_4Sb_2O_7 \cdot 7H_2O$, was verified by determining their thermodynamic stability by measuring the solubility in the ternary system at a constant temperature. An X-ray study of these substances was performed and, in spite of a somewhat decreased content of water of crystallization ($Li_3SbO_4 \cdot 3.8H_2O$ and $Na_4Sb_2O_7 \cdot 6.8H_2O$), all the interference lines could be indexed in a hexagonal or tetragonal system.

The constitution of the hydrates $M^ISbO_3 \cdot xH_2O$ ($M^I = Li$, Na) has already been verified and corresponds to the hexahydroxoantimonates $M[Sb(OH)_6]$ [2—4, 9]. However, it follows from the i.r. spectra that the isolated hexahydroxoantimonates also contain water of crystallization. The preparations obtained here had an average composition of $M[Sb(OH)_6] \cdot 0.5H_2O$. During thermal decomposition of these substances, water begins to dissociate at the relatively high temperature of 490—510 K, with simultaneous decomposition of the inner coordination sphere of the $[Sb(OH)_6]^-$ anion. Similar to other authors [9, 27], we did not succeed in obtaining the anhydrous salts $M[Sb(OH)_6]$. The i.r. spectra indicate that the $Li_3SbO_4 \cdot 4H_2O$ and $Na_4Sb_2O_7 \cdot 7H_2O$ hydrates also contain both constitutional water and water of hydration. Assuming a coordination number of 6 for antimony in antimonates [9, 29], the constitutional formulae $Li_3[SbO_2(OH)_4] \cdot 2H_2O$ and $Na_2[SbO(OH)_5] \cdot H_2O$ can be proposed for the lithium and sodium compounds, respectively. This ratio of constitutional water and water of hydration follows not only from the coordination number of antimony, but also from the intensities of the absorption bands assigned to the OH vibrations in SbOH and H_2O. Compared with the higher hydrate $Na_4Sb_2O_7 \cdot 7H_2O$ (or $6.8H_2O$), the lower hydrate $Na_4Sb_2O_7 \cdot 2.3H_2O$ exhibits a band for OH in SbOH with about half the intensity, whereas the OH bands in H_2O are completely absent. This corresponds to a ratio of constitutional water to water of hydration of about 5:2 in the higher hydrate, as required by the proposed constitutional formula. The higher lithium hydrate, $Li_3SbO_4 \cdot 4H_2O$ (or $3.8H_2O$), has a water content similar to that of the lower hydrate and there are no substantial differences in the band intensities of the two substances; for this reason, Table 7 does not contain the bands for the lower hydrate. Similar to the analogous potassium compound [11], for the sodium compound the validity of the above constitutional formulae is supported by the works of *Jander* and *Ostmann* [30], who detected the existence of the $[SbO(OH)_5]^{2-}$ anion at pH > 12 in a study of antimonate solutions.

All the substances studied are thermally very stable. During the thermal decomposition up to temperatures of 850—1050 K, only dehydration to the anhydrous products without reduction of antimony was observed, similar to potassium antimonates [11]. The presence of constitutional water up to such high temperatures was verified by the i.r. spectra and by analyses of the products collected at temperatures about 150 K lower than the final decomposition temperature.

References

1. Glemser, O. and Rieck, G., *Z. Anorg. Allg. Chem. 297*, 175 (1958).
2. Hammet, L. P. and Pauling, L., *J. Amer. Chem. Soc. 55*, 3053 (1933).
3. Pauling, L., *J. Amer. Chem. Soc. 55*, 1895 (1933).
4. Schrewelius, N., *Z. Anorg. Allg. Chem. 238*, 241 (1938).
5. Beintema, J., *Rec. Trav. Chim. Pays-Bas 71*, 111 (1937).
6. Beintema, J., *Proc. Acad. Sci.* (Amsterdam) *38*, 1015 (1937); *Chem. Abstr. 30*, 1281 (1936).
7. Beintema, J., *Proc. Acad. Sci.* (Amsterdam) *39*, 241 (1936); *Chem. Abstr. 30*, 3697 (1936).
8. Asai, T., *Bull. Chem. Soc. Jap. 48*, 2677 (1975).
9. Siebert, H., *Z. Anorg. Allg. Chem. 301*, 161 (1959).
10. Edstrand, M. and Ingri, N., *Acta Chem. Scand. 8*, 1021 (1954).
11. Drátovský, M. and Karlíček, J., *Collect. Czech. Chem. Commun.*, in press.
12. Urazov, G. G., Lipshii, B. M., and Lovchikov, V. S., *Zh. Neorg. Khim. 4*, 439 (1959).
13. Balicheva, T. G. and Roi, N. I., *Zh. Neorg. Khim. 17*, 142 (1972).
14. Colin, J. M. and Lefebvre, J., *C. R. Acad. Sci., Ser. C 271*, 503 (1970).
15. Colin, J. M. and Lefebvre, J., *C. R. Acad. Sci., Ser. C 271*, 280 (1970).
16. Montmory, M. C., Durif-Varambou, A., and Paré, X., *Bull. Soc. Fr. Mineral. Cristallogr. 86*, 434 (1963).
17. Stewart, D. J. and Knop, O., *Can. J. Chem. 48*, 1323 (1970).
18. Hong, H. Y. P., Kalafas, J. A., and Goodenough, J. B., *J. Solid State Chem. 9*, 345 (1974).
19. Blasse, G., *Z. Anorg. Allg. Chem. 326*, 44 (1963).
20. Ananyev, N. I. and Polyvyannii, I. R., *Tr. Inst. Met. Obogashch., Akad. Nauk Kaz. SSR 13*, 96 (1965); *Chem. Abstr. 68*, 26450a (1968).
21. Ananyev, N. I., Polyvyannii, I. R., Demyanikov, I. G., and Suleymanov, K., *Tr. Inst. Met. Obogashch., Akad. Nauk Kaz. SSR 21*, 35 (1967); *Chem. Abstr. 68*, 45670p (1968).
22. Schwedes, B. and Hoppe, R., *Z. Anorg. Allg. Chem. 393*, 136 (1972).
23. Jander, G. and Brüll, W., *Z. Anorg. Allg. Chem. 158*, 321 (1926).
24. Johnson, E. A. and Newman, E. J., *Analyst 80*, 631 (1955).
25. Podlahová, J., Kratochvíl, B., and Loub, J., *Programs for X-ray calculations for the HP 9830 A calculator* (in Czech). Charles University, Prague, 1975.
26. Frank, R., *Rev. Chim. Miner. 10*, 795 (1973).
27. Balicheva, T. G. and Roi, N. I., *Zh. Strukt. Khim. 12*, 415 (1971).
28. Lisichkin, I. N., Kerembekov, A. V., Kerembekova, N. A., and Manashirov, O. Ya., *Zh. Neorg. Khim. 16*, 2133 (1971).
29. Balicheva, T. G. and Roi, N. I., *Zh. Neorg. Khim. 17*, 2959 (1972).
30. Jander, G. and Ostmann, H. J., *Z. Anorg. Allg. Chem. 315*, 241, 250 (1962).

Translated by M. Štulíková