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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis and Properties of $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$

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Abstract—Conditions for the synthesis of the water-soluble lead thiosulfate complex $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ were determined. The complex synthesized was characterized by UV and IR spectroscopy and X-ray phase and thermal analyses. Thermolysis schemes were proposed on the basis of the IR and mass spectra of the thermal decomposition products.

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The interaction of equivalent amounts of $Pb(NO_3)_2$ or $Pb(CH_3COO)_2$ with $Na_2S_2O_3$ in aqueous solutions yields poorly soluble compounds PbS_2O_3 [1] and $Pb_3(S_2O_3)_2(CH_3COO)_2$ [2]. These compounds are dissolved in an $Na_2S_2O_3$ excess to form lead thiosulfate complex ions $[Pb(S_2O_3)_2]^{2-}$, $[Pb(S_2O_3)_3]^{4-}$, and $[Pb(S_2O_3)_4]^{6-}$ [3].

The purpose of this work is to recover water-soluble lead thiosulfate complexes in the solid phase and characterize them.

EXPERIMENTAL

The following reagents were used: $Na_2S_2O_3 \cdot 5H_2O$ (pure for analysis grade), $Pb(NO_3)_2$ (pure for analysis grade), and PbS_2O_3 prepared by reacting solutions of $Pb(NO_3)_2$ and $Na_2S_2O_3$ [1].

Lead thiosulfate complexes were synthesized using two methods. In method (1), exact weighed portions of $Na_2S_2O_3 \cdot 5H_2O$ and $Pb(NO_3)_2$ were dissolved in a minimum volume of water and combined by pouring a solution of $Pb(NO_3)_2$ solution to a solution of $Na_2S_2O_3$; the relevant reaction is

$$Pb(NO_3)_2 + xNa_2S_2O_3 \longrightarrow Na_{(2x-2)}[Pb(S_2O_3)_x] + 2NaNO_3, \quad (1)$$

where $x = 2$–4.

Reaction (1) proceeded in two stages: poorly soluble PbS_2O_3 was first formed in the solution (the solubility product was 4×10^{-7}) and then dissolved in an $Na_2S_2O_3$ excess.

In method (2), a PbS_2O_3 powder was dissolved in a saturated solution of $Na_2S_2O_3$; the relevant reaction is

$$PbS_2O_3 + yNa_2S_2O_3 \longrightarrow Na_{2y}[Pb(S_2O_3)_{(y+1)}], \quad (2)$$

where $y = 1$–3.

Lead thiosulfate PbS_2O_3 formed then the solutions were combined according to method (1) and the PbS_2O_3 powder used in method (2) are completely dissolved only when the molar ratio $Pb^{2+} : S_2O_3^{2-} = 1 : 4$ or higher. At other ratios insoluble PbS_2O_3 remains in the solution.

Thus, the lead thiosulfate complexes were recovered to the solid phase from solutions with the molar ratio $Pb^{2+} : S_2O_3^{2-} = 1 : 4$.

On heating and storage solutions of the lead thiosulfate complexes decompose to form PbS, which makes impossible their isolation by the evaporation of the solvent.

The lead thiosulfate complexes can be isolated from solutions using alcohol. When ethanol is used, the lead thiosulfate complexes are isolated as an oily liquid, which is separated and treated with absolute ethanol (without additional treatment, the liquid decomposes with time to form PbS). The oily liquid gradually transforms into a powder, which is filtered off, washed, and dried in air.

A drawback of method (1) is the necessity to reprecipitate the product because of its contamination with $NaNO_3$, which enchances the decomposition of the lead thiosulfate complexes. In this case, the yield of the product decreases.

The product is isolated as a nonhygroscopic white powder. The yield of the lead thiosulfate complexes in method (2) is 75%.

The compositions and structures of the compounds synthesized were determined by elemental and thermal analyses and IR spectroscopy.

The complexes were analyzed for lead [4] and sulfur [5]. The amount of water was determined from thermal analysis data.

For $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ anal. calcd. (%): Pb, 22.98; S, 28.45; H_2O, 11.98.

Found (%): Pb, 23.1; 23.02; S, 28.40; 28.35; H_2O, 11.81.

Thus, according to the elemental and thermal analyses, the synthesized compound is formulated as $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ (sodium tetrathiosulfatoplumbate hexahydrate).

X-ray diffraction patterns were measured on a Shimadzu XRD 6000 diffractometer (CuK_α radiation).

IR spectra as KBr pellets were recorded on a Nicolet 6700 IR spectrometer in the range 400–4000 cm^{-1} at room temperature.

The electronic absorption spectra of solutions were recorded on an Evolution 600 spectrophotometer using 1-cm quartz cells.

Thermogravimetric studies were carried out on an SDT Q600 analyzer in the temperature range from 20 to 800°C under a nitrogen or air atmosphere. Thermal decomposition products were identified using IR absorption spectra recorded for samples stored before and after the corresponding endo- or exotherms in a vacuum or in air.

Gases evolved upon the thermal decomposition were analyzed using a TRACE DSQ chromatograph/mass spectrometer.

RESULTS AND DISCUSSION

The X-ray phase study showed that the compounds synthesized by methods (1) and (2) were alike, being one individual substance that possessed a characteristic X-ray pattern containing no lines of the starting components (Table 1).

The individual character of the compound was also proved by IR spectra. The frequencies observed in the IR spectra of the compound and their assignments to the vibrations of atomic groups are given in Table 2.

According to [1], the vibration ν_{as}(SO) is the most fruitful for the determination of the structure of thiosulfate compounds: >1175 cm^{-1} (S bridging), 1175–1130 cm^{-1} (S coordinated), ~1130 cm^{-1} (ionic $S_2O_3^{2-}$), and <1130 cm^{-1} (O coordinated). The shift of the ν_s(SO) vibration to higher frequencies than 1000 cm^{-1} indicates the coordination through the sulfur atom, and the shift to below 1000 cm^{-1} indicates the coordination through the oxygen atom. As can be seen from the data in Table 2, the thiosulfate group is coordinated to the lead atom through the sulfur and oxygen atoms and acts as a bidentate ligand.

The 3300–3600 cm^{-1} range of the IR spectrum contains two peaks with maxima at 3395 and 3517 cm^{-1} associated with ν(OH) of water molecules. The presence of two maxima may arise from the nonequivalence of water molecules in the structure of sodium tetrathiosulfatoplumbate hexahydrate as to the distance from the metal atom and involvement in hydrogen bonding.

The compound synthesized is highly soluble in water. At concentrations of 0.5 mol/L and higher, sodium tetrathiosulfatoplumbate hexahydrate is dissolved with the formation of a minor amount of PbS, and the solution turns brown. On storage, the highly concentrated solutions decompose with time to form PbS.

At a solution concentration of 0.1 mol/L, platy pearly round-shaped crystals precipitate from the solutions after 8–10 h. The IR spectrum of the compound isolated from the solution is identical to that of PbS_2O_3 (Table 2). This indicates that in an aqueous solution the complex undergoes hydrolysis and decomposes.

It should be noted that PbS_2O_3 prepared by reacting solutions of $Pb(NO_3)_2$ and $Na_2S_2O_3$ has no pronounced crystal structure, unlike PbS_2O_3 formed by the hydrolysis of sodium tetrathiosulfatoplumbate hexahydrate.

The electronic absorption spectra of PbS_2O_3, $Na_2S_2O_3$, and sodium tetrathiosulfatoplumbate hexahydrate are shown in Fig. 1. The spectrum of sodium tetrathiosulfatoplumbate hexahydrate, as well as that of PbS_2O_3, is characterized by the presence of two absorption bands in the UV region: one is the charge-transfer band from thiosulfate ions to solvent molecules with a maximum at 215 nm, which is also observed in the spectrum of $Na_2S_2O_3$, and the other is the charge-transfer band from thiosulfate ions to lead ions with a maximum at 256 nm. The electronic absorption spectrum of sodium tetrathiosulfatoplumbate hexahydrate differs from that of PbS_2O_3 by the bathochromic shift of the adsorption edge at 215 nm, which is related to an increase in the amount of the thiosulfate ions surrounding the lead ion.

The study of the thermolysis of the compound in air and in a nitrogen atmosphere showed that the thermal decomposition of sodium tetrathiosulfatoplumbate hexahydrate proceeded in three stages (Figs. 2, 3). Heating first results in removal of water of crystallization. Second, the dehydrated complex decomposes at the second stage. At the third stage, the decomposition products are oxidized (in air) or removed (in nitrogen).

The thermolysis is accompanied by the formation of volatiles. According to the mass-spectrometric data, the thermolysis products contains ions with the following mass numbers: 48, 64, 80, 96, 128, 160, 192, 224, and 256. The peaks in the mass spectrum corresponding to the masses 48 and 64 amu are attributed to the fragmentation radical ion SO^+ and sulfur dioxide SO_2^+. The presence in the mass spectra of the molecular ion S_8^+ with the mass number 256 and its fragmentation from S_8 to S_2 (m/z = 224, 192, 160, 128, 96, and 64) indicate the formation of sulfur upon the thermolysis of sodium tetrathiosulfatoplumbate hexahydrate. The mass spectrum also contains a low-intensity peak with the mass number 80, which may be assigned to sulfur trioxide SO_3^+.

The DTA curves in the range 20–90°C contain two endotherms with maxima at 52 and 88°C corresponding to the stepped dehydration of sodium tetrathiosulfatoplumbate hexahydrate. The weight loss in air is 11.5% under a nitrogen atmosphere 11.81%, which

Table 1. Interplanar spacings and line intensities for $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$

d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
12.133	5	3.605	5	2.247	8
11.841	9	3.537	24	2.236	5
11.539	32	3.503	18	2.227	9
10.961	29	3.474	16	2.202	11
10.644	33	3.442	28	2.193	6
10.132	26	3.378	5	2.167	7
9.709	89	3.356	15	2.122	9
7.622	13	3.290	10	2.095	13
7.459	100	3.275	7	2.085	10
6.736	66	3.222	38	2.072	15
6.532	5	3.202	25	2.063	5
6.412	7	3.114	28	2.053	13
6.329	6	3.091	19	2.045	16
6.233	5	3.021	17	2.034	5
5.756	14	2.993	21	2.018	10
5.668	48	2.978	24	2.010	5
5.619	59	2.958	12	1.986	14
5.514	47	2.926	54	1.978	12
5.460	52	2.888	24	1.970	10
5.387	6	2.864	39	1.942	5
5.102	25	2.833	63	1.922	14
4.995	5	2.799	29	1.914	10
4.944	14	2.762	7	1.887	12
4.715	10	2.739	14	1.878	15
4.643	5	2.714	50	1.868	16
4.575	20	2.680	19	1.861	13
4.458	8	2.648	21	1.852	6
4.431	10	2.579	6	1.836	6
4.334	100	2.558	5	1.822	7
4.262	25	2.537	21	1.812	7
4.163	14	2.486	10	1.803	6
4.099	10	2.453	12	1.790	7
4.048	29	2.416	10	1.775	6
3.981	14	2.406	19	1.742	10
3.948	5	2.361	7	1.736	9
3.831	5	2.350	22	1.705	5
3.778	48	2.323	5	1.697	11
3.719	28	2.311	10	1.691	9
3.664	7	2.257	6	1.679	7

Table 2. Maxima of the vibration frequencies (cm^{-1}) and their assignment in the IR spectra of $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$, $Na_2S_2O_3$, PbS_2O_3, and the compound formed by the hydrolysis of $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$

$Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$	$Na_2S_2O_3$ [1]	PbS_2O_3 [1]	Compound formed by $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ hydrolysis	Band assignment
3526				ν(OH)
3396				
1631				δ(OH)
1594				
1151	1160	1140	1141	ν_{as}(SO)
1126	1130	1116	1119	
1027	1002	988	988	ν_s(SO)
1011				
694	680	645	645	δ_s(SO)
680	668	624	625	
643				
551	555	541	542	δ_{as}(SO)
542	535	516	517	
439	338	434	435	ν(SS)

corresponds to the removal of six water molecules per molecule of the compound and the formation of anhydrous sodium tetrathiosulfatoplumbate (the calculated loss is 11.98%).

The dehydration of sodium tetrathiosulfatoplumbate hexahydrate in both nitrogen and air is accompanied by partial decomposition and removal of the decomposition products, as observed in the TG curves. The nonequivalence of the water molecules in sodium tetrathiosulfatoplumbate hexahydrate in the IR spectra of the residues becomes more pronounced as temperature increase (Fig. 4, curve *1*). According to the IR spectra, the complete dehydration of sodium tetrathiosulfatoplumbate hexahydrate occurs at 115°C in both cases.

The first changes in the IR spectra of the residues arising from the decomposition of the thiosulfate groups of sodium tetrathiosulfatoplumbate hexahydrate appear at 90°C (Fig. 4, curve *1*). These changes are due to the splitting of the absorption bands in the frequency regions of ν_{as}(SO) and ν_s(SO). Visually sodium tetrathiosulfatoplumbate retains its original white color up to 120°C.

The heating in the range 115–180°C is accompanied by the distortion of the sodium tetrathiosulfatoplumbate structure, which is seen from the changes in the IR spectra. The compound becomes brown.

In both cases, the complete decomposition of sodium tetrathiosulfatoplumbate occurs in the range 180–350°C. The absorption bands characteristic of the thiosulfate groups gradually disappear from the IR spectra, the absorption band at 1120–1150 cm^{-1} becomes broader, and the absorption band with the maximum at 625 cm^{-1} assigned to the bending vibra-

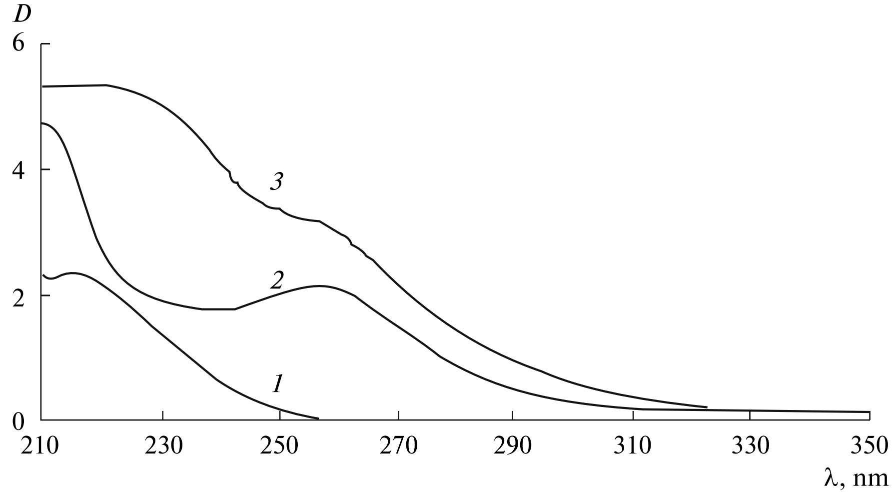

Fig. 1. Electronic absorption spectra of (*1*) $Na_2S_2O_3$ (5×10^{-4} mol/L), (*2*) PbS_2O_3 (5×10^{-4} mol/L), and (*3*) $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ (5×10^{-4} mol/L).

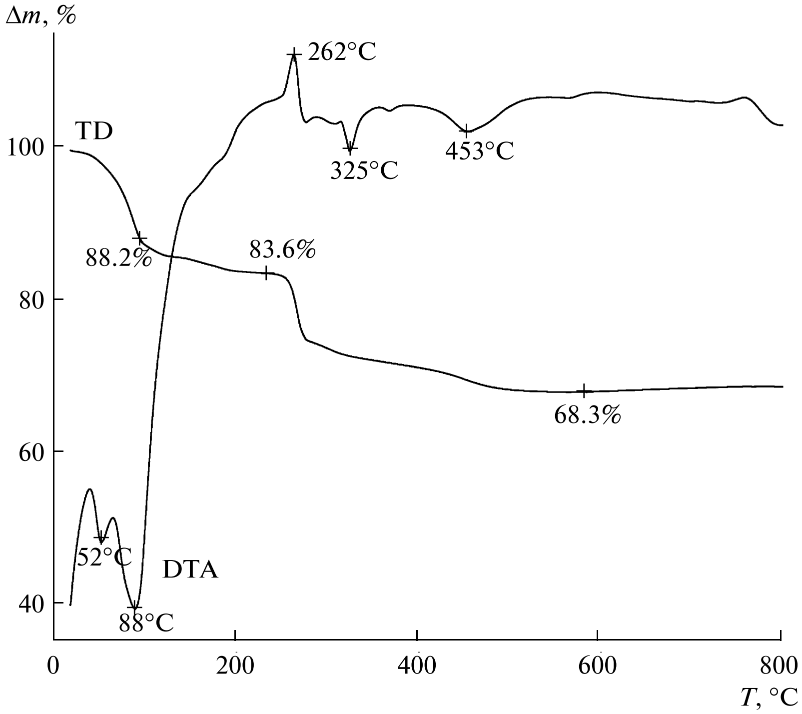

Fig. 2. Thermal curves for $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ in a nitrogen atmosphere.

tions δ(SO) of the sulfate group appears (Fig. 4, curves *2* and *3*). The sodium tetrathiosulfatoplumbate residues formed in a vacuum contain elementary sulfur. In both cases, the residue turns black.

The DTA curve exhibits composite features accompanied by a weight loss: an exotherm at 262°C and an endotherm at 325°C with a total weight loss of 31.7% upon thermolysis in a nitrogen atmosphere, or two partially overlapped exotherms at 275 and 285°C with a total loss of 26.7% upon thermolysis in air.

It is known that the weakest bond in the thiosulfate group is the S–S bond [6]. Most likely, the decomposition of the thiosulfate groups of sodium tetrathiosulfatoplumbate begins from the cleavage of this bond. According to [7], the thermolysis of PbS_2O_3 proceeds in two stages. At the first stage PbS and SO_3 are formed, and at the second stage SO_3 reacts with PbS_2O_3 to form $PbSO_4$, S, and SO_2.

Basing on the literature data and experimental results, we may assume that the exotherms at 262°C (Fig. 2) and 274°C (Fig. 3) are due to the oxidation of the thiosulfate groups with sulfur trioxide SO_3. Because of the concurrence of sodium tetrathiosulfatoplumbate decomposition and oxidation and the more vigorous manifestation of the exotherms, there are no endotherms of decomposition in the DTA curves.

The second exotherm (at 285°C) (Fig. 3) is associated with the oxidation of the thiosulfate groups to sulfate groups with the evolution of S, which is almost completely oxidized in air to SO_2. The endotherm at 325°C (Fig. 2) is assigned to the decomposition of the thiosulfate groups that have not been oxidized with SO_3.

The exotherm at 388°C (Fig. 3) and the endotherm at 453°C (Fig. 2) correspond to the removal of S: in the first case, due to oxidation to SO_2 (the weight loss is 0.5%), and in the second case, due to sublimation (the loss is 6.5%).

The weight increase in the TG curves after 400°C (Fig. 3) is related to the oxidation of PbS with air oxygen and the formation of $PbSO_4$, which is confirmed by the IR spectra of the residues obtained at 800°C (Fig. 4, curve *4*).

Thus, the thermal decomposition of sodium tetrathiosulfatoplumbate hexahydrate may be presented as follows:

$$Na_6[Pb(S_2O_3)_4] \cdot 6H_2O \longrightarrow Na_6[Pb(S_2O_3)_4] + 6H_2O,$$

$$Na_6[Pb(S_2O_3)_4] \longrightarrow PbS + SO_3 + 3Na_2S_2O_3,$$

$$Na_2S_2O_3 + SO_3 \longrightarrow Na_2SO_4 + S + SO_2.$$

In a nitrogen atmosphere:

$$2Na_2S_2O_3 \longrightarrow Na_2SO_4 + Na_2S + S + SO_2.$$

In air:

$$2Na_2S_2O_3 + O_2 \longrightarrow 2Na_2SO_4 + 2S,$$

$$3S + 3O_2 \longrightarrow 3SO_2.$$

The overall equations for sodium tetrathiosulfatoplumbate hexahydrate decomposition are as follows:

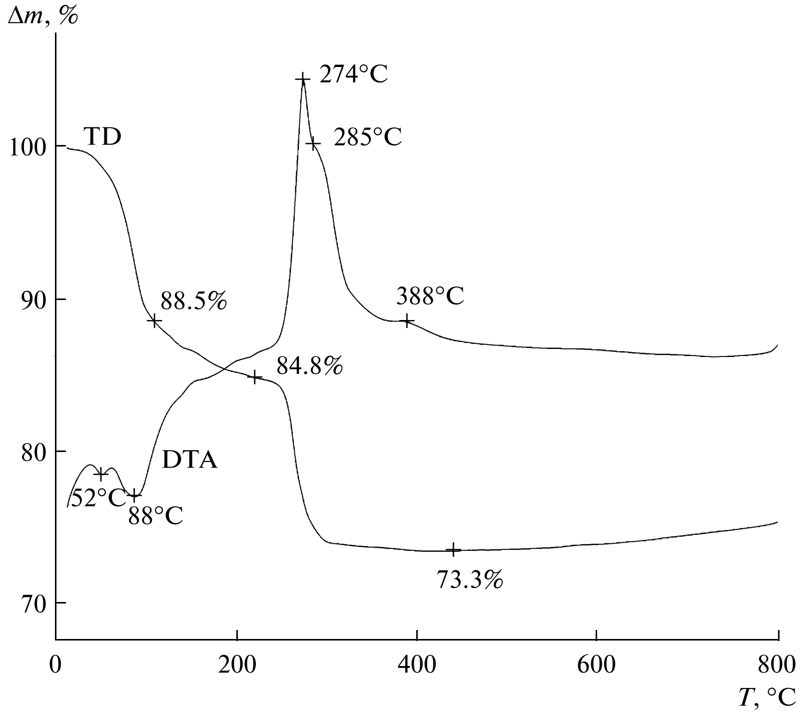

Fig. 3. Thermal curves for $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ in air.

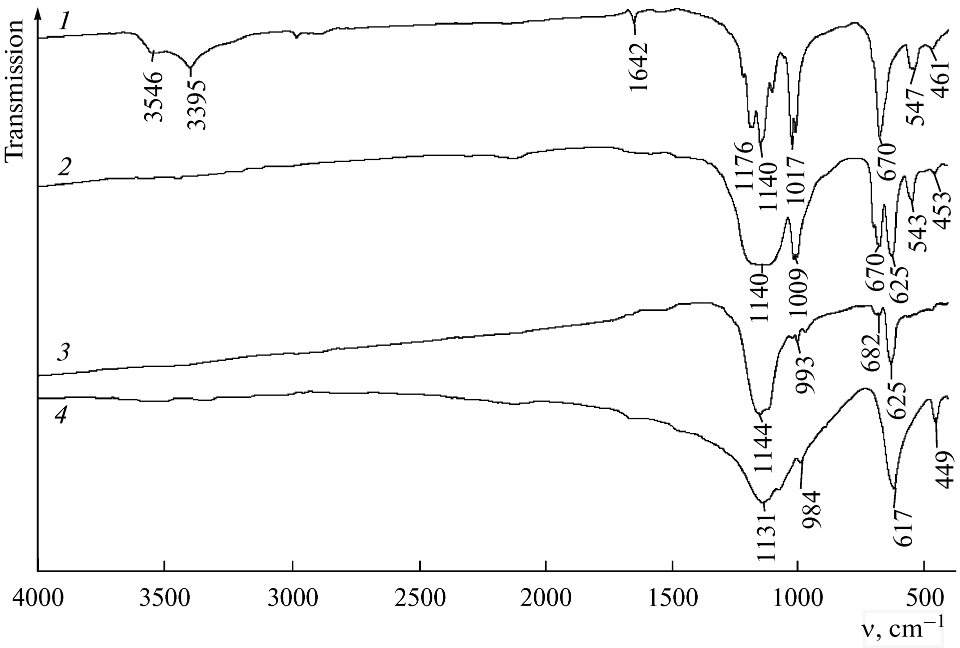

Fig. 4. IR spectra of $Na_6[Pb(S_2O_3)_4] \cdot 6H_2O$ residues after thermolysis: (*1*) in a vacuum at temperatures higher than 90°C, (*2*) in air at temperatures higher than 220°C, (*3*) in a vacuum at temperatures higher than 220°C, and (*4*) in air at temperatures higher than 800°C.

in a nitrogen atmosphere:

$$Na_6[Pb(S_2O_3)_4] \cdot 6H_2O \longrightarrow PbS + 2Na_2SO_4 + Na_2S + 2S + 2SO_2 + 6H_2O,$$

in air:

$$Na_6[Pb(S_2O_3)_4] \cdot 6H_2O + 4O_2 \longrightarrow PbS + 3Na_2SO_4 + 4SO_2 + 6H_2O.$$

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