

Synthesis of monoselenanedisulfanediphosphonate by the reaction of selenous acid with thiophosphate in the presence of ascorbic acid

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The reaction between selenous acid, H_2SeO_3 , potassium dihydrogenmonothiophosphate, KH_2SPO_3 , and ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$, in the solution of acetic acid proceeds with the formation of monoselenanedi(monothiophosphate) – monoselenanedisulfanediphosphonate, $\text{Se}(\text{SPO}_3)_2^{4-} - \text{SeS}_2\text{P}_2\text{O}_6^{4-}$, which in certain conditions is isolated from the reaction mixture as the crystalline salt *trans*-dipyridine-*bis*(dimethylglyoximato)cobalt(III) trihydrogenmonoselenane-disulfanediphosphonate dihydrate, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$. The isolated compound is characterized by the chemical analysis, XRD pattern, thermogravimetric and differential thermal analysis methods, and IR spectra. The dehydration of the isolated compound proceeds at a temperature of ~55–100 °C and its decomposition begins at ~120 °C. The final product of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ decomposition at high temperature is cobalt(II) metaphosphate, $\text{Co}(\text{PO}_3)_2$. The IR spectra of the isolated compound showed the maxima of absorption bands characteristic of monoselenanedisulfanediphosphonate anion at 255; 278; 360, 386, 390; 424, 442; 470, 514, 589; 652, 693, 744, 769; 917, 953, 980, 1 037; 1 070, 1 092, 1 147, 1 173 and 1 238 cm^{-1} ; they are assigned to δ (S–Se–S), ν (Se–S), ν_r (PO_3), ν (P–S), δ_{as} (O–P–O), δ_s (O–P–O), ν_s (P–O), ν_{as} (P–O), respectively.

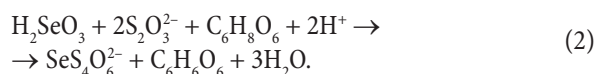
Key words: monoselenanedisulfanediphosphonate, formation, thermogravimetry, IR spectra

INTRODUCTION

In the study [1], the Norris and Fay reaction between selenous acid and thiosulfate [2, 3],



was modified seeking to prevent formation of tetrathionate, $\text{S}_4\text{O}_6^{2-}$, by changing a part (2 moles) of a reductor – thiosulfate, $\text{S}_2\text{O}_3^{2-}$, by reductor ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$:



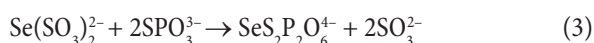
The reaction product – monoselenopentathionate anion, $\text{SeS}_4\text{O}_6^{2-}$, was isolated as a salt *trans*-dianiline-*bis*(dimethyl-

glyoximato)cobalt(III), $[\text{Co}(\text{DH})_2\text{A}_2]_2\text{SeS}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$; the compound isolated was characterized by the thermogravimetric methods and IR absorption spectra. First salts of monoselenopentathionate were synthesized by O. Foss [3] by the reaction (1).

The analog of monoselenopentathionate anion, $^{-}\text{O}_3\text{S}-\text{S}-\text{Se}-\text{S}-\text{SO}_3^{-}$, is monoselenanedisulfane-diphosphonate ion, $\text{SeS}_2\text{P}_2\text{O}_6^{4-} - ^{-}\text{O}_3\text{P}-\text{S}-\text{Se}-\text{S}-\text{PO}_3^{2-}$, which was identified for the first time by German scientists [4] in the reaction between monoselenopentathionate, $\text{Se}(\text{S}_2\text{O}_3)_2^{2-}$, and monothiophosphate, SPO_3^{3-} , using ionphoresis and labelled atoms S^{35} , P^{32} , Se^{75} .

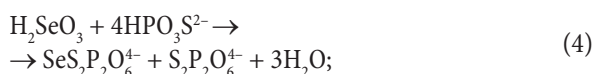
This anion in the study [5] was isolated as barium salt in the reaction of $\text{Se}(\text{S}_2\text{O}_2\text{CH}_3)_2$ and $\text{Na}_3\text{PO}_3\text{S}$, acting on the reaction mixture by saturated solution of $\text{Ba}(\text{OH})_2$. In our previous study [6], monoselenanedisulfanediphosphonate was received by the reaction of selenotrithionate with monothiophosphate

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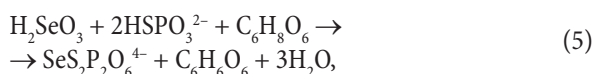
and isolated as a salt *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III), $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$.

In the studies [7, 8], thiosulfate in the reaction (1) was replaced by monothiophosphate and conditions under which the reaction proceeds with the formation of 2 products – monoselenane-disulfanediphosphonate, $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$, and disulfanediphosphonate, $\text{S}_2\text{P}_2\text{O}_6^{4-}$, were determined:



both these anions were isolated as barium salts.

The aim of the present study was in the last reaction to replace two moles of monothiophosphate by ascorbic acid seeking to receive only monoselenanedisulfanediphosphonate, $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$:



to isolate this anion as a salt of *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III) and to characterize the reaction product – $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ by the methods of thermal analysis and IR spectra. To achieve this goal, it was needed to optimize conditions of the reaction (5) and conditions for its product isolation.

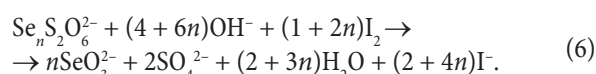
EXPERIMENTAL

The following chemically and analytically pure chemicals have been used: selenous acid, H_2SeO_3 , ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$, hydrogen chloride acid, acetic acid, propyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, potassium hydroxide, KOH, potassium bromide, KBr, potassium bromate, KBrO_3 , potassium iodide, KI, potassium hydrogencarbonate, KHCO_3 , starch and standard 0.1 mol/l sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, iodine solutions, indicator bromocresol green. Potassium dihydrogenmonothiophosphate, $\text{KH}_2\text{PO}_3\text{S}$, was prepared as described by Feher and Vial [8].

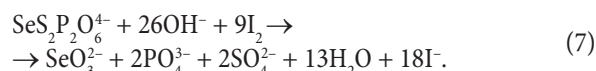
Trans-dipyridine-bis(dimethylglyoximato)cobalt(III) acetate, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{CH}_3\text{COO}$, was prepared as described in [9].

Sulfur in isolated *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III) trihydrogenmonoselenanedisulfanediphosphonate dihydrate, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, was determined by the classical gravimetric method in the form of BaSO_4 .

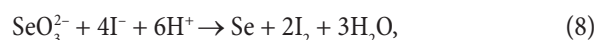
For determination of selenium, we applied known in the chemistry of selenopolythionates reaction of oxidation by iodine in hydrogencarbonate medium. It is known [10] that iodine in hydrogencarbonate medium can oxidize selenopolythionates, $\text{Se}_n\text{S}_2\text{O}_6^{2-}$, to selenite and sulfate according to the overall equation:



We have determined that, analogically, iodine in hydrogencarbonate medium can oxidize monoselenanedisulfanediphosphonate, $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$, to selenite, sulfate and phosphate according to the equation



For the analysis in hydrogencarbonate medium, a sample was dissolved in 50% alcohol (ethyl or propyl) and 20 ml of 0.1 mol/l solution of I_2 containing dissolved 2 g of potassium hydrogencarbonate, KHCO_3 , added. After 10–15 min, a reaction mixture was acidified with acetate buffer solution (pH = 4.6) until slightly acidic reaction and excess of iodine back titrated with thiosulfate. Then the reaction mixture was acidified to strongly acidic medium by adding 20 ml 23% HCl and iodine liberated



the amount of which is in proportion to the amount of selenite ions, was again titrated with thiosulfate.

Selenium was also determined iodometrically in another way. A sample was oxidized by bromine to selenous acid, which has been determined by the reaction (8). The sample was dissolved in a mixture of propyl alcohol and water (1 : 1) or 0.1 mol/l HCl.

Cobalt was determined in the form of metaphosphate, $\text{Co}(\text{PO}_3)_2$, after thermal decomposition of a sample in a platinum crucible at a temperature of 950 °C.

The X-ray diffraction pattern of synthesized $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ was recorded by a DRON-6 X-ray diffractometer (Russia) using the graphite-monochromatized Cu-K α radiation source ($\lambda = 1.54178 \text{ \AA}$) under a voltage of 30 kV and a current of 30 mA. The XRD pattern was recorded with a step of 0.05° from 2θ 3° to 65° (Fig. 1).

The thermal decomposition of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and its pyrolysis process were studied by a NETZSCH derivatograph STA 409 PC in air atmosphere. Parameters: 40 mg of a sample, 750 °C temperature scale. Speed of temperature increase to 180 °C – 5 °C/min and from 180 to 750 °C – 10 °C/min; ethalon – an empty crucible.

IR spectra have been recorded by a spectrometer Perkin-Elmer (USA) GX system FT-IR in the region 200–3 600 cm^{-1} (tablets with CsI and KBr).

RESULTS AND DISCUSSION

For realization of the reaction (5), according to the results of preliminary experiments, the medium of 0.3 mol/l acetic acid was chosen. Monoselenanedisulfanediphosphonate, $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$, anion, as an analog of monoselenopentathionate,

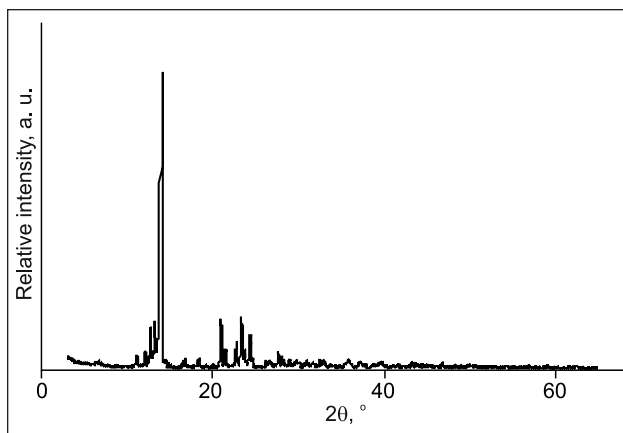


Fig. 1. XRD pattern of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$

$\text{SeS}_4\text{O}_6^{2-}$, is more stable in an acidic medium [3]. It was noticed [11] that chalcogendiphosphonic compounds are better soluble in water, crystallize harder and decompose faster than selenopolythionates with liberation of selenium and sulfur.

In the present study, the reagents (selenous and ascorbic acids, and potassium dihydrogenmonothiophosphate) were taken for the formation of 10 mmol of monoselenanedisulfanediphosphonate.

1.28 g (10 mmol with an excess of 5%) of H_2SeO_3 was dissolved in 200 ml 0.3 mol/l CH_3COOH . A small excess of selenous acid has been used in synthesis of monoselenopentathionate by the reaction (1) [3] since thiosulfate catalyzes decomposition of $\text{SeS}_4\text{O}_6^{2-}$. Therefore, one could expect that monothiophosphate may catalyze decomposition of monoselenanedisulfanediphosphonate ions too. A solution (1) was obtained, its $\text{pH} = 2$, it was cooled to 0–4 °C.

A solution (2) was prepared by dissolution of 1.77 g (10 mmol) of ascorbic acid in 75 ml of water; then a solution of potassium dihydrogenmonothiophosphate, $\text{KH}_2\text{PO}_3\text{S}$, prepared by dissolution of 3.04 g (20 mmol) of $\text{KH}_2\text{PO}_3\text{S}$ in 75 ml of water was added into it.

The solution (2) was slowly added to the solution (1), and a clear yellowish-green solution of reaction products was obtained. The concentration of monoselenanedisulfanediphosphonate, $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$, in the solution prepared was 10 mmol in 350 ml of the reaction products solution; such concentration is maximal-critical, since the solution of higher concentration decomposes fast with liberation of sulfur and selenium.

A solution of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{CH}_3\text{COO}$ (10 g in 150 ml H_2O) was added into a clear solution of reaction products, and the crystallization of dipyridine-*bis*(dimethylglyoximate) cobalt(III) trihydrogenmonoselenanedisulfanediphosphonate dihydrate, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, started. For completion of the crystallization, a mixture was kept in a refrigerator at 0–4 °C for two days. The crystals obtained were filtered, washed with a little amount of cold water and dried in a desiccator over calcium chloride until the constant weight. 3.5 g of the product were obtained that correspond to 45% yield based on the amount of $\text{KH}_2\text{PO}_3\text{S}$ used.

Found, %: Se – 10.18, 10.07; S – 8.78; P – 7.50; Co – 7.13; H_2O (thermogravimetrically at ~100 °C) – 4.06%; calcination residue ($\text{Co}(\text{PO}_3)_2$) after calcination at 950 °C in a platinum crucible – 26.23%.

Calculated for $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, %: Se – 10.03; S – 8.14; P – 7.87; Co – 7.48; H_2O – 4.57; calcination residue – 27.5%.

The compound synthesized was studied by the methods of gravimetric and differential thermal analysis. Its thermogram is shown in Fig. 2.

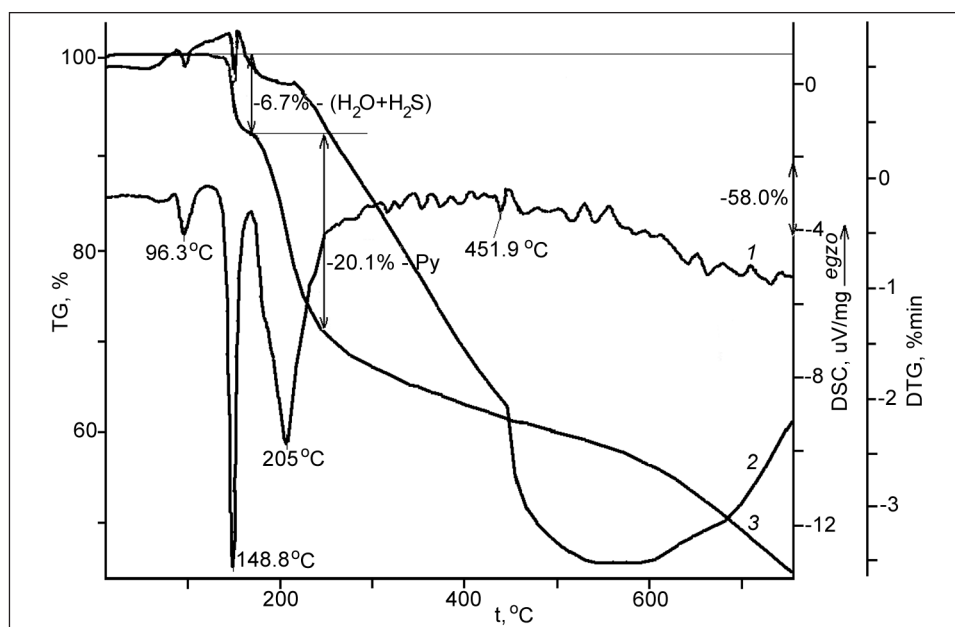


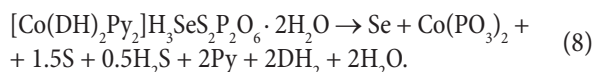
Fig. 2. DTG (1), DSC (2) and TG (3) curves of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ thermal decomposition

Dehydration of the compound $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ begins at 55–60 °C (beginning of a small endothermic effect in a DSC curve) and continues until temperature reaches ~100 °C; this process is reflected by the peak of endothermic effect with a minimum at 96.3 °C. Loss of mass in an interval of temperature 55–100 °C is ~4.06% and corresponds to liberation of 2 water molecules (4.57%). Thermal decomposition of dehydrated compound begins just after the end of dehydration at a temperature of ~120 °C (beginning of a strong endothermic effect with a minimum at 148.8 °C). Loss of mass in an interval of temperature 55–150 °C is 6.70% and corresponds to liberation of 2 water molecules and 0.5 molecule of H_2S (6.73%). Hydrogen sulfide was identified by heating a sample in a closed test tube with $\text{Pb}(\text{CH}_3\text{COO})_2$ paper, which becomes black because of PbS formation.

At higher temperatures, the oxidation of organic ligands takes place and a sample becomes as a black melt; therefore to identify liberation of separate products of decomposition at high temperature (Se, S, pyridine, dimethylglyoxime) is practically impossible. But loss of mass in an interval of temperature 160–240 °C ~20.1% corresponds to liberation of pyridine (20.09%).

Calcination residue at a temperature of 950 °C – 26.23% corresponds to formation of cobalt(II) metaphosphate (calculated 27.5%) as the final product of thermolysis.

Thermal decomposition of the compound $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ from analogy with thermal decomposition of trihydrogentrisulfanediphosphonate monohydrate of the same cation, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{S}_3\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$, [12] may be presented by the equation:



Formation of hydrogen chalcogenide (sulfide, selenide) during thermal decomposition of acidic salts of thiophosphorus compounds was fixed in our previous studies [6, 7,

11–14] of hydrogenmonothiophosphates and hydrogenpolysulfanediphosphonates of various cations.

Cobalt(II) metaphosphate, $\text{Co}(\text{PO}_3)_2$, as the final product of cobalt(III) complex cations polysulfanediphosphonates, was identified by X-ray diffraction and IR spectra [6, 11–14].

IR spectra of isolated in the present study $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ recorded by the compensation method (absorption of a complex cation eliminated) are presented in Fig. 3; the values of absorption peaks maximums (cm^{-1}) and their assignment to particular vibrations are given in the Table.

The bonds Se–S, P–S and P–O are in monoselenanedisulfanediphosphonate anion, $^{-2}\text{O}_3\text{P–S–Se–S–PO}_3^{-}$, and the vibrations in these bonds are reflected by absorption peaks in IR spectra.

In the spectra of selenopolythionates that contain chains of divalent sulfur-selenium atoms with SO_3 groups on the ends [15–17], like in the spectra of thiosulfate, selenosulfate [18], polythionates and other sulfur and selenium oxygen compounds [15, 19–23], deformation and valence vibrations in the bond S–O are in the region 1250–500 cm^{-1} and the vibrations of ν (Se–S), δ (S–Se–S), γ_r (SO_3) – in the region 500–200 cm^{-1} .

In the IR spectra of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, the vibrations in P–O bonds were found in the region 1238–470 cm^{-1} , and we assigned the region 390–255 cm^{-1} to ν (Se–S), ν (P–S), δ (S–Se–S), γ_r (PO_3) vibrations.

For assignment of peaks in the IR spectra of the compound studied we used data received earlier when studying IR spectra of phosphorus sulfides, P_4S_3 ir P_4S_5 [24], barium polysulfanediphosphonates, $\text{Ba}_n\text{S}_n\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ($n = 9–25$) [20], cobalt complex cations hexadecasulfanediphosphonates, $[\text{Co}(\text{DH})_2(\text{NH}_3)_2]\text{H}_3\text{S}_{16}\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_6](\text{H}_3\text{S}_{16}\text{P}_2\text{O}_6)_3$, [14] and a number of monothiophosphates and polysulfanediphosphonates [6, 7, 11, 14, 20]. In [11] a review of results on syntheses, thermogravimetric studies of thiophosphorus compounds and IR spectra of compounds of this type, re-

Table. Absorption peaks of anions (cm^{-1}) in IR spectra of reaction (5) product, selenosulfate, barium monoselenanedisulfanediphosphonate, potassium monoselenopentathionate and their assignment

Product of reaction (5)*	SeSO_3^{2-} [24]	$\text{Ba}_n\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ [9]	$\text{K}_2\text{SeS}_4\text{O}_6$ [21, 25]	Assignment
255			228–247	δ (S–Se–S)
278	277–281		256–280	ν (Se–S)
360, 386, 390				γ_r (PO_3)
424, 442		425		ν (P–S)
			440–450	ν (S–S)
	522		510–550	δ_{as} (S–O)
470, 514, 589		560		δ_{as} (O–P–O)
	616–652		580–730	δ_3 (S–O)
652, 693, 744, 769		575, 630, 670		δ_3 (O–P–O)
	994–1019		1010–1036	ν_3 (S–O)
917, 953, 980, 1037		860		ν_3 (P–O)
	1128–1150		1210–1226	ν_{as} (S–O)
1070, 1092, 1147, 1173, 1238		1200, 1214, 1242		ν_{as} (P–O)

* – $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ isolated in the present work

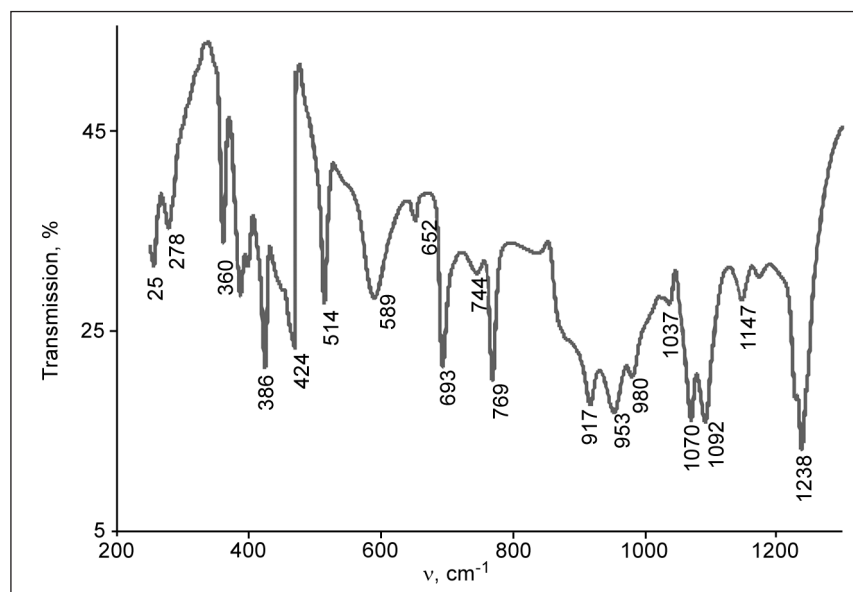


Fig. 3. IR spectra of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$

ceived in an earlier studies of our group and in the studies of other authors, were given.

It is known [19, 24, 25] that vibrations $\nu(\text{P-S})$ and $\nu(\text{S-S})$ in IR spectra correspond to unclear peaks at 260–500 and 400–550 cm^{-1} , respectively. Therefore one could expect that the peaks of $\nu(\text{P-S})$ should be at slightly lower frequencies than the peaks of $\nu(\text{S-S})$.

In vibrational spectra of monothiophosphates and diamidomonothiophosphates, the peaks of $\nu(\text{P-S})$ vibrations were found at 400–440 cm^{-1} , in the Raman spectra of sodium and lithium tetraorthophosphates – at 413 and 418 cm^{-1} , and in IR spectra of P_4S_3 and P_4S_5 – at 435 and 451 cm^{-1} [11, 24]. Therefore in the spectra of the compound studied in the present work, we assigned the peaks at 424 and 442 cm^{-1} to vibrations $\nu(\text{P-S})$.

We assign the peaks at 360–390 cm^{-1} from the analogy with the studied spectra of monothiophosphates and polysulfanediphosphonates [11, 14, 20] to rotational vibrations of PO_3 groups, $\gamma_r(\text{PO}_3)$; the peaks of these vibrations in the spectra of barium polysulfanediphosphonates, $\text{Ba}_2\text{S}_n\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, are at 310–400 cm^{-1} [20].

We assign the peaks at 255 or 278 cm^{-1} from the analogy with the studied spectra of monothiophosphates and polysulfanediphosphonates [11, 14] to deformation vibrations in the bonds S-Se-S , $\delta(\text{S-Se-S})$ and valence vibrations in the bonds Se-S , $\nu(\text{Se-S})$.

It is not problematic to identify the peaks of $\delta_{as}(\text{O-P-O})$ and $\delta_s(\text{O-P-O})$ vibrations that in the spectra of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ are at 470–589 cm^{-1} and 652–769 cm^{-1} .

The peaks of deformation vibrations O-P-O in IR spectra are at 300–660 cm^{-1} [21], but in the spectra of ionic phosphates [22] they most frequently appear at $\sim 500 \text{ cm}^{-1}$.

In the spectra of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ presented in [23], the peaks of these vibrations are at 540–740 cm^{-1} and in the

spectra of $\text{Ba}_2\text{S}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, $\text{Ba}_2\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Ba}_2\text{TeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ – at $\sim 500\text{--}650 \text{ cm}^{-1}$ [5].

The peaks of $\delta(\text{O-P-O})$ vibrations of studied by us [6, 7, 11, 14, 20] monothiophosphates and polysulfanediphosphonates are at 443–617 cm^{-1} and 536–722 cm^{-1} . But the clearest peaks of $\delta_{as}(\text{O-P-O})$ in the spectra of $\text{Ba}_2\text{S}_n\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ($n = 9\text{--}25$) and trichalcogenodiphosphonates [11, 20] are at ~ 540 , ~ 560 and 447–550 cm^{-1} , respectively, and in our recorded spectra of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ – at 470–589 cm^{-1} .

The clearest peaks of $\delta_s(\text{O-P-O})$ vibrations in the spectra of $\text{Ba}_2\text{S}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{S}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Ba}_2\text{S}_n\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ($n = 9\text{--}25$) [11, 20] were found at 570, 624, 590 and 608–610 cm^{-1} , respectively; in our recorded spectra of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ – at 652–769 cm^{-1} .

The peaks of valence vibrations of the P-O bond in IR spectra are at 900–1200 cm^{-1} [21]. In the spectra of inorganic phosphates two clear peaks of $\nu(\text{P-O})$ are at ~ 980 and 1000–1080 cm^{-1} [22]. The PO_3 group in IR spectra appears as clear peaks at 962–1010 and 970–1140 cm^{-1} [22]. A peak at higher frequencies corresponds to antisymmetric valence vibrations in the bond P-O [22].

In studied by us spectra of $\text{Ba}_2\text{S}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Ba}_2\text{S}_n\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ($n = 9\text{--}25$) [11, 20], the peaks of $\nu_s(\text{P-O})$ vibrations were found at 908–984, 875–943 and 845–1015 cm^{-1} , respectively, and of $\nu_{as}(\text{P-O})$ vibrations – at 1028–1148, 1032–1140 and 1068–1206 cm^{-1} , respectively.

Vibrations of $\nu_s(\text{P-O})$ in the spectra of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ correspond to the peaks at 917–1037 cm^{-1} , and vibrations $\nu_{as}(\text{P-O})$ – to the peaks at 1070–1238 cm^{-1} (Table).

Summarizing the presented data, we may state that the IR spectra of the compound isolated in the present study is of the same type as the spectra of the compounds of the same

origin described earlier, among them di- and polysulfanediphosphonates. It confirms that the compound isolated in the present study is *trans*-dipyridine-*bis*(dimethylglyoximato)cobalt(III) trihydrogenmonoselenane-disulfanediphosphonate dihydrate, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$.

CONCLUSIONS

1. The reaction of selenous acid, monothiophosphate and ascorbic acid in the solution of acetic acid proceeds with the formation of monoselenanedisulfanediphosphonate, $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$, which is isolated as the crystalline salt *trans*-dipyridine-*bis*(dimethylglyoximato)cobalt(III) trihydrogenmonoselenanedisulfanediphosphonate dihydrate, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$.

2. The compound received by a new reaction is characterized by IR absorption spectra in which the maxima of peaks characteristic to anion are at 255; 278; 360, 386, 390; 424, 442; 470, 514, 589; 652, 693, 744, 769; 917, 953, 980, 1 037; 1 070, 1 092, 1 147, 1 173, 1 238 cm^{-1} ; these peaks are assigned to vibrations δ (S–Se–S), ν (Se–S), ν_r (PO_3), ν (P–S), δ_{as} (O–P–O), δ_s (O–P–O), ν_s (P–O), ν_{as} (P–O), respectively. It confirms that the compound isolated is monoselenane-disulfanediphosphonate.

3. The thermogravimetric study of the compound $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ showed that its dehydration occurs in the temperature range of ~55–100 °C, and the decomposition of the dehydrated compound begins at ~120 °C. The final product of the $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ decomposition at ~950 °C temperature is cobalt metaphosphate, $\text{Co}(\text{PO}_3)_2$.

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References

- F. Savickas, V. Janickis, *Chemical Technology*, **3**(56), 35 (2010).
- J. F. Norris, H. Fay, *Amer. Chem. J.*, **18**, 703 (1895).
- O. Foss, *Acta Chem. Scand.*, **3**, 435 (1949).
- E. Blasius, N. Spannhake, *Z. Anorg. Allg. Chem.*, **399**, 331 (1973).
- H. Wagner, R. Muller, *Z. Anorg. Allg. Chem.*, **429**, 270 (1977).
- F. Savickas, V. Janickis, *Chemical Technology*, **1**(14), 54 (2000).
- F. Savickas, V. Janickis, D. Nizevičienė, R. Rumša, *Chemical Technology*, **2**(51), 75 (2009).
- F. Feher, F. Vial, *Z. Anorg. Allg. Chem.*, **335**, 113 (1963).
- I. Soos, G. Varhelyi, M. Somay, *Studia Univ. Babeş-Bolyai, Ser. Chem.*, **8**(2), 51 (1963).
- V. J. Janickis, J. V. Janickij, E. J. Pacauskas, *Zh. Neorgan. Khimii*, **2**(6), 1341 (1957).
- V. Janickis, F. Savickas, *Chemical Technology*, **3**(45), 5 (2007).
- F. Savickas, V. Janickis, *Chemical Technology*, **2**(11), 13 (1999).
- F. Savickas, V. Janickis, *Chemical Technology*, **2**(28), 13 (2003).
- F. Savickas, V. Janickis, D. Nizevičienė, *Chemical Technology*, **2**(36), 82 (2005).
- V. J. Janickis, *Formation, Structure and Physical-chemical Properties of Sulfane and Selenane Derivatives*. Doctoral Dissertation, Kaunas (1983).
- V. J. Janickis, J. V. Janickij, *Trans. Lithuanian Acad. Sci. Ser. B*, **6**(157), 43 (1986).
- V. J. Janickis, J. V. Janickij, *Trans. Lithuanian Acad. Sci. Ser. B*, **2**(159), 40 (1987).
- P. Klæboe, A. Martinsen, J. Songstad, *Acta. Chem. Scand.*, **31 A**, 56 (1977).
- E. R. Clark, A. J. Collet, *J. Chem. Soc. (A)*, **N 10**, 1594 (1969).
- V. Janickis, F. Savickas, *Chemical Technology*, **1**(22), 28 (2002).
- K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, New York-London (1963).
- L. J. Bellamy, *Infrared Spectra of Complex Molecules*, London (1978).
- R. A. Nyquist, R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, New York and London (1971).
- G. Nickless, *Inorganic Sulphur Chemistry*, Amsterdam-London-New York (1968).
- R. S. Steudel, *Z. Naturforsch.*, **306**(2), 281 (1975).

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MONOSELENANDISULFANDIFOSFONATO SINTEZĖS REAKCIJA TARP SELENITO IR TIOFOSFATO ESANT ASKORBO RŪGŠČIAI

Santrauka

Reakcija tarp selenito rūgšties (H_2SeO_3), kalio dihidromonotiofosfato (KH_2SPO_3) ir askorbo rūgšties ($\text{C}_6\text{H}_8\text{O}_6$) acto rūgšties tirpale vyksta susidarant monoselenandi(monotiofosfato) – monoselenandisulfandifosfonato ($\text{Se}(\text{SPO}_3)_2^{4-} - \text{SeS}_2\text{P}_2\text{O}_6^{4-}$) jonams, kurie tam tikromis sąlygomis iš reakcijos mišinio išskirti kristalinės *trans*-dipiridino-*bis*(dimetilglioksimato)kobalto(III) trihidromonoselenandisulfandifosfonato dihidrato, $[\text{Co}(\text{DH})_2\text{Py}_2]\text{H}_3\text{SeS}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, druskos pavidalo. Gautas junginys charakterizuotas cheminės, termogravimetrinės, diferencinės terminės analizės metodais ir IR absorbcijos spektru. Nustatyta, kad junginio dehidracija įvyksta ~55–10 °C temperatūroje, o dehidratuoto junginio skilimas prasideda ~120 °C temperatūroje. Galutinis junginio skaidymo aukštoje ~950 °C temperatūroje produktas yra kobalto(II) metafosfatas ($\text{Co}(\text{PO}_3)_2$). Spektroskopinis tyrimas parodė, kad išskirto junginio $\text{SeS}_2\text{P}_2\text{O}_6^{4-}$ anijonui būdingų absorbcijos smailių maksimumai yra ties 255; 278; 360, 386, 390; 424, 442; 470, 514, 589; 652, 693, 744, 769; 917, 953, 980, 1 037; 1 070, 1 092, 1 147, 1 173 ir 1 238 cm^{-1} . Šios smailės atitinkamai priskirtos virpesiams: δ (S–Se–S), ν (Se–S), ν_r (PO_3), ν (P–S), δ_{as} (O–P–O), δ_s (O–P–O), ν_s (P–O), ν_{as} (P–O).