Figure 8. Pmr spectra (60 MHz) of Ni(3-*sec*-C₄H₉-sal)₂bmp in the azomethine region demonstrating the signal assignments for the diastereoisomers: (a) total mixture; (b) Ni(3-(+)-*sec*-C₄H₉-sal)₂-RS-bmp; (c) Ni(3-(+)-*sec*-C₄H₉-sal)₂-S-bmp; (d) Ni(3-(+)-*sec*-C₄H₉-sal)₂-R-bmp.

Λ(+,+) signals due to the onset of the Δ ⇌ Λ interconversion. Hence, the complexes exhibit the stereochemical integrity anticipated, at least up to 90°. Because their contact shifts are decidedly non-Curie in behavior, equilibrium 6 obtains and structural

rearrangment occurs without racemization at the metal. The interconversion sequence **21** ⇌ **22** ⇌ **21**, for example, is to be contrasted with **16** ⇌ **17** ⇌ **18**, which invariably occurs with bis-chelate complexes and produces structural rearrangement and racemization. The complete set of thermodynamic and contact shift data for nickel(II) complexes of type **20** is available
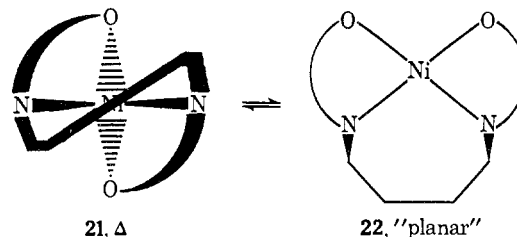
elsewhere.[29]

The foregoing examples have been considered in order to provide at least a partial indication of the extreme sensitivity of isotropic shifts to subtle structural differences and their consequent utility in the study of the stereochemistry and structural equilibria of paramagnetic metal complexes. Use of the isotropic shift method in the investigation of structural and electronic properties of transition metal complexes is very rapidly increasing, and it may be safely anticipated that significant and new applications of the method will be forthcoming in the near future.

Some Aspects of the Chemistry of Polythionates and Selenopolythionates

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In 1841 the French chemist Langlois heated a saturated solution of potassium bisulfite with elemental sulfur for a long time and obtained a salt which differed in properties from salts of sulfur acids known at that time. Unlike the expected product, thiosulfate, this salt did not decompose in dilute acids and gave no precipitate with barium salts. Analysis showed it to have the composition $K_2S_3O_6$. By treating it with $HClO_4$, which precipitated the potassium ion as $KClO_4$,

Langlois obtained in solution the first polythionic acid, the trithionic. Langlois studied the decomposition of the new acid and found that upon warming it produced sulfuric acid, sulfur dioxide, and elemental sulfur.

A year later Fordos and Gelis discovered the tetrathionic acid $H_2S_4O_6$, obtained by oxidation of thiosulfate with iodine—a reaction now familiar to every chemist. They obtained crystalline sodium and barium tetrathionates and from the latter, after precipitation of barium with sulfuric acid, solutions of tetrathionic acid. Its properties proved to be like those of Langlois'

acid, except that upon decomposition it liberated twice the amount of elemental sulfur.

These two discoveries opened the long history of the chemistry of polythionates. For over a century many chemists have been working on these peculiar compounds; many investigators were especially interested in the so-called Wackenroder's liquid, obtained by the reaction of sulfurous acid with hydrogen sulfide. Textbooks of inorganic chemistry frequently associate polythionic acids with Wackenroder's liquid. It contains mainly the penta- and the tetrathionic acids and only minor amounts of the tri- and hexathionic acids. The literature on polythionates up to 1927 has been reviewed by Kurtenacker,[2a] and there is a more recent review by Goehring.[2b]

During the long history of polythionates their structure was discussed by many authors. Blomstrand[3] and Mendelejeff[4] were the first to formulate these compounds with unbranched sulfur chains terminated by sulfonate groups. Later many workers preferred formulas with branched sulfur chains, mostly on the ground that the fourth, fifth, etc., sulfur atoms are readily given off by the action of several reagents without destruction of the whole molecule or anion. The long dispute on the structure of the polythionates was decided by the excellent work of Foss and coworkers.[5] Their careful structure determinations by X-ray methods carried out on several tetrathionates, pentathionates, and hexathionates proved these compounds consisted of unbranched nonplanar sulfur chains terminated by sulfonate groups.

Sulfur can be partially substituted by selenium in polythionic acids. Such compounds are called selenopolythionic acids. Until 1949 a definite proof of the presence of only one such compound, selenotrithionic acid, was known; its salts ($K_2SeS_2O_6$) were synthesized as early as the 19th century (Rathke in 1865). In 1949 the Norwegian chemist Foss isolated the first salts of selenopentathionic ($H_2SeS_4O_6$) and telluropentathionic ($H_2TeS_4O_6$) acid.[6,7] The latter is to date the only known tellurium counterpart of polythionates. The selenopentathionate and telluropentathionate anions, as Foss established by X-ray methods, are likewise unbranched and nonplanar chains S–S–Se–S–S and S–S–Te–S–S, respectively, with sulfo groups at the chain ends.[5]

In this paper we give a short Account of work in the area of polythionates and selenopolythionates carried out in our laboratory since 1952. We begin with some remarks on the nomenclature used in the field.

In earlier literature selenotrithionate was called "selenodithionate" and selenopentathionate "seleno-

tetrathionate" according to the number of sulfur atoms in the molecule. At present in the nomenclature used by us and many other authors[5,8] "tri-, tetra-, penta-," etc., denote the total number of sulfur and selenium atoms. Such names emphasize that selenium substitutes sulfur atoms in the corresponding compounds.

In recent years some German authors call polythionates "sulfanedisulfonates," as was proposed by Schmidt in 1957.[9] This nomenclature stresses that polythionic acids must be regarded as derivatives of sulfanes, i.e., hydrogen polysulfides. In analogy selenopolythionates should be called "selenanedisulfonates." This nomenclature is logical; however we do not use it because it is not yet generally accepted.
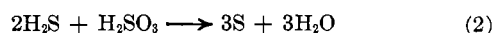
Higher Polythionic Acids

Several authors[10,11] have reported solutions containing polythionic acids of order six or more. However, conclusions were based on indirect analysis and the attempts to isolate these acids were unsuccessful. For example, in 1937 we could show that high polythionic acids containing up to 14 sulfur atoms in the molecule are present in so-called Gil–Beato solutions.[11] These solutions are obtained by introducing a concentrated solution of sodium thiosulfate into cooled concentrated hydrochloric acid.

In 1952 a crystalline salt of octathionic acid—benzidineoctathionate—was synthesized in our laboratory.[12] Compounds of composition approximately corresponding to benzidine salts of hepta- and nonathionic acids were also reported.[13] These results encouraged further research in the area of higher polythionic acids.
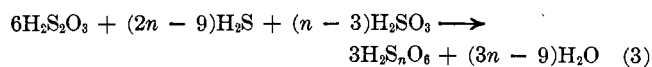
The previously discovered reaction producing[14] hexathionic acid (eq 1) was combined with the reaction

$$2H_2S_2O_3 + H_2S + H_2SO_3 \longrightarrow H_2S_6O_6 + 3H_2O \qquad (1)$$
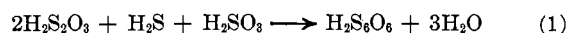
producing elemental sulfur (eq 2). This clarified

$$2H_2S + H_2SO_3 \longrightarrow 3S + 3H_2O \qquad (2)$$

the conditions under which high polythionic acids are formed (eq 3). The formation follows the above

$$6H_2S_2O_3 + (2n - 9)H_2S + (n - 3)H_2SO_3 \longrightarrow$$
$$3H_2S_nO_6 + (3n - 9)H_2O \qquad (3)$$

equation almost stoichiometrically without separation of elemental sulfur.

Following this procedure it was possible to obtain polythionic acid solutions of various sulfuration levels, up to nearly 20 sulfur atoms per molecule. These acids were isolated in the form of crystalline salts with organic cations of large radii, such as nitron ($C_{20}H_{16}N_4$)

(2) (a) A. Kurtenacker, Abegg's Handbuch der Anorganischen Chemie, IV (1), S. Hirzel Leipzig, 1927, p 541; (b) M. Goehring, Fortschr. Chem. Forsch., 2, 444 (1952).
(3) C. W. Blomstrand, Chem. Jetztzeit, 157 (1869).
(4) D. I. Mendelejeff, J. Russ. Chem. Soc., 2, 276 (1870); Ber., 3, 870 (1870).
(5) O. Foss, Advan. Inorg. Chem. Radiochem., 2, 237 (1960).
(6) O. Foss, Acta Chem. Scand., 3, 435 (1949).
(7) O. Foss, ibid., 3, 708 (1949).

(8) Gmelin's Handbuch der Anorganischen Chemie, 8 Aufl. Syst. No. 10, Selen B, Gmelin-Verlag, Clausthal-Zellerfeld, 1949, p 185.
(9) M. Schmidt, Z. Anorg. Allg. Chem., 289, 175 (1957).
(10) A. Kurtenacker and K. Matejka, ibid., 229, 19 (1936).
(11) J. Janickis, ibid., 234, 193 (1937).
(12) J. Janickis and J. Valančiunas, Zh. Obshch. Khim., Sb., 1, 734 (1953).
(13) J. Janickis and E. Pacauskas, Zh. Obshch. Khim., 23, 1449 (1953).
(14) J. Janickis and J. Valančiunas, ibid., 24, 790 (1954).

and dimethylphenylbenzylammonium $(C_{15}H_{18}N^+)$.[15] We obtained dimethylphenylbenzylammonium polythionates with up to 13 sulfur atoms and nitron polythionates up to 18 sulfur atoms. These salts are crystalline, insoluble in water, but soluble in ethanol. They can be recrystallized without change in composition. When dry they are quite stable. The composition was established by determination of sulfur (as $BaSO_4$ after combustion by melting with Na_2O_2, Na_2CO_3, and K_2CO_3) and of nitrogen by the well-known Dumas micro method as used in organic analysis. The results agree well with calculated values. Nevertheless, we cannot be sure that the products represent pure compounds and not mixtures of homologs because the analytical methods give only the average sulfur content. The same is valid for benzidinepolythionates mentioned above. We agree with Foss[5] that the only safe way to ascertain the purity of a higher polythionate appears to be by chromatography or electrophoresis. However, the importance of the present investigations is that they directly prove the existence of polythionic acids of a high degree of sulfuration.

The reaction mechanism of polythionic acid synthesis (eq 3) is undoubtedly complicated. It probably takes place through a series of intermediate compounds important among which are sulfanemonosulfonic acids, i.e., compounds of a general composition $H_2S_xO_3$. Several high polythionic acids were obtained from these compounds by Schmidt[9] at about the same time as by us. We were successful in showing the formation of sulfanemonosulfonic acids during the decomposition of thiosulfate in acidic solutions.[16] These experiments support the decomposition mechanism as proposed by Davis[17] on the basis of kinetic data.

We were not able to undertake X-ray structure determinations on polythionates of high sulfuration level. However, we can hardly doubt that their structure is unbranched like the lower homologs.[5] Such a structure is supported by the synthesis of the octathionic, decathionic, and dodecathionic acids carried out by Schmidt[9] by oxidation of the corresponding sulfanemonosulfonic acids with iodine according to eq 4.

$$2H_2S_xO_3 + I_2 \longrightarrow H_2S_{2x}O_6 + 2HI \qquad (4)$$
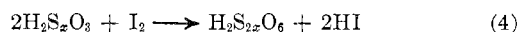
Selenopolythionic Acids

Until recently selenopolythionates were known with only one selenium atom in the molecule. In 1954 potassium diselenotetrathionate $(K_2Se_2S_2O_6)$, i.e., tetrathionate with two sulfur atoms substituted by selenium, was synthesized in our laboratory.[18] It crystallizes as yellow needles with one molecule of water and is easily soluble in water. This compound is formed by oxidation of selenosulfate (K_2SeSO_3) with iodine or, better, with hydrogen peroxide (eq 5).

$$2SeSO_3^{2-} + H_2O_2 + 2H^+ \longrightarrow Se_2S_2O_6^{2-} + 2H_2O \qquad (5)$$

Diselenotetrathionate is also formed in certain other reactions such as the reaction between selenious and sulfurous acids. Reduction of selenites with sulfur dioxide, a widely used reaction in analytical chemistry, is a complicated process involving intermediate compounds. By introduction of SO_2 into selenite solution a yellow color is developed and selenium is slowly precipitated, although not always quantitatively. Various hypotheses were proposed about the nature of the yellow intermediate compound but without convincing experimental data.

It is very probable that the yellow compound formed while mixing selenites with sulfurous acid is diselenotetrathlonic acid. Under proper conditions the reaction proceeds almost stoichiometrically according to eq 6. It is possible to synthesize potassium diseleno-

$$2H_2SeO_3 + 5H_2SO_3 \longrightarrow H_2Se_2S_2O_6 + 3H_2SO_4 + 3H_2O \qquad (6)$$

tetrathionate rather conveniently by means of the above reaction.[19]

The investigation of this reaction and of formation and decomposition reactions of previously unrecorded selenopolythionates became possible only after development of suitable analytical methods for determination of selenothionates in mixtures with various by-products and products of their decomposition, such as selenosulfate, selenite, and sulfite.

The analytical procedure developed[20] is based mainly on combinations of several iodometric titrations carried out under different conditions. For instance, iodine oxidizes selenopolythionates of the $Se_nS_2O_6^{2-}$ type and selenosulfate in acidic solution (HCl, H_2SO_4) to sulfate with separation of selenium. The iodine consumption is 2 equiv/mol of each of these compounds and 2 equiv/mol of sulfite as well. The latter, if present, may be bound with formaldehyde to prevent its reaction with iodine. Under these conditions selenite liberates 4 equiv of iodine. Selenosulfate decomposes in acidic solution or in the presence of formaldehyde into sulfite and selenium. The separated selenium may be weighed or dissolved in sulfite, oxidized with bromine, and determined iodometrically as selenite.

In weakly alkaline solutions (bicarbonate) iodine oxidizes all compounds mentioned to selenite and sulfate. But now the iodine consumption differs for various compounds. Selenosulfate and selenotrithionate consume six, diselenotetrathionate consumes ten, and higher selenopolythionates described below consume still more iodine equivalents per mole. On acidifying the solution after this titration the selenite

(15) J. Janickis, J. Valančiunas, and O. Tučaite, Zh. Neorg. Khim., 3, 2087 (1958).

(16) J. Valančiunas and J. Janickis, Dokl. Akad. Nauk SSSR, 145, 1052 (1962).

(17) R. E. Davis, J. Amer. Chem. Soc., 80, 3565 (1958).

(18) J. Janickis and V. Zelionkaité, Zh. Obshch. Khim., 25, 841 (1955).

(19) J. Janickis and V. Zelionkaité, Zh. Neorg. Khim., 3, 1755 (1958).

(20) J. Janickis, V. Zelionkaité, and E. Pacauskas, ibid., 2, 1341 (1957).

formed liberates the equivalent amount of iodine which can be titrated with thiosulfate. This gives the total selenium content of the sample.

In some cases it is useful to combine the iodometric procedures with the polarographic determination of selenosulfate.[21] In this way diselenotetrathionate may also be determined after its treatment with an excess of sulfite which gives selenotrithionate and seleno-sulfate (eq 7).

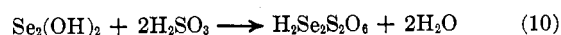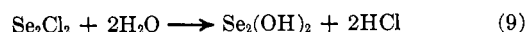$$Se_2S_2O_6{}^{2-} + SO_3{}^{2-} \longrightarrow SeS_2O_6{}^{2-} + SeSO_3{}^{2-} \qquad (7)$$
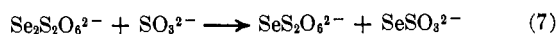
It may be added that it is not yet possible to determine the individual selenopolythionates in mixtures containing these compounds with more than two selenium atoms in the molecule. In this case the analytical methods give the average selenium content only. Nevertheless, the methods outlined above enabled us to investigate series of previously unrecorded seleno-polythionates and their formation and decomposition reactions.

Diselenotetrathionate and triselenopentathionate are formed by oxidation of selenosulfate with selenious acid in strongly acidic solution according to eq 8.

$$4SeSO_3{}^{2-} + H_2SeO_3 + 4H^+ \longrightarrow Se_2S_2O_6{}^{2-} + Se_3S_2O_6{}^{2-} + 3H_2O \qquad (8)$$

The products of reaction were isolated as potassium diselenotetrathionate and nitron triselenopenta-thionate.[22]

Reactions 5 and 8 suggest the treatment of seleno-polythionic acids as hydrogen polyselenide (selenane H_2S_x) derivatives. Their structure is visualized as chains of selenium atoms with sulfo groups at the chain ends. This structure is supported by the fact that diselenotetrathionate is formed as a primary product of selenosulfate anodic oxidation[23] and also during the hydrolysis of selenium chloride in sulfurous acid solutions.[24]

$$Se_2Cl_2 + 2H_2O \longrightarrow Se_2(OH)_2 + 2HCl \qquad (9)$$

$$Se_2(OH)_2 + 2H_2SO_3 \longrightarrow H_2Se_2S_2O_6 + 2H_2O \qquad (10)$$

The above-mentioned selenopolythionates turned out to be the first members of a homologous series $Se_nS_2O_6{}^{2-}$. Mixtures of selenopolythionic acids with two to six selenium atoms in a molecule were obtained in a reaction between potassium selenotrithionate and selenious acid in a strongly acidic (HCl) solution. By fractional precipitation with nitron acetate we were able to isolate the nitron salts of all acids in this series from these mixtures. By metathesis with dichloro-bisethylenediaminecobalt(III) chloride in methanol the nitron salts were converted into the corresponding water-soluble dichlorobisethylenediaminecobalt seleno-

polythionates $(Co(en)_2Cl_2)_2Se_nS_2O_6$, where $2 \leq n \leq 6$.[25]

The nitron salts are yellow needles, the complex cobalt salts green, small, longish crystals, becoming yellowish with increasing selenium content. The composition was established by determination of sulfur, selenium, and nitrogen or cobalt, respectively. When dry, these compounds are stable for several weeks, but they are all sensitive to light which causes slow separa-tion of red selenium.

The reactions of selenotrithionate and diselenotetra-thionate could be investigated employing relatively easily prepared potassium salts.[26,27] Investigation of the reactions of higher selenopolythionates (where $n > 2$) was possible only by employing the above-mentioned complex cobalt salts.[25] Nitron salts are practically insoluble in water, and salts with simple cations, i.e., alkaline metals, are difficult to isolate, because of their instability and high solubility. Ap-parently a large diameter cation is required to stabilize the Se-rich anion.

The principal reactions of the selenopolythionates under various conditions were studied. In neutral aqueous solutions, dilute acids, and weakly alkaline solutions (bicarbonate) these compounds slowly de-compose, releasing selenium (eq 11). In strongly
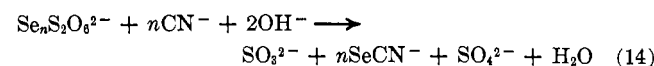
$$Se_nS_2O_6{}^{2-} \longrightarrow xSe + Se_{n-x}S_2O_6{}^{2-} \qquad (11)$$

alkaline solutions the decomposition is fast and pro-ceeds stoichiometrically according to eq 12.

$$2Se_nS_2O_6{}^{2-} + 6OH^- \longrightarrow$$
$$2SeSO_3{}^{2-} + (2n - 3)Se + SeO_3{}^{2-} + 2SO_3{}^{2-} + 3H_2O \qquad (12)$$
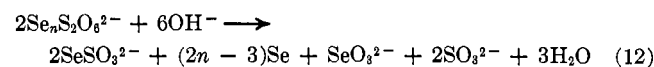
Iodine oxidizes these selenopolythionates in bi-carbonate solution to selenite and sulfate, and in acidic solution (HCl) Se is separated according to eq 13.

$$Se_nS_2O_6{}^{2-} + I_2 + 2H_2O \longrightarrow nSe + 2HSO_4{}^- + 2HI \qquad (13)$$
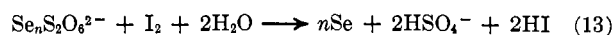
Alkaline cyanide causes decomposition reaction 14.

$$Se_nS_2O_6{}^{2-} + nCN^- + 2OH^- \longrightarrow$$
$$SO_3{}^{2-} + nSeCN^- + SO_4{}^{2-} + H_2O \qquad (14)$$

This reaction is suitable for the determination of the molar concentration of these compounds in a solution by titration with iodine after treatment with cyanide.

The compounds react with silver nitrate to give a black silver selenide precipitate and sulfuric acid.

The selenopolythionates described above apparently have a symmetrical structure of general composition $Se_n(SO_3)_2{}^{2-}$. Although no structure analysis has been made, an unbranched structure of the selenium chain is likely.

Recently we synthesized several asymmetric seleno-polythionates with three sulfur atoms in the molecule of the composition $Se_nS_3O_6{}^{2-}$ or $[Se_n(SO_3)(S_2O_3)]^{2-}$. A well-known reaction in the chemistry of polythionates was employed for this synthesis (eq 15). This reaction

(21) V. Zelionkaité and J. Janickis, *Lietuvos TSR Mokslu Akad. Darbai, Ser. B,* No. 4 (20), 71 (1959).

(22) J. Janickis and V. Zelionkaité, *Zh. Neorg. Khim.,* **2,** 1349 (1957).

(23) J. Janickis and E. Pacauskas, *Lietuvos TSR Mokslu Akad. Darbai, Ser. B,* No. 3 (26), 195 (1961).

(24) J. Janickis and D. Reingardas, *Lietuvos TSR Aukštuju. Mokyklu Mokslo Darbai, Chem.,* **2,** 47 (1962).

(25) V. Zelionkaité, J. Janickis, and D. Kudarauskiené, *Lietuvos TSR Mokslu Akad. Darbai, Ser. B,* No. 1 (36), 103, 117 (1964).

(26) V. Zelionkaité, J. Janickis, and J. Šuliakiené, *Lietuvos TSR Aukštuju Mokyklu Mokslo Darbai, Chem.,* **3,** 93 (1963).

(27) J. Janickis and V. Zelionkaité, *Lietuvos TSR Mokslu Akad. Darbai, Ser. B,* No. 4 (20), 79 (1959).

$$S_nO_6{}^{2-} + S_2O_3{}^{2-} \rightleftarrows S_{n+1}O_6{}^{2-} + SO_3{}^{2-} \qquad (15)$$
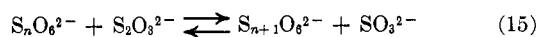
is regarded as a replacement of one sulfite group by a thiosulfate group (eq 16).

$$S_{n-2}(SO_3)_2{}^{2-} + S_2O_3{}^{2-} \rightleftarrows [S_{n-2}(SO_3)(S_2O_3)]^{2-} + SO_3{}^{2-} \quad (16)$$
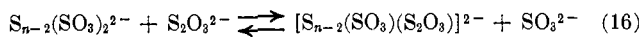
Under certain conditions (acidic solution containing formaldehyde to combine with the sulfite formed) selenothionate exchanges one sulfite group for a thiosulfate group according to eq 17, forming monoseleno-

$$Se_n(SO_3)_2{}^{2-} + S_2O_3{}^{2-} \longrightarrow [Se_n(SO_3)(S_2O_3)]^{2-} + SO_3{}^{2-} \quad (17)$$
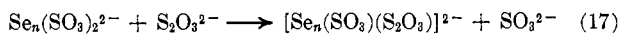
tetrathionate, diselenopentathionate, or triselenohexathionate, respectively. These compounds were isolated in a way similar to that used for the compounds of the series described previously as crystalline dichlorobisethylenediaminecobalt(III) salts $(Co(en)_2Cl_2)_2$-$Se_nS_3O_6$, where $1 \leq n \leq 3$.[28]

The reactions of the asymmetric selenopolythionate series differ from the reactions of $Se_nS_2O_6{}^{2-}$ discussed earlier. In acidic solutions these compounds consume only 1 equiv of iodine/mol. Decomposition by cyanide takes place by formation of thiosulfate instead of sulfite, as in eq 14, according to eq 18. Silver nitrate

$$Se_nS_3O_6{}^{2-} + nCN^- + 2OH^- \longrightarrow$$
$$S_2O_3{}^{2-} + nSeCN^- + SO_4{}^{2-} + H_2O \quad (18)$$
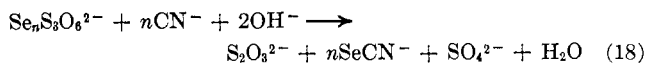
gives a black precipitate containing selenium and one-third of the sulfur content of the sample as Ag_2S.

The reactions of these compounds as well as their synthesis indicate the presence of one thiosulfate group in the anion $Se_nS_3O_6{}^{2-}$. Therefore the structure $[Se_n(SO_3)(S_2O_3)]^{2-}$ may be assigned to those compounds.

Quite recently we isolated the monoselenotetrathionates $(SeS_3O_6{}^{2-})$ of dianilinebisdimethyglyoximecobalt(III) and di-o-toluidinebisdimethylglyoximecobalt(III) from an acidified mixture of potassium selenotrithionate and sodium thiosulfate (ratio 1:1) in the presence of formaldehyde by direct (i.e., without employing nitron) fractional precipitation with the cation sulfates.[29] Chemical analysis showed the ratio Co:Se:S = 2:1:3, in agreement with the formulas. One can be sure that these compounds are not mixtures of selenotrithionate and selenopentathionate because after treatment with cyanide they consume exactly 1 equiv of iodine, i.e., the decomposition follows eq 18. Under the same conditions a hypothetical mixture ought to consume 1.5 equiv of iodine because selenotrithionate yields sulfite with cyanide, while selenopentathionate, like monoselenotetrathionate, yields thiosulfate.[30] The monoselenotetrathionates of the complex cobalt cations mentioned crystallize with two molecules of water each and are slightly soluble in water.

(28) V. Zelionkaité, J. Janickis, J. Jatautaité, and D. Reingardas, Lietuvos TSR Mokslu Akad. Darbai, Ser. B, No. 1 (44), 3 (1966).

(29) V. Zelionkaité and V. Janickis, Lietuvos TSR Mokslu Akad. Darbai, Ser. B, in press.
(30) O. Foss, Acta Chem. Scand., 4, 1241 (1950).