EXPERIMENTAL

The absorption spectra of 10^{-4}-10^{-5} mole/liter solutions of the compounds in toluene were measured with an SF-4A spectrophotometer. The IR spectra of KBr pellets were measured with a UR-20 spectrometer at 700-4000 cm^{-1} (with NaCl and LiF prisms).

Diethyl Thiophenebis(methylenephosphonate) (I). A mixture of 41 g (0.37 mole) of bis(chloromethyl)thiophene, 77 ml (0.45 mole) of triethyl phosphite, and 150 ml of dry p-xylene was refluxed for 10 h, after which the p-xylene was removed by vacuum distillation to give 85 g (97%) of I as a red oil.

2,5-Distyrylthiophene (IVa). Sodium methoxide (a solution of 1.5 g of sodium in the minimum amount of absolute methanol) was added in portions to a solution of 10 g (0.025 mole) of I in 40 ml of dimethylformamide (DMF), and the mixture was allowed to stand for 15 min. A solution of 5.5 g (0.05 mole) of benzaldehyde in 15 ml of DMF was then added, and the mixture was allowed to stand for another 15 h. The resulting precipitate was removed by filtration and an additional amount of the reaction product was isolated from the filtrate by the addition of water. The product was purified by two crystallizations with activated charcoal from cyclohexane and subsequent chromatography of a solution in benzene on aluminum oxide to give 2.2 g (30%) of a yellow powder with mp 197°C. Compounds IVb-h were similarly synthesized (Table 1).

LITERATURE CITED

1. West German Patent No. 2301410 (1974); Chem. Abstr., 81, 171369 (1974).
2. Ng. H. Nam, Ng. Ph. Buu-Hoi, and Ng. D. Xuong, J. Chem. Soc., No. 6, 1690 (1954).
3. M. El-Kerdawy, M. N. Tolba, and A. El-Agamey, Acta Pharm. Jugosl., 26, 141 (1976); Ref. Zh. Khim., 21Zh377 (1976).
4. L. Ya. Malkes, L. V. Shubina, and Yu. M. Vinetskaya, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Vol. 1, Kharkov (1967), p. 78.
5. I. I. Lapkin and L. P. Borodina, Zh. Org. Khim., 8, 725 (1972).
6. M. G. Voronkov, A. N. Pereferkovich, M. P. Gavar, and G. V. Ozolin', Khim. Geterotsikl. Soedin., 9, 1183 (1970).
7. A. Arcoria, S. Fisichella, C. Scarlata, and M. Tore, J. Heterocycl. Chem., 10, 643 (1973).
8. Yu. K. Yur'ev and D. Ékkhardt, Zh. Obshch. Khim., 31, 3536 (1961).
9. L. Horner, H. Hoffmann, and H. Wippel, Chem. Ber., 91, 61 (1958); L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, Chem. Ber., 92, 2499 (1959).
10. N. N. Zatsepina, Yu. L. Kaminskii, and I. F. Tupitsyn, Reakts. Sposobn. Org. Soedin., 6, 778 (1969).
11. A. J. Speziale and D. E. Bissing, J. Am. Chem. Soc., 85, 3878 (1963).

CONDENSED HETEROAROMATIC SYSTEMS THAT INCLUDE A THIOPHENE RING

36.* NEW COMPLEXING AND CHELATE COMPOUNDS OF THE BENZO[b]THIOPHENE SERIES WITH SELENIUM AS THE DONOR

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UDC 547.735:541.49

New complexing compounds, viz., 2-formylbenzo[b]thiophene-3-selenol and 3-formylbenzo[b]thiophene-2-selenol, and some derivatives involving the selenium atom and the formyl group, as well as complexes of divalent nickel and copper based on them, were obtained. The tautomerism of the isomeric formylthiopheneselenols was studied by means of IR spectroscopy, and it was shown that 3-formylbenzo[b]thiophene-2-selenol, in contrast to 2-formylbenzo[b]thiophene-3-selenol, exists in the form of a mixture of two tautomers.

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* See [1] for communication 35.

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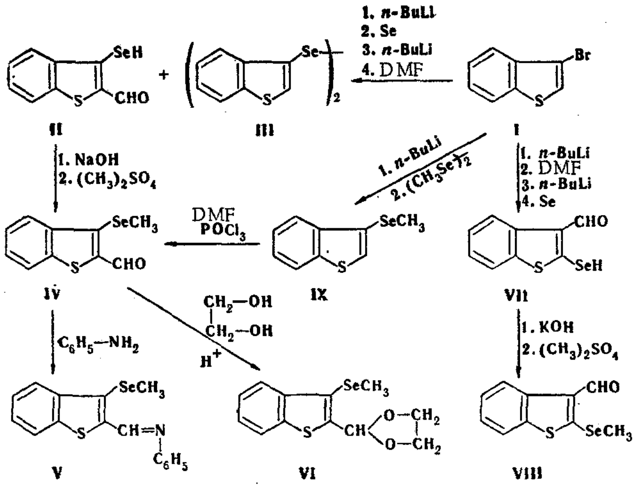
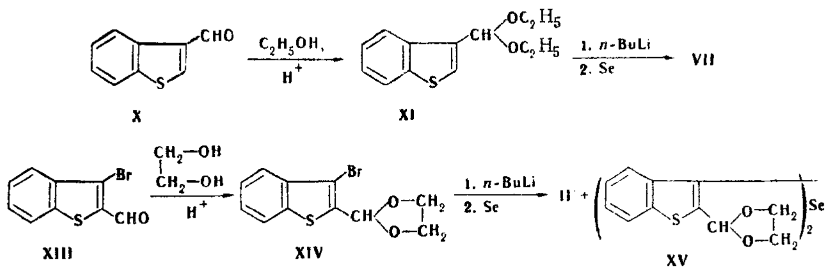
The difference in the lengths of the bonds of sulfur and selenium atoms with carbon in organic compounds is a factor involved in their strengths. The fact that selenides of the furan, thiophene, and selenophene series with an alkylselenide group in the α position of the ring readily split out this group under the influence of organolithium compounds even at low temperatures and that, moreover, the $C_{arom}-Se$ bond is also easily cleaved by the action of excess bromine [2] may serve as an example. Thus an a priori prediction or an attempt to draw a parallel in the mechanisms of the reactions of organoselenium and organosulfur compounds is to a certain extent risky, and only experiments can give an accurate answer to the questions that arise in such cases. Of great significance here is the difference in the degree of polarization of the $C=S$ and $C=Se$ bonds [3], which has a pronounced effect on the tautomeric equilibrium of the complexing compounds. It is also known that replacement of the donor sulfur atom by selenium in complexes leads to an increase in the complexes [4].

In our laboratory we have studied complexes based on benzo[b]thiophenes that have an oxygen or sulfur atom as one of the donors [5-7]. It seemed of interest in this respect to study complexing compounds of the benzo[b]thiophene series in which the selenium atom is one of the coordination centers. The first task was to develop a method for the preparation of compounds of this type, to study their tautomerism, and to obtain complexes from them. For the synthesis of 2-formylbenzo[b]thiophene-3-selenol (II) and 3-formylbenzo[b]thiophene-2-selenol (VII) we used the methods proposed in our laboratory for the preparation of the corresponding sulfur analogs [8]; these methods involve the one-step introduction of selenium and a formyl group in the 2 and 3 positions of benzo[b]thiophene. The use of this method for the preparation of aldehyde II (Scheme 1, Pathway A) leads to the formation of a mixture of 25% II and up to 8% bis(benzo[b]thien-3-yl) diselenide (III), which is the product of oxidation of benzo[b]thiophene-3-selenol; aldehyde VII is formed in up to 21% yield by this method. Products of alkylation of the selenium atom, viz., 2-formyl-2-methylselenobenzo[b]thiophene (VIII) and 2-formyl-3-methylselenobenzo[b]thiophene (IV), were obtained by the action of dimethyl sulfate on the sodium salt of aldehyde II and the sodium salt of aldehyde VII. Aldehyde IV was also obtained by an independent method. The data from PMR, IR, and UV spectroscopy are in agreement with the IV and VIII structures and with the structures of some derivatives involving the aldehyde group (V and VI). The low yields of aldehydes II and VII prompted us to synthesize the isomeric aldehydes by a different method, which includes the preparation of acetal XI and bromoacetal XIV with subsequent treatment of them with n-BuLi and Se (Scheme 1, Pathway B). The yield in the last step in the preparation of aldehyde VII by this method was ~19%, whereas a mixture of 10% II and 15% of a substance whose structure, according to the data from the PMR and IR spectra, can be depicted by formula XV is formed in the preparation of aldehyde II. The formation of isomeric aldehydes II and VII by this method in even lower yields and the increase in the number of steps make their preparation by method A (Scheme 1) preferable.

Scheme 1



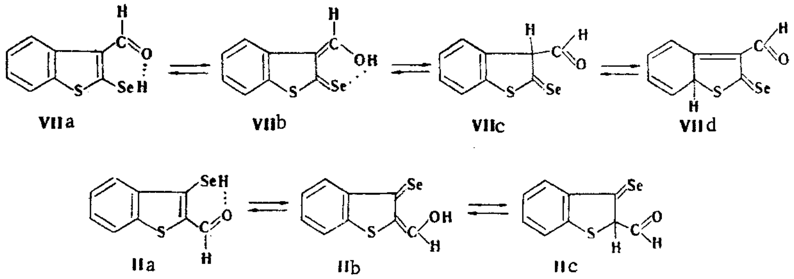
Pathway A



Pathway B

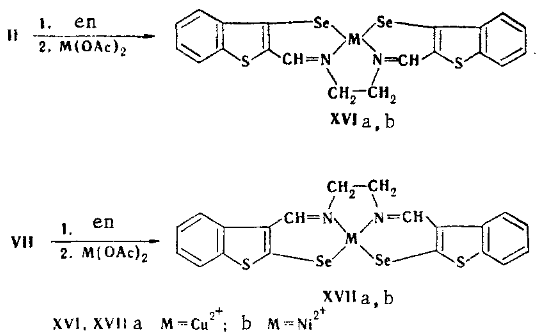
Aldehydes II and VII are potentially capable of existing in several theoretically possible tautomeric forms (a-d) or an equilibrium mixture of them (Scheme 2). We were unable to study the structures of II and VII by PMR spectroscopy because of their low solubilities. The IR-spectroscopic data provide evidence that isomeric aldehydes II and VII exist in the solid state and in solutions of various concentrations primarily in enol forms IIb and VIIb with an intramolecular hydrogen bond. This is indicated by the broad band at 3400 cm^{-1} for II and at 3450 cm^{-1} for VII, which can be assigned to the intramolecular vibrations of the hydroxy group. The absence of tautomeric form IIa is confirmed by the fact that the IR spectrum does not contain the absorption band at ~1500 cm^{-1} that is characteristic for other benzo[b]thiophene derivatives with a formyl group in the 2 position of the thiophene ring such as, for example, XIII ($\nu_{C=C}$ 1507 cm^{-1}) and IV ($\nu_{C=C}$ 1490 cm^{-1}). In the case of isomer VII the presence of a band at 1465 cm^{-1}, which is also present in the spectrum of its 3-formyl-2-methylselenobenzo[b]thiophene derivative (VIII) and is characteristic for the vibrations of the C = C bond of the thiophene ring, indicates the presence of tautomer VIIa. This is also confirmed by the presence of two bands at 1645 and 1670 cm^{-1}, which are characteristic for a formyl group in the 3 position of benzo[b]thiophene (e.g., in the case of 3-formyl-2-methylselenobenzo[b]thiophene $\nu_{C=O}$ 1650 cm^{-1}). On the basis of the material presented above, it may be assumed that 2-formylbenzo[b]thiophene-3-selenol preferably exists in the IIb form, whereas its isomer exists in the form of a mixture of two tautomers (VIIa and VIIb).

Scheme 2



Complexes with the compositions XVIa,b and XVIIa,b were obtained by reaction of aldehydes II or VII with ethylenediamine (en) and acetates (Scheme 3):

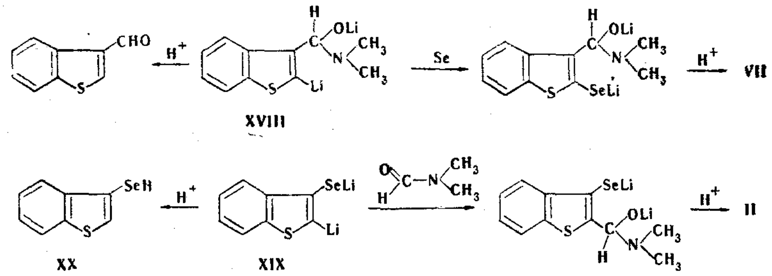
Scheme 3



XVI, XVII a M = Cu^{2+}; b M = Ni^{2+}

In contrast to the sulfur analogs, which are formed via Scheme 1 in up to 80% yields (e.g., 3-formylbenzo[b]-thiophene-2-thiol [7]), the isomeric aldehydes II and VII, as noted above, are formed only in yields that do not exceed 21%. A possible explanation for this may be the steric hindrance that develops when an Se atom is introduced in intermediate XVIII, which is formed as a result of the addition of a second equivalent of n-BuLi (Scheme 4) or dimethylformamide (DMF) to XIX, which is formed as an intermediate in the final stage of the one-step synthesis via Pathway A.

Scheme 4



The formation of intermediates, viz., 3-formylbenzo[b]thiophene (X) and benzo[b]thiophene-3-selenol (XX), in no less than 60% yields indicates the complexity of the reaction precisely in the second step of the synthesis.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Varian DA-60-IL spectrometer (60 MHz) with tetramethylsilane as the internal standard. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The mass spectra were recorded with a Varian MAT CH-6 spectrometer at an ionizing-electron energy of 70 eV. The molecular weights of the isomeric aldehydes were measured with an ÉP-75 precision ebulliograph.

2-Formylbenzo[b]thiophene-3-selenol (II). A 29.4-g (0.138 mole) sample of 3-bromobenzo[b]thiophene (I) in 45 ml of absolute ether was added at −70°C to an ether solution of 8.82 g (0.138 mole) of n-butyllithium. After 15 min, 10.9 g (0.138 mole) of powdered selenium was added to the mixture at −70°C, after which the cooling bath was removed. After 30 min (after the selenium had dissolved), a second equivalent of n-butyllithium (8.82 g) was added at −30°C. After 5 min at −30°C, 10.1 g of dry DMF in 18 ml of absolute ether was added, and the mixture was stirred at −10°C for 30 min. It was then treated with 50 ml of water, and the aqueous layer was separated. The ether layer was washed with water, and the combined water layers were acidified with dilute HCl. The resulting yellow precipitate was removed by filtration, dried over P_2O_5, and recrystallized from hexane to give 8.3 g (25%) of aldehyde II with mp 115-116°C. UV spectrum: λ_{max} (in alcohol) 225 nm (log ε 4.30); (in chloroform) 243 nm (log ε 4.31). IR spectrum: 3400 cm^{-1} (– OH ...). M_{ebull} 250. Found: C 45.2; H 2.5; S 13.2; Se 32.5%. C_9H_6OSSe. Calculated: C 44.8; H 2.5; S 13.3; Se 32.7%. M 241.

The hexane-insoluble residue in the preparation of II was recrystallized from toluene to give diselenide III with mp 120-120.5°C and $[M^{+\cdot}]$ 424. Found: C 45.6; H 2.7; S 15.2; Se 37.4%. $C_{16}H_{10}S_2Se_2$. Calculated: C 45.3; H 2.4; S 15.1; Se 37.2%.

2-Formyl-3-methylselenobenzo[b]thiophene (IV). Excess dimethyl sulfate (15 ml) was added with stirring to a solution of 2.2 g (0.009 mole) of aldehyde II in 150 ml of 1 N aqueous NaOH, and the mixture was heated at 70°C for 30 min. It was then cooled and extracted thoroughly with benzene. The benzene extracts were washed with a saturated solution of Na_2CO_3 and twice with water and dried over $MgSO_4$. The benzene was removed by distillation, and the residue began to crystallize. It was recrystallized from ether to give 1.61 g (69%) of light-yellow crystals of IV with mp 73.5-74°C. UV spectrum: λ_{max} (in chloroform) 308 nm (log ε 4.18). IR spectrum: 1675 cm^{-1} (C = O). PMR spectrum (in $CDCl_3$): 10.47 (1H, s, CH = O), 7.3-8.3 (4H, m, H_{arom}), and 2.33 ppm (3H, s, CH_3). $[M^{+\cdot}]$ 255. Found: C 47.1; H 3.2, S 12.3; Se 30.8%. $C_{10}H_8OSSe$. Calculated: C 47.1; H 3.2; S 12.6; Se 30.9%. M 255.

2-Formyl-3-methylselenobenzo[b]thiophene Dioxolane (VI). A 3.1-g (0.04 mole) sample of freshly distilled ethylene glycol and two crystals of p-toluenesulfonic acid were added to a solution of 9.8 g (0.38 mole) of IV in 50 ml of benzene, and the mixture was refluxed for 5 h with a Dean–Stark trap. It was then washed with Na_2CO_3 solution and water and dried over $MgSO_4$, the benzene was removed by distillation, and the residue was distilled to give 10.8 g (96%) of VI as a light-yellow liquid with bp 176-178°C (2.0-2.5 mm) and n_D^{20}

1.6601, which crystallized on standing to give a product with mp 54-55°C (from ether). IR spectrum: The band characteristic for a formyl group is absent. PMR spectrum (in C_6D_6): 6.9-8.2 (4H, m, H_{arom}), 6.63 (1H, s, C–H), 3.58 (4H, m, CH_2-CH_2), and 1.89 ppm (3H, s, CH_3). Found: C 48.7; H 4.3%. $C_{12}H_{12}O_2SSe$. Calculated: C 48.2; H 4.1%.

2-Formyl-3-methylselenobenzo[b]thiophene Anil (V). A 0.93-g (0.01 mole) sample of aniline was added to a solution of 1.7 g (0.007 mole) of IV in 60 ml of benzene, and the mixture was refluxed for 2 h with a Dean–Stark trap. The benzene was removed by distillation, and the residue was recrystallized from alcohol to give anil V in quantitative yield in the form of light-yellow needles with mp 93-94°C. UV spectrum: λ_{max} (in chloroform) 345 nm (log ε 4.23). PMR spectrum (in $CDCl_3$): 9.17 (1H, s, CH=N–), 7.2-8.2 (4H, m, H_{arom}), and 2.20 ppm (3H, s, CH_3). [$M^{+\cdot}$] 330. Found: C 58.2; H 4.1; N 4.4; S 9.5; Se 23.5%. $C_{16}H_{13}NSSe$. Calculated: C 58.2; H 4.0; N 4.2; S 9.7; Se 23.9%. M 330.

3-Methylselenobenzo[b]thiophene (IX). An 8.95-g (0.14 mole) sample of n-butyllithium in 80 ml of ether was added at –70°C in a stream of argon to a solution of 30 g (0.14 mole) of I in 100 ml of absolute ether. After 15 min, 26.3 g (0.14 mole) of dimethyldiselenide in 40 ml of absolute ether was added with stirring, the cooling bath was removed, and the mixture was stirred for 1 h. A total of 100 ml of 25% aqueous NH_4Cl solution was then added at –5°C, and the mixture was again stirred for 15 min. The ether layer was separated, and the aqueous layer was extracted thoroughly with ether. The ether extracts were washed with water and dried over $MgSO_4$, the ether was removed by distillation, and the residue was distilled in vacuo to give 25.3 g (79.5%) of IX with bp 127-128°C (2.5-3 mm) and n_D^{20} 1.6869; judging from the results of gas–liquid chromatography (GLC), IX contained up to 7.5% starting I. Found: C 47.2; H 3.1%. C_9H_8SSe. Calculated: C 47.6; H 3.5%.

2-Formyl-3-methylselenobenzo[b]thiophene (IV). A 14.1-g (0.105 mole) sample of N-methylformaniline was added with stirring to 15 g (0.098 mole) of $POCl_3$, and the mixture was stirred at 60°C for 30 min. A 21.7-g (0.079 mole) sample of IX was added dropwise, and the mixture was stirred at 60°C for 4 h. It was then hydrolyzed with water, and the aqueous mixture was extracted with ether. The ether extracts were washed with water and dried over $MgSO_4$, the ether was removed by distillation, and the residue was recrystallized from alcohol to give 14.5 g (60%) of aldehyde IV with mp 73.5-74°C. No melting-point depression was observed for a mixture of this product with a sample of IV obtained by a different method. Found: C 47.2; H 3.2; S 12.3; Se 30.8%. $C_{10}H_8OSSe$. Calculated: C 47.1; H 3.2; S 12.6; Se 30.9%.

3-Formylbenzo[b]thiophene-2-selenol (VII). A cooled (to –70°C) solution of 19.6 g (0.092 mole) of I in 30 ml of absolute ether was added with stirring at –70°C in a stream of argon to an ether solution of 5.88 g (0.091 mole) of n-butyllithium (49.3 ml), and the mixture was then stirred for 30 min, after which, 6.7 g of dry DMF in 12 ml of absolute ether was added at –70°C, and a second equivalent (5.88 g) of n-butyllithium was added at –30°C. The mixture was stirred at –30°C for 30 min, after which 7.26 g of powdered selenium was added at –25°C, and the mixture was stirred at 20°C until the selenium had dissolved completely. The solution was hydrolyzed with water, the ether layer was washed with water, and the combined aqueous extracts were acidified with dilute HCl to pH 3. The precipitate was removed by filtration, washed with water, and dried over P_2O_5 to give 4.68 g (21%) of VII with mp 109-111°C. Reprecipitation from a solution in alcoholic alkali by the addition of dilute HCl gave a product with mp 137-138°C. UV spectrum: λ_{max} (in alcohol) 228 nm (log ε 4.27); (in chloroform) 243 nm (log ε 4.30). IR spectrum: 3450 cm^{-1} (–OH...). Mebull 248. Found: C 45.0; H 2.4; S 13.3; Se 32.3%. C_9H_6OSSe. Calculated: C 44.8; H 2.5; S 13.3; Se 32.7%. M 241.

3-Formyl-2-methylselenobenzo[b]thiophene (VIII). A 2-g (0.008 mole) sample of VII was added to a hot solution of 5 g (0.089 mole) of KOH in 100 ml of ethanol, and the mixture was heated until all of the VII had dissolved. The solution was filtered, and the filtrate was treated in portions with 12.6 g (0.1 mole) of dimethyl sulfate. The mixture was cooled and treated with 200 ml of water, and the aqueous mixture was extracted with benzene. The extract was washed with a saturated solution of Na_2CO_3 and water and dried over $MgSO_4$. The benzene was removed by distillation, ether was added to the residue, and the resulting precipitate was removed by filtration and recrystallized from acetone to give 1.5 g (71%) of VIII with mp 96-97°C. UV spectrum: λ_{max} (in chloroform) 318 nm (log ε 3.85). IR spectrum: 1650 cm^{-1} (C=O). PMR spectrum, $(CD_3)_2CO$: 10.35 (1H, s, CH=O), 7.2-8.4 (4H, m, H_{arom}), and 2.5 ppm (3H, s, CH_3). [$M^{+\cdot}$] 255. Found: C 47.1; H 3.2; S 12.3; Se 30.7%. $C_{10}H_8OSSe$. Calculated: C 47.1; H 3.2; S 12.6; Se 30.9%. M 255.

3-Formylbenzo[b]thiophene (X). This compound, with bp 117-120°C (2 mm) and mp 56.5-57°C (mp 56-57°C [9]), was obtained in 50% yield by the method in [9].

3-Formylbenzo[b]thiophene Diethylacetal (XI). A mixture of 9.18 g (0.057 mole) of aldehyde X, 8.58 g (0.058 mole) of freshly distilled ethyl orthoformate, 27 ml of absolute alcohol, and one to two drops of concentrated HCl was refluxed for 4h, after which the alcohol was removed by distillation, and the residue was distilled to give 11.3 g (84%) of XI with bp 119-120°C (2 mm) and n_D^{20} 1.5585. Found: C 65.9; H 6.8; S 13.9%. $C_{13}H_{16}O_2S$. Calculated: C 66.1; H 6.8; S 13.6%.

3-Formylbenzo[b]thiophene-2-selenol (VII). A solution of 9.44 g (0.04 mole) of acetal XI in 15 ml of absolute ether was added with stirring at −30°C in a stream of nitrogen to a solution of 2.6 g (0.041 mole) of n-butyllithium in 25 ml of ether. The mixture was then stirred for 30 min at −30°C, after which 3.13 g (0.04 mole) of powdered Se was added, and the mixture was stirred at 20°C for 4 h. It was then hydrolyzed with water, and the ether layer was washed twice with water. The combined aqueous layers were acidified with a 1 N HCl solution, and the yellow precipitate was removed by filtration and dried over P_2O_5. Reprecipitation from a solution in 1 N alcoholic alkali by the addition of HCl solution gave 1.8 g (19%) of VII with mp 137-138°C. No melting-point depression was observed for a mixture of this product with a sample of the compound obtained via Pathway A (Scheme 1).

2-Formylbenzo[b]thiophene (XII). This compound, with bp 125-126°C (3 mm) and mp 33°C (mp 34-34.5°C [10]), was obtained in 74% yield by the method in [10].

3-Bromo-2-formylbenzo[b]thiophene (XIII). This compound, with mp 117-118°C (mp 118-118.5°C [11]), was obtained in 70% yield by the method in [11]. IR spectrum: 1665 cm^{-1} (C = O).

3-Bromo-2-formylbenzo[b]thiophene Dioxolane (XIV). A mixture of 17.9 g (0.075 mole) of XIII, 6 g (0.097 mole) of ethylene glycol, two crystals of p-toluenesulfonic acid, and 80 ml of absolute benzene was refluxed with a Dean – Stark trap for 5 h, after which the solution was washed with a saturated solution of Na_2CO_3 and water and dried over $MgSO_4$. The benzene was removed by distillation, and the residue was distilled to give 21 g (98.5%) of XIV with bp 173-175°C (4 mm). Found: C 46.2; H 3.1%. $C_{11}H_9O_2BrS$. Calculated: C 46.3; H 3.2%.

2-Formylbenzo[b]thiophene-3-selenol (II). A solution of 16.1 g (0.057 mole) of acetal XIV in 25 ml of absolute ether was added in a stream of argon at −70°C to a solution of 3.65 g (0.057 mole) of n-butyllithium in 33 ml of ether, after which 4.45 g (0.057 mole) of powdered selenium was added at −30°C, and the mixture was stirred for 30 min. The cooling bath was then removed, and the mixture was stirred for another 4 h and worked up as in the preparation of aldehyde VII to give 1.36 g (10%) of II with mp 115-116°C. No melting-point depression was observed for a mixture of this product with a sample obtained via Pathway A. The ether layer was washed with water and dried over $MgSO_4$, the ether was removed by distillation, and the residue was recrystallized from benzene to give 2.0 g (15%) of XV with mp 177-178°C. PMR spectrum (C_6D_5): 6.75-8.10 (8H, m, H_{arom}), 6.70 (2H, s, CH), and 3.5 ppm (8H, m, CH_2). $[M^{+\cdot}]$ 489. Found: C 45.1; H 3.9; Se 15.7%. $C_{22}H_{18}O_4S_2Se$. Calculated: C 54.0; H 3.7; Se 16.1%. M 489.

N,N'-{Bis(3-selenobenzo[b]-2-thenylidene)ethylenediaminato} Cu(II). (XVIa). A 6.5-g (0.027 mole) sample of II was dissolved by heating in 100 ml of DMF, after which 0.24 g (0.014 mole) of ethylenediamine was added, and the resulting solution was heated at 100°C for 20 min. A hot filtered solution of 2.8 g (0.014 mole) of $Cu(OAc)_2 \cdot H_2O$ in 10 ml of DMF was added to the hot solution, and the precipitate that formed in the course of 10 h was removed by filtration to give 4.7 g (61.5%) of complex XVIa (golden-brown crystals). Recrystallization from bromobenzene gave a product with mp 284-286°C (dec.). Found: C 42.2; H 2.5; S 11.6; Se 28.2; Cu 10.9%. $C_{20}H_{14}N_2S_2Se_2Cu$. Calculated: C 42.3; H 2.5; S 11.3; Se 27.8; Cu 11.2%.

N,N'-{Bis-(3-selenobenzo[b]-2-thenylidene)ethylenediaminato} Ni (II) (XVIb). The nickel chelate was obtained in 65% yield by a method similar to that used to prepare chelate XVIa. The cherry-red crystals decomposed above 360°C. Found: C 42.7; H 2.7; S 11.5; Se 27.9; Ni 10.6%. $C_{20}H_{14}N_2S_2Se_2Ni$. Calculated: C 42.7; H 2.5; S 11.4; Se 28.1; Ni 10.4%.

N,N'-{Bis(2-selenobenzo[b]-3-thenylidene)ethylenediaminato} Cu (II) (XVIIa). This complex was similarly obtained in 52% yield. The dark-brown needles had mp 293-294°C (from bromobenzene). Found: C 42.0; H 2.3; S 11.4; Se 28.0; Cu 11.0%. $C_{20}H_{14}N_2S_2Se_2Cu$. Calculated: C 42.3; H 2.5; S 11.3; Se 28.1; Cu 11.2%.

N,N'-{Bis(2-selenobenzo[b]-3-thenylidene)ethylenediaminato} Ni (II) (XVIIb). The nickel chelate was similarly obtained in 49% yield and decomposed above 360°C (from dimethylacetamide). Found: C 42.5; H 2.7; S 11.4; Se 28.4; Ni 10.2%. $C_{20}H_{14}N_2S_2Se_2Ni$. Calculated: C 42.7; H 2.5; S 11.4; Se 28.0; Ni 10.4%.

LITERATURE CITED

1. L. M. Skolnikova (Scolnikova), A. E. Obodovskaya, B. E. Zavodnik, N. B. Rannev, and V. P. Litvinov, Chem. Scr., 9, 183 (1976).

2. V. P. Litvinov, A. N. Sukiasyan, and Ya. L. Gol'dfarb, Khim. Geterotsikl. Soedin., No. 6, 723 (1972).
3. H. G. Mautner, J. Am. Chem. Soc., 78, 5298 (1956).
4. D. C. Goodall, J. Chem. Soc., No. 6, 890 (1969).
5. V. P. Litvinov, Ya. L. Gol'dfarb, and É. G. Ostapenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2279 (1974).
6. Ya. L. Gol'dfarb, V. P. Litvinov, V. S. Bogdanov, G. V. Isagulyants, É. G. Ostapenko, and A. A. Greish, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2284 (1974).
7. V. P. Litvinov, N. N. Petukhova, Ya. L. Gol'dfarb, and A. S. Chegolya, USSR Inventor's Certificate No. 405897 (1972); Byul. Izobr., No. 45, 98 (1973).
8. V. P. Litvinov, Ya. L. Gol'dfarb, V. V. Zelentsov, L. G. Bogdanova, and N. N. Petukhova, Khim. Geterotsikl. Soedin., No. 5, 486 (1974).
9. V. P. Mamaev and O. P. Shkurko, Zh. Obshch. Khim., 31, 3288 (1961).
10. D. A. Shirly and M. J. Danzig, J. Am. Chem. Soc., 74, 2935 (1952).
11. W. Ried and H. Bender, Ber., 88, 34 (1955).

CONDENSED HETEROAROMATIC SYSTEMS THAT INCLUDE A THIOPHENE RING

37.* PREPARATION OF ISOMERIC FORMYL-SUBSTITUTED SELENOLS OF THE BENZO[b]THIOPHENE SERIES

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Isomeric 2-formylbenzo[b]thiophene-3-selenol and 3-formylbenzo[b]thiophene-2-selenol and their sulfur analogs were obtained by nucleophilic substitution of the bromine atom in 3-bromo-2-formylbenzo[b]thiophene or the isomeric 2-bromo-3-formylbenzo[b]thiophene by a hydroselenide or hydrosulfide group by the action of an alcohol solution of NaSeH or NaSH, as well as by the action of selenourea with subsequent alkaline hydrolysis. Various Schiff bases were obtained from the isolated formyl-substituted selenols and thiols by two methods, and complexes with divalent Zn, Cd, and Ni were obtained by reaction of the Schiff bases with the corresponding metal acetates.

We have previously [1] obtained 2-formylbenzo[b]thiophene-3-selenol (I) and 3-formylbenzo[b]thiophene-2-selenol (II) by organolithium synthesis by the method developed for the analogous compounds with a sulfur atom [2]. However, in contrast to the 80% yields obtained for the analogous sulfur-containing isomers, the yields in the preparation of the selenium compounds were only 21%.

Further development of our research on the structures and properties of derivatives of isomeric formyl-substituted selenols I and II and complexes based on them required us to improve the methods for their synthesis in order to increase the yields and to decrease the amounts of side products, which hinder the synthesis and isolation of pure ligands and complexes. On the basis of the literature data we concluded that the most convenient methods are those based on nucleophilic substitution of a labile Cl or Br atom by a hydroselenide group. 3-Bromo-2-formylbenzo[b]thiophene (III) and 2-bromo-3-formylbenzo[b]thiophene (IV), which were obtained by the methods in [3] and [4], respectively, served as the starting compounds. We initially used selenourea (Method A), which judging from the data in [5], leads to the formation of selenols in good yields, as the nucleophilic agent. However, the synthesis of formyl-substituted selenols I and II by this method is accompanied by the significant formation of side products that are insoluble in alcoholic alkali solution; this can be explained by the possible condensation of the amino group of selenourea with the formyl group, as well as by nucleophilic substitution of the bromine in IV by the amino group of selenourea [4]. Nevertheless formyl-substituted selenols I and II were obtained in 40-45% yields after two reprecipitations from an alcoholic alkali solution by acidification with dilute HCl.

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* See [1] for communication 36.

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