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SYNTHESIS, STRUCTURES, AND REDOX PROPERTIES OF SOME NEW DITHIOCARBAMATES
THAT INCLUDE A HETEROAROMATIC RING

Ya. L. Gol'dfarb,* É. G. Ostapenko, V. G. Vinogradova, UDC 547.496.2'727'734'739':
A. N. Zverev, A. V. Polyakov, A. I. Yanovskii, 543.253:539.26
D. S. Yufit, and Yu. T. Struchkov

New Cu, Ni, Pb, Zn, Co, Fe, Mn, Sb, and Bi dithiocarbamates that include 2-thenyl and 2-furfuryl radicals were synthesized. The potentials of polarographic oxidation on a rotating platinum electrode were determined for them and for the previously synthesized N-substituted unsymmetrical dithiocarbamates of the same metals. The results of x-ray diffraction analysis of bis-(di-2-thenyldithiocarbamato)nickel(2⁺) are presented and discussed.

It is known [1, 2] that chelate compounds of metals having a variable valence with sulfur-containing M(N, S) and M(S, S) chelate nodes inhibit the oxidation of hydrocarbons by oxygen and stabilize a number of polymers under conditions of thermal-oxidative destruction and photodestruction. A correlation between the inhibiting activity and the potentials of polarographic oxidation of chelates has been established for some classes of such chelate compounds [3]. In this connection the synthesis of compounds of this type and the investigation of their properties and inhibiting activities are of considerable interest.

In the present research we accomplished the synthesis of 12 new dithiocarbamates (XIII-XXIV) by the successive conversion of furfural (I) or 2-formylthiophene (II) to azomethines (III, IV) [4, 5] and amines (VIII, IX) (see Table 1).

By reducing azomethines III and IV in the presence of NaBH₄ we attempted to obtain amine V (X = O) and its thiophene analog VI (X = S). However, according to the results of gas-liquid chromatography (GLC), V and VI were not detected in the reduction products, and only amines VIII and IX were isolated.

Amine V, which is the product of hydrogenation of azomethine III over platinum [6], is not converted to ligand VII (M₁ = NH₄, Na, or K), evidently because of steric hindrance. Amines VIII and IX, the structures of which are similar to the structure of amine V, are readily converted to alkali-metal salts of N,N-disubstituted dithiocarbamic acids.

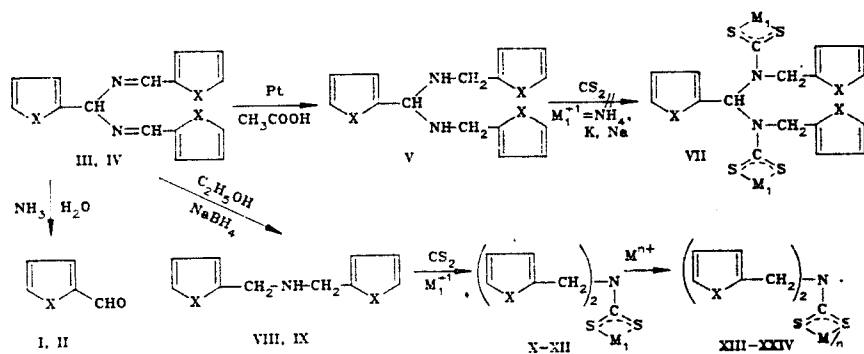
*Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow 117977. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 7, pp. 902-909, July, 1987. Original article submitted February 3, 1986.

TABLE 1. Characteristics of the Synthesized Dithiocarbamates $[(RCH_2)_2N-CS_2Met]_n$ (XIII-XXIV)

Comp. number	Met(n)	Form and color	$T_{dec}, ^\circ C$	Found, %				Empirical formula	Calculated, %				Yield, %
				C	H	Met	S(N)		C	H	Met	S(N)	
XIII	Co(III)	Green crystals	178-179	49.0	3.8	7.1	23.4	$C_{33}CoH_{30}N_3O_6S_6$	48.6	3.7	7.2	23.6	98
XIV	Fe(III)	Black powder	168-170	9.0	3.8	7.1	23.6	$C_{33}H_{30}FeN_3O_6S_6$	48.8	3.7	6.9	23.7	83
XV	Mn(III)	Black powder	131-132	46.7	3.8	9.7	22.6	$C_{22}H_{20}MnN_2O_4S_4$	47.2	3.6	9.8	22.9	78
XVI	Zn(II)	White crystals	197-198	46.4	3.8	11.7	22.4	$C_{22}H_2N_2O_4S_4Zn$	46.4	3.5	11.5	22.5	79
XVII	Pb(II)	Yellow crystals	148-149	37.1	2.9	29.0	18.0	$C_{22}H_{20}N_2O_4PbS_4$	37.1	2.8	29.1	18.0	95
XVIII	Ni(II)	Green crystals	209-210	47.1	3.6	10.9	22.9	$C_{22}H_{20}N_2NiO_4S_4$	46.9	3.6	10.4	22.8	99
XIX	Cu(II)	Green crystals	213-214	7.0	3.7	11.1	22.4	$C_{22}CuH_{20}N_2O_4S_4$	46.5	3.6	11.2	22.6	86
XX	Bi(III)	Yellow crystals	180-181	37.4	2.9	20.1	36.0	$BiC_{33}H_{30}N_3S_{12}$	37.3	2.8	19.7	36.2	73
XXI	Zn(II)	White crystals	223-224	41.6	3.2	10.6	40.2	$C_{22}H_{20}N_2S_{12}Zn$	41.6	3.2	10.3	40.4	95
XXII	Ni(II)	Green crystals	224-225	42.1	3.2	9.4	41.0	$C_{22}H_{20}N_2NiS_8$	42.0	3.2	9.4	40.9	92
XXIII	Cu(II)	Dark-green crystals	205-206	42.1	3.3	10.1	40.3	$C_{22}CuH_{20}N_2S_8$	41.8	3.2	10.0	40.6	94
XXIV	Sb(III)	Yellow crystals	143-144	40.7	3.2	12.4	39.2	$C_{33}H_{30}N_3S_{12}Sb$	40.6	3.1	12.5	39.5	63

*R = 2-furyl for XIII-XIX, and R = 2-thienyl for XX-XXIV.



I, III, V, VII, VIII, X, XIII-XIX X=O; II, IV, IX, XI, XII, XX-XXIV X=S; X, XI $M_1=NH_4^+$; XII $M_1=K^+$; XIII-XIX $M=Co, Fe, Mn, Zn, Pb, Ni, Cu$; XX-XXIV $M=Bi, Zn, Ni, Cu, Sb$

Dithiocarbamates XIII-XXIV, which are readily soluble in organic solvents, were obtained from these salts (ligands) by an exchange reaction with the corresponding salts of other metals.

The structures of the synthesized dithiocarbamates were confirmed by the results of x-ray diffraction analysis in the case of XXII. It is bis(di-2-thienyldithiocarbamate)nickel(2⁺). The structure of the molecule is shown in Fig. 1; the bond lengths and bond angles are presented in Tables 3 and 4. The nickel atom has distorted square-planar coordination with four sulfur atoms; interchelate bond angle $S(1)NiS(2)$ is $79.54(6)^\circ$. The $Ni-S(1)$ [2.197(1) Å] and $Ni-S(2)$ [2.200(2) Å] bond lengths are close to those observed in other dithiocarbamate complexes of nickel, for example, 2.198 Å and 2.210 Å in $Ni[S_2CN(CH_2CH=CH_2)_2]_2$ [7].

The geometry of the dithienyldithiocarbamate ligand is virtually the same as that found in other structurally investigated dithiocarbamate complexes [7-10]. The $S(1)S(2)C(1)NC(2)C(7)$ atoms (plane A) are coplanar with an accuracy of 0.009 Å; the deviation of the nickel atom from plane A is 0.074 Å. The $S(1)-C(1)$ and $S(2)-C(1)$ bond lengths are identical and are 1.709(6) Å; this constitutes evidence for delocalization of the electron density in the chelate ligate. The $N-C(1)$ [1.323(6) Å], $N-C(2)$ [1.474(7) Å], and $N-C(7)$ [1.489(7) Å] distances are close to the corresponding values in other dithiocarbamates. Thus, for example, they are 1.231, 1.490, and 1.492 Å, respectively, in $Cu[S_2CN(iso-Pr)_2]_2$ [10]. The thienyl substituents are situated on the same side relative to plane A. The $S(3)C(3)C(4)C(5)C(6)$ and $S(4)C(8)C(9)-C(10)C(11)$ planes of the thiophene rings form dihedral angles of $96.76(7)^\circ$ and $70.4(1)^\circ$, respectively, with plane A.

In decoding the structure (see the experimental section) it was found that ~80% of the crystal is constructed from the molecules depicted in Fig. 1 and ~20% is constructed from molecules that differ with respect to -180° rotation of the thienyl substituents about the $C(2)-C(3)$ and $C(7)-C(8)$ bonds. This disorderliness leads to apparent distortion of the bond lengths and bond angles in both rings: the bonds with the participation of the $S(3)$ and $S(4)$ atoms [$S(3)-C(3)$ 1.677(5) Å, $S(3)-C(6)$ 1.668(6) Å, $S(4)-C(8)$ 1.697(5) Å, and $S(4)-C(11)$

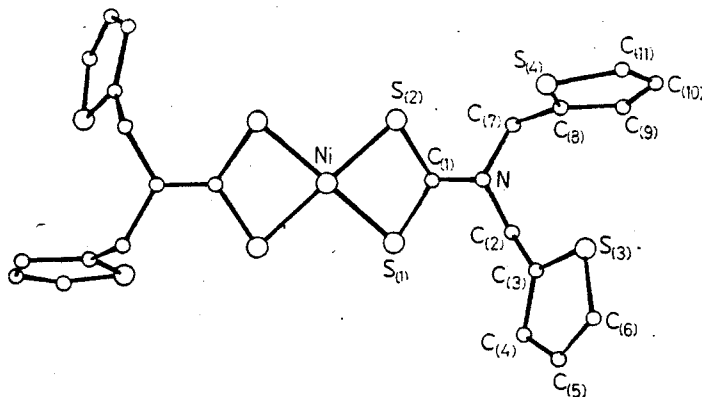


Fig. 1. Structure of the XXII molecule (the hydrogen atoms are not shown).

TABLE 2. Bond Lengths d (Å)

Bond	d
Ni—S(1)	2,197(1)
Ni—S(2)	2,200(2)
S(1)—C(1)	1,709(6)
S(2)—C(1)	1,709(6)
S(3)—C(3)	1,677(5)
S(3)—C(6)	1,668(6)
S(4)—C(8)	1,697(5)
S(4)—C(11)	1,666(7)
N—C(1)	1,323(6)
N—C(2)	1,474(7)
N—C(7)	1,489(7)
C(2)—C(3)	1,500(8)
C(3)—C(4)	1,489(7)
C(4)—C(5)	1,437(7)
C(5)—C(6)	1,319(9)
C(7)—C(8)	1,493(7)
C(8)—C(9)	1,501(7)
C(9)—C(10)	1,457(8)
C(10)—C(11)	1,313(9)

1.666(7) Å] are shortened and the angles at these atoms [$C(3)S(3)C(6)$ $93.5(3)^\circ$ and $C(8)S(4)C(11)$ $92.1(3)^\circ$] are increased while the bonds with the participation of the $C(4)$ and $C(9)$ atoms [$C(3)-C(4)$ 1.489(7) Å, $C(4)-C(5)$ 1.437(7) Å, $C(8)-C(9)$ 1.501(7) Å and $C(9)-C(10)$ 1.457(8) Å] are elongated and the corresponding angles [$C(3)C(4)C(5)$ $105.3(5)^\circ$ and $C(8)C(9)C(10)$ $104.7(5)^\circ$] are decreased as compared with the geometrical parameters of the thiophene molecule: S—C 1.718 Å C=C 1.352 Å, C—C 1.455 Å, CSC 91.3° and CCC 111.8° [11]. The structure of trans-dichlorobis[tri(2-thienyl)phosphine]palladium(2⁺) is distinguished by similar character of the disorderliness of the 2-thienyl groups [12]; an approximately equal contribution of both forms, which also differ with respect to 180° rotation of the thienyl groups, was detected in it, and the deviations of the bond angles and bond lengths from the corresponding values in the thiophene molecule are even greater.

The oxidation half-wave potentials for dithiocarbamates XIII–XXIV and for the previously described XXV–XXXVI [2] and XXXVII [13] were determined in acetonitrile on a platinum rotating electrode.

It is known [14–16] that the dithiocarbamates of metals are capable of undergoing both reduction and oxidation on various electrodes. The parameters of the oxidation of metal dithiocarbamates on solid electrodes characterize their reactivities. In [16] it was shown that the half-wave potential of the first one-electron step in the oxidation of chelates changes symbatically with respect to the ionization potentials of the dithiocarbamates.

In the case of anode oxidation under the experimental conditions the investigated dithiocarbamates give one or two oxidation waves, half-wave potentials (E_1 and E_2), and limiting currents ($i_{lim 1}$ and $i_{lim 2}$), which are presented in Table 4. Data previously obtained [1, 14] for diethyldithiocarbamates of the same metals are included in Table 4 for comparison.

TABLE 3. Bond Angles (deg)

Angle	ω	Angle	ω	Angle	ω
S(1)NiS(2)	79,54(6)	S(1)C(1)N	124,1(4)	C(2)C(3)C(4)	124,5(5)
NiS(1)C(1)	84,9(2)	S(2)C(1)N	125,1(4)	C(7)C(8)C(9)	125,6(5)
NiS(2)C(1)	84,8(2)	NC(2)C(3)	115,1(5)	C(3)C(4)C(5)	105,3(5)
C(3)S(3)C(6)	93,5(3)	NC(7)C(8)	112,4(5)	C(8)C(9)C(10)	104,7(5)
C(8)S(4)C(11)	92,1(3)	S(3)C(3)C(2)	123,7(4)	C(4)C(5)C(6)	116,7(6)
C(1)NC(2)	121,6(5)	S(4)C(8)C(7)	122,0(4)	C(9)C(10)C(11)	115,7(6)
C(1)NC(7)	120,6(5)	S(3)C(3)C(4)	111,7(4)	C(5)C(6)S(3)	112,7(5)
C(2)NC(7)	117,7(5)	S(4)C(8)C(9)	112,4(4)	C(10)C(11)S(4)	115,1(5)
S(1)C(1)S(2)	110,8(3)				

Two oxidation waves are observed for all of the Ni(II) and Fe(III) complexes, one wave was observed for the Zn(II), Pb(II), Sb(III), and Mn(III) complexes, and two waves were recorded in two cases and one wave was recorded in two cases for the Cu(II) complexes. A wave without an inflection, which passes into the background wave, was observed for Bi complex XX at potentials >1.2 V.

In order to verify the diffusion nature of the current in the region of the first oxidation waves we studied the dependence of i_{lim} on the concentration in the case of complex XXV in acetonitrile and complexes XXV, XXVII, and XXXV in acetonitrile-ethylbenzene (1:1), as well as the dependence of the magnitude of the limiting current on the square root of the angular rate of rotation of the electrode. In all cases we observed a linear dependence, which confirms the diffusion nature of the current. In acetonitrile-ethylbenzene the half-wave potentials for both waves are shifted 5-8% to the positive region as compared with the results in acetonitrile; this is evidently due to an increase in the resistance of the solution. We also observed an appreciable decrease in the i_{lim} values in the mixture.

It follows from Table 4 that potential E_1 for the investigated complexes ranges from +0.4 V to +1.2 V and is determined by the nature of the metal-complexing agent. The Mn(III) and Fe(III) complexes are oxidized most readily, and the Zn(II) and Co(III) complexes are oxidized with the greatest difficulty.

In [15] it was noted that for the first wave the potential of oxidation of dithiocarbamates depends markedly on the $3d^n$ configuration of the central metal ion and that among the octahedral complexes of Mn(III), Fe(III), Co(III), and Cr(III) the most stable complexes should be the Co(III) and Cr(III) complexes with filled and half-filled t_2 shells. Similarly, Ni(II) complexes with a d^8 shell will be more stable than Cu(II) complexes (d^9), but Zn(II) complexes with a d^{10} shell should display the greatest resistance to electrical oxidation. The data presented in Table 4 confirm that this principle is also observed for dithiocarbamates with heteroaromatic rings in the ligands.

The nature of the substituents in the ligand has a relatively slight effect on the E_1 value for complexes of the same metal. However, the investigated dithiocarbamates with hetaryl substituents in the ligand are oxidized with somewhat greater difficulty than the corresponding diethyldithiocarbamates (see Table 4). In series of chelates formed by the same metal [Cu(II), Co(III), Fe(III), and Zn(II)] the complexes with substituents $R^1 = \text{cyclohexyl}$ and $R^2 = 2\text{-thienyl}$ are oxidized most easily. Complexes of Ni(II), for which the oxidation potential is virtually independent of the character of the substituent in the ligand, constitute an exception.

A certain effect of the substituent in the ligand on the oxidation potentials of dithiocarbamates was also pointed out in [15]. However, the absence of a simple relationship between potential E_1 and the sum of the Taft constants for R^1 and R^2 was noted; for the six investigated metals the dichlohexyl complexes were found to be the most easily oxidized, and the dibenzyl complexes were oxidized with the greatest difficulty.

According to the data in [16], in most cases for diethyldithiocarbamates [complexes of Fe(III), Ni(II), and Cu(II), and sometimes Zn(II) and Pd(II)] the first wave of oxidation on a platinum electrode corresponds to the detachment of one electron; a complex cation containing the metal ion in the formally highest oxidation state is formed in this case:

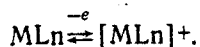


TABLE 4. Half-Wave Potentials (E_1) and Limiting Currents (i_{lim1}) in the Anode Oxidation on a Rotating Pt Electrode of Metal Dithiocarbamates at 25°C in Acetonitrile (complex concentration $5 \cdot 10^{-4}$ mole/liter)

Compound	Met**	E_1 , V	i_{lim1} , μA	E_2 , V	i_{lim2} , μA
XV	Mn(III)	+0,38	0,53	—	—
Etdtc	Mn(III)	+0,19	—	—	—
XIV	Fe(III)	+0,47	0,82	+1,49	0,42
XXXI	Fe(III)	+0,37	0,22***	+1,68	0,53
Etdtc	Fe(III)	+0,26	—	—	—
XXIII	Co(III)	+1,02	1,13	+1,71	2,37
XXIX	Co(III)	+0,92	0,26***	—	—
Etdtc	Co(III)	+0,80	—	—	—
XXII	Ni(II)	+0,63	0,20***	+0,97	0,17
XVIII	Ni(II)	+0,66	0,60	+0,96	0,14
XXVIII	Ni(II)	+0,61	0,13***	+0,94	0,10
XXX	Ni(II)	+0,62	1,00	+0,92	0,31
XXXII	Ni(II)	+0,60	0,60	+0,95	0,12
XXXIII	Ni(II)	+0,62	0,87	+1,04	0,28
XXXIV	Ni(II)	+0,61	0,70	+0,90	0,17
XXXV	Ni(II)	+0,62	0,88	+0,97	0,11
XXV	Ni(II)	+0,62	0,90	+1,01	0,70
Etdtc	Ni(II)	+0,60	1,24	—	—
XXIII	Cu(II)	+0,54	0,24***	—	—
XIX	Cu(II)	+0,53	1,20	+1,80	0,65
XXVII	Cu(II)	+0,45	0,36***	+1,70	0,38
XXXVI	Cu(II)	+0,47	1,37	—	—
Etdtc	Cu(II)	+0,43	—	—	—
XXI	Zn(II)	+1,20	0,66***	—	—
XVI	Zn(II)	+1,17	—	—	—
XXVI	Zn(II)	+1,13	0,41***	—	—
Etdtc	Zn(II)	+1,01	—	—	—
XXIV	Sb(III)	+0,88	0,58	—	—
Etdtc	Sb(III)	+0,73	—	—	—
XVII	Pb(II)	+1,08	0,96	—	—
Etdtc	Pb(II)	+0,80	—	—	—
XXXVII	—	+1,01	0,58	—	—

*Etdtc pertains to diethyldithiocarbamate

**XXV, XXX, XXXVI R^1 = p-hydroxyphenyl, XXVI-XXIX, XXXI-XXXIII, XXXV R^1 = cyclohexyl, XXXIV R^1 = tert-butyl; XXV-XXIX, XXXI, XXXIV, XXXVI R^2 = 2-thienyl, XXX R^2 = 2-furfuryl, XXXII R^2 = 2-benzo[b]selenophen-2-yl, XXXIII R^2 = 2-benzo[b]thienyl, XXXV R^2 = 2-methoxy-5-ethyl-3-thienyl. XXV-XXXVI.

***The concentration of the complex was $1 \cdot 10^{-4}$ mole/liter.

The formation of the corresponding Ni(III) derivative was demonstrated by EPR spectroscopy [17].

From a comparison of the i_{lim1} values of the investigated dithiocarbamates and nickel diethyldithiocarbamate, for which the one-electron nature of the first oxidation wave on a platinum electrode was demonstrated, it may be concluded that the oxidation of complexes of Fe(III), Co(III), Cu(II), and Pb(II) and most complexes of Ni(II) has one-electron character in the first step.

For Zn(II) complexes it may be assumed that the first and subsequent oxidation waves merge and that elevated i_{lim1} values are observed as a consequence of this. Our results, as well as the literature data, in general are in agreement with the assumption regarding the nature of the first oxidation wave. The introduction of electron-donor substituents, all things being equal (the charge of the central metal atom, the structure of the complex, etc.), should facilitate electrical oxidation.

The subsequent steps in electrical oxidation are due to oxidation of the products formed in the first step [16].

In [18] it was established that radical particles, which subsequently undergo dimerization with the formation of the corresponding thiuram disulfide, are formed in the oxidation of sodium diethyldithiocarbamate on a platinum electrode. A comparison of potential E_2 for Ni

complex XXII (+0.97 V) with half-wave potential E_1 for thiuram disulfide XXXVIII makes it possible to assume that the second step of the oxidation of Ni complex XXII corresponds to the oxidation of the thiuram disulfide formed in the first step. For the remaining investigated nickel complexes potentials E_2 (from +0.90 to +1.04 V) are rather close to the E_2 values of complex XXII (correspondingly, E_1 of thiuram disulfide XXXVIII). The corresponding thiuram disulfides are evidently formed in the electrical oxidation of these complexes.

Potentials E_2 for the Fe(III), Co(III), and Cu(II) complexes have substantially more positive values (by 0.5-0.8 V) than the oxidation potential of XXXVIII, and an unambiguous interpretation of them is difficult.

EXPERIMENTAL

X-Ray Investigation of Bis(di-2-thenyldithiocarbamate)nickel(2⁺). The XXII crystals were monoclinic with (at +20°C) $a = 5.4063(4)$ Å, $b = 15.768(1)$ Å, $c = 15.185(2)$ Å, $\beta = 91.966(7)^\circ$, $Z = 2$, and space group $P2_1/c$ with the molecule in a separate position at the center of symmetry.

The parameters of the unit cell and the intensities of 971 independent reflections with $F^2 \geq 3\sigma$ were measured with a Hilger-Watts four-circle automatic diffractometer (+20°C, λ Mo K_α , graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 30^\circ$).

The structure was decoded by the heavy-atom method: for the initial assignment of the signs of the reflections we used the contribution of the Ni atom positioned at the center of symmetry 0, 0, 0, after which all of the nonhydrogen atoms were localized in successive approximations of syntheses of the electron density. Refinement of the structure by the method of least squares, initially in the isotropic approximation and then in the anisotropic approximation, led to $R = 0.055$. However, the distribution of the bond lengths in the thienyl rings and the high temperature factors of the S atoms indicated their possible disorderliness. Further refinement with the use of mixed f curves with different contributions of the S and C atoms for the $S(3)$, $S(4)$, $C(4)$, and $C(9)$ atoms led to a substantial decrease in the R factor; the highest accuracy was achieved with the use of $f_1 = 0.2f_C + 0.8f_S$ and $f_2 = 0.8f_C + 0.2f_S$ curves for the $S(3)$, $S(4)$, $C(4)$, and $C(9)$ atoms, respectively. All of the hydrogen atoms were revealed in differential synthesis and were included in the refinement with fixed temperature factors $B_{iso} = 5$ Å². The final R factor was 0.033, and the weighted R factor was 0.034. All of the calculations were made with an Eclipse S/200 computer from INEXTL programs [19]. The coordinates of the atoms are presented in Table 5.

The polarographic measurements were made with a Radelkis OH-102 polarograph (Hungary) via a two-electrode scheme. A platinum-disk rotating electrode with an operating area of 0.5 mm² served as the indicator electrode; the rate of rotation was 430 rpm. The reference electrode was a saturated calomel electrode. After several recordings of the polarogram, the Pt electrode. After several recordings of the polarogram, the Pt electrode was cleaned with fine emery paper and washed with ethanol and distilled water. The oxidation of the investigated substances was carried out in acetonitrile and acetonitrile-ethylbenzene (1:1) in an Ar atmosphere at 25°C. The concentrations of the dithiocarbamates and the disulfide in solution were $1 \cdot 10^{-4}$ and $5 \cdot 10^{-4}$ mole/liter, and the concentration of the inert electrolyte $[N(C_2H_5)_4ClO_4]$ was 0.1 mole/liter. The rate of polarization of the electrode was 1.5 V/min, and the range of the change in the potential was from 0 V to +2 V. The half-wave potential was determined graphically.

The acetonitrile and ethylbenzene were purified by the methods in [14]. Industrial furfural (I) and 2-formylthiophene (II) [20] were used as the starting compounds. Azomethines III and IV were obtained by the reaction of aldehydes I and II with excess 25% ammonium hydroxide [4, 5]. Compounds III and IV, which were liberated after many days in the reaction with ammonium hydroxide were removed by filtration, washed with methanol and ether, and air dried.

Di(2-furfuryl)amine (VIII). A 26.6-g (0.65 mole) sample of $NaBH_4$ was added gradually with stirring and water cooling to a solution of 87.2 g (0.325 mole) of azomethine III in 600 ml of alcohol, after which the reaction mixture was diluted with 1.2 liters of water. Amine VIII was extracted with ether, and the ether extract was washed with water and dried with KOH. The ether was removed by distillation, and the residue was fractionated in vacuo. Amine VIII had bp 90-91°C (0.13 mm) [bp 126-128°C (10 mm)] [21] and $n_D^{20} 1.5183$ and was obtained in 84% yield.

TABLE 5. Coordinates of the Atoms ($\times 10^4$; $\times 10^3$ for H)

Atom	x	y	z	Atom	x	y	z
Ni	0	0	0	C ₍₉₎	-6605(8)	-1319(3)	3725(4)
S ₍₁₁₎	-1359(3)	856(1)	1018(1)	C ₍₁₀₎	-4968(12)	-1891(5)	4222(5)
S ₍₂₎	-2662(3)	-836(1)	638(1)	C ₍₁₁₎	-3017(11)	-2156(4)	3810(5)
S ₍₃₎	-1969(4)	348(2)	3832(2)	H ₍₂₁₎	-534(9)	125(4)	211(4)
S ₍₄₎	-2755(3)	-1779(2)	2792(2)	H ₍₂₂₎	-681(9)	71(4)	278(4)
N	-4855(8)	51(3)	1913(3)	H ₍₄₎	-220(10)	223(4)	275(5)
C ₍₁₎	-3217(9)	24(4)	1286(4)	H ₍₅₎	88(9)	229(4)	401(4)
C ₍₂₎	-5224(9)	822(4)	2442(4)	H ₍₆₎	113(9)	86(4)	473(4)
C ₍₃₎	-3144(9)	1033(4)	3083(4)	H ₍₇₁₎	-804(9)	-50(4)	227(4)
C ₍₄₎	-1970(8)	1884(3)	3171(3)	H ₍₇₂₎	-631(9)	-107(4)	155(4)
C ₍₅₎	-108(11)	1795(4)	3864(4)	H ₍₉₎	-784(10)	-97(4)	387(5)
C ₍₆₎	71(12)	1047(4)	4248(4)	H ₍₁₀₎	-538(9)	-198(3)	479(4)
C ₍₇₎	-6423(9)	-700(4)	2097(4)	H ₍₁₁₎	-193(9)	-244(4)	404(4)
C ₍₈₎	-5414(9)	-1214(4)	2853(4)				

Di(2-thenyl)amine (IX). This compound was similarly obtained in 81% yield and had bp 142-143°C (1.3 mm) [bp 150-152°C (10 mm) [22]].

Dithiocarbamates XIII, XVI-XIX, and XXI-XXIII. An equimolar amount of CS₂ and excess 25% ammonium hydroxide were added to the amine (VIII or IX), after which the calculated amount of a solution of the metal chloride, acetate, or nitrate in the same solvent was added to the resulting aqueous ammoniacal solution of N,N-disubstituted dithiocarbamic acid. The resulting precipitates were removed by filtration, washed with alcohol and ether, and air dried. The compounds obtained were recrystallized; XIII and XVI-XIX from benzene, XXI from toluene, and XXII and XXIII from DMF.

Dithiocarbamates XIV, XV, XX, and XXIV. The calculated amounts of CS₂, ammonia, and the metal salt dissolved in water were added successively to amine VIII. Precipitated dithiocarbamate XIV was washed with methanol and ether and dried, while precipitated XV was dissolved in methanol, precipitated with n-hexane, separated, and air dried. Dithiocarbamate XX was obtained from amine IX in DMF under similar conditions. Compound XX was precipitated by the addition of ether to the reaction mass; the crystals were washed with acetone and ether and air dried. Dithiocarbamate XXIV was similarly obtained from calculated amounts of amine IX, CS₂, KOH, and SbCl₃ in absolute methanol. The XXIV was isolated from the reaction mass by precipitation with water and dissolved in acetone. The acetone solution was filtered, and water was added to the filtrate until crystallization commenced. The XXIV crystals were precipitated at -2°C; they were separated, washed with n-hexane, and air dried.

In preparation for elementary analysis the compounds were dried in vacuo at 20-30°C below their melting points.

N,N,N',N'-Tetra(2-thenyl)thiuram Disulfide (XXXVII). A 0.38-g (5 mmole) sample of CS₂ was added to 1.05 g (5 mmole) of amine IX, the resulting N,N-disubstituted dithiocarbamic acid was dissolved in 10 ml of methanol, and the solution was treated with 0.61 ml (5 mmole) of 28% H₂O₂. Water (0.6 ml) was added to the reaction mass, and the liberated oil was separated and dissolved (with heating) in a mixture of 80% methanol and 20% acetone. The crystals of XXXVIII that precipitated after the solution was cooled were separated and air dried to give a product with mp 131-132 C (mp 129-130 C [13]) in 33% yield.

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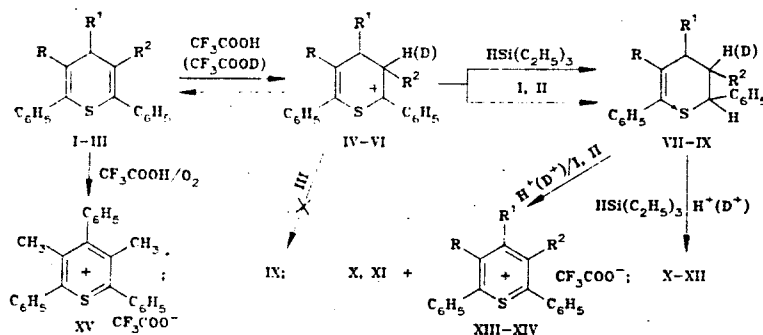
PECULIARITIES OF THE STEREOCHEMISTRY OF THE DISPROPORTIONATION, IONIC,
AND CATALYTIC HYDROGENATION OF POLYSUBSTITUTED 4H-THIOPYRANS

N. I. Kozhevnikova and V. G. Kharchenko

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The configuration of the thiacyclohexane obtained in the ionic and catalytic hydrogenation of 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran was established. It is shown that the stereochemistry of these reactions differs for penta- and tetrasubstituted 4H-thiopyrans in that the stereochemistry of the cited processes and the stereochemistry of disproportionation are the same for each of the poly-substituted 4H-thiopyrans.

In contrast to tetrasubstituted 4H-thiopyrans I and II, 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran (III) does not disproportionate with trifluoroacetic acid but is converted quantitatively to thiopyrylium trifluoroacetate XV with the participation of oxygen [1]:



I, IV, VII, X, XIII R=CH₃, R¹=C₆H₅, R²=H; II, V, VIII, XI, XIV R=R²=CH₃, R¹=H;
III, VI, IX, XII R=R²=CH₃, R¹=C₆H₅.

3,5-Dimethyl-2,4,6-triphenylthiacyclohexane (XII), which should be formed in the case of disproportionation of thiopyran III, can be obtained only by the action of the CF₃COOH/HSi-(C₂H₅)₃ hydrogenating pair on this unsaturated sulfide or as a result of its catalytic hydro-

N. G. Chernyshevskii Saratov State University, Saratov 410601. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 7, pp. 910-911, July, 1987. Original article submitted January 3, 1986.