THE SYNTHESIS AND SOME REACTIONS OF THIOPHENE SULFIDES

XVII. The Synthesis and Reactions of 2-Mercapto-3-thenylidenecyclohexylamine and Its Zinc Chelate*

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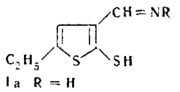
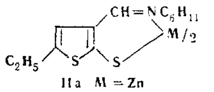
The reaction of some electrophilic reagents (bromine, acetyl chloride, and acetic anhydride) and of butyllithium on the zinc chelate of 2-mercapto-3-thenylidenecyclohexylamine (IIIa) is examined. Bromination and acetylation of IIIa lead to fission of the chelate ring and the formation of a complex of thienoisothiazolium bromide with $ZnBr_2$ (VIII), and the corresponding dithienodithiocine (X). Butyllithium combines with the C=N double bond of the chelate ring (IIIa), with the formation of the chelate XIII.

Investigations into the reactivity of chelated compounds, and in particular of those formed by aromatic ligands with external donor atoms, are relevant to a number of most interesting but hitherto little investigated questions of the chemistry of complex compounds. There is in fact in these systems the possibility of observing the finest distinctions in behavior dependent, on the one hand, on changes in the type of metal, its valency state and coordination number, and on the other hand on the nature of the ligand. The deficiency of data relating to this question may in part be attributed to the limited number of types of chelate containing aromatic or heteroaromatic rings (while this work was being carried out, a short communication [1] appeared on the bromination of copper chelates of salicylaldehyde and of 8-hydroxyquinoline with cupric bromide. In the first case, treatment of the reaction product with hydrochloric acid gave 5-bromosalicylaldehyde).

Special interest pertains to chelate containing thiophene or furan rings which are able (as distinct from the benzene ring) readily to undergo reactions not only with electrophilic, but also with some nucleophic reagents. The character of the process here is dependent to a large extent on the stability of the chelate ring which, as shown in the case of the metal acetylacetonates [2], is determined by the nature of the metal and, to a lesser extent, by exchanging one reagent for another [3].

Some information has been given [4] on the reaction of bromine and N-bromosuccinimide with 2-mercapto-5-alkyl-3-thenylideneimines of type I and their zinc and nickel chelates IIa and IIb.


Ia R = H
Ib R = cyclo $-C_6H_{11}$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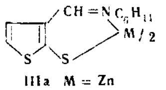
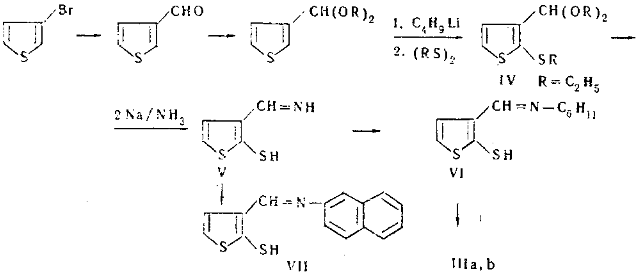
IIb M = Ni

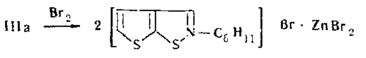

IIIa M = Zn
IIIb M = Ni

The presence of substituents in the 5-position of the thiophene ring in this system precluded the possibility of substitution at this reactive center of the molecule. Therefore, we undertook the preparation of chelates of type II with one free α-position in the thiophene ring, according to the scheme.

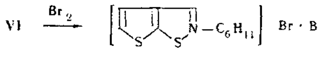


2-Ethylmercapto-3-thiophenealdehyde diethyl acetal (IV) was obtained in 74% yield by the successive reaction of butyllithium and diethyl disulfide with 3-thiophenealdehyde diethyl acetal. If, instead of diethyl disulfide, sulfur and ethyl iodide were used [5], the yield of the sulfide IV fell to 34%. The acetal IV and 2 equivs. of sodium in liquid ammonia, under the conditions described previously [6], afforded 2-mercapto-3-thenylideneimine (V). Reaction of this with primary amines gave, as with its homolog Ia, the Schiff's bases (VI and VII), which gave with metal acetates the chelates, for example IIIa and IIIb. Compounds Ia and V differ in that Ia has a definite melting point, while V does not melt on heating to 360° C, apparently because of its ability to polymerize at the α-position of the thiophene ring by virtue of the iminomethyl group.

Investigations into the reaction of bromine in chloroform with the zinc chelate IIIa showed that, as also in the case of its 5-substituted homolog [4], attack occurred initially on the chelate ring, leading to the eventual formation of 2-cyclohexylthieno[3,2-d]isothiazolium bromide, which separated as the complex with zinc bromide (VIII). The same bicyclic system is formed on bromination of the Schiff's base (VI) as the perbromide IX. The UV spectra of VIII and IX resemble closely those of their homologs bearing substituents in the 5-position (cf. 4). Thus, in neither case is the substitution of the α-hydrogen atom of the thiophene ring observed.



VIII



IX

It seemed preferable to attempt to introduce another type of substituent into the α-position of the complex

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*For part XVI, see [16].

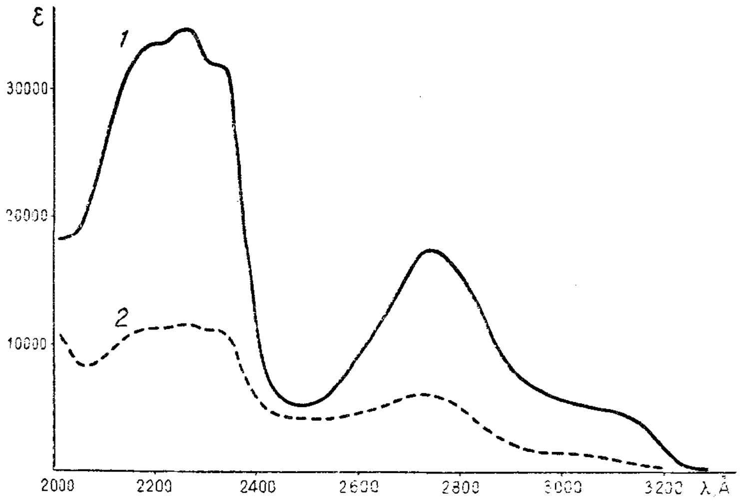


Fig. 1. UV Spectra (in ethanol): 1) complex of 2-cyclohexylthieno[3, 2-d]isothiazolium bromide with $ZnBr_2$ (VIII) 2) 2-cyclohexylthieno[3, 2-d]isothiazolium bromide perbromide (IX).

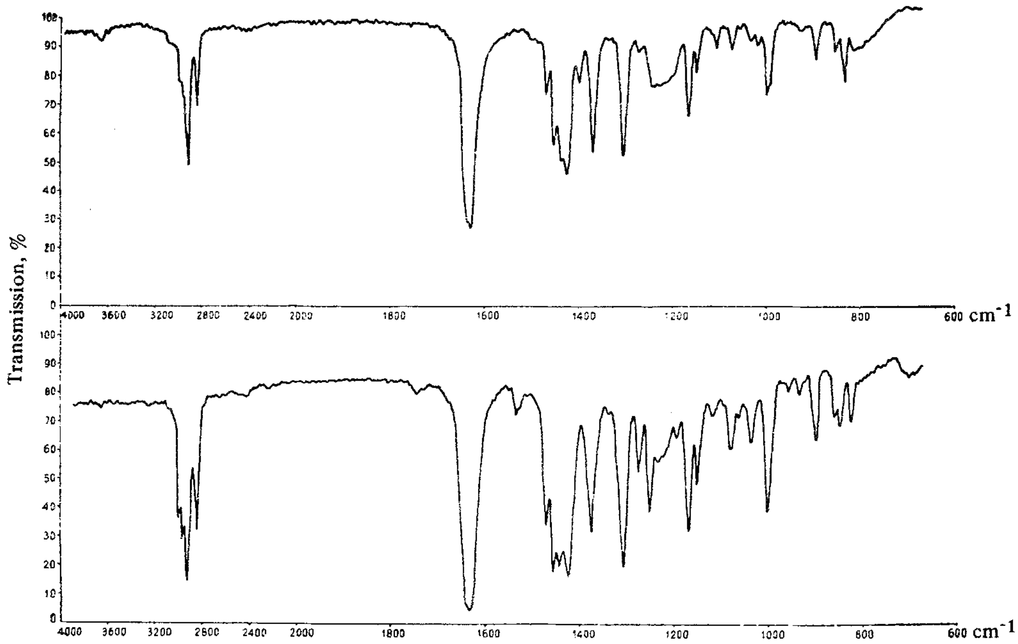


Fig. 2. IR Spectra (in $CHCl_3$): 4, 9-di(N-acetyl-N-cyclohexylamino)-4H, 9H-dithieno[2, 3-b: 2', 3'-f]-5, 10-dithiocine (X); 2) 4, 9-di-(N-acetyl-N-cyclohexylamino)-2, 7-diethyl-4H, 9H-dithieno[2, 3-b: 2', 3'-f]-5, 10-dithiocine (XI).

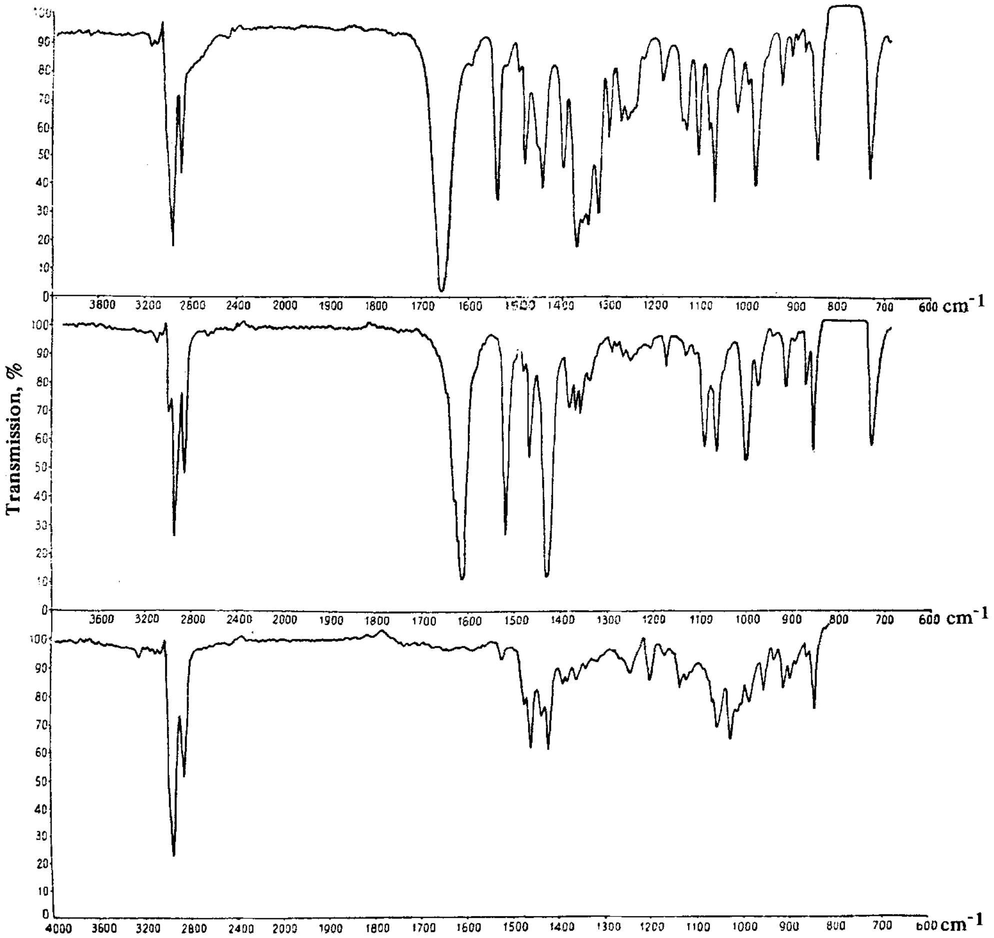


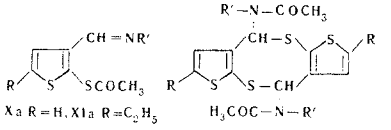
Fig. 3. IR Spectra (in $CHCl_3$): 1) 2-mercapto-3-thenylidenecyclo hexylamine (VI); 2) bis(2-mercapto-3-thenylidenecyclohexylamine)zinc (IIIa); 3) bis[2-mercapto-3-(α-butyl)thenylidenecyclo hexylamine]zinc (XIII).

IIIa, under different conditions. For this purpose, we chose acylation with acetic anhydride in the presence of boron trifluoride etherate, which had been used successfully to introduce the acetyl group in metal acetonylacetonates without disruption of the chelate ring [7]. In this case also, however, the desired end was not achieved, since we succeeded in isolating from the reaction mixture only a colorless compound containing no metal, mp 202–203° C (X), having the composition $C_{13}H_{17}NOS_2$. The same compound was obtained by the direct treatment of the Schiff's base VI with acetic anhydride:

$$\text{IIIa} \xrightarrow[BF_3\cdot(C_2H_5)_2O]{(CH_3CO)_2O} \underset{\text{X}}{(C_{13}H_{17}NOS_2)_2} \xleftarrow{(CH_3CO)_2O} \text{VI}$$

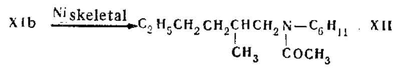
2-Mercapto-5-ethyl-3-thenylidenecyclohexylamine (Ib) and acetic anhydride similarly afforded the acetylated compound (XI) with the composition $C_{15}H_{21}NOS_2$, mp 193–195° C. It is interesting that, on treatment of Ib with acetyl chloride, we succeeded only in isolating cyclohexylamine hydrochloride and not the corresponding acetyl derivative. Acetyl chloride therefore causes the rapid breakdown of the chelate rings of both complexes **IIa** and **IIIa**, with the formation of derivatives XI and X.

As regards the reaction with acetic anhydride in the absence of BF_3 etherate, chelates of types II and III show similar properties, but the reaction proceeds somewhat more slowly; after brief contact they remain unchanged, and only on prolonged treatment (from several hours to several days) is fission of the ring observed with formation of X and XI. It may be suggested that X and XI are the S-acyl derivatives (Xa and XIa). However, the considerably reduced melting points by comparison with the starting Schiff's bases Ib and VI, and also the absence in the IR spectra (Fig. 2) of absorption bands characteristic of phenylthioacyl derivatives, and the presence of bands in the 1630 cm^{-1} region as observed for the C=O group in N,N-disubstituted amides make this suggestion improbable. At the present time, the results of molecular weight determinations and reductive desulfurization by Raney nickel of compound XI leading to the formation of N-2-methylhexyl-N-cyclohexylacetamide (XII) agree best with the dithienodithiocine structure XIb arising, apparently, by migration from the sulfur to the nitrogen atom.


Xa R = H, XIa R = C_2H_5

Xb R = H, XIb R = C_2H_5

R′ = cyclo – C_6H_{11}

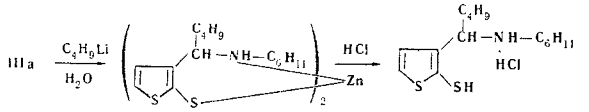


$$\text{XIb} \xrightarrow{\text{Ni skeletal}} C_2H_5CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle COCH_3}{\underset{|}{N}}-C_6H_{11} \quad \text{XII}$$

To summarize, it may be said that the presence in the chelates of type III, of the extremely reactive heterocyclic ring with a free α-position does not result in any change in the position of electrophilic attack in comparison with their unsubstituted analogs. As in similar systems, the process involving the chelate ring predominates, leading ultimately to ring fission. Deactivation of the thiophene ring apparently plays a major part in the effect under examination. It may be suggested that the metal atom, maintaining the coplanarity essential for maximum conjugation, interacts synergetically with the nitrogen atom in withdrawing electrons from the aromatic system. In this connection, it is interesting to note that, according to [8], a proton has greater effect than a metal in this situation.

It was naturally to be supposed that metallo-organic compounds, being nucleophilic reagents, might attack other centers in the molecules of the complexes **IIIa** and its homolog **IIa**. Actually, in these chelate it is possible for coordination to occur at the thiophene sulfur atom, a process preceded by the metallation of the thiophene ring by n-butyllithium (BL) [9]. Such a directed process would lead in the case of the chelate **IIIa** after carbonation, to the formation of the corresponding carboxylic acid.

The results of our experiments on the reaction of BL with chelates of the type of II and III still do not give a full picture of the reactions occurring under these conditions. Brief treatment (1–2 hr) of **IIIa** with 2 equiv. of BL, followed by treatment with water, led to almost total recovery of unchanged material. A similar picture is observed with the chelate **IIa**. If, however, the number of equivalents of BL and the time of reaction were increased, for example by keeping a solution of **IIIa** and BL in the propertions 1 : 4 in ether solution overnight, then a small quantity of a colorless crystalline solid, mp 180–182° C, was obtained. By its elemental analysis and molecular weight, this compound has the formula XIII. Under the same conditions, the chelate **IIa** did not give a pure product.



XIII

XIV

The amount of **XIII** was increased substantially by using 8 equivs. of BL, the yield in some cases reaching 50%. The structure of **XIII**, formed by the combination of 2 molecules of BL with the chelate **IIIa**, is also in agreement with the changes in the IR spectrum of the latter. The spectrum of **XIII** shows no absorption band due to the coordinated C=N bond which occurs clearly in the spectrum of the starting chelate **IIIa** at 1607 cm^{-1}, and a band appears in the 3235 cm^{-1} region, possibly due to stretching of the coordinated NH group (Fig. 3). Treatment of the chelate **XIII** with conc. HCl gives a hydrochloride containing no metal, the composition of which corresponds to compound **XIV**. The observed conversion represents yet another example of the combination of metallo-organic compounds with the azomethine bond, described for aromatic and aliphatic aldimines [10], and for pyridine bases [11, 12]. Since, however, the nitrogen atom in the chelate **IIIa** is coordinated, being part of the chelate ring, the formation of XIII must apparently proceed by some mechanism other than those described. We note in this connection that addition of even 2 equiv. of BL to a suspension of the chelate **IIIa** in ether results in immediate dissolution of the chelate which, as has already been pointed out, may be recovered on treatment with water.

The remaining unanswered question is; does the BL coordinate with the sulfur atom of the thiophene ring at any stage of the reaction? Experiments carried out to answer this question led to the following results: with 2 equivs. of BL at the boil for 1–2 hr, followed by treatment with carbon dioxide, the chelate IIIa was recovered unchanged; no carboxylic acid was observed either after treatment with 8 equivs. of BL and keeping overnight. In this case, the product was an oil, from which on treatment with acid there was separated a little of the hydrochloride XIV.

It may therefore be stated that, in the competition for the butyllithium between the sulfur atom of the thiophene and the coordinated azomethine group, the conditions favor the latter.

EXPERIMENTAL

2-Ethylmercapto-3-thiophenealdehyde diethyl acetal (IV). To 77 g (0.42 mole) of 3-thiophenealdehyde [13] in 150 ml of dry ether at −40° C was added a solution of 27 g (0.42 mole) of butyllithium in 220 ml of ether, also previously cooled to −40° C. The reaction mixture was stirred for 30 min at −30° C, kept for 1 hr without cooling, and a solution of 51.5 g (0.42 mole) of diethyl disulfide in 75 ml of ether added at −40° C. The resulting white suspension was stirred for 2 hr without cooling, kept overnight and hydrolyzed with water. The aqueous layer was separated, extracted with ether, the ether extract washed with 10% NaOH and water, and dried over magnesium sulfate. Distillation afforded 75.2 g (74% yield) of the acetal **IV**, bp 113–114° C (3 mm); n_D^{20} 1.5239; d_4^{20} 1.0867. Found, %: C 53.70, 53.69; H 7.28, 7.38; S 26.31, 26.23; MR_D 69.38. Calculated for $C_{11}H_{18}O_2S_2$, %: C 53.61; H 7.36; S 26.03; MR_D 69.09.

2-Ethylmercapto-3-thiophenealdehyde 2,4-dinitrophenylhydrazone, mp 167–168° C (from ethanol). Found, %: C 44.48, 44.53; H 3.59, 3.54; S 18.14, 18.29. Calculated for $C_{13}H_{12}N_4O_4S_2$, %: C 44.30; H 3.43; S 18.20. **Semicarbazone,** mp 194–195° C (from ethanol). Found, %: N 18.16, 17.96. Calculated for $C_8H_{11}N_3OS_2$, %: N 18.35.

2-Mercapto-3-thenylideneimine (V). Prepared as previously described [6] from 20 g (0.081 mole) of the acetal **IV** and 3.75 g (0.163 g-at) of sodium in 200 ml of liquid ammonia, in 83% yield. Sparingly soluble in hot ethanol, chloroform, and ethyl acetate, soluble in dimethylformamide and tetrahydrofuran. After two recrystallizations from ethyl acetate, the imine did not melt on heating on a block at 360° C. Found, %: C 41.86, 41.95; H 3.43, 3.38; S 44.45, 44.43. Calculated for $C_5H_5NS_2$, %: C 41.93; H 3.52; S 44.77.

2-Mercapto-3-thenylidenecyclohexylamine (VI). A suspension of 9.5 g (0.066 mole) of the imine **V** in 30 ml of ethanol and 6.6 g (0.067 mole) of cyclohexylamine were heated for several minutes until the solid had completely dissolved, filtered, and cooled to give yellow crystals of the Schiff's base. Yield 12.9 g (87%) of **VI**, which after two crystallizations from ethyl acetate melted at 103.5–105° C. Found, %: C 58.72, 58.86; H 6.67, 6.53; S 28.41, 28.56. Calculated for $C_{11}H_{15}NS_2$, %: C 58.62; H 6.71; S 28.46.

2-Mercapto-3-thenylidene-β-naphthylamine (VII). Prepared as described above, from a suspension of the imine **V** in ethyl acetate and an alcoholic solution of β-naphthylamine. After two recrystallizations from ethyl acetate, obtained as red crystals, mp 169.5–170.5° C. Found, %: C 66.51, 66.59; H 4.16, 4.07; S 23.93, 23.71. Calculated for $C_{15}H_{11}NS_2$, %: C 66.88; H 4.11; S 23.81.

Bis(2-mercapto-3-thenylidenecyclohexylamine)zine (IIIa). To a hot alcoholic solution of 3.7 g (0.016 mole) of the Schiff's base **VI** was added a solution of 1.8 g (0.01 mole) of zinc acetate in methanol. The lustrous yellow crystals were filtered off and twice reprecipitated from chloroform with methanol to give 3.7 g (87%) of the zinc chelate **IIIa**, mp 224–225° C. Found, %: C 51.10, 51.40; H 5.50, 5.38; S 24.99, 24.70; Zn 12.83, 13.10. Mol. wt. 516.7 (by the ebullioscopic method, in benzene). Calculated for $C_{22}H_{28}N_2S_4Zn$, %: C 51.40; H 5.48; S 24.95; Zn 12.72; mol. wt. 514.1.

Bis(2-mercapto-3-thenylidenecyclohexylamine)nickel (IIIb). Obtained in similar way to the chelate **IIIa** from the Schiff's base **VI** and nickel acetate in methanol. After two reprecipitations from chloroform with methanol, violet crystals mp 207–208.5° C. Found, %: C 51.81; 51.81, H 5.57, 5.43; Ni 11.75, 11.80. Calculated for $C_{22}H_{28}N_2S_4Ni$, %: C 52.07; H 5.56; Ni 11.57.

(2-Mercapto-3-thenylidenecyclohexylamine)copper. From 2.2 g (0.01 mole) of the Schiff's base **VI** and 1 g (0.008 mole) of copper acetate in methanol there was obtained 1.3 g of the Cu (I)-chelate of 2-mercapto-3-thenylidenecyclohexylamine, mp 270–280° C (decomp.) after two recrystallizations from dimethylformamide. Found, %: C 45.57, 45.60; H 4.72, 4.71; S 22.04, 21.84; Cu 21.49, 22.01. Calculated for $C_{11}H_{14}NS_2Cu$, %: C 45.88; H 4.90; S 22.07; Cu 22.08.

The action of bromine on bis(2-mercapto-3-thenylidenecyclohexylamine)zinc (IIIa). To 0.5 g (1 mM) of the chelate **IIIa** in 5 ml of chloroform was added gradually 0.3 g (2 mM) of bromine in 1 ml of chloroform. The mixture was kept for 1 hr at 20° C, the precipitate filtered off, washed with chloroform and twice recrystallized from a mixture of alcohol and ether. The resulting complex of 2-cyclohexylthieno[3,2-d]isothiazolium bromide and zinc bromide (VIII) melted at 195–196° C. Found, %: C 32.05, 32.02; H 3.39, 3.42. Calculated for $C_{22}H_{28}Br_2N_2S_4 \cdot ZnBr_2$, %: C 31.69; H 3.38.

2-Cyclohexylthieno[3,2-d]isothiazolium bromide perbromide (IX). To a solution of 0.4 g (1.8 mM) of 2-mercapto-3-thenylidenecyclohexylamine in 5 ml of chloroform was added gradually 0.6 g (3.7 mM) of bromine in 2 ml of chloroform. The mixture was heated for 30 min at 40–50° C, and the chloroform removed in vacuo to give 0.85 g of the perbromide **IX** as a brown powder which after two recrystallizations from chloroform melted at 110–111° C. Found, %: C 29.11, 29.15; H 3.01, 3.18; Br 51.82, 51.32; S 13.85, 13.73. Calculated for $C_{11}H_{14}Br_3NS_2$, %: C 28.47; H 3.04; Br 51.66; S 13.82.

4,9-Di(N-acetyl-N-cyclohexylamino)-4H,9H-dithieno[2,3-b:2',3'-f]-5,10-dithiocine (Xb). A 0.4 g (1.8 mM) quantity of the Schiff's base **VI** in 5 ml of chloroform and 1 ml of freshly-distilled acetic anhydride were kept for 12 hr at 20° C. The solution was filtered and evaporated in vacuo giving 0.6 g of a red oil, which on treatment with chloroform and ether was converted into a colorless powder. After two reprecipitations from chloroform with ether, the dithienothiocine **X** melted at 202–203° C. Found, %: C 57.80, 57.69; H 6.45, 6.25; S 23.78, 23.64. Calculated for $C_{26}H_{34}N_2O_2S_4$, %: C 58.38; H 6.41; S 23.98.

4,9-Di(N-acetyl-N-cyclohexylamino)-2,7-diethyl-4H,9H-dithieno[2,3-b:2',3'-f]-5,10-dithiocine (XIb). Obtained similarly to **X** from the Schiff's base **Ib** in 50% yield. After two reprecipitations from chloroform with ether, it was obtained as colorless crystals, mp 193–194.5° C. Found, %: N 4.83, 4.72; mol. wt. 566, 605 (determined cryoscopically in bromoform). Calculated for $C_{30}H_{42}N_2O_2S_4$, %: N 4.74; mol. wt. 590.9.

Acylation of bis(2-mercapto-3-thenylidenecyclohexylamine)zinc (IIIa). To 0.5 g (1 mM) of the chelate **IIIa** in 15 ml of benzene and 0.24 g (2.4 mM) of acetic anhydride was added dropwise under a stream of nitrogen 0.3 ml of boron trifluoride etherate. The mixture became turbid, and a yellow oil separated. After 1 hr, 15 ml of an aqueous solution of potassium acetate was added, and the mixture stirred for 15 min. The organic layer was separated, washed with water and dried over $MgSO_4$. Removal of the benzene gave 0.5 g of red oil, which on treatment with a mixture of alcohol and ether was converted into a white powder. After reprecipitation from chloroform with ether, the acetyl derivative melted at 203–205° C (decomp). A mixed mp with the dithienothiocine X obtained from 2-mercapto-3-thenylidenecyclohexylamine (see above) gave no depression. Found, %: S 23.97; 23.68. Calculated for $C_{26}H_{34}N_2O_2S_4$, %: S 23.98.

The action of acetic anhydride on bis(2-mercapto-3-thenylidenecyclohexylamine)nickel (IIIb). A 0.5 g (1 mM) quantity of the chelate IIIb in 5 ml of chloroform and 1 ml of acetic anhydride were kept at room temperature for several days. The violet color of the solution gradually faded, and a yellow precipitate separated. The solvent was distilled off in vacuo, the residue washed repeatedly with hot water until a sample gave a negative test for nickel, filtered off and twice reprecipitated from chloroform with dry ether to give 0.3 g of metal-free colorless powder, mp 202–203° C. A mixed mp with a sample of the dithienothiocine X obtained previously gave no depression.

The action of acetyl chloride on bis(2-mercapto-5-ethyl-3-thenylidenecyclohexylamine)nickel (IIb). To 0.5 g (about 1 mM) of the chelate IIb in 5 ml of chloroform was added 0.26 ml (a twofold excess) of acetyl chloride (in order to remove acidic impurities, the acetyl chloride was treated with K_2CO_3 before distilling). The violet color of the solution faded rapidly and a yellow solid separated. The solid was filtered off (nickel chloride), and the filtrate washed with water and 10% Na_2CO_3, and dried over $MgSO_4$. After removal of the chloroform there was obtained 0.25 g of the di(ethylthieno)dithiocine XI, mp 193–195° C (after reprecipitation from chloroform with ether). Found, %: C 60.23, 60.19; H 7.38, 7.14; S 21.54, 21.45. Calculated for $C_{30}H_{42}N_2O_2S_4$, %: C 60.97; H 7.16; S 21.70. A mixed mp with a sample of XI obtained previously (see above) gave no depression.

Reductive desulfurization of the di(ethylthieno)dithiocine XIb. A suspension of 3 g (0.005 mole) of the dithiocine XIb and 20 g of skeletal nickel in 150 ml of ethanol was stirred for 5 hr at 60–70° C. A sample of the filtrate at this point gave a negative test for sulfur. The solid was filtered off and washed with ethanol, the ethanol distilled off, the residue dissolved in ether, and dried over $MgSO_4$. Removal of the ether gave 2.15 g of a clear oil, n_D^{25} 1.4780, which on distillation afforded 1.8 g (63.5%) of 2-methylcyclohexylacetamide (XII), bp 134–135.5° C (3 mm); n_D^{25} 1.4775. Found, %: C 75.18, 75.09; H 12.00, 12.09. Calculated for $C_{15}H_{29}NO$, %: C 75.25; H 12.21.

The action of acetyl chloride on 2-mercapto-5-ethyl-3-thenylidenecyclohexylamine (Ib). A mixture of 0.5 g (2 mM) of the Schiff's base Ib, and 0.2 ml of freshly-distilled acetyl chloride was kept for 12 hr. The solvent was removed in vacuo, the residue washed with ether and reprecipitated from alcohol with dry ether to give 0.2 g (74%) of cyclohexylamine hydrochloride, mp 205–206° C. Found, %: C 52.72, 53.02; H 10.54, 10.42. Calculated for $C_6H_{13}N \cdot HCl$, %: C 53.13; H 10.40. A mixed mp with a sample of the hydrochloride obtained by heating cyclohexylamine with conc. hydrochloric acid with mp 205–206° C gave no depression [in literature, mp 206° C].

The action of butyllithium on bis(2-mercapto-3-thenylidenecyclohexylamine)zinc (IIIa). To a suspension of 1 g (2 mM) of the chelate IIIa in 20 ml of ether was added gradually, in a stream of nitrogen, 1 g (8 equiv.) of butyllithium in ether. After the addition of 2 equiv. of butyllithium, the chelate dissolved completely. The solution was boiled for 1 hr, kept overnight and hydrolyzed with water, with cooling. The ether layer was separated, the aqueous layer extracted thoroughly with chloroform, the combined solutions washed with water and dried over magnesium sulfate. Removal of the solvents gave 1.3 g of a dark-colored oil, which on trituration with ethanol gave a white powder. The powder was filtered off and twice reprecipitated from chloroform with ether or pentane giving 0.3 g of bis[2-mercapto-3-(α-butyl)-thenylcyclohexylamine]zinc (XIII), mp 180–182.5° C. Found, %: C 57.07; 57.14; H 7.39; 7.76; S 19.56; 20.06; Zn 10.58; 10.51. mol. wt. 644.9 (by the ebullioscopic method in benzene). Calculated for $C_{30}H_{48}N_2S_4Zn$, %: C 57.16; H 7.67; S 20.35; Zn 10.37; mol. wt. 630.3.

2-Mercapto-3-(α-butyl)thenylcyclohexylamine (XIV). A 0.1 g quantity of the chelate XIII and 2 ml of conc. HCl were boiled for 10–15 min. The precipitate was filtered off, washed with water and twice reprecipitated from ethanol with dry ether to give 0.06 g (54%) of the hydrochloride XIV, mp 160–162° C. Found, %: C 56.41; 56.21; H 8.40; 8.56; Cl 10.56; 10.54. Calculated for $C_{15}H_{25}NS_2 \cdot HCl$, %: C 56.30; H 8.20; Cl 11.08.

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