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The Synthesis and Properties of New Complex-forming Thiophen Derivatives

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The review deals with the methods of synthesis and properties of new heterocyclic ligands-mercaptoaldimine derivatives of thiophen, thienothiophen, and thionaphthene. Data on the preparation and certain reactions of metal chelate complexes of mercaptoaldimines are presented. The tautomerism and the ^{1}H NMR spectra of mercaptoaldimine derivatives of thiophen are discussed.
The bibliography includes 100 references.

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I. INTRODUCTION

In recent years there has been a fresh spurt in the development of the chemistry of complex compounds. New experimental techniques, in particular infrared, ^{1}H NMR, and ESR spectroscopy, and especially the exceptional importance which complex formation has acquired as a special method of activating simple molecules acting as ligands, have undoubtedly played a significant role in stimulating interest in the field of complex compounds. Complex formation also makes it possible to transfer a metal from one part of a biological substrate to another or to remove from the organism a metal with toxic properties [1]. A new branch of organic chemistry, based on the modification of the organic molecule by coordination with a metal, has been developing at an increasing rate and attention has been concentrated on the organic part of the complex, while previously interest was directed almost exclusively to the study of the properties of the coordinated metal ions. Many relevant problems have been discussed in reviews and monographs [2-7].

Chelate compounds, the chemical and physical properties of which vary within extremely wide limits as a function of the coordinating centres of the ligands and the nature, valence state, and the coordination number of the central atom, are of special interest. In Collman's extensive studies [8], this has been demonstrated for a large number of metal acetylacetonates. Functional groups, in particular nitro-, acyl, and chloromethyl, and other groups, can be introduced into some of these compounds by electrophilic substitution reactions, the properties of the group becoming sharply altered as a result of the bond formed with the chelate ring. For example, the aldehyde group loses its capacity to form oxides, hydrazones, etc. and does not react with methylmagnesium iodide; the sulphide group is not oxidised by hydrogen peroxide. In view of the chemical behaviour of acetylacetonates, some investigators refer to their properties as pseudoaromatic. In this connection one can mention the recent work of Japanese investigators [9], who, wishing to compare the aromatic properties of the furan and chelate rings, studied the nitration and bromination of chromium(III) and cobalt(III) trisfuroylacetonates and obtained only the chelate ring substitution products.

Chelates the ligand component of which is a bifunctional derivative of a heteroaromatic compound constitute a group which has so far been little investigated. New possibilities have arisen in practice and in research not only as a result of the ability to vary the ring heteroatom but also owing to its capacity for involvement in complex formation together with atoms outside the ring. This branch of the chemistry of complex compounds has attracted the attention of the authors of the present review.

II. SYNTHESIS AND PROPERTIES OF SULPHIDE DERIVATIVES OF THIOPHEN

Thiophen is a heterocyclic compound with pronounced aromatic properties. During the decades elapsed since its discovery (1883) by Victor Meyer, the chemistry of thiophen has been treated in terms of the concept of its complete analogy with benzene. This approach, which is in many respects justified and is to some extent in keeping with the present general concept of aromaticity, suffers from the disadvantage that certain specific features of the chemical behaviour of thiophen remained undiscovered or were ignored. However, with the development of new theoretical views in organic chemistry and the adoption of modern physical methods for the investigation of organic molecules, differences between the properties of the thiophen and benzene systems were discovered; these are due, in particular, to differences between their geometry or the influence of the heteroatom as a unit different from the other units in the closed chain of the heterocycle.

In the light of these data, it is of considerable interest to investigate analogous bifunctional benzene and thiophen (or furan, etc.) derivatives as regards their capacity to form chelates and the chemical behaviour of the latter. One of the types of ligands for this purpose may be analogues of salicylaldehyde and its Schiff bases containing the mercapto-group instead of the hydroxy group [structures (I) and (II)].

It is noteworthy that in recent years there has been an increasing interest in complexes where one of the coordinating centres is a sulphur atom [10]:



(I) (II)

It appeared useful to employ 2-alkyl-5-mercaptothiophens for the synthesis of compounds of type (I). [11] However, it is known that in the analogous thiophenol system a second functional group cannot be introduced into the ring because, under the influence of both electrophilic and nucleophilic agents, the mercapto-group is the first to be altered. For example, under nitration and bromination conditions, thiophenol is converted into a disulphide [12,13] and in the Friedel–Crafts acetylation it yields phenyl thioacetate, which does not react further even at 150°C. [14] Individual cases of the ring alkylation of aromatic thiols in the presence of boron trifluoride have been described but under these conditions too the intermediate products are complexes of the thiol and the catalyst in which the mercapto-group is blocked [15].

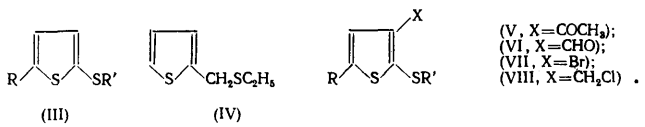
Thus, it is evident that, in order to introduce a second functional group into the molecule of an aromatic mercaptan, it is necessary to protect the mercapto-group by substituents which can be readily eliminated in the final stage. However, the use for this purpose of the corresponding mercaptals, disulphides or *S*-acylated mercaptothiophens did not yield satisfactory results [14,16,17]. On the other hand, alkyl aryl sulphides readily undergo electrophilic substitution but the dealkylation necessary for the above purpose has been rarely employed [18].

Ring-substituted thiophenols have been synthesised from sulphides formed by the reaction of thiophenols with 3-nitrobenzylideneacetophenone [16]. The use of this method for the synthesis of 3-substituted mercaptothiophens proved relatively inaffective. Thus the reaction of *N*-methylformanilide and phosphoryl chloride did not result in the introduction of the formyl group into the thiophen ring of β-[(5-ethyl-2-thienylmercapto)-β-(3-nitrophenyl)]propiophenone and the acetylation of this sulphide led to the formation of its cyclodehydration products [11].

The required result was achieved only when alkyl thienyl sulphides were employed as the starting materials. In this case the problem reduced to the introduction of the corresponding functional group into the 3-position of the thiophen ring and the subsequent dealkylation of the alkylthio-group in such a way that the resulting mercapto-group remained linked to the ring. Since alkyl thienyl sulphides are key compounds in this process, it is desirable to examine initially the methods of their synthesis and some of their properties.

Alkyl 2-thienyl sulphides are formed in high yields when thiophen and its homologues with at least one substituted α-position are treated in succession with butyl-lithium, elemental sulphur, and an alkyl halide [19,20]. Other methods of synthesis of similar sulphides, which also do not require a preliminary halogenation of the thiophen, are based on the use of thiyl radicals [21,22] or thiocyanatothiophens [23].

When 2-alkyl-5-alkylthiothiophens (III) were acetylated with acetyl chloride in the presence of $SnCl_4$ or with acetic anhydride and phosphoric acid [19], formulated by the Wilsmeyer method† [24], and brominated, the corresponding derivatives (V), (VI), and (VII) containing a new substituent in the 3-position were isolated:



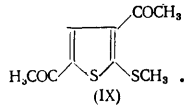
(III) (IV) (V, X=$COCH_3$); (VI, X=CHO); (VII, X=Br); (VIII, X=CH_2Cl).

where R and R′ = alkyl.

This is evidence that alkylthio-groups have a more powerful activating effect than alkyl groups. It is interesting to note that, on competitive acylation of a mixture of thiophen and 2-methylthiothiophen with acetyl chloride [26], 2-acetothienone and 5-methylthio-2-acetothienone were isolated in yields of 15 and 48% respectively.

On chloromethylation of type (III) sulphides, a 3,4-di-(chloromethyl)-substituted derivatives was isolated together with the monochloromethyl-substituted derivative (VIII). [27]

When 2-methylthiothiophen was acetylated, a small amount of a diacetyl derivative, probably with structure (IX), was detected in addition to 5-methylthio-2-acetothienone:



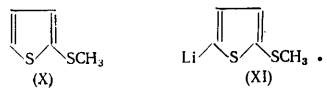
(IX)

Kinetic data for hydrogen exchange between an acid and 2- and 3-methylthiothiophens deuterated in specified positions may serve as a measure of the activating effect of the alkylthio-group in electrophilic substitution reactions of methylthiothiophens [28]. The results obtained show that in 2-methylthiothiophen the second α-position is strongly activated and the 3-position less so. The methylthio-group in the 3-position increases the rate of exchange in the 2-position by two powers of 10 more than in the 4-position. The rates of exchange of β-atoms in 2-ethylthio-5-methylthiophen also differ by approximately two powers of 10. The data quoted above for the site of acetylation, formylation, and bromination of 2-alkyl-5-alkylthiothiophens are also at least qualitatively consistent with these findings.

As already mentioned, the capacity of thiophen and certain types of its alkyl- or aryl-substituted derivatives for metallation, for example when treated with lithium alkyl, is important for synthetic purposes in the thiophen series. According to hypotheses put forward at one time [29,30], the first stage in this reaction is coordination of the metallating agent to the heteroatom with a lone electron pair; this determines the site where the metal is introduced and limits or excludes the effect of substituents [31]. Therefore the problem of the site of metallation of alkyl thienyl sulphides, the molecules of which contain two formally bivalent sulphur atoms, cannot be solved unambiguously *a priori*, particularly since their benzene analogue (thioanisole) yields on metallation exclusively the product of substitution in the side chain [32,33].

† Sulphides of type (IV) have an interesting property: when acted upon by *NN*-dimethylformamide or phosphoryl chloride, they do not yield the corresponding aldehydes but are cleaved with the formation of thienyl chloride and amidomercaptals [25].

In contrast to methyl phenyl sulphide, methyl 2-thienyl sulphide (X) readily gives the lithio-derivative (XI) when acted upon by butyl-lithium. Similar results were obtained also for the sulphide (IV) [34] although the possibility of substitution in the thiophen ring appeared unlikely in this case:



(X) (XI)

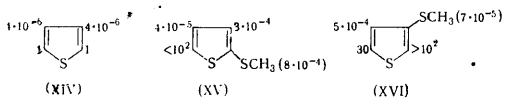
In a similar reaction involving protophilic substitution the alkylthio-group also has an activating effect. This is evident, for example, from the finding that, in an experiment involving the metallation of an equimolar mixture of thiophen and the sulphide (X) with a deficiency of butyl-lithium followed by carboxylation, it is possible to isolate only the acid (XII): [20]



(XII) (XIII)

The β-hyrodgen atoms in the thiophen group are not substituted at all under the influence of butyl-lithium, as in the case of 2,5-dimethylthiophen, or are substituted only with difficulty. The acid (XIII) could be obtained in only 27% yield from 2-methyl-5-methylthiothiophen [20].

All these observations are consistent with measurements of the rate of hydrogen–deuterium exchange between bases and methylthiothiophens containing a deuterium atom in a specified position in the molecule [35]. The formulae quoted below characterise the relative mobilities of the hydrogen atoms in all the C–H bonds in thiophen and isomeric methylthiothiophens:



(XIV) (XV) (XVI)

The rate constant for the exchange of the deuterium atom in the 2-position of unsubstituted thiophen with dimethyl sulphoxide catalysed by an alkali metal t-butoxide was adopted as a unit in formulae (XIV), (XV), and (XVI). Attention should be drawn to data concerning the mobility of hydrogen atoms in the methylthio-groups themselves. Evidently the rate of exchange involving these groups is smaller by several powers of ten than the rate of exchange of the ring α-hydrogen atom. In the case of thioanisole the opposite relations are obtained [36].

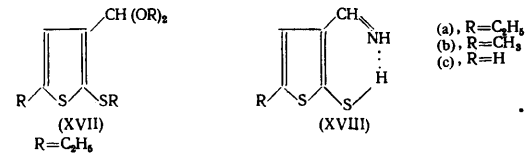
III. MERCAPTOALDIMINE DERIVATIVES OF THIOPHEN

1. Effect of Sodium in Liquid Ammonia on the Diethylacetals of 5-Alkyl-2-Alkylthiothiophen-3-aldehydes

As mentioned above, in order to obtain substituted mercaptothiophens of types (I) and (II) from β-substituted sulphides of type (VI), it is necessary to have an effective means of dealkylating the alkylthio-groups without affecting the bond between the exocyclic sulphur atom ahd the thiophen ring.

In the search for such a method, the discovery of the capacity of alkyl thienyl sulphides for dealkylation under the influence of sodium in liquid ammonia (Na/NH_3) with formation of the corresponding mercaptans in yields of 50–80% [37] (depending on the nature of the alkyl group) has played an important role. In order to "protect" the aldehyde group under the dealkylation conditions, compound (VI) was converted into the acetal (XVII), since it is known that aliphatic acetals do not react with aqueous and liquid ammonia and with aliphatic amines up to 130°C and are stable also in relation to sodium in liquid ammonia [38,39].

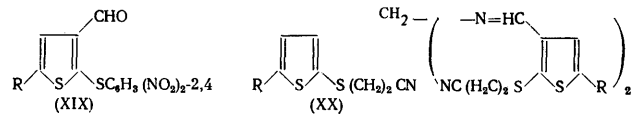
When two equivalents of sodium in liquid ammonia were allowed to react with the acetal (XVII) and the resulting aqueous alkaline solution was treated with HCl, a high yield was obtained of a nitrogen-containing crystalline compound—the mercaptoaldimine (XVIIIa)‡—instead of the expected mercaptoacetal (or aldehyde). [40] Its homologues (XVIIIb) [41] and (XVIIIc) [42] were obtained similarly:



(XVII) (XVIII) (a), R=C_2H_5 (b), R=CH_3 (c), R=H

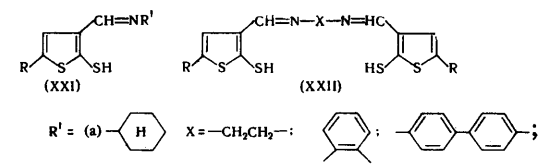
R=C_2H_5

When the mercaptoaldimine (XVIIIa) is treated with acid or alkali, ammonia is split off, which is consistent with its structure; in an acid medium, the product is a coloured polymer without nitrogen, which retains the capacity to form derivatives via the mercapto- and aldehyde groups, identical with the analogous derivatives obtained directly from (XVIIIa). On reduction with lithium aluminium hydride, (XVIIIa) is converted in high yields into 5-ethyl-2-mercapto-3-thenylamine [43]. One of the typical properties of compound (XVIIIa), reflecting the characteristics of its structure, is its instability under conditions where the hydrogen atoms of the mercapto-group are substituted under the influence of any reagent. For example, the reaction with 1-chloro-2,4-dinitrobenzene in an alkaline medium results in the formation of the formylsulphide (XIX) and the reaction with acrylonitrile gives the hydramide (XX): [40]



(XIX) (XX)

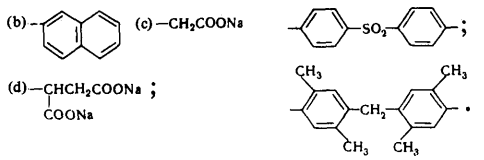
The formation of hydramides is known to be characteristic of extremely unstable aromatic imines [44] and is observed also when ammonia acta on thiophen-2-aldehyde and furfural [45]. On the other hand, reaction of compound (XVIIIa) with primary amines results in the formation, with evolution of ammonia, of stable di- and tetra-functional *N*-substituted mercaptoaldimines of types (XXI) and (XXII)—the thiophen analogues of the Schiff bases of thiosalicylaldehyde [40,41]. In the light of the above data, it becomes evident that the very existence and stability of compounds of type (XVIII) may be attributed to the formation of an intramolecular hydrogen bond stabilising the molecule (see Section III, 2):



(XXI) (XXII)

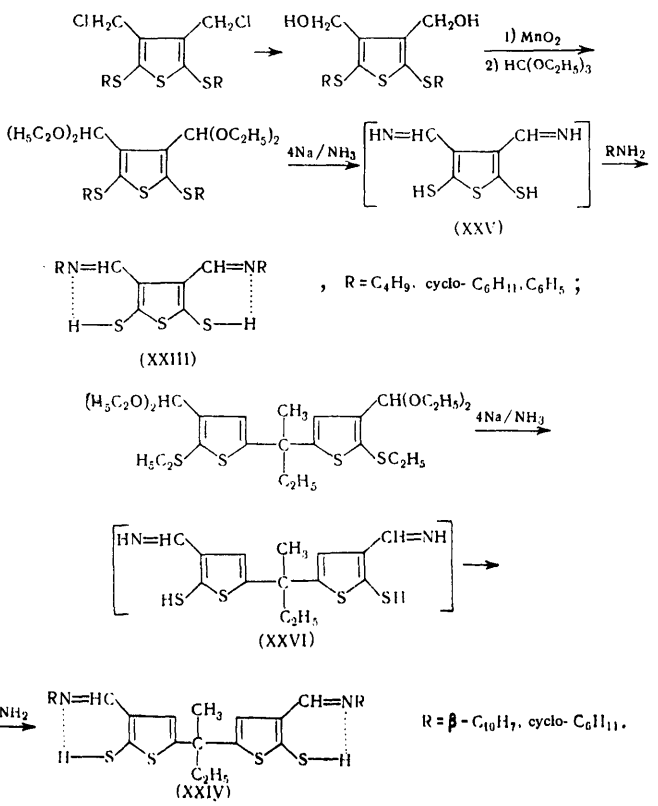
R' = (a) H X = $-CH_2CH_2-$; ; ;

‡ For brevity, here and henceforth compounds of type (XVIII) are called mercaptoaldimines although it has been shown [61] that they exist predominantly in another tautomeric form.



Compounds (XXIc) and (XXId), obtained from sodium glycinate and aspartate [41], are readily soluble in water, which in some cases may be an important condition for the applicability of a complex-forming agent.

Apart from the mercaptoaldimines described above, the derivatives (XXIII) and (XXIV) with analogous structure and four coordinating centres in one or in two thiophen rings separated by a methylene bridge have been obtained [46,47]. Such tetrafunctional compounds may be of interest in the synthesis of coordination polymers. The pathways in their synthesis are illustrated below:



It is noteworthy that satisfactory analyses have not been obtained for the bismercaptoaldimines (XXV) and (XXVI), since they are infusible powdery substance, probably with an oligomeric structure, and are difficult to purify. However, their capacity to evolve ammonia under the influence of alkalis and amines with formation in the latter case of readily crystallisable Schiff bases (XXIII) and (XXIV) may serve as confirmation of the structure attributed to them. One can therefore postulate that, when Na/NH_3 is allowed to act on compounds containing two acetal and two sulphide groups, reactions similar to those observed for the acetal (XVII) take place.

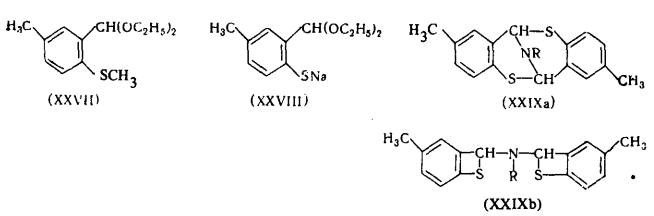
The problem of the mechanism of the formation of mercaptoaldimines of type (XVIII) cannot yet be regarded as finally elucidated. Nevertheless the available data [48] permit certain conclusions concerning the process.

1. When two equivalents of sodium in liquid ammonia are allowed to act on the alkylthioacetal (XVII), the acetal group is unchanged and only the dealkylation of the alkylthio-group with formation of the corresponding mercaptide takes place. (The mercaptoacetal was isolated as mercury mercaptide.)

2. The mercaptoaldimine (XVIII) is a product of the conversion of the mercaptide in the presence of an acid and ammonia.

3. The stability of mercaptoaldimines is due to the specific relative positions of the mercapto- and aldimine groups, which make possible the formation of a hydrogen bond or an inner salt. For other relative positions of the groups in the initial alkylthioacetal, for example, in the acetal of 5-ethylthiothiophen-2-aldehyde, a mercaptoaldimine is not formed. In this case the reaction reaches completion only after the addition of six equivalents of sodium, since sodium is consumed in the dissociation of the C–S bonds and in the reduction of the acetal group to a methyl group. Examples of similar reduction reactions have been described for certain aromatic ketals [49,50].

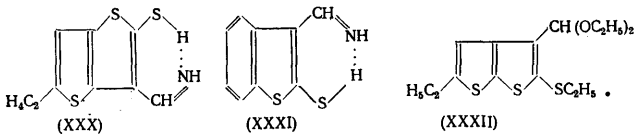
In the light of the foregoing facts, the results obtained in the study of the effect of sodium in liquid ammonia on benzene analogues of the alkylthioacetals (XVII) are of interest. When two equivalents of sodium in liquid ammonia are allowed to act on the acetal (XXVII), the product is, as for the thiophen acetal (XVII), the mercaptide (XXVIII) (obtained in quantitative yield), which reacts with ammonia and amines to give compounds (XXIXa) or (XXIXb). [51] Compound (XXIX, R = H) is formed also when Na/NH_3 is allowed to act on 3-methyl-6-methylthiobenzaldehyde [52]. Therefore in such cases the final product is not a benzene analogue of mercaptoaldimines of type (XVIII):



This may be due to differences between the geometries of the thiophen and benzene rings. Indeed, when a hydrogen atom in the benzene ring is substituted by a sulphur atom, a molecular model analogous to that of compound (XVIIIa), in which the nitrogen and sulphur atoms are linked by a hydrogen bond§, cannot be constructed. In thiophen, such a possibility exists, since its external valence angles are larger. An indirect confirmation of this interpretation comes from the fact that furan, the geometry of which is similar to that of thiophen, forms stable mercaptoaldimines as a result of the reactions described above [57].

§ Here one must again emphasise that these considerations apply only to mercaptoaldimines unsubstituted at the nitrogen atom. The synthesis, infrared spectra, and certain metal chelates of Schiff bases of *o*-mercaptobenzaldehyde were described recently [55,56].

Using the above method for the synthesis of mercaptothenylideneamines (XVIII), the mercaptoaldimines (XXX) and (XXXI), derived from 2-ethylthieno[3,2-*b*]thiophen and thionaphthene respectively, were obtained[58]:



(XXX) (XXXI) (XXXII)

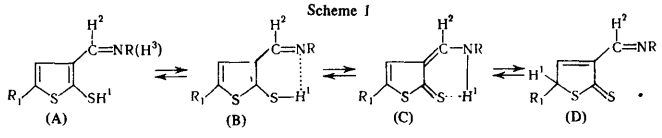
They are coloured crystalline compounds and, like (XVIIIa), form Schiff bases with β-naphthylamine and the corresponding chelates with zinc and nickel salts.

The attempt to synthesise the mercaptoaldimine from the acetal (XXXII) obtained from 2-ethylthieno[2,3-*b*]thiophen was unsuccessful[59].

2. Tautomerism of Mercaptoaldimine Derivatives of Thiophen

In a discussion of problems concerning the structure and chemical behaviour of mercaptoaldimines, one cannot exclude from consideration the possibility of a tautomeric equilibrium (see Scheme 1).

Scheme 1



(A) (B) (C) (D)

Together with the tautomeric forms A, C, and D, there is also a form B, which differs from A only by the presence of a hydrogen bond. Its inclusion in the scheme appears to be valid, since it can be regarded as intermediate between forms A and C.

The tautomerism of mercaptoaldimines in solution has been investigated by proton magnetic resonance (^{1}H NMR).[60,61] The signal from the ^{1}H proton has a chemical shift of 12–14 p.p.m., which indicates the presence of a strong intramolecular bond between H^1 and N or S. The formation of a chelate ring (structures B and C) is also confirmed by data for compounds in which R = H. In the spectra of these compounds both protons linked to the nitrogen atom have different shifts. The H^1 proton, the signal of which is at a lower field (by 2–2.5 p.p.m.), is rigidly fixed, while the other proton is involved in intermolecular exchange, since, on replacement of the ^{14}N isotope by ^{15}N, the H^1 signal becomes a well resolved quartet, while the H^3 signal remains broad.

The values of δH^1 leads to the conclusion that there are no appreciable amounts of the tautomer A and the fine structure of the signal due to the thiophen ring protons and the substituent R_1 shows that there are no appreciable amounts of the tautomer D.

The problem of the location of the H^1 proton within the limits of the chelate ring is of considerable interest. Namely whether it is linked by a covalent bond to the sulphur atom and hence by a hydrogen bond to the nitrogen atom or conversely, i.e. whether we are dealing with structure B or C. Experimental data confirmed the second hypothesis. The fact that the H^1 proton is located predominantly at the nitrogen atom is confirmed by the following observations.

a. In the spectra recorded at frequencies of 60 and 100 MHz, the distance between the signal lines corresponding to the H^1 and H^2 protons remained unchanged, which indicates the occurrence of spin–spin coupling between them (J_{H^1,H^2} = 13–15 Hz).

b. The study of the ^{1}H NMR of the products of the substitution of H^1 by a methyl group or deuterium leads to the same conclusion. Such substitution results in the merging of the components of the H^2 doublet into a singlet in addition to the disappearance of the H^1 signal.

c. When the ^{14}N isotope is replaced by ^{15}N, a constant $J_{^{15}N,H^1}$ = 85–87 Hz is observed for the spectrum. Consequently, even if there is an equilibrium at room temperature (see Scheme 1), it is appreciably displaced towards the tautomer C. This equilibrium may be shifted somewhat towards A or B by increasing the temperature.

Thus the compounds initially assigned to the class of mercaptoaldimines can be more correctly regarded as substituted 4-thiolen-2-thiones.

It is noteworthy that a change of solvent hardly affects the parameters of the spectra of these compounds.

The H^1 chemical shifts depend appreciably on the nature of the substituent at the nitrogen atom. The highest value of δH^1 and probably the longest hydrogen bonds are observed for aromatic substituents[61]. δH^1 increases in the sequence

$$H < n\text{-}C_4H_9 < \text{cyclo-}C_6H_{11} < C_6H_5 < \beta\text{-naphthyl.}$$

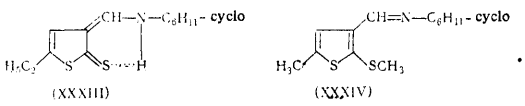
A significant change in the spectra of mercaptoaldimines is observed when they are heated above room temperature: the fine structures of the H^1 and H^2 signals disappear, the H^1 signal broadens so much that it vanishes altogether, and the H^2 signal is converted from a doublet into a broad signal, which is converted into a narrow singlet as the temperature is raised. These findings may be accounted for on the hypothesis that an increase of temperature entails a change in the contents of different forms in the equilibrium mixture.

The study of the H^1 NMR spectra of mercaptoaldimines of the furan series[62] showed that, as in the analogous thiophen derivatives, they have a strong intermolecular hydrogen bond C–S...HN. The H^1 proton (the numbering of the protons and the designation of the tautomeric forms is the same as for the thiophen derivatives) in the chelate ring is located predominantly at the nitrogen atom.

In general, when carbon tetrachloride and dioxan are employed as solvents, a situation similar to that for the analogous thiophen compounds is observed, but in polar solvents, for example in dimethyl sulphoxide (DMSO), the dipole moment of which is 4.3 D,[63] they exist in two forms. Under the influence of DMSO, the spectrum becomes "doubled". One can therefore postulate that, under the influence of this solvent, the intramolecular bond dissociates in some of the type C molecules, but the spin–spin coupling between the H^1 and H^2 protons persists. Thus the replacement of sulphur in the ring by oxygen leads to a weakening of the hydrogen bond in the chelate ring.

The characteristics of thiophen mercaptoaldimines as compounds with an intramolecular hydrogen bond are reflected in their polarographic behaviour. This has been shown for 5-ethyl-2-mercapto-3-thenylidenecyclohexylamine (5-ethyl-3-cyclohexylaminomethylene-1-thiolen-2-thione) and compound (XXXIII).[64] As a result of the protonation of the azomethine atom, it is reduced in

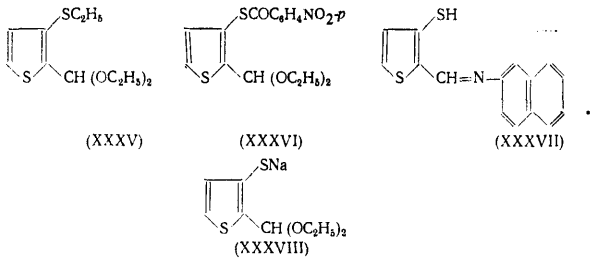
dimethylformamide (DMF) much more readily than compound (XXXIV), in which the hydrogen atom has been substituted and therefore the formation of an intermolecular hydrogen bond is ruled out:



(XXXIII) (XXXIV)

3. Effect of Sodium in Liquid Ammonia on the Diethylacetal of 3-Ethylthiothiophen-2-aldehyde

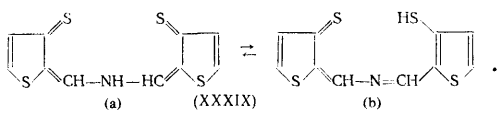
If the possibility of the occurrence of structures of types A–C (Scheme 1) depended ultimately only on the geometry of the ring, one might expect that the acetals of 3-alkylthiothiophen-2-aldehydes (XXXV) should be converted into the isomeric mercaptoaldimines (XVIII). However, the different relative positions of the functional groups in the thiophen ring might entail differences in reactivity. In contrast to the observations for the acetal (XVII), with the acetal (XXXV), the reaction reached completion after the addition of six equivalents of sodium and a high yield of 3-mercapto-2-methylthiophen was obtained[65]:



(XXXV) (XXXVI) (XXXVII) (XXXVIII)

If the amount of added sodium is restricted to two equivalents, it is possible to isolate from the resulting mixture 20–30% of the initial acetal and the dealkylation product in the form of the *p*-nitrobenzoyl derivative (XXXVI) or the Schiff base (XXXVII). Thus the processes involving two equivalents of sodium are in broad outline analogous for the acetals (XVII) and (XXXV) and lead to identical products, but they differ as regards quantitative relations.

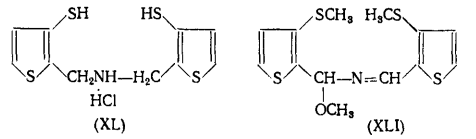
A different situation is observed when an acid is allowed to act on an alkaline solution of the mercaptide (XXXVIII) in the presence of ammonia. At pH ~ 8, under conditions analogous to those in the formation of compound (XVIII), a substance with the composition $C_{10}H_7NS_4$ is isolated and not the mercaptoaldimine. The structure of this compound can be best represented by the formulae (XXXIXa) and (XXXIXb), which reflect its tautomeric nature[66]:



(a) (XXXIX) (b)

This representation is supported by the following data. The molecule of compound (XXXIX) is found to have one active hydrogen atom; its infrared spectrum contains absorption bands in the region 1135–1157 cm^{-1}, which are characteristic of the –C=C–C=S group[67] and a band in the region of 3300 cm^{-1}, which may be assigned to the stretching vibrations of the secondary amino-group. The ^1H NMR spectrum of compound (XXXIX) in dimethyl sulphoxide corresponds better to structure (XXXIXa) than to structure (XXXIXb).

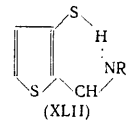
When compound (XXXIX) was treated with lithium aluminium hydride, an amine was obtained, isolated as the hydrochloride (XL). Compound (XXXIX) also yields an acetyl derivative, the reductive desulphuration of which with Raney nickel yields *NN*-dipentylacetamide. All these findings are consistent with formula (XXXIXa), although, as already mentioned, one cannot rule out a tautomeric equilibrium (see above):



(XL) (XLI)

An interesting reaction, confirming the presence in the molecule of (XXXIX) of an $\alpha\beta$-unsaturated thione group, occurs with methyl iodide in a methanol solution of potassium hydroxide. The resulting product probably has the structure (XLI), the formation of which can be accounted for by the 1,4-addition of methanol to the C=C–C=S molecular fragment.

On reaction with amines, compound (XXXIX) yields Schiff bases (XLII), one molecule of (XXXIX) giving two molecules of a new base. This process may be interpreted in different ways, in particular by regarding it as the aminolysis of (XXXIX) with a stage involving addition to the C= N bond[68] or it can be treated, by analogy with the reaction of (XXXIX) with methanol, as 1,4-addition:



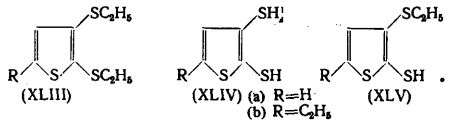
(XLII)

IV. SYNTHESIS OF DIMERCAPTOTHIOPHENS

An interesting type of complex, formed by α-dithiones or α-dithiols, which have unusual physical and chemical properties owing to their specific electronic structure, was discovered comparatively recently[69–75]. Compounds of this type, in particular the dimercapto-derivatives of benzene[76], can also be used as starting materials for further syntheses.

Of the four possible dimercaptothiophens, Gronowitz described 3,4-dimercaptothiophen[77]. His attempts to obtain the 2,4- and 2,3-isomers from the corresponding bromomercaptothiophens and also 2,5-dimercaptothiophen

from 2,5-dilithiothiophen or from magnesium bromide derivatives were unsuccessful[77,78]. The synthesis of 2,3-dimercaptothiophen derivatives was achieved by the dealkylation of di(alkylthio)-compounds of type (XLIII) with sodium in liquid ammonia[79]:



(XLIII) (XLIV) (a) R=H (b) R=C_2H_5 (XLV)

The reaction takes place smoothly and treatment with four equivalents of sodium per mole of the bis-sulphide resulted in the isolation of the corresponding dithiols (XLIVa) and (XLIVb) in a yield of 60–80%. These are viscous, coloured, liquids which vacuum-distil with decomposition. Since the bis-sulphides (XLIII) contain two identical functional groups in different positions in the thiophen ring, the problem arises whether they are dealkylated by sodium in liquid ammonia in any specific order.

Comparatively recently it has been suggested[80,81] that the mode of cleavage of an organic sulphide by alkali metals depends to a considerably degree on the numerical values of the acidities of the mercaptide ions and carbanions formed. In the case of di(alkylthio)thiophens of type (XLIII), which have the same aliphatic group linked to the sulphur atom, the principal factor determining the order of dealkylation is probably the stabilities of the resulting thiophen-2-thiol or thiophen-3-thiol. Evidently the first is stabilised to a greater extent, since the delocalisation of the negative charge extends over the entire aromatic ring, while in the 3-isomer the delocalisation is restriced to the π-electron 1,3-system[82]:

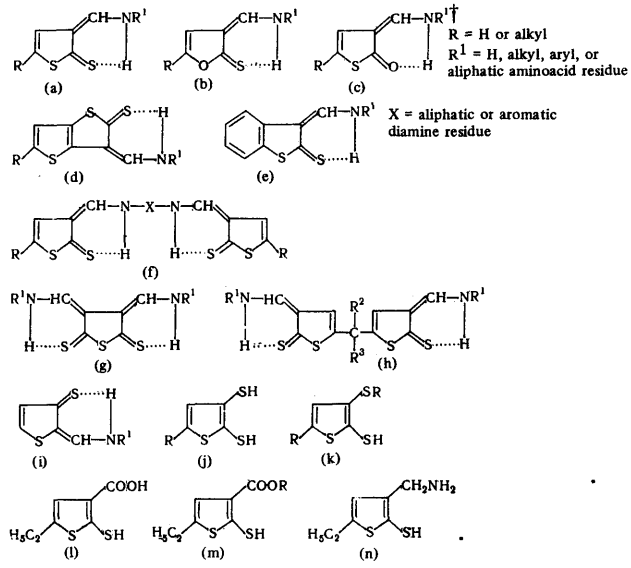


In fact when 2,3-di(ethylthio)thiophen and 4,5-di(ethylthio)-2-ethylthiophen were treated with two equivalents of sodium in liquid ammonia, the corresponding mercaptosulphides (XLVa) and (XLVb) were isolated in a yield up to 80%.[83] That the latter are α-mercapto-derivatives of thiophen was confirmed by ^{1}H NMR data. It was found that the cleavage products (XLIIIa) and (XLIIIb) have chemical shifts and spectra identical with those of 3-ethylthio-2-mercaptothiophen and 2-ethyl-4-ethylthio-5-mercaptothiophen respectively, which were obtained by an independent method.

The delocalisation effect probably plays a decisive role in determining the mode of cleavage of bis-sulphide derivatives of thiophen with different alkylthio-substituents, for example 2-butylthio-3-ethylthiothiophen. If it is assumed that the ease of removal of the primary alkyl group as carbanions decreases in the sequence $CH_3 > C_2H_5 > C_4H_9$,[81] then the ethyl group should be preferentially eliminated from this bis-sulphide with formation of 2-butylthio-3-mercaptothiophen. However, the only product isolated in the reaction of this bis-sulphide with sodium in liquid ammonia was 3-ethylthio-2-mercaptothiophen.

V. TYPES OF LIGANDS AND CERTAIN CHELATE COMPOUNDS

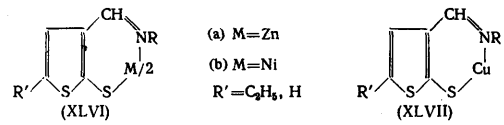
The formulae of the principal types of di- and tetrafunctional complex-forming compounds synthesised by the authors are given below¶:



5-Ethyl-2-mercaptothiophen-3-carboxylic acid (l)—the thiophen analogue of thiosalicylic acid—was obtained in 90% yield by the action of two equivalents of sodium in liquid ammonia on 5-ethyl-2-ethylthiothiophen-3-carboxylic acid[41]. The acid (l) forms a disulphide and in an alkaline medium is alkylated at the mercapto-group. Esterification in the presence of hydrogen chloride results in the formation of the corresponding esters (m).[85]

Some of the synthesised thiophen derivatives of types (a), (b), (c), (d), (e), (f), (i), (k), and (m) have been used to prepare chelate complexes with copper, zinc, and nickel ions. They were obtained by the reaction of the ligands in a suitable solvent with aqueous methanol solutions of the metal acetate or by the "method of nascent reagents"[86]. The data concerning the chelate complexes isolated are described in the literature[41,42,59].

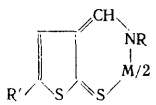
Compounds of the type (a) form with zinc and nickel ions the chelates (XLVIa) and (XLVIb) in which the ligand : metal ratio is 2 : 1, while in the copper complexes (XLVII) and in the complexes (XLVIII) of tetradentate ligands of type (f) the ratio is 1 : 1.

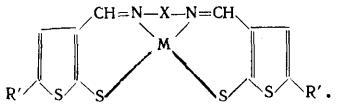


(XLVI) (a) M=Zn (b) M=Ni R'=C_2H_5, H (XLVII)

¶ For brevity only one of the possible tautomeric forms is quoted. For compounds (d), (e), and (h), the ^{1}H NMR spectra were not investigated and the thione structures are quoted by analogy.

† Compounds with the structure (c), which are oxygen analogues of mercaptoaldimine derivatives of thiophen, are formed when primary amines react with *NN*-disubstituted 5-alkyl-3-aminomethylene-4-thiolen-2-ones[84].

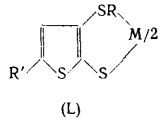

(XLIX)

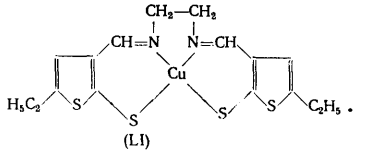

(XLVIII)

These are brightly coloured crystalline compounds fairly readily soluble in the usual organic solvents, for example in benzene and chloroform.

The infrared spectra of chelates of type (XLVI) contain stretching vibration bands in the region 1595–1610 cm^{-1}, which may be assigned to the vibrations of the coordinated C=N group [41] (cf. Trompson and Busch [87]). However, one should bear in mind that the structure of the metal chelates represented by formulae (XLVI), (XLVIII), etc. is not the only one possible, since the tautomerism characteristic of the corresponding ligands can also obtain in the chelate complexes formed by them. The problem of which form, (XLVI) or (XLIX), predominates under particular conditions must be regarded as open at the present time.

On interaction with nickel and copper acetates in methanol, dimercaptothiophen (j) forms black infusible powders insoluble in the usual solvents [79]. Probably they are polymeric (oligomeric) complexes analogous to the polymeric bisdithioglyoxalnickel complexes [69]. On the other hand, alkylthiomercaptothiophens (m) form with nickel acetate the chelate compounds (L) in which the metal : ligand ratio is 1 : 2. In contrast to the complexes formed by dimercaptothiophen (j), they have definite melting points:


(L)

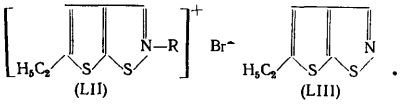

(LI)

Valuable information about the type of metal–ligand bond in complexes may be obtained from ESR spectra. This of course applies only to paramagnetic compounds incorporating a metal atom (ion) with one or several unpaired electrons. An example of such a compound is [bis-(5-ethyl-2-mercapto-3-thenylidene)ethylenediaminato]copper(II) (LI), in which the immediate environment of the central metal atom resembles that in copper(II) complexes with the Schiff bases of salicylaldehyde.

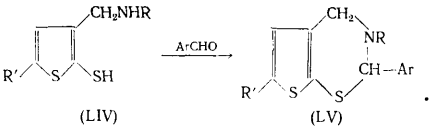
The ESR spectrum of this complex [88] contains, apart from the four lines generated as a result of the interaction of the unpaired electron spin with the spins of the copper nuclei [63,65], an additional hyperfine 11-line structure. Detailed analysis of the spectrum combined with a comparison with the literature data led to the conclusion that these 11 additional hyperfine structure lines are due to the pair interactions of the unpaired electron spin with the spins of the nuclei of ^{14}N and the CH protons.

VI. SOME REACTIONS OF THE MERCAPTOALDIMINES AND THEIR CHELATES

The presence in mercaptoaldimines of type (XVIII) of two highly reactive functional groups linked to adjacent carbon atoms of the thiophen ring creates interesting possibilities for the synthesis of new condensed bicyclic compounds. One of the ways in which such systems can be obtained consists in simple bromination of compound (XVIII) by an equimolar amount of bromine in chloroform. The reaction is accompanied by the evolution of hydrogen bromide and probably proceeds via a stage involving the formation of sulphene bromide, which undergoes ring closure to the bicyclic system (LII): [43]


(LII) (LIII)

As a result of hydrolysis, compound (LII, R = H) loses HBr, yielding 5-ethylthieno[3,2-*d*]isothiazole (LIII), which has also been obtained by the oxidation of 5-ethyl-2-mercapto-3-thenylamine (LIVa) with iodine. Mercaptothenylamines (LIVa) and (LIVb), formed in high yields when the corresponding mercaptoaldimines are reduced with lithium aluminium hydride [43], are also capable of entering into reactions leading to the formation of condensed systems. Thus they react with aldehydes to form derivatives belonging to the class of 3,4-dihydrothieno-1,3-thiazines (LV): [89]


(LIV) (LV)

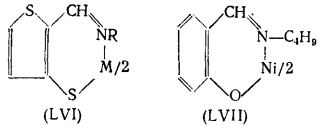
(a) R = H
(b) R = cyclo-C_6H_{11}; R′ = C_2H_5.

The above examples do not of course exhaust the possibilities of the use of different types of thiophen derivatives in syntheses. They illustrate only one of the developments in the chemistry of these compounds.

At the same time, as noted in the introduction, the study of the reactivities of the coordinated ligands examined is of greatest interest. Here we may note that we are at present only at the beginning of the development of this field.

On the basis of studies related to this field, Jones [90–93] arrived at the following most general conclusion: coordination does not alter the orientation of the substitution in the organic part of the ligand, but, by influencing the nature of the transition state, can cause appreciable changes in the rate of reaction. For example, many electrophilic substitution reactions of bis-(8-hydroxyquinolinato)copper take place more readily than with the free ligand [93].

Chelates of type (XLVI) and (LVI) can be regarded as condensed systems, one of the rings of which includes a metal ion as a unit. The problem of the reactivity of such compounds, which are readily susceptible to the action of both electrophilic and nucleophilic agents since they incorporate the thiophen ring, is of considerable interest:

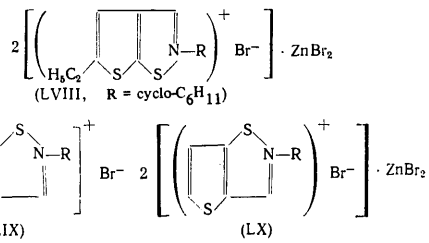

(LVI) (LVII)

(a) M = Zn; (b) M = Ni; R = cyclo-C_6H_{11}.

Treatment of bis-(salicylidenebutylaminato)nickel (LVII) with *N*-bromosuccinimide (NBS) is known to yield a dibromo-derivative [94,95], but the question of its structure remains open. It has been shown only recently [96] that initially bromine enters the 5-position of each ring and on subsequent bromination also the 3-position. The complex with cobalt(III) reacts similarly. Thus, when bromine is introduced by treatment by NBS, the chelate ring (LVII)

is not cleaved. A different behaviour is observed when the chelates (XLVI) and (LVI) are subjected to attack by bromine and NBS.[97] The nickel chelate (XLVIb, R = cyclo-C_6H_{11}, R′ = C_2H_5) reacts with two moles of bromine in chloroform to form 2-cyclohexyl-5-ethylthieno[3,2-*d*]-isothiazolium bromide, which is isolated from the mixture as the perbromide; as stated above, this compound is also obtained by the direct action of bromine on the corresponding ligand. The results are similar when NBS is employed as a brominating agent. When the zinc chelate (XLVIa, R = cyclo-C_6H_{11}, R′ = C_2H_5) is treated with bromine, a complex of thienoisothiazolium bromide with zinc bromide (LVIII) is formed.

In contrast to (XLVI), in the complexes (LVI) there are two hydrogen atoms in each thiophen ring potentially capable of being substituted by electrophilic agents. Consequently, one might expect here the formation of bromination products if the rate of substitution exceeded the rate of reaction of the electrophilic agent with the chelate ring. However, when the nickel chelate (LVIb) is treated with two moles of bromine or NBS in chloroform, the chelate ring is in fact also cleaved and 2-cyclohexylthieno[2,3-*d*]isothiazolium bromide (LIX) is formed in a mixture with its perbromide[97]:



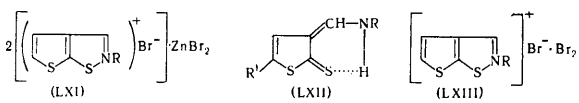
(LVIII, R = cyclo-C_6H_{11})

(LIX) (LX)

The zinc chelate (LVIa) reacts with bromine similarly to the nickel chelate, forming the complex (LX).

Summarising, one may say that the nickel and zinc chelates of both types (XLVIa and XLVIb, R = cyclo-C_6H_{11}, R′ = C_2H_5) and (LVI) are unstable under conditions corresponding to bromination with bromine and NBS.

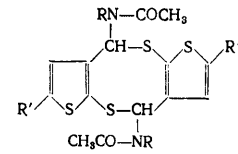
The study of the action of bromine in chloroform on the chelate (XLVIa, R = cyclo-C_6H_{11}, R′ = H)[42] showed that, as for the homologue substituted in the 5-position, the chelate ring is the primary site of attack, which ultimately leads to the formation of the complex (LXI) with zinc bromide. A similar bicyclic system is obtained also when the Schiff base (LXIIa) is brominated, the reaction product being isolated as the perbromide (LXIII). Consequently in both cases the α-hydrogen atom in the thiophen ring is not substituted:



(LXI) (LXII) (LXIII)

(a) R′ = H; (b) R′ = C_2H_5, R = cyclo-C_6H_{11}.

Together with bromination, the action of acetic anhydride in the presence of boron trifluoride-ether was investigated; this method has been successfully employed for the acetylation of metal acetylacetonates[98]. However, it proved impossible to introduce the acetyl group into the thiophen ring of the chelate (XLVIa, R = cyclo-C_6H_{11}, R′ = H) under these conditions. The final product isolated was a substance for which the structure of dithienodithiocine (LXIVa) was proposed on the basis of infrared spectra and data for reductive desulphuration; it is also formed when compound (LXIIa) is treated with acetic anhydride. A homologue of compound (LXIVa), compound (LXIVb), was obtained under the same conditions:

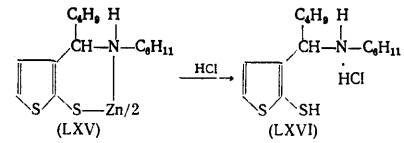


(LXIVa, R′ = H); (LXIVb, R′ = C_2H_5, R = cyclo-C_6H_{11})

Summarising, one can also say that the presence of an unsubstituted α-position in chelates of type (XLVI) does not entail a change in the direction of electrophilic attack compared with their substituted analogues. In such systems the process involving the chelate ring, which ultimately results in its decomposition, also predominates. The deactivation of the thiophen ring probably plays a significant role in this phenomenon, but one cannot rule out *a priori* an effect of the geometrical parameters of the condensed chelate ring, which may influence its stability.

It is quite evident that organometallic compounds behaving as nucleophilic agents can act also on other centres in the molecule of the type (XLVIa) complex. In principle, these chelates may be capable of coordination via the thiophen sulphur atom. As mentioned above, some investigators believe that such a process is a preliminary stage in the metallation of the thiophen ring by organometallic compounds, for example n-butyl-lithium.

By treating the chelate (XLVIa, R = cyclo-C_6H_{11}, R′ = H) with an excess of butyl-lithium, compound (LXV) was obtained[42], which on treatment with hydrogen chloride yields the hydrochloride (LXVI). The formation of compound (LXV) might have been regarded as an example of the addition of an organometallic compound to the azomethine bond, which is characteristic of aromatic and aliphatic aldimines[99] and pyridine bases[100]:



(LXV) (LXVI)

However, since the nitrogen atom in the initial chelate is coordinated, forming a unit of the chelate ring, compound (LXV) is probably formed by another mechanism. In order to determine whether butyl-lithium is coordinated to the ring sulphur atom at any stage, a study was made of the reaction of the chelate (XLVIa, R′ = H) with butyl-lithium and carbon dioxide but carboxylic acid was never detected.

Here one should note that, in an examination of the reactions of type (XLVI) chelates, one cannot rule out the possibility of their involvement in the reactions in the tautomeric form (XLIX).

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In undertaking this review, the authors wished to draw attention to the methods of preparation and certain properties of complex-forming compounds which in a certain sense may be regarded as new. The metal chelates mentioned in the review, the number of which is fairly limited have been treated mainly as derivatives indicating the complex-forming properties of the compounds synthesised. The problem of their steric structure and other physical properties as well as the synthesis of other chelate compounds of this series will be the subject of future investigations.

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