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Dithiocarboxylic Acids, Their Esters, and Metal Dithiocarboxylates

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The present state of the chemistry of dithiocarboxylic acids is described and methods for the synthesis of both the acids themselves and their esters and metal dithiocarboxylates are discussed. Data are presented on the properties and applications of these substances.

The bibliography includes 350 references.

CONTENTS

I. INTRODUCTION

By analogy with the carboxy-group COOH, the sulphur-containing functional group CSSH is called the dithiocarboxy-group. For this reason, the compounds R-CSSH, in which the organic moiety is linked to the dithiocarboxy-group by a carbon–carbon bond, should be called dithiocarboxylic acids. This term is in fact used in the English and American chemical literature†.

The names of the individual examples of compounds of this class are devised in accordance with the principles of the IUPAC nomenclature on the basis of the name of the corresponding hydrocarbon.

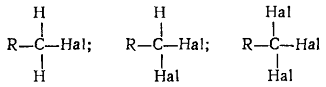
The first example of dithiocarboxylic acids (C_6H_5CSSH) was synthesised more than 100 years ago in 1866[1]. However, due attention was not devoted to compounds of this class for a long time. This can be apparently partly accounted for by the low stability in air of many dithiocarboxylic acids and partly by the unpleasant smell of these substances (particularly the alkyl derivatives) which has been very strikingly described by the first investigators[2].

The chemistry of dithiocarboxylic acids began to develop vigorously in the 1960's. During the last 6–7 years, approximately as many studies have been published as during the previous 100 years. Certain reviews have also been published[3-6], but these do not cover all the aspects of the chemistry of dithiocarboxylic acids. The present paper surveys the literature on dithiocarboxylic acids, their esters, and metal dithiocarboxylates up to 1973 (and partly also 1974).

II. METHODS FOR THE SYNTHESIS OF DITHIOCARBOXYLIC ACIDS

1. Synthesis from Compounds Containing a Halogenomethyl Group

Compounds containing mono-, di-, and tri-halogenomethyl groups may be used as the starting materials of the synthesis of dithiocarboxylic acids:



$$R{-}\overset{H}{\underset{H}{C}}{-}Hal;\qquad R{-}\overset{H}{\underset{Hal}{C}}{-}Hal;\qquad R{-}\overset{Hal}{\underset{Hal}{C}}{-}Hal\qquad ,$$

(I) (II) (III)

where R is an organic group and Hal a halogen. Compounds (III) can also be used in syntheses with R = H. In all cases, the syntheses are carried out in alcoholic solutions.

The monohalogeno-derivatives (I) react with finely dispersed sulphur in the presence of alkali metal alkoxides. The alkoxide ion, being a strong base, cleaves the eight-membered ring of the sulphur molecule under these conditions[7,8] and gives rise to the chemically highly reactive ion $CH_3O{-}S{-}S_6{-}S^-$, which reacts with the monohalogeno-derivative (I). The dithiocarboxylic acids are synthesised in accordance with the following overall equation:

$$R{-}CH_2Hal + 2S + 2NaOCH_3 \rightarrow R{-}CSSNa + NaHal + 2CH_3OH.$$

After the solution has been acidified, the corresponding dithiocarboxylic acid is isolated. Benzenedithiocarboxylic, 4-chlorobenzenedithiocarboxylic, and 2,6-dichlorobenzenedithiocarboxylic acids have been obtained by this method in methanol solutions[7,9,10].

On interaction with ethanol solutions of KHS, the dihalogeno-derivatives (II) give rise to the corresponding potassium dithiocarboxylates as side products in addition to the disulphide[1,11]:

$$3R{-}CHHal_2 + 7KHS \rightarrow (R{-}CH_2S)_2 + R{-}CSSK + 3H_2S + 6KHal.$$

This method is also of historical importance—it was in fact used to synthesise the first dithiocarboxylic acid[1].

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†The following section of the original Russian text has been omitted here. However, in the Russian literature compounds containing the carboxy-group are traditionally called carbonic acids and in the present paper the term "dithiocarbonic acids" is used instead of the systematic term "dithiocarboxylic acids".

The trihalogeno-derivatives (III) can be converted into dithiocarboxylate ions by treatment with alkali metal sulphides, hydrogen sulphides, or trithiocarbonates in ethanol or methanol solutions:

$$\mathrm{R{-}CHal_3 + 2K_2S \rightarrow R{-}CSSK + 3KHal;}$$
$$\mathrm{R{-}CHal_3 + 4KHS \rightarrow R{-}CSSK + 3KHal + 2H_2S;}$$
$$\mathrm{R{-}CHal_3 + 2Na_2CS_3 \rightarrow R{-}CSSNa + 3NaHal + 2CS_2.}$$

On subsequent acidification, the corresponding dithiocarboxylic acids are isolated in a free form. The rapidly polymerising dithiocarboxylic acid HCSSH was obtained by this procedure from chloroform and potassium sulphide in ethanol solution[12–14]. It can be obtained in a purer form by carrying out the synthesis in the absence of air and in methanol solutions[15,16].

$C_6H_5CCl_3$ can be converted into benzenedithiocarboxylic acid by treatment with potassium sulphide[17,18] or hydrogen sulphide[19] in ethanol solutions and by potassium sulphide in methanol solution[20]. When sodium trithiocarbonate is used[21,22], the synthesis is carried out in aqueous methanol solution.

Chlorobenzenedithiocarboxylic[17], pyridine-4-dithiocarboxylic[23], quinoline-2-dithiocarboxylic, and quinoline-4-dithiocarboxylic[24] acids have been obtained similarly.

2. Interaction of Organometallic Compounds with Carbon Disulphide.

The first attempts to obtain dithiocarboxylic acids by the interaction of carbon disulphide with organosodium and organozinc compounds were unsuccessful[25]. When triethylaluminium was used, only traces of ethanedithiocarboxylic acid were obtained[26]. Later it was shown that organolithium and organosodium compounds can be used successfully to synthesise dithiocarboxylic acids[27,28]. The reactions with carbon disulphide were then carried out in ethyl ether solutions in an atmosphere of nitrogen:

$$\mathrm{R{-}Me + CS_2 \rightarrow R{-}CSSMe.}$$

Lithium naphthalene-1-dithiocarboxylate $C_{10}H_7CSSLi$ and sodium diphenylmethanedithiocarboxylate $(C_6H_5)_2CHCSSNa$ were obtained in this way.

Organomagnesium compounds have found the widest applications in the synthesis of dithiocarboxylic acids and were proposed for this purpose at the beginning of the century[2,29–32]. Here the starting materials are the corresponding halogeno-derivatives, which react with metallic magnesium in an ethereal medium:

$$\mathrm{R{-}Hal + Mg \rightarrow R{-}MgHal.}$$

Some workers recommend that this reaction be carried out in the absence of air, for example, in an atmosphere of nitrogen[33]. The addition of carbon disulphide to a solution of organomagnesium compound results in the formation of dithiocarboxylates:

$$\mathrm{R{-}MgHal + CS_2 \rightarrow R{-}CSSMgHal.}$$

The dithiocarboxylic acids can be isolated in a free state by treating the reaction mixture with hydrochloric acid.

The diethers of poly(ethylene glycols) have also been proposed as solvents instead of ethyl ether. For example, pyridine-2-dithiocarboxylic acid has been obtained[34] in solution of the dimethyl ether of diethylene glycol. The synthesis can also be achieved in tetrahydrofuran[24].

Organomagnesium compounds have been used to synthesise the following dithiocarboxylic acids: methanedithiocarboxylic[32,35], ethanedithiocarboxylic[2], propanedithiocarboxylic[2], 2-methylpropanedithiocarboxylic[2], 3-methylbutanedithiocarboxylic[2], cyclohexanedithiocarboxylic[36], phenylmethanedithiocarboxylic[29,30,37], hydropinenedithiocarboxylic[31], benzenedithiocarboxylic[18,30,33,38–43], 2-methylbenzenedithiocarboxylic[33,41], 4-methylbenzenedithiocarboxylic[33,41,44,45], 4-chlorobenzenedithiocarboxylic[41,44], 4-bromobenzenedithiocarboxylic[30,47], 5-isopropyl-2-methylbenzenedithiocarboxylic[48], naphthalene-1-dithiocarboxylic[30,33,39,41,49], naphthalene-2-dithiocarboxylic[41,47,50], pyrroledithiocarboxylic[41,51–53], indole-3-dithiocarboxylic[41,52,53], 2-methylindole-3-dithiocarboxylic[52], pyridine-2-dithiocarboxylic[34], quinoline-2-dithiocarboxylic[24], and thiophen-2-dithiocarboxylic[41]. Alkanedithiocarboxylic acids are obtained by this procedure in very low yields (5–25%). The yields of compounds with aromatic groups are very much higher (usually between 40% and 80%) (see also Ref. 54).

3. Interaction of Aldehydes with Hydrogen and Ammonium Polysulphides

Aromatic aldehydes and hydrogen polysulphide form brownish-yellow or reddish resinous products in the presence of condensing agents such as zinc chloride, hydrogen chloride, sulphuric acid, etc. The products are ground and treated with an aqueous or alcoholic solution of KOH and the insoluble residues are filtered off. The filtrate consists of a solution of the corresponding potassium dithiocarboxylate[55–57]. The following dithiocarboxylic acids have been synthesised by this method: benzenedithiocarboxylic[57], 2-hydroxybenzenedithiocarboxylic[55,57], 2- and 4-methoxybenzenedithiocarboxylic[55,57], and furan-2-dithiocarboxylic[58].

The method has not found more extensive applications probably for the simple reason that dithiocarboxylic acids can be obtained from aldehydes more conveniently by the reaction of the latter with ammonium polysulphide. This reaction was used for the first time to synthesise benzenedithiocarboxylic acid[59]. A concentrated solution of ammonia and copper powder was added to an ethanol solution of benzaldehyde, after which the latter was saturated with hydrogen sulphide. Later it was suggested that ammonium polysulphide be prepared beforehand. Dithiocarboxylic acids are synthesised by adding the solution to an aldehyde or to an ethanol solution of an aldehyde[58,60]:

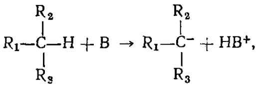
$$\mathrm{R{-}CHO + (NH_4)_2S_2 \rightarrow R{-}CSSNH_4 + NH_4OH.}$$

After acidification with hydrochloric acid, the free dithiocarboxylic acids are obtained.

The following dithiocarboxylic acids have been synthesised by this method: benzenedithiocarboxylic[45,58], 2-chlorobenzenedithiocarboxylic[41,45], 4-chlorobenzenedithiocarboxylic[45], 2-hydroxybenzenedithiocarboxylic[41,45,58,61,62], 4-hydroxybenzenedithiocarboxylic[41,45], 4-methoxybenzenedithiocarboxylic[41,45,58,61,62]; 3,4-dihydroxybenzenedithiocarboxylic[61,62], 4-hydroxy-3-methoxybenzenedithiocarboxylic[45,58,61,62], 3,4-methylenedioxybenzenedithiocarboxylic[45,58,61,62], 4-aminobenzenedithiocarboxylic[45], 4-dimethylaminobenzenedithiocarboxylic[45], 4-acetamidobenzenedithiocarboxylic[41], 3-sulphobenzenedithiocarboxylic[63], 4-hydroxy-3-sulphobenzenedithiocarboxylic[63], 1-phenylethylene-2-dithiocarboxylic[62], naphthalene-2-dithiocarboxylic[64], furan-2-dithiocarboxylic[42,58,61,62,65], and thiophen-2-dithiocarboxylic[41]. The yields are usually between 20 and 45%.

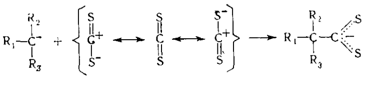
4. Reactions of CH acids with Carbon Disulphide (with Xanthates and Trithiocarbonates)

In the presence of a sufficiently strong base, CH acids react with carbon disulphide to form dithiocarboxylate ions. It is suggested that the reaction proceeds via a mechanism[66-69] which begins with a protolytic reaction:

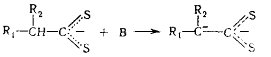


$$R_1R_2R_3C{-}H + B \rightarrow R_1R_2R_3C^- + HB^+,$$

where B is the base and HB^+ the conjugate acid. This is followed by the electrophilic addition of carbon disulphide via its carbon atom to the base (carbanion) $R_1R_2R_3C^-$:

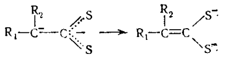


If the initial compound with $R_3 = H$ contains an activated methylene group $R_1R_2CH_2$, then substances of this kind initially react only via the mechanism described above, which results in the formation of $R_1R_2CH{-}CSS^-$. However, when the dithiocarboxylate ion is still a fairly strong CH acid, the following protolytic reaction takes place:



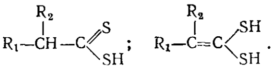
$$R_1R_2CH{-}CSS^- + B \rightarrow R_1R_2C^-{-}CSS^-$$

The subsequent redistribution of charges in such cases yields the dianions of ene-1,1-dithiols:



$$R_1R_2C^-{-}CSS^- \rightarrow R_1R_2C{=}C(S^-)_2$$

Here one must note that the treatment of ene-1,1-dithiolate ions with acids can lead to their reconversion into dithiocarboxylate ions[70]. The dithiocarboxylic acids themselves and the ene-1,1-dithiols are isomers:



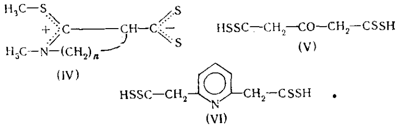
$$R_1R_2CH{-}C(S)SH;\quad R_1R_2C{=}C(SH)_2.$$

It follows from the foregoing that, in those cases where $R_3 = H$ (or $R_3 = R_2 = H$) in the initial compound dithiocarboxylic acids can occur in the synthesis only as intermediates.

NaOH, KOH, alkoxides [CH_3ONa, C_2H_5ONa, $(CH_3)_3CONa$, and $(CH_3)_2(C_2H_5)CONa$], sodamide ($NaNH_2$), sodium hydride (NaH), and in some cases even metallic sodium are used as bases. Ammonia in the form of a concentrated aqueous solution or in the liquid state sometimes plays the role of this component. Depending on the properties of the reactants, the solvents may be hydrocarbons (pentane, benzene), alcohols (methanol, ethanol), ethers (ethyl ether, dioxan, tetrahydrofuran), acetone, acetonitrile, dimethyl sulphoxide, dimethylformamide, and dimethylacetamide.

Many dithiocarboxylic acids or the corresponding ene-1,1-dithiols have been synthesised by the above method. The starting materials in these processes were aldehydes ($R_1 = CHO$, $R_3 = H$)[71], ketones ($R_1 = RCO$, $R_3 = H$)[38,72-85], nitromethane ($R_1 = NO_2$, $R_2 = R_3 = H$)[86-88], phenols, naphthols, hydroxyquinoline[67,89-91], malonic acid derivatives ($R_3 = H$)[69,76,82,92-101], pyrrole, pyridine, indole, quinoline, and their derivatives[76,102-108], ketimines of cyclohexanone and cyclopentanone [$R_2 = -(CH_2)_n - \underset{|}{C}{=}N - R$, $R_3 = H$][109,110], compounds with the sulphonyl group ($R_1 = RSO_2$, $R_3 = H$)[111], sodium cyclopentadienide (R_1R_2 = cyclopentadienide ion, $R_3 = H$)[112,113], and pyrazolone derivatives (R_1R_2 = the residue of pyrazolone derivative, $R_3 = H$).[114-116]

Dithiocarboxylic acids have been obtained by this method also in the reaction of carbon disulphide with the Reissert compound[117], with dinitrotoluene[76], and with the quaternary salts derived from heterocyclic nitrogen compounds[118,119]. Dithiocarboxylic acids which are stable dipoles of type (IV)[120,121], and even the bisdithiocarboxylic acids (V)[122] and (VI)[76] have also been obtained:



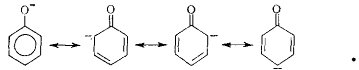
(IV) (V) (VI)

$$HSSC{-}CH_2{-}CO{-}CH_2{-}CSSH$$

A variety of the above method for the synthesis of dithiocarboxylic acids is that consisting of heating phenols with alkali metal xanthates or trithiocarbonates. On increase of temperature, these reactants decompose into carbon disulphide and the alkoxide (sulphide):

$$C_2H_5{-}O{-}CSSK \rightarrow CS_2 + C_2H_5OK;$$
$$Na_2CS_3 \rightarrow CS_2 + Na_2S.$$

Alkoxide or sulphide ions play the role of a strong base, the presence of which is necessary for reaction with carbon disulphide. The site of addition of carbon disulphide is determined under these conditions by the existing resonance or tautomeric forms of the corresponding phenoxide ion, for example:

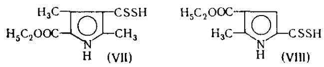


Evidently the addition should take place in the *ortho*- or *para*-positions.

The following dithiocarboxylic acids have been obtained by this method: 4-hydroxybenzenedithiocarboxylic[123], 2,4-dihydroxybenzenedithiocarboxylic[124-127], 2-4-dihydroxy-6-methylbenzenedithiocarboxylic[123], 2, 3, 4- and 2,4,6-trihydroxybenzenedithiocarboxylic[125, 127], 1-hydroxynaphthalene-2-dithiocarboxylic[128], and 8-hydroxyquinoline-7-dithiocarboxylic[124]. The method of synthesis using a xanthate suffers from the disadvantage that the syntheses must be performed at high temperatures and pressures.

5. Other Methods for the Synthesis of Dithiocarboxylic Acids

Under the conditions of the Friedel–Crafts synthesis (with anhydrous aluminium chloride as the catalyst), pyrrole derivatives react with carbon disulphide. The acids (VII) and (VIII) have been obtained in this way[129]:

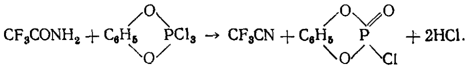


(VII) (VIII)

Dithiocarboxylic acids can be synthesised by hydrolysing their esters. Ethane-, methane-, benzene-, 4-methylbenzene-, and phenylmethane-dithiocarboxylic acids as well as HSSC–CSSH have been obtained by treating the corresponding esters with alcoholic KOH solution[130]. 3-Antipyrine-4-dithiocarboxylic acid was obtained after heating its ethyl ester for 1 h on a water bath with a 10% alcoholic KOH solution[131]. The 4-dithiocarboxylic acids of antipyrine[132] and isoantipyrine[133] have been prepared by heating their ethyl esters with an ethanol solution of KHS

(1–2 h, on a water bath). In order to obtain benzenedithiocarboxylic acid, its methyl ester was hydrolysed overnight at room temperature with NaHS solution[134].

Trifluoromethanedithiocarboxylic acid has been synthesised from trifluoroacetamide, which was initially converted into the nitrile by treatment with 1,2-phenylenedioxyphosphorus trichloride[135]:



$$CF_3CONH_2 + C_6H_5(O)_2PCl_3 \rightarrow CF_3CN + C_6H_5(O)_2P(=O)Cl + 2HCl.$$

The nitrile was then thiolysed[136,137] with a mixture of liquid H_2S and HCl (40°C, 28 atm, 2–3 days):

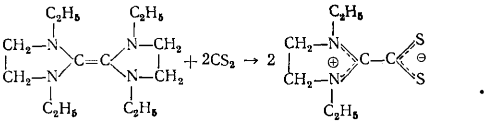
$$CF_3CN + H_2S \rightarrow CF_3CSNH_2;$$
$$CF_3CSNH_2 + H_2S + HCl \rightarrow CF_3CSSH + NH_4Cl.$$

Cyanodithioformate ions are formed[138,139] when cyanide ions interact with carbon disulphide in a dimethylformamide solution:

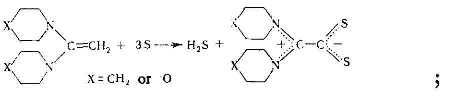
$$CN^- + CS_2 \rightarrow NC{-}CSS^-.$$

Cyanodithioformic acid $(NCCSSH)_X$ is obtained by the subsequent addition of concentrated hydrochloric acid.

The synthesis of dithiocarboxylic acids derived from peraminoethylenes is very unusual[140]. The reaction takes place exothermically with 98% yield in accordance with the following equation:



Analogous zwitter-ions were obtained[141] as a result of the interaction of certain compounds containing an active methylene group with elemental sulphur:

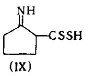


III. THE PROPERTIES AND APPLICATIONS OF DITHIOCARBOXYLIC ACIDS

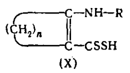
1. Physical properties

Dithioformic and cyanodithioformic acids are weakly coloured polymeric substances[13,14,16,138,139,142]. The radius of the dithioformate ion has been calculated from the measured conductivities of the solutions[143].

Aliphatic dithiocarboxylic acids as well as phenylmethanedithiocarboxylic acids are orange oily liquids[2,30,32,130]. This is also true of trifluoromethanedithiocarboxylic acid[136,137]. Cyclohexanedithiocarboxylic acid is a reddish-brown liquid[36]. The dithiocarboxylic acids obtained from iminopentane (IX)[84] and its derivatives[85] and also from cyclopentene and cyclohexene (X) derivatives[109] are crystalline substances melting between 66° and 117°C:



(IX)



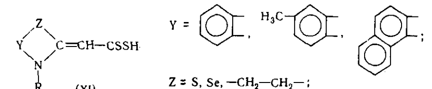
(X)

$n = 3; 4$.

Benzenedithiocarboxylic acid and its halogeno-, methyl, and isopropyl derivatives are red or red-violet oily liquids[1,30,38,44,48,55,57,130]. 4-Hydroxy- and 3,4-dihydroxybenzenedithiocarboxylic acids are likewise oily liquids[62,123,144]. 2-Hydroxy- and 2,4-dihydroxybenzenedithiocarboxylic acids have been obtained in the form of a thick, red, rapidly solidifying mass[144,145]. The latter acid forms a yellow crystalline monohydrate[125,126,146]. 2,3,4-Trihydroxy-[125,128], 4-methoxy-[55,57,62], 4-hydroxy-3-methoxy-[62,147], 3,4-methylenedioxy-[62,148], and 4-hydroxy-3-sulpho-benzenedithiocarboxylic[63] acids are likewise crystalline. Naphthalene-1- and naphthalene-2-dithiocarboxylic acids are dark-red oily liquids[30,33,149,150], while 1-hydroxynaphthalene-2-dithiocarboxylic acid is a dark-yellow crystalline substance[89,128].

Furan-2-[62,65,148], pyrrole-2-[51,52], and indole-3-dithiocarboxylic[52] acids are red oily liquids but the dithiocarboxylic acids obtained from certain pyrrole[108], indole[104], pyridine[103], and quinoline[102] derivatives are crystalline substances. Dithiocarboxylic acids of type (XI) are yellow crystalline substances (m.p. between 200° and 288°C)[119] like the dithiocarboxylic acids obtained from pyrazolone derivatives (m.p. between 115° and 230°C)[114–116, 132].

Zwitter-ionic dithiocarboxylic acid has been obtained in the form of dark-red substances melting at 178–179°C[140] and 233–236°C[141]:



(XI)

$Z = S, Se, {-}CH_2{-}CH_2{-};$
$R = CH_3{-}, C_6H_5{-}CH_2{-}$.

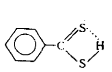
Dithiocarboxylic acids are sparingly soluble in water, dissolving more or less readily in organic solvents.

2. Absorption Spectra

The electronic absorption spectra of dithiocarboxylic acids differ little from those of their esters[151,152]. The electronic absorption spectra of methane-[152], ethane-[153], cyclohexane-[154], phenylmethane-[155,156], benzene-[152,156,157], 4-chlorobenzene-[157], 4-methylbenzene-[158], 2-hydroxybenzene-[145], 4-hydroxybenzene-[144,159], 2,4-dihydroxybenzene-[144,146], 2,3,4-trihydroxybenzene[144], 4-hydroxy-3-methoxybenzene-[147], naphthalene-1- and naphthalene-2-[150], pyrrole- and indole-[160,161], and quinoline-2- and quinoline-4-dithiocarboxylic[162] acids are available in the literature. Other publications quote only numerical data characterising the absorption maxima (wavelengths and molar extinction coefficients). Such data are available for methane-, trimethylmethane-, phenylmethane-, benzene- and 4-methylbenzene-dithiocarboxylic acids[163], for acids (IX)[85] and (X)[109], and for zwitter-ionic dithiocarboxylic acids.

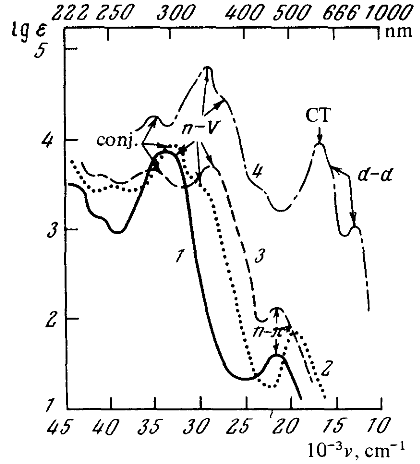
The absorption bands in the electronic spectra of phenylmethane- and benzene-dithiocarboxylic acids have been assigned[156] (see Figure).

The low-intensity band ($\epsilon < 100$) observed in the visible spectra has been assigned to $n-\pi^*$ transitions. Resolution of this band in the absorption spectrum of benzenedithiocarboxylic acid into two components led to the conclusion that there is a hydrogen bond in the dithiocarboxy-group, as in formula (XII)[164]; the energy of this bond is 4.5 ± 0.5 kcal mole^{-1}:



(XII)

The ultraviolet spectra of phenylmethane- and benzenedithiocarboxylic acids as well as the spectra of the corresponding anions (see Figure) contain a high-intensity band, which has been assigned to $n-V$ transitions[156]. In the spectra of benzenedithiocarboxylic acid and its anion, there is a second high-intensity absorption band, which has been assigned to $\pi-\pi^*$ transitions in the conjugated system of the benzene ring with the dithiocarboxy-group (in the Figure, it is designated by "conj."). These absorption band assignments were extended also 4-chloro- and 4-methyl-benzenedithiocarboxylic acids[165].



Electronic absorption spectra: 1) phenylmethanedithiocarboxylic acid in carbon tetrachloride; 2) benzenedithiocarboxylic acid in ethyl ether; 3) benzenedithiocarboxylic acid in water; 4) nickel benzenedithiocarboxylate in chloroform[157].

Vibrational spectra. A spectrum in the range 526–4000 cm^{-1} was obtained[142] for the dithioformic acid trimer $(HCSSH)_3$. There are numerical data for the same part of the spectrum of the polymeric acid $(HCSSH)_x$.[16,142] The absorption at 2500 cm^{-1} has been assigned to ν(S–H) and that at 1166 and 1048 cm^{-1} to the stretching and deformation vibrations of the CSC group.

The spectrum of cyanodithioformic acid $(NC-CSSH)_x$ was recorded in the range 526–4000 cm^{-1}.[166] The (C≡N) band was found at 2250 cm^{-1}, which led to the conclusion that the polymerisation of this acid as well as that of dithioformic acid involves the C═S group.

The spectra of liquid (400–10 000 cm^{-1}) and gaseous (750–10 000 cm^{-1}) methanedithiocarboxylic acid have been obtained[167] and the following assignments of the absorption wavenumbers have been made: 2481 cm^{-1} to ν(SH), 1216 cm^{-1} to ν(C═S), 581 cm^{-1} to ν(C–S) and 860 cm^{-1} tentatively to δ(SH). Calculation of the normal vibration wavenumbers for this acid on a computer[168] led to the following assignments:

2976 cm^{-1} to CH stretch.;
2918 cm^{-1} to CH stretch.;
2481 cm^{-1} to SH stretch.;
1431 cm^{-1} to CH def.;
1357 cm^{-1} to CC stretch. + CH def.;
$\left\{\begin{matrix}1192\\1216\end{matrix}\right.$ cm^{-1} to CC stretch. + SCC def. + SCS def. + CH def.;
$\left\{\begin{matrix}1072\\1107\end{matrix}\right.$ cm^{-1} to SCC def. + SCS def. + SH def.;
903 cm^{-1} to CC stretch.+ CS stretch.+ SH def.;
$\left\{\begin{matrix}860\\873\end{matrix}\right.$ cm^{-1} to CS stretch. + CH def.;
581 cm^{-1} to CS stretch.;
406 cm^{-1} to CCS def.

The spectra of solutions of trifluoromethanedithiocarboxylic acid in carbon tetrachloride and in carbon disulphide have been obtained (670–4000 cm^{-1})[169] as well as numerical data for the absorption wavenumbers[136,137,169]. The following assignments have been made:

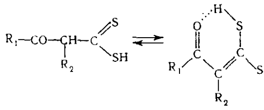
2577-2580 cm^{-1} to ν(SH);
1253 cm^{-1} to $\nu_{\mathrm{asym}}(CS_2)$;
933-945 cm^{-1} to δ(SH)?
690-691 cm^{-1} to $\nu_{\mathrm{sym}}(CS_2)$.

The vibrational spectrum of benzenedithiocarboxylic acid[20] contains intense absorption bands at 1690 and 1270 cm^{-1}. The shift of ν(SH) on passing from the spectrum of its 20% solution in carbon tetrachloride indicates[170] the existence of the hydrogen bond S–H...S [see also formula (XII)].

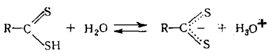
The vibrational absorption spectra of 2-hydroxy-[145], 4-hydroxy-[123], and 2,4-dihydroxy-benzenedithiocarboxylic[123,146] acids have likewise been published. The following assignments have been made for the last acid[146]: 2530 cm^{-1} to ν(SH); 1250–1240 cm^{-1} to δ(OH), ν(C═S)?; 685 cm^{-1} to ν(C–S)? The study of the spectrum of 2-hydroxybenzenedithiocarboxylic acid led to the conclusion that there is an intramolecular hydrogen bond in this compound[145].

3. Chemical Properties

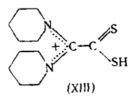
There may be a tautomeric equilibrium between dithiocarboxylic acids and the corresponding ene-1,1-dithiols. The equilibrium has been detected[171] in the dithiocarboxylic acids obtained by the reaction between carbon disulphide and ketones:



Dithiocarboxylic acids enter into a protolytic interaction with water molecules:



In an alkaline medium, where hydronium ions combine with hydroxide ions, the dithiocarboxylic acids, which are sparingly soluble in water, therefore dissolve in the form of dithiocarboxylate ions:



(XIII)

The strongest dithiocarboxylic acid is compound (XIII) ($pK_a \simeq -2$).[141] The pK_a values for other dithiocarboxylic acids vary in the range from 1 to 3 (see Table). $pK_1 < 2$ and $pK_2 \simeq 5.2$ have been found for nitromethanedithiocarboxylic acid[88] (pK_2 corresponds to the second dissociation involving the conversion of the dithiocarboxylate ion into the ene-1,1-dithiolate ion).

Dithiocarboxylic acids are extremely reactive. They undergo intense colour reactions with textiles and form dark stains on leather[30,32,172]. On storage, many dithiocarboxylic acids decompose rapidly or are oxidised. For example, an ethereal solution of benzenedithiocarboxylic acid may be stored without significant changes for more than 1 h only in an atmosphere of an inert gas[172]. This by no means applies to all dithiocarboxylic acids. There are also extremely stable representatives of compounds of this class, for example the dithiocarboxylic acids obtained from derivatives of pyrazolone[114-116, 132], 4-hydroxy-3-methoxybenzenedithiocarboxylic acid[147], and the acids (X), (XI), and (XII).

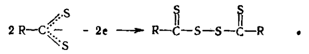
The pK_a values for dithiocarboxylic acids in aqueous solutions.

No.	Acid	pK_a	References
1	Dithioformic	0.85	143
2	Methanedithiocarboxylic	2.55	152
3	Ethanedithiocarboxylic	2.65±0.05	153
4	1-Oxopropanedithiocarboxylic	2.15	77
5	Phenylmethanedithiocarboxylic	2.05±0.04	155
6	Benzenedithiocarboxylic	1.92±0.06	157
7	4-Chlorobenzenedithiocarboxylic	1.7	157
8	4-Methylbenzenedithiocarboxylic	2.3	157
9	2-Hydroxybenzenedithiocarboxylic	1.60±0.06	145
10	4-Hydroxybenzenedithiocarboxylic	2.58±0.07	144
11	2,4-Dihydroxybenzenedithiocarboxylic	1.91±0.08	144
12	2,3,4-Trihydroxybenzenedithiocarboxylic	1.72±0.04	144
13	3,4-Methylenedioxybenzenedithiocarboxylic	2.29±0.07	148
14	Furan-2-dithiocarboxylic	2.04±0.04	148

When nitromethane-[86], 2,4-dihydroxybenzene-[124, 126], 2,3,4-trihydroxybenzene[125], and 1-hydroxynaphthalene-2-dithiocarboxylic[128] acids are heated with concentrated aqueous solutions of alkalis, sulphur is split off and the corresponding carboxylic acids are formed.

The reducing action of amalgamated zinc on benzene-, 4-methoxybenzene-, and phenylmethane-dithiocarboxylic acids has been investigated in hydrochloric acid solutions. Under these conditions, benzenedithiocarboxylic acid is largely converted after interaction for 10 min into phenylmethanethiol ($C_6H_5CH_2SH$) (yield 25%); stilbene and benzoic acids are also formed and a considerable proportion of the substance char. When the above three dithiocarboxylic acids are reduced polarographically, three waves are observed in each individual instance. The first corresponds to the reduction of the disulphide formed in the solution of the supporting electrolyte, the second to the reduction of the thiocarbonyl group, and the third to the reduction of the dithiocarboxylate ion[54].

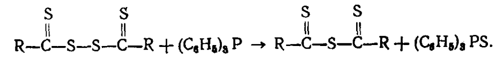
When cyclohexane-[36], 4-methylbenzene-[44], and 8-hydroxyquinoline-7-dithiocarboxylic[124] acids are treated with strong oxidising agents ($KMnO_4$, HNO_3), the corresponding carboxylic acids are formed. On oxidation of alkali metal dithiocarboxylates under milder conditions (with iodine, hydrogen peroxide, and atmospheric oxygen), the products are usually disulphides, which precipitate:



$$2\,R{-}C{\overset{\cdot\cdot S}{\underset{\cdot\cdot S}{\langle}}}{}^{-} - 2e \longrightarrow R{-}\overset{S}{\overset{\|}{C}}{-}S{-}S{-}\overset{S}{\overset{\|}{C}}{-}R\ .$$

The disulphides containing aliphatic groups are as a rule yellow, while those containing aromatic and heterocyclic groups are red. Dithioformic acid gives rise to a polymeric disulphide[12, 173].

Disulphides can be converted into monosulphides by treatment with triphenylphosphine[174]:



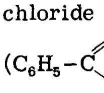
$$R{-}\overset{S}{\overset{\|}{C}}{-}S{-}S{-}\overset{S}{\overset{\|}{C}}{-}R + (C_6H_5)_3P \rightarrow R{-}\overset{S}{\overset{\|}{C}}{-}S{-}\overset{S}{\overset{\|}{C}}{-}R + (C_6H_5)_3PS.$$

A solution of bis-(1-thionaphthoyl) disulphide in fused naphthalene exhibits thermochromic properties, i.e. the colour of the solution changes as the temperature is altered[175,176]. This is explained by the formation of free radicals:

$$C_{10}H_7{-}CS{-}S{-}S{-}CS{-}C_{10}H_7 \rightleftarrows 2C_{10}H_7{-}CS{-}S^{\cdot}.$$

A 0.005% benzene solution or a 0.05% chloroform solution of bis-(2-hydroxythiobenzoyl) disulphide have been suggested as reagents for the extraction-colorimetric determination of microgram amounts of nickel[177].

Dithiocarboxylic acids react with ammonia derivatives such as amines, hydroxylamine, hydrazine, and semicarbazide. The reaction with primary amines $R'NH_2$ yields the corresponding thioamides RCSNHR'. This has been used for the thioacylation of uracil and pyrimidine derivatives[178]. The corresponding derivatives of dithiocarboxylic acid obtained from pyrazolones[114,115,131] and the acids $RCOCH_2CSSH$ have also been synthesised[179,180]. As a result of interaction with dithiocarboxylic acids, 1,2-phenylenediamine yields substituted benzimidazoles[181]. In the presence of an oxidising agent (elemental iodine), dithiocarboxylic acids react with cyclohexylamine and the products are again thioamides[39,182]. The reaction of aromatic dithiocarboxylic acids with hydroxylamine gives rise to the oximes RCH=NOH, [46, 183] while the reaction between hydroxylamine and non-aromatic dithiocarboxylic acids gives rise to the nitriles RCN.[183] Aromatic dithiocarboxylic acids react with hydrazine to form the hydrazones $RCH{=}NNH_2$ and the reactions with methyl-, phenyl-, and methylphenyl-hydrazines result in the formation of the corresponding substituted hydrazones[23,48,114,183-186]. Aliphatic dithiocarboxylic acids react with these reagents to form the thiohydrazides $RCSNHNH_2$. The reaction between semicarbazide and aromatic dithiocarboxylic acids leads to the formation of the semicarbazones $RCH{=}NNHCONH_2$.[47,183]

Benzenedithiocarboxylic acid reacts with thionyl chloride ($SOCl_2$) to form[38, 43, 134] thiobenzoyl chloride ( $C_6H_5{-}C{\overset{\nearrow S}{\underset{\searrow Cl}{}}}$). 4-Methyl-, 3-chloro-, 4-chloro-, and 4-methoxy-benzenedithiocarboxylic acids as well as thiophen-2-dithiocarboxylic acid react similarly[187].

4. Applications of Dithiocarboxylic Acids

Dithiocarboxylic acids can be used in organic synthesis as thioacylating agents. Their reactions with azolides constitute the basis of one of the methods for the synthesis of thioamides[188]. Substituted methane dithiocarboxylic acids can serve as the starting materials for the synthesis of compounds with sulphur-containing rings[189].

Dithioformic acid has been used as a reagent for the introduction of sulphur into proteins[190]. Various dithiocarboxylic acids have been suggested as effective agents accelerating the vulcanisation of raw rubber[58,60,61,191]. Copolymerisation with benzenedithiocarboxylic acid makes it possible to increase the elasticity and to improve other properties of many polymers[192,193]. Hydroxy-derivatives of benzenedithiocarboxylic acid exhibit bactericidal and fungicidal properties and can find appropriate applications[91].

IV. DITHIOCARBOXYLIC ACID ESTERS

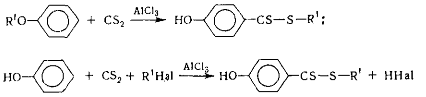
1. Methods of Synthesis

The esters can be obtained from the corresponding dithiocarboxylic acids. Historically, this is the first method for the synthesis of the esters, but it is still used on a fairly large scale. The esters are sometimes obtained by alkylating the dithiocarboxylic acids themselves[109,119], but normally their salts are used for this purpose: the sodium[41,44,48,54,79,194-197], potassium[13,18,19,24,57,82,115,116,132,144,198-200], silver[57], ammonium[146,201], and magnesium halide salts RCSSMgHal, obtained in the synthesis of dithiocarboxylic acids using organomagnesium compounds[37,40,202,205]. The zwitter-ionic dithiocarboxylic acids react directly with methyl iodide[121,141]. Dimethyl sulphate[44,48,54,57,66,82,108,109,115,116,119,132,144,195,197,199,202,203,205], diethyl sulphate[24,108,203,204], methyl iodide[13,121,141,146,196,200,206], ethyl iodide[13,57,200], propyl iodide[13], butyl iodide[44], 4-nitrobenzyl bromide[44], monochloroacetic acid[18,19,37,40,41,198], and diazomethane[108,109,129] are used as alkylating agents.

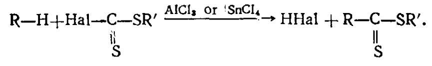
The Friedel–Crafts synthesis of dithiocarboxylic acid esters is used in several versions. The reaction of pyrazolone derivatives with carbon disulphide and ethyl bromide gives rise to the ethyl esters[132,133,207,208]:

$$\mathrm{R{-}H + C_2H_5Br + CS_2 \xrightarrow{AlCl_3} HBr + R{-}CS{-}S{-}C_2H_5}.$$

The esters of aromatic dithiocarboxylic acids containing the OH group in the aromatic moiety can be obtained in two ways[208,209,210]:

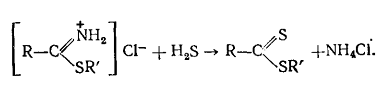


Esters of halogenodithiocarbonic acid may be used in the Friedel–Crafts synthesis instead of carbon disulphide[211,212]:



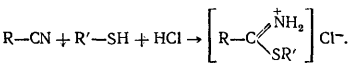
$$\mathrm{R{-}H + Hal{-}\underset{\underset{S}{\|}}{C}{-}SR' \xrightarrow{AlCl_3\ or\ SnCl_4} HHal + R{-}\underset{\underset{S}{\|}}{C}{-}SR'}.$$

Another group of methods for the synthesis of dithiocarboxylic acid esters is based on the interaction of the salts of thioiminoesters with carbon disulphide in an anhydrous medium:



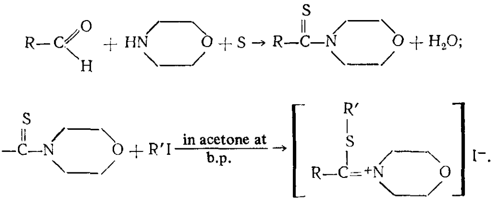
$$\left[\mathrm{R{-}C{\genfrac{}{}{0pt}{}{\overset{+}{N}H_2}{SR'}}}\right]\mathrm{Cl^- + H_2S \rightarrow R{-}C{\genfrac{}{}{0pt}{}{S}{SR'}} + NH_4Cl}.$$

Ethyl ester was initially proposed as a solvent for this reaction[130], but higher yields are obtained in dry pyridine[213]. The thioiminoester salts required for the synthesis can be obtained by adding hydrogen chloride to a mixture of equivalent amounts of a nitrile and a thiol[214,215]:



$$\mathrm{R{-}CN + R'{-}SH + HCl \rightarrow} \left[\mathrm{R{-}C{\genfrac{}{}{0pt}{}{\overset{+}{N}H_2}{SR'}}}\right]\mathrm{Cl^-}.$$

When R = H, i.e. when HCN reacts with thiols, the products are the corresponding dithioformic acid derivatives[216]. The product of the addition of HCN to ketones, i.e. $\mathrm{R_1R_2C(OH)CN}$ react with thiols to form thioiminoester salts of the type $\left[\mathrm{R_1R_2C(OH){-}C{\genfrac{}{}{0pt}{}{\overset{+}{N}H_2}{SR'}}}\right]\mathrm{Cl^-}$ which can also be used[217] to synthesise the corresponding dithiocarboxylic acid esters $\mathrm{R_1R_2C(OH)CSSR'}$. Treatment of the latter with thionyl chloride ($\mathrm{SOCl_2}$) leads to the substitution of the hydroxy-group by chlorine[217]. It has been suggested recently[218] that thioiminoester salts be obtained from the thioamides $\mathrm{R\overset{\overset{S}{\|}}{C}NH_2}$ and ethyl thiochloroformate ($\mathrm{Cl\overset{\overset{O}{\|}}{C}SC_2H_5}$). Thioiminoester salts in which the hydrogen atoms at the nitrogen atom have been substituted by hydrocarbon groups, i.e. $\left[\mathrm{R{-}C{\genfrac{}{}{0pt}{}{\overset{+}{N}R_3R_4}{SR'}}}\right]\mathrm{Cl^-}$ can also be used to synthesise dithiocarboxylic acid esters[219,220]. In the specific instance of morpholine, the latter can be represented by the fragment $\mathrm{=\overset{+}{N}{\genfrac{}{}{0pt}{}{R_3}{R_4}}}$.[54,134,197,221]. Thioiminoester salts can be obtained[221] as follows:

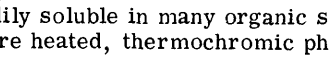


Methods have also been proposed for the synthesis of dithiocarboxylic acid esters by the interaction of unsaturated compounds with thiols[222,223] or with dithiocarboxylic acids[224]. On heating, 2-mercapto-1,1-diphenyl-2-phenylthioethylene is transformed into the phenyl ester of diphenylmethanedithiocarboxylic acid[225]. Methods have also been developed for the synthesis of fluoro-substituted dithiocarboxylic acids[226].

2. Properties of the Esters

The esters RCSSR′, in which both organic groups are aliphatic, are yellow or orange oily liquids. This also applies to cyclohexane- and phenylmethane-dithiocarboxylic acids. However, the esters of dithioformic acid (R = H) are trimeric and therefore crystalline[13,200]. If R is an aromatic group and R′ an aliphatic group, the esters can be both liquid and crystalline red substances. The esters with both groups are aromatic crystalline substances.

If the group R contains substituents capable of splitting off a proton, the ester can exist in two forms, involved in tautomeric equilibrium[171,227,228]:



$$\mathrm{R{-}S{\genfrac{}{}{0pt}{}{S}{S{-}R'}} \rightleftarrows R_1{=}C{\genfrac{}{}{0pt}{}{SH}{S{-}R'}}};\ \mathrm{R{=}R_1H}.$$

Dithiocarboxylic acid esters are insoluble in water, but are usually readily soluble in many organic solvents. When such solutions are heated, thermochromic phenomena may be observed. For example, a solution of methyl naphthalene-1-dithiocarboxylate in ethyl benzoate or ethyl oxalate as well as a solution of phenyl diphenylmethanedithiocarboxylate in xylene change colour on heating. When the solutions are cooled, the initial colour is restored[27,229].

The electronic absorption spectra of the esters differ little from those of the acids themselves[152]. The absorption spectra of the methyl esters of ethane-[205], cyclohexane-[230], benzene-[230], 2,4-dihydroxybenzene-[146], naphthalene-1-[229,230], and naphthalene-2-dithiocarboxylic[230] acids, the ethyl esters of methane- and benzene-dithiocarboxylic acids[152], and the phenyl esters of benzene-, 4-hydroxybenzene-, 2,4,6-trimethylbenzene-, and 2-thiophen-dithiocarboxylic[212] acids have been published.

Characteristic absorption maxima at 1050 and 1240 cm^{-1} have been observed in the vibration spectra of the methyl, ethyl, and phenyl esters of aromatic dithiocarboxylic acids[212]. The absorption wavenumbers of the ethyl and isobutyl esters of methanedithiocarboxylic acid as well as the ethyl and butyl esters of ethanedithiocarboxylic acid have been published[213]. The spectra themselves have been published only for the methyl esters of 3-methyl-1-phenyl-5-pyrazolone-4-dithiocarboxylic acid (500–4000 cm^{-1})[199] and 2,4-dihydroxybenzenedithiocarboxylic acid (685 to 3800 cm^{-1})[146].

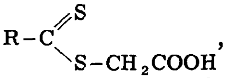
The magnetic permeability of ethyl methanedithiocarboxylate has been determined[231] as well as the NMR chemical shifts of the protons in the ethyl esters of methane-, phenylmethane-, and benzene-dithiocarboxylic acids and methanebis(dithiocarboxylic) acid[232]. The chemical shifts of carbon-13 have also been determined in the last instance[233].

Among the chemical properties of the esters, their ability to hydrolyse to the corresponding dithiocarboxylic acids has already been noted. However, the effect of hydrolysing agents can also lead to monothiocarboxylic or even carboxylic acids[132,203,208,234].

When the methyl esters of aliphatic and aromatic dithiocarboxylic acids are reduced with amalgamated zinc in hydrochloric acid, the main reaction product is the sulphide RCH_2SCH_3, in which the thiono-sulphur atom of the ester has been replaced by two hydrogen atoms[54]. In the polarographic reduction[54] of these esters, the half-wave potentials were in the range between −1 and −1.5 V. The half-wave potentials have also been determined for a number of phenyl esters[212], ranging from −0.95 to −1.30 V.

3. Applications of the Esters

The esters are usually much more stable than the dithiocarboxylic acids themselves. For this reason, they frequently constitute the form in which dithiocarboxylic acids are stored and actually used (for example, for thioacylation[235,236]). The carboxymethyl esters



$R{-}C(=S){-}S{-}CH_2COOH$

, which form water-soluble alkali metal salts, are particularly convenient for this purpose[37,40,41,237]. When necessary, the dithiocarboxylic acids can be obtained by hydrolysing the esters[130].

The ability of the esters to condense with nitriles, which are CH acids, and to undergo self-condensation can be used also in organic synthesis[238]. The esters can also serve as the starting materials in the synthesis of keten thioacetals[239] or as intermediates in the synthesis of dyes[119,196]. The dyes obtained from the esters of dithiocarboxylic acids of type (XI) proved to be extremely valuable sensitisers in the manufacture of photographic materials[119]. It has been stated in the literature that the esters can be used as antioxidants in lubricating oils[224] and also as bactericidal and fungicidal agents[91].

V. METAL DITHIOCARBOXYLATES

1. Synthesis and Properties

There is an ionic bond between the anion and cation in alkali and alkaline earth metal dithiocarboxylates. For this reason, they are readily soluble in water. Aqueous solutions of the dithiocarboxylates are usually obtained by the reaction of dithiocarboxylic acids with solutions of alkalies. Many sodium and potassium dithiocarboxylates are stable in aqueous solutions for several months[45]. However, alkali metal cyanodithioformates decompose rapidly in aqueous solutions[138] and alkali metal trifluoromethanedithiocarboxylates cannot be obtained at all because of the strong electron-attracting influence of the trifluoromethyl group[137]. Sodium benzenedithiocarboxylate[42,156] and phenylmethanedithiocarboxylate[156] have been obtained in a solid form by the vacuum evaporation of their aqueous solutions, while evaporation of methanol solutions yielded potassium dithioformate[15,240]. Potassium pyridine-4-dithiocarboxylate has been obtained in the solid state by adding ethyl ether to an evaporated methanol solution of the salt[23].

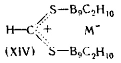
Ammonium dithiocarboxylates are also readily water-soluble ionic compounds. Only ammonium 2-aminocyclopent-1-ene-1-dithiocarboxylate is precipitated from ammonia solutions[84,241]. Quaternary ammonium dithiocarboxylates can be obtained in a crystalline form. In many instances, they are precipitated when aqueous solutions of sodium dithiocarboxylate and the quaternary ammonium halide are mixed. The corresponding salts of naphthalene-1-[49,149,242], naphthalene-2-[50,64], 2-hydroxybenzene-[145], 1-hydroxynaphthalene-2-[243], and indole-3-dithiocarboxylic[53] acids have been obtained in this way. In other instances, cooling or extraction with chloroform followed by the addition of another solvent which causes precipitation are used to isolate the reaction product. Quaternary ammonium salts of thioformic[240] and benzene-, 4-chlorobenzene-, 4-methylbenzene-[244], phenylmethane-[245], quinoline-2-, and quinoline-4-dithiocarboxylic[24] acids have been obtained by this procedure. In the synthesis of tetraethylammonium cyanodithioformate, tetraethylammonium hydroxide is used instead of the corresponding halide[138].

A series of tetraphenylphosphonium[53,148,153,240], tetraphenylarsonium[15,24,139,149,154,240,242], and triphenyltin[240] dithiocarboxylates have also been synthesised. The solubilities of certain 'onium naphthalene-[149], pyrrole- and indole-dithiocarboxylates[246] have been determined.

The introduction of transition or non-transition metal ions into aqueous solutions of ionic dithiocarboxylates often gives the corresponding dithiocarboxylate chelate complexes. The latter are insoluble in water and are precipitated. Among non-transition elements, gallium, indium, thallium, germanium, tin, lead, arsenic, antimony, bismuth, and selenium ions react with dithiocarboxylate ions. Among transition metals, dithiocarboxylate chelates are formed by vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, osmium, rhodium, iridium, palladium, platinum, copper, silver, gold, zinc, cadmium, and mercury ions. The dithiocarboxylates of the majority of platinum metals are formed slowly at the usual temperature, but the reactions can be accelerated by heating. It has been stated in the literature that dithiocarboxylate ions interact with zirconium ions[108]. Among the actinides, uranium interacts with dithiocarboxylate ions.

Metal dithiocarboxylates can also be obtained from organometallic compounds as a result of the dissociation of the C–M bonds and the insertion of carbon disulphide at the site of the break; part of the review of Butler and Fenster[247] is devoted to this problem. Such reactions also include the interaction between organometallic compounds and carbon disulphide, used to synthesise dithiocarboxylic acids (see Section II). It has been stated in the literature that dialkyl-aluminium-, -gallium, and -indium dithiocarboxylates can be obtained in this way[248], although later the same author synthesised these substances by a different method[249]. The method has been used successfully to prepare manganese and rhenium dithiocarboxylatocarbonyls having the general formula $RCSSM(CO)_4$, where R = CH_3, C_6H_5, $CH_3C_6H_4$, ClC_6H_4, $C_6H_5CH_2$, or $(C_6H_5)_3C$.[250-253] However, the attempts to obtain triethyl-lead ethanedithiocarboxylate from tetraethyl-lead and carbon disulphide were unsuccessful[254]. Manganese and rhenium dithiocarboxylatocarbonyls can also be synthesised from the corresponding dithiocarboxylic acids (benzene-[20,255,256] and trifluoromethanedithiocarboxylic acids[135]) or their chlorides (C_6H_5CSCl).[257]

In addition, the following complexes containing dithioformate ions as ligands have been obtained from mixed dithiocarboxylates: $Re(CO)_2(HCSS)[P(C_6H_5)_3]_2$,[258] $[Ru(HCSS)_2][P(C_6H_5)_3]_2$,[259] and compound (XIV).[260-262] Their structures have been elucidated by X-ray diffraction:


(XIV)

; M = Co, Fe .

2. Absorption Spectra

The first electronic absorption spectra of metal dithiocarboxylates were already obtained in the 1920's[152]. However, the bulk of the data on these spectra have been published the last 7–8 years. The spectra or numerical data characterising the absorption maxima of a number of metal dithioformates[15,240], methane-[152,153,163,263], ethane-[153], trimethylmethane-[163], phenylmethane-[155,156,163,263-268], cyclohexane-[154], benzene-[152,156,163,264,269-274], 2-hydroxybenzene-[275], 4-hydroxybenzene-[159,276], 2,4-dihydroxybenzene-[277,278], 2,3,4-trihydroxybenzene-[277], 4-hydroxy-3-methoxybenzene-[147], 4-chlorobenzene-[270,271,274,279], 4-methylbenzene-[163,270-274], napthalene-1-[280], 1-hydroxynaphthalene-2-[243], pyrrole- and indole-[281], and 2-aminocyclopent-1-ene-1-dithiocarboxylates[84] have been described in the literature.

Comparison of the absorption spectrum of the dithioformate ion with that of the thioloformate ion $HCOS^-$ led[240] to the following assignments: 225 nm to the $n-\sigma^*$ transitions, 331 nm to the $\pi-\pi^*$ transitions, and 386 nm to the $n-\pi^*$ transitions.

The electronic absorption spectra of lead, indium, chromium(III), cobalt(III), rhodium(III), iridium(III), nickel(II), palladium(II), and platinum(II) benzene- and phenylmethane-dithiocarboxylates led to the conclusion[156] that the chromophoric groups MS_4 in the ML_2 complexes have the square planar structure, while in the ML_3 complexes the MS_6 chromophores are pseudo-octahedral. A preliminary assignment was also made of the absorption bands (the Figure presents as an example the spectrum of nickel benzenedithiocarboxylate).

The bands in the ranges 208–222 and 250–268 nm were assigned to the vibrations of the benzene ring. One or several intense bands in the range 295–345 nm were assigned to the $n-V$ transitions. The bands which originate from the electronic transitions in the conjugated system of the benzene ring and the dithiocarboxylate group are located between those of the benzene ring and the $n-V$ transitions. In the range 333–455 nm, there are bands which are missing from the spectra of the free ligands. They were assigned to the charge-transfer (CT) bands. In the spectra of the transition metal compounds, there are weak absorption bands above 455 nm due to the $d-d$ transitions in the MS_4 and MS_6 chromophores.

Later, approximately the same assignments were made in the electronic absorption spectra of vanadium[263], nickel, and zinc[163] methanedithiocarboxylates, nickel trimethylmethanedithiocarboxylate[163], iron[264], vanadium[263], nickel, and zinc[163] benzenedithiocarboxylates, vanadium[263], nickel, and zinc[163] 4-methylbenzenedithiocarboxylates, and iron[264], vanadium[263], nickel, and zinc[163] phenylmethanedithiocarboxylates.

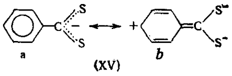
The electronic absorption spectra of arsenic, bismuth, indium, gallium, antimony, mercury(II), lead, tin(II), zinc, and platinum(II) 2,4-dihydroxybenzenedithiocarboxylates led to the conclusion[278] that the absorption band in the range 390–420 nm arises as a result of $n-\pi^*$ transitions. This is nevertheless difficult to accept, since this band is intense (the molar extinction coefficients are between 4×10^4 and 8×10^4).

The vibrational spectra or the wavenumbers in these spectra have been published for a number of metal dithioformates[15,240], cyanodithioformates[166], and methane-[168,252,253,263,282], 2-aminocyclopent-1-ene-1-[84,283], benzene-[252,253,263,284-288], 4-methylbenzene-[253,263,289], 4-chlorobenzene-[253], 4-isopropylbenzene-[289], 2,4-dihydroxybenzene-[290], and naphthalene-1-dithiocarboxylates[285]. The following assignments were made in the spectrum of potassium dithioformate[240] (the wavenumbers are in cm^{-1}): 1250 to $\delta_{asym}(SCS)$, 988 to $\nu_{asym}(SCS)$, and 848 to $\nu_{sym}(SCS)$.

Comparison of the spectra of sodium and lead methanedithiocarboxylates with those of their deuterated analogues led to the following assignments[282]: 1141 to $\rho(CH_3)$, and $\nu_{asym}(CSS)$, 602 to $\nu_{sym}(CSS)$, 464 to $\omega(CSS)$, 372 to $\delta(CSS)$, and 348 to $\rho(CSS)$. The following assignments were made in the spectra of mixed methanedithiocarboxylatocarbonyl complexes[252,253]: 1146 to $\nu_{asym}(CS_2)$ and 616 to $\nu_{sym}(CS_2)$. Calculation[168] of the normal vibrations of the methanedithiocarboxylate ion and its deuterated analogue permitted the following assignments:

2976 cm^{-1} to CH stretch.;
2915 cm^{-1} to CH stretch.;
1449 cm^{-1} to CH def.;
1349 cm^{-1} to CC stretch. + CH def.;
1141 cm^{-1} to CC stretch. + CS stretch. + SCS def. + CCS def.;
1115
1065 cm^{-1} to CS stretch. + SCC def. + CH def.;
983 cm^{-1} to CH def.;
865 cm^{-1} to CS stretch. + SCC def. + CH def.;
602 cm^{-1} to CS stretch. + CS stretch.;
372 cm^{-1} to SCS def. + SCC def.;
348 cm^{-1} to SCC def.

A number of studies have been made on the spectra of benzenedithiocarboxylates, but the assignments are not unambiguous. In the spectra of lead, cadmium, and thallium benzenedithiocarboxylates, the wavenumbers in the range 940–1000 cm^{-1} are attributed to the vibrations in the CS_2 group[284]. In the study[286,287] of the spectra of nickel(II), palladium(II), cobalt(III), chromium(III), indium, rhodium(III), lead, and iron(III) benzenedithiocarboxylates, comparison with the spectra of the complexes of the deuterated analogues led to the following assignments: 980–1000 to $\nu_{asym}(CSS)$; 940–950 to $\nu_{sym}(CSS)$; 660–670 to $\delta(CSS)$; 360–370 to $\nu_{asym}(MSS)$; and 310–320 to $\nu_{sym}(MSS)$. Furthermore, the differences between the vibrational wavenumbers of the benzene ring in various complex-forming agents led to the conclusion that the contribution of the resonance form of the ligands (XVb) increases with increase of the electron affinity of the central ion:



(XV)

A subsequent study[288] of the spectra of potassium, thallium(I), lead, cadmium, mercury(II), and indium benzenedithiocarboxylate nevertheless provided a justification for a new assignment of certain wavenumbers. The 585–589 cm^{-1} was assigned to the γ(CSS) vibrations and the 320–330 cm^{-1} band to the δ (CSS) vibrations. Objections were raised against the assignment of the 950 cm^{-1} band to the $\nu(CS_2)$ vibrations and of the 670 cm^{-1} band to the δ (CSS) vibrations. The band at 300–350 cm^{-1} was assigned to the latter.

The following assignments were made in the spectra of mixed benzenedithiocarboxylatocarbonyl complexes[252,253]: 1267 to $\nu_{asym}(CS_2)$; 613–631 to $\nu_{sym}(CS_2)$. Assignments were also made in the spectra of 4-methylbenzene-[253,289], 4-chlorobenzene-[253], and 4-isopropylbenzene-dithiocarboxylates[289]. The 1220–1260 cm^{-1} and 590 cm^{-1} bands in the spectra of 2,4-dihydroxybenzenedithiocarboxylates were assigned to the stretching vibrations in the CS_2 group. The bands in the range 970–990 cm^{-1} were assigned to the vibrations of the same group.

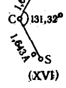
The bands in the range 990–1020 cm^{-1} in the spectra of naphthalene-1-dithiocarboxylates[285] were assigned to the stretching vibrations of the CSS group.

The Structure of Metal Dithiocarboxylates

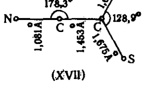
The magnetic properties of iron(III), benzene- and phenylmethane-dithiocarboxylates indicate the presence of low-spin complexes[264,291]. Cobalt(III), indium, rhodium(III), palladium(II), iridium(III), and platinum(II) phenylmethanedithiocarboxylates are diamagnetic, while the corresponding chromium(III) complexes are paramagnetic[156]. Nickel(II), platinum(II), copper(II), zinc, and cadmium 2-aminocyclopent-1-ene-1-dithiocarboxylates are also diamagnetic, which indicates a square planar coordination of the sulphur atoms[283,292]. Magnetic moment measurements have shown[263,293] that vanadium functioning as the complex-forming agent in methane-, phenylmethane-, benzene-, and 4-methylbenzene-dithiocarboxylates is in the +4 state of oxidation. Judging from their magnetic properties[163], nickel methane-, trimethylmethane-, phenylmethane-, benzene-, and 4-methylbenzene-dithiocarboxylates are low-spin complexes. The magnetic permeability of copper(I) naphthalene-1-dithiocarboxylate has also been determined[294].

The number of ESR data is so far small[263,295,296].

A number of metal dithiocarboxylates have been investigated by X-ray diffraction and their structures have been elucidated. The principal data obtained in the study of potassium dithioformate[297] are presented in formula (XVI). In the mixed dithioformatocarbonyl complexes[258,259], the C–S bond length is in the range 1.64–1.70 Å. The data obtained for the cyanodithioformate ion[298,299] are presented in formula (XVII):



(XVI)

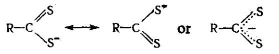


(XVII)

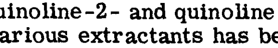
The sulphur atoms around the central atom in zinc benzenedithiocarboxylate $Zn(C_6H_5CSS)_2$ form a strongly distorted tetrahedron[300], while in vanadium benzenedithiocarboxylate $V(C_6H_5CSS)_4$ and phenylmethanedithiocarboxylate $V(C_6H_5CH_2CSS)_4$ they form an almost ideal dodecahedron[263,301,302] and in chromium benzenedithiocarboxylate $Cr(C_6H_5CSS)_3$ a distorted octahedron[303]. Crystalline nickel trimethylmethanedithiocarboxylate $Ni[(CH_3)_3CCSS]_2$ is dimeric, since bonds are formed between the nickel atoms and the sulphur atoms in another molecule[304]. The coordination of the sulphur atoms is square planar. Nickel phenylmethanedithiocarboxylate $Ni(C_6H_5CH_2CSS)_2$ is also dimeric, but in this case there is a bond between the nickel atoms[305]. The sulphur atoms surrounding each nickel atom are located in the same plane. Nickel benzenedithiocarboxylate $Ni(C_6H_5CSS)_2$ is a trimer formed by bonds between the nickel atoms and the sulphur atoms in another molecule[306]. The coordination of sulphur atoms about the nickel is square planar.

In dimeric palladium benzenedithiocarboxylate $Pd(C_6H_5CSS)_2$, there are bonds between the palladium and the sulphur atoms in another complex molecule[307]. However, the platinum 4-isopropylbenzenedithiocarboxylate dimer $Pt(C_3H_7C_6H_4CSS)_2$ is formed as a result of bonds between the platinum atoms[289,308]. The sulphur atoms in this compound form a square antiprism, two faces of which contain platinum atoms. Two ligands are then in the bridging positions and are linked to both platinum atoms.

In all the dithiocarboxylates investigated by X-ray diffraction, the two bonds between carbon and sulphur are virtually identical, which indicates the equalisation of electron density:



The length of the bond between the carbon of the dithiocarboxy-group and the carbon of the group R depends on the nature of the latter. If it is aliphatic (this also applies to $C_6H_5CH_2$), the length of this bond corresponds to that of a single bond. However, if the group is aromatic (C_6H_5), the bond length is in the range 1.5–1.5 Å, which indicates a partial double bond character of the linkage, i.e. conjugation over the entire ligand, which is consistent with the conclusions reached in the study of vibrational spectra [see formula (XV)]. Thus three resonance forms contribute to the structure of the ligand:



4. Complex Metal Dithiocarboxylates in Solution

Complex dithiocarboxylates can be extracted from an aqueous medium by organic solvents. The extractability of metal benzene-[309], naphthalene-1-[310], pyrrole- and indole-[53], and quinoline-2- and quinoline-4-dithiocarboxylates[162] by various extractants has been tested qualitatively. The dependence of the optical density of the extract on the pH of the aqueous phase has been elucidated for the extraction of cyclohexane-[154], phenylmethane-[155,265–268], benzene-[269,274], 2-hydroxybenzene-[148,275], 4-hydroxybenzene-[159,276], 2,4-dihydroxybenzene-[277,278], 2,3,4-trihydroxybenzene-[277], 3,4-methylenedihydroxybenzene-[148], 4-chlorobenzene-[270,271,274,279], 4-methylbenzene-[270-274], naphthalene-1-[280], naphthalene-2-[50], furan-2-[148], indole-, and pyrrole-dithiocarboxylates[281,311]. Many of these are extracted from an extremely acid medium.

The molecular weights of chromium(III), cobalt(III), indium, rhodium(III), palladium(II), iridium(III), and platinum(II) phenylmethane- and benzene-dithiocarboxylates dissolved in benzene have been determined by the osmometric method[156], which has also been used to determine the molecular weights of iron(III) phenylmethane- and benzene-dithiocarboxylates in chloroform solutions[264]. The molecular weights of vanadium methane-, phenylmethane, benzene-, and 4-methylbenzene-dithiocarboxylates[263], nickel methane-, trimethylmethane-, phenylmethane-, and benzene-dithiocarboxylates[163], and of the mixed complex[20] $C_6H_5CSSMn(CO)_4$ in solutions have also been determined. Polymeric species were not detected, with the exception of nickel trimethylmethanedithiocarboxylate.

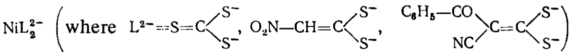
The usual methods have been employed to determine the compositions of the dithiocarboxylates extracted: the isomolar series [continuous variations], molar ratios, equilibrium shift, and other methods as well as the dependence of the formation function[312] and the Leden function[313] on the excess of ligands. In most cases, the composition of the complexes is consistent with the valence of the complex-forming agent[147,159,267-271,273-275,277,278,280,287,311]. However, there are exceptions. For example, nickel forms several compounds[159,276], bivalent cobalt reacts in proportions of 1 : 3,[159,267,270,275,277,287], and molybdenum(V, VI) reacts in proportions of 1 : 2 or 1 : 3.[147,275,277,280]

The stability constant of osmium 2-aminocyclopent-1-ene-1-dithiocarboxylate (2.5×10^9) has been determined in aqueous ethanol[314]. The two-phase stability constants of a number of dithiocarboxylates (the ratios of the concentrations of the complexes in the organic phase to the products of the concentrations of metal ions and free ligands in the aqueous phase) have been determined for a number of dithiocarboxylates. The constants for naphthalene-1-dithiocarboxylates in the water–chloroform system[315] are between 10^9 and 10^{40}. The two-phase stability constants of hydroxybenzenedithiocarboxylates found in the water–3-methylbutanol system[316] are in the range from 10^9 to 10^{22} and those of 2,4-dihydroxybenzenedithiocarboxylates[278] are in the range between 10^5 and 10^{16}.

Attempts have been made at a chromatographic separation of naphthalene-1-dithiocarboxylates using toluene–heptane mixtures as the solvent[317,318].

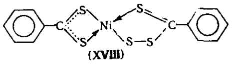
5. Metal Perthiocarboxylates

At the end of the 1940's, it was observed[319] that nickel benzenedithiocarboxylate $(C_6H_5CSS)_2Ni$ combines with sulphur to form a compound in which there are 5 sulphur atoms for each nickel atom. Immediately after the establishment of this fact, it was suggested that the compound formed is a dinuclear complex of nickel(IV).[319-321]. However, the study of the reactions involving the addition of elemental sulphur to ene-1,1-dithiol complexes of nickel



$$NiL_2^{2-}\ \left(\text{where } L^{2-} = S{=}C(S^-)_2,\ O_2N{-}CH{=}C(S^-)_2,\ (C_6H_5{-}CO)(NC)C{=}C(S^-)_2\right)$$

showed that the nickel remains bivalent under these conditions and the sulphur atom is inserted in the four-membered chelate ring, expanding it into a five-membered ring[322]. This suggested that sulphur adds similarly to nickel benzenedithiocarboxylate. Somewhat later, it was shown[323] that this does indeed entail the formation of nickel benzeneperthiocarboxylate benzenedithiocarboxylate(XVIII):



(XVIII)

A number of other perthiocarboxylate dithiocarboxylates as well as perthiocarboxylates of metals such as zinc, nickel, iron(III), cobalt(III), palladium(II), and platinum(II) have also been obtained[292,324-327]. For this purpose, zinc perthiocarboxylates are synthesised first. The corresponding aldehyde RCHO in tetrahydrofuran solution is treated with $(NH_4)_2S_2$ and the resulting perthiocarboxylate ions are precipitated in the form of the nickel complex $(RCSSS)_2Zn$. The latter complex is used to synthesise the perthio-complexes of other elements with the aid of the corresponding double decomposition reactions.

Nevertheless, one should note that the formation of perthio-complexes has also been observed in the direct interaction of bivalent nickel and cobalt ions with 2-aminocyclopent-1-ene-1-dithiocarboxylate ions; one molecule of the reactant then decomposes and liberates a sulphur atom, which is necessary for the formation of the five-membered chelate ring[292].

The electronic absorption spectra of a number of perthio- and perthio-dithio-complexes have been published[163,324,326]. On passing from nickel benzenedithiocarboxylate to the benzeneperthiocarboxylate benzenedithiocarboxylate, the charge-transfer band undergoes a hypsochromic shift (approximately 60 nm) and, on passing to the nickel bis(perthio)-complex, the shift is even greater (approximately 180 nm).[324]

X-Ray diffraction analysis of zinc[328], nickel[326-328], and iron(III)[325,329], perthiocarboxylate complexes has shown that all the atoms of the five-membered chelate ring are in the same plane.

6. Applications of Metal Dithiocarboxylates

In view of their high stability in air and in aqueous alkaline solutions, quaternary ammonium, phosphonium, and arsonium dithiocarboxylates can be used as a convenient form for the storage of dithiocarboxylic acids. These compounds have also been proposed as analytical reagents[242].

Dithiocarboxylates are used in analytical chemistry to detect and determine the corresponding elements. Sodium antipyrine-, 3-antipyrine-, and isoantipyrine-dithiocarboxylates have been proposed for the detection of nickel ions[330]. Tervalent arsenic can be detected with the aid of tetraethylammonium naphthalene-1-dithiocarboxylate[331].

Palladium cyclohexanedithiocarboxylate can be used for the extraction-photometric determination of this element[154]. Palladium benzenedithiocarboxylate[332], iron 4-methyl- and 4-chloro-benzenedithiocarboxylates[165], molybdenum 4-hydroxy-3-methoxy-benzenedithiocarboxylate[147], nickel 4-hydroxy-benzenedithiocarboxylate[276], arsenic naphthalene-1-dithiocarboxylate[333], nickel 2-hydroxynaphthalenedithiocarboxylate[334], and nickel 2-aminocyclopent-1-ene-1-dithiocarboxylate[241] have been suggested for the extraction-photometric determination of the corresponding elements. In the case of nickel 1-hydroxynaphthalenedithiocarboxylate[335] and osmium 2-aminocyclopent-1-ene-1-dithiocarboxylate[314], photometric measurements are made on ethanol solutions in which the solubility of these complexes is fairly high. Nickel 2-hydroxynaphthalenedithiocarboxylate can also be used for the gravimetric determination of nickel[334].

Several methods for the quantitative determination of the elements with the aid of antipyrine-, 3-antipyrine-, and isoantipyrine-dithiocarboxylic acids have been proposed. Nickel[330] and cobalt[336] can be determined gravimetrically with the aid of these reagents. A solution of cobalt antipyrine-4-dithiocarboxylate in pyridine is suitable for the photometric determination of cobalt[337]. A chloroform solution of nickel antipyrine-4-dithiocarboxylate can be used for the determination of mercury: the decrease of colour intensity on shaking with solutions of mercury salts is proportional to the amount of mercury[338]. The double decomposition reaction occurring when an aqueous solution of nickel nitrate is shaken with chloroform solutions of bismuth, lead, and thallium antipyrine-4-dithiocarboxylates can be used for the photometric determination of the last three elements[339].

Many metal dithiocarboxylates are highly effective fungicides and can be used to protect fruit trees from fungal disease. Nitromethane-[87,340], benzene-[341], chlorobenzene- (from mono- to penta-chlorobenzene-)[342,343], and 2-hydroxynaphthalene-dithiocarboxylates[341] have been proposed for this purpose. Metal dithiocarboxylates can be used as accelerators of the vulcanisation of raw rubber. It is postulated that they promote the cleavage of the eight-membered sulphur molecule in this process[344].

Various impurity elements can be removed from the surface of silicon $p-n$ structures in the form of 2,4-dihydroxybenzenedithiocarboxylates, which greatly increases the breakdown potential and reduces the leakage current[345]. Water-soluble salts can be freed from heavy metal impurities by adding an ethanol solution of 2,4-dihydroxybenzenedithiocarboxylic acid: the dithiocarboxylates of the impurity elements pass to the solid phase together with the precipitated acid[346].

Tetraethylammonium napthalene-1-dithiocarboxylate, which is an effective flotation agent for many sulphide minerals, has been proposed as the collector in the flotation of ores[347].

VI. QUANTUM-MECHANICAL CALCULATIONS

The energy of the $\pi-\pi^*$ transition in the dithiocarboxylate group has been calculated by the Hückel method[348]. The result obtained agrees well with the experimental absorption of sodium methanedithiocarboxylate.

The energies of the lowest vacant and the highest occupied molecular orbitals have been calculated for nine dithiocarboxylic acids[349]. The energies of the lowest vacant levels are correlated with the polarographic half-wave potentials of dithiocarboxylic acids and their esters[350]. The results of the calculation of the energies of the $n-\pi^*$ and $\pi-\pi^*$ transitions in the molecules of 19 dithiocarboxylic acids agree satisfactorily with the experimental data obtained from the electronic absorption spectra of the corresponding methyl esters[230].

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