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METAL COMPLEXES OF THIO-β-DIKETONES

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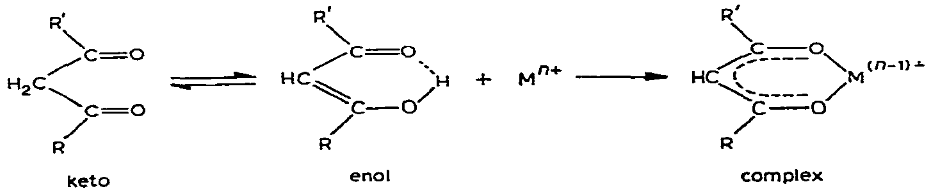
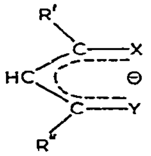
CONTENTS

A. INTRODUCTION

β-Diketones have been used as chelating agents for many years and compounds of these ligands with nearly all the metals and metalloids are known [1–4]. Replacement of the acidic proton from the enol form by a metal cation will produce a six-membered chelate ring with the two donor oxygen atoms.



This β-difunctional system provides an opportunity for comparison of relative donor properties of atoms in that oxygen can be replaced by other atoms giving metal complexes where the donors are, for example, nitrogen, sulphur, and selenium. In certain cases complexes can be prepared although the free monomeric ligand is unknown [7,8].



X = O,	Y = NR	β-ketoamine[5]
X = O,	Y = S	monothio-β-diketone[6]
X = S,	Y = S	dithio-β-diketone[7]
X = O,	Y = Se	monoseleno-β-diketone
X = Se,	Y = Se	diseleno-β-diketone[8]
X = S,	Y = NR	β-aminothione[9]

The metal complexes using the ligands with oxygen—sulphur and sulphur—sulphur donor atoms will be considered in this review and compared with complexes derived from the parent β-diketone.

B. LIGAND SYNTHESIS

The reaction between hydrogen sulphide and acetylacetone in alcoholic solution in the presence of hydrogen chloride as catalyst was first studied in 1906 [10]. The product, isolated as a colourless solid, was the dithioacetylacetone dimer (Fig. 1).

By the reaction of ethyl acetoacetate with hydrogen sulphide, Mitra [11] successfully prepared ethyl thioacetoacetate.

$$CH_3COCH_2COC_2H_5 + H_2S \xrightarrow[0^\circ C]{HCl/C_2H_5OH} CH_3CSCH_2CO_2C_2H_5$$

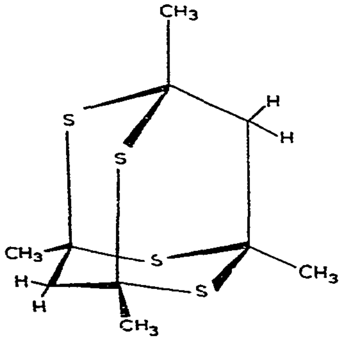


Fig. 1. Structure of the dithioacetylacetone dimer.

This compound had been previously prepared, in poor yield, by treating ethyl chlorocrotonate with potassium hydrosulphide [12].

$$CH_3C(Cl){:}\,CHCO_2C_2H_5 + KSH \rightarrow CH_3C(SH){:}\,CHCO_2C_2H_5$$

The related reaction of ethyl benzoylacetate with hydrogen sulphide gives ethyl thiobenzoylacetate [13]. Monothioacetylacetone was first obtained by the base-catalysed reaction of acetylacetone with hydrogen sulphide [14], and more recently the acid-catalysed reactions of these two reagents has been extensively used by Livingstone and co-workers to give a variety of substituted monothio-β-diketones [6,15,16].

The major obstacle in the preparation of thio-β-diketones by the treatment of β-diketones with hydrogen sulphide is the prevention of the formation of byproducts similar to the dithioacetylacetone dimer shown above. These are readily formed from the thio-β-diketones in solution and to limit the replacement of both oxygen atoms by sulphur and the consequent dimerisation, dilute solutions of the diketone must be used. In addition, the concentration of hydrogen chloride in the solution needed to provide reasonable conversion to the thio derivative depends upon the enol concentration of the β-diketone (Table 1) [6].

TABLE 1

Concentration of hydrogen chloride required to convert the β-diketone to the monothio derivative in the presence of hydrogen sulphide

Compound	*Enol form in alcohol** %	*Concentration of hydrogen chloride required at −10°*
$CH_3COCH_2CO_2C_2H_5$	13	Very dilute
$C_6H_5COCH_2CO_2C_2H_5$	27	Very dilute
$CH_3COCH_2COCH_3$	84	Dilute
$C_6H_5COCH_2COCH_3$	94	Concentrated
$C_6H_5COCH_2COC_6H_5$	90–100	Concentrated
$C_4H_3SCOCH_2COCF_3$	100	Supersaturated

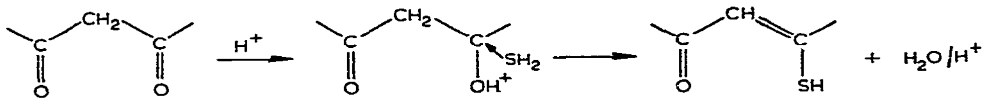
* These values are based on Meyer's original determinations[17]

The observation that the larger enol concentration requires a higher acid concentration suggests that the hydrogen sulphide is reacting with the diketo tautomer.

The order of preference in asymmetric β-diketones for the site of attack by hydrogen sulphide appears to be[6]

$$CH_3 > C_6H_5 > OC_2H_5 \qquad \text{and} \qquad C_4H_3S > CF_3$$

This order of groups adjacent to the attacked carbonyl could indicate that the reaction is not nucleophilic otherwise the site adjacent to the CF_3 group would be preferred In such a highly acidic solution the reactive species could be the H_3S^+ ion [18]. The other suggested mechanism involves protonation of the β-diketone [19].



Site preference in this case would be determined by which carbonyl group is protonated. This would be the one furthest away from the most electron-withdrawing group, giving rise to the order found above

In all cases investigated of the reaction with asymmetrical β-diketones, $R'COCH_2COR$ only one of the possible isomers is obtained To distinguish which isomers were formed mass spectrometry was used [6]. This limitation on the formation of isomers is an obvious disadvantage of this method of preparation. In addition, although the yields are generally good, because the reactant solution must be dilute a practical limitation is imposed

A second method of preparation involves the Claisen condensation of thiono- or dithio-esters with ketones of the general formula CH_3COR [20–22].

$$R'CSOC_2H_5 + CH_3COR \xrightarrow[Et_2O]{Na\,NH_2} R'CSCH_2COR + C_2H_5OH \text{ (Na salts)}$$

$$R'CSSC_2H_5 + CH_3COR \xrightarrow[Et_2O]{Na\,NH_2} R'CSCH_2COR + C_2H_5SH \text{ (Na salts)}$$

The better starting materials, thiono-esters, can be easily synthesised from nitriles

$$R'CN + C_2H_5OH + HCl \xrightarrow{Et_2O} R'C(OC_2H_5)\cdot NH.HCl \xrightarrow[py]{H_2S} R'CSOC_2H_5$$

This method enables any specific thio-β-diketone to be prepared. The ligands are yellow or orange liquids and solids most of which have an unpleasant odour Table 2 contains a list of thio-β-diketones prepared to date.

TABLE 2

Monothio-β-diketones, $R^1CSCH_2COR^2$, prepared to date

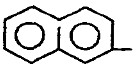
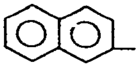
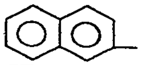
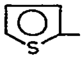
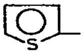
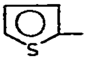
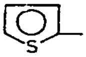
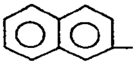
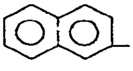
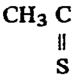
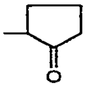
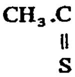
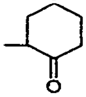
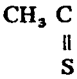
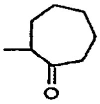
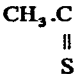
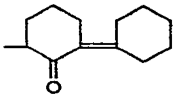
R^1	R^2	Mp./b.p (°C)	Ref
CH_3	OCH_3	Not purified	49
CH_3	OC_2H_5	75–80/12 mm 75–80/9 mm	11 6
CH_3	CH_3	50–55/10 mm (6)	6, 14, 21, 22
CH_3	CF_3	50/20 mm	15
CH_3	C_6H_5	25–26 (21), 28 (6)	6, 21, 22
CH_3	$t\text{-}C_4H_9$	90–92/15 mm	21
CH_3		44–45	21
CH_3		97–98	21
C_6H_5	OC_2H_5	102/0 7 mm	6, 13

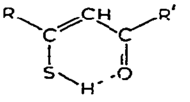
TABLE 2 (continued)

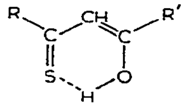
R'	*R²*	*M.p./b.p. (°C)*	*Ref.*
C_6H_5	CH_3	61–62	21, 22
C_6H_5	C_6H_5	82 (20)	6, 20, 22, 48
C_6H_5	CF_3	95/5 mm	39
C_6H_5		108–109	21
t-C_4H_9	CH_3	87–89/15 mm	77
t-C_4H_9	t-C_4H_9	50–60/8 mm 71–73/0.7 mm	6, 77 77
iso-C_3H_7	CH_3	79–80/15 mm	21
iso-C_3H_7		34–36	21
p-$CH_3C_6H_4$	CF_3	Decomposed	16
p-$CH_3OC_6H_4$	CF_3	Decomposed	16
p-BrC_6H_4	CF_3	110/2 mm	16
	CH_3	75–76	21
	CF_3	74	6
		86–86.5	21
	CF_3	102/1 mm	16
	CH_3	86 -87	21
	C_6H_5	114–115	21
 $CH_3\underset{\underset{S}{\|}}{C}$		80–83/0 5 mm	77
 $CH_3.\underset{\underset{S}{\|}}{C}$		90–92/0 1 mm	21
 $CH_3\underset{\underset{S}{\|}}{C}$		110–112/0 8 mm	77
 $CH_3.\underset{\underset{S}{\|}}{C}$		69	21

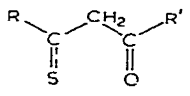
The nomenclature of these compounds can be based either on a systematic method or by using a prefix on the trivial name of the parent β-diketone. Because of the extensive use of trivial names for common β-diketones the latter system has already been used widely The systematic nomenclature is made more difficult by the possible existence of three tautomeric forms The problems which arise in giving trivial names to unsymmetrical thio-β-diketones can be overcome by placing the prefix thio before the relevant part of the name. Thus $C_6H_5CSCH_2COCH_3$ becomes thiobenzoylacetone and $C_6H_5COCH_2CSCH_3$ benzoylthioacetone In this review the trivial names will be used as far as possible

C STRUCTURE OF THE LIGANDS

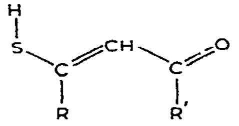
Like their oxygen analogues, mono-thio-β-diketones almost certainly exist in tautomeric forms, the most probable structures being

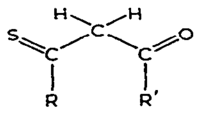

cis thioenol

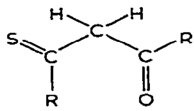

cis enol


cis thioxo

As well as these tautomers, several *trans* forms are also possible, for example







Ferraro et al [23], using dipole moment measurements, concluded that in ethyl thioacetoacetate the preferred orientation of the tautomers is *trans*. They suggest that the presence of the sulphur atom leads to considerable steric hindrance in the *cis* forms

The remaining studies have centered on the distribution between the keto and enol forms and in this respect the conclusions reached by various workers are rather confusing Most of the results have involved the interpretation of either NMR or infrared spectra of the compounds although some earlier data were obtained using a titrimetric procedure for the estimation of the thioenol content [13,24].

The NMR spectra indicate a predominance of the enol form, there being no evidence for any methylene proton signal [13,26–28] and as only one band is observed in the enol–thioenol proton region there is a significant concentration of only one isomer [22–25] Whether this proton is attached to the sulphur (thioenol) or oxygen (enol) atom is more difficult to decide. The shift of the signal to higher τ values on comparison with the dioxygen analogues suggests the presence of the thioenol form [22,25] However, this is contradicted by an intensive study of the isomeric ligands thiobenzoylacetone and benzoylthioacetone [26]. In both compounds the methyl resonance is split by interaction with the vinyl proton [$J \sim ½$ c/sec] but in the case of thiobenzoylacetone this was further split by the enol–thioenol proton [$J = 0.32$ c/sec] Also, only in this compound did the enol–thioenol hydrogen resonance show unresolved splitting presumably by the methyl group. These interactions suggest that both compounds exist in the enol rather than the thioenol form.

The appearance of a broad band at 2450 cm^{-1} in the infrared spectra of several liquid thio-β-diketones suggests the presence of an intramolecularly hydrogen bonded thiol group [13,22,29]. The strong carbonyl absorption at 1675 cm^{-1} in ethyl thiobenzoylacetate has been assigned to the carbonyl group of this thioenol tautomer while a weaker band at 1740 cm^{-1} was thought to arise from the presence of the thioxo isomer [13]

The electronic spectra support the conclusion that little of the thioxo tautomer is present. This is based on the observed molar extinction coefficients ($\epsilon \sim 100$) of a band in the range 420–500 nm arising from transitions in the multiple linkages of the functional groups [47]. In the thioxo form this band has a much lower extinction coefficient, for example ethyl thiobenzoylacetate, $\epsilon = 1\ 6$ [13]

The thio-β-diketones are stronger acids than the parent β-diketones [21,30–32] and these results together with the ease of oxidation to disulphides certainly indicate the presence of a small equilibrium amount of thioenol form, further work is required before the structure of these compounds is fully understood.

D REACTIONS OF MONOTHIO-β-DIKETONES WITH METAL COMPOUNDS

In favourable conditions, reaction of thio-β-diketones with metal salts (halides and acetates have been commonly used), leads to the formation of complexes. Although complexation occurs readily with nearly all metals, the reaction is accompanied, in the majority of cases, by oxidation–reduction reactions of the metal – ligand system The two reaction types may occur concurrently and the products depend very much on the thio-β-diketone used, the metal, especially its oxidation state, and the reaction conditions.

The oxidation of thiols to disulphides is promoted by metal ions [33], in particular by those having high oxidation states Thus, in general, attempts to prepare manganese (III) complexes have resulted in complete oxidation of the ligand [34]. In some cases, as with iron(III), complexing occurs alongside oxidation. Increases in temperature favour the oxidation reactions

Sometimes reaction with a metal in a low oxidation state causes reduction of some of the ligand and formation of a metal complex of a higher oxidation state For example, reactions of titanium(III) chloride with thiodibenzoylmethane produces a strong smell of hydrogen sulphide and a titanium(IV) compound [29] Further examples of oxidation of the metal are provided by the conversion of iron(II) to iron(III) [34], and that only one ferrous complex, bis(thiodibenzoylmethanato)bispyridineiron(II) is known [35]. Similar oxidation from cobalt(II) to (III) occurs readily and the only reported cobaltous complex is bis(thiodibenzoylmethanato)cobalt(II) [35].

The ease of ligand oxidation is also variable depending upon the terminal groups R and R′. Of the thio-β-diketones, thiodibenzoylmethane is one of the harder to oxidise and forms particularly stable compounds. So while tris(thiodibenzoylmethanato)iron(III) is easily prepared and quite stable, tris(thioacetylacetonato)iron(III) can only be obtained in low yield and the solid decomposes over a few weeks at room temperature in vacuo [29]. This point is further emphasised by results of thio-β-diketone complexes of copper. From Table 3 it can be seen that the substituents play an important part in determining the oxidation state of the product. This behaviour of the ligand may be attributed to variation of the electron density on the two donor atoms [34] The increase of electron density on the sulphur atom facilitating the oxidation of the ligand

However, despite the complications introduced by ligand oxidation reactions, metals

TABLE 3

Copper complexes of monothio-β-diketones $R^1CSCH_2COR^2$

R^1	R^2	*Copper(I)*	*Copper(II)*	*Ref*
p-$CH_3C_6H_4-$	$-CF_3$	X	X	16
p-$CH_3OC_6H_4-$	$-CF_3$	X	X	16
p-BrC_6H_4-	$-CF_3$	X	X	16
C_4H_3O-	$-CF_3$	O	X	16
C_6H_5-	$-C_6H_5$	O	X	34
CH_3-	$-CH_3$	X	O	34
CH_3-	$-OC_2H_5$	X	O	34
CH_3-	$-CF_3$	X	O	15

X = complex known, O = complex unknown

complex readily with monothio-β-diketones. Several types of bonding with metal, paralleling the observed bonding in β-diketonates, can occur

(i) Chelation, involving bonding through both oxygen and sulphur as an anion.
(ii) Donation, through sulphur only as an anion.
(iii) Donation, through oxygen only as an anion.
(iv) Donation, through carbon as an anion.
(v) Addition, without loss of hydrogen, involving either chelation or simple donation.

Of these five alternatives (i), (iv) [4] and (v) [36] occur for β-diketones. With thio-β-diketones, chelation of type (i) occurs readily, and of the other alternatives only type (ii) has been observed to date Since the thio-β-diketones are stronger acids than β-diketones and the latter do not form many addition compounds, bonding of type (v) is unlikely.

Chelation is achieved with most metals by direct reaction of a metal halide, or acetate, in a suitable solvent with the thio-β-diketone. Sometimes the presence of a base, triethylamine, pyridine, etc., improves the reaction. The metal chelates are usually deeply coloured compounds, insoluble in water, slightly soluble in alcohols and benzene and easily soluble in chloroform and acetone

Table 4 lists typical metal complexes prepared so far. Interest has centered mainly on metals in the first transition series but a few elements in the other series and the lanthanons [37] have been studied. Although the range of ligands and metals on which work has been published is extensive, information on structure and other physical properties is scant. Some metals, particularly nickel, palladium, platinum, and iron, have received more detailed investigation.

E STEREOCHEMISTRY

Detailed stereochemistry of thio-β-diketone metal complexes has not received much attention. However, the structure of bis(thiodibenzoylmethanato)palladium(II) and the corresponding platinum compound have been determined by X-ray crystallography [38]. These compounds have the *cis* square planar structure.

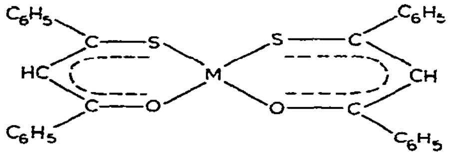
TABLE 4

Typical thio-β-diketone metal complexes

Element	*Complex*	*Ref*
Titanium(IV)	$Ti(PhCSCHCOPh)_2Cl_2$	29
	$[Ti(PhCSCHCOPh)_3]^+$	29
Vanadium(IV)	$VO(PhCSCHCOPh)_2H_2O$	35, 88
	$V_2O_2(C_4H_3SCSCHCOCF_3)_4$	15
Vanadium(III)	$V(PhCSCHCOCH_3)_3$	40
	$V(PhCSCHCOPh)_3$	29
Chromium(III)	$Cr(PhCSCHCOPh)_3$	29
Manganese(III)	$Mn(t\text{-}BuCSCHCO\text{-}t\text{-}Bu)_3$	34
Manganese(II)	$Mn(PhCSCHCOPh)_2(py)_2$	35
Iron(III)	$Fe(PhCSCHCOPh)_3$	34, 35
	$Fe(CH_3CSCHCOCH_3)_3$	29, 59
	Others	15, 58, 59
Iron(II)	$Fe(PhCSCHCOPh)_2(py)_2$	35
Cobalt(III)	$Co(PhCSCHCOPh)_3$	24, 46, 48
	$Co(CH_3CSCHCOCH_3)_3$	22, 34
	Others	15, 18, 22, 86
Cobalt(II)	$Co(PhCSCHCOPh)_2$	35
Nickel(II)	$Ni(PhCSCHCOPh)_2$	6, 34, 46, 48
	$Ni(CH_3CSCHCOCH_3)_2$	6, 34
	Others	15, 16, 39, 49, 86
Copper(II)	$Cu(PhCSCHCOPh)_2$	46, 48
	$Cu(CH_3CSCHCOPh)_2$	22
	Others	16, 34
Copper(I)	$Cu(p\text{-}CH_3C_6H_4CSCHCOCF_3)$	16
	Others	15, 16, 34
Zinc(II)	$Zn(PhCSCHCOPh)_2$	34, 46, 48
	Others	15, 22, 39
Ruthenium(IV)	$Ru(PhCSCHCOPh)_4$	35
Ruthenium(III)	$Ru(PhCSCHCOPh)_3$	35
Rhodium(III)	$Rh(PhCSCHCOPh)_3$	34, 46
Palladium(II)	$Pd(PhCSCHCOPh)_2$	34, 46, 48
	$Pd(CH_3CSCHCOCH_3)_2$	22
	Others	15, 39, 49
Silver(I)	$Ag(PhCSCHCOPh)$	34, 46
Cadmium(II)	$Cd(PhCSCHCOPh)_2$	34, 46
	Others	15, 34
Osmium(IV)	$Os(PhCSCHCOPh)_4$	35
Osmium(III)	$Os(PhCSCHCOPh)_3$	35

TABLE 4 (continued)

Element	*Complex*	*Ref*
Platinum(II)	$Pt(PhCSCHCOPh)_2$	34, 46
	Others	15, 39
Mercury(II)	$Hg(PhCSCHCOPh)_2$	34
	Others	15
Beryllium(II)	$Be(PhCSCHCOPh)_2$	55
Gallium(III)	$Ga(PhCSCHCOPh)_3$	46
Indium(III)	$In(PhCSCHCOPh)_3$	46
Thallium(I)	Tl(PhCSCHCOPh)	46
Tin(IV)	$Sn(PhCSCHCOPh)_2Cl_2$	46
Tin(II)	$Sn(PhCSCHCOPh)_2$	46
Lead(II)	$Pb(PhCSCHCOPh)_2$	46, 48
	Others	15
Bismuth(III)	$Bi(PhCSCHCOPh)_3$	46



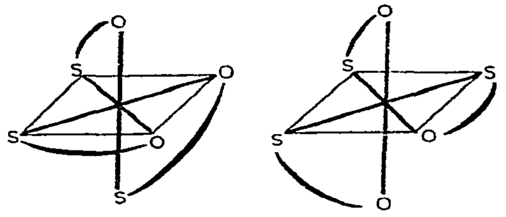
where M = Pd, Pt In the palladium complex the Pd–S bond lengths are 2 26 and 2.22 Å, and the S–Pd–S angle is close to 90°.

All nickel(II) chelates of thio-β-diketones are diamagnetic [6] and readily add two molecules of an aromatic base to form adducts such as bis(thioacetyltrifluoroacetonato)-bispyridinenickel(II) [39] which are paramagnetic [$\mu_{eff} = 3.15$ B.M] and presumably six-coordinate The nickel chelates are therefore also square planar, probably with a similar structure to the palladium and platinum compounds. In contrast, bis(acetylacetonato) nickel(II) is trimeric, each nickel atom being six-coordinate [3] and paramagnetic.

Studies of the NMR spectra of some tris six-coordinate metal chelates have revealed their qualitative stereochemistry [40]. The vanadium(III) and cobalt(III) chelates with ligands of the type, CH_3COCH_2CSR, where R = CH_3, C_6H_5, *iso*-C_3H_7, *t*-C_4H_9, show only one resonance attributable to the vinyl and one for the methyl groups in their NMR spectra This result is consistent with the compounds existing in the *cis* (*facial*) form, Fig. 2.

The lability of the vanadium(III) compounds ensures an equilibrium isomer distribution. Equilibrium constant determinations on the corresponding asymmetric β-diketone complexes indicate preferential stability of the *trans* (*meridinal*) form [41]. Existence of the compounds as *cis* isomers in the case of thio-β-diketone complexes may arise from non-bonded S—S interactions

The structure and stereochemistry of other common thio-β-diketone metal chelates have not been studied to date. However, the ruthenium(IV) and osmium(IV) chelates of



cis (facial) cis (meridinal)

Fig 2 Isomeric forms of *cis*-tris(thio-β-diketone) complexes

thiodibenzoylmethane are considered to be eight-coordinate The diamagnetism of the ruthenium compound indicates it has a cubic structure [35].

F SPECTRAL STUDIES

Studies of the vibrational and electronic spectra of thio-β-diketones and their metal chelates have provided information on the structure and mode of bonding between the metal and ligand.

(i) Vibrational spectra

Much of the work on infrared spectroscopy is based on analogy with β-diketone complexes. Livingstone et al [6] made the first tentative assignments of the bands in thio-β-diketones following the work of Reyes and Silverstein on ethyl thiobenzoylacetate and previous published assignments of β-diketones Uhlemann and Thomas [21] drew similar conclusions for a number of thio-β-diketones. These correlations are given in Table 5.

TABLE 5

Infrared absorption bands of monothio-β-diketones

Group	*Absorption band* *(cm^{-1})*
$\nu(\mathrm{C}\overset{\text{---}}{\text{—}}\mathrm{O})$	1670 – 1590
$\nu(\mathrm{C}\overset{\text{---}}{\text{—}}\mathrm{C})$	1638 – 1530
$\nu(\mathrm{C}\overset{\text{---}}{\text{—}}\mathrm{S})$	1270 – 1190
$\nu(\mathrm{C}—\mathrm{S})$ + $\delta(\mathrm{CH_3})$	837 – 805
$\nu(\mathrm{C}{=}\mathrm{O})$ (ketonic)	1730 – 1720

Nickel(II) chelates were also investigated by Livingstone et al. [6] who found that, whereas the first strong band below 2000 cm^{-1} in the free ligand occurs at 1670–1590

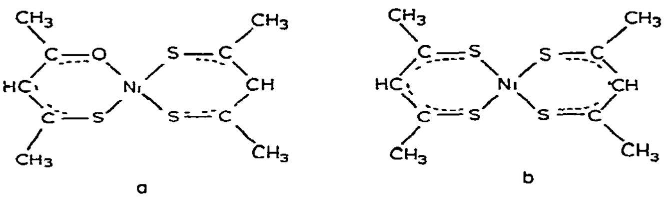


Fig 3 Nickel(II) complexes with monothioacetylacetone and dithioacetylacetone

cm^{-1} (ν (C = O)), the first strong band in the spectra of the nickel chelate occurs slighttly lower, 1590 – 1540 cm^{-1}. In contrast to the free ligand assignments this band is attributed to the C $\overset{\cdots}{-}$ C stretch. This was based on Nakamoto's results on metal acetylacetonates [42]. However, the assignments by Nakamoto concerning the relative positions of the C $\overset{\cdots}{-}$ O and C $\overset{\cdots}{-}$ C stretching vibrations in metal chelates have been shown to be in error by ^{18}O substitution in tris(acetylacetonato)chromium(III) [43]. In fact the higher frequency band being susceptible to ^{18}O substitution confirms the earlier work on metal acetylacetonates in assigning this band as a C $\overset{\cdots}{-}$ O stretch. This latter result is confirmed for thio-β-diketonates by the infrared spectra of the nickel chelates shown in Fig. 3(a) and (b). In bis(dithioacetylacetonato)nickel(II), Fig. 3(b), no infrared absorption band, excluding C — H, appears above 1500 cm^{-1} but the appearance of a strong band at 1550 cm^{-1} in (monothioacetylacetonato) (dithioacetylacetonato) nickel(II), Fig. 2(a), confirms the assignment of the latter band as ν(C = O) [19,44]. Although quantitative calculations on chelates of monothio-β-diketones have not been reported, some normal coordinate analyses have been carried out on a series of square planar chelates of divalent metals with dithioacetylacetone. These calculations [19,45] show that the C $\overset{\cdots}{-}$ S stretching frequency occurs at 700 cm^{-1}. By comparison the C $\overset{\cdots}{-}$ S stretching frequency in bis(monothioacetylacetonato) nickel(II) is reassigned at 720 and 660 cm^{-1} In addition the Ni — S and Ni — O stretching frequencies are also given. The revised assignments for bis(monothioacetylacetone) nickel(II) are in Table 6. A strong band at ~ 1260 cm^{-1} which is present in all thio-β-diketonates is notably absent from these assignments. The reassignment of the ν(C = S) in bis(monothioacetylacetonato) nickel(II) makes Livingstone's original conclusion that the C $\overset{\cdots}{-}$ S vibration in thioacetylacetone and other compounds lies in the region of 1270 cm^{-1} dubious.

The infrared spectra of other metal chelates with a variety of thio-β-diketones have been recorded with assignments following those of Livingstone. Uhlemann and Thomas [46] attributed the band at ~ 1540 cm^{-1} to the C $\overset{\cdots}{-}$ C stretching vibration of the chelate ring and the band at ~ 1590 cm^{-1} to ν(C = O) in monothiodibenzoylmethane complexes However, the band at ~ 1590 cm^{-1} may be due to an in-plane skeletal vibration of the phenyl rings and the 1540 cm^{-1} band to the C $\overset{\cdots}{-}$ O vibration These suggestions are consistent with the revised assignments on bis(monothioacetylacetonato) nickel(II)

From a comparison of the spectra of the ligands and their metal complexes it can be seen that chelation causes a drop in frequency of the carbonyl stretching mode, Table 7. In infrared studies with metal β-diketonates correlations have been drawn between the

TABLE 6

Infrared assignments of bis(thioacetylacetonato) nickel(II)

Frequency (cm^{-1})	*Assignment*
1562	$\mathrm{C} \overset{\cdots}{—} \mathrm{O}$ stretch
1473	$\mathrm{C} \overset{\cdots}{—} \mathrm{C}$ stretch
1415	CH_3 deformation
1370	CH_3 deformation
1360	
1335	C — C stretch
1310	C — H in plane bend
1292	
1025	CH_3 rocking mode
810	C — H out of plane bed
721	C — S stretch
661	C — S stretch
495	Ni — O stretch
487	
365	Ni — S stretch

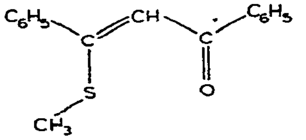
carbonyl stretching frequency, or the metal–oxygen stretching frequency, and the thermodynamic stability constants [42]. No such correlations have yet been attempted with thio-β-diketonates.

In contrast to the chelate compounds, the spectra of complexes of silver(I) copper(I), cadmium(II), and mercury(II) are indicative of coordination to the metal through sulphur only. These compounds show a strong carbonyl absorption above 1600^{-1} attributed to a non-coordinated $\mathrm{C} \overset{\cdots}{—} \mathrm{O}$ group [34,46] The spectra of thiodibenzoylmethane complexes of silver, cadmium and mercury closely resemble that of S-methyl-1,3-diphenyl-3-mercaptoprop-2-en-1-one [34], I, which has a carbonyl absorption at 1640 cm^{-1}. These observations indicate only weak bonding, if any, between the oxygen donot atom and the metal

TABLE 7

Carbonyl absorption of monothioacetylacetone and its metal chelates.

Compound	*$\mathrm{C} \overset{\cdots}{—} \mathrm{O}$ frequency (cm^{-1})*	*Ref*
$CH_3CSCH_2COCH_3$	1645	34
$Ni(CH_3CSCHCOCH_3)_2$	1566	34
$Co(CH_3CSCHCOCH_3)_2$	1580	34
$[Ti(CH_3CSCHCOCH_3)_3]^+$	1525	29
$Fe(CH_3CSCHCOCH_3)_3$	1565	29



I

Although copper forms only a copper(II) chelate with thiobenzoylmethane, copper(I) complexes of other thio-β-diketones, for example, ethyl thioacetoacetate [34], thioacetyltrifluoroacetone [15], have been isolated These compounds again exhibit a strong carbonyl absorption above 1600 cm^{-1} indicating non-coordinated C ⩵ O. A comparison of the carbonyl vibrations in the silver, mercury, and cadmium compounds is made in Table 8

To date no work on the Raman spectra of the ligands or their complexes has been published.

TABLE 8

Infrared spectra of non-chelated metal complexes of thiodibenzoylmethane

Compound	*C ⩵ O frequency (cm^{-1})*	*Ref*
$PhCSCH_2COPh$	1555	34
$PhC(SCH_3)CHCOPh$	1640	34
Ag(PhCSCHCOPh)	1615	34, 46
$Hg(FhCSCHCOPh)_2$	1630, 1622	34, 46
$Cd(PhCSCHCOPh)_2$	1605, 1595	34, 46
$Cu(PhCSCHCOPh)_2$	1550*	34

* For comparison, previously assigned as C ═ C.

(ii) Electronic spectra

Published work on the ultraviolet and visible spectra of metal complexes of thio-β-diketones has been largely centred on the nickel(II) chelates, which have similar spectra to other square planar nickel(II) complexes. Also, the conclusions reached on the bonding of class B metals from the infrared spectra are supported by the electronic spectra of these compounds.

The electronic spectra of a large number of monothio-β-diketones have been recorded by Uhlemann and Thomas [21] and Chaston and Livingstone [47]. High-intensity bands are observed in two regions 290—400 nm and 350—460 nm which are associated with π→π* transitions of the ligand hydrogen-bonded chelate ring. The spectrum of thiodibenzoylmethane is shown in Table 9 together with the assignments made by Chaston [47]. Initial studies on thiodibenzoylmethane included the recording of absorption maxima of several metal chelates as being in the range 410—415 nm [48]. The assignment of ligand π→π*,

TABLE 9

Electronic absorption spectrum of thiobenzoylmethane

Chloroform solution		*Isooctane solution*		*Assignment*
Wavelength (nm)	*ε (mole^{-1} l^{-1}.cm^{-1})*	*Wavelength (nm)*	*ε (mole^{-1} l^{-1}.cm^{-1})*	
490	240	505	170	
413	17,800	408	12,500	$\mathrm{C} \overset{\text{---}}{=} \mathrm{S}$
330	12,700	325	11,000	$\mathrm{C} \overset{\text{---}}{=} \mathrm{O}$
265	8,000	263	7,600	

metal–ligand charge transfer and *d–d* transitions has been made for nickel(II) complexes by Uhlemann and Thomas [21], Chaston et al. [17,49]. The position of the charge transfer and $\pi \rightarrow \pi^*$ transitions are, as expected, very much dependent upon the ring substituents whereas the *d–d* bands are more constant. The assignments of these bands are summarised in Table 10. The first $\pi \rightarrow \pi^*$ transition in the nickel(II) chelates occurs at slightly higher wavelength than in the free ligand consistent with chelation. From the positions of the two *d–d* transitions in relation to these transitions in other nickels(II) chelates with sulphur ligands the following spectrochemical order was constructed.

TABLE 10

Electronic spectra of nickel(II) chelates of monothio-β-diketones

λ (nm)	ε (mole^{-1}.l^{-1} cm^{-1})	*Assignment*
680 – 630	< 100	$d - d$
~ 500	< 100	$d - d$
570 – 400	< 5,000	$d - L_{\pi^*}$
480 – 380	< 7,000	$d - L_{\pi^*}$
500 – 300	< 10,000	$L_\pi - d$
450 – 300	< 50,000	$L_\pi - L_{\pi^*}$
370 – 240	< 50,000	$L_\pi - L_{\pi^*}$ or $L_\sigma - d$

$\mathrm{dtp} < \mathrm{CH_3} — \mathrm{OCH_3} \sim \mathrm{C_6H_5} — \mathrm{OC_2H_5} \sim \mathrm{CH_3} — \mathrm{OC_2H_5} < \mathrm{C_4H_3S} — \mathrm{CF_3} < \mathrm{C_6H_5} — \mathrm{C_6H_5} \sim \mathrm{exan} \sim \mathrm{CH_3} — \mathrm{C_6H_5} \sim t\mathrm{C_4H_9} — t\mathrm{C_4H_9} < \mathrm{CH_3} — \mathrm{CH_3} < \mathrm{dtc}$ $\mathrm{R^1} — \mathrm{R^2} = \mathrm{R^1CSCH_2COR^2}$, dtp = diethyl dithiophosphate, exan = ethyl xanthate and dtc = diethyl dithiocarbamate.

Investigations of the electronic spectra of the class B metal complexes with thiodibenzoylmethane confirm bonding through sulphur only as indicated by infrared spectroscopy[47]. The lower wavelength of the $\pi \rightarrow \pi^*$ transition of the ligand in the silver(I) and cadmium(II) complexes compared to the free ligand and the zinc complex is indicative of less delocalisation of the π-electron system. This conclusion is consistent with bonding through sulphur only In addition, the mercury(II) compound gave an electronic spectrum closely resembling that of the *S*-methyl derivative of thiodibenzoylmethane

(iii) Nuclear magnetic resonance spectra

Little work has appeared concerning proton magnetic resonance data on metal chelates of monothio-β-diketones These data together with the relevant results on the free ligands are given in Table 11. Little variation can be seen in the chemical shifts on chelation of the ligand. This is expected in the complexes studied to date, and is similar to the results found in β-diketonates where no ring current can occur around the chelate ring[50]. Since the presence of a ring current in some β-diketonates of transition metals is still the subject of much discussion, further studies on the proton magnetic resonance spectra of monothio-β-diketonates of the earlier transition metals should prove fruitful.

The use of these spectra in the elucidation of the stereochemistry of complexes has already been mentioned (section E) but because of several isomeric species, arising from the ligand asymmetry, in equilibria in solution the NMR spectra are often complex

TABLE 11

Proton magnetic resonance spectra of some monothio-β-diketone complexes

Compound	*Chemical shift in $CDCl_3$ solution*				*Ref*
	CH	*CH_3CS*	*CH_3CO*	*C_6H_5*	
$C_6H_5CSCH_2COC_6H_5$	2.52			2.00, 2.21	25
Zn^{II} complex	2.45			2.01, 2.21	25
Co^{III} complex	2.53			1.99, 2.16	25
Ni^{II} complex	2.54			2.04, 2.33	25
$CH_3CSCH_2COCH_3$	3.64	7.65	7.87		26
Co^{III} complex	3.70	?	7.80		22
$C_6H_5CSCH_2COCH_3$	3.29		7.78		26
Co^{III} complex	3.42		7.65		40

(iv) Magnetic properties

The replacement of an oxygen atom in a β-diketone by sulphur will obviously affect the physical properties of the ligand and especially its metal complexes introducing, as it does, additional steric and electronic factors The properties of the metal complex which are most sensitive to these changes are the electronic spectra and magnetism Thus it has been shown above that the ligands can be grouped in the spectrochemical series with related sulphur donor ligands. Concerning the magnetic properties of the complexes, it was observed that spin-pairing occurred more readily with these ligands than with the corresponding β-diketones, for example nickel(II) [6]. The factors which affect the magnetic properties of complexes have been fully discussed elsewhere [53], and are beyond the scope of this review, however, a brief discussion of those factors involved in spin-pairing is worth consideration.

In a number of electronic configurations the ground state cannot be uniquely defined as it is dependent upon the strength of the ligand field, the system changing from a maximum value of the total spin quantum number to lower values as the ligand field strength (Δ) increases Octahedral configurations where this change of spin state is possible are d^4, d^5, d^6 and d^7. In these configurations spin-pairing occurs by the transfer of one or two electrons from the higher e_g orbitals to the lower t_{2g} orbitals. The gain in energy of the system resulting in this transfer of electron is, however, offset by the increased Coulombic repulsion energy between the electrons now in the t_{2g} orbitals and the loss of quantum mechanical exchange energy as a result of the spin-pairing process This combination of Coulombic and exchange energy can be represented by π, the "mean spin-pairing energy" of d electrons. These two energy terms Δ and π set the limits for spin-pairing to occur, i e. $\Delta > \pi$, low spin, $\Delta < \pi$, high spin. Estimated values of π are available for the first-row transition metals based on Racah parameters for the free metal ions [54]. However, as the interelectronic repulsion in the metal ion is affected by ligand coordination (nephelauxetic effect) these free-ion values may be drastically reduced For example, Fe^{3+}, free ion, $\pi = 30{,}000\ cm^{-1}$ $[Fe(H_2O)_6]^{3+}$ $\pi \simeq 22{,}500\ cm^{-1}$, $[Fe(dtc)_3]^{3+}$ $\pi \simeq 14{,}000\ cm^{-1}$ [55] Thus although the ligand field strength of water is greater than that of diethyldithiocarbamate (dtc) the variation in the magnitude of π allows the weaker ligand to cause spin pairing of the d electrons. In the case of the thio-β-diketonates the sulphur atom, by its increased polarisability and the participation of its d orbitals in π-bonding with the metal, will reduce the value of π below that of the corresponding β-diketonates and so enhance the possibility of spin-paired complexes

When the mean pairing energy, π, is of the same order as the ligand field parameter Δ then the phenomenon of spin isomerism occurs. The magnetic properties of these systems show a substantial variation with temperature as the relative population of the high and low-spin states vary. A full discussion of this topic in octahedral metal complexes has been published [55] and it was shown that in this "crossover" situation the mean pairing energy and the ligand field parameter are related by

$$\Delta\ (\text{high spin}) < \pi < \Delta\ (\text{low spin})$$

It should also be noted that Δ is temperature dependent increasing as the temperature is reduced [56]. So as the temperature is decreased the equilibrium will tend to shift towards the low-spin state.

The complexes which have been most fully studied in this context are the iron(III) dithiocarbamates [57], discovery of spin isomerism in the tris(thio-β-diketonate) iron(III) chelates was made by Ho and Livingstone [58], and some of their results are shown in Fig 4 This work has been extended by Cox et al. [59] and their results agree closely with those of

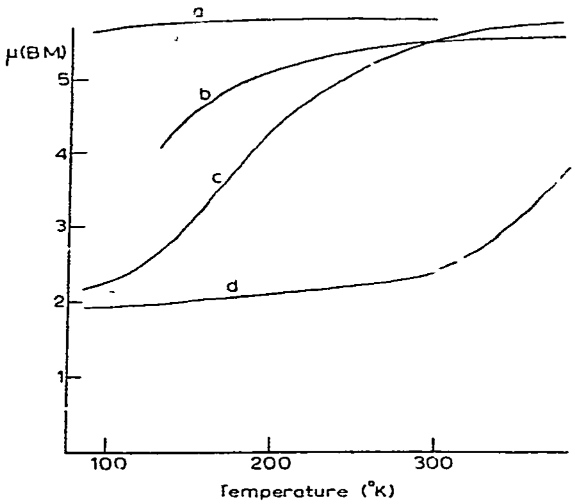


Fig 4. Magnetic moments of iron(III) monothio-β-diketonates from Ho and Livingstone [58]. a, $Fe(C_6H_5CSCHCOOC_2H_5)_3$; b, $Fe(C_4H_3SCSCHCOCF_3)_3$; c, $Fe(C_6H_5CSCHCOC_6H_5)_3$; d, $Fe(C_6H_5CSCHCOCF_3)_3$.

Ho, (Fig. 5 and Table 12) Several interesting variations in the properties of individual complexes are noteworthy. Firstly, the ethyl thiobenzoylacetate complex is totally high-spin and obeys the Curie–Weiss law. Secondly, tris(monothioacetylacetonato) iron(III) shows a remarkably rapid change of spin state at ~ 140°K. This probably indicates the

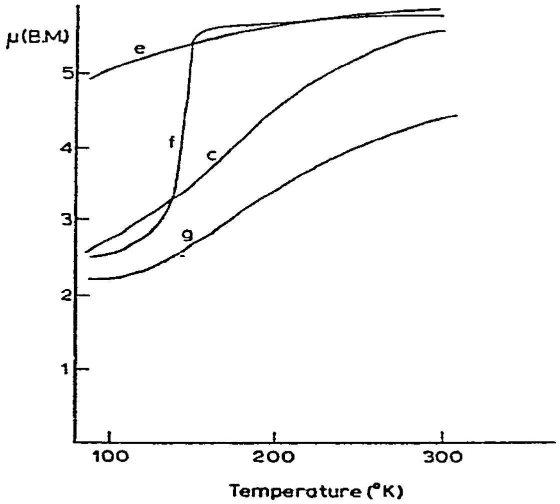


Fig. 5. Magnetic moments of iron(III) monothio-β-diketonates, Cox et al [59]. c, $Fe(C_6H_5CSCHCOC_6H_5)_3$, e, $Fe(C_6H_5CSCHCOCH_3)_3$; f, $Fe(CH_3CSCHCOCH_3)_3$; g, $Fe(CH_3CSCHCOC_6H_5)_3$.

TABLE 12

Magnetic data of iron(III) complexes Fe(R^1CSCHCOR^2)$_3$

$R^1=R^2=Ph$		$R^1=CH_3, R^2=Ph$		$R^1=Ph, R^2=CH_3$		$R^1=R^2=CH_3$	
T (°K)	*(BM)*	*T (°K)*	*(BM)*	*T (°K)*	*(BM)*	*T (°K)*	*(BM)*
300.1	5.50	300.4	4.35	300.5	5.75	301.0	5.66
265.3	5.28	265.4	4.03	265.4	5.68	265.5	5.66
229.5	4.88	229.7	3.69	229.4	5.63	230.5	5.68
193.4	4.35	193.8	3.16	193.0	5.60	194.0	5.60
157.4	3.64	157.2	2.59	157.0	5.38	157.5	5.58
119.5	3.04	119.6	2.34	118.8	5.17	119.3	2.65
98.0	2.84	98.2	2.26	97.5	5.02	98.7	2.53
89.6	2.86	89.3	2.24	87.0	4.95	91.2	2.66

presence of a phase change although no independent evidence of this has yet been obtained. Thirdly, the chelates of the isomeric thio(benzoylacetonates) show complementary behaviour. As in the case of the dithiocarbamates the terminal alkyl groups slightly affect the ligand field strength and thus the proportion of the spin-paired isomer, at equilibrium. Ho and Livingstone [60] have suggested that electron-withdrawing groups in the terminal positions of the ligand increase the tendency towards spin-pairing.

TABLE 13

Mossbauer parameters for iron(III) complexes Fe(R^1CSCHCOR^2)$_3$

Compound	*300°K*				*80°K*			
	High spin		*Low spin*		*High spin*		*Low spin*	
	$\Delta E^{\dagger}$ *(mm/sec)*	$\delta^{\dagger}$ *(mm/sec)*	ΔE *(mm/sec)*	δ *(mm/sec)*	ΔE *(mm/sec)*	δ *(mm/sec)*	ΔE *(mm/sec)*	δ *(mm/sec)*
$R^1 = R^2 = Ph$	0.61	0.65			0.93	0.65	1.90	0.60
$R^1=R^2=CH_3$	0.21	0.75					1.93	0.64
$R^1=Ph, R^2=CH_3$				*	0.00	0.85	1.68	0.58
$R^1=CH_3, R^2=Ph$	0.56	0.60	1.47	0.57			1.91	0.61

† ΔE is the quadrupole splitting, δ is the chemical isomeric shift relative to disodium pentanitrosylferrate(II).

* Room-temperature spectrum too weak to measure.

The magnetic studies of Cox et al. [59] have been accompanied by an investigation of the Mössbauer spectra of these compounds (Table 13, Fig. 6). For the first time, individual spin isomers have been observed for iron(III) at a single temperature. This indicates that the relaxation time required to change from one spin state to the other is long compared to the effective quadrupole period. This long relaxation period also allows the identification of

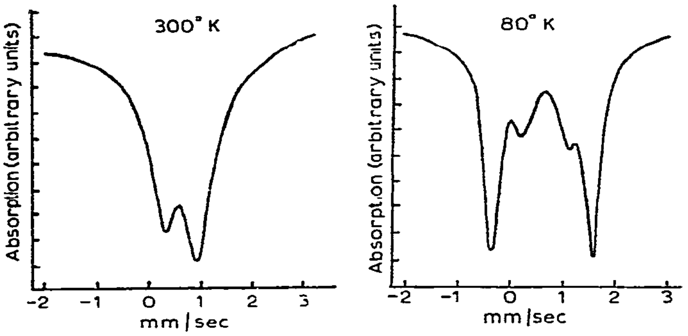


Fig 6. Mössbauer spectra of tris(thiodibenzoylmethanato) iron(III)

both spin states in the ESR spectrum [61]. For the iron(III) complexes shown in Table 13, two distinct resonances were observed at $g \approx 4$ and $g \approx 2$, which could be associated with the high-spin and low-spin states. Different intensity—temperature relationships of these two signals implies that two different species are involved, and the assignment of the $g = 2$ signal to the low-spin form is supported by resolution of 3-fold anisotropy expected for an $S = ½$ system The line at $g = 4$ is known to occur in high-spin complexes ($S = 5/2$) of certain stereochemistry, one of which is the pseudo-octahedral *mer*-MA_3B_3 (C_{2v}) [62] Thus the ESR spectra strongly support the magnetic and Mossbauer evidence for spin isomerism in these iron(III) thio-β-diketonates.

The magnetic properties of other metal chelates have to date been restricted to single moment determinations [35]. However, it is interesting to note that the only reported complex of manganese(II), $Mn(C_6H_5CSCHCOC_6H_5)_2py_2$, is high-spin (6.09 B.M), and tris(thiodipivaloylmethanato)manganese(III) is also reported as high-spin [34].

G STABILITY AND BONDING PREFERENCES

The acid dissociation constants of many of the thio-β-diketones have been determined [21,30–32,63,64] These show that the thio-β-diketones are stronger acids than the parent β-diketones, Table 14

TABLE 14

pK_D Values for some thio-β-diketones

Compound	*Thio-β-diketone (in 75% aqueous dioxan)*	*Parent-β-diketone (in 75% aqueous dioxan)*
$C_6H_5CSCH_2COC_6H_5$	11.40[30], 11 14[31], 9 38[32]	13.75[90], 10 90[32]
$CH_3CSCH_2COCH_3$	10 20[30], 10 26[31]	12.75[90]
$C_6H_5CSCH_2COCH_3$	10 45[30]	12 85[90]
$C_6H_5COCH_2CSCH_3$	10 40[30], 10 43[31]	12.85[90]
Others	[21]	

The stepwise and overall stoichiometric stability constants of several bivalent metal chelates with these ligands have been determined potentiometrically [30–32,63,64]. The results show that although thio-β-diketones are stronger acids than analogous β-diketones, some metals, particularly the late transition and class B metals form more stable complexes with the thioderivatives. Thus for magnesium(II), beryllium(II), manganese(II), copper(II) and the lanthanons [37] the β-diketone chelate is more stable than the thio-analogue. The position is reversed for the chelates of nickel(II), cadmium(II), zinc(II) and lead(II). It has been suggested [32] that this arises from π-bonding between *d* orbitals of transition metal ions and the vacant *d* orbitals on the sulphur atom. The order of stability of the metal chelates of thio-β-diketones is found to be Cu > Ni > Zn > Pb > Cd and Cu > Ni > Zn > Co. This is the same order as found for β-diketonates.

Magnetic studies of the iron chelates have shown that substituent groups in the chelate ring affect the ligand field strength, i.e. the charge density on the oxygen and sulphur donor atoms. The effects of substituent groups are also reflected to some extent in the preference for the formation of copper(I), class B, or copper(II), class A, complexes. Ligands containing the CF_3–CO grouping easily form copper(I) derivatives whilst other ligands prefer copper(II) [16]. However, it does not seem possible, at present, to make any generalisations on the effects of the substituents.

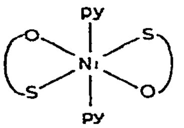
The spectroscopic studies of the complexes of copper(I), silver(I), cadmium(II), and mercury(II) indicate that the ligand is bonded through only the sulfur atom. This may involve the sulphur atoms bonding to more than one metal atom and the compounds may exist as polymers. Certainly many of their physical properties are consistent with a polymeric formulation This type of behaviour is expected for these strong class B acceptors. Other examples of bonding through sulphur only are found in the adducts of aromatic bases and phosphines with some metal chelates ($M = Ni^{II}, Pd^{II}, Pt^{II}, Zn^{II}$) [39].

H. REACTIONS OF THIO-β-DIKETONE CHELATES

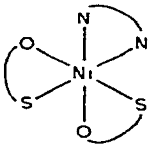
Metal acetylacetonates are known to undergo a wide range of chemical reactions. These include further addition of ligands [3], exchange of β-diketone residues from one metal to another [66], and electrophilic substitution in the chelate ring [67]. Thio-β-diketones also undergo reactions of these types

(i) Adduct formation

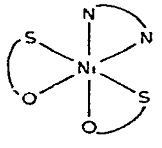
Livingstone and co-workers have made extensive studies of the reactions of aromatic bases and phosphines with chelates of nickel(II) and other metals. They found that reaction of pyridine with diamagnetic nickel chelates gave paramagnetic adducts such as bis-(ethyl thioacetoacetato) bispyridinenickel(II), μ_{eff} = 3 0 B M. [6]. This work was later extended to include other aromatic bases for example γ-picoline, 1,10-phenanthroline, 2,2′-dipyridyl and 2,2′,2″-terpyridyl [49]. Whereas the pyridine and picoline adducts easily lost base on exposure to air and decomposed on heating, the adducts of the chelating bases were quite stable. The structure proposed for the pyridine adduct was



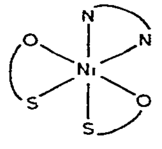
The adducts of the bidentate or tridentate aromatic bases pose more complicated questions concerning their structure. Adducts of dipyridyl and phenanthroline may have one of the following configurations, but for 2-methyl-1,10-phenanthroline there is considerable steric hindrance in these structures



cis OO, *cis* SS



cis OO, *trans* SS



trans OO, *cis* SS

Adducts of terpyridyl could also have one of these structures with one nitrogen uncoordinated, providing one of the rings is no longer coplanar with the others. The loss of resonance energy that results from this would make it very unlikely to occur The other alternatives involve seven-coordinate nickel or one of the thio-β-diketone residues becoming monodentate. This is certainly indicated in bis(methylthioacetoacetato)terpyridylnickel(II) which has a strong infrared absorption band attributed to uncoordinated $C=O$ at 1700 cm^{-1}. In this case one ligand is bonded via sulphur only. However, in the spectrum of the apparently analogous compound bis(thioacetylacetonato)terpyridylnickel (II) no such band is observed. This investigation has been extended to cover adducts of nickel, palladium, platinum, zinc, cadmium, mercury and lead complexes with thio-β-diketones containing CF_3CO— [39] In contrast to the adducts formed with non-fluorinated thio-β-diketonato–nickel complexes and monodentate bases, these new adducts were stable up to their melting points. This extra stability is attributed to the electron-withdrawing power of the trifluoromethyl group

The presence of strong infrared bands above 1600 cm^{-1} in the spectra of bis(trifluoroacetylthioacetonato)terpyridylnickel(II) and bis(thiothenoyltrifluoroacetonato)terpyridylnickel(II) again indicates bonding of one of the thio-β-diketone residues through sulphur only. Similar infrared bands are displayed by other adducts including $ML_2(PPh_3)_2$, ML_2(dipy), ML_2(phen) where $L = C_6H_5CSCHCOCF_3$, $CH_3CSCHCOCF_3$, or $C_4H_3SCSCHCOCF_3$, and M = Pt, Pd, and ML_2(terpy), $L = C_4H_3SCSCHCOCF_3$, M = Hg, Zn. Although the infrared spectra indicate that in all of these chelates the metal–oxygen bond is very easily broken the structure of the adducts is not revealed.

(ii) Lability of the metal chelates

Many metal β-diketonates react with metal halides undergoing an exchange process where the β-diketone residue moves from one metal atom to another. An example of this is the reaction of tris(acetylacetonato)iron(III) with titanium tetrachloride [66]

$$TiCl_4 + Fe(CH_3COCHCOCH_3)_3 \longrightarrow [Ti(CH_3COCHCOCH_3)_3]\ [FeCl_4]$$

Thio-β-diketonates undergo exactly analogous reactions [29].

Here it is perhaps relevant to discuss the possibilities of thio-β-diketones replacing β-diketones or vice versa in metal chelates Chaston et al. [49] have observed that acetylacetone will not replace thioacetylacetone from square planar bis(thioacetylacetonato)-nickel(II) but after addition of pyridine to give the octahedral complex replacement does occur. The authors conclude that four-coordinate nickel(II) has more B character than the six-coordinate species The reverse reaction of thioacetylacetone replacing acetylacetone is observed for managanese(III) and iron(III) [29].

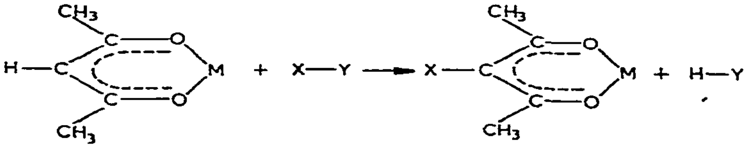
$$Mn(CH_3COCHCOCH_3)_3 + 3\ C_6H_5CSCH_2COC_6H_5 \xrightarrow[H_2O]{Et_3N} Mn(C_6H_5CSCHCOC_6H_5)_3 +$$
$$+ CH_3COCHCOCH_3 \text{ (Salt with } Et_3N)$$

$$Fe(CH_3COCHCOCH_3)_3 + 3\ Na(C_6H_5CSCHCOC_6H_5) \xrightarrow{H_2O} Fe(C_6H_5CSCHCOC_6H_5)_3 +$$
$$+ Na(CH_3COCHCOCH_3)$$

Though manganese(III) and iron(III) are both class A ions the thio-β-diketone replaces the β-diketone. The reaction path, however, may be determined by the extreme insolubility of the tris(thiodibenzoylmethanato) metal products in water. The resulting crude manganese (III) complex cannot be recrystallised since solutions decompose rapidly to the disulphide. It seems probable, therefore, that the oxidation of the thio-β-diketones by metal ions involves chelation. This exchange reaction may prove a useful method of preparing thio-β-diketonates

(iii) Reaction of the chelate ring

Metal acetylacetonates undergo electrophilic substitution reactions which suggest that the chelate ring has some aromatic character [67].



where X = I, Br, Cl, SCN, NO_2, CHO, etc , Y = R, H, etc. and M = Cr^{III}, Co^{III}, Rh^{III}, Be^{II}, Cu^{II}, Al^{III} Analogous reactions have now been reported for some thio-β-diketonates of cobalt(III) [22]. *N*-Bromosuccinimide has been used to brominate tris(thioacetylacetonato)-cobalt(III) and tris(thiobenzoylacetylacetonato)cobalt(III) to give the tribromo derivatives.

I. APPLICATIONS OF METAL CHELATES

Compared with the β-diketonates, few applications of the monothio-β-diketonates have been published. The major field of application will probably be, like the oxygen compounds, in analytical chemistry where their properties of intense colour and solubility in nonpolar solvents can be used to advantage. As mentioned earlier, significant differences between the physical properties of complexes of the sulphur and oxygen ligands will ensure that, for some purpose, the sulphur ligands will be preferred. For example, it has been suggested that thiothenoyltrifluoracetone could be used as a colorimetric reagent for lead, zinc, and cadmium with which it forms coloured chelates, whereas the β-diketonates of these elements are colourless [18]. Very little has been published on the quantitative aspects of the use of these ligands, i.e. stability of colour, possible interferences, Beers law dependence, but the technique has been used for the quantitative estimation of cobalt [89].

The solubility of the metal chelates in nonpolar solvents together with the low solubility of the ligands in aqueous solution allows the extraction of metal ions from an aqueous to an organic phase. The use of β-diketones in solvent extraction is a well-known analytical technique [69]. Uhlemann and Mueller [68,70,89,91] have studied the extraction of a few metals with thio-β-diketones and have shown that copper(II), nickel(II) and cobalt (II) can easily be extracted into *n*-heptane or carbon tetrachloride from solutions of higher acidity than with the corresponding β-diketone (Table 15).

TABLE 15

pH of 50% extraction of metals from aqueous solution

Compound	*pK*	*Copper*	*Cobalt*	*Nickel*	*Lead*	*Zinc*	*Ref*
$C_4H_3SCSCH_2COCF_3$	4.10	0.5	3.7	4.1	4.5	4.7	91
$C_4H_3SCOCH_2COCF_3$	6.23		4.0	3.8	3.2		69
$C_6H_5CSCH_2COC_6H_5$	6.30	0.6	6.0	5.7			68
$C_6H_5COCH_2COC_6H_5$	9.35	2.9	6.6	6.4			69
iso-$C_3H_7CSCH_2COCH_3$	7.56	0.5	5.5	5.0			68

However, during the extraction of cobalt(II) oxidation occurs to cobalt(III). At present difficulties arising from oxidation of the ligands limit the use of these reagents for solvent extraction.

Gas chromatography is a branch of analytical chemistry for which β-diketones have been tested over a number of years with only a limited success. The ability to separate metallic elements by means of gas chromatographic techniques is obviously of great importance in analysis and for many years various β-diketones have been tried. The main problem is that the metal complexes tend to decompose on the column and quantitative recovery is not achieved. To reduce this decomposition, complexes of fluorinated β-diketones having a lower volatilisation temperature have been used [71]. A preliminary communication has indicated that thio-β-diketones may be superior to the oxygen analogues for this technique [72]. Using thioacetylacetone complexes of cobalt(II), nickel(II) and palladium(II) symmetrical peak shapes were observed on the chromatographic trace. This indicates little decomposition and thus provides a good prospect for quantitative analysis. It is interesting that the elements chosen are ones which have not been successfully chromatographed using β-diketones and the column temperature of 240°C shows that, under these conditions, the complexes are thermally stable. Similar thermal stability has been found with chelates of thiothenoyltrifluoroacetone with these elements [18].

From these few published examples it can be seen that these ligands will provide a useful addition to the range of reagents available to the analytical chemist, supplementing the already wide use of β-diketones in this field.

J. DITHIO-β-DIKETONES

Monomeric dithio-β-diketones are unknown; attempts to prepare them by the reaction of hydrogen sulphide with a β-diketone in hydrogen chloride saturated alcohol results in the formation of dimers of which the dithioacetylacetone dimer is an example, Fig. 1. The isolation of this type of product shows that substitution of both oxygen atoms of the β-diketone is possible and that the monomeric dithio-β-diketones may be formed initially in solution

By reacting hydrogen sulphide with acetylacetone in the usual manner and in the presence of a metal chloride, Martin and Stewart [7] successfully prepared dithioacetylacetonates of cobalt(II), nickel(II), palladium(II) and platinum(II)

$$4\,H_2S + 2\,CH_3COCH_2COCH_3 + M^{2+} \xrightarrow[EtOH]{HCl} M(CH_3CSCHCSCH_3)_2 + 2\,H^+ + 4\,H_2O$$

The tris dithioacetylacetone complexes of iron(III), ruthenium(III) and osmium(III) have also been prepared by a similar method [65]. These compounds are, like the monothio derivatives, deeply coloured and readily soluble in organic solvents. The nickel(II) compound is diamagnetic and the cobalt(II) compound is also low-spin, $\mu_{eff} = 2.3$ BM. An X-ray structural analysis of these two chelates has shown they are isostructural [73] and a detailed structure of the cobalt(II) complex is shown in Fig. 7 . Mixed chelates of the mono- and dithioacetylacetone ligands have also been prepared, for example (monothioacetylacetonato)-(dithioacetylacetonato)nickel(II)[44]. Application of the above reaction to rhodium(III) and iridium(III) compounds gives the crimson tris(dithioacetylacetonates) [74]. The tris-chelate of cobalt(III) is readily prepared by the reaction of tris(dithioacetylacetonato) cobalt(II) with acetylacetone and hydrogen sulphide in the presence of air. A mixed ligand intermediate, (monothioacetylacetonato)bis(dithioacetylacetonato)cobalt(III) was also prepared [74]. The isolation of this complex and the mixed nickel(II) chelate indicates that replacement of the second oxygen atom takes place by reaction of a monothioacetylacetone—

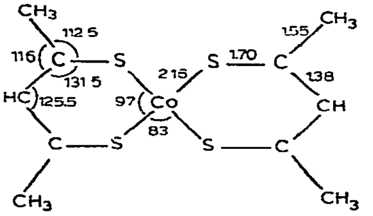


Fig. 7. X-ray structure of bis(dithioacetylacetonato)cobalt(II)

metal chelate with hydrogen sulphide and that the monomeric dithioacetylacetone is not formed in solution [19]. A very recent publication [87] of the X-ray structure of tris(dithioacetylacetonato)iron(III) has indicated a distorted octahedral arrangement of the six sulphur atoms round the iron, the authors also confirmed an earlier report [75] that the compound is low-spin The low value of the magnetic moment at room temperature μ_{eff} = 2 00 BM together with the ESR and Mossbauer spectra suggests that the site symmetry is lower than octahedral although the Fe — S bond lengths are similar. In addition to the complexes of dithioacetylacetone, nickel(II) and cobalt(II) chelates of other ligands such as dithiobenzoylacetone, dithiodibenzoylmethane and dithio-1,1,1-trifluoroacetylacetone have been prepared [76]. Dithioderivatives of the metal chelates of 1,1,1,5,5,5-hexafluoroacetylacetone and ethylacetoacetate were not obtained. However, the nickel(II) complex of methyldithioacetoacetate can be prepared by the autocondensation of methyl thionoacetate, $CH_3CS(OCH_3)$ in the presence of sodamide.

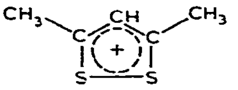
$$2\ CH_3CS(OCH_3) \xrightarrow{NaNH_2} (CH_3CSCHCSCH_3)\,Na + NH_3 + CH_3OH$$

$$\downarrow Ni^{2+}$$

$$Ni(CH_3CSCHCSCH_3)_2$$

Two independent normal coordinate analyses of the vibrations of the divalent chelates of dithioacetylacetone have been carried out [19,45] The results obtained are substantially in agreement. In both cases the $C \mathrel{\overset{\cdots}{=}} S$ stretching frequencies are calculated as being close to 700 cm^{-1} and the M — S stretching frequencies are around 380 cm^{-1} It has been concluded that the M — S bonds are weaker than those in other sulphur chelates [45]

In addition to the simple chelates, the reaction of hydrogen sulphide with acetylacetone in the presence of a hydrogen halide and metal ions gives another class of compound with the empirical formula $M(C_5H_7S_2)Cl_4$ ($M = Fe^{II}$ [75], Mn^{II}, Hg^{II} [78]) Analogous bromo compounds have also been prepared for $M = Mn^{II}$, Fe^{II}, Co^{II}, Cu^{II}, Zn^{II} and Cd^{II} [79]. These compounds have contrasting physical properties to the bis(dithioacetylacetonato)metal chelates. They are high-spin and relatively insoluble in organic solvents The violet iron–chlorine compound, $Fe(C_5H_7S_2)Cl_4$ dissolves readily in water, the resulting solution containing ferrous ions, chloride ions, and 3,5-dimethyldithiolium ions.



X-ray structural analyses [80,81] have shown that the iron compound is di(3,5-dimethyldithiolium) tetrachloroferrate(II), $[C_5H_7S_2]_2^{+}[FeCl_4]^{2-}$. The manganese(II) zinc(II), and cobalt(II) compounds are isomorphous with this structure [80]. The S - - - Cl distances in the iron complex are shorter than the sum of the Van der Waals radii of these two atoms This is consistent with the observed charge transfer transition from the tetrachloroferrate anion to the dithiolium cation at 20,000 cm^{-1}, which gives rise to the deep violet colour of the compound [83]. Further confirmation of the structure comes from the Mossbauer spectrum which is typical of the tetrachloroferrate(II) anion [83]

Compounds of this second type can also be prepared from the simple dithiochelates, for example, halogenation of a dithioacetylacetone chelate produces a dithiolium salt [83,84].

$$Co(CH_3CSCHCSCH_3)_2 + 2\,Br_2 \xrightarrow{CCl_4} (C_5H_7S_2)_2CoBr_4$$

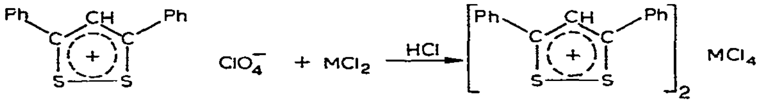
$$Ni(CH_3CSCHCSCH_3)_2 + 2\,Cl_2 \longrightarrow (C_5H_7S_2)_2NiCl_4$$

Bromination of a bis(dithioacetylacetone) chelate may give compounds with six bromine atoms per metal [84].

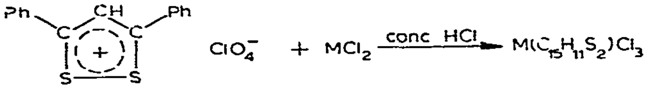
$$Ni(CH_3CSCHCSCH_3)_2 + 3\,Br_2 \longrightarrow Ni(C_5H_7S_2)_2Br_6$$

The structure of this type of complex is not known.

As expected, these salts can be prepared from the metal halide and a dithiolium salt [83,85]

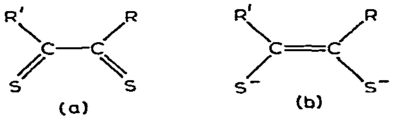


where M = Co^{II}, Cu^{II}, Cd^{II}.



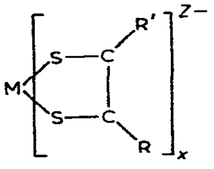
where M = Zn^{II}, Mn^{II}, Cu^{II}. These salts can be converted to the simple dithio-β-diketone chelates by reduction with sodium borohydride [84,85]

It is interesting at this stage to compare the chelates of dithio-β-diketones with those of dithio-α-diketones. The latter ligands may be regarded as coordinating either as dithio-α-diketones (a) or as 1,2-dithioethylene dianions (b). The chemistry of these metal complexes has been recently reviewed elsewhere [97,98] and only the broad outlines will be included here.



Both four- and six-coordinated neutral complexes of divalent [92] and trivalent metals respectively have been prepared. The former are square planar whereas the six-coordinate species favour a trigonal prismatic coordination rather than an octahedral structure The non-bonded S - - - S distances are constant for a series of metals [96] and it has been suggested that these non-bonded interactions help to stabilise the prismatic structure

The most interesting property of all these chelates is the ready participation in electron transfer reactions to give ionic species [93–95].



$x = 2$ $Z = 0, 1, 2$
$x = 3$ $Z = 0, 1, 2, 3$

M = Ni, Co, Pd, etc.
R', R = Ph, CH_3, CF_3, CN

These reactions normally occur without change of geometry and allow the study of similar complexes in a series of formal oxidation states although, like the 2,2'-dipyridyl complexes, traditional concepts of oxidation state are difficult to apply in these cases. Thus it is considered [99] in the case of maleonitrile dithiol ($R' = R = CN$) that in the dianionic complex $[Ni(S_2C_2(CN)_2)_2]^{2-}$ the ligands approach the dithiolate structure (b).

Although chelates of dithio-β-diketones have not been reduced to ionic species they are readily oxidised to compounds containing dithiolium cations These dithiolium complexes and the neutral chelates, although they have different structures, are readily interconvertible via redox processes. This phenomenon of ligand reduction is a property of the π-system of the chelate ring as it occurs with donor atoms other than sulphur [98]. Thus, it may be possible to oxidise chelates of monothio-β-diketone in this manner.

It is interesting to note that the only tris(dithio-β-diketone) complex structure recorded so far Fe(SacSac)$_3$ has a distorted octahedral configuration, perhaps the non-bonded S - - - S interactions play a part in determining its structure?

K. SELENO-β-DIKETONES

Metal chelates of diselenoacetylacetone have been synthesised by the reaction of hydrogen selenide with acetylacetone in the presence of metal ions Bis(diselenoacetylacetonato) nickel(II) is a diamagnetic, red crystalline solid [8]. The infrared spectrum is completely consistent with a structure analogous to that of bis(dithioacetylacetonato) nickel(II) [19].

Compounds containing the 3,5-dimethyldiselenolium ion are also known. Attempts to prepare bis(diselenoacetylacetonato)cobalt(II) have so far resulted in the formation of the diselenolium salt, $(C_5H_7Se_2)_2CoCl_4$. The electronic absorption spectrum and the magnetic moment of 4.6 BM provide evidence for the tetrachlorocobaltate(II) ion [8].

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REFERENCES

1 J.P. Fackler, Jr., *Progr. Inorg. Chem.*, 7 (1966) 361.
2 R.M. Pike, *Coord. Chem. Rev*, 2 (1967) 163.
3 D.P. Graddon, *Coord. Chem. Rev.*, 4 (1969) 1
4 D Gibson, *Coord. Chem. Rev.*, 4 (1969) 225
5 R.H. Holm, G.W. Everett, Jr. and A. Chakravorty, *Progr. Inorg. Chem.*, 7 (1966) 83.
6 S H H. Chaston, S E Livingstone, T N Lockyer, V A. Pickles and J.S. Shannon, *Australian J Chem*, 18 (1965) 673.
7 R.L. Martin and I.M. Stewart, *Nature*, 210 (1966) 622.
8 G.A. Heath, R.L. Martin and I M. Stewart, *Inorg. Nucl. Chem. Letters*, 5 (1969) 169.
9 D.H Gerlach and R.H. Holm, *J. Amer. Chem. Soc.*, 91 (1969) 3457.
10 E Fromm and P. Zierch, *Chem. Ber.*, 39 (1906) 3599.

11 S.K. Mitra, *J. Indian Chem Soc.*, 10 (1933) 71.
12 S K Mitra, *J. Indian Chem. Soc.*, 8 (1931) 471.
13 Z. Reyes and R M. Silverstein, *J. Amer. Chem. Soc.*, 80 (1958) 6367
14 R. Mayer, G. Hiller, M Nitzchke and J. Jentsch, *Angew. Chem. (Intern. Ed. Engl.)*, 2 (1963) 370.
15 R.K.Y. Ho, S E. Livingstone and T.N. Lockyer, *Australian J. Chem.*, 19 (1966) 1179.
16 R.K.Y. Ho and S.E. Livingstone, *Australian J. Chem.*, 21 (1968) 1781.
17 K.H. Meyer, *Chem. Ber.*, 45 (1912) 2843.
18 E.W. Berg and K.P. Reed, *Anal. Chim. Acta*, 36 (1966) 372
19 C.G Barraclough, R L. Martin and I M Stewart, *Australian J. Chem.*, 22 (1969) 891
20 E Uhlemann and H Mueller, *Angew Chem (Intern. Ed Engl.)*, 4 (2) 154.
21 E. Uhlemann and Ph. Thomas, *J Prakt Chem.*, 34 (1966) 180.
22 A. Yokoyama, S. Kawanishi, M. Ouikuma and H. Tanaka, *Chem. Pharm. Bull (Tokyo)*, 15 (1967) 540.
23 C F. Ferraro, J J Draney and M. Cefola, *J. Amer. Chem Soc*, 75 (1953) 1206
24 S.K. Mitra, *J. Indian Chem. Soc*, 15 (1938) 205.
25 G. Klose, M. Mueller and E. Uhlemann, *Z Naturforsch.*, 19b (1964) 952.
26 G. Klose, J. Marki, Ph. Thomas and E. Uhlemann, *Tetrahedron*, 22 (1966) 2695.
27 K Arnold, G Klose, Ph. Thomas and E Uhlemann, *Tetrahedron*, 25 (1969) 2957.
28 K. Arnold and G. Klose, *Tetrahedron*, 25 (1969) 3775
29 M. Cox and J. Darken, unpublished results
30 K. Arnold, G Klose, Ph. Thomas and E Uhlemann, *Z. Anorg. Allgem. Chem.*, 364 (1969) 153.
31 S E Livingstone and E A. Sullivan, *Australian J. Chem.*, 22 (1969) 1363
32 A. Manane and K. Saito, *Bull Chem Soc Japan*, 41 (1968) 2419
33 C.K Jørgensen, *Inorganic Complexes*, Academic Press, New York, 1963, p 134
34 S H H Chaston and S.E. Livingstone, *Australian J Chem.*, 20 (1967) 1065
35 E. Uhlemann and Ph. Thomas, *Z Naturforsch*, 23b (1968) 275.
36 A.L Allred and D W. Thompson, *Inorg Chem*, 7 (1968) 1196
37 N K Dutt, K. Nag and T. Sheshadri, *J Inorg Nucl Chem*, 31 (1969) 1435
38 E A. Shugam, L.M. Shkol'nikova and S.E Livingstone, *Zh Strukt Khim*, 8 (1967) 550
39 R K.Y. Ho, S E Livingstone and T N. Lockyer, *Australian J Chem.*, 21 (1968) 103.
40 R.H. Holm, D.H. Gerlach, J G. Gordon and M G McNamee, *J. Amer. Chem. Soc.*, 90 (1968) 4184
41 R.C. Fay and T S. Piper, *J Amer Chem Soc*, 84 (1962) 2303.
42 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.
43 S Pinchas, B.L Silver and I Lanlicht, *J Chem Phys*, 46 (1967) 1506
44 A Ouchi, M Hyodo and Y Takahashi, *Bull Chem Soc Japan*, 40 (1967) 2819
45 O Siiman and J Fresco, *Inorg Chem.*, 8 (1969) 1849
46 E Uhlemann and Ph Thomas, *Z Anorg Allgem Chem*, 356 (1967) 71
47 S H H. Chaston and S E. Livingstone, *Australian J. Chem.*, 20 (1967) 1079
48 E Uhlemann, G Klose and H Mueller, *Z Naturforsch*, 19b (1964) 962.
49 S H H. Chaston, S E. Livingstone and T N Lockyer, *Australian J Chem*, 19 (1966) 1401
50 R C. Fay and N Serpone, *J Amer. Chem. Soc*, 90 (1968) 5701
51 R H Holm and F A Cotton, *J Amer. Chem Soc*, 80 (1958) 5658
52 R.C. Fay and N. Serpone, *Inorg Chem.*, 8 (1969) 2379
53 B N Figgis and J Lewis, *Progr Inorg Chem*, 6 (1964) 37
54 J S Griffith, *J Inorg Nucl. Chem*, 2 (1956) 229
55 A.H. Ewald, R.L Martin, I.G Ross and A H White, *Proc Roy. Soc (London), Ser A*, 280 (1964) 235.
56 O.G. Holmes and D S McClure, *J. Chem. Phys*, 26 (1957) 1686
57 R.L Martin and A H White, in R.L. Carlin (Ed), *Transition Metal Chemistry*, Vol. 4., Arnold, London, 1968, p. 113.
58 R K.Y. Ho and S E. Livingstone, *Australian J Chem*, 21 (1968) 1987
59 M. Cox, J Darken, B.W. Fitzsimmons, A.W Smith, L F. Larkworthy and K A Rogers, *Chem. Commun.*, (1970) 105.

60 R.K.Y. Ho and S.E Livingstone, *Chem. Commun.*, (1968) 217.

61 S A Cotton and J.F. Gibson, private communication.

62 J.S. Griffith, *Mol Phys*, 8 (1969) 213.

63 E. Uhlemann and W.W Suchan, *Z Anorg Allgem. Chem*, 342 (1966) 41

64 S H.H. Chaston and S.E. Livingstone, *Australian J. Chem.*, 19 (1966) 2305

65 G.A. Heath and R.L. Martin, *Australian J. Chem.*, 23 (1970) 1721

66 M. Cox, J. Lewis and R S Nyholm, *J. Chem. Soc, Suppl*, 2 (1964) 6113

67 J P. Collman, in R L Carlin (Ed.), *Transition Metal Chemistry*, Vol 2, Arnold, London, 1966.

68 E. Uhlemann and H Mueller, *Anal Chim Acta*, 41 (1968) 311

69 J Stary, *Solvent Extraction of Metal Chelates*, Pergamon, Oxford, 1964.

70 E. Uhlemann and H Mueller, *Z. Chem.*, 9 (1969) 114.

71 R E. Sievers and R W Moshier. *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.

72 W.I. Stephen, I J. Thomson and P.C. Uden, *Chem. Commun.*, (1969) 269.

73 R. Beckett and B.F. Hoskins, *Chem. Commun.*, (1967) 909.

74 G.A. Heath and R.L. Martin, *Chem. Commun.*, (1969) 951.

75 K. Knauer, P. Hemmerich and J D.W van Voorst, *Angew Chem. (Intern Ed. Engl)*, 6 (1967) 262

76 A. Ouchi, M. Nakatani and Y Takahashi, *Bull Chem. Soc Japan*, 41 (1968) 2044.

77 E. Uhlemann and Ph. Thomas, *Z. Chem.*, 7 (1967) 430

78 A. Furihashi, K. Watanuki and A. Ouchi, *Bull Chem. Soc. Japan*, 41 (1968) 110

79 A. Furihashi, T. Takeuchi and A. Ouchi, *Bull Chem. Soc Japan*, 41 (1968) 2049.

80 R. Mason, E D. McKenzie, G.B. Robertson and G A. Rusholme, *Chem. Commun.*, (1968) 1673

81 H.C. Freeman, G H.W. Milburn, C.E. Nockolds, P. Hemmerich and K. Knauer, *Chem. Commun.*, (1969) 54.

83 G A. Heath, R.L. Martin and I M. Steward, *Australian J. Chem.*, 22 (1969) 83.

84 A Furihashi, K. Watanuki and A Ouchi, *Bull Chem. Soc Japan*, 42 (1969) 260

85 Y. Takahashi, M Nakatani and A Ouchi, *Bull Chem. Soc Japan*, 42 (1969) 274.

86 R K.Y. Ho, S E. Livingstone and T.N. Lockyer, *Australian J. Chem.*, 18 (1965) 1927

87 R. Beckett, G A. Heath, B F. Hoskins, B P. Kelly, R.L Martin, I A G Ross and P.L Weickhardt, *Inorg. Nucl. Chem. Letters*, 6 (1970) 357

88 R A. Bozis and B J McCormick, *Chem. Commun*, (1968) 1592

89 E. Uhlemann and H. Mueller, *Anal Chim. Acta*, 48 (1969) 115.

90 A E. Martell, *Stability Constants of Metal Ion Complexes, Section II, Chemical Society Special Publication 17*, London, 1964.

91 E Uhlemann and H Mueller, *Z. Chem.*, 8 (1968) 185

92 G.N Schrauzer and V. Mayweg, *J Amer. Chem. Soc.*, 84 (1962) 3221.

93 A. Davidson. N. Edelstein, R H. Holm amd A H. Maki, *J Amer Chem. Soc.*, 85 (1963) 2029

94 H.B. Gray, R. Williams, I. Bernal and E Billig, *J. Amer. Chem. Soc*, 84 (1962) 3596

95 H.B Gray and E. Billig, *J Amer. Chem. Soc*, 85 (1963) 2019.

96 J S Wood, *Coord Chem. Rev.*, 2 (1967) 403.

97 S E. Livingstone, *Quart. Rev.*, 19 (1965) 386.

98 L.F. Lindoy, *Coord. Chem. Rev.*, 4 (1969) 41

99 G.N. Schrauzer and H N. Rabinowitz, *J. Amer Chem. Soc*, 90 (1968) 4297.