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MONOTHIO-β-DIKETONES AND THEIR METAL COMPLEXES *

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CONTENTS

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* Editor's footnote: Two articles dealing with the same subject appear in this issue; although there is some overlap, the reviews being written independently, the approach and emphasis are sufficiently different to warrant publication of both contributions. Hopefully, their simultaneous publication in the same issue will provide both a useful and complete coverage of the topic concerned

A. INTRODUCTION

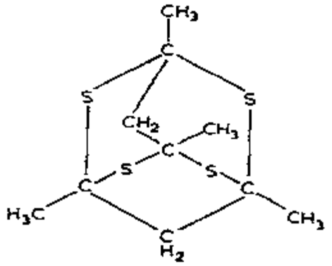
The chelating ability of acetylacetone was first reported by Werner [1] seventy years ago and metal complexes of acetylacetone and many other β-diketones have been extensively studied [2–4] The first metal complexes of monothio-β-diketones were reported by the author in 1964 [5] The replacement of one oxygen of the β-diketone by sulphur gives rise to metal chelates having properties in many instances considerably different from those of the complexes formed by the parent β-diketone

Monothio-β-diketones and their metal complexes have previously been briefly reviewed [6]. However, these two reviews were not devoted entirely to this subject and furthermore, a considerable body of work has appeared since their publication A review by Cox and Darken[7] precedes this article in this Journal.

B. PREPARATION OF MONOTHIO-β-DIKETONES

(i) By reaction of hydrogen sulphide on β-diketones

The first recorded attempt to prepare thio derivatives of a β-diketone was made by Fromm and Ziersch who prepared the colourless dimer (I) from acetylacetone and hydrogen sulphide in alcohol in the presence of hydrogen chloride [8]. Ethyl thioacetoacetate (II, R = Me; R′ = OEt) was prepared by Mitra [9] by passing hydrogen sulphide for 6 h into a solution of ethyl acetoacetate in alcohol, which had been saturated with hydrogen chloride at −10°C Ethyl thiobenzoylacetate (III, R = Ph, R′ = OEt) was prepared by a modification of Mitra's method by Reyes and Silverstein [10] who reported that this compound, which is blue, is decolorized on contact with air owing to dissolution of oxygen The decolorization is not due to polymerization, since the infrared and NMR spectra of the blue and decolorized forms are identical. Reyes and Silverstein concluded that the compound exists solely in the intramolecular hydrogen-bonded thienol form (III).



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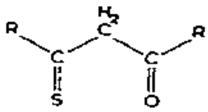

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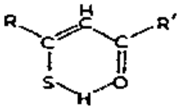
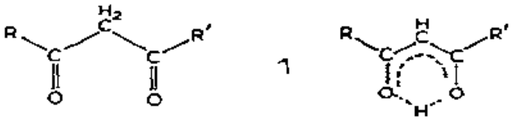


(III)

The base-catalyzed reaction of hydrogen sulphide on β-diketones has been investigated [11]. The monothio-derivative of acetylacetone was obtained in 24% yield by the treatment of a solution of acetylacetone (0.5 mole) in methanol or dimethylsulphoxide (100 ml) with morpholine (0.05 mole) followed by the rapid passage of hydrogen sulphide through the mixture for 7 h [11].

Monothio-β-diketones can be prepared from β-diketones by the action of hydrogen sulphide, a low concentration (2.5% in alcohol) is used to avoid the formation of polymers such as (I). Nevertheless, the conditions are rather critical. For example, benzoylacetone and dibenzoylmethane are not converted to their monothio derivatives by Mitra's method However, if hydrogen sulphide is passed for 30 min into a solution of the β-diketone at −10°C followed by the passage of hydrogen chloride for 5 min, the monothio-β-diketones are obtained On the other hand, thenoyltrifluoroacetone requires saturation of the alcohol solution with hydrogen sulphide and hydrogen chloride at −70°C [12].

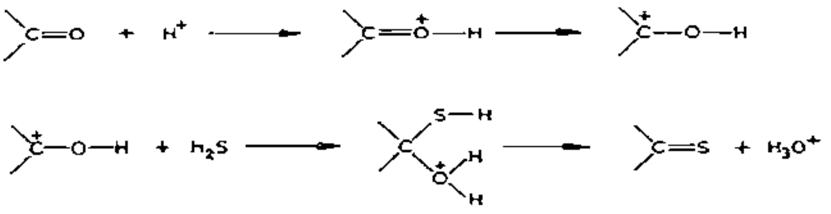
At room temperature, β-diketones and β-keto-esters are in tautomeric equilibrium between the diketo form (IV) and the chelated hydrogen-bonded form (V) [13,14]. In polar solvents the concentration of the diketo form is increased [13,15]



(IV) (V)

There appears to be a relationship between the amount of enol form present in alcohol solution and the concentration of hydrogen chloride necessary to bring about conversion to the thio derivative This is summarized in Table 1 of the preceding article [7] It was also suggested that reaction with hydrogen sulphide occurs only with the diketo tautomer (IV) Consequently, higher concentrations of hydrogen chloride are required for those β-diketones which exist predominantly in the enol form in order to provide the more polar conditions necessary to shift the tautomeric equilibrium in favour of the diketo form [12].

The reaction can be represented as follows [16]:



In the case of a β-diketone (IV) when R ≠ R′, it has been shown that the nucleophilic attack by hydrogen sulphide takes place at the ketonic group attached to R, if the electron-withdrawing power of R is less than that of R′ [12,16]. Thus the monothio-β-diketone (III) is obtained as the only isomer, as shown in Table 1

TABLE 1

Monothio-β-diketones which have been obtained in only one isomeric form RC(SH)=CHCOR′ by the action of hydrogen sulphide on $RCOCH_2COR'$

R	*R′*	*Ref*
Me	Ph	12
C_4H_3S,	CF_3	12
Me	CF_3	17
Ph	CF_3	18
p-BrC_6H_4	CF_3	19
C_4H_3O	CF_3	19
Ph	p-ClC_6H_4	16
Ph	p-$MeOC_6H_4$	16
Ph	C_4H_3S	16
p-ClC_6H_4	p-$MeOC_6H_4$	16
p-ClC_6H_4	C_4H_3S	16

Since the experimental conditions for the preparation of monothio-β-diketones are rather critical, they are given here The method which has been found to be most satisfactory is as follows [12,19] Hydrogen sulphide is passed for 20 min into a solution of the β-diketone (5 g) in alcohol (200 ml) at −70°C followed by dry hydrogen chloride for 10 min The reaction flask is fitted with a calcium chloride drying tube and the contents are allowed to come to room temperature, then stood for 15 h If the product is a solid, the reaction mixture is poured into ice-water (500 ml) and the resulting red crystalline product is filtered off and recrystallized from light petroleum. If the product is an oil, the reaction mixture, after standing, is extracted with light petroleum. The extract, after concentration to small volume (100 ml), is dissolved in alcohol (150 ml), and then treated with a solution of lead acetate trihydrate (3 g) in 80% alcohol (200 ml) Water (200 ml) is added to the mixture, which is then warmed on the steam bath for 15 min The lead complex is filtered off, dried over phosphorus pentoxide, and suspended in light petroleum (300 ml) while hydrogen sulphide is passed through for 15 min The precipitated lead sulphide is filtered off, and the red filtrate is dried, the solvent is removed under reduced pressure, and the crude product is distilled under reduced pressure to give the pure monothio-β-diketone

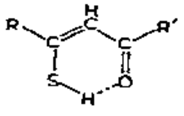
Purification via the lead complex has the added advantage that any *gem*-dithiol, which may also be formed in the reaction between hydrogen sulphide and the β-diketone, particularly above −40°C, is removed, since, although the lead complex of the *gem*-dithiol is formed, it is unstable and decomposes to give the lead complex of the monothio-β-diketone and lead sulphide [20].

The monothio-β-diketones which have been reported are listed by Cox and Darken[7] in their Table 2.

(ii) By condensation of ketones with thionic esters

Monothio-β-diketones can readily be obtained in yields exceeding 50% by a Claisen-type condensation of ketones with thionic esters, RC(S)OMe, or dithionic esters, RC(S)SMe. The ketone is added to a suspension of sodamide in ether and, after 15 min, an ethereal solution of the thionic ester is added dropwise. The mixture is allowed to stand 15 h and then the sodium salt of the monothio-β-diketone is extracted with water. Carbon dioxide is passed into the aqueous solution and the monothio-β-diketone separates out [21,22].

This method has the added advantage in that, where the two structural isomers (VI) and (VII) are possible, both isomers can be prepared in good yield, whereas the reaction of hydrogen sulphide on the β-diketone yields only one isomer (vide supra). Uhlemann and his co-workers have synthesized a considerable number of monothio-β-diketones by this method, many of them in both isomeric forms (see Table 2, ref. 7)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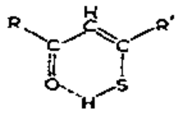
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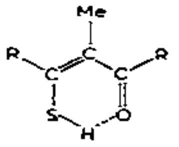
C. OTHER COMPOUNDS CONTAINING THE GROUPING –C(SH)=CHCO–

Other compounds containing the grouping –C(SH)=CHCO– are listed in Table 2 They can act as chelating agents and form metal complexes similar to those formed by monothio-β-diketones.

D α-SUBSTITUTED MONOTHIO-β-DIKETONES

The α-C-methyl substituted monothio-β-diketones (VIII, R = Me, Ph) have been prepared by the action of hydrogen sulphide on the corresponding β-diketones [28] The complexing ability of these ligands appears to be much weaker than that of other monothio-β-diketones, this appears to be due to steric hindrance caused by the methyl group attached to the central carbon atom. Where the terminal groups are phenyl, there is severe interaction between the central methyl group and the benzene rings. A similar steric effect obtains in 2-methyl-1,3-diphenylpropane-1,3-dione; however, the interaction can be relieved to some extent by a bending of the molecule, as shown in (IX), with a concomitant shortening of the oxygen–oxygen distance [29]. With the thio derivative VIII (R = Ph), the larger size of the sulphur atom prevents any appreciable bending of the molecule [28].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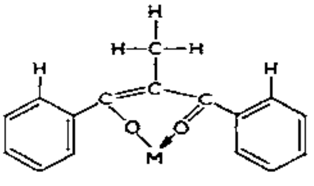
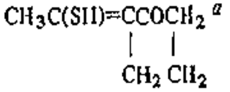
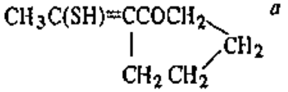
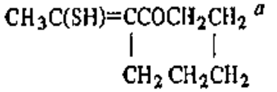

(IX)

TABLE 2

Other compounds containing the grouping - C(SH)=CHCO-

Compound	*Formula*	*M p or b p*	*Ref*
Ethyl thioacetoacetate	$CH_3C(SH){=}CHCOOEt^a$	75–80/9 mm	9
Ethyl thiobenzoylacetate	$PhC(SH){=}CHCOOEt^a$	102/0 7 mm	10
Ethyl 3-(4-nitrophenyl)-3-mercaptopropenoate	$p\text{-}ClC_6H_4C(SH){=}CHCOOEt$	130–4/5 mm	23
Ethyl 3-(4-methoxyphenyl)-3-mercaptopropenoate	$p\text{-}NO_2C_6H_4C(SH){=}CHCOOEt$	*b*	23
Ethyl *o*-mercaptobenzoate	$p\text{-}MeOC_6H_4C(SH){=}CHCOOEt$	*b*	23
iso-Propyl *o*-mercaptobenzoate	$o\text{-}HSC_6H_4COOEt$	*b*	24
iso-Amyl *o*-mercaptobenzoate	$o\text{-}HSC_6H_4COOPr^i$	*b*	24
S-Ethyl *o*-mercaptothiobenzoate	$o\text{-}HSC_6H_4COOAm^i$	*b*	24
S-iso-Propyl *o*-mercaptothiobenzoate	$o\text{-}HSC_6H_4COSEt$	145–7/7 mm	24
S-iso-Amyl *o*-mercaptothiobenzoate	$o\text{-}HSC_6H_4COSPr^i$	125/4 mm	24
S-Ethyl *β*-mercaptothiocinnamate	$o\text{-}HSC_6H_4COSAm^i$	148–52/4 mm	24
S-iso-Propyl *β*-mercaptothiocinnamate	$PhC(SH){=}CHCOSEt$	163	25
S-Benzyl *β*-mercaptothiocinnamate	$PhC(SH){=}CHCOSPr^i$	127	25
N-Ethyl *β*-mercaptocinnamamide	$PhC(SH){=}CHCOSCH_2Ph$	150	25
N-Phenyl *β*-mercaptocinnamamide	$PhC(SH){=}CHCONHEt$	136–7	26
N-Phenyl *β*-mercaptocinnamamide	$PhC(SH){=}CHCONHPh$	107–8	26
2-Thioacetylcyclopentanone	 $\begin{array}{l}CH_3C(SH){=}CCOCH_2^{\,a}\\ \qquad\qquad\;\; \vert \quad \vert\\ \qquad\qquad\;\; CH_2\,CH_2\end{array}$	80–3/0.5 mm	27
2-Thioacetylcyclohexanone	 $\begin{array}{l}CH_3C(SH){=}CCOCH_2\diagdown\;\;\;^{a}\\ \qquad\qquad\;\; \vert \qquad\quad CH_2\\ \qquad\qquad\;\; CH_2\,CH_2\diagup\end{array}$	90–2/0 1 mm	22
2-Thioacetylcycloheptanone	 $\begin{array}{l}CH_3C(SH){=}CCOCH_2CH_2^{\,a}\\ \qquad\qquad\;\; \vert \qquad\quad \vert\\ \qquad\qquad\;\; CH_2\,CH_2CH_2\end{array}$	110–2/0 8 mm	27

[a] Thioenol form [b] Not reported.

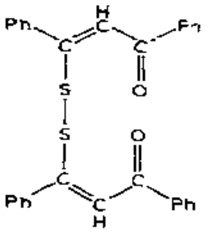
E. PHYSICAL MEASUREMENTS ON MONOTHIO-β-DIKETONES

(i) Infrared spectra

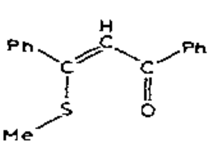
The infrared spectra of monothio-β-diketones display three characteristic bands which have been assigned as follows [12,22] 1670–1590 cm^{-1} $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, 1638–1530 cm^{-1} $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, and 1267–1190 cm^{-1} $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ The spectra of crystalline monothio-β-diketones show no absorption in the range 1760–1700 cm^{-1}, attributable to $\nu(\mathrm{C}{=}\mathrm{O})$ (ketonic), indicating that in the solid state, these compounds exist almost entirely in the thioenol tautomeric form (III). The absence of a sharp SH absorption at ca 2570 cm^{-1} indicates strong chelation of the thiol proton [12]

(ii) Electronic spectra

Most monothio-β-diketones are red, whereas the sodium salt the disulphide (X), and the *S*-methyl derivative (XI) of 3-mercapto-1,3-diphenylprop-2-en-1-one (III, R = R′ = Ph) are yellow. The red colour of (III, R = R′ = Ph) is due to a band at 505 nm (ε, 170), this is an R-band associated with the C–SH group of the hydrogen-bonded thioenol tautomer (III). This grouping is absent in the sodium salt, the disulphide (X), and the *S*-methyl derivative (XI). The spectrum of (III, R = R′ = Ph) displays a strong band at 408 nm (ε, 14500), this is a K-band associated with the $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ chromophore, corresponding to a π ⟶ π* transition. There is also another strong band at 325 nm (ε, 11000) which occurs in the same region and with half the intensity of the K-band in dibenzoylmethane It is considered to be due to the conjugated system associated with the C = O chromophore [30].



(X)

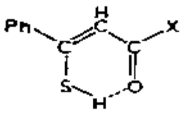


(XI)

The band at ca. 315 nm in the spectra of ethyl β-mercaptothiocinnamate and *N*-phenyl-β-mercaptocinnamamide has been ascribed to the enthiol form (XII; X = SEt or NHPh) The intensity of this band decreases with increasing solvent polarity as follows. $\mathrm{CCl_4} >$ n-hexane $> \mathrm{CHCl_3} > 99\%$ EtOH $> 75\%$ EtOH. This indicates that in the more polar solvents there is tautomerism between the thioenol form (XII) and the thioxo form (XIII) [31].

(iii) Mass spectra

The mass spectrum of (III; R = R′ = Ph) is characterized by an intense molecular ion at *m/e* 240 accompanied by an intense M-1 ion at *m/e* 239. This is due to the formation



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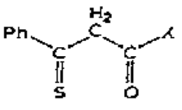
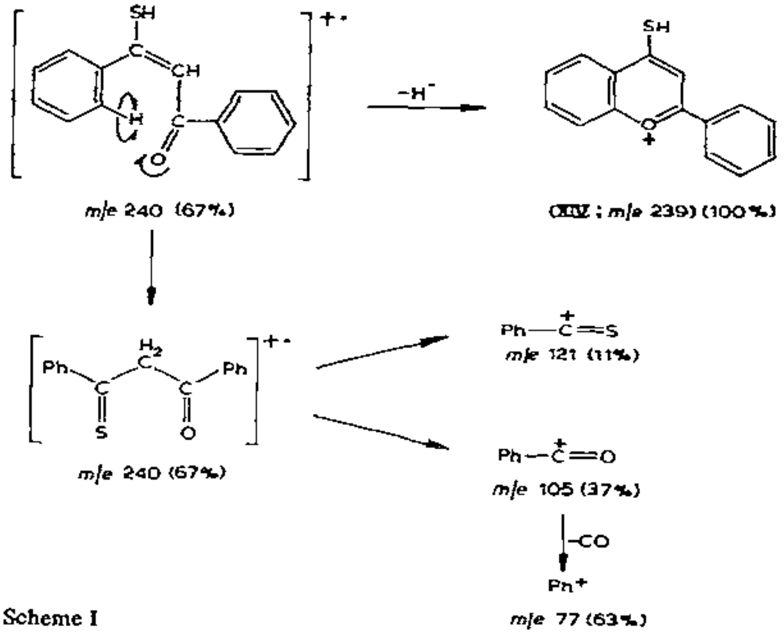


(XIII)

of a five-membered resonance-stabilized cyclic ion (XIV) Other peaks in the spectrum which occur at m/e 121, 105. and 77 are due to ions formed by homolytic cleavage reactions, as shown in Scheme I[12].



Scheme I

(iv) Dissociation constants

Measurements on monothio-β-diketones in dioxan–water solutions with varying mole fraction (n_2) of dioxan have shown that the values of the dissociation constant (pK_D) vary linearly with n_2 over a range of n_2 from 0.18 to 0.44 The monothio-β-diketones are stronger acids than β-diketones, having pK_D values 2.0–2.7 log units lower than their oxygen analogues [32,33]. The values of pK_D, in 74.5 vol.% of dioxan, obtained for some β-diketones and their sulphur analogues are given in Table 3.

F. METAL COMPLEXES OF MONOTHIO-β-DIKETONES

Metal ions known to form complexes with monothio-β-diketones are listed in Table 4. With the exception of vanadium (IV) and manganese (II), all the metal ions listed form neutral complexes of the type ML_n (LH = monothio-β-diketone; n = oxidation state of

TABLE 3

Values of pK_D for monothio-β-diketones RC(SH)=CHCOR′ and their oxygen analogues in 74.5 vol % dioxan at 30°C

R	*R′*	*Monothio-β-diketone*	*β-Diketone*
Ph	Ph	11.14 [32,35], 11.40 [33]	13.75 [34]
Me	Ph	10.43 [35], 10.40 [33]	12.85 [34]
Me	Me	10.26 [32], 10.20 [33]	12.60 [32]
Ph	Me	10.45 [33]	
C_4H_3S [a]	CF_3	7.05 [32]	8.64 [36]
C_4H_3S	Me	10.40 [33]	
Me	C_4H_3S	10.00 [33]	12.35 [34]
C_4H_3S	C_4H_3S	10.80 [33]	
Me	Bu^t	10.65 [33]	
Bu^t	Me	12.02 [33]	
Me	$C_{10}H_7$ [b]	11.20 [33]	
$C_{10}H_7$	Me	10.70 [33]	
Ph	$C_{10}H_7$	11.45 [33]	
$C_{10}H_7$	Ph	11.30 [33]	

[a] C_4H_3S = 2-thienyl [b] $C_{10}H_7$ = 2-naphthyl.

the metal). Nickel complexes have been isolated with nearly all the monothio-β-diketones listed (Table 2, ref. 7) [12,17–19,22]. However, for most of the other metal ions, complexes are known only with 3-mercapto-1,3-diphenyl-prop-2-en-1-one (III, R = R′ = Ph) [37–39].

The nickel complexes are brown, diamagnetic, square-planar, and insoluble in water but readily soluble in most polar and non-polar organic solvents On the other hand, most nickel complexes of β-diketones are green, paramagnetic, octahedral, and, at most, sparingly soluble in organic solvents, although a few red, diamagnetic complexes of sterically hindered ligands have been prepared [3,4]. It has been recently observed [40] that the replacement of oxygen by sulphur in bis-chelate complexes of cobalt(II) and nickel(II) has two important structural consequences, viz. depolymerization and the stabilization of the planar form.

Attempts to prepare monothio-β-diketone complexes of vanadium(III) and chromium(II), even in the absence of air, result in the formation of complexes of vanadium(IV) and chromium(III) [38,41]. When monothiodibenzoylmethane (III; R = R′ = Ph) is treated with manganese(II) acetate in alcohol, even in the presence of hypophosphorous acid, the disulphide (X) is formed With manganese(III) acetate the ligand is oxidized to the disulphide so rapidly that the maganese(III) complex cannot be isolated. However, the manganese(III) complex of 5-mercapto-2,2,6,6-tetramethylhept-4-en-3-one (III; R = R′ = CMe_3) has been obtained [38].

If cobalt(II) salts are treated with monothio-β-diketones without precautions to exclude air, the cobalt(III) complexes are readily formed. However, the cobalt(II) complexes of monothioacetylacetone, thiobenzoylacetone, and monothiodipivaloylmethane have been obtained by the use of thoroughly dried and degassed solvents under rigorously anaerobic conditions [42]. The cobalt(II) complex of monothiodibenzoylmethane has been obtained from an aqueous alcohol solution containing piperidine at 20°C [39].

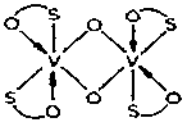
TABLE 4

Metal ions known to form neutral complexes with monothio-β-diketones

VA	*VIA*	*VIIA*	*VIII*			*IB*	*IIB*	*IIIB*	*IVB*	*VB*
										P(III)
V(IV)	Cr(III)	Mn(II) Mn(III)	Fe(II) Fe(III)	Co(II) Co(III)	Ni(II)	Cu(I) Cu(II)	Zn(II)	Ga(III)		As(III)
	Mo(III)		Ru(III) Ru(IV)	Rh(III)	Pd(II)	Ag(I)	Cd(II)	In(III)	Sn(II) Sn(IV)	Sb(III)
			Os(III) Os(IV)		Pt(II)		Hg(II)	Tl(I)	Pb(II)	Bi(III)

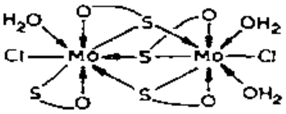
The iron(II) complex of monothiodipivaloylmethane has been obtained under anaerobic conditions [42]. The iron(II) and manganese(II) complexes, FeL_2py_2 and MnL_2py_2 (LH = PhC(SH)=CHCOPh), have been obtained from pyridine solution below 15°C; at higher temperatures oxidation occurs [39].

Both six- and five-coordinate complexes are known with vanadium(IV). The compound VOL_2 (LH = C_4H_3SCSH=$CHCOCF_3$) is dimeric in nitrobenzene and its infrared spectrum shows no ν(V=O) absorption in the region 900–1000 cm^{-1}, accordingly, it was assumed to have the μ-dioxo-bridged structure (XV) [17] The compounds VOL_2 (LH = RCSH=CHCOR′, R = Ph, R′ = Ph, OEt; R = Me, R′ = Ph), which are monomeric in benzene or methylene chloride, display ν(V=O) in the range 984–996 cm^{-1} and are considered to have a square-pyramidal configuration [43].



(XV)

The only molybdenum(III) complexes which have been reported are those having the empirical formulae $Mo_2L_4Cl_2(H_2O)_3$ (LH = RCSH=CHCOR′, R = Ph, R′ = Ph, OEt, R = 2-thienyl, R′ = CF_3). They are considered to have the tris-μ-thiolo-bridged structure (XVI) in which the molybdenum atoms are eight-coordinate. All have anomalously low magnetic moments [44].



(XVI)

Ruthenium and osmium form complexes with monothiobenzoylmethane of the type ML_3 and ML_4 (M = Ru, Os). In the ruthenium(IV) and osmium(IV) complexes the metal atom is considered to be eight-coordinate [39]

In the copper(I), silver(I), and thallium(I) complexes ML the monothio-β-diketone is most likely bound to the metal via the sulphur atom only The compounds are insoluble and probably polymeric with sulphur bridges [17,37,38].

Of interest are the tris-ligand complexes of monothiodibenzoylmethane with the Group VB elements, phosphorus, arsenic, antimony, and bismuth. Whereas the antimony and bismuth complexes are readily soluble in benzene, chloroform, and alcohol, the phosphorus and arsenic complexes are not. In the former the ligand is chelated through both sulphur and oxygen but the infrared data indicate that the ligand is bound through sulphur only in the arsenic complex and through oxygen only in the phosphorus compound. This difference in the mode of coordination is manifested in their reaction with water. The phosphorus compound is hydrolyzed within a few minutes, whereas the arsenic complex is unaffected by long contact with boiling water [37]

G. PHYSICAL MEASUREMENTS ON METAL COMPLEXES OF MONOTHIO-β-DIKETONES

(i) Infrared spectra

The infrared spectra of the complexes ML_n display five characteristic bands which have been assigned as listed in Table 5 [12,37,38]. There is some doubt about the assignments of $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and it is possible that these assignments should be interchanged. There is also a band of medium intensity in the range 820–790 cm^{-1}, no similar band occurs in the spectra of β-diketone complexes. This band was tentatively assigned as $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ stretching coupled with another mode, possible C–H deformation [12,37], but this assignment needs further confirmation.

TABLE 5

Characteristic infrared bands of metal complexes of monothio-β-diketones

Band (cm^{-1})	*Assignment*
1590–1525	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1542–1458	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1270–1220	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
499–437	$\nu(\mathrm{M} - \mathrm{O})$
399–376	$\nu(\mathrm{M} - \mathrm{S})$

The copper(I), silver(I), cadmium(II), and mercury(II) complexes, like the *S*-methyl derivative (XI), display $\nu(\mathrm{C} = \mathrm{O})$ at 1640–1605 cm^{-1} but no absorption in the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{M} - \mathrm{O})$ regions. This indicates that in these complexes the ligand is bound through sulphur only. The silver and mercury complexes are almost certainly two-coordinate, however, the low solubility of the cadmium complexes indicates that they are probably four-coordinate and polymeric with sulphur bridges [19,38].

The spectrum of the arsenic(III) complex of (III; R = R′ = Ph) displays $\nu(\mathrm{C} = \mathrm{O})$ at 1640 cm^{-1}, indicating that the carbonyl group is not coordinated [37].

(ii) Electronic spectra

The electronic spectra of a considerable number of nickel(II) complexes of monothio-β-diketones have been measured. The band at 14400–15600 cm^{-1} (ϵ, ca. 200) and the shoulder at 19000–22800 cm^{-1} have been assigned as $d - d$ transitions of square-planar coordinated nickel(II), while the five more intense bands occurring at higher frequencies are regarded as charge-transfer bands [22,30]. The position of the lowest energy band at ca. 15000 cm^{-1} has been used to place the various monothio-β-diketones among other sulphur ligands in the spectrochemical series as follows [45]: dtp $<$ Me–OMe $\simeq$ Ph–OEt $\simeq$ Me–OEt $<$ $\mathrm{C_4H_3S{-}CF_3}$ $<$ Ph–Ph $\simeq$ exan $\simeq$ Me–Ph $\simeq$ $\mathrm{Bu^t{-}Bu^t}$ $<$ Me–Me $<$ dtc (dtp = diethyldithiophosphate; exan = ethyl xanthate; dtc = *N,N′*-diethyldithiocarbamate).

Whereas palladium(II) complexes are usually more deeply coloured than their platinum(II) analogues, the platinum complexes of monothio-β-diketones are darker than the corresponding palladium complexes. The lowest frequency band of the palladium complex of monothiodibenzoylmethane occurs at 22400 cm^{-1} while the platinum complex displays a weak shoulder at 17000 and a maximum at 19600 cm^{-1}. The $M \rightarrow L_{\pi *}$ charge-transfer band of the nickel complex occurs at 18000 cm^{-1} [30]. The order of increasing frequency of the $M \rightarrow L_{\pi *}$ band for maleonitriledithiol and cyanide complexes is: $Ni \simeq Pt < Pd$ [46,47]. In this respect monothio-β-diketones resemble maleonitriledithiol and cyanide.

The spectra of the green complexes $VO(RCS{=}CHCOR')_2$ (R = Ph, R' = Ph, OEt, R = Me, R' = Ph) display two absorptions below 18000 cm^{-1}, viz. a shoulder at 10500–12100 cm^{-1} and a band at 14700–17300 cm^{-1}, which have been assigned provisionally as the $d_{xy} \rightarrow d_{xz}, d_{yz}$ and the $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, respectively. The two intense bands above 20000 cm^{-1} are considered to be charge-transfer bands [43].

The spectrum of the iron(II) complex $Fe(Me_3CS{=}CHCOCMe_3)_2$ shows a maximum at 10500 cm^{-1}, indicative of a tetrahedral configuration [42].

The spectra of the cobalt(II) complexes $Co(MeCS{=}CHCOCMe)_2$ and $Co(PhCS{=}CHCOCMe)_2$ in chloroform solution display a maximum at 7300 cm^{-1} with a shoulder at ca. 9500 cm^{-1}, denoting a tetrahedral configuration. On the other hand, the solid-state spectrum of $Co(Me_3CS{=}CHCOCMe_3)_2$ (λ_{max}, 8300 cm^{-1}) is indicative of a square-planar structure. Nevertheless, in toluene solution the spectrum progressively changes towards a typical tetrahedral spectrum as the temperature is raised [42].

(iii) Magnetic moments

The moments of the vanadium(IV) complexes lie within the range 1.72–1.78 B.M. and are consistent with the expected value for a d^1 ion [17,43]. The complex $Cr(PhCS{=}CHCOPh)_3$ has a moment of 3.8 B.M., usual for chromium(III) [41]. The manganese(III) compound $Mn(Me_3CS{=}CHCOCMe_3)_3$ is spin-free [38].

The cobalt(III) and nickel(II) complexes are diamagnetic [12,19,38]. The cobalt(II) complex $Co(Me_3CS{=}CHCOCMe_3)_2$ is spin-paired with a moment of 2.93 B.M. but in chloroform solution the moment ranges from 3.17 B.M. at 294°K to 3.65 B.M. at 318°K. The compounds $Co(MeCS{=}CHCOCMe)_2$ and $Co(PhCS{=}CHCOCMe)_2$ are spin-free with moments of 4.45 and 4.59 B.M., respectively, indicating a tetrahedral configuration [42]. Several copper(II) complexes of the type CuL_2 are known and their moments are normal, lying within the range 1.84–1.93 B.M. [17,19]

The iron(II) complex $Fe(Me_3CS{=}CHCOCMe_3)_2$ has a moment of 5.18 B.M. in toluene, the moment was not measured in the solid state [42].

The iron(III) complexes display anomalous magnetic behaviour, their room-temperature moments varying between 2.3 and 5.8 B.M. (see Table 6). The ethyl thiobenzoylacetate complex behaves as a normal paramagnetic and obeys the Curie–Weiss law with $\theta = -8$°K. The moments of the other complexes are temperature-dependent, due to a thermal equilibrium between the nearly equi-energetic spin-paired (t_{2g}^5) and spin-free ($t_{2g}^3 e_g^2$) configurations of the iron atoms, resulting from the approximately equal magnitudes of the ligand field (Δ) and the pairing energy (π) in these complexes. The ligand field, and consequently the magnetic behaviour, are sensitive to the nature of R and R'; electron-withdrawing groups appear to be the most effective in increasing the population of the spin-paired configuration [48].

TABLE 6

Magnetic data on $Fe(RCS{=}CHCOR')_3$ complexes

R	*R'*	*μ* (*298° K*)	*Temp. range* (*°K*)	*Range of μ*
Ph	CF_3	2.31	80–373	1.86 – 3.65
p-BrC_6H_4	CF_3	3.10	80–378	2.06 – 4.45
p-MeC_6H_4	CF_3	3.45	80–378	2.11 – 5.06
p-$MeOC_6H_4$	CF_3	3.44	80–375	2.70 – 4.65
2-Thienyl	CF_3	5.49	133–368	4.13 – 5.58
2-Furyl	CF_3	5.61	80–373	4.07 – 5.70
Ph	Ph	5.50	80–403	2.18 – 5.77
Ph	OEt	5.82	93–293	5.67 – 5.82

Some measurements have been made in complexes of metals of the second and third transition series. The molybdenum(III) complexes $Mo_2L_4Cl_2(H_2O)_3$ (LH = monothio-β-diketone), which are considered to have the thiolo-bridged structure (XVI), have anomalously low moments ranging from 0.3 to 1.1 B.M. Most octahedral complexes of molybdenum(III), for which magnetic measurements have been made, have moments lying between 3.66 and 3.88 B.M., as expected for the d^3 configuration with no orbital contribution to the moment. The low moments of the monothio-β-diketone complexes and of some other thiolo-bridged molybdenum(III) complexes are considered to be due to metal–metal interaction either directly or via the bridging atoms.[44]

OsL_3 (LH = PhCS=CHCOPh) has a moment of 1.66 B.M., indicating a spin-paired (t_{2g}^5) octahedral complex; osmium(III) complexes normally have moments within the range 1.6–1.95 B.M. ESR measurements on the corresponding ruthenium(III) complex indicate the presence of one unpaired electron (i.e. the t_{2g}^5 configuration).[39]

The moment of OsL_4 is 1.89 B.M., while RuL_4 is diamagnetic. The diamagnetism of the ruthenium complex may indicate a cubic environment and the moment of the osmium complex indicates the presence of two unpaired electrons.[39] Octahedral osmium(IV) complexes, which presumably have the t_{2g}^4 configuration, have room-temperature moments within the range 1.2–1.7 B.M., far below the spin-only value of 2.84 B.M. Osmium(IV) has a high spin–orbit coupling constant λ; this means that kT/λ is quite small at room temperature, leading to a magnetic moment which is low at ordinary temperatures and strongly temperature-dependent[49]. Little is known about the magnetism of eight-coordinate osmium(IV).

(iv) Mossbauer spectra

Mossbauer spectra have been obtained at 300 and 80° K for the complexes $Fe(RCS{=}CHCOR')_3$ (R = Ph, Me, R′ = Ph, Me), which display a thermal equilibrium between the $^6A_1$ ($t_{2g}^3e_g^2$) and the $^2T_2$ (t_{2g}^5) spin isomers. Both spin isomers were detected in all four compounds, although not always at both temperatures. This is in contrast to tris-(*N,N*-dialkyldithiocarbamato)iron(III) complexes for which unfavourable relaxation times prevent the detection of the isomers by Mossbauer spectroscopy. The Mossbauer parameters[50] for the monothio-β-diketone complexes are given by Cox and Darken[7] in Table 13. It can be seen from the Table that the low-spin ($^2T_2$) isomers have much larger quadrupole splittings (ΔE) than the high-spin ($^6A_1$) isomers at the same temperature.

(v) NMR spectra

Data obtained from the NMR spectra of acetylacetonate, β-ketoimine, and monothioacetylacetonate complexes of nickel(II) in pyridine solution show that the contact shifts are a sensitive function of the heteroatom and that the extent of σ-delocalization increases as $N < O < S$, while the π-delocalization decreases as $N > O > S$. The observed increase in σ-spin delocalization parallels in reverse order the relative positions of the ligands in the spectrochemical series viz. β-ketoimine > acetylacetone > monothioacetylacetone[51].

The NMR spectra are further discussed below (Section H).

(vi) ESR spectra

ESR measurements have been made on three vanadium(IV) complexes of the type $VO(RCS{=}CHCOR')_2$. The spectra are similar to those of other VO^{2+} complexes. The g_0 values are somewhat higher (~0.005) than those found for β-diketone complexes, consistent with a greater electron delocalization in the monothio-β-diketone complexes relative to β-diketone complexes[43].

The values of the isotropic hyperfine splittings A_0 for vanadium(IV) complexes decrease in the order: β-diketone (~110*G*) > monothio-β-diketone (~96*G*) > *N,N*-dialkyldithiocarbamate (~90*G*) > maleonitriledithiolate (~70*G*). This sequence is consistent with the greater degree of covalency of (*b*) class (sulphur) compared to (*a*) class (oxygen) donors[43].

(vii) X-ray structural analyses

A preliminary structural investigation on $Ni(Me_3CS{=}CHCOCH_3)_2$ indicated that the compound probably has a *trans* arrangement[52].

Although it was earlier reported that a preliminary X-ray structural determination on the isomorphous palladium and platinum complexes $M(PhCS{=}CHCOPh)_2$ (M = Pd, Pt) showed that these compounds had a *trans*-configuration[45], this was in error. Both complexes are *cis* square-planar, the Pd–S distances are 2.26 and 2.22Å[53].

The crystal structure of monothiodibenzoylmethanato-π-methylallylpalladium(II), $(\pi\text{-}C_4H_7)Pd(PhCS{=}CHCOPh)$, has been determined by a three-dimensional X-ray crystallographic analysis. The Pd–O and Pd–S distances are 2.067 and 2.291 Å, respectively. The Pd–C distances are 2.08, 2.15, and 2.21 Å to the three carbon atoms of the methylallyl backbone. The long Pd–C bond length of 2.21 Å is opposite the sulphur atom and may be ascribed to a *trans* effect[54].

The Pd–S bond length in *cis*-$Pd(PhCS{=}CHCOPh)_2$ (2.26 Å) and in the allyl complex

(2 29 Å) is much shorter than the value of 2 49 Å calculated from the observed Pd—O distance and the difference between the sulphur and the oxygen covalent radii. This pronounced shortening is indicative of considerable Pd—S π-bonding The difference between the geometry of the monothio-β-diketone chelate ring and that obtaining in the β-diketone analogues reflects the asymmetry induced in the former by the presence of the large sulphur atom [54]

(viii) Dipole moments

The dipole moments of the nickel(II), palladium(II), and platinum(II) complexes of monothiobenzoylmethane (LH), obtained from static polarization measurements in benzene solution, were found to be as follows. NiL_2, 2.45D, PdL_2, 3 63D, PtL_2, 2 97D Dielectric relaxation measurements in benzene solution gave the following values for the dipole moments NiL_2, 1 2 ± 0.1D, PdL_2, 1 3 ± 0 1D, PtL_2, 1.2 ± 0 1D. The appreciably higher values obtained from static polarization measurements are considered to be due to abnormally high atomic polarization in these complexes [55] Similar high atomic polarization has been found for many β-diketone complexes [56].

Since the X-ray structure determination has shown the palladium and platinum complexes to have the *cis*-configuration in the crystalline state [53], the non-zero values for the dipole moments can be taken as evidence for the existence of the *cis*-form in solution In an attempt to ascertain if both isomers were present in solution, the NMR spectra were measured but, due to insufficient solubility, the signal due to the vinyl protons could not be detected with certainty It appears that only one isomer is present in solution, since attempts to separate the *cis—trans* isomers by thin-layer chromatography were unsuccessful It is considered that the complexes exist in solution solely in the *cis*-form, since only a small dipole moment would be expected for the *cis*-isomer and the electronegativity difference between the oxygen and sulphur atoms would not be great because these atoms form part of a pseudo aromatic ring in the complex The relatively high value of the dielectric relaxation times (ca 80 × 10^{-12} sec) is indicative of a non-planar arrangement of the phenyl groups [55], this is in keeping with the results obtained from the X-ray structure determination [53]

(ix) Stability constants

Stepwise formation constants (k_1 and k_2) and overall stability constants (β_n) have been measured for eight bivalent metal complexes of monothiobenzoylmethane and for five metal complexes of benzoylthioacetone and for the zinc complexes of another eleven monothio-β-diketones. The measurements were made at 30°C in 74.5 vol.% dioxan—water with perchlorate, nitrate, or chloride salts of the metals. These results, together with the values of $\log \beta_2$ for the corresponding β-diketone complexes, are given in Table 7.

Livingstone and Sullivan [35] determined the stoicheiometric stability constants with chloride and with perchlorate as supporting electrolyte (figures for the latter are listed in Table 7). Stoicheiometric stability constants are thermodynamic stability constants which are valid for a standard state, defined by the composition of the solution [57]. Thermodynamic stability constants may be obtained from the stoicheiometric constants by the

TABLE 7

Stability constants of metal complexes of monothio-β-diketones and β-diketones in 74.5 vol % dioxan at 30°C

R	*R'*	*Metal ion*	*Monothio-β-diketone complex*			*β-Diketone complex*
			log k_1	*log k_2*	*log β_2*	*log β_2*
Ph	Ph	Cu(II)			22.15 [32]	25.00 [32]
			9.90 [35]	11.22 [35]	21.12 [35]	25.10 [34]
					22.6 [33]	
Ph	Ph	Ni(II)			21.65 [32]	20.18 [34]
			9.95 [35]	10.80 [35]	20.72 [35]	
					22.2 [33]	
Ph	Ph	Zn(II)	8.84 [35]	9.08 [35]	17.92 [35]	19.64 [34]
			10.23 [33]	10.06 [33]	20.29 [33]	
Ph	Ph	Pb(II)			17.4 [35]	18.79 [34]
			10.11 [33]	9.61 [33]	19.72 [33]	
Ph	Ph	Cd(II)	9.04 [35]	8.65 [35]	17.70 [35]	16.63 [58]
			10.40 [33]	10.08 [33]	20.48 [33]	
Ph	Ph	Be(II)	9.38 [33]	7.97 [33]	17.35 [33]	26.03 [34]
Ph	Ph	Mn(II)	7.43 [33]	7.31 [33]	14.74 [33]	17.79 [34]
Ph	Ph	UO_2^{2+}	10.43 [33]	9.47 [33]	19.81 [33]	
Me	Ph	Cu(II)	10.22 [35]	10.00 [35]	20.22 [35]	23.01 [32]
Me	Ph	Ni(II)	9.73 [35]	9.67 [35]	19.40 [35]	18.00 [32]
Me	Ph	Zn(II)	8.23 [35]	8.27 [35]	16.50 [35]	
			9.48 [33]	9.29 [33]	18.77 [33]	
Me	Ph	Pb(II)	8.26 [35]	7.16 [35]	15.42 [35]	16.35 [32]
Me	Ph	Cd(II)	8.23 [35]	7.80 [35]	16.04 [35]	14.54 [58]
Ph	Me	Zn(II)	9.57 [33]	9.45 [33]	19.02 [33]	
Me	$C_{10}H_7$ [a]	Zn(II)	10.28 [33]	9.68 [33]	19.96 [33]	
$C_{10}H_7$ [a]	Me	Zn(II)	9.88 [33]	9.53 [33]	19.41 [33]	
Me	C_4H_3S [b]	Zn(II)	9.19 [33]	9.03 [33]	18.22 [33]	
C_4H_3S	Me	Zn(II)	9.46 [33]	9.24 [33]	18.70 [33]	
Ph	$C_{10}H_7$	Zn(II)	10.47 [33]	10.10 [33]	20.57 [33]	
$C_{10}H_7$	Ph	Zn(II)	10.37 [33]	10.12 [33]	20.49 [33]	
Me	t-Bu	Zn(II)	9.61 [33]	9.53 [33]	19.14 [33]	
t-Bu	Me	Zn(II)	10.36 [33]	10.24 [33]	20.60 [33]	
Me	Me	Zn(II)	9.33 [33]	9.29 [33]	18.62 [33]	
C_4H_3S	C_4H_3S	Zn(II)	9.76 [33]	9.51 [33]	19.27 [33]	

[a] $C_{10}H_7$ = 2-naphthyl. [b] C_4H_3S = 2-thienyl.

use of the appropriate activity coefficients but there can be some uncertainty in the actual values assigned. Livingstone and Sullivan found that the thermodynamic stability constants are 1.6–1.8 log units greater than the stoicheiometric values under the conditions they used. The values quoted by Uhlemann et al.[33] for the zinc, lead, and cadmium complexes are appreciably higher than those reported by Livingstone and Sullivan but Uhlemann's values are the thermodynamic stability constants. Similarly, the stability constants of the β-diketone complexes, determined by Van Uitert et al.[34] and quoted for comparison in Table 7, are thermodynamic constants.

From the stability data, certain generalizations can be made. With sodium perchlorate as the supporting electrolyte the stability order is Cu > Ni > Zn > Cd > Pb. This sequence differs from the Mellor–Maley series[59], Cu > Ni > Pb > Zn > Cd, which has been found to hold almost universally for oxygen and nitrogen ligands. Class (*a*) metal ions, by definition, form stronger complexes with oxygen than with sulphur donors, whereas the reverse is true for (*b*) class metal ions[6,60]. The (*a*) class metal ions beryllium(II) and manganese(II) form stronger complexes with β-diketones than with their monothio analogues. However, in view of the ready oxidation of manganese(II) in the presence of monothio-β-diketones (vide supra), the values for manganese(II) must be accepted with reserve. The metal ions, nickel(II), zinc(II), cadmium(II), and lead(II) form stronger complexes with monothio-β-diketones, showing their (*b*) class character. The situation with copper(II) is interesting in that $\log \beta_2$ is greater for β-diketones than for their monothio derivatives. This indicates that copper(II) is definitely (*a*) class with respect to these ligands. On the other hand, copper(I) is class (*b*) in that it readily forms complexes with sulphur, phosphorus, and arsenic ligands.

The copper(II) and nickel(II) complexes are unusual, since the values for $\log K_{av}$ are greater than pK_D for the ligand. This situation is rare.

The data obtained by Uhlemann et al.[33] for the zinc complexes show that the greater the value of pK_D, the greater the value of $\log \beta_2$.

Stability measurements have been made for nine rare earth complexes of benzoylthioacetone (see Table 8). The measurements were made on the perchlorates at 0.1 *M* ionic strength in 3:1 acetone–water solution at 30°C[61]. As for other rare earth complexes,

TABLE 8

Stability constants of rare earth metal complexes of 3-mercapto-1-phenylbut-2-en-1-one MeC(SH)=CHCOPh in 3:1 (v/v) acetone–water at 30°C

Metal ion	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_3$
Y^{3+}	3.85	3.42	3.18	10.45
La^{3+}	3.42	2.98	2.70	9.10
Pr^{3+}	3.71	3.34	2.97	10.02
Nd^{3+}	3.80	3.41	3.16	10.37
Sm^{3+}	4.03	3.55	3.11	10.69
Gd^{3+}	3.92	3.38	3.02	10.32
Dy^{3+}	4.00	3.57	3.28	10.85
Er^{3+}	4.18	3.70	3.45	11.33
Yb^{3+}	4.33	3.82	3.55	11.70

the values of log β_3 rise from lanthanum to samarium and fall to gadolinium, then increase again, while the value for yttrium lies between those of neodymium and samarium. The average value of log β_3 for benzoylacetone is 18, whereas for benzoylthioacetone it is ca. 11, indicating the class (*a*) character of the rare earth ions.

H. ADDUCTS OF METAL COMPLEXES OF MONOTHIO-β-DIKETONES

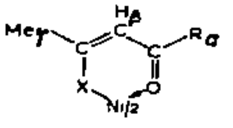
Adducts of nickel(II), palladium(II), platinum(II), zinc(II), mercury(II), and lead(II) complexes of monothio-β-diketones with pyridine, α-picoline, γ-picoline, 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 2,2′,2″-terpyridyl, or triphenylphosphine have been described [18,45]

The adducts of the nickel complexes are paramagnetic (μ, 3 05–3.34 B M.) and their reflectance spectra exhibit bands at ca. 10500 cm^{-1} and 14500–18700 cm^{-1}, which are characteristic of octahedral nickel(II) The terpyridyl adducts display $\nu(C = O)$ at ca. 1650 cm^{-1}, indicating that one carbonyl group is not coordinated and that terpyridyl is acting as a tridentate Consequently, the nickel atom is six-coordinate in these terpyridyl adducts [45].

The phenanthroline, bipyridyl, and bistriphenylphosphine adducts of the palladium(II) and platinum(II) complexes also display $\nu(C = O)$ at ca. 1650 cm^{-1}, indicating that the carbonyl groups of the monothio-β-diketone ligands are not coordinated and that the metal atom is four-coordinate Indeed the complex $Pd(C_4H_3SCS{=}CHCOCF_3)_2(Ph_3P)$ displays $\nu(C = O)$ at 1646 cm^{-1} and $\nu(C \cdots O)$ at 1490 cm^{-1}, indicating the presence of both bidentate (S,O-bonded) and unidentate (S-bonded) monothio-β-diketone [18]

Both five- and six-coordinate zinc complexes have been isolated, viz ZnL_2pic and ZnL_2pic$_2$ ($L = C_4H_3SCS{=}CHCOCF_3$, pic = α- and γ-picoline) [18].

The NMR spectra of the pyridine adducts of the nickel complexes $Ni(MeCX{=}CHCOR)_2py_2$ ($X = O, S, NR'$, $R = Me, Ph$, $R' = Me, Ph$, or *p*-tolyl) have been measured [51]. The observed contact shifts for the β-diketone and monothio-β-diketone complexes are listed in Table 9. The symbols α, β, and γ refer to the structure (XVII) The



(XVII)

variation in X from O to S affects primarily the γ-CH_3 group, causing a shift of 22–24 ppm. Although the highest bonding π-orbital must contain some unpaired spin due to the positive β-CH shifts for all the adducts, one additional spin-transferral mechanism must be present and its magnitude differs with the nature of X It is considered likely that this secondary mechanism is ligand-to-metal spin transfer into the highest bonding σ-orbital [51].

I HALOGENATION REACTIONS OF METAL COMPLEXES OF MONOTHIO-β-DIKETONES

The chromium(III), cobalt(III), rhodium(III), and palladium(II) complexes of acetyl-

TABLE 9

Contact shifts for $Ni(MeCX{=}CHCOR)_2py_2$

X	*R*	*Contact shifts (ppm)*		
		α-CH_3	*β-CH*	*γ-CH_3*
O	Me	−2.95	+18.50	−2.95
O	Ph		+19.28	−3.36
S	Me	−3.00	+14.54	−25.90
S	Ph		+15.05	−27.33

acetone undergo electrophilic substitution at the central carbon atom of the ligand, indicating the aromatic nature of the chelate ring [62–66]. The cobalt(III) complexes of thioacetylacetone and monothiodibenzoylmethane react with *N*-bromosuccinimide to yield the tribromo derivatives $Co(RCS{=}CBrCOR)_3$ (R = Me, Ph) The NMR spectrum of $Co(CH_3CS{=}CHCOCH_3)_3$ has a signal at 6.26 ppm, attributable to the vinylic proton This signal was not observed in the spectrum of the bromination product. The attempted bromination of complexes of some other metals was unsuccessful [67].

Attempts to effect halogen substitution at the central atom of the ligand in the nickel(II), cobalt(III), copper(II), and palladium(II) complexes of monothiobenzoylmethane by reaction with *N*-chloro-, *N*-bromo-, and *N*-iodo-succinimides under a variety of conditions led to oxidation of the ligand and the isolation of indefinite products [68].

5 ANALYTICAL APPLICATIONS

A radio-isotope dilution method, involving the use of monothiodibenzoylmethane, has been developed for the determination of mercury in quantities above 0.5 μg. A known amount of ^{203}Hg-labelled standard mercuric chloride solution is added to the unknown mercury sample solution at pH ~ 4. A sub-stoicheiometric amount of monothiodibenzoylmethane is added and the mercury complex is extracted with chloroform. The standard ^{203}Hg solution is treated in the same manner and from the measured activities of both solutions the amount of mercury in the unknown solution can be calculated Other metals do not interfere [69].

Cobalt, nickel, lead, and zinc can be extracted with 10^{-3} *M* thiothenyltrifluoroacetone in toluene from weakly acid solutions. Copper can be similarly extracted from strongly acid solutions [70].

The extraction of copper, nickel, and cobalt with thioisobutyrylacetone, $Pr^iCSH{=}CHCOMe$, in toluene has been studied over a range of pH. Copper is quantitatively extracted at pH 2.5, whereas no nickel or cobalt is extracted below pH 3.5. However, the reagent is not suitable for analytical application because it is easily oxidized [71].

A method has been described for the extraction and photometric determination of cobalt with monothiodibenzoylmethane. Interfering metals can be separated by re-extraction with sodium hydroxide/sodium cyanide, except in the case of copper. In the presence of thiourea, copper and manganese do not interfere in up to ten-fold amounts. Zinc can be kept in solution by means of ammonia and ammonium thiocyanate but iron must be separated by ether extraction [72].

The gas chromatography of the metal complexes $M(MeCS{=}CHCOCMe)_2$ (M = Co,Ni,Pd) has been effected. The symmetrical peaks obtained indicate that gas chromatography of these compounds could have analytical applications. The general chromatographic characteristics were found to be superior to those of most volatile metal tris(β-ketonates) [73].

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