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Review

DIPOLE MOMENT MEASUREMENTS ON METAL COMPLEXES OF MONOTHIO-β-DIKETONES *

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Summary

Dipole moments have been reported for over 200 monothio-β-diketone complexes, Met(RCS=CHCOR$'$)$_n$ (n = 2, 3). The data show that the nickel(II), palladium(II), platinum(II), and copper(II) complexes are *cis*-square-planar, the zinc(II) complexes are tetrahedral, and the chromium(III), iron(III), ruthenium(III), cobalt(III), and rhodium(III) complexes are *facial* (*cis*)-octahedral. Measurements of the dipole moments of a considerable number of the metal complexes by both the static polarization and dielectric relaxation methods have shown that atomic polarization is ca. 0.3 D in square-planar, 0.5 D in tetrahedral, and 0.9 D in octahedral complexes.

A large number of complexes, Met(RCS=CHCOR$'$)$_n$ (R = phenyl or X-substituted phenyl; R$'$ = CF_3) have been studied. The difference in the values of the dipole moments depend upon: (a) the magnitude and vector direction of the Ph—X bond moments; (b) the inductive effect arising from the difference in electron density of the C^1 and C^5 carbon atoms of the ligand moiety — this is affected by the nature and position of the substituent X on the phenyl ring; (c) the change in moment brought about by the mesomeric effect of the substituent X.

Introduction

β-Diketones exhibit keto-enol tautomerism so that in solution the diketo form I is in equilibrium with the enol forms II and III. In the presence of a metal ion M^{n+} at the appropriate pH the proton can be replaced by the metal

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* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

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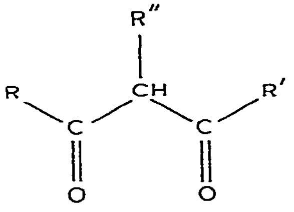
ion to produce a chelate complex IV in which there is delocalization of the C=C and C=O bonds.



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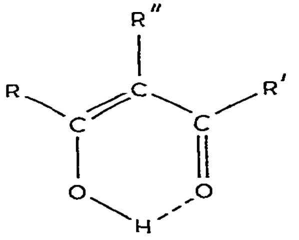

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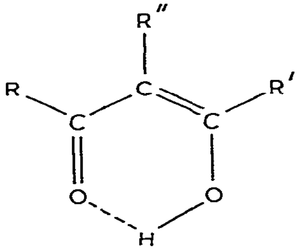

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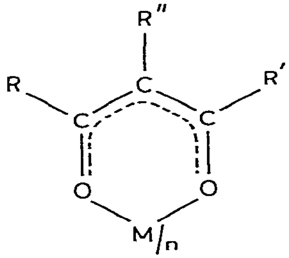

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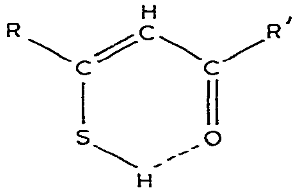
The first β-diketone complexes were reported in 1887 by Combes [1] who prepared several metal complexes of acetylacetone (I; R = R′ = CH_3, R″ = H). Metal chelates of β-diketones have been investigated very extensively and the subject has been reviewed by Morgan and Moss [2], Harris and Livingstone [3], Fackler [4], Gibson [5], and more recently by Mehrotra et al. [6]. However, it was not until 1964 that the first metal complexes of monothio-β-diketones were reported by Chaston and Livingstone [7]. In the solid state and in solution monothio-β-diketones exist entirely in the thienol form (V). The absence of a sharp SH absorption in the infrared spectra indicates strong chelation of the thiol proton and, as with β-diketones, there is delocalization of the C=C and C=O bonds [8].



(V)

Monothio-β-diketones readily form stable complexes with class (b) metal ions such as Mo^{III}, Rh^{III}, Ni^{II}, Pd^{II}, Pt^{II}, Hg^{II}, and Pb^{II}. Although complexes with most borderline metals, viz., Fe^{III}, Ru^{III}, Os^{III}, Co^{III}, Cu^{II}, Zn^{II}, Cd^{II}, In^{III}, Sn^{II}, and Sn^{IV} are known, reported complexes of class (a) metals are relatively few. Nevertheless, complexes of V^{III}, V^{IV}, and Cr^{III} have been reported. Complexes of monothio-β-diketones have been reviewed by Cox and Darken [9], Livingstone [10], and Mehrotra et al. [6]. However, of these, only the review by Mehrotra refers to measurements of the dipole moments, and then only to the earlier work. Consequently, the time is opportune for the appearance of a review dealing with the quite considerable number of dipole moment measurements of monothio-β-diketone complexes which have now been reported.

Measurement of dipole moments

The dipole moment μ of a molecule is defined as the product of the distance d between the centres of positive and negative charges and the magnitude of one of the charges q:

$$\mu = d \times q$$

The charges in molecules are of the order of 10^{-10} esu and interatomic distances are of the order of 10^{-8} cm; consequently, dipole moments have traditionally been expressed in Debye (D), where

$$1\ \mathrm{D} = 1 \times 10^{-18}\ \text{esu cm}$$

In SI (Système International) units

$$1\ \mathrm{D} = 3.33564 \times 10^{-30}\ \mathrm{C\ m}.$$

Values for the dipole moments of inorganic compounds vary from 0—14 D, while the dipole moments of some proteins have been reported to be in excess of 200 D [11].

The distortion polarization, P_D, is temperature independent and is equal to the sum of the electronic polarization, P_E, and the atomic polarization, P_A ($P_D = P_E + P_A$). The electronic polarization is the distortion of the electrons relative to the nuclei; the atomic polarization is a process involving polarization of the atoms leading to changes in bond angles and bond lengths. Polar molecules possess a permanent dipole moment, μ, and under the influence of an electric field this gives rise to orientation polarization, P_O, which is temperature dependent.

Thus for a non-polar molecule the total molar polarization, P_T, is equal to the distortion polarization ($P_T = P_E + P_A$). However, for a polar molecule:

$$P_T = P_E + P_A + P_O\ .$$

For polar molecules $P_O > P_E$ and it is usually assumed that P_A is ca. 5% P_E but for some metal complexes P_A has been found to exceed 50% P_E. This can cause difficulties in the determination of P_O and hence the true value of the dipole moment.

Most dipole-moment determinations on metal complexes have been made by the static polarization method, which involves the measurement of the dielectric constant and the refractive index of solutions of the metal complex in a nonpolar solvent at various concentrations. This method gives the value of $P_T - P_E$, i.e. $P_O + P_A$. It has the disadvantage that the value of P_A cannot be determined. For many simple compounds the value of P_A is 5—10% of the value of P_E, which can be determined from the molar refractivity. In many instances P_A is ignored and the P_O is taken to be $P_T - P_E$. As stated above, the assignment of P_A as ca. 10% P_E is not always valid, since measurement of a number of acetylacetonato complexes by the gas dielectric temperature-variation method showed that for some of these complexes $P_A > 50\% P_E$.

The dipole moments of some metal complexes have been determined from dielectric relaxation measurements. Incremental loss tangents ($\Delta \tan \delta$) of benzene solutions of the metal complexes are measured at various radio frequencies by the method of Roberts and von Hippel [12,13]. This method has the advantage that it gives the dipole moment due to orientation polarization only without the need to estimate the value of P_A.

Discussion of published results

The first measurements of the dipole moments of metal complexes of monothio-β-diketones were made by Eddy et al. [14], who measured the nickel, palladium, and platinum complexes of V (R = R′ = Ph). The values ranged from 2.45 D for the nickel complex to 3.63 D for the palladium complex. An X-ray structural determination had shown that the palladium and platinum complexes have a *cis*-square-planar configuration in the solid state [15]. The appreciable values found for the dipole moments suggested strongly that these complexes exist in the *cis* form in solution also.

In a subsequent study by Livingstone and coworkers [16] the dipole moments of the nickel(II), palladium(II), platinum(II), copper(II), iron(III), and cobalt(III) complexes of seven monothio-β-diketones were measured by both the static polarization and dielectric relaxation methods. The latter method, as stated above, has the advantage of giving a value for the dipole moment without the uncertainty associated with the allowance made for atomic polarization. The values for the dipole moments, μ_s and μ_d, obtained by the static polarization and dielectric relaxation methods, respectively, together with the relaxation times (τ) for the square-planar complexes are listed in Table 1 and those for the octahedral complexes are given in Table 2.

Square-planar complexes

For the square-planar complexes, τ increased generally in the order (R, R′): (Me, CF_3) < (Me, Ph) ≃ (C_4H_3S, CF_3) < (Ph, Ph) ≃ (*p*-MeC_6H_4, CF_3) ≃ (*p*-BrC_6H_4, CF_3). A comparison of the relative sizes of these ligands, obtained from molecular models, showed that the order is in accordance with increasing bulk of the ligand. Furthermore, the octahedral complexes had generally greater values of τ than the square-planar complexes, consistent with their greater bulk. For the square-planar complexes of a given ligand, τ values were approximately constant over the range of metals examined. This is to be expected, since the metal atom has little effect on the size of the complex molecule if the configuration remains the same.

Molecular weight determinations on three of the complexes showed them to be monomeric in benzene and it was assumed that the other complexes are also monomeric.

The observed values of μ_s compared with μ_d were on average 0.31 D greater

TABLE 1

DIPOLE MOMENTS (μ) AND RELAXATION TIMES (τ) OF SQUARE-PLANAR METAL COMPLEXES Met(RCS=CHCOR′)$_2$

R	R′		Ni	Pd	Pt	Cu
Me	Ph	μ_s(D)	2.89	2.58	[a]	3.43
		μ_d(D)	2.69	2.45		3.19
		τ(ps)	112	125		120
Ph	Ph	μ_s(D)	2.45	2.48	2.97	3.46
		μ_d(D)	2.28	2.16		2.64
		τ(ps)	108	169	80	189
Me	CF_3	μ_s(D)	4.14	4.39	[a]	
		μ_d(D)	4.08	4.29		
		τ(ps)	66	77		
C_4H_3S [b]	CF_3	μ_s(D)	5.74	5.88	6.09	4.96
		μ_d(D)	5.44	5.56	5.67	4.09
		τ(ps)	135	115	137	121
Ph	CF_3	μ_s(D)	4.92	5.02	5.35	4.39
		μ_d(D)	4.65	4.88	4.90	3.93
		τ(ps)	137	155	133	137
p-MeC_6H_4	CF_3	μ_s(D)	5.84	5.91	6.16	5.12
		μ_d(D)	5.35	5.54	5.62	4.63
		τ(ps)	168	173	170	175
p-BrC_6H_4	CF_3	μ_s(D)	2.85	2.97	3.21	2.45
		μ_d(D)	2.56	2.92	3.01	2.18
		τ(ps)	162	210	185	148

[a] The Pt complex could not be isolated. [b] C_4H_3S = 2-thienyl.

for the square-planar and 0.91 D greater for the octahedral complexes. These differences were attributed to the contribution made by atomic polarization. Consequently, the lower value, viz. μ_d, can be regarded as the more correct value for the dipole moment.

The appreciable values obtained for the dipole moments of the nickel, palladium, platinum, and copper complexes indicate a *cis*-square-planar configuration. Further evidence for the *cis*-configuration is provided by the substantially higher moments obtained for complexes of the ligands having R′ = CF_3. In these instances the more electronegative carbonyl and CF_3 groups are at the same end of the ligand moiety, thus a higher moment would be expected than when R′ = Ph. This is further supported by the observation that when R′ = p-BrC_6H_4, values for the moments of all the square-planar complexes were lowered by ca. 2 D, indicating that the moment of the p-BrC_6H_4 group is opposing that of the CF_3 group. X-Ray structural determinations have established *cis*-square-planar structures for the nickel(II) complexes of 1-(4-bromophenyl)-3-mercaptoprop-2-en-1-one (V; R = H, R′ = p-BrC_6H_4) [17], 4-mercapto-5-methylhex-3-en-2-one

TABLE 2

DIPOLE MOMENTS (μ) AND RELAXATION TIMES (τ) OF OCTAHEDRAL COMPLEXES $Met(RCS{=}CHCOR')_3$

R	R'		Fe	Co
Me	Ph			
		μ_s(D)	4.81	3.27
		μ_d(D)	4.29	2.68
		τ(ps)	71	192
Ph	Ph			
		μ_s(D)	4.29	3.84
		μ_d(D)	3.30	2.05
		τ(ps)	105	171
Me	CF_3			
		μ_s(D)	^{a}	5.40
		μ_d(D)		5.05
		τ(ps)		116
C_4H_3S	CF_3			
		μ_s(D)	7.00	7.14
		μ_d(D)	5.82	6.55
		τ(ps)	177	215
Ph	CF_3			
		μ_s(D)	6.03	6.54
		μ_d(D)	5.51	5.41
		τ(ps)	236	190
p-MeC_6H_4	CF_3			
		μ_s(D)	6.85	7.36
		μ_d(D)	5.74	6.15
		τ(ps)	233	237
p-BrC_6H_4	CF_3			
		μ_s(D)	3.59	3.62
		μ_d(D)	2.46	2.88
		τ(ps)	164	196

[a] The complex could not be isolated.

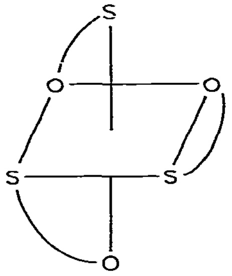
(V; R = Pr^i, R' = Me) [18], 1,1,1-trifluoro-4-mercaptopent-3-en-2-one (V; R = Me, R' = CF_3) [19] and 4-mercaptopent-3-en-2-one (V; R = R' = Me) [20].

For the complexes of nickel, palladium, and platinum the values of μ_s and μ_d are usually constant within 0.3—0.4 D for any particular ligand. Slight variations can be attributed to differences in electronegativities of the metals and variations in the extent of distortion from a square-planar configuration. For the copper complexes μ_s and μ_d generally differed by more than 0.8 D from the mean value obtained for the nickel, palladium, and platinum complexes of the same ligand. This difference is almost certainly due to significant distortion from the square-planar towards the tetrahedral configuration.

Das et al. [16] carried out a group dipole-moment analysis on the square-planar complexes on the basis that the dipole moment μ_d is composed of three types of group moment μ_i, each inclined at an angle Φ_i to μ: these are the two group moments $\mu_{R\text{-ch}}$ and $\mu_{R'\text{-ch}}$ and the metal—chelate ring moment $\mu_{Met\text{-}ch}$.

Octahedral complexes

Values for the dipole moments μ_s and μ_d, for the iron(III) and cobalt(III) complexes were found to be considerably higher than those for square-planar complexes of the same ligand. Although a higher moment would be expected for the *facial*-isomer VI than for the *meridional*-isomer VII, the dipole-moment data cannot establish either isomer unequivocally. However, earlier PMR studies on some vanadium(III) and chromium(III) complexes of the monothio-β-diketones RC(SH)=CHCOCF$_3$ (R = Me, Pr^i, Bu^i, Ph) indicated that these complexes have the *facial*-octahedral configuration with all sulfur atoms *cis* [21]. Subsequent X-ray structural data have established the *facial*-configuration for the iron(III) complex of V (R = Ph, R′ = CF$_3$) [22] and the cobalt(III) complex of V (R = Ph, R′ = CF$_3$) [23].



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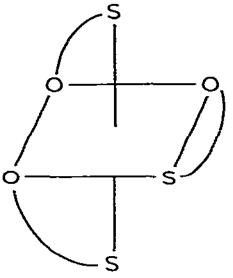

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Tetrahedral complexes

Filipczuk et al. [24] determined the values of μ_s, μ_d, and τ for a number of zinc complexes of monothio-β-diketones; the results are listed in Table 3.

X-Ray crystal structure determinations on the zinc complexes of 1-ethoxy-2-mercaptoprop-2-en-1-one (V; R = H, R′ = OEt) and 1,1,1-trifluoro-4-mercaptopent-3-en-2-one (V; R = CH$_3$, R′ = CF$_3$) have established a tetrahedral configuration for these two zinc complexes [25].

The relaxation times obtained for the zinc complexes [24] (see Table 3) are similar to those obtained for the nickel, palladium, platinum, and copper complexes (see Table 1) for the same ligand, indicating that a similar volume is swept out by the molecular rotation of both the square-planar complexes and the tetrahedral zinc complexes.

The average difference in the values of μ_s and μ_d for the zinc complexes was found to be 0.50 D for a given ligand, although this difference varied appreciably. The difference is attributed to the value of atomic polarization included in the value of μ_s. Group dipole-moments for the metal-chelate rings were calculated and found to be similar to those obtained for the square-planar complexes. The magnitude and direction of these ring moments are dependent on the presence of a CF$_3$ group as the R′ substituent [24].

Complexes of monothio-β-diketones containing the CF$_3$ group

Further studies were made by Das and Livingstone and coworkers [26—32] on the dipole moments of the complexes formed by a wide range of monothio-

TABLE 3

DIPOLE MOMENTS (μ) AND RELAXATION TIMES (τ) OF TETRAHEDRAL COMPLEXES $Zn(RCS{=}CHCOR')_2$

R	R′	μ_s(D)	μ_d(D)	τ(ps)
Me	Ph	3.37	3.02	120
Ph	Ph	3.29	2.72	189
Me	CF_3	3.37	2.41	74
C_4H_3S	CF_3	3.57	3.45	120
Ph	CF_3	3.07	2.75	130
p-MeC_6H_4	CF_3	3.65	3.21	145
p-BrC_6H_4	CF_3	2.46	1.77	175

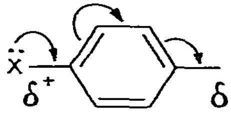
β-diketones, $RC(SH){=}CHCOCF_3$, with nickel(II), palladium(II), platinum(II), copper(II), and zinc(II) (see Table 4) and with the octahedral metals chromium(III), iron(III), ruthenium(III), cobalt(III), and rhodium(III) (see Table 5). The results given are those obtained for μ_s and no correction has been made for atomic polarization, which is ca. 0.3 D for square-planar, ca. 0.5 D for tetrahedral, and ca. 0.9 D for octahedral complexes (vide supra).

For the square-planar complexes and the cobalt complexes — the only octahedral complexes for which data are available for a large number of ligands — the dipole moments decrease if the R groups are arranged in the order:
$p\text{-EtOC}_6\text{H}_4 > 5\text{-MeC}_4\text{H}_2\text{S} > p\text{-MeOC}_6\text{H}_4 > m\text{-F}, p\text{-MeOC}_6\text{H}_3 > m,p\text{-Me}_2\text{C}_6\text{H}_3 \simeq p\text{-EtC}_6\text{H}_4 \simeq m,m\text{-(MeO)}_2\text{C}_6\text{H}_3 > p\text{-MeC}_6\text{H}_4 \simeq p\text{-Bu}^t\text{C}_6\text{H}_4 \simeq p\text{-Pr}^i\text{C}_6\text{H}_4 > \text{C}_4\text{H}_3\text{S} > \beta\text{-C}_{10}\text{H}_7 \simeq m\text{-MeOC}_6\text{H}_4 \simeq m\text{-MeC}_6\text{H}_4 > \text{Ph} > \text{Pr}^i > \text{Bu}^i > \text{Me} > 5\text{-ClC}_4\text{H}_2\text{S} > m\text{-ClC}_6\text{H}_4 > m\text{-BrC}_6\text{H}_4 > p\text{-FC}_6\text{H}_4 > p\text{-ClC}_6\text{H}_4 > p\text{-BrC}_6\text{H}_4 > m,p\text{-Cl}_2\text{C}_6\text{H}_3$.

The positions of the R groups $m,p\text{-(MeO)}_2\text{C}_6\text{H}_3$ and $m,m,p\text{-(MeO)}_3\text{C}_6\text{H}_2$ vary slightly with different metals.

This series can be better understood if we consider only the ligands having R = phenyl or substituted phenyl; the series reduces to:
$p\text{-EtOC}_6\text{H}_4 > p\text{-MeOC}_6\text{H}_4 > m\text{-F}, p\text{-MeOC}_6\text{H}_3 > m,p\text{-Me}_2\text{C}_6\text{H}_3 \simeq p\text{-EtC}_6\text{H}_4 \simeq m,m\text{-(MeO)}_2\text{C}_6\text{H}_3 > p\text{-MeC}_6\text{H}_4 \simeq p\text{-Bu}^t\text{C}_6\text{H}_4 > p\text{-Pr}^i\text{C}_6\text{H}_4 > m\text{-MeOC}_6\text{H}_4 \simeq m\text{-MeC}_6\text{H}_4 > \text{Ph} > m,m,p\text{-(MeO)}_3\text{C}_6\text{H}_2 > m\text{-ClC}_6\text{H}_4 > m\text{-BrC}_6\text{H}_4 > p\text{-FC}_6\text{H}_4 > > p\text{-ClC}_6\text{H}_4 > p\text{-BrC}_6\text{H}_4 > m,p\text{-Cl}_2\text{C}_6\text{H}_3$.

The differences in the values of the dipole moments of the metal complexes depend on a number of factors among which are: (a) the magnitude and vector direction of the Ph—X bond moments; (b) the inductive effect arising from the difference in electron density of the C^1 and C^5 carbon atoms [*] of the ligand moieties; this will be affected by the nature and position of the substituent X on the phenyl ring; (c) the change in moment brought about by the mesomeric effect (VIII) of the substituent X.



(VIII)

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[*] The C^1 atom is part of the CF_3 group and the C^5 atom is the phenyl carbon atom attached to the C^4 atom.

TABLE 4

DIPOLE MOMENTS μ_S(D) OF SQUARE-PLANAR AND TETRAHEDRAL METAL COMPLEXES Met(RCS=CHCOCF$_3$)$_2$

R	Square-planar				Ref.	Tetrahedral	Ref.
	Ni	Pd	Pt	Cu		Zn	
Me	4.14	4.39			16	3.37	24
Pr^i	4.48	4.75	4.90	3.85	27	2.82	27
Bu^i	4.38	4.64	4.89	3.64	27	2.70	27
β-$C_{10}H_7$ [a]	5.47	5.55	5.68		27	3.48	27
Ph	4.92	5.02	5.35	4.39	16	3.07	24
m-ClC_6H_4	4.07	4.09	4.38	3.59	26,27	3.00	27
m-BrC_6H_4	3.93	4.01	4.32	3.55	26,27	2.90	27
p-FC_6H_4	2.92	3.28	3.54		26	1.96	27
p-ClC_6H_4	2.89	3.20	3.42		26	2.10	27
p-BrC_6H_4	2.85	2.97	3.21	2.45	16	2.46	24
m,p-$Cl_2C_6H_3$	2.80	2.97	3.01	2.45	26,27	2.16	27
m-MeC_6H_4	5.33	5.55	5.68	4.66	26,27	3.37	27
p-MeC_6H_4	5.84	5.91	6.16	5.12	16	3.65	24
p-EtC_6H_4	5.94	6.07	6.34	5.26	29	3.85	29
p-$Pr^iC_6H_4$	5.80	5.98	6.38		30	3.77	30
p-$Bu^tC_6H_4$	5.84	5.91	6.31		30		
m,p-$Me_2C_6H_3$	6.05	6.32	6.20	5.46	28	3.76	28
m-$MeOC_6H_4$	5.43	5.88	5.64	4.91	28	3.94	28
p-$MeOC_6H_4$	6.70	7.16	6.73	6.02	28	4.80	28
p-$EtOC_6H_4$	6.95	7.23	7.36	6.36	29	4.81	29
m,m-$(MeO)_2C_6H_3$	5.87	5.96		5.50	29	4.13	29
m,p-$(MeO)_2C_6H_3$	5.62	6.45	6.07	5.24	28	3.96	28
m,m,p-$(MeO)_3C_6H_2$	4.32	4.48		3.98	29	3.38	29
m-F,*p*-$MeOC_6H_3$	6.24	6.48	6.62	5.70	30	4.89	30
C_4H_3S [b]	5.74	5.88	6.09	4.96	16	3.57	24
5-ClC_4H_2S	4.12	4.25	4.32		30		
5-MeC_4H_2S	6.90	7.20	7.31	6.21	30	4.63	30

[a] β-naphthyl. [b] 2-thienyl.

(a) Ph—X bond moments. The conformation adopted by the *meta*-substituted phenyl ring with respect to the chelate ring affects the vector direction of the Ph—X bond moments. Because of the lack of molecular symmetry these bond moments do not cancel entirely in either the square-planar or the octahedral complexes, since the line of action of the group moment does not pass through the C^5 atom.

The square-planar complexes having R = *m*-XC_6H_4 (X = Cl, Br) have dipole moments ca. 1 D greater than those having R = *p*-XC_6H_4, while the octahedral complexes show a difference of ca. 1.4 D. The marked difference in moment between complexes with *meta*- and *para*-substituted phenyl groups can be attributed to a preferred conformation of the phenyl ring whereby the Ph—X group moment lies close to the plane of the chelate rings and on the same side as the CF_3 groups. In other words, there can be little rotation of the phenyl rings. This is further substantiated by the values of the moments of the complexes having R = *m,p*-$Cl_2C_6H_3$. These moments are only 0.1—0.4 D less than the moments of the complexes with R = *p*-ClC_6H_4. If there is restriction to rotation of the phenyl rings and if the phenyl rings have a similar conformation to that in the

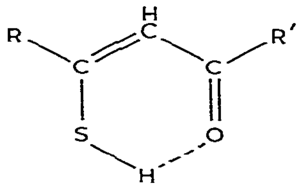
TABLE 5

DIPOLE MOMENTS μ_S(D) OF OCTAHEDRAL METAL COMPLEXES Met$(\mathrm{RCS{=}CHCOCF_3})_3$

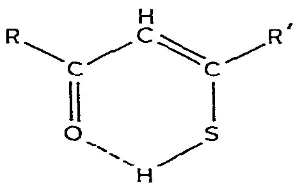
R	Cr	Fe	Ru	Co	Rh	Ref.
Me				5.40		16
β-$\mathrm{C_{10}H_7}$	6.19	6.09	6.69	6.90	7.16	27,31,32
Ph	6.27	6.03	6.11	6.54	6.52	16,27,32
m-$\mathrm{ClC_6H_4}$		4.91	4.83	5.11		26,27
m-$\mathrm{BrC_6H_4}$		4.70	4.55	5.08		26,27
p-$\mathrm{FC_6H_4}$		3.68		3.79	4.13	26,27
p-$\mathrm{ClC_6H_4}$		3.52		3.72		26,27
p-$\mathrm{BrC_6H_4}$		3.59		3.62		16
m,p-$\mathrm{Cl_2C_6H_3}$				3.29		26
m-$\mathrm{MeC_6H_4}$		6.62	6.20	6.79		26,27
p-$\mathrm{MeC_6H_4}$		6.85	6.91	7.36	7.16	16,27
p-$\mathrm{EtC_6H_4}$				7.43		29
p-$\mathrm{Pr^iC_6H_4}$				7.29		30
p-$\mathrm{Bu^tC_6H_4}$				7.36		30
m,p-$\mathrm{Me_2C_6H_3}$				7.75		28
m-$\mathrm{MeOC_6H_4}$				6.91		28
p-$\mathrm{MeOC_6H_4}$				8.57	8.14	28
p-$\mathrm{EtOC_6H_4}$				8.71		29
m,m-$\mathrm{(MeO)_2C_6H_3}$				7.08		29
m,p-$\mathrm{(MeO)_2C_6H_3}$				6.89	7.04	28
m,m,p-$\mathrm{(MeO)_3C_6H_2}$				5.15		29
m-F, p-$\mathrm{MeOC_6H_3}$				7.62		30
$\mathrm{C_4H_3S}$	7.07	7.00	6.91	7.14	7.19	16,27,32
5-$\mathrm{ClC_4H_2S}$				5.20		30
5-$\mathrm{MeC_4H_2S}$				8.67		30

complexes with R = m-$\mathrm{ClC_6H_4}$, molecular models show that the m-X—Ph bond moments in the two phenyl rings are inclined at ca. 170°, thereby almost cancelling each other. A small departure from coplanarity of the chelate and phenyl rings could offset any enhancement of the molecular moment by contribution from the *meta*-chloro-groups.

(b) The inductive effect. Because of the high electronegativity of fluorine, the electron density at C^1 is always lower than at C^5 and C^4. This contention is supported by the fact that the product obtained by the action of hydrogen sulfide on fluorinated β-diketones is the isomer IX (R = $\mathrm{CF_3}$) and there is no evidence that the isomer X is produced even in small yield. It has been reported that nucleophilic attack by hydrogen sulfide takes place at the ketonic group attached to R if the electron-withdrawing power of R is less than that of R′ [8,10,33].



(IX)



(X)

The substituents F, Cl, and Br on the phenyl group are electrophilic, whereas the substituents Me, Et, Pr^i, Bu^t, MeO, and EtO are nucleophilic (+*I* effect). Accordingly, when alkyl substituents are introduced into a phenyl group, either at the *para*- or *meta*-position, they increase the electron density at the C^5 atom relative to that when R = Ph. Consequently, on the basis of the inductive effect alone, complexes having R = p-MeC_6H_4 and m-MeC_6H_4 would be expected to have higher dipole moments than those of the ligand having R = Ph. The experimental results are in accord with this postulate. The replacement of Me by Et brings about a small increase in the dipole moment, but substitution of Me by Pr^i or Bu^t has virtually no effect on the dipole moment, indicating that the nucleophilic (+*I*) effects of Me, Pr^i and Bu^t are approximately equal. However, the introduction of the substituent MeO or EtO at the *para*-position causes a substantial increase in the dipole moment (0.6—1.2 D for square-planar and 1.0—1.7 D for octahedral complexes), indicating the strongly nucleophilic nature (large +*I* effect) of the methoxy and ethoxy groups.

On the other hand, the halogens, F, Cl, or Br, being strongly electrophilic (—*I* effect), when substituted at *para*- or *meta*-positions, produce lower electron density at the C^5 atom relative to that when R = Ph. Thus substitution of halogen in the phenyl ring at either the *para*- or *meta*-positions would be expected to lower the dipole moment of the complex, although the lowering would be expected to be smaller for *meta*-substitution. This has indeed been found to be so: *para*-substitution brings about a reduction of ca. 2.0 D in the value of the dipole moment for square-planar and ca. 2.7 D for octahedral complexes; *meta*-substitution causes a lowering of ca. 1.0 D and 1.6 D, respectively.

Substitution at *para*- and *meta*-positions alters the electron density at the C^5 atom to different extents [34]. A *para*-methyl group produces a higher electron density at the C^5 atom than a *meta*-methyl group. Accordingly, metal complexes with R = p-MeC_6H_4 will be expected to have higher dipole moments than those having R = m-MeC_6H_4. This difference has been found to be ca. 0.4 D for square-planar and ca. 0.6 D for octahedral complexes. Similarly, metal complexes with R = p-$MeOC_6H_4$ have appreciably higher moments than those with R = m-$MeOC_6H_4$: ca. 1.2 D for square-planar and ca. 1.7 D for octahedral complexes. *para*-Halogeno-substitution has the reverse effect: it decreases the electron density at the C^5 atom to a greater extent than *meta*-halogeno-substitution. Thus when R = m-XC_6H_4, the metal complexes have higher moments than when R = p-XC_6H_4 (X = F, Cl, or Br). When R = m,p-$Cl_2C_6H_3$, both substituents lower the electron density at the C^5 atom leading to the lowest values for the dipole moments of monothio-β-diketone complexes.

In complexes where R = m,p-$(MeO)_2C_6H_3$ and m,m,p-$(MeO)_3C_6H_2$, steric factors effect the value of the dipole moment. The carbon atom of the methoxy group is not coplanar with the phenyl ring. This non-linearity of the Me—O—C_6H_4 bonds causes steric hindrance which prevents free rotation of the methoxy groups when R = m,p-$(MeO)_2C_6H_3$ and m,m,p-$(MeO)_3C_6H_2$ but not when R = m,m-$(MeO)_2C_6H_3$. This steric effect may influence the dipole moment in two ways: (a) by orienting the lone-pair orbitals in a direction such that delocalization of lone-pair electrons into the π-orbitals of the aromatic nucleus is restricted; and (b) by aligning the methoxy-groups in a favoured orientation, thereby producing an additional component of electric moment which reduces the group moment $\mu_{R\text{-ch}}$ [28,29]. Consequently, m,p-$(MeO)_2C_6H_3$ falls below p-$(MeO)_2C_6H_4$ and m,m,p-$(MeO)_2C_6H_3$ falls below m,m-$(MeO)_2C_6H_3$ in the dipole-moment series given above.

(c) The mesomeric effect. The electronegativities of the halogens decrease in the order: F > Cl > Br. In terms of the inductive effect the dipole moments of the metal complexes should decrease as the R substituent is changed as follows: p-BrC_6H_4 > p-ClC_6H_4 > p-FC_6H_4. However, the observed dipole moments are in the reverse order for each metal, although the differences are slight. It appears likely that the mesomeric effect operates in these complexes, since the phenyl ring is attached to a chelate ring containing considerable electron delocalization, i.e., aromatic character, and to which is attached the strongly electron-withdrawing CF_3 group. The mesomeric moment arising from the effect shown in VIII operates in a direction towards the chelate ring and would be greatest for the F and least for the Br substituent. Thus the mesomeric effect operates in the reverse direction to the inductive effect and tends to make the dipole moments decrease in the order: p-FC_6H_4 > p-ClC_6H_4 > p-BrC_6H_4, i.e. in the order observed. It follows that the mesomeric effect outweighs the inductive effect for complexes of the ligands with *para*-substituted halogens.

Complexes of monothio-β-diketones containing the CHF_2 group

Das [35] recently reported the dipole moments of some metal complexes of three new difluoro monothio-β-diketones containing the CHF_2 group. The results are listed in Table 6 together with the dipole moments of the metal complexes of the analogous ligands containing the CF_3 group.

The values obtained for the dipole moments when R′ = CHF_2 are 1.4—1.9 D lower for the square-planar complexes, and 2.2 D lower for the one cobalt complex measured, compared to the corresponding complexes containing the CF_3 group. The dipole moment of the zinc complex containing the CHF_2 group was found to be 0.46 D lower than for the corresponding complex of the CF_3 ligand. These lower values are attributed to the smaller electron-withdrawing

TABLE 6

DIPOLE MOMENTS μ_S(D) OF METAL COMPLEXES OF THE FLUORINATED MONOTHIO-β-DIKETONES RC(SH)=CHCOR′ (R′ = CHF_2, CF_3; RC(SH)=CHCOR′ = LH)

R	Complex	R′	
		CHF_2	CF_3
Ph	NiL_2	3.27 [a]	4.92 [b]
p-MeC_6H_4	NiL_2	3.95 [a]	5.84 [b]
	CuL_2	3.19 [a]	5.12 [b]
C_4H_3S	NiL_2	3.87 [a]	5.74 [b]
	CuL_2	3.54 [a]	4.96 [b]
	ZnL_2	3.11 [a]	3.57 [c]
	CoL_3	4.95 [a]	7.14 [b]

[a] Ref. 35. [b] Ref. 16. [c] Ref. 24.

TABLE 7

DIPOLE MOMENTS OF METAL COMPLEXES OF THE FLUORINATED MONOTHIO-β-DIKETONES RC(SH)=CHCOR' (R = C_3H_7, C_2F_5, CF_3; RC(SH)=CHCOR' = LH)

R	Complex	R'		
		C_3F_7	C_2F_5	CF_3
Ph	NiL_2	5.38 [a]	5.35 [a]	4.92 [b]
	PdL_2	5.63 [a]	5.55 [a]	5.02 [b]
	CoL_3	6.68 [a]	6.54 [a]	6.54 [b]
β-$C_{10}H_7$	NiL_2	6.07 [a]	5.86 [a]	5.47 [b]
	PdL_2	6.24 [a]	6.00 [a]	5.55 [b]
	CoL_3	7.36 [a]	7.20 [a]	6.90 [c]
C_4H_3S	NiL_2	6.31 [a]	5.94 [a]	5.74 [b]
	PdL_2	6.38 [a]	6.18 [a]	5.88 [b]
	CoL_3	7.60 [a]	7.48 [a]	7.14 [b]

[a] Ref. 36. [b] Ref. 16. [c] Ref. 31.

power of CHF_2 group vis-a-vis that of the CF_3 group, leading to a lower group moment $\mu_{R'\text{-ch}}$ for the former.

Complexes of monothio-β-diketones containing the perfluoroalkyl groups C_2F_5 and C_3H_7

In a recent publication, Das [36] reported the dipole moments of the nickel(II), palladium(II), and cobalt(III) complexes of the perfluoro ligands RC(SH)=CHCOR' (R = Ph, β-$C_{10}H_7$, C_4H_3S; R' = C_2F_5, C_3F_7). The results are listed in Table 7 together with the dipole moments of the analogous complexes containing R' = CF_3.

The replacement of CF_3 by C_2F_5 and C_3F_7 causes an increase in the dipole moment of the square-planar complexes of ca. 0.4 D and ca. 0.6 D, respectively, and somewhat smaller increases in the case of the cobalt complexes.

Conclusion

The observed dipole moments of all the nickel(II), palladium(II), and copper(II) complexes of monothio-β-diketones indicate unequivocally that these complexes possess a *cis*-square-planar configuration in solution. The appreciably lower values obtained for the copper complexes compared with the values for the nickel, palladium, and platinum complexes of the same ligand suggest some distortion from square-planar towards a tetrahedral configuration in the case of the copper complexes, since the tetrahedral zinc complexes have considerably lower values. X-Ray structural determinations have confirmed the *cis*-square-planar configuration for one palladium, one platinum, and four nickel complexes. The tetrahedral structure of two zinc complexes has also been confirmed by X-ray crystal analysis. Recent ^{13}C and ^{19}F NMR studies [37,38] have confirmed the *cis*-square-planar structure for several nickel, palladium, and platinum complexes and the tetrahedral configuration for six zinc complexes of fluorinated monothio-β-diketones in chloroform solution.

A *facial* (*cis*)-octahedral structure has been established for two iron(III) and one cobalt(III) complex in the solid state. And ^{13}C and ^{19}F NMR measurements on four cobalt(III) complexes of fluorinated monothio-β-diketones have confirmed the *facial*-octahedral structure in chloroform solution [37,38]. The dipole-moment data support the assignment of a *facial*-octahedral structure to the chromium(III), iron(III), ruthenium(III), cobalt(III), and rhodium(III) complexes.

The preference for the *cis*-square-planar and *facial*-octahedral configurations among these complexes has been explained [16] as arising from strong d_π—d_π bonding between the metal and sulfur atoms in monothio-β-diketone complexes. Transition metal ions can form two π-bonds at 90° and consequently, of the isomeric *cis* and *trans* complexes wherein only two (the sulfur atoms) of the four donor atoms can form d_π—d_π bonds, the *cis*-isomer is the more stable [39]. An alternative explanation is that the *cis* configuration is due to weak non-bonded S—S interaction [20].

References

1 A. Combes, Ann. Chim., 12 (1887) 199; Compt. Rend., 105 (1887) 869.
2 G.T. Morgan and H.W. Moss, J. Chem. Soc., 105 (1914) 189.
3 C.M. Harris and S.E. Livingstone in F.P. Dwyer and D.P. Mellor (Eds.), Chelating Agents and Metal Chelates, Academic Press, New York, 1964, p. 100.
4 J.P. Fackler, Progr. Inorg. Chem., 7 (1966) 361.
5 D. Gibson, Coordination Chem. Rev., 4 (1969) 225.
6 R.C. Mehrotra, R. Bohra and D.P. Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, New York, 1978.
7 S.H.H. Chaston and S.E. Livingstone, Proc. Chem. Soc., (1964) 111.
8 S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer, V.A. Pickles and J.S. Shannon, Australian J. Chem., 18 (1965) 673.
9 M. Cox and J. Darken, Coordination Chem. Rev., 7 (1971) 29.
10 S.E. Livingstone, Coordination Chem. Rev., 7 (1971) 59.
11 C.P. Smyth, Dielectric Behaviour and Structure, McGraw Hill, New York, 1955.
12 S. Roberts and A. von Hippel, J. Appl. Phys., 17 (1946) 610.
13 R.J.W. Le Fèvre and E.P.A. Sullivan, J. Chem. Soc., (1954) 2873.
14 L.P. Eddy, J.W. Hayes, S.E. Livingstone, H.L. Nigam, and D.V. Radford, Australian J. Chem., 24 (1971) 1071.
15 E.A. Shugam, L.M. Shkol'nikova and S.E. Livingstone, Zhur. strukt. Khim., 8 (1967) 550.
16 M. Das, S.E. Livingstone, S.W. Filipczuk, J.W. Hayes and D.V. Radford, J. Chem. Soc. Dalton Trans., (1974) 1409.
17 L. Kutchabsky and L. Beyer, Z. Chem., 11 (1971) 30.
18 J. Sieler, P. Thomas, E. Uhlemann and E. Hohne, Z. Anorg. u. Allgem. Chem., 380 (1971) 160.
19 D.C. Craig, M. Das, S.E. Livingstone and N.C. Stephenson, Cryst. Struct. Commun., 3 (1974) 283.
20 O. Siiman, D.D. Titus, C.D. Cowman, J. Fresco and H.B. Gray, J. Amer. Chem. Soc., 96 (1974) 2353.
21 R.H. Holm, D.H. Gerlach, J.G. Gordon and M.C. McNamee, J. Amer. Chem. Soc., 90 (1968) 4184.
22 B.F. Hoskins and C.D. Pannan, Inorg. Nucl. Chem. Lett., 11 (1975) 409.
23 J. Ollis, M. Das, V.J. James, S.E. Livingstone and K. Nimgirawath, Cryst. Struct. Commun., 5 (1976) 679.
24 S.W. Filipczuk, J.W. Hayes, D.V. Radford, M. Das and S.E. Livingstone, J. Chem. Soc. Dalton Trans., (1975) 886.
25 B.F. Hoskins and C.D. Pannan, Inorg. Nucl. Chem. Lett., 11 (1975) 405.
26 M. Das and S.E. Livingstone, J. Chem. Soc. Dalton Trans., (1975) 452.
27 M. Das, S.E. Livingstone, J.H. Mayfield, D.S. Moore and N. Saha, Australian J. Chem., 29 (1976) 767.
28 M. Das and S.E. Livingstone, J. Chem. Soc. Dalton Trans., (1977) 663.
29 M. Das, Inorg. Chim. Acta, 36 (1979) 79.
30 M. Das, J. Inorg. Nucl. Chem., 43 (1981) 1803.
31 S.E. Livingstone, Proc. 3rd Internat. Congr. Iranian Chem. Soc., Shiraz, Iran, 1975, p. 168.
32 S.E. Livingstone and J.E. Oluka, Australian J. Chem., 29 (1976) 1913.
33 M. Das and S.E. Livingstone, Inorg. Synthesis, 16 (1976) 206.

34 C.K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, 2nd edn. 1969.
35 M. Das, Transition Metal Chem., 5 (1980) 17.
36 M. Das, Inorg. Chim. Acta, 48 (1981) 33.
37 M. Das and D.T. Haworth, J. Inorg. Nucl. Chem., 43 (1981) 515.
38 D.T. Haworth, D.L. Maas and M. Das, J. Inorg. Nucl. Chem., 43 (1981) 1807.
39 D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel and L.E. Sutton, J. Chem. Soc., (1954) 332.