Dipole-moment Measurements on Metal Chelate Complexes. Part I. Dipole-moment and Dielectric-relaxation Measurements on Square-planar and Octahedral Metal Complexes of Seven Mercapto-β-diketones

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Dipole moments have been determined for iron(III), cobalt(III), nickel(II), palladium(II), platinum(II), and copper(II) complexes of the mercapto-β-diketones RC(SH)⁚CH·C(O)R′ [R = Me or Ph, R′ = Ph; R = Me, C_4H_3S (2-thienyl), Ph, *p*-MeC_6H_4, or *p*-BrC_6H_4, R′ = CF_3] from both static-polarization and dielectric-relaxation measurements. The moments clearly indicate *cis*-square-planar configurations for the nickel, palladium, platinum, and copper complexes, but do not distinguish unequivocally between *facial*- and *meridional*-octahedral configurations for the iron and cobalt complexes. Group dipole moments for the R substituents, except 2-thienyl, in the square-planar complexes have been derived from the dipole-moment data. The effect of the CF_3 group is discussed in terms of its influence on the electron density in the chelate ring.

METAL complexes of mercapto-β-diketones, (I), were first reported in 1964.[1] Since then these complexes have been extensively studied and have been the subject of three recent reviews.[2-4] An *X*-ray crystallographic study showed that palladium(II) and platinum(II) complexes of 1,3-diphenyl-3-mercaptoprop-2-en-1-one (I; R = R′ = Ph) have a *cis*-square-planar configuration.[5] *X*-Ray structural determinations have also established *cis*-square-planar structures for nickel(II) complexes of 1-(4-bromophenyl)-3-mercaptoprop-2-en-1-one (I; R =

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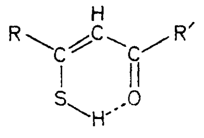
H, R′ = *p*-BrC_6H_4),[6] 4-mercapto-5-methylhex-3-en-2-one (I; R = Pr^i, R′ = Me),[7] and 1,1,1-trifluoro-4-mercaptopent-3-en-2-one (I; R = Me, R′ = CF_3).[8]



(I)

Dipole moments of the nickel(II), palladium(II), and platinum(II) complexes of ligand (I; R = R′ = Ph) have been reported.[9] Values obtained from dielectric-relaxation measurements (1·2—1·3 D) * were considered to indicate a *cis*-square-planar configuration for these complexes in benzene solution. No evidence was obtained to indicate that any of the *trans*-form was present in solution.[9] Jensen's early work [10] on the measurement of dipole moments of a number of palladium(II) and platinum(II) complexes established the occurrence of *cis–trans*-isomerism in these complexes. Dipole moments have since been determined for a wide range of square-planar and tetrahedral metal complexes, but for only a few octahedral complexes.[11] It is noteworthy that nickel(II) complexes of the mercapto-esters ethyl thioglycolate, hexadecyl thioglycolate, and ethyl thioacetylacetate have dipole moments of 2·4, 2·6, and 4·5 D, respectively.[12] These values suggest a *cis*-configuration for these complexes.

We have determined dipole moments of iron(III), cobalt(III), nickel(II), palladium(II), platinum(II), and copper(II) complexes of seven mercapto-β-diketones [I; R = Me or Ph, R′ = Ph; R = Me, $\text{C}_4\text{H}_3\text{S}$ (2-thienyl); Ph, *p*-MeC_6H_4, or *p*-BrC_6H_4, R′ = CF_3] in order to ascertain whether the *cis*-configuration is favoured in the square-planar complexes and to observe the variation in moment of the square-planar and octahedral complexes with change in R and R′ substituents of the ligand, (I). Metal complexes often have appreciable atomic polarization; [9,10,13-29] indeed some β-diketone complexes are known to display 'anomalously' high atomic polarization.[11] Consequently, we have determined dipole moments of the mercapto-β-diketone complexes by both static-polarization and dielectric-relaxation measurements. The latter method [30-33] has the advantage of giving a value for the dipole moment without the uncertainty associated with the allowance made for atomic polarization. Atomic polarization in these complexes will be discussed in a subsequent publication.

EXPERIMENTAL

The mercapto-β-diketones (I; R = Me or Ph, R′ = Ph; R = Me, $\text{C}_4\text{H}_3\text{S}$, Ph, *p*-$\text{MeC}_6\text{H}_4$, or *p*-$\text{BrC}_6\text{H}_4$, R′ = CF_3) were prepared as previously described.[34-36]

Preparation of the Complexes.—Metal complexes were prepared by the general methods given below. Analyses, which were all within one per cent of calculated values, are listed in Supplementary Publication No. SUP 20993 (23 pp., 1 microfiche).†

Iron(III). Anhydrous iron(III) chloride (1 g, 6·2 mmol) in ethanol (20 cm^3) was added to a solution of the appropriate mercapto-β-diketone (I) (18·6 mmol) in ethanol (50 cm^3). Addition of water (50 cm^3) caused deposition of a black solid, which was filtered off and recrystallized from a 1 : 1 mixture of acetone and ligroin to give the iron(III) complex; yield 30—60%.

Cobalt(III). Cobalt(II) diacetate tetrahydrate (1 g, 4 mmol) in hot ethanol (100 cm^3) was added to a solution of (I) (12 mmol) in ethanol (100 cm^3). A deep brown solution resulted. Air was passed through this solution for 6 h. The black deposit which formed was then filtered off and recrystallized from acetone to give the cobalt complex; yield 30—60%.

Nickel(II). Nickel(II) diacetate tetrahydrate (1 g, 4 mmol) in hot ethanol (70 cm^3) was added to a solution of

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* 1 D = 3·336 × 10^{-30} C m.

† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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(I) (8 mmol) in ethanol (30 cm^3). The resulting brown precipitate was filtered off and recrystallized from ligroin to give the nickel complex which was dried *in vacuo* over silica gel; yield 30—40%.

When the ligand (I; R = Me, R′ = CF_3) was used, no precipitate was formed. In this case water (50 cm^3) was added to the reaction mixture and the complex was extracted with ligroin. The extract was dried over anhydrous sodium sulphate and then concentrated to small bulk. On cooling, the extract gave brown crystals of the nickel complex; yield 70%.

Palladium(II). Dipotassium tetrachloropalladate(II) (1·6 g, 4·9 mmol) in water (50 cm^3) was added to a solution of (I) (9·8 mmol) in acetone (50 cm^3). The resulting orange precipitate was filtered off and recrystallized from acetone to give reddish orange crystals of the palladium complex; yield 40—65%.

Platinum(II). Dipotassium tetrachloroplatinate(II) (2·5 g, 6 mmol) in water (60 cm^3) was added to a solution of (I) (12 mmol) in acetone (60 cm^3). The reaction mixture was heated under reflux for 15 min during which the red complex began to deposit. After the mixture had cooled, water (60 cm^3) was added with stirring. The complex was filtered off and recrystallized from acetone to give dark red crystals; yield 40—50%.

Copper(II). Copper(II) diacetate monohydrate (1 g, 5 mmol) in hot ethanol (100 cm^3) was added to a solution of (I) (10 mmol) in ethanol (50 cm^3). The mixture was cooled and the resulting brown precipitate was filtered off and recrystallized from ligroin to give the copper complex; yield 20—50%.

Carbon and hydrogen were determined by Dr. E. Challen of the Microanalytical Laboratory, School of Chemistry, University of New South Wales. Sulphur and bromine were determined by the Australian Microanalytical Service, Melbourne. Platinum was determined by ignition of the complex. The other metals were determined by standard analytical procedures after the complex had been decomposed by a mixture of concentrated sulphuric and nitric acids.

AnalaR grade benzene was purified by partial freezing (twice), followed by drying by passage through a chromatographic column packed with B.D.H. 4A molecular sieves (1/16 in pellets). The sieves were cleaned before use by washing with benzene, followed by heating at 350 °C. For benzene at 25 °C the dielectric constant, ε, density, *d*, and refractive index, *n*, for sodium light are 2·2725, 0·87378 g cm^{-3}, and 1·4973, respectively.[37]

Determination of Dipole Moments.—From static-polarization measurements. Dielectric-constant measurements were made on a Wissenschaftlich-Technische Werkstatten dipolemeter DM01, fitted with a gold-plated cell, thermostatted at 25 ± 0·1 °C. The dipolemeter was calibrated against benzene and cyclohexane. All manipulations of solvent and solutions were made by means of a filling device in an inert atmosphere, obtained by flushing the cell with dry nitrogen. Measurements were made at five different concentrations of the metal complex in benzene. The dielectric constant, ε, and refractive index, *n*, were measured for the solvent and solution. Concentrations were expressed as weight fractions w_2. Incremental quantities, indicated by the prefix Δ, are differences between properties measured for the solvent and solution at the concentration w_2. The determining equation has the form (1), where μ is the dipole moment, $\boldsymbol{k}$ the Boltzmann

$$\mu^2 = \frac{27\boldsymbol{k}T}{4\pi N} \times \frac{1}{d(2 + \varepsilon)^2} \times (a_\epsilon - a_n)M_2 \qquad (1)$$

constant, *N* the Avagadro number, *d* the density of the solvent, a_ϵ and a_n are gradients of Δε and $\Delta(n^2)$, respectively, when plotted as ordinate against w_2 as abscissa, and M_2 is the molecular weight of the solute. Refractive-index measurements were made on an Abbe 60 refractometer with white light. The reproducibility of values for the dipole moment is ±0·1 D.

From dielectric-relaxation measurements. Incremental-loss tangents (Δ tan δ) of dilute benzene solutions of the solutes were measured at the frequencies 1·140, 3·040, and 8·540 GHz on a Central Research Laboratory (Red Wing, Minn., U.S.A.) dielectrometer fitted with machined copper cells suitable for liquid samples. This instrument employs the standing-wave method of Roberts and von Hippel[38] and has been described previously.[39] The gradient of the plot of Δ tan δ against ω_2 was obtained at each frequency. Values of the dipole moment and relaxation time, τ, were reduced from the best-fit curve to the Debye equation as adapted by Le Fèvre and Sullivan.[40] Values of dipole moments obtained in this way are referred to as μ_d, to distinguish them from values obtained from static-polarization measurements (μ_s).

Molecular weights were determined in benzene solution at 25 °C with a Mechrolab vapour-pressure osmometer model 301A. Calibration was made with benzil for the range of concentrations used (0·003—0·01M).

RESULTS AND DISCUSSION

Incremental dielectric constants, refractive indices, and loss tangents for the solutes, together with dielectric constants and loss factors for the solutions, are listed in SUP 20993. Calculated dipole moments μ_s and μ_d, together with relaxation times, are given in Table 1. Oligomerization is known to occur in solution with a number of metal complexes of β-diketones.[41] However, the results of molecular-weight determinations on three of the present complexes (Table 2) show that the complexes are monomeric in benzene solution and it is assumed that this holds for all the complexes studied. Dipole moments of a cobalt(III), nickel(II), palladium(II), and copper(II) complex were determined by the static-polarization method at different temperatures (Table 3). No significant variation of the moments with temperature was observed; this suggests the absence of a *cis–trans*-equilibrium in solution. A similar lack of temperature dependence of the dipole moment has been found for *cis*-bis(acetylacetonato)dichlorotin(IV).[42]

Relaxation Times.—Di Carlo *et al.*[29] have noted that, in order to establish relaxation times (τ) with good

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precision, it is necessary to measure dielectric absorptions at frequencies in the vicinity of maximum absorption on the Debye curve ($f_{\max.}$). From the form of the Debye equation,[40] it is apparent that this will also be true for dipole moments measured from dielectric-relaxation data. For the majority of the present complexes the lowest frequency used, 1·140 GHz, is close to $f_{\max.}$ and hence the τ and μ_d values are considered to be more accurate than those obtained previously in these laboratories [9] when only two frequencies 3·109 and 9·400 GHz, were employed. τ Values were found to exhibit a greater range than was observed previously, due to variations in size of the ligand, the configuration of the complex, and the co-ordination number of the metal atom.

TABLE 1

Dipole moments (μ) and relaxation times (τ) of metal complexes with mercapto-β-diketone ligands RC(SH):CH·C(O)R′, (I)

R	R′		Fe^{III}	Co^{III}	Ni^{II}	Pd^{II}	Pt^{II}	Cu^{II}
Me	Ph							
		μ_s/D	4·81	3·27	2·89	2·58	*a*	3·43
		μ_d/D	4·29	2·68	2·69	2·45		3·19
		τ/ps	71	192	112	125		120
Ph	Ph							
		μ_s/D	4·29	3·84	2·45	2·48	2·97 [b]	3·46
		μ_d/D	3·30	2·05	2·28	2·16	1·2 [b]	2·64
		τ/ps	105	171	198	169	80 [b]	189
Me	CF_3							
		μ_s/D	*c*	5·40	4·14	4·39	*a*	
		μ_d/D		5·05	4·08	4·29		
		τ/ps		116	66	77		
C_4H_3S	CF_3							
		μ_s/D	7·00	7·14	5·74	5·88	6·09	4·96
		μ_d/D	5·82	6·55	5·44	5·56	5·67	4·69
		τ/ps	177	215	135	115	137	121
Ph	CF_3							
		μ_s/D	6·03	6·54	4·92	5·02	5·35	4·39
		μ_d/D	5·51	5·41	4·65	4·88	4·90	3·93
		τ/ps	236	190	137	155	133	137
p-MeC_6H_4	CF_3							
		μ_d/D	6·85	7·36	5·84	5·91	6·16	5·12
		μ_s/D	5·74	6·15	5·35	5·54	5·62	4·63
		τ/ps	233	257	168	173	170	175
p-BrC_6H_4	CF_3							
		μ_d/D	3·59	3·62	2·85	2·97	3·21	2·45
		μ_s/D	2·46	2·88	2·56	2·92	3·01	2·18
		τ/ps	164	196	162	210	185	148

[a] The Pt^{II} complex could not be isolated. [b] From ref. 9. [c] The Fe^{III} and Cu^{II} complexes of this ligand cannot be prepared by the general method (see ref. 35).

TABLE 2

Molecular weights of metal complexes with ligands (I) in benzene

			M	
Complex	R	R′	Found	Calc.
$[NiL_2]$	Me	CF_3	361	397
$[PdL_3]$	C_4H_3S	CF_3	547	581
$[CuL_2]$	Me	Ph	394	418

TABLE 3

Effect of temperature on dipole moments of metal complexes with ligands (I)

			μ_s/D		
Complex	R	R′	10	25	40 °C
$[CoL_3]$	p-MeC_6H_4	CF_3	7·14	7·36	
$[NiL_2]$	Ph	CF_3	4·80	4·92	
$[PdL_2]$	C_4H_3S	CF_3	5·86	5·88	5·63
$[CuL_2]$	C_4H_3S	CF_3	5·14	4·96	4·92

For the square-planar complexes, τ increased generally in the order (R,R′): (Me,CF_3) < (Me,Ph) $\simeq$ (C_4H_3S,CF_3) < (Ph,Ph) $\simeq$ (p-MeC_6H_4,CF_3) $\simeq$ (p-BrC_6H_4,CF_3). A comparison of the relative sizes of these ligands obtained by use of space-filling molecular models shows that the order is in accordance with increasing bulk of the ligand, the largest ligands giving rise to the largest values of τ. Furthermore, the octahedral complexes had, in general, greater values of τ than the square-planar complexes, consistent with their greater bulk. However, observed values for the relaxation times of the iron complexes, (I; R = Me or Ph, R′ = Ph), were anomalously low. This could arise from some decomposition of these complexes in solution; consequently, perhaps less reliability should be placed on the results obtained for these two complexes.

For square-planar complexes of a given ligand, τ values were approximately constant over the range of metals examined. This result is not unexpected, since the nature of the metal atom has little effect on the actual size of the complex, unless there is a change in configuration. A notable exception occurs with the ligand (I; R = p-BrC_6H_4, R′ = CF_3). For this ligand τ values ranged from 148 ps for the copper complex to 210 ps for the palladium complex. This large variation may be indicative of conformational changes associated with the complexes of this ligand. These changes were not so apparent from the dipole moments, presumably because of cancellation of opposing dipole-moment vectors. Further studies, in which *ortho*- and *meta*-substituted phenyl groups are employed as R substituents, are being undertaken for the purpose of establishing more precisely the conformations of substituted phenyl groups.

Dipole Moments.—Observed values of μ_s compared to μ_d were 0·14—0·82 D greater for the square-planar complexes and 0·35—1·81 D greater for the octahedral complexes. These differences are attributed to the contribution made by atomic polarization which is appreciable in some cases. In the conformational analysis, which is detailed below, μ_d is taken as the more correct value for the dipole moment.

Square-planar complexes. The appreciable values obtained for 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, hence a higher moment would be expected than when R′ = Ph. This conclusion 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. For the square-planar and octahedral complexes of a given metal when R′ = CF_3, the moments decreased in the order for the substituent R: *p*-$MeC_6H_4 \simeq C_4H_3S$ > Ph > Me ≫ *p*-BrC_6H_4.

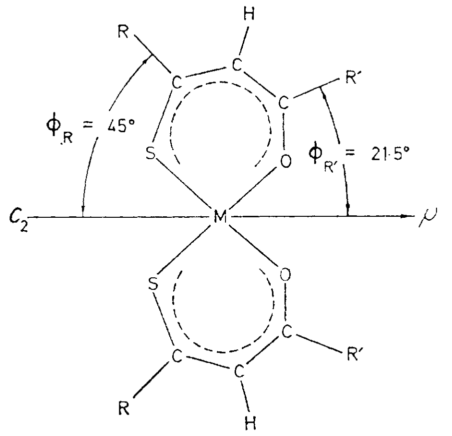
Values of μ_d for the nickel, palladium, and platinum complexes of the ligand (I; R = R′ = Ph) were previously reported as 1·2, 1·3, and 1·2 D, respectively, and values of τ were 80, 80, and 90 ps, respectively.[9] The values of μ_d for the nickel and palladium complexes have now been redetermined and found to be 2·28 and 2·16 D, respectively, while the τ values were found to be 198 and 169 ps, respectively (see Table 1). As stated above, the earlier measurements were obtained at only two frequencies, 3·109 and 9·400 GHz. Consequently, the previously reported values of μ_d and τ for the platinum complex are now considered to be much too low.

For the complexes of nickel, palladium, and platinum the value of μ_d is usually constant within 0·3 D for any particular ligand. Slight variations can be attributed to differences in electronegativities of the metals and/or variations in the extent of distortion from a square-planar configuration. For the copper complexes 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 attributed to significant distortion from the square-planar towards the tetrahedral configuration, since data obtained for a corresponding series of zinc complexes,[43] which are known to be tetrahedral,[44] show an even greater difference.

The model, (II), used for group dipole-moment analysis is based on *X*-ray crystallographic determination of the solid-state structure of the nickel complex $[Ni\{MeCS\colon CH\cdot C(O)CF_3\}_2]$.[8] This complex crystallizes in the monoclinic system and is *cis*-square planar with a C_2 axis of symmetry passing midway between the oxygen atoms, through the nickel atom, and midway between the sulphur atoms.[8] For the model used for the calculations, it was assumed that bond angles and distances do not change when the complex is dissolved in benzene, and that these are identical for all the complexes studied. Although there are, no doubt, minor structural differences among the complexes, it seems probable that the effect of these on the values of the group moments will be small.

An inspection of Table 1 permits the *direction* of the molecular dipole moment to be established. When the R group of each complex is changed from *p*-MeC_6H_4 to *p*-BrC_6H_4, the moment decreases significantly; the direction of the *p*-BrC_6H_4 group moment is away from the chelate ring, while that of the *p*-MeC_6H_4 group moment is towards the chelate ring. Thus the dipole moment acts along the C_2 axis *from* the side of the molecule containing the sulphur atoms *to* the side containing the oxygen atoms.

Group-moment analysis is simplified if it is recognized that the molecular dipole moment μ 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 $\mu_{M\text{-ch}}$ (here defined as the metal–ligand moment less contributions from groups R and R′). Thus μ is given by equation (2).



(II)

FIGURE 1. Structural model for square-planar complexes based on data from ref. 8

$$\mu = \Sigma 2\mu_i \cos\phi_i \qquad (2)$$

The inclination of $\mu_{M\text{-ch}}$ to μ cannot be determined, but ϕ_i for the R group is available from the structural model. For a given metal, it is assumed that when the R group moment is subtracted from μ the resulting group moment does not change, provided R′ remains the same. Therefore μ, the difference between the dipole moments, μ_1 and μ_2, of two complexes of a given metal with the same R group is given by equation (3).

$$\mu = \mu_2 - \mu_1 = 2\cos\phi_R[(\mu_{R\text{-ch}})_1 - (\mu_{R\text{-ch}})_2] \qquad (3)$$

In order to calculate the various R group moments, it is necessary to know, or to have a reliable estimate of, one such group moment. We found that the most reasonable estimates of R group moments were obtained when $\mu_{Ph\text{-ch}}$ was taken as zero.* Values of group moments determined on this basis are given in Table 4. A negative value for the group moment indicates that the moment is directed towards the chelate ring. Any change in the assumed value for $\mu_{Ph\text{-ch}}$ caused an identical change in each of the derived group moments.

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* When any other basis for these calculations was used, *e.g.* $\mu_{Me\text{-ch}}$ 0·00 or −0·35 D, a less internally consistent set of group moments was obtained.

[43] M. Das, S. E. Livingstone, S. W. Filipczuk, J. W. Hayes, and D. V. Radford, unpublished work.

[44] B. F. Hoskins, personal communication.

When R′ = Ph, the same procedure leads to values for $\mu_{\mathrm{Me\text{-}ch}}$ of −0·3, −0·2, and −0·4 D for the nickel, palladium, and copper complexes, respectively. Group-moment values (Table 4) for R = *p*-MeC_6H_4 are close to the numerical value of the dipole moment for toluene (0·37 D[45]), and group-moment values for R = *p*-BrC_6H_4 are likewise similar to that for bromobenzene (1·53 D[45]). When R = Me, although the magnitude of the group moment is typical of that found for methyl groups,[37] the direction (away from the chelate ring) is opposite to that normally observed for a methyl group in an aromatic system. When R′ = Ph rather than CF_3, the direction of the methyl-group moment is as expected, *i.e.* towards the chelate ring. This seems to indicate that the negative hyperconjugative effect of the CF_3 group predominates over the hyperconjugative effect of the methyl group, resulting in the apparent reversal of direction.[46]

TABLE 4

Calculated group moments (D) derived from μ_d for square-planar metal complexes [M{RCS⁚CH·C(O)R′}$_2$] (R′ = CF_3)

	Ni	Pd	Pt	Cu
$\mu_{\mathrm{Me\text{-}ch}}$	0·41	0·43		
$\mu_{p\text{-}\mathrm{MeC_6H_4\text{-}ch}}$	−0·51	−0·48	−0·52	−0·51
$\mu_{p\text{-}\mathrm{BrC_6H_4\text{-}ch}}$	1·51	1·42	1·37	1·27

Values of $\mu_{\mathrm{C_4H_3S\text{-}ch}}$ are not given in Table 4 because of the possibility of rotation about the C–C bond joining the thiophene and chelate rings. It is noteworthy that in the case where there is symmetrical conformation of the two thienyl groups, *i.e.* where components of the thienyl-group moments normal to the C_2 axis cancel, values of the components of the two thienyl-group moments along the C_2 axis are in the range 0·68—0·79 D. These values do not seem unreasonable in view of the dipole moment of thiophen.[45]

The R′ group moments are not accessible from the above type of calculation since, as has already been noted, there appears to be a difference in electron distribution in the chelate ring when R′ = CF_3 from that obtaining when R′ = Ph. However, an estimate of the CF_3 group moment in some complexes of B sub-group metals with β-diketones (2·56 D) has been used by Moore and Nelson[47] and a similar value (2·52 D) for this moment has been obtained in substituted aromatic systems.[46] The change in electron distribution in the metal–chelate ring due to the influence of the CF_3 group could be regarded as a change in the magnitude and direction of the group moment $\mu_{\mathrm{M\text{-}ch}}$. Using values for $\mu_{\mathrm{R'\text{-}ch}}$ of 2·56 and 0·00 D when R′ is CF_3 and Ph, respectively, we have calculated the components of $\mu_{\mathrm{M\text{-}ch}}$ along the C_2 axis (Table 5). A positive value indicates that the component is acting in the same direction as μ.

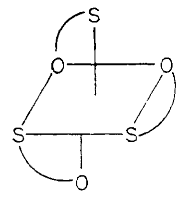
The near-zero values for the nickel, palladium, and platinum complexes where R′ = CF_3 (Table 5) indicate that the two $\mu_{\mathrm{M\text{-}ch}}$ group moments in the molecule almost cancel and, since $\mu_{\mathrm{M\text{-}ch}}$ values are considered to be large (*e.g.* 6—9 D [14,17,37,47]), the angle between $\mu_{\mathrm{M\text{-}ch}}$ and the normal to the C_2 axis must be small. For the corresponding copper complex the direction of action of $\mu_{\mathrm{M\text{-}ch}}$ apparently lies at an angle greater than 90° to μ. Determination of the angle cannot be made, since no reliable estimates of $\mu_{\mathrm{M\text{-}ch}}$ exist. When R′ = Ph, it is clear that $\mu_{\mathrm{M\text{-}ch}}$ acts at a smaller angle to μ, *i.e.* along a line closer to the metal–oxygen bond, as would be expected from the greater electronegativity of oxygen compared to sulphur.

TABLE 5

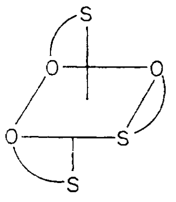
Components of $\mu_{\mathrm{M\text{-}ch}}$ along the C_2 axis for metal complexes with ligands (I)

	Ni	Pd	Pt	Cu
R′ = CF_3	−0·06	0·06	0·07	−0·42
R′ = Ph	1·14	1·08		1·32

Octahedral complexes. Values of the dipole moments, μ_s and μ_d, for the iron(III) and cobalt(III) complexes are higher than those of square-planar complexes of the same ligand. Although a higher moment would be expected for the *facial*-isomer (III) than for the *meridional* isomer (IV), dipole-moment data do not allow unequivocal assignment of configuration for the octahedral complexes. Lack of crystal structure data for these complexes prevents a conformational analysis such as that undertaken for the square-planar complexes.



(III)



(IV)

However, since the *fac*-isomer has all three sulphur atoms mutually *cis*, it seems the most probable structure.

Conclusion.—Observed dipole moments of the nickel(II), palladium(II), platinum(II), and copper(II) complexes indicate unequivocally that these complexes possess a *cis*-square-planar configuration. It is probable that the metal atom forms d_π–d_π bonding with the sulphur but not the oxygen atoms of the mercapto-β-diketone ligands. A later transition-metal ion can form two π-bonds at right angles and consequently, of the isomeric *cis*- and *trans*-complexes wherein only two of the four donor atoms can form d_π–d_π bonds, the *cis*-isomer is the more stable.[48] Values of dipole moments found for the

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[45] A. L. McClellan, ‘ Tables of Experimental Dipole Moments,’ Freeman, San Fancisco, 1963.

[46] K. E. Calderbank and R. K. Pierens, *J.C.S. Perkin II*, 1972, 293.

[47] C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 1969, **8**, 143.

[48] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 1954, 332.

iron(III) and cobalt(III) complexes do not distinguish between *fac*- and *mer*-octahedral configurations. However, since the *fac*-isomer has all three sulphur atoms mutually *cis*, it seems the most probable structure. It is hoped that more information concerning metal–chelate ring moments will be obtained from an examination of tetrahedral zinc complexes of the mercapto-β-diketones, (I), and similar ligands. This study is now in progress.

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