# Dipole-moment Measurements of Metal Chelates. Part II.[1] Dipole Moments of Nickel(II), Palladium(II), Platinum(II), and Cobalt(III) Complexes of Six Fluorinated Mercapto-β-diketones

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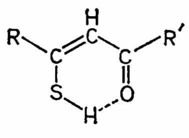
Dipole moments have been determined by static polarization measurements for the nickel(II), palladium(II), platinum(II), and cobalt(III) chelates of the fluorinated mercapto-β-diketones $\mathrm{RC(SH){:}CHCOCF_3}$ (R = *m*-$\mathrm{MeC_6H_4}$, *m*-$\mathrm{ClC_6H_4}$, *m*-$\mathrm{BrC_6H_4}$, *p*-$\mathrm{FC_6H_4}$, *p*$\mathrm{ClC_6H_4}$, and *m,p*-$\mathrm{Cl_2C_6H_3}$). The moments indicate *cis*-square-planar configurations for the nickel, palladium, and platinum complexes and suggest a *facial*-octahedral configuration for the cobalt complexes. The variation of the dipole moments with R is considered to be dependent on: (*a*) the magnitude and vector directions of the Ph–X bond moments; (*b*) the inductive effect of the *meta*- and *para*-substituent on the phenyl ring; and (*c*) the mesomeric effect of the substituent X.

IN a recent communication[1] we reported the dipole moments of the nickel(II), palladium(II), platinum(II), copper(II), iron(III), and cobalt(III) complexes of the mercapto-β-diketones (I; R′ = Ph, R = Me or Ph; R′ = $\mathrm{CF_3}$, R = Me, 2-thienyl, Ph, *p*-$\mathrm{MeC_6H_4}$, or *p*-$\mathrm{BrC_6H_4}$). The moments obtained by the static polarization method for the nickel, palladium, platinum, and copper complexes ranged from 2·45 to 6·09 D. These appreciable values indicate a *cis*-square-planar configuration which was confirmed for the complex $\mathrm{Ni(MeCS{:}CHCOCF_3)_2}$ by an *X*-ray crystal structure analysis.[2] The moments of the iron(III) and cobalt(III) complexes ranged from 3·27 to 7·36 D, suggesting a *facial* (II) rather than a *meridional* (III) octahedral structure. The *facial* structure has been established for $\mathrm{Fe(PhCS{:}CHCOCF_3)_3}$ by an *X*-ray study.[3] Evidence



(I)

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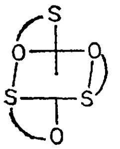
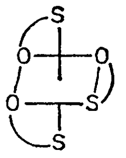
[1] M. Das, S. E. Livingstone, S. W. Filipczuk, J. W. Hayes, and D. V. Radford, *J.C.S. Dalton*, 1974, 1049.

[2] D. C. Craig, M. Das, S. E. Livingstone, and N. C. Stephenson, *Crystal Struct. Comm.*, 1974, **3**, 283.

[3] B. F. Hoskins and C. D. Pannan, personal communication.

from p.m.r. measurements has indicated that the cobalt(III) and vanadium(III) complexes of the mercapto-β-diketones $\mathrm{RC(SH){:}CHCOCF_3}$ (R = Me, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$, or Ph) have the *facial* configuration (II) with all sulphur atoms mutually *cis*.[4]


(II)


(III)

We have determined the dipole moments of metal chelates of fluorinated mercapto-β-diketones $\mathrm{RC(SH){:}CHCOCF_3}$, where R is a *meta*- or *para*-substituted phenyl group, in order to study the effect of the substituent on the value of the dipole moment. Mercapto-β-diketones with *ortho*-substituted phenyl groups were found to be unreactive toward metal ions, presumably because of steric hindrance. With the *p*-nitro-ligand $p\text{-}\mathrm{O_2NC_6H_4C(SH){:}CHCOCF_3}$ forms metal chelates which are insoluble in benzene and other organic solvents;[5] consequently, the dipole moments cannot be determined by measurements on solutions of these complexes.

## RESULTS AND DISCUSSION

Dipole moments were determined by static polarization measurements for the nickel(II), palladium(II), platinum(II), and cobalt(III) chelates of 1,1,1-trifluoro-4-mercapto-4-(3-methylphenyl)but-3-en-2-one (I; R = $m$-$\mathrm{MeC_6H_4}$, R′ = $\mathrm{CF_3}$), 4-(3-chlorophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (I; R = $m$-$\mathrm{ClC_6H_4}$, R′ = $\mathrm{CF_3}$), 4-(3-bromophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (I; R = $m$-$\mathrm{BrC_6H_4}$, R′ = $\mathrm{CF_3}$), 4-(4-fluorophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (I; R = $p$-$\mathrm{FC_6H_4}$, R′ = $\mathrm{CF_3}$), 4-(4-chlorophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (I; R = $p$-$\mathrm{ClC_6H_4}$, R′ = $\mathrm{CF_3}$), and 4-(3,4-dichlorophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (I; R = $m,p$-$\mathrm{Cl_2C_6H_3}$, R′ = $\mathrm{CF_3}$). The dipole moments are listed in the Table together with moments previously reported[1] for related metal complexes. Data for incremental dielectric constants and refractive indices are given in Supplementary Publication No. 21242 (7 pp.).*

In our earlier study[1] of 38 metal complexes of mercapto-β-diketones we found that the values for the dipole moments obtained from static polarization measurements compared to those obtained from dielectric relaxation measurements were 0·14—0·82 D greater for square-planar complexes and 0·35—1·21 D greater for the octahedral complexes. These differences were attributed to the contribution made by atomic polarization. The appreciable values obtained for the dipole moments of the metal complexes listed in the Table indicate a *cis*-square-planar configuration for the nickel, palladium, and platinum chelates and suggest a *facial*-octahedral structure for the cobalt chelates. For a given ligand the moments of the square-planar complexes decrease in the order: Pt > Pd > Ni. This is the order of decreasing b class character.[6,7] It is noteworthy that the melting points also decrease in this order.[8]

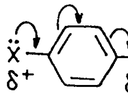
Dipole moments μ(D) for metal complexes of fluorinated mercapto-β-diketones $\mathrm{RC(SH){:}CHCOCF_3}$

| R | $\mathrm{Ni^{II}}$ | $\mathrm{Pd^{II}}$ | $\mathrm{Pt^{II}}$ | $\mathrm{Co^{III}}$ |
|---|---|---|---|---|
| $p$-$\mathrm{MeC_6H_4}$ * | 5·84 | 5·91 | 6·16 | 7·36 |
| $\mathrm{C_4H_3S}$ * | 5·74 | 5·88 | 6·09 | 7·14 |
| $m$-$\mathrm{MeC_6H_4}$ | 5·33 | 5·55 | 5·68 | 6·79 |
| Ph * | 4·92 | 5·02 | 5·35 | 6·54 |
| $m$-$\mathrm{ClC_6H_4}$ | 4·07 | 4·09 | 4·38 | 5·11 |
| $m$-$\mathrm{BrC_6H_4}$ | 3·93 | 4·01 | 4·32 | 5·08 |
| $p$-$\mathrm{FC_6H_4}$ | 2·92 | 3·28 | 3·54 | 3·79 |
| $p$-$\mathrm{ClC_6H_4}$ | 2·89 | 3·20 | 3·42 | 3·72 |
| $p$-$\mathrm{BrC_6H_4}$ * | 2·85 | 2·97 | 3·21 | 3·62 |
| $m,p$-$\mathrm{Cl_2C_6H_3}$ | 2·80 | 2·97 | 3·01 | 3·29 |

* Dipole moment data from ref. 1.

For all metal ions studied the dipole moments decrease if the R groups are arranged in the order: $p$-$\mathrm{MeC_6H_4}$ > 2-thienyl ($\mathrm{C_4H_3S}$) > $m$-$\mathrm{MeC_6H_4}$ > Ph > $m$-$\mathrm{ClC_6H_4}$ ⩾ $m$-$\mathrm{BrC_6H_4}$ > $p$-$\mathrm{FC_6H_4}$ ⩾ $p$-$\mathrm{ClC_6H_4}$ ⩾ $p$-$\mathrm{BrC_6H_4}$ > $m,p$-$\mathrm{Cl_2C_6H_3}$.

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 directions of the Ph–X bond moments; (*b*) the inductive effect arising from the difference in electron density of the $\mathrm{C^1}$ and $\mathrm{C^5}$ 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 (IV) of the substituent X.



(IV)

(*a*) Ph–X *Bond Moments*.—The conformation adopted by the *meta*-substituted phenyl ring with respect to the chelate ring will affect the vector direction of the Ph–X bond moments. Because of the lack of molecular symmetry these bond moments will 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 $\mathrm{C^5}$ atom. Furthermore,

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* See Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue for details of the Scheme.

† The $\mathrm{C^1}$ atom is part of the $\mathrm{CF_3}$ group and the $\mathrm{C^5}$ atom is the phenyl or thienyl carbon atom attached to the $\mathrm{C^4}$ atom.

[4] R. H. Holm, D. H. Gerlach, J. G. Gordon, and M. C. McNamee, *J. Amer. Chem. Soc.*, 1968, **90**, 4184.

[5] M. Das and S. E. Livingstone, *Austral. J. Chem.*, 1974, **27**, 749.

[6] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

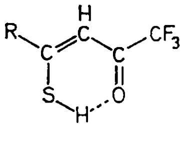
[7] S. E. Livingstone, *Quart. Rev.*, 1965, **19**, 386.

[8] M. Das and S. E. Livingstone, *Austral. J. Chem.*, 1974, **27**, 2109.

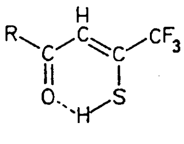
calculations in progress[9] indicate that changes in the R and R′ moieties can cause marked changes in the direction of the metal chelate ring moment.

The square-planar complexes having R = *m*-$\mathrm{XC_6H_4}$ have dipole moments *ca.* 1 D greater than those having R = *p*-$\mathrm{XC_6H_4}$, while the octahedral complexes show a difference of *ca.* 1·4 D. This 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 $\mathrm{CF_3}$ groups. In other words, there can be little or no rotation of the phenyl rings. This is further substantiated by the values of the moments of the complexes having R = *m*,*p*-$\mathrm{Cl_2C_6H_3}$. These moments are only 0·1—0·4 D less than the moments of the complexes with R = *p*-$\mathrm{ClC_6H_4}$. If there is restriction to rotation of the phenyl rings and if the phenyl rings have a similar conformation to that in the complexes with R = *m*-$\mathrm{ClC_6H_4}$, molecular models and *X*-ray data[2] indicate 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 the $C^1$ is always lower than that at $C^5$ (I; R′ = $\mathrm{CF_3}$). This contention is supported by the fact that the product obtained by the action of hydrogen sulphide on fluorinated β-diketones is the isomer (V) and there is no evidence that the isomer (VI) is produced even in small yield. It has been shown that 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′ (structure I).[10,11]



(V)



(VI)

Metal complexes of mercapto-β-diketones (IV) with nucleophilic (Me) and electrophilic (F, Cl, or Br) or substituents on the phenyl group have been studied in this survey and dipole moments compared with those of the metal complexes of (V; R = Ph). Since the methyl group is nucleophilic (+*I* effect) when it is introduced into a phenyl group, either at the *para*- or *meta*-position, it increases the electron density at the $C^5$ atom relative to that when R = Ph. Consequently, it would be expected on the basis of the inductive effect alone that complexes of ligands having R = *p*-$\mathrm{MeC_6H_4}$ and *m*-$\mathrm{MeC_6H_4}$ will have higher dipole moments than those of the ligand having R = Ph. The experimental results are in accord with this postulate. On the other hand, strongly electronegative halogens (—*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 would be expected similarly to lower the dipole moment of a metal complex. This also is in accord with the experimental data.

Substitution at *para*- and *meta*-positions alters the electron density at the $C^5$ atom to different extents.[12] A *para*-methyl group produces a higher electron density at the $C^5$ atom than a *meta*-methyl group. Accordingly, metal complexes of (V; R = *p*-$\mathrm{MeC_6H_4}$) will be expected to have higher dipole moments than those having R = *m*-$\mathrm{MeC_6H_4}$. *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*-$\mathrm{XC_6H_4}$, the metal complexes have higher moments than when R = *p*-$\mathrm{XC_6H_4}$ (X = F, Cl, or Br). When R = *m*,*p*-$\mathrm{Cl_2C_6H_3}$, both substituents lower the electron density at the $C^5$ atom leading to the lowest dipole moments for the metal complexes.

(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*-$\mathrm{BrC_6H_4}$ > *p*-$\mathrm{ClC_6H_4}$ > *p*-$\mathrm{FC_6H_4}$. However, the observed dipole moments are in the reverse order for each metal ion, although the differences are slight and sometimes within experimental error. It is not unreasonable to assume that the mesomeric effect operates in these complexes, since the phenyl ring is attached to a chelate ring with some aromatic character and to which is attached a $\mathrm{CF_3}$ group. The mesomeric moment arising from the effect shown in (IV) operates in a direction toward the chelate ring and would be greatest for F and least for Br. 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*-$\mathrm{FC_6H_4}$ > *p*-$\mathrm{ClC_6H_4}$ > *p*-$\mathrm{BrC_6H_4}$, *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.

It is noteworthy that when R = 2-thienyl, the dipole moments of the metal complexes lie between those of complexes having R = *p*-$\mathrm{MeC_6H_4}$ and those having R = *m*-$\mathrm{MeC_6H_4}$.

A recent study of the dipole moments of the β-diketones $\mathrm{RCOCH_2COCF_3}$ has revealed that the moments decrease according to the nature of R in the sequence: *p*-$\mathrm{MeC_6H_4}$ > *m*-$\mathrm{MeC_6H_4}$ > *o*-$\mathrm{MeC_6H_4}$ and increase in the order of *p*-$\mathrm{ClC_6H_4}$ < *m*-$\mathrm{ClC_6H_4}$ < *o*-$\mathrm{ClC_6H_4}$.[13] Dipole moments of the β-diketones and

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

[10] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**, 673.

[11] S. E. Livingstone, *Co-ordination Chem. Rev.*, 1971, **7**, 59.

[12] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, 2nd edn., 1969.

[13] M. Das and S. E. Livingstone, unpublished data.

of the metal complexes of their monothio-analogues appear to vary in the same manner; however, metal complexes of mercapto-β-diketones with *ortho*-substituted phenyl groups could not be isolated.

## EXPERIMENTAL

*Preparation of the Complexes.*—The preparation of the mercapto-β-diketones and their metal complexes, together with the analytical data, have been reported previously.[8,14]

*Determination of Dipole Moments.*—Dipole moments were determined by the static-polarization method. Dielectric-constant measurements were made on a Wissenschaftlich-Technische Werkstätten dipolemeter DMO1 at 25 ± 0·1 °C, as previously described.[1] Refractive-index measurements were obtained with an Abbe 60 refractometer with white light.

[4/1392 *Received*, 10*th July*, 1974]

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[14] M. Das and S. E. Livingstone, *Austral. J. Chem.*, 1974, **27**, 749.