Dipole-moment Measurements on Metal Chelate Complexes. Part 4.† The Effect of Substitution in the Phenyl Ring on the Dipole Moments of Metal Chelates of Fluorinated Mercapto-β-diketones containing a Phenyl Group

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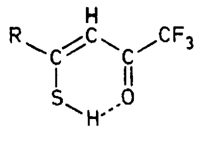
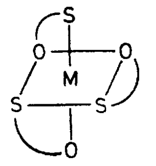
Dipole moments have been determined from static-polarization measurements for the nickel(II), palladium(II), platinum(II), copper(II), zinc(II), cobalt(III), and rhodium(III) chelate complexes of the fluorinated mercapto-β-diketones RC(SH):CHCOCF$_3$ [R = *p*-MeOC$_6$H$_4$, *m*-MeOC$_6$H$_4$, *m,p*-(MeO)$_2$C$_6$H$_3$, and *m,p*-Me$_2$C$_6$H$_3$]. The moments indicate *cis*-square-planar conformations for the complexes of Ni, Pd, Pt, and Cu, and a *facial*-octahedral configuration for those of Co and Rh. For all the metal complexes with methyl substitution of the phenyl ring the dipole moments decrease if the R groups are arranged in the order: *m,p*-Me$_2$C$_6$H$_3$ > *p*-MeC$_6$H$_4$ > *m*-MeC$_6$H$_4$ > Ph. However, for methoxy-substitution the order is: *p*-MeOC$_6$H$_4$ > *m,p*-(MeO)$_2$C$_6$H$_3$ > Ph. The anomalous position of *m,p*-(MeO)$_2$C$_6$H$_3$ is ascribed to steric hindrance preventing free rotation of the methoxy-groups and leading to a lower group moment $\mu_{\text{R-ch}}$.

We have previously reported dipole moments of the chromium(III), iron(III), ruthenium(III), cobalt(III), rhodium(III), nickel(II), palladium(II), platinum(II), copper(II), and zinc(II) complexes of a range of mercapto-β-diketones (1).[1-5] The relatively large values of the dipole moments were considered to indicate a *cis*-square-planar configuration for the complexes of Ni, Pd, Pt, and Cu and a *facial*-octahedral configuration (2) for those of Cr, Fe, Ru, Co, and Rh. The appreciably lower values obtained for the dipole moments of the zinc complexes were considered to be consistent with a tetrahedral configuration. *X*-Ray crystal-structure determinations on metal chelates of mercapto-β-diketones have confirmed the *cis*-square-planar configuration for a palladium(II),[6] a platinum(II),[6] and four nickel(II) complexes,[7-10] the *facial*-octahedral configuration for a cobalt(III)[11] and two iron(III) complexes,[12] and a tetrahedral configuration for a zinc(II) complex.[13]



(1)



(2)

The dipole moments were determined by static-polarization measurements on solutions of the metal complexes in benzene. The dipole moments of 45 of the complexes were also determined by dielectric-relaxation measurements.[1,3] The values obtained by the latter method are lower than those determined by the former by 0.06—0.82, 0.35—1.21, and 0.12—0.69 D ‡ for square-planar, octahedral, and tetrahedral complexes, respectively. These differences were attributed to the contribution made by atomic polarization, since the value obtained by the dielectric-relaxation method is independent of atomic polarization.

In our studies we have observed the effect of substitution in the phenyl ring of (1; R = Ph) on the dipole moments of the metal complexes. The effects of both nucleophilic and electrophilic substituents at the *para* and *meta* positions were studied. It was found that the dipole moments of all the square-planar and octahedral metal complexes of (1) investigated decrease if the R groups are arranged in the order: *p*-MeC$_6$H$_4$ > *m*-MeC$_6$H$_4$ > Ph > *m*-ClC$_6$H$_4$ > *m*-BrC$_6$H$_4$ > *p*-FC$_6$H$_4$ > *p*-ClC$_6$H$_4$ > *p*-BrC$_6$H$_4$ > *m,p*-Cl$_2$C$_6$H$_3$.[2,4] This order was explained in terms of: (*a*) the magnitude and direction of the Ph–X bond moments (X = F, Cl, Br, H, or Me); (*b*) the inductive effect arising from differences in electron density at the C^1 and C^5 carbon atoms of the ligand; and (*c*) the change in moment brought about by the mesomeric effect of the substituent X.[2]

We have now investigated the effects of *p*-MeO, *m*-MeO, *m,p*-(MeO)$_2$, and *m,p*-Me$_2$ substitution on the dipole moments of the metal chelates.

RESULTS AND DISCUSSION

The new fluorinated β-diketones 1,1,1-trifluoro-4-(*m*-methoxyphenyl)-, 4-(*m,p*-dimethoxyphenyl)-1,1,1-trifluoro-, and 4-(*m,p*-dimethylphenyl)-1,1,1-trifluoro-butane-2,4-dione were obtained and used as starting materials for the preparation of the mercapto-β-diketones.

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† Part 3 is ref. 3.

‡ Throughout this paper: 1 D = 3.336 × 10^{-30} C m.

[1] M. Das, S. E. Livingstone, S. W. Filipczuk, J. W. Hayes, and D. V. Radford, *J.C.S. Dalton*, 1974, 1409.

[2] M. Das and S. E. Livingstone, *J.C.S. Dalton*, 1975, 452.

[3] S. W. Filipczuk, J. W. Hayes, D. V. Radford, M. Das, and S. E. Livingstone, *J.C.S. Dalton*, 1975, 886.

[4] M. Das, S. E. Livingstone, J. H. Mayfield, D. S. Moore, and N. Saha, *Austral. J. Chem.*, 1976, **29**, 767.

[5] S. E. Livingstone and J. E. Oluka, *Austral. J. Chem.*, 1976, **29**, 1913.

[6] E. A. Shugam, L. M. Shkol'nikova, and S. E. Livingstone, *Zhur. strukt. Khim.*, 1967, **8**, 550.

[7] L. Kutschabsky and L. Beyer, *Z. Chem.*, 1971, **11**, 30.

[8] J. Sieler, P. Thomas, E. Uhlemann, and E. Höhne, *Z. anorg. Chem.*, 1971, **380**, 160.

[9] O. Siiman, D. D. Titus, C. D. Cowman, J. Fresco, and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, **96**, 2353.

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

[11] J. Ollis, M. Das, V. J. James, S. E. Livingstone, and K. Nimgirawath, *Crystal Struct. Comm.*, 1976, **5**, 679.

[12] B. F. Hoskins and C. D. Pannan, *Inorg. Nuclear Chem. Letters*, 1974, **11**, 409.

[13] B. F. Hoskins and C. D. Pannan, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 405.

The new mercapto-β-diketones, 1,1,1-trifluoro-4-mercapto-4-(*p*-methoxyphenyl)-, 4-(*m,p*-dimethoxyphenyl)-1,1,1-trifluoro-4-mercapto- and 4-(*m,p*-dimethylphenyl)-1,1,1-trifluoro-4-mercapto-but-3-en-2-one [1; R = *p*-$MeOC_6H_4$, *m,p*-$(MeO)_2C_6H_3$, and *m,p*-$Me_2C_6H_3$] were prepared. Compound (1; R = *m*-$MeOC_6H_4$) was not purified but the crude material was used in the preparation of the metal complexes.

Dipole moments of the metal complexes of the mercapto-β-diketones were determined from static-polarization measurements. The values are given in the Table together with moments previously reported for related metal complexes for comparison. Data for incremental dielectric constants and refractive indices are given in Supplementary Publication No. SUP 21968 (8 pp).* No corrections were applied for the contribution due to atomic polarization. Our earlier results indicate that the average values for atomic polarization are 0.32, 0.85, and 0.49 D for square-planar, octahedral, and tetrahedral complexes, respectively.

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

R	Ni^{II}	Pd^{II}	Pt^{II}	Cu^{II}	Zn^{II}	Co^{III}	Rh^{III}
p-$MeOC_6H_4$	6.70	7.16	6.73	6.02	4.80	8.57	8.14
m,p-$Me_2C_6H_3$	6.05	6.32	6.20	5.46	3.76	7.75	*a*
p-MeC_6H_4	5.84 [b]	5.91 [b]	6.16 [b]	5.12 [b]	3.65 [c]	7.36 [b]	7.16 [d]
m,p-$(MeO)_2C_6H_3$	5.62	6.45	6.07	5.24	3.96	6.89	7.04
m-$MeOC_6H_4$	5.43	5.88	5.64	4.91	3.94	6.91	*a*
m-MeC_6H_4	5.33 [e]	5.55 [e]	5.68 [e]	4.66 [d]	3.37 [d]	6.79 [e]	
Ph	4.92 [b]	5.02 [b]	5.35 [b]	4.39 [b]	3.06 [c]	6.54 [b]	6.52 [d]

[a] Compound could not be isolated. [b] Data from ref. 1. [c] Data from ref. 3. [d] Data from ref. 4. [e] Data from ref. 2.

For all the metal complexes studied with methyl substitution on the phenyl ring the dipole moments decrease if the R groups are arranged in the order: *m,p*-$Me_2C_6H_3$ > *p*-MeC_6H_4 > *m*-MeC_6H_4 > Ph. This is the order expected on the basis of the inductive effect. The nucleophilic methyl group (+*I* effect) at either the *meta*- or *para*-position increases the electron density at the C^5 atom, *i.e.* the phenyl carbon atom attached to the C^4 atom of (1). However, a *p*-methyl group produces a higher electron density at the C^5 atom than a *m*-methyl group, leading to a higher dipole moment for the metal complex. Furthermore, methyl substitution at both *meta*- and *para*-positions will lead to an even greater electron density at the C^5 atom than that produced by a *p*-methyl group alone. Hence the complexes with R = *m,p*-$Me_2C_6H_3$ have the highest dipole moments among those with methyl substituents on the phenyl ring.

In the case of methoxy-substitution the dipole moments of complexes of a given metal ion decrease in the order: *p*-$MeOC_6H_4$ > *m,p*-$(MeO)_2C_6H_3$ > *m*-$MeOC_6H_4$ > Ph. The only exception is the cobalt(III) complex with R = *m,p*-$(MeO)_2C_6H_3$, which has a moment 0.02 D less than its analogue with R = *m*-$MeOC_6H_4$. Now the methoxy-group has a greater +*I* effect than the methyl group. This is manifested by the complexes with R = *p*-$MeOC_6H_4$ having greater dipole moments than those with R = *p*-MeC_6H_4. The same is true for complexes with *meta*-substitution. However, an anomaly occurs in that the complexes with R = *m,p*-$(MeO)_2C_6H_3$ have lower moments than the corresponding complexes with R = *p*-$MeOC_6H_4$. Moreover, except for the palladium and zinc complexes, the moments are lower for those complexes having R = *m,p*-$(MeO)_2C_6H_3$ than for those with R = *m,p*-$Me_2C_6H_3$.

These anomalous results can be explained by the fact that in methyl-substituted complexes the carbon atom of the methyl group is coplanar with the phenyl ring, whereas this is not so for the methoxy-groups. In the latter case the Me–O–C_6H_3 bond angle is not 180°. Molecular models indicate that this non-linearity leads to steric hindrance which prevents free rotation of the two methoxy-groups in the *m,p*-$(MeO)_2C_6H_3$ moiety. This steric effect preventing free rotation of the methoxy-groups 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 orienting the methoxy-groups in a favoured orientation thereby producing an additional component of electric moment which reduces the group moment μ_{R-ch}.

EXPERIMENTAL

Preparation of β-*Diketones*.—The following β-diketones, which were obtained as colourless crystals, were prepared in 40—50% yields by the general method previously given for fluorinated β-diketones:[14] 1,1,1-trifluoro-4-(*p*-methoxyphenyl)butane-2,4-dione,[15] m.p. 55 °C (Found: C, 53.5; H, 4.0. Calc. for $C_{11}H_9F_3O_3$: C, 53.7; H, 3.7%); 1,1,1-*trifluoro*-4-(m-*methoxyphenyl*)*butane*-2,4-*dione*, m.p. 38 °C (Found: C, 53.9; H, 4.0. $C_{11}H_9F_3O_3$ requires C, 53.7; H, 3.7%); 4-(m,p-*dimethoxyphenyl*)-1,1,1-*trifluorobutane*-2,4-*dione*, m.p. 85—86 °C (Found: C, 52.1; H, 4.0. $C_{12}H_{11}F_3O_4$ requires C, 52.2; H, 4.0%); 4-(m,p-*dimethylphenyl*)-1,1,1-*trifluorobutane*-2,4-*dione*, m.p. 30—32 °C (Found: C, 58.7; H, 4.7. $C_{12}H_{11}F_3O_2$ requires C, 59.0; H, 4.5%).

Preparation of Mercapto-β-*diketones*.—The following mercapto-β-diketones were prepared in 50—65% yields from the appropriate β-diketones by the general method previously described:[14] 1,1,1-*trifluoro*-4-*mercapto*-4-(p-*methoxyphenyl*)*but*-3-*en*-2-*one*, red oil (Found: C, 51.0; H, 3.75; S, 12.0. $C_{11}H_9F_3O_2S$ requires C, 50.4; H, 3.5; S, 12.2%); 4-(m,p-*dimethylphenyl*)-1,1,1-*trifluoro*-4-*mercaptobut*-3-*en*-2-*one*, red oil (Found: C, 56.2; H, 4.9; S, 12.4. $C_{12}H_{11}F_3OS$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[14] M. Das and S. E. Livingstone, *Austral. J. Chem.*, 1974, **27**, 1177.

[15] R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem.*, 1968, **21**, 1787.

requires C, 55.4; H, 4.3; S, 12.3%); 4-(m,p-*dimethyoxyphenyl*)-1,1,1-*trifluoro*-4-*mercaptobut*-3-*en*-2-*one*, red crystals, m.p. 66 °C (Found: C, 49.5; H, 3.9; S, 11.0. $C_{12}H_{11}F_3O_3S$ requires C, 49.3; H, 3.8; S, 11.0%). As the latter compound is a solid, it was not purified *via* the lead complex but the crude material, which was obtained when the reaction mixture was poured into water, was dried and recrystallized from light petroleum. 1,1,1-Trifluoro-4-mercapto-4-(*m*-methoxyphenyl)but-3-en-2-one was not purified *via* the lead complex. In this case the crude oil was used for the preparation of the metal complexes.

Preparation of Metal Complexes.—The metal complexes were prepared by the general methods given below. The complexes were dried *in vacuo* over silica gel. Analyses, which were all within 1% of calculated values, are listed in SUP 21968. Analyses for carbon and hydrogen were by the Microanalytical Laboratory, University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne. Metals were determined by standard gravimetric procedures.

Nickel(II). Nickel acetate tetrahydrate (1 g, 4 mmol) in hot ethanol (70 cm^3) was added to a solution of the appropriate mercapto-β-diketone (1) (8 mmol) in ethanol (30 cm^3). The resulting brown precipitate was filtered off and recrystallized from ligroin to give the nickel complex, yield 30—50%.

Palladium(II). Potassium tetrachloropalladate(II) (1.6 g, 4.9 mmol) in water (50 cm^3) was added to a solution of (1) (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 45—65%.

Platinum(II). Potassium tetrachloroplatinate(II) (2.5 g, 6 mmol) in water (60 cm^3) was added to a solution of (1) (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 product was filtered off and recrystallized from acetone to give dark red crystals of the platinum complex, yield 60—80%.

Copper(II). Copper(II) acetate monohydrate (1 g, 5 mmol) in hot ethanol (100 cm^3) was added to a solution of (1) (10 mmol) in ethanol (50 cm^3). The mixture was cooled and the resulting brown product was filtered off and recrystallized from ligroin to give the copper complex, yield 35—50%.

Zinc(II). Zinc acetate dihydrate (1.44 g, 4.5 mol) in hot ethanol (80 cm^3) was added to a solution of (1) (9 mmol) in ethanol (50 cm^3). Water (100 cm^3) was added to the cooled mixture and the resulting yellow precipitate was filtered off and recrystallized from ligroin to give deep yellow crystals of the zinc complex, yield 30—40%.

Cobalt(III). Cobalt(II) acetate tetrahydrate (1 g, 4 mmol) in hot ethanol (75 cm^3) was added to a solution of (1) (12 mmol) in ethanol (100 cm^3). Air was passed through the resulting deep brown solution for 6 h. The black product which had deposited was then filtered off and recrystallized from acetone to give black crystals of the cobalt complex, yield 40—65%.

Rhodium(III). Rhodium(III) chloride trihydrate (1 g, 3.7 mmol) in ethanol (30 cm^3) was added to a solution of (1; R = p-MeOC$_6$H$_4$) (11 mmol) in ethanol (25 cm^3). The mixture was kept at reflux for 4 h and then allowed to stand in the refrigerator overnight. The brown crystals of *tris*[1,1,1-*trifluoro*-4-*mercapto*-4-(p-*methoxyphenyl*)*but*-3-*en*-2-*onato*]*rhodium*(III) were separated by filtration and washed with a little ice-cold ethanol, yield 40%.

Determination of Dipole Moments.—Dipole moments were determined by static-polarization measurements on benzene solutions at 25 ± 0.1 °C, as previously described.[1] Benzene (AnalaR) was purified as previously described.[1]

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