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Dipole Moments of some Metal Complexes of Four New Monothio-β-Diketones

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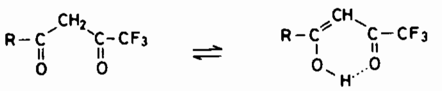
Dipole moments have been determined by static polarization measurements for the nickel(II), copper(II), zinc(II), palladium(II), platinum(II) and cobalt(III) chelates of the fluorinated monothio-β-diketones $RC(SH)\!=\!CHCOCF_3$ [$R = 4'\text{-}C_2H_5C_6H_4$, $4'\text{-}C_2H_5OC_6H_4$, $3',5'\text{-}(CH_3O)_2C_6H_3$ *and* $3',4',5'\text{-}(CH_3O)_3C_6H_2$]. *The moments indicate* cis-*square-planar configurations for the nickel, palladium and platinum complexes. The zinc complexes have tetrahedral structures and the configurations of copper complexes lies between square-planar and tetrahedral structures. The cobalt complexes perhaps have facial-octahedral configurations. The presence of steric hindrance when R is* $3',4',5'\text{-}(CH_3O)_3C_6H_2$ *lower the dipole moments. Such hindrance is absent with R as* $3',5'\text{-}(CH_3O)_2C_6H_3$.

Introduction

The metal complexes of β-diketones (I) are generally solvated, polymeric and insoluble in organic solvents [1], but those of monothio-β-diketones(II) are anhydrous, monomeric and soluble in organic solvents. Because of these useful properties we have reported the dipole moments of many transition metal complexes of fluorinated monothio-β-diketones [2–6]. Some copper bischelates of fluorinated β-diketones are soluble in benzene and their dipole moments were reported [7–9].



(I)

(II)

In the course of these investigations we have studied the effect of substituents in the phenyl ring of $PhC(SH)\!=\!CHCOCF_3$ on the dipole moments of their metal complexes. Nucleophilic substituents (methyl and methoxy) at the *para* and *meta* positions of the phenyl ring increase the dipole moments of their metal complexes, the group at *para* position increases the value to a greater extent than that by the group at *meta* position. Electrophilic substituents (chloro and bromo) in the phenyl ring decrease the values of dipole moments of their metal complexes, the group at the *para* position decreases the value by a greater amount than the group at the *meta* position. Interesting results were obtained when R = *m,p*-$X_2C_6H_3$ (X = CH_3 and CH_3O). For all the metal complexes studied with methyl substituents on the phenyl ring the dipole moments decrease if the R groups are arranged in the order: *m,p*-$(CH_3)_2C_6H_3$ > *p*-$CH_3C_6H_4$ > *m*-$CH_3C_6H_4$ > C_6H_5. This is the order expected on the basis of induction effect. In the cases of methoxy substituents the dipole moments of complexes of a given metal decrease in the order: *p*-$CH_3OC_6H_4$ > *m,p*-$(CH_3O)_2C_6H_3$ > *m*-$CH_3OC_6H_4$ > C_6H_5. Since both methyl and methoxy groups are nucleophilic they should follow the same order. The anomalous result in the cases with R = *m,p*-$(CH_3O)_2C_6H_3$ is ascribed to steric hindrance preventing free rotation of the methoxy groups.

We have now prepared four new fluorinated β-diketones and their monothio derivatives. The dipole moments of metal complexes of these monothio-β-diketones are discussed in this report.

Experimental

Preparation of the β-Diketones

The β-diketones were prepared by Claisen condensation of the substituted acetophenone and ethyl trifluoroacetate, catalyzed by sodium methoxide.

Substituted acetophenone ($RCOCH_3$; 0.2 mol) and ethyl trifluoroacetate ($CF_3COOC_2H_5$; 0.2 mol) were added to a solution of sodium methoxide (prepared by the reaction of 5 g sodium and 30 ml methanol in 250 ml dry ether). The mixture was allowed to stand at room temperature overnight. It was then acidified with saturated $KHSO_4$ solution (pH paper). A saturated aqueous copper acetate solution (400 ml) was then added, and the mixture was heated on a steam bath to drive off ether. The green bis(β-diketonato)copper was filtered and washed with 95% alcohol.

Hydrogen sulphide was passed for 90 min through the suspension of air-dried copper complex in 500 ml ether. The copper sulphide was filtered off with the aid of cellulose powder. The filtrate, after drying over anhydrous sodium sulphate, was evaporated to remove the solvent. The residue was cooled to room temperature to find out whether the β-diketone is a solid or liquid. The solid β-diketones were recrystallized from absolute alcohol and the liquid β-diketone was purified by distillation:

1,1,1-trifluoro-4-(4′-ethoxyphenyl)butane-2,4-dione (I; R = 4′-$C_2H_5OC_6H_4$), m.p. 51.5 °C (Found: C, 55.57; H, 4.21; $C_{12}H_{11}F_3O_3$ requires, C, 55.40; H, 4.26%). 1,1,1-trifluoro-4-(3′,5′-dimethoxyphenyl)-butane-2,4-dione [I; R = 3′,5′-$(CH_3O)_2C_6H_3$], m.p. 73 °C (Found: C, 52.10; H, 3.92. $C_{12}H_{11}F_3O_4$ requires C, 52.18; H, 4.01%.).

1,1,1-trifluoro-4-(3′,4′,5′-trimethoxyphenyl)butane-2,4-dione [I; R = 3′,4′,5′-$(CH_3O)_3C_6H_2$], m.p. 91 °C (Found: C, 50.82; H, 4.13; $C_{13}H_{13}F_3O_5$ requires C, 50.98; H, 4.28%).

1,1,1-trifluoro-4-(4′-ethylphenyl)butane-2,4-dione (I; R = 4′-$C_2H_5C_6H_4$), b.p. 242 °C (Found: C, 58.98; H, 4.38. $C_{12}H_{11}F_3O_2$ requires C, 59.00; H, 4.50%).

Preparation of the Monothio-β-diketones

Dry hydrogen sulphide was passed at a rapid rate for 30 min through a solution of the β-diketone (4 g) in dry absolute alcohol (400 ml), cooled to −70 °C in an alcohol-dry ice bath. Dry hydrogen chloride was then passed for 15 min. The flask was fitted with a calcium chloride tube to prevent access of moisture. The mixture was allowed to stand at room temperature for about 20 hours. The red solution was poured slowly, with stirring, into 400 g ice–water mixture. The monothio-β-diketone was extracted with petroleum ether (b.p. 40–60 °C).

For isolating solid 1,1,1-trifluoro-4-mercapto-4-(3′,5′-dimethoxyphenyl)but-3-en-2-one [II; R = 3′,5′-$(CH_3O)_2C_6H_3$], the combined ether extracts of three batches (after drying over anhydrous sodium sulphate) were evaporated to a small volume (60 ml) and then cooled in ice. The solid was filtered and recrystallized from petroleum ether. The red crystals melt at 66 °C (Found, C, 49.28; H, 3.70; S, 11.11. $C_{12}H_{11}F_3O_3S$ requires C, 49.31; H, 3.79; S, 10.97%).

1,1,1-Trifluoro-4-mercapto-4-(3′,4′,5′-trimethoxyphenyl)but-3-en-2-one [II; R = 3′,4′ 5′-$(CH_3O)_3C_6H_2$] was isolated by a similar procedure. The red solid melts at 91 °C (Found: C, 48.81; H, 3.92; S, 10.08. $C_{13}H_{13}F_3O_4S$ requires C, 48.43; H, 4.06; S, 9.95%).

4-(4′-Ethoxyphenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (II; R = 4′-$C_2H_5OC_6H_4$) was separated as lead complex by adding an alcoholic solution (100 ml) of equivalent lead acetate trihydrate to the petroleum ether extract, followed by the addition of 200 ml water. The mixture was heated for 10 min and then cooled in ice. The lead complex was filtered and washed with hot water. The dried lead complex of three batches was suspended in 300 ml petroleum ether and hydrogen sulphide passed for 90 min. The lead sulphide was removed by filtration. The red filtrate, after drying over anhydrous sodium sulphate, was evaporated off to get the liquid product (Found: C, 52.33; H, 4.23. $C_{12}H_{11}F_3O_2S$ requires C, 52.18; H, 4.01%).

4-(4′-Ethylphenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-one (II; R = 4′-$C_2H_5C_6H_4$) was obtained as a red liquid by evaporating off the solvent from the dried petroleum ether extract (Found: C, 55.63; H, 4.58. $C_{12}H_{11}F_3OS$ requires C, 55.40; H, 4.26%). It could not be purified via lead complex.

Preparation of the Complexes

Nickel(II)

Nickel acetate tetrahydrate (1 g, 4 mmol) in hot ethanol (70 ml) was added to a solution of the monothio-β-diketone (8 mmol) in warm ethanol (30 ml). The mixture was cooled in ice and the resulting brown precipitate filtered off. It was recrystallized from 1:1 acetone–petroleum ether mixture. When R = 4′-$C_2H_5C_6H_4$, the crude product was recrystallized from 50 ml petroleum ether.

Palladium(II)

A filtered solution of potassium tetrachloropalladate(II) (1.5 g, 4.6 mmol) in water (60 ml) was added to a solution of the monothio-β-diketone (9.2 mmol) in acetone (60 ml). The resulting orange precipitate was filtered off and recrystallized from acetone.

Platinum(II)

A filtered solution of potassium tetrachloroplatinate(II) (1.5 g, 3.6 mmol) in water (60 ml) was added to a solution of the monothio-β-diketone (7.2 mmol) in acetone (60 ml). The mixture was refluxed for 15 min and cooled in ice. The filtered red precipitate was recrystallized from acetone.

Copper(II)

Copper acetate monohydrate (1 g, 5 mmol) in hot ethanol (100 ml) was added to a solution of the monothio-β-diketone (10 mmol) in warm ethanol (50 ml). The mixture was cooled in ice. The filtered brown precipitate was recrystallized from acetone–petroleum ether mixture. When R = 4′-$C_2H_5C_6H_4$, the addition of 10 ml water to the reaction mixture precipitated the complex which was recrystallized from 50 ml petroleum ether.

TABLE I. Analytical Data for the Complexes.

R	Compound	% Found				% Calculated			
		C	H	Met	S	C	H	Met	S
4′-$C_2H_5C_6H_4$	NiL_2	49.58	3.52	10.01	10.89	49.94	3.49	10.18	11.11
	PdL_2	46.16	3.11	16.62	10.15	46.10	3.20	17.03	10.26
	PtL_2	40.83	2.88	27.01	9.13	40.40	2.82	27.33	8.99
	CuL_2	49.68	3.51	11.18	10.75	49.53	3.46	10.92	11.02
	ZnL_2	49.57	3.44		11.29	49.42	3.45		10.98
	CoL_3	52.06	3.75	6.85	11.41	51.68	3.61	7.04	11.50
4′-$C_2H_5OC_6H_4$	NiL_2	47.63	3.01	9.65	10.33	47.33	3.31	9.64	10.53
	PdL_2	43.78	2.87	15.87	9.65	43.90	3.07	16.20	9.76
	PtL_2	38.49	2.62	25.85	8.57	38.67	2.70	26.17	8.60
	CuL_2	47.06	3.21	10.52	10.20	46.95	3.28	10.35	10.44
	ZnL_2	46.90	3.13		10.22	46.82	3.27		10.41
	CoL_3	48.76	3.18	6.73	10.66	48.90	3.42	6.66	10.87
3′,5′-$(CH_3O)_2C_6H_3$	NiL_2	44.79	2.99	9.28	9.64	44.96	3.14	9.15	10.00
	PdL_2	41.78	2.73	15.21	9.02	41.85	2.93	15.45	9.31
	CuL_2	44.69	3.00	9.90	9.97	44.63	3.12	9.84	9.92
	ZnL_2	44.16	3.13		9.68	44.49	3.11		9.90
	CoL_2	46.47	3.15	6.17	10.07	46.34	3.24	6.32	10.31
3′,4′,5′-$(CH_3O)_3C_6H_2$	NiL_2	44.66	3.33	8.54	9.00	44.53	3.45	8.37	9.14
	PdL_2	41.55	3.08	14.00	8.88	41.70	3.23	14.21	8.56
	CuL_2	44.47	3.42	9.12	8.90	44.23	3.43	9.00	9.08
	ZnL_2	44.23	3.38		8.95	44.12	3.42		9.06
	CoL_3	45.82	3.35	5.53	9.14	45.79	3.55	5.73	9.40

Zinc(II)

Zinc acetate dihydrate (1 g, 4.5 mmol) in hot ethanol (100 ml) was added to a warm solution of the monothio-β-diketone (9 mmol) in ethanol (30 ml). The addition of 100 ml water to the cooled mixture precipitated the yellow complex which was recrystallized from petroleum ether. When R = 3′,5′-$(CH_3O)_2C_6H_3$ and 3′,4′,5′-$(CH_3O)_3C_6H_2$, the addition of water to the cooled reaction mixture separated the product in colloidal form which was extracted by petroleum ether. The extract, after drying over anhydrous sodium sulphate, was concentrated to a small volume and cooled. The yellow solid was recrystallized from petroleum ether.

Cobalt(III)

Cobalt(II) acetate tetrahydrate (1 g, 4 mmol) in ethanol (150 ml) was added to a solution of the monothio-β-diketone (12 mmol) in warm ethanol (50 ml). The deep brown solution was filtered and air passed through the solution for about three hours. The black deposit was filtered and washed with ethanol.

Analytical data for the complexes are shown in Table I.

Determination of Dipole Moments

Dipole moments were calculated from the measurements of dielectric constants and refractive indices of the compounds in benzene solutions at five different concentrations. The solvent was purified by recrystallizing BDH analar grade benzene twice, and drying it with BDH molecular sieves. The dielectric constants were measured using a Wissenschaftlich-Technische Werkstatten Dipolemeter Type DM 01 with Type DFL-1 cell. The instrument was calibrated with pure, dry benzene and cyclohexane. Refractive indices were measured in an Abbe 60 Refractometer. All measurements were done at 25 °C.

The dielectric constant, ϵ, and refractive index, n, were measured for solvent and solutions. The values of $\Delta\epsilon$ (difference between the values of the solution and solvent) and $\Delta(n^2)$ were plotted against the weight fractions of the solutions. The slopes of the graphs give a_ϵ and a_n. M is the molecular weight of the compound. The dipole moment, μ, was calculated by the equation [10–13],

$$\mu^2 = \frac{27kT}{4\pi N}\,\frac{1}{ds(2+\epsilon_s)^2}\,(a_\epsilon - a_n)\,M$$

TABLE II. Dipole Moments of the Metal Complexes of $RC(SH){=}CHCOCF_3$.

R	NiL_2	PdL_2	PtL_2	CuL_2	ZnL_2	CoL_3
3',5'-Dimethoxyphenyl	5.87	5.96		5.50	4.13	7.08
3',4',5 -Trimethoxyphenyl	4.32	4.48		3.98	3.38	5.15
4'-Ethylphenyl	5.94	6.07	6.34	5.26	3.85	7.43
4'-Ethoxyphenyl	6.95	7.23	7.36	6.36	4.81	8.71
Phenyl	4.92[a]	5.02[a]	5.35[a]	4.39[a]	3.06[b]	6.54[a]
4'-Methylphenyl	5.84[a]	5.91[a]	6.14[a]	5.12[a]	3.65[b]	7.36[a]
4'-Methoxyphenyl	6.70[c]	7.16[c]	6.73[c]	6.02[c]	4.80[c]	8.57[c]
3',4'-Dimethoxyphenyl	5.62[c]	6.45[c]	6.07[c]	5.24[c]	3.96[c]	6.89[c]
3'-Methoxyphenyl	5.43[c]	5.88[c]	5.64[c]	4.91[c]	3.94[c]	6.91[c]

[a] Reference 2. [b] Reference 4. [c] Reference 6.

k is the Boltzmann constant, N the Avogadro number, d_s the density and ϵ_s the dielectric constant of benzene. At 25 °C the above equation can be simplified to

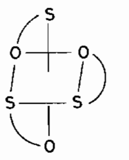
$$\mu = 0.0959\sqrt{(a_\epsilon - a_n)M}\ \text{Debye}$$

Results and Discussion

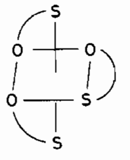
Dipole moments of the metal complexes of the monothio-β-diketones were determined from static polarization measurements. The values are given in Table II together with the moments previously reported for related metal complexes for comparison. Metal complexes have an appreciable value for atomic polarization [14–16]. Dipole moments determined by the static polarization method include the contribution due to this effect and are probably less than 0.5 D for bis-chelate and 1.0 D for tris-chelate. No correction was applied.

The appreciably large values of dipole moments indicate *cis*-square-planar configuration for the complexes of nickel, palladium and platinum. For a given ligand the dipole moments decrease in the order: Pt > Pd > Ni, although the variation is within 0.3 Debye. This is the order of decreasing *b* class character [17]. Preferential formation of *cis* structure in the transition metal complexes of sulphur containing ligands is probably due to d_π–d_π bonding between the metal and sulphur atoms [18]. The dipole moments of copper complexes are about 0.4–0.8 Debye lower than the mean values for the nickel, palladium and platinum complexes of the same ligand. This difference has been attributed to significant distortion from the square-planar towards the tetrahedral configuration in the case of the copper complexes. Further lower values for zinc complexes are due to their tetrahedral structure. X-ray structure determination has confirmed the *cis* configuration for nickel [19–22], palladium [23], and platinum [23] complexes of some monothio-β-diketones.

The relatively high values obtained for the dipole moments of CoL_3 indicate the facial-octahedral (III) rather than meridional-octahedral (IV) configuration. It is interesting to note that three sulphur atoms are at right angles to the metal in the facial structure and thus in correct position for d_π–d_π bonding with the metal atom. X-ray studies of the tris-chelates of cobalt [24] and iron [25] of some monothio-β-diketones confirmed their facial structures. Holm *et al.* had postulated the facial configuration on the basis of p.m.r. studies on some tris(monothio-β-diketonato)cobalt [26].



III



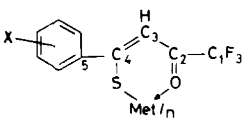
IV

A strongly nucleophilic substituent, such as methoxy group, at the *para* position of phenyl ring increases the dipole moment of the metal complexes. The carbon atom of the methoxy group is not coplanar with the phenyl ring. This non-linearity of CH_3–O–C_6H_4 bonds causes steric hindrance which prevents free rotation of the methoxy groups in 3',4'-$(CH_3O)_2C_6H_3$ and 3',4',5'-$(CH_3O)_3C_6H_2$. 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 orienting the methoxy groups in a favoured orientation thereby producing an additional component of electric moment which reduces the group moment $\mu_{R\text{-}ch}$. Such interference is absent in 3',5'-$(CH_3O)_2C_6H_3$ and thus the dipole moment increases. In the case of methoxy-substitution the dipole moments of complexes of a given metal ion decrease in the order:

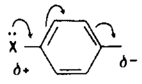
$4'\text{-}CH_3OC_6H_4 > 3',5'(CH_3O)_2C_6H_3 > 3',4'\text{-}(CH_3O)_2C_6H_3 > 3'\text{-}CH_3OC_6H_4 > C_6H_5\ 3',4',5'\text{-}(CH_3O)_3C_6H_2$.

The dipole moments of metal complexes are increased by a small amount when methyl and methoxy groups at the *para* position of phenyl ring are replaced by ethyl and ethoxy groups, respectively. This is indicative of the greater nucleophilic (+I effect) properties of C_2H_5 and C_2H_5O compared to CH_3 and CH_3O groups, respectively. The ethoxy is a stronger nucleophile than the ethyl group.

The effect of substituents on the dipole moments arises from a) the magnitude and direction of Ph–X bond moments; (b) the induction effect giving rise to a difference of electron density of the C1 and C5 carbon atoms of the ligand moieties (V) – 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 (VI) of the substituent X; and (d) the steric hindrance.



V



VI

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