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Dipole Moments of some Transition Metal Complexes of Five New Monothio-β-Diketones

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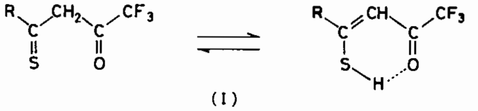
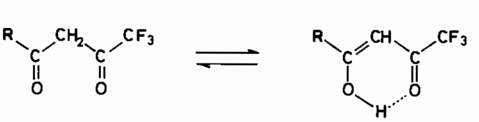
Dipole moments of cobalt(III), nickel(II), palladium(II), platinum(II), copper(II) and zinc(II) complexes of five new monothio-β-diketones $RC(SH)=CHCOCF_3$ *(R = 2'-methoxyphenyl, 2',4'-dimethoxyphenyl, 2',5'-dimethoxyphenyl, 2',3',4'-trimethoxyphenyl and 2',4',5'-trimethoxyphenyl) were determined by static-polarization measurements. The moments clearly indicate* cis-*square-planar configurations for the nickel, palladium and platinum complexes. The zinc complexes have tetrahedral structures and the copper complexes perhaps have distorted* cis-*square-planar structures. The* ^1H *and* ^{19}F *NMR data confirm the* facial *configurations for the cobalt(III) complexes. The dipole moment values for the complexes vary with R: 2',3',4'-trimethoxyphenyl > 2',4'-dimethoxyphenyl > 2',4'5'-trimethoxyphenyl > 2',5'-dimethoxyphenyl > 2'-methoxyphenyl.*

Introduction

In the last few years we have studied the effect of substitution, both electrophilic and nucleophilic, in the phenyl ring of $PhC(SH)=CHCOCF_3$ (I; R = Ph) on the dipole moment of their metal complexes [1–7]. In the course of these studies we have investigated the effect of substitution at the *para* and *meta* positions of the phenyl ring. The nucleophilic substituents (methoxy and methyl) at the *para* and *meta* positions of the phenyl ring increase the dipole moments of the metal complexes, the group at the *para* position increasing the value to a greater extent than the group at the *meta* position. The electrophilic substituents (chloro and bromo) in the phenyl ring decrease the values of the dipole moments of the metal complexes, the group at the *para* position decreasing the value by a greater amount than the group at the *meta* position.


(I)


(II)

In continuation of our above studies we have now prepared five new β-diketones with methoxy substituents at the *ortho* position of the phenyl ring and their monothio derivatives. The dipole moments of some metal complexes of these monothio-β-diketones are presented in this report.

Experimental

Preparation of the β-Diketones

The β-diketones(II) with R as 2'-methoxyphenyl, 2',4'-dimethoxyphenyl, 2',5'-dimethoxyphenyl and 2',3',4'-trimethoxyphenyl were prepared by the general method described previously [6]. In the preparation of the β-diketone with R as 2',4',5'-trimethoxyphenyl the step involving its isolation as the copper(II) complex was omitted. Instead, after acidification with $KHSO_4$ solution, the mixture was heated on a water bath to remove the ether and the solid β-diketone was recrystallized from absolute alcohol.

1,1,1-Trifluoro-4- (2'-methoxyphenyl) butane-2,4-dione [II; $R = 2'\text{-}CH_3OC_6H_4$], m.p. 43 °C (*Anal.* Found: C, 53.32; H, 3.61%. $C_{11}H_9F_3O_3$ requires C, 53.65; H, 3.68%).

1,1,1-Trifluoro-4- (2',4'-dimethoxyphenyl) butane-2,4-dione [II; $R = 2',4'\text{-}(CH_3O)_2C_6H_3$], m.p. 93 °C (*Anal.* Found: C, 51.86; H, 3.83%. $C_{12}H_{11}F_3O_4$ requires C, 52.18; H, 4.01%).

1,1,1-Trifluoro-4- (2',5'-dimethoxyphenyl) butane-2,4-dione [II; $R = 2',5'\text{-}(CH_3O)_2C_6H_3$], m.p. 68 °C (*Anal.* Found: C, 52.23; H, 3.83%. $C_{12}H_{11}F_3O_4$ requires C, 52.18; H, 4.01%).

1,1,1-Trifluoro-4- (2',3',4'-trimethoxyphenyl)butane-2,4-dione [II; $R = 2',3',4'\text{-}(CH_3O)_3C_6H_2$], m.p. 64 °C (*Anal.* Found: C, 50.59; H, 4.14%. $C_{13}H_{13}F_3O_5$ requires C, 50.98; H, 4.28%).

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1,1,1-Trifluoro-4- (2′,4′,5′-Trimethoxyphenyl)-butane -2,4-dione [II; R = 2′,4′,5′-$(CH_3O)_3C_6H_2$], m.p. 138 °C (*Anal.* Found: C, 50.96; H, 4.32%. $C_{13}H_{13}F_3O_5$ requires C, 50.98; H, 4.28%).

The molecular weights of these β-diketones were determined by EI mass spectrometry.

Preparation of the Monothio-β-diketones

The monothio-β-diketones(I) with R = 2′-methoxyphenyl, 2′,4′-dimethoxyphenyl, 2′,5′-dimethoxyphenyl and 2′,3′,4′-trimethoxyphenyl are liquids and were prepared by the general method described previously [6]. The compounds were not purified via the lead complex. The impure ligands were used for the preparation of metal complexes.

For the preparation of 1,1,1-trifluoro-4-mercapto-4-(2′,4′,5′-trimethoxyphenyl)but-3-en-2-one [I; R = 2′,4′,5′-$(CH_3O)_3C_6H_2$] a solution of 1.5 g β-diketone in 350 ml absolute ethyl alcohol was used [6]. The monthio-β-diketone was extracted with 200 ml petroleum ether (40–60 °C). The extracts of four batches were combined, dried and evaporated to 50 ml. The hot solution was filtered and cooled in ice for 30 min. The shiny red crystalline solid was filtered and dried. It melted at 66 °C (*Anal.* Found: C, 48.52; H, 4.04; S, 9.9%. $C_{13}H_{13}F_3O_4S$ requires C, 48.43; H, 4.06; S, 9.95%). The molecular weight of the monothio-β-diketone was determined by mass spectrometry. The presence of RCS in the EI mass spectrum indicated the position of the sulphur atom in the ligand.

Preparation of the Complexes

Metal complexes were prepared by the general methods reported earlier [4, 6]. The analytical data for the complexes are shown in Table I.

Analyses

Carbon and hydrogen were determined by the Microanalytical Laboratory, School of Chemistry, The University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne. Platinum was determined by ignition of the complex and cobalt as $CoSO_4$. The other metals were determined by gravimetric procedures after the complex had been decomposed by a mixture of Conc. H_2SO_4 and HNO_3 (nickel and palladium by dimethylglyoxime, and copper as $Cu(en)_2HgI_4$. Molecular weights were determined in benzene solutions with a Mechrolab vapour pressure osmometer model 301A.

Determination of the Dipole Moments

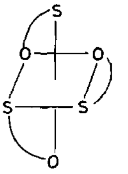
Dielectric constants were measured at 25 °C with a WTW Dipolemeter Type DM 01 with DFL-1 cell. Refractive indices were obtained at 25 °C with an Abbe 60 Refractometer. The detailed procedure of the calculation of the dipole moments was described in our earlier reports [6, 8].

Results and Discussion

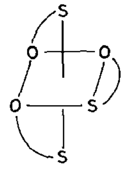
Dipole moments of the metal complexes determined from the static-polarization measurements are shown in Table II. The values of some related compounds are also shown in the table for the purpose of comparison. Metal chelates generally have an appreciable value for the atomic polarization due to vibration of the chelate ring with respect to the rest of the molecule and increases with the increasing number of chelate rings [9, 10]. Its effects on dipole moments of the metal chelates are less than 0.5 D for bischelates and 1.0 D for trischelates [1, 3]. Dipole moments determined by the static-polarization method include the contribution of atomic polarization and no corrections were applied to the values shown in Table II.

Oligomerization is common with metal chelates of β-diketones, both in solid and solution [11], but when one oxygen of the β-diketone is replaced by a sulphur atom the metal chelates become monomeric as evident from the molecular weight determinations in their benzene solutions (Table I).

The monothio-β-diketones are unsymmetrical bidentate ligands. They can form either *cis* or *trans* isomers in square planar and *facial* or *meridional* geometry in octahedral complexes.



Facial



Meridional

The appreciable values of the dipole moments indicate *cis*-square-planar configurations for the complexes of nickel(II), palladium(II) and platinum(II). For a given ligand the values increase in the order: Ni < Pd < Pt, although the variation is within 0.6 D. This is the order of increasing *b* class character for these metals [12]. Preferential formation of *cis* structures in the transition metal complexes of sulphur containing ligands is probably due to d_π–d_π bonding between the metal and sulphur atoms [13]. The electron filled *d* orbitals of the transition metal act as a donor and the vacant *d* orbitals of sulphur atoms act as an acceptor. For such bonding the sulphur–metal–sulphur angle must be about 90 °C, resulting in *cis* structures for these complexes. An alternate explanation for the *cis* structure is that it may be due to a weak nonbonded S···S interaction [14]. The *cis* configuration of the platinum(II) complexes also could be attributed to the *trans* effect of the sulphur atom. X-ray structure determinations have confirmed the *cis* configuration for some nickel(II) [14–16], palladium(II) [17] and platinum(II)

TABLE I. Analytical and Molecular Weight Data of the Complexes of $RC(SH)=CHCOCF_3$.

R	Compound	% Found				% Calcd				Molecular Weight	
		C	H	S	Metal	C	H	S	Metal	Found	Calcd
2′-Methoxyphenyl	NiL_2	45.11	2.78	11.2	9.97	45.45	2.77	11.03	10.11	600	581
	PdL_2	41.53	2.35	9.9	16.91	42.01	2.56	10.20	16.92		
	PtL_2	36.64	2.28		26.97	36.82	2.25		27.19		
	CuL_2	45.00	2.83	11.2	11.01	45.08	2.75	10.94	10.84		
	ZnL_2	45.02	2.96	11.0		44.95	2.74	10.91		620	588
	CoL_3	46.89	2.92	11.7	7.07	47.04	2.87	11.41	6.99		
2′,4′-Dimethoxyphenyl	NiL_2*	44.71	3.21	10.1	9.20	44.96	3.14	10.00	9.15		
	PdL_2	41.40	2.83	9.5	15.21	41.85	2.93	9.31	15.45	656	689
	PtL_2	37.02	2.80		24.56	37.09	2.59		25.10	731	777
	CuL_2	44.64	3.12	9.8	10.04	44.63	3.12	9.92	9.84		
	ZnL_2	44.30	2.97	10.0		44.49	3.11	9.90		700	648
	CoL_3	46.13	3.20	9.9	6.07	46.34	3.24	10.31	6.32		
2′,5′-Dimethoxyphenyl	NiL_2	45.16	3.26	9.8	9.14	44.96	3.14	10.00	9.15	620	641
	PdL_2	42.05	3.20	9.0	14.98	41.85	2.93	9.31	15.45		
	CuL_2	44.68	3.22	9.6	9.71	44.63	3.12	9.92	9.84	605	646
	ZnL_2	44.93	3.36	9.7		44.49	3.11	9.90			
	CoL_3	46.25	3.22	10.4	6.34	46.34	3.24	10.31	6.32		
2′,3′,4′-Trimethoxyphenyl	NiL_2	44.63	3.50	9.2	8.40	44.53	3.45	9.14	8.37		
	PdL_2	41.76	3.13	8.5	14.11	41.70	3.23	8.56	14.21		
	PtL_2	37.24	3.06		22.56	37.29	2.89		23.28		
	CuL_2	44.78	3.64	9.1	8.95	44.23	3.43	9.08	9.00	760	706
	ZnL_2	43.98	3.42	9.1		44.12	3.42	9.06			
	CoL_3	45.58	3.51	10.0	5.79	45.79	3.55	9.40	5.73	1000	1022
2′,4′,5′-Trimethoxyphenyl	NiL_2	44.71	3.54	9.1	8.40	44.53	3.45	9.14	8.37		
	PdL_2	41.78	3.04	8.6	14.14	41.70	3.23	8.56	14.21		
	PtL_2	37.21	2.99		22.80	37.29	2.89		23.28		
	CuL_2	44.21	3.70	9.3	8.89	44.23	3.43	9.08	9.00		
	CoL_3	45.67	3.79	9.6	5.87	45.79	3.55	9.40	5.73		

*Compound was dried at 90 °C for 1½ hours to get the anhydrous product.

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$_3$
2'-Methoxyphenyl	5.64	5.95	6.15	4.82	3.70	6.75
2',4'-Dimethoxyphenyl	6.89	7.32	7.45	6.22	4.78	8.44
2',5'-Dimethoxyphenyl	5.90	6.20	*	5.24	3.93	7.10
2',3',4'-Trimethoxyphenyl	7.41	7.57	7.78	6.83	5.21	8.97
2',4',5'-Trimethoxyphenyl	6.00	6.30	6.46	5.50	*	7.14
Phenyl	4.92[a]	5.02[a]	5.35[a]	4.39[a]	3.06[b]	6.54[a]
4'-Methoxyphenyl	6.70[c]	7.16[c]	6.73[c]	6.02[c]	4.80[c]	8.57[c]
3'-Methoxyphenyl	5.43[c]	5.88[c]	5.64[c]	4.91[c]	3.94[c]	6.91[c]
3',4'-Dimethoxyphenyl	5.62[c]	6.45[c]	6.07[c]	5.24[c]	3.96[c]	6.89[c]
3',5'-Dimethoxyphenyl	5.87[d]	5.96[d]		5.50[d]	4.13[d]	7.08[d]
3',4',5'-Trimethoxyphenyl	4.32[d]	4.48[d]		3.98[d]	3.38[d]	5.15[d]

*Compound could not be isolated. [a]Data from ref. 1. [b]Data from ref. 3. [c]Data from ref. 4. [d]Data from ref. 6.

[17] complexes of monothio-β-diketones. Such *cis* structures were also found in the nickel(II) complexes of some sulphur containing bidentate Schiff bases [18].

The dipole moments of the copper(II) complexes are about 0.75–1.09 D lower than the mean value for the nickel(II), palladium(II) and platinum(II) complexes of the same ligand. This difference is not due to the presence of *cis–trans* equilibrium in solution as no significant variation of the dipole moment with temperature was observed (Table III). No information is available about the crystal structure of bis(monothio-β-diketonato)copper(II) compounds. A planar centrosymmetric and dimeric structure for the bis(monothio-β-diketonato)copper(II) compounds was suggested by Toy *et al.* from the esr studies of the compounds in a series of frozen solvents [19]. The presence of appreciable dipole moment and the existence of monomeric species in benzene solution do not agree with their structure. These lower values of the dipole moment of copper(II) complexes may be due to distortion from a *cis*-square-planar towards a tetrahedral configuration, since data obtained for the corresponding zinc(II) complexes, which are known to be tetrahedral [20], show further lower values.

TABLE III. Effect of Temperature on the Dipole Moments of Copper(II) Complexes of RC(SH)=CHCOCF$_3$.

R	10°	25°	40 °C
2',5'-Dimethoxyphenyl	5.18	5.24	5.40
2',4',5'-Trimethoxyphenyl	5.43	5.50	5.45
2',4'-Dimethoxyphenyl	6.43	6.22	6.26

TABLE IV. ^{1}H and ^{19}F NMR Chemical Shift* Data of Co(RCSCHCOCF$_3$)$_3$.

R	Methine proton chemical shift δ (p.p.m.)	Fluorine chemical shift δ (p.p.m.)
2'-Methoxyphenyl	6.98	−74.65
2',4'-Dimethoxyphenyl	7.01	−74.51
2',5'-Dimethoxyphenyl	6.99	−74.66
2',3',4'-Trimethoxyphenyl	7.01	−74.62
2',4',5'-Trimethoxyphenyl	7.08	−74.53

*Proton and fluorine shifts are relative to an internal reference of TMS and external reference of CFCl$_3$, respectively. ^{1}H and ^{19}F NMR were recorded in CDCl$_3$, and were taken with JEOL-FX-100-S and Varian EM-360 60 MHz spectrometers, respectively.

The *facial* octahedral CoL$_3$ should have higher dipole moment than the *meridional* octahedral one. But it is not possible from the dipole moment alone to deduce their structure. The ^{1}H and ^{19}F NMR studies of these complexes were carried out in order to distinguish between *facial* and *meridional* structures. Since the ligands are unsymmetrical the *facial* octahedral configuration should give only one ^{19}F resonance for the three equivalent CF$_3$ groups. In the *meridional* octahedral structure the three non-equivalent CF$_3$ groups should give three ^{19}F resonances. Only one ^{19}F resonance was observed with the present CoL$_3$ complexes and thus confirms their *facial* structures (Table IV). Similarly, the single ^{1}H resonance for the methine proton also confirms their *facial* structures. Such *facial* structures of other tris(monothio-β-diketonato)cobalt(III) were reported from ^{13}C and ^{19}F NMR studies [21–23]. ^{1}H NMR data were used to determine the *facial* octahedral structure of M(S-O)$_3$ complexes where M = Co(III) and Sb(III) [24, 25]. X-ray studies of trischelates of cobalt(III) [26] and iron(III) [27] of some monothio-β-diketones confirmed their *facial* structures. It is interesting to note that three sulphur atoms are at right angles to the metal in the *facial* structure and thus in the correct position for d_π–d_π bonding.

The values of dipole moment of the complexes of a given metal ion depends on R and decreases in the order: 2',3',4'-trimethoxyphenyl > 2',4'-dimethoxyphenyl > 2′,4′,5′-trimethoxyphenyl > 2′,5′-dimethoxyphenyl > 2′-methoxyphenyl. The change in the dipole moments arises mainly from the induction and mesomeric effects of the substituents as discussed in our earlier report [2]. These effects depend on the position of the substituents. 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 when two methoxy groups are in vicinal positions and prevent free rotation of the methoxy groups as in 2′,3′,4′-$(CH_3O)_3C_6H_2$ and 2′,4′,5′-$(CH_3O)_3C_6H_2$.

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