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Dipole Moments of Copper(II) Chelates of Some Fluorinated β-Diketones

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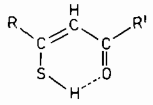
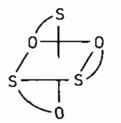
Dipole moments have been determined by static polarization measurements for the copper(II) chelates of the fluorinated β-diketones $RCOCH_2COCF_3$ (R = 2-thienyl, Ph, p-MeC_6H_4, p-ClC_6H_4, m-ClC_6H_4, p-BrC_6H_4, and m-BrC_6H_4). The moments, which range from 2.47 to 4.82D, indicate a cis-square-planar structure for the copper chelates. The variation of the dipole moments with R is considered to be dependent on (a) the Ph–X bond moment, (b) the inductive effect of the meta- and para-substituent X, and (c) the mesomeric effect of X (X = Cl, Br, Me).

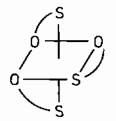
Introduction

We have made an extensive study of the dipole moments of the nickel(II), palladium(II), platinum(II), copper(II), iron(III), and cobalt(III) chelates of a wide range of monothio-β-diketones (I).[1,2,3]


(I)

The values of the dipole moments indicate a *cis*-square-planar configuration for the nickel, palladium, platinum, and copper complexes. X-ray structure determinations have confirmed the *cis*-square-planar configuration for the palladium and platinum complexes of (I) where R = R′ = Ph[4] and for the nickel complexes of (I) where R = H, R′ = *p*-Br C_6H_4[5]; R = Pr^i, R′ = Me;[6] and R = Me, R′ = CF_3.[7] The dipole moments of the iron(III) and cobalt(III) chelates range from 3.27 to 7.36D (1 Debye = 3.336 × 10^{-30} Cm), suggesting a *facial* structure (II), with the three sulphur atoms mutually *cis*, rather than a *meridional* structure (III) for these octahedral complexes.[2,3]


(II) facial


(III) meridional

The *facial* configuration has been established for the iron(III) complex of (I) where R = Ph and R′ = CF_3 by an X-ray structural determination.[8]

For all the metal chelates of monothio-β-diketones having R′ = CF_3 it has been found that the values of the dipole moments decrease if the R groups are arranged in the order:

p-MeC_6H_4 > 2-thienyl (C_4H_3S) > m-MeC_6H_4 > Ph > m-ClC_6H_4 ≧ m-BrC_6H_4 > p-FC_6H_4 ≧ p-ClC_6H_4 ≧ p-BrC_6H_4 > m,p-$Cl_2C_6H_3$

The variation in the values of the dipole moments with change in the R group depend on: (*a*) the magnitude and vector directions of the Ph–X moments (X = F, Cl, Br, Me); (*b*) the inductive effect of the *meta-* and *para*-substituent X on the phenyl ring; and (*c*) the mesomeric effect of substituent X.[3]

Whereas metal chelates of monothio-β-diketones are usually quite soluble in non-polar solvents, the metal chelates of β-diketones mostly have low solubilities in solvents such as benzene and consequently their dipole moments cannot be measured. However, the copper(II) chelates of the fluorinated β-diketones $RCOCH_2COCF_3$ (R = C_4H_3S, Ph, p-MeC_6H_4, m-MeC_6H_4, p-ClC_6H_4, m-ClC_6H_4, p-BrC_6H_4, and m-BrC_6H_4) are moderately soluble in benzene and we have determined their dipole moments in order to obtain information about their configurations.

Experimental

Preparation of the β-Diketones

Thenoyltrifluoroacetone was obtained from Aldrich Chemical Company, Milwaukee. The other β-diketones were prepared by Claisen condensation of the substituted acetophenone and ethyl trifluoroacetate by the general method previously described for the preparation of fluorinated β-dikctoncs.[9,10]

1,1,1-Trifluoro-4-phenylbutane-2,4-dione, m.p. 40° C (Found: C, 55.9; H, 3.6. Calc. for $C_{10}H_7F_3O_2$: C, 55,5; H, 3,3%).

1,1,1-Trifluoro-4-(4′-methylphenyl)butane-2,4-dione, m.p. 42° C (Found: C, 57.7; H, 3.9. Calc. for $C_{11}H_9F_3O_2$: C, 57.4; H, 3.9%).

1,1,1-Trifluoro-4-(3′-methylphenyl)butane-2,4-dione, b.p. 244° C/760 mm (Found: C, 57.75; H, 4.1. Calc. for $C_{11}H_9F_3O_2$: C, 57.4; H, 3.9%).

4-(4′-Chlorophenyl)-1,1,1-trifluorobutane-2,4-dione, m.p. 61° C (Found: C, 48.3; H, 2.4; Cl, 14.1. Calc. for $C_{10}H_6ClF_3O_2$; C, 47.9; H, 2.4; Cl, 14.1%).

4-(3'-Chlorophenyl)-1,1,1-trifluorobutane-2,4-dione, m.p. 39° C (Found: C, 48.2; H, 2.4; Cl, 14.5. Calc. for $C_{10}H_6ClF_3O_2$; C, 47.9; H, 2.4; Cl, 14.1%).

4-(4'-Bromophenyl)-1,1,1-trifluorobutane-2,4-dione, m.p. 56° C (Found: C, 40.6; H, 2.2. Calc. for $C_{10}H_6BrF_3O_2$: C, 40.7; H, 2.0%).

4-(3'-Bromophenyl)-1,1,1-trifluorobutane-2,4-dione, m.p. 39° C (Found: C, 40.8; H 2,2; Br, 26.9. Calc. for $C_{10}H_6BrF_3O_2$: C, 40.7; H, 2.1; Br, 27.1%).

Preparation of the Copper Chelates

A filtered solution of copper(II) acetate monohydrate (1 g; 5 mmol) in hot alcohol (70 ml) was added to a solution of the β-diketone (10 mmol) in alcohol (30 ml). The mixture was cooled and allowed to stand at 0° C for 2 hr. The resulting green crystals of the copper complex were filtered off, washed with a small quantity of ice-cold alcohol, and dried *in vacuo;* yield, 50–80%. The analytical data are listed in Table I.

Determination of Dipole Moments

The dipole moments were determined from static polarization measurements.[11, 12] The dielectric constant measurements were made on a Wissenschaftlich-Technische Werkstätten 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 solution were made by means of a filling device in an inert atmosphere, obtained by flushing of the cell with dry nitrogen.

Measurements were made at several different concentrations of the metal chelate in benzene. The dielectric constant ε and the refractive index n were measured for the solvent and the solution. Concentrations are expressed as weight fractions w_2.

The determining equation has the form:

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

where μ is the dipole moment; k is the Boltzmann constant; N is the Avagadro number; d is the density of the solvent; a_ε and a_n are the slopes of $\Delta\varepsilon$ and $\Delta(n^2)$, respectively, when plotted as the ordinate against w_2 as the abscissa; and M_2 is the molecular weight of the solute.

Analar grade benzene was purified by partial freezing (twice), followed by drying by means of passage through a chromatographic column packed with BDH 4A molecular sieves (1.5 mm 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 and the density d are 2.2725 and 0.87378, respectively.[12]

The refractive index measurements were obtained with an Abbe 60 refractometer with white light.

The reproducibility of the values for the dipole moments is ± 0.1D.

Molecular Weight Determinations

Molecular weights were determined in benzene solution at 25° C with a Mechrolab vapour pressure osmometer model 301A.

Analyses

Carbon and hydrogen were determined by Dr. E. Challen of the Microanalytical Laboratory, School of Chemistry, University of New South Wales. Chlorine, bromine, and sulphur were determined by the Australian Microanalytical Service, Melbourne. Copper was determined as $[Cu(en)_2]HgI_4$ after decomposition of the complex with a mixture of sulphuric and nitric acids.

Results and Discussion

Dipole moments were determined by static polarization measurements for the copper(II) complexes of eight fluorinated β-diketones. The dipole moments are listed in Table II. The data for incremental dielectric constants and refractive indices are given in Table III.

TABLE I. Analytical Data for Copper Complexes $Cu(RCO{=}CHCOCF_3)_2$.

R	C		H		Cu		Other	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found (%)
Ph	48.6	48.4	2.5	2.7				
C_4H_3S	38.0	37.8	1.6	1.7	12.6	12.5	12.7[a]	12.5
p-MeC_6H_4	50.6	50.5	3.1	3.2	12.2	12.2		
m-MeC_6H_4	50.6	51.2	3.1	3.2	12.2	12.2		
p-ClC_6H_4	42.7	42.7	1.8	1.9	11.3	11.1	12.6[b]	12.8
m-ClC_6H_4	42.7	42.9	1.8	1.8	11.3	11.3	12.6[b]	12.6
p-BrC_6H_4	36.9	36.8	1.6	1.8	9.8	9.7	24.5[c]	24.3
m-BrC_6H_4	36.9	37.3	1.6	1.7	9.8	9.8	24.5[c]	24.2

[a] Sulphur analysis. [b] Chlorine analysis. [c] Bromine analysis.

TABLE II. Dipole Moments of Copper Complexes of Fluorinated β-Diketones Cu(RCO=CHCOCF$_3$)$_2$.

R	μ(D)
C$_4$H$_3$S	4.82
p-MeC$_6$H$_4$	4.54
m-MeC$_6$H$_4$	4.30
Ph	4.01
m-ClC$_6$H$_4$	3.74
m-BrC$_6$H$_4$	3.72
p-ClC$_6$H$_4$	2.80
p-BrC$_6$H$_4$	2.47

Oligomerization is known to occur in solution with some metal complexes of β-diketones.[13] Consequently, molecular weights were determined for four of the copper complexes used in this study. The results, which are listed in Table IV, show that the complexes are monomeric in benzene solution.

In a previous study[2] of square-planar metal monothio-β-diketonates, M(RCS=CHCOCF$_3$)$_2$ (M = Ni, Pd, Pt, Cu), we found that the values for the dipole moments obtained from static polarization measurements were 0.14–0.82D greater than the values obtained from dielectric relaxation measurements. The difference in values – in most instances <0.4D – was attributed to the contribution made by atomic polarization, since the dielectric relaxation method gives a value for the dipole moment which does not include a component arising from atomic polarization.

After allowance has been made for atomic polarization, which is probably less than 0.5D, the values of the dipole moments of the copper chelates of the fluorinated β-diketones (see Table II) are quite appreciable, *viz.* from 2.0 to 4.3D. These values are much too high for a *trans*-square-planar configuration, which would have a moment close to zero, and indicate a *cis*-square-planar configuration. The values are comparable with those obtained by the static polarization method (without a correction for atomic polarization) for the dipole moments of the copper(II) chelates of the corresponding monothio-β-diketones, *viz.* when R = C$_4$H$_3$S, μ, 4.96D; R = p-MeC$_6$H$_4$, μ, 5.12D; R = Ph, μ, 4.39D; R = p-BrC$_6$H$_4$, μ, 2.45D.[3] The slightly higher values obtained for the monothio-β-diketone complexes can be attributed to the greater electronegativity of oxygen compared to sulphur, since in the monothio-β-diketone complexes the sulphur atom is attached to the 4-Carbon atom of the ligand, *i.e.* on the side of the square-plane farthest from the electron-withdrawing CF$_3$ group; consequently, the metal–oxygen and CF$_3$ moments reinforce each other.

The dipole moments of two copper chelates were determined at three different temperatures (see Table V). No significant variation of the dipole moment

TABLE III. Data on Incremental Dielectric Constants and Refractive Indices for Solutions of Copper Chelates Cu(RCO=CHCOCF$_3$)$_2$ in Benzene at 25° C.

R						
Ph	$10^5 w_2$	450	367	271	187	93
	$10^4 \Delta\varepsilon$	172	140	102	72	36
	$10^4 \Delta(n^2)$	15	11.5	8.5	5.5	2
C$_4$H$_3$S	$10^5 w_2$	457	369	277	184	93
	$10^4 \Delta\varepsilon$	255	207	153	103	54
	$10^4 \Delta(n^2)$	–	–	17	11	5.5
p-MeC$_6$H$_4$	$10^5 w_2$	459	365	276	180	89
	$10^4 \Delta\varepsilon$	214	171	129	83	46
	$10^4 \Delta(n^2)$	–	12	9	6	3
m-MeC$_6$H$_4$	$10^5 w_2$	–	365	273	181	92
	$10^4 \Delta\varepsilon$	–	146	110	73	37
	$10^4 \Delta(n^2)$	–	6	–	3	–
p-ClC$_6$H$_4$	$10^5 w_2$	451	358	273	180	91
	$10^4 \Delta\varepsilon$	83	66	50	34	17
	$10^4 \Delta(n^2)$	–	12	–	6	–
m-ClC$_6$H$_4$	$10^5 w_2$	–	363	273	182	88
	$10^4 \Delta\varepsilon$	–	109	81	54	27
	$10^4 \Delta(n^2)$	–	12	9	6	3
p-BrC$_6$H$_4$	$10^5 w_2$	456	366	278	183	95
	$10^4 \Delta\varepsilon$	57	46	34	23	12
	$10^4 \Delta(n^2)$	–	6	–	3	–
m-BrC$_6$H$_4$	$10^5 w_2$	–	367	273	181	91
	$10^4 \Delta\varepsilon$	–	93	69	46	23
	$10^4 \Delta(n^2)$	–	12	9	6	3

TABLE IV. Molecular Weights of Copper Complexes $Cu(RCO{=}CHCOCF_3)_2$ in Benzene.

R	*M* (obs)	*M* (theor)
C_4H_3S	468	506
Ph	484	494
p-MeC_6H_4	501	521
p-BrC_6H_4	663	652

TABLE V. Effect of Temperature on Dipole Moments of Copper Complexes $Cu(RCO{=}CHCOCF_3)_2$.

R		μ (D)	
	10°	25°	40° C
C_4H_3S	4.85	4.82	5.17
p-MeC_6H_4	4.59	4.54	4.66

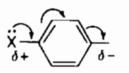
with temperature was observed. This suggests the absence of a *cis–trans* equilibrium in solution or, if there is an equilibrium, it has a very small enthalpy associated with it. A similar lack of temperature dependence of the dipole moment has been found for *cis*-$Cu(MeCS{=}CHCOPh)_2$[2] and *cis*-$SnCl_2(MeCO{=}CHCOMe)_2$.[14]

Zinc monothio-β-diketonates, which are tetrahedral, have dipole moments 1.8–2.2D lower than their nickel analogues, which are *cis*-square-planar.[15] On the other hand, the moments of the copper complexes are *ca.* 0.6D lower than their nickel analogues. This difference has been attributed to a significant distortion of the copper complexes from *cis*-square-planar towards the tetrahedral configuration.[2] From the data it is not possible to state that the copper complexes of the fluorinated-β-diketones investigated in this study are similarly distorted towards the tetrahedral configuration. Hence, they can be regarded as essentially *cis*-square-planar.

The dipole moments of the copper complexes of the fluorinated β-diketones decrease if the R groups are arranged in the order:

$$C_4H_3S > p\text{-}MeC_6H_4 > m\text{-}MeC_6H_4 > Ph > m\text{-}ClC_6H_4 > m\text{-}BrC_6H_4 > p\text{-}ClC_6H_4 > p\text{-}BrC_6H_4.$$

Except for the relative positions of C_4H_3S and *p*-MeC_6H_4 this is the order observed for the nickel(II), palladium(II), and platinum(II) complexes of the corresponding fluorinated monothio-β-diketones. This order has been explained for a *cis*-square-planar configuration in terms of (*a*) the magnitude and vector directions of the Ph–X bond moment, (*b*) the inductive effect of the *meta*- and *para*-substituent X on the phenyl ring, and (*c*) the mesomeric effect (IV) of the substituent X (X = Cl, Br, Me).[3]



(IV)

mesomeric effect of X

It has been suggested that the *cis* configuration, adopted by the nickel, palladium, platinum, and copper chelates of monothio-β-diketones, is favoured because the metal ion can form d_π–d_π bonds with sulphur but not with oxygen and that this metal–sulphur π-bonding is only possible if the SMS angle is approximately 90° C, *i.e.* if the two ligands are *cis.*[2] On the basis of infrared evidence metal–sulphur π-bonding has been postulated to occur in the monothio-β-diketone complexes $NEt_4[M(CO)_4(C_4H_3SCS{=}CHCOCF_3)]$ (M = Cr, Mo, W).[16] The occurrence of a *cis* configuration in the copper complexes of the fluorinated β-diketones suggests that π-bonding may be present in these complexes also. Oxygen, unlike sulphur, cannot normally form π-bonds. However, because of the highly conjugated nature of the metal-chelate ring, especially when there are aromatic substituents on the 4-carbon atom, π-bonding may indeed occur thus accounting for the preference for the *cis* configuration.

References

1 L. P. Eddy, J. W. Hayes, S. E. Livingstone, H. L. Nigam, and D. V. Radford, *Austral. J. Chem., 24,* 1071 (1971).

2 M. Das, S. E. Livingstone, S. W. Filipczuk, J. W. Hayes, and D. V. Radford, *J. Chem. Soc. Dalton Transactions,* 1409 (1974).

3 M. Das and S. E. Livingstone, *J. Chem. Soc. Dalton Transactions,* in press.

4 E. A. Shugam, L. M. Shkol'nikova, and S. E. Livingstone, *Zhur. strukt. Khim., 8,* 550 (1967).

5 L. Kutschabsky and L. Beyer, *Z. Chem. 11,* 30 (1971).

6 J. Sieler, P. Thomas, E. Uhlemann, and E. Höhne, *Z. anorg. allgem. Chem., 380,* 160 (1971).

7 D. C. Craig, M. Das, S. E. Livingstone, and N. C. Stephenson *Cryst. Struct. Commun., 3,* 283 (1974).

8 B. F. Hoskins and C. D. Pannan, personal communication.

9 R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem., 21,* 1781 (1968).

10 M. Das and S. E. Livingstone, *Austral. J. Chem., 27,* 1177 (1974).

11 G. J. Moody and J. D. R. Thomas, *"Dipole Moments in Inorganic Chemistry",* Arnold, London, 1971.

12 R. J. W. Le Fevre, *"Dipole Moments",* Methuen, London, 1953.

13 D. P. Graddon, *Coordination Chem. Rev. 4,* 1 (1969).

14 V. Doron and C. Fischer, *Inorg. Chem., 6,* 1917 (1967).

15 S. W. Filipczuk, J. W. Hayes, D. V. Radford, M. Das, and S. E. Livingstone, *J. Chem. Soc. Dalton Transactions,* in press.

16 G. H. Barnett and M. K. Cooper, *Inorg. Chim. Acta, 7,* 613 (1973).