Dipole-moment Measurements on Metal Chelate Complexes. Part III.† Dipole-moment and Dielectric-relaxation Measurements on some Tetrahedral Zinc(II) Complexes of Seven Mercapto-β-diketones

By **Stephen W. Filipczuk, John W. Hayes,*** and **Donald V. Radford**, School of Chemistry, University of Sydney, N.S.W. 2006, Australia
Manoranjan Das and **Stanley E. Livingstone**, School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033, Australia

Dipole moments and relaxation times have been determined for tetrahedral zinc(II) complexes of the mercapto-β-diketones RC(SH):CH·C(O)R′ [R = Me or Ph, R′ = Ph; R = Me, C_4H_3S (2-thienyl), Ph, *p*-MeC_6H_4, or *p*-BrC_6H_4, R′ = CF_3] from both static-polarization and dielectric-relaxation measurements. Group dipole moments for the R substituents have been derived and found to agree with the corresponding values for a series of square-planar complexes studied earlier. Group dipole moments for the metal–chelate rings have been calculated by comparison of results obtained for the square-planar and tetrahedral complexes. The magnitude and direction of these ring moments are dependent on the presence of a CF_3 group as R′ substituent.

In a previous paper [1] we reported dipole-moment and dielectric studies on iron(III), cobalt(III), nickel(II), palladium(II), platinum(II), and copper(II) complexes of the mercapto-β-diketones RC(SH):CH·C(O)R′ [R = Me or Ph, R′ = Ph; R = Me, C_4H_3S (2-thienyl), Ph, *p*-MeC_6H_4, or *p*-BrC_6H_4, R′ = CF_3]. Group dipole moments for all of the R substituents (except 2-thienyl) were obtained but no group dipole moment for the metal–chelate ring could be calculated.

In this work we have undertaken similar studies on tetrahedral zinc(II) complexes with the same ligands in the hope that further information on the metal–chelate ring group moment may be obtained.

EXPERIMENTAL

Preparations.—The mercapto-β-diketones were prepared as previously described.[2-4]

The zinc(II) *complexes.* Zinc(II) acetate dihydrate (1·44 g, 4·5 mmol) in hot alcohol (80 cm^3) was added to a solution of the mercapto-β-diketone (9 mmol) in alcohol (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 yellow *crystals* of the zinc complex, yield 20—30%. When R = Me or Ph and R′ = CF_3, addition of water did not precipitate the complex. In these cases the complex was extracted from the mixture with ligroin. The extract, after being dried over anhydrous sodium sulphate, was concentrated to small bulk (30—40 cm^3), which, on cooling, gave yellow *crystals* of the zinc complex, yield 60—70%.

Analyses and Molecular-weight Determinations.—These were carried out as described previously.[1] All analyses, which were within 1% of the calculated values, and molecular-weight determinations on three of the compounds are listed in Supplementary Publication No. SUP 21299 (7 pp.).‡ The *M* values indicate that these complexes are monomeric in benzene solution and it is assumed that this holds for the other four complexes. Benzene (AnalaR) was purified as described previously; [1] at 25 °C the dielectric constant, ε, density, *d*, and refractive index, *n*, for sodium light are 2·2725, 0·87378 g cm^{-3}, and 1·4973 respectively.[5]

Determination of Dipole Moments.—Dipole moments were determined by both static-polarization and dielectric-relaxation measurements at frequencies of 1·140, 3·040, and 8·540 GHz by methods described previously.[1] In the follow-

---

† Part II, M. Das and S. E. Livingstone, *J.C.S. Dalton*, 1975, 452.

‡ For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

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

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

[3] R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, 1966, **19**, 1179; 1968, **21**, 103.

[4] R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem.*, 1968, **21**, 1781.

[5] R. J. W. Le Fevre, 'Dipole Moments,' Methuen, London, 1953.

ing discussion μ_s refers to dipole moments determined from static-polarization measurements and μ_d those from the dielectric-relaxation measurements.

RESULTS AND DISCUSSION

Incremental dielectric constants ($\Delta\varepsilon$), refractive indexes (Δn^2), and loss tangents for the solutes (Δ tan δ), together with dielectric constants (ε') and loss factors (ε'') for the solutions for various weight fractions (w_2), are listed in SUP 21299. Values of ψ ($= \Sigma\Delta \tan \delta/\Sigma w_2$) at each frequency, the calculated dipole moments μ_s and μ_d, and the relaxation times, τ, are listed in Table 1. In all cases the results were found to fit a Debye curve within experimental error.

TABLE 1

Values of ψ, dipole moments (μ_s and μ_d), and relaxation times (τ) for the complexes $[Zn\{RCS\dot{:}CH\cdot C(O)R'\}_2]$

R	R′	ψ			μ_s/D	μ_d/D	τ/ps
		a	b	c			
Me	Ph	0·530	0·390	0·174	3·37	3·02	120
Ph	Ph	0·319	0·169	0·082	3·29	2·72	189
Me	CF_3	0·290	0·335	0·182	3·37	2·41	74
C_4H_8S	CF_3	0·533	0·382	0·190	3·57	3·45	120
Ph	CF_3	0·346	0·238	0·068	3·07	2·75	130
p-MeC_6H_4	CF_3	0·471	0·295	0·150	3·65	3·21	145
p-BrC_6H_4	CF_3	0·109	0·062	0·025	2·46	1·77	175

[a] At 1·140 GHz. [b] At 3·040 GHz. [c] At 8·540 GHz.

Relaxation Times.—Since the frequency of maximum absorption lies within the range of the three frequencies used to make dielectric-relaxation measurements, the relaxation times determined from these measurements are well defined.[1,6] The values listed in Table 1 are very similar to those for the square-planar complexes of Pd^{II}, Pt^{II}, Ni^{II}, and Cu^{II} studied previously.[1] This is reasonable when one considers the similarity in the volume swept out by an overall molecular rotation in the two cases.

Dipole Moments.—The observed values of μ_s were larger than those of μ_d as found previously. This difference is attributed to high atomic polarization in these complexes [1] and therefore μ_d is taken as the true value of the dipole moment. This subject will form the basis of a subsequent communication. When R′ = CF_3, values of the dipole moments for the zinc complexes have a smaller range and are smaller in magnitude than those for the corresponding square-planar complexes of platinum(II), palladium(II), and nickel(II). As has been noted previously,[1] dipole moments for the copper(II) complexes have intermediate values, probably indicating a distortion from the square-planar configuration. When R′ = Ph these trends are not observed.

Determination of Metal–Chelate Ring Group Dipole Moments.—Group dipole moments for the metal–chelate rings were deduced from the dipole-moment data by use of the approach outlined below. As in the previous work [1] the molecular dipole moment, μ, is considered to have components which are defined as follows: $\mu_{R\text{-}ch}$ and $\mu_{R'\text{-}ch}$, the group dipole moments attributable to the R and R′ groups respectively; and $\mu_{M\text{-}ch}$, the group dipole moment attributable to the chelate ring less the contributions from the R and R′ groups. Values of $\mu_{R\text{-}ch}$ and $\mu_{R'\text{-}ch}$ for this series of complexes, calculated using the method described before,[1] are listed in Table 2. These values are similar to those obtained for the corresponding square-planar complexes. Table 3 gives values of the components of $\mu_{M\text{-}ch}$ along the C_2 axis for complexes in which R′ = CF_3 and Ph for the zinc complexes studied in this paper and mean values for the square-planar complexes studied in ref. 1.

TABLE 2

Calculated group dipole moments derived from μ_d for the complexes $[Zn\{RCS\dot{:}CH\cdot C(O)R'\}_2]$

R	R′	$\mu_{R\text{-}ch}$/D
Ph	CF_3	0·00
Me	CF_3	0·46
p-MeC_6H_4	CF_3	−0·62
p-BrC_6H_4	CF_3	1·33
Me	Ph	0·41

TABLE 3

Components of $\mu_{M\text{-}ch}$ along the C_2 axis derived from μ_d for zinc(II) and square-planar complexes

	R′ = CF_3	R′ = Ph
Zn	−0·55	1·36
Mean for square-planar complexes (from ref. 1)	0·00	1·11

A positive value indicates a component acting from the metal towards the oxygen atoms, a negative value in the opposite direction.

Crystal-structure data on two model compounds, bis(1-ethoxy-3-mercaptoprop-2-en-1-one)zinc(II) (tetrahedral) [7] and bis(1,1,1-trifluoro-4-mercaptopent-3-en-2-one)nickel(II) (square planar),[8] are available, and it has been assumed that these solid-state dimensions also apply, where relevant, to the solutes investigated in this work. From these data it is found that the sulphur–metal–oxygen bond angles within the chelate rings are approximately equal (99·3 and 96·1°) for the tetrahedral and square-planar molecules respectively. In the following calculations it has been assumed that for a given R′ group the magnitude and direction, relative to the atoms of the chelate ring, of $\mu_{M\text{-}ch}$ in both the tetrahedral and square-planar cases are equal. (From

---

[6] E. N. Di Carlo, E. Watson, C. E. Varga, and W. I. Chamberlain, *J. Phys. Chem.*, 1973, **77**, 1073.

[7] C. D. Pannan and B. F. Hoskins, University of Melbourne, personal communication.

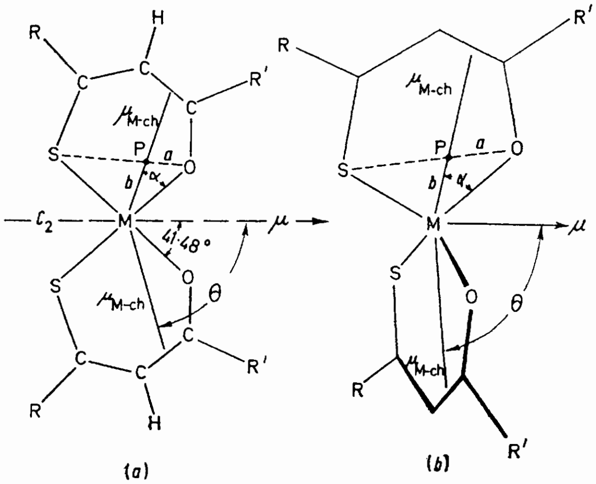
[8] D. C. Craig, M. Das, S. E. Livingstone, and N. C. Stephenson, *Cryst. Struct. Comm.*, 1974, **3**, 283.

previous work [1] it is evident that in these complexes the presence of a CF_3 substituent causes a different electron distribution in the ring compared to that with the other substituents.)

In order to determine $\mu_{M\text{-ch}}$, equations can be set up which relate the molecular dipole moment, less the contributions from the R and R′ groups, to the magnitude and direction of $\mu_{M\text{-ch}}$ for both the tetrahedral and square-planar cases. Since we have assumed that the magnitude of $\mu_{M\text{-ch}}$ is the same in both cases, its value may be obtained by simultaneous solution of the two equations. Figure (*a*) illustrates the square-planar case; μ lies along the molecular C_2 axis and the metal–oxygen bond is inclined at an angle of 41·48° to that axis. The angle between $\mu_{M\text{-ch}}$ and the metal–oxygen bond is α. Thus we obtain equation (1), where μ_{sp}' is the molecular

$$\mu_{sp}' = 2\mu_{M\text{-ch}} \cos(\alpha + 41{\cdot}48°) \qquad (1)$$

dipole moment, less the contributions from the R and R′ groups, for the square-planar case.



Structural models based on data from refs. 8 and 9: (*a*) square-planar complexes; (*b*) tetrahedral complexes

Figure (*b*) illustrates the tetrahedral case. The direction of μ has been taken as collinear with the line passing through the metal atom, M, and a point midway between the oxygen atoms of the two ligands; its direction cosines can be obtained from the crystallographic data.[7] P Is the point of intersection of the line of action of $\mu_{M\text{-ch}}$ and the line joining the sulphur and oxygen atoms in the same ligand. The direction cosines of $\mu_{M\text{-ch}}$ may be expressed in terms of *a* and *b* (again from the crystallographic data [7]) where *a* is the distance between P and the oxygen atom in the same ligand and *b* is the distance between P and M. The cosine of the angle θ, the inclination of $\mu_{M\text{-ch}}$ with respect to μ, is given by the sum of the products of the direction cosines of the two vectors. Although the crystallographic data indicate that the two chelate rings are slightly twisted from the regular tetrahedral configuration, calculation of θ for each of the chelate rings shows a difference of less than 0·5°, well within the experimental error in this work. Thus we obtain equation (2), where μ_{tet}' is the value corresponding to μ_{sp}' in the tetrahedral case.

$$\begin{aligned}\mu_{tet}' &= 2\mu_{M\text{-ch}} \cos\theta \\ &= 2\mu_{M\text{-ch}}(0{\cdot}6639 \cos\alpha - 0{\cdot}3454 \sin\alpha) \qquad (2)\end{aligned}$$

Simultaneous solution of equations (1) and (2) gives $\mu_{M\text{-ch}} = 3{\cdot}27$ D (acting away from the metal) and $\alpha = 28{\cdot}7°$ for complexes in which R′ = Ph, while $\mu_{M\text{-ch}} = 3{\cdot}04$ D (acting towards the metal) and $\alpha = 48{\cdot}5°$ for complexes in which R′ = CF_3.* In view of the electronegativity differences between oxygen and sulphur it is expected that, all other things being equal, $\mu_{M\text{-ch}}$ inclines towards the oxygen atom rather than the sulphur atom. This is indeed the case when R′ = Ph where $\alpha = 28{\cdot}7°$, the mean sulphur–metal–oxygen angle being 97·6°. The direction of action of $\mu_{M\text{-ch}}$ in these complexes, away from the metal, is in accord with a greater electron density on the ligand atoms than that on the metal. When R′ = CF_3, however, the line of action of $\mu_{M\text{-ch}}$ almost bisects the sulphur–metal–oxygen angle (α 48·5°). Apparently the highly electronegative CF_3 group has reduced the electron density in the chelate ring in such a way that the density on the oxygen side of the ring is reduced to give this value of α.†

In view of the likely nature of d_π–d_π bonding between the sulphur and metal atoms (suggested to explain the *cis*-configuration in the square-planar complexes [1]), the electrons on the sulphur atom are expected to be less mobile than those on the oxygen atom. Further the direction of action of $\mu_{M\text{-ch}}$ is towards the metal, the reverse of that when R′ = Ph. It is proposed that this reversal in direction arises from depletion of the electron density on the three carbon atoms of the chelate ring by the CF_3 group, leaving the sulphur and oxygen atoms less deficient in electron density than these ring carbon atoms.

The magnitude of $\mu_{M\text{-ch}}$ is closer to the values proposed by Moore and Nelson [9] for the metal–chelate ring group dipole moments in pentane-2,4-dione, 1,3-diphenylpropane-1,3-dione, and 1,1,1,5,5,5-hexafluoropentane-2,4-dione complexes of thallium, indium, and tin than the earlier estimates which were of the order of 6—9 D.[5,10,11]

We thank J. S. Dryden for use of the C.S.I.R.O. National Measurement Laboratory dielectrometer during the course of this work, and B. F. Hoskins and C. D. Pannan of the University of Melbourne for permission to use unpublished crystal-structure data.

[4/2110 *Received, 14th October*, **1974**]

---

* 1D ≈ 3·336 × 10^{-30} C m.

† A referee kindly pointed out to us that probably a large portion of the moment, when R′ = Ph, arises from the contribution of the lone pairs on the oxygen atoms. Reduced electron density on the oxygen (when R′ = CF_3) will result in the lone pairs being more tightly held and consequently will produce a reduction in the contribution to the moment from the lone-pair electrons.

[9] C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 1969, **8**, 143.
[10] I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1938, 1269.
[11] J. McQueen and J. W. Smith, *J. Chem. Soc.*, 1956, 1821.