

ATOMIC POLARIZATION IN METAL CHELATES

II.* DIELECTRIC LOSS MEASUREMENTS ON SOME DIKETONE CHELATES OF TiN(IV)

By J. W. HAYES,[†] W. H. NELSON,^{†‡} and D. V. RADFORD[†]

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Abstract

Dipole moments and relaxation times determined by dielectric loss measurements at 3·109 and 9·400 GHz are reported for bis(pentane-2,4-dionato)dimethyltin(IV) and its dimethyl and diphenyl analogues with tropolone. All of these compounds show true orientation polarization in accord with the assignment of *cis* structures. High atomic polarizations are observed in all cases and it is suggested that this may be a characteristic of metal chelates in general.

In Part I of this series¹ we reported dielectric loss and dipole moment measurements on bis(pentane-2,4-dionato)diphenyltin(IV) $[\text{Ph}_2\text{Sn}(\text{acac})_2]$ (1). The discrepancy between the dipole moment determined by the static polarization (or "refractivity") method and that from the dielectric loss measurements was attributed to a high value of the atomic polarization (125 cm^3). The existence of true orientation polarization was taken as evidence for a *cis* configuration in this chelate.

In this paper we report dielectric loss measurements at 25° on dilute benzene solutions of bis(pentane-2,4-dionato)dimethyltin(IV) $[\text{Me}_2\text{Sn}(\text{acac})_2]$ (2), bistropolonatotdiphenyltin(IV) $[\text{Ph}_2\text{Sn}(\text{tr})_2]$ (3), and bistropolonatotdimethyltin(IV) $[\text{Me}_2\text{Sn}(\text{tr})_2]$ (4).

Experimental

Materials

All complexes with the exception of the two tropolone compounds were prepared using the methods of Moore and Nelson.² The tropolone complexes were those prepared for another investigation.³ Purities were checked by melting point and elementary analysis.

A.R. grade benzene was purified by partial freezing; the remelted solid was stored over sodium. In the tables concentrations are shown as weight fractions, w_2 . Incremental loss tangents, $\Delta \tan \delta$, are the differences between loss tangents measured for solutions and solvent. For benzene at 25°C the dielectric constant and density are,⁴ in order, 2·2725, 0·87378.

* Part I, *Inorg. Chem.*, 1970, 9, 400.

[†] School of Chemistry, University of Sydney, N.S.W. 2006.

[‡] Present address: Department of Chemistry, University of Rhode Island, Kingston, R.I. 02881, U.S.A.

¹ Hayes, J. W., Le Fèvre, R. J. W., and Radford, D. V., *Inorg. Chem.*, 1970, 9, 400.

² Moore, C. Z., and Nelson, W. H., *Inorg. Chem.*, 1969, 8, 138.

³ Aroney, M. J., and Nelson, W. H., *Inorg. Chem.*, in press.

⁴ Le Fèvre, R. J. W., "Dipole Moments," (Methuen: London 1953).

Dielectric Loss Measurements

Incremental loss tangents were measured at the frequencies 3.109 and 9.400 GHz. Determinations at the lower frequency were made with equipment similar to that described previously by Le Fèvre and Sullivan.⁵ Microwave power from a klystron oscillator was fed via attenuators and a signal sampler to the cavity which was equipped with a Teflon cup to hold liquid dielectrics. The sample arm of the signal sampler was connected to a Marconi Instruments Ltd digital frequency counter TF 2410/TM 8094 capable of frequency measurement to 3.4 GHz. This was used to measure Δf , the width of the "Q curve" of the cavity at half power, and hence the "Q" of the cavity.

Measurements at 9.400 GHz were obtained with apparatus described by Aroney *et al.*⁶

The value of the dipole moment and relaxation time for each complex were obtained from the Debye curve⁵ of best fit with the aid of an I.B.M. 7040 computer.

TABLE 1
INCREMENTAL LOSS TANGENTS FOR SOLUTIONS IN BENZENE AT 25°C

$\psi = \Sigma \Delta \tan \delta / \Delta \omega_2$								
$10^5 \omega_2$	$10^3 \times \Delta \tan \delta^a$	$10^3 \times \Delta \tan \delta^b$	$10^5 \omega_2$	$10^3 \times \Delta \tan \delta^a$	$10^3 \times \Delta \tan \delta^b$	$10^5 \omega_2$	$10^3 \times \Delta \tan \delta^a$	$10^3 \times \Delta \tan \delta^b$
[Me ₂ Sn(acac) ₂]			[Ph ₂ Sn(tr) ₂]			[Me ₂ Sn(tr) ₂]		
388	0.64	1.01	322	1.36	0.70	160	0.81	0.48
1066	1.66	2.53	536	2.30	0.81	364	2.13	0.96
1687	2.55	3.77	835	3.66	1.56	467	2.72	1.12
2165	3.23	4.74	1262	5.32	1.99	960	5.70	2.57
						1678	10.29	4.89
$\psi(3.109 \text{ GHz}) = 0.152$			$\psi(3.109 \text{ GHz}) = 0.43$			$\psi(3.109 \text{ GHz}) = 0.60$		
$\psi(9.400 \text{ GHz}) = 0.227$			$\psi(9.400 \text{ GHz}) = 0.17$			$\psi(9.400 \text{ GHz}) = 0.28$		

^a At 3.109 GHz.

^b At 9.400 GHz.

TABLE 2
DIPOLE MOMENTS (μ), RELAXATION TIMES (τ), AND POLARIZATIONS (${}_oP$, ${}_AP$) FROM OBSERVATIONS ON SOLUTIONS IN BENZENE AT 25°C

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

Solute	$\mu_{\text{loss}} (\text{D})$	τ_{ps}	${}_oP (\text{cm}^3)$	$\mu_{\text{static}} (\text{D})$	${}_AP (\text{cm}^3)$
[Ph ₂ Sn(acac) ₂]	2.55 ^a	61 ^a	133 ^a	3.78 ^b	160
[Me ₂ Sn(acac) ₂]	1.76	19	63	2.95 ^b	115
[Ph ₂ Sn(tr) ₂]	3.5	113	251	4.60 ^c	182
[Me ₂ Sn(tr) ₂]	3.0 ₅	63	190	3.65 ^c	83

^a From ref. 1.

^b From ref. 2.

^c From ref. 3.

The experimental data for compounds (2)–(4) are listed in Table 1 and the calculated dipole moments (μ_{loss}) and relaxation times (τ) are given in Table 2. Included in Table 2 are the values for compound (1) from previously published data.^{1,2} Values of true orientation polarization (${}_oP$) were calculated from these dipole moments. Estimates of atomic polarization (${}_AP$) were made by subtracting these values of ${}_oP$ from the apparent values derived from measurement of dipole moment by static polarization techniques (μ_{static}).^{2,3} In all of these calculations the molar refraction has been assumed to be equal to the electronic polarization and hence these values of ${}_AP$ are minimum estimates.

⁵ Le Fèvre, R. J. W., and Sullivan, E. P. A., *J. chem. Soc.*, 1954, 2873.

⁶ Aroney, M. J., Chio, H., Le Fèvre, R. J. W., and Radford, D. V., *Aust. J. Chem.*, 1970, 23, 199.

Discussion

Values of μ_{loss} in Table 2 show that all of these complexes are definitely polar. This is in accord with the assignment of *cis* structures to these compounds and in agreement with the conclusions of Moore and Nelson.² The existence of *cis-trans* equilibria has not been ruled out by any of the measurements so far made^{2,7,8} but the regularities observed in μ_{static} (within experimental error) would indicate that the *trans* form is either absent or always present in the same proportion along with the *cis* form.

Atomic polarizations for these compounds are all high. This appears to be a characteristic of metal chelates where the ligand is of the diketone type,⁹⁻¹⁹ and may be characteristic of metal chelates in general.^{11,20} It has been suggested by Coop and Sutton¹⁰ that bending of the metal-oxygen bonds in pentane-2,4-dionate complexes is largely responsible for the high values of A_P in these compounds. This has been supported by recent dielectric loss^{14,15,17,19} and far-infrared refractive index measurements^{16,18} on several metal- β -diketone complexes. In this context our results with the tropolonates are interesting. The aromatic ring in tropolone would be expected to make this ligand more rigid than the pentane-2,4-dione. Consequently the high A_P in the tropolone complexes suggests that "flapping" of the whole ligand about an axis though the tin-oxygen bonds may account for this polarization. However, it is significant that quite different values of A_P are obtained when the non-chelated ligands bonded to tin are changed from phenyl to methyl. This effect is particularly noticeable in the case of the tropolonate complexes although the experimental error may be as high as $\pm 25 \text{ cm}^3$.

The values of relaxation time listed in Table 2 show a decrease of expected order of magnitude when, for a given chelating ligand the non-chelated phenyl ligands are changed to methyl ligands. For the pentane-2,4-dionates this change is 42 ps while the tropolonates show a change of 50 ps.

Further studies with a view to the estimation of atomic polarization in other metal chelates are in progress.

⁷ McGrady, M. M., and Tobias, R. S., *J. Am. chem. Soc.*, 1965, **87**, 1909.

⁸ Nelson, W. H., and Martin, D. F., *J. inorg. Nucl. Chem.*, 1965, **27**, 89.

⁹ Finn, A. E., Hampson, G. C., and Sutton, L. E., *J. chem. Soc.*, 1938, 1254.

¹⁰ Coop, I. E., and Sutton, L. E., *J. chem. Soc.*, 1938, 1269.

¹¹ McQueen, J., and Smith, J. W., *J. chem. Soc.*, 1956, 1821.

¹² Meredith, C. C., Westland, L., and Wright, G. F., *J. Am. chem. Soc.*, 1957, **79**, 2385.

¹³ Podleschka, P., Westland, L., and Wright, G. F., *Can. J. Chem.*, 1958, **36**, 574.

¹⁴ Dasgupta, S., and Smythe, C. P., *J. Am. chem. Soc.*, 1967, **89**, 5532.

¹⁵ DiCarlo, E. N., Stronski, R. E., and Varga, C. E., *J. phys. Chem.*, 1969, **73**, 3433.

¹⁶ Nelson, R. D., and White, C. E., *J. phys. Chem.*, 1969, **73**, 3439.

¹⁷ Le Fèvre, R. J. W., Radford, D. V., and Saxby, J. D., *Inorg. Chem.*, 1969, **8**, 1532.

¹⁸ Haigh, J., and Sutton, L. E., *Chem. Commun.*, 1970, 296.

¹⁹ Eddy, L. P., Hayes, J. W., Livingstone, S. E., Nigam, H. L., and Radford, D. V., *Aust. J. Chem.*, 1971, **24**, 1071.

²⁰ Angel, R., Hayes, J. W., and Radford, D. V., unpublished data.