

believed to remove the degeneracy of the ground state and an esr signal is then observed in these hexachloro complexes.²²

Certain values of theoretical interest can be calculated for molybdenum(V) compounds if it is assumed that the d^1 electron is in the $b_2(d_{xy})$ orbital.²³

The values of K , χ , β^2 , and $P_{\text{complex}} (= \beta^2 P_{\text{ion}})$ are listed in Table III. K and χ are the isotopic contact term in reciprocal centimeters and atomic units, respectively, and β^2 is the molecular orbital coefficient for the b_2 orbital. The β^2 values indicate that the electron is a b_2 electron and spends more time in the d_{xy} orbital in dialkoxo than oxo complexes. The other values, $-K$, $-\chi$, and $\beta^2 P$, are comparable to those obtained for other molybdenum(V) complexes.^{10,12,23}

TABLE III
ISOTOPIC CONTACT TERMS, K AND χ , β^2 , AND P
FOR MOLYBDENUM(V) COMPLEXES IN GLASSES AT 78°K

Compound	$10^4(-K)$, cm ⁻¹	$10^4(-\chi)$, cm ⁻¹	$10^4 P$, cm ⁻¹	β^2
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	39.6	5.07	48.5	0.881
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	39.5	5.05	49.9	0.908
$[(C_2H_7)_4N](MoOCl_4)$	45.9	5.87	44.6	0.810
$[(C_4H_9)_4N](MoOCl_4)$	46.5	5.95	44.5	0.809

In the cases of the tetraethylammonium salts of the tetrachlorodimethoxomolybdate(V) and the tetrachlorodiethoxomolybdate(V) ions in solutions in the appropriate alcohols, which had been saturated with HCl, the experimental g and A values could be used to calculate the molecular orbital coefficients N_{π_1} , N_{π_2} , and N_{σ_2} in the equations

$$|B_2\rangle^* = N_{\pi_2}(d_{xy} - \lambda_{\pi_2}\phi_{b_2})$$

$$|B_1\rangle^* = N_{\sigma_2}(d_{x^2-y^2} - \lambda_{\sigma_2}\phi_{b_1})$$

$$|E\rangle^* = N_{\pi_1}[d_{zz}(\text{or } d_{yz}) - \lambda_{\pi_1}^o\phi_e^o - \lambda_{\pi_1}^a\phi_e^a]$$

These calculations were carried out exactly as in our work with the monoalkoxo complexes of vanadium(IV)⁷ and in the work of Manoharan and Rogers¹³ on molybdenyl-halo complexes. In the cases of the tungsten(V) compounds anisotropic A values could not be determined well enough to permit such calculations.

For the methoxo complex we took the following values as those of molybdenyl complexes: $S_{b_2} = 0.12$, $S_{b_1} = 0.16$, $S_e = 0.20$, $\xi_{\text{metal}} = 820$ cm⁻¹, $\xi_{\text{ligand}} = 587$ cm⁻¹, and $P = 55.0$. The energies of the $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions⁸ are 11.7 and 21.8×10^3 cm⁻¹, respectively. In the case of the ethoxo complex the same "molybdenyl values" were used for the overlap integrals, spin-orbit coupling constants, and " P ," and the transition energies were taken from spectra⁸ and equaled 12.1 and 21.5×10^3 cm⁻¹.

In the methoxo case $N_{\pi_1} = 0.968$, $N_{\pi_2} = 0.939$, $N_{\sigma_2} = 0.864$, and the spin density in the equatorial $3p_{\pi}$ orbital is 4.3%. For the ethoxo complex we found $N_{\pi_1} = 0.947$, $N_{\pi_2} = 0.967$, $N_{\sigma_2} = 0.811$, and a spin density of 2.8%.

(23) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

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The Structure of Bis(2,4-pentanedionato)diphenyltin(IV)

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The structure of the octahedral complex bis(2,4-pentanedionato)diphenyltin(IV) $[(C_6H_5)_2Sn(acac)_2]$ was studied in 1965 by McGrady and Tobias¹ and by Nelson and Martin,² both groups suggesting a *trans* disposition of the phenyls. The evidence was, however, not conclusive. Nelson and Martin² reported the dipole moment of this complex in benzene and in cyclohexane solutions as 3.78 and 4.02 D, respectively. Mainly on the basis of their failure to obtain an optical resolution, they ascribed a *trans* configuration to the complex, and they attributed the apparent orientation polarization to anomalously high atomic polarization effects arising principally from the presence of 2,4-pentanedionato chelate rings.³ They concluded that either the *trans* isomer is present alone in solution or alternatively the rate of racemization and/or isomerization is very rapid. Recently Moore and Nelson,⁴ noting the temperature variation of the measured dipole moment for a number of structurally related Sn complexes, have inferred by analogy that $(C_6H_5)_2Sn(acac)_2$ probably exists as the *cis* isomer. The purpose of this work was to apply the method of dielectric relaxation to ascertain if the observed disparity² between the measured total molar polarization and molecular refraction is attributable to a large atomic polarization or to the existence of a permanent electric moment.⁵⁻⁸ Accordingly dielectric absorption measurements have been made on solutions of $(C_6H_5)_2Sn(acac)_2$ in benzene at frequencies of 3109 and 9400 MHz.

Experimental Section

The complex was prepared from diphenyltin dichloride (Fluka *purum* grade) and sodium 2,4-pentanedionate⁹ (mp 226°), as described by McGrady and Tobias¹ except that the reagents

- (1) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).
- (2) W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965).
- (3) I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).
- (4) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, **8**, 138 (1969).
- (5) P. Debye, "Polar Molecules," Dover Publications, New York, N. Y., 1929.
- (6) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., London, 1952.
- (7) M. Davies, "Molecular Behaviour," Pergamon Press, London, 1965.
- (8) R. J. W. Le Fèvre, *et al.*, numerous publications, 1954-1969.
- (9) C. F. Hatch and G. Sutherland, *J. Org. Chem.*, **13**, 249 (1948).

were dissolved in a 2:1 ethanol-benzene mixture dried over magnesium ethoxide. The product, mp 122°, had an infrared absorption spectrum identical with that reported by McGrady and Tobias.¹ *Anal.* Calcd for C₂₂H₂₄O₄Sn: C, 56.08; H, 5.14; Sn, 25.20. Found: C, 56.23; H, 5.60; Sn, 26.9.

The solvent was AR grade benzene purified by partial freezing; the remelted solid was stored over sodium.

Procedures described elsewhere¹⁰⁻¹³ were used in making the measurements summarized in Tables I and II. Concentrations

TABLE I

INCREMENTAL DIELECTRIC CONSTANTS, DENSITIES, AND REFRACTIVE INDICES FOR SOLUTIONS OF (C₆H₅)₂Sn(acac)₂ IN BENZENE AT 25°

10 ⁵ w ₂	676	880	931	935	1206	2095
10 ⁴ Δε	221	277	299	...	380	557
10 ⁶ Δd	233	321	414	688
10 ⁴ Δ(n ²)	15	18	21	42

TABLE II

INCREMENTAL LOSS TANGENTS FOR SOLUTIONS OF (C₆H₅)₂Sn(acac)₂ IN BENZENE AT 25°

		(a) 3109 MHz				
10 ⁵ w ₂		880	1206	2095		
10 ³ Δ tan δ		2.589	4.363	6.713		
		(b) 9400 MHz				
10 ⁵ w ₂		676	931	935	1206	1587 2095
10 ³ Δ tan δ		0.864	1.437	1.471	2.565	2.929 3.928

are shown as weight fractions w₂. Incremental quantities, indicated by the prefix Δ, are the differences between properties measured for solutions and solvent. Suffixes 1 and 2 refer, respectively, to solvent and solute. For benzene at 25°, and w₂ = 0, the dielectric constant, density, and refractive index (Na light) are,¹⁰ in order, ε₁ 2.2725, d₁ 0.87378, and n₁ 1.4973.

Results and Discussion

Mean values (± standard variations) of quotients drawn from Table I are Δε/w₂ = 3.09 ± 0.24, Δd/w₂ = 0.3399 ± 0.0024, and Δn²/w₂ = 0.200 ± 0.019, so that at infinite dilution the total polarization and molecular refraction of the solute follow¹⁰⁻¹² as 372 ± 22 cm³ and 114 ± 2 cm⁻³, respectively. Its apparent dipole moment falls in 0.1 D steps from 3.6 to 3.1 D (±0.2 D) as the distortion polarization is increased 1.0, 1.1, ..., 1.5 times the molecular refraction. However, from ref 14 and 15 it seems that only about 14 cm³ of atomic polarization should be attributed to each 2,4-pentanedionato chelate group; when this is the case μ emerges as 3.35 ± 0.2 D.

Table II reports dielectric loss measurements which give mean values of (Δ tan δ)/w₂ of 0.325 at 3109 MHz and 0.17 (±0.03 standard variation) at 9400 MHz. Such results strongly suggest that (C₆H₅)₂Sn(acac)₂ in benzene solution exhibits an orientation polarization which is large and "real." The two values just quoted

for (Δ tan δ)/w₂ are found—by accepting the Debye model for a solute behaving as a rigid dipole in a low viscosity, nonpolar solvent¹⁶ and by using the equations given by Le Fèvre and Sullivan¹²—to be consistent with a relaxation time τ of 61 × 10⁻¹² sec and a dipole moment of 2.5 D. A τ of this order is reasonable for a solute molecule of the size of (C₆H₅)₂Sn(acac)₂—compare 62 × 10⁻¹² sec for (C₆H₅)₃CCl and 51 × 10⁻¹² sec for C₈H₈Rh(acac).¹⁷

The dipole moment deduced from the dielectric loss measurements is lower than others suggested above by the refractivity method; however the correct allowance to make for atomic polarization is unknown. Only if this allowance is slightly larger than the molecular refraction can the same moment be deduced from the data of Tables I and II. No precedent exists to justify making such a suggestion.

Accordingly we conclude that bis(2,4-pentanedionato)diphenyltin(IV) dissolved in benzene is, in fact, polar with a dipole moment lying between 2.5 and 3.6 D. It follows that in solution the complex cannot exist as the (nonpolar) *trans* form alone but must prefer the *cis* configuration although the existence of a mixture of *cis* and *trans* forms (with the former predominant) cannot be precluded. Further studies of this nature on other organometallic complexes are in progress.

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(16) W. Jackson and J. G. Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).

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

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Identification of the "Lead(II) Hydroxide" of Robin and Théolier

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The uncertain status of the existence of lead(II) hydroxide, Pb(OH)₂, has been pointed out by Robin and Théolier,¹ who claimed to have made it by the thermal decomposition, at 280–300°, of a basic salt precipitated by ammonium hydroxide from a solution of lead(II) nitrate. The thermogravimetric curve of the basic salt resembled that given by Duval² and showed two stages of weight loss, the second corresponding exactly to that expected for the dehydration of Pb(OH)₂. In earlier studies of basic lead(II) nitrates precipitated by sodium hydroxide Nicol³ obtained a

(1) J. Robin and A. Théolier, *Bull. Soc. Chim. France*, 680 (1956).

(2) C. Duval, *Anal. Chim. Acta*, **4**, 159 (1950).

(3) A. Nicol, *Compt. Rend.*, **226**, 810 (1948).

(10) R. J. W. Le Fèvre, "Dipole Moments," Methuen and Co. Ltd., London, 1953.

(11) A. D. Buckingham, J. Y. H. Chau, H. C. Freeman, R. J. W. Le Fèvre, N. Rao, and J. Tardif, *J. Chem. Soc.*, 1405 (1956).

(12) R. J. W. Le Fèvre and E. P. A. Sullivan, *ibid.*, 2873 (1954).

(13) R. J. W. Le Fèvre, D. V. Radford, and H. K. The, to be submitted for publication.

(14) A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938).

(15) R. S. Armstrong, C. G. Le Fèvre, and R. J. W. Le Fèvre, *ibid.*, 371 (1957).