obtaining and interpreting the nuclear magnetic resonance spectra, Dr. H. D. Hoberecht for mass spectral analyses, and Dr. R. C. Rittner for elemental analyses.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL,
AND HUNTER COLLEGE, THE CITY UNIVERSITY OF NEW YORK,
NEW YORK, NEW YORK 10021

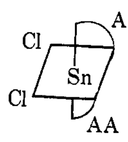
A Study of the Temperature Dependence of the Dipole Moment of Dichlorobis(acetylacetonato)tin(IV)

BY VERA DORON[1] AND CHAVA FISCHER

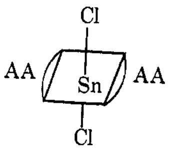
Received March 27, 1967

The stereochemistry of bis(acetylacetonato)tin(IV) complexes has been the subject of a number of recent publications.[2-6]

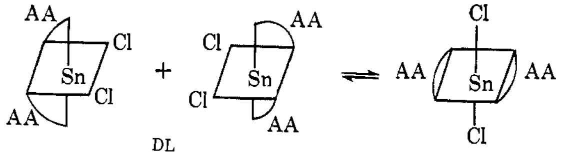
The *cis* structure (Ia) for dichlorobis(acetylacetonato)tin(IV) has been proposed on the basis of nmr evidence[3] alone. Dipole moment measurements carried out by the present authors and others[7] seem to be in agreement with the earlier proposed structure. It should be pointed out at this time that related compounds of tin such as $(C_6H_5)_2Sn(AA)_2$ (AA = acetylacetonate) have been assigned[6] the *trans* configuration in solution though a dipole moment of approximately 4 D. was reported. Whether this moment is due to a high induced polarization as suggested[6] or whether there is a permanent moment present can only be decided by a study of the temperature dependence of the dipole moment.



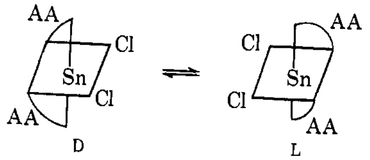
Ia



Ib



(I)



(II)

The present study was initially undertaken in an effort to shift a possible *cis–trans* (I) equilibrium which may occur in solution. The data indicate that within the temperature range (30–79°) no shift occurs as evidenced by the constant value of the dipole moment (Table I).

TABLE I

THE DIPOLE MOMENTS OBTAINED FOR $Sn(AA)_2Cl_2$ AT VARIOUS TEMPERATURES

Temp, °C	$(\Delta/C)_0$	C_2	$\epsilon_{12} - n_{12}^2$	μ, D.[d,e]
30[a]	5.789×10^3	1.90×10^{-5}	1.10×10^{-1}	6.90
34[b]	5.148×10^3	2.35×10^{-6}	1.21×10^{-2}	6.57
77.5[a]	4.048×10^3	2.10×10^{-6}	8.5×10^{-3}	6.35
79[c]	4.413×10^3	2.90×10^{-6}	1.28×10^{-2}	6.65

[a] Measurements were carried out on freshly prepared solutions at the given temperatures. [b] The solution was equilibrated at 79° for 3 days and rapidly cooled to the given temperature. [c] The solution was equilibrated at 79° for 3 days; then measurements were carried out at the given temperature. [d] The dipole moments were calculated using the equation

$$\mu^2 = \text{constant}\left(\frac{T}{(\epsilon_1 + 2)(n_1^2 + 2)}\right)\left(\frac{\Delta}{C_2}\right)_0$$

where constant $= 27k/4\pi N$ and $k = 1.38 \times 10^{-16}$, $N = 6.02 \times 10^{23}$, and T varies as indicated in the table. $(\Delta/C_2)_0$ is the value of the slope obtained by plotting C_2, the concentration of solute in moles/ml of solution, against Δ, where $\Delta = \epsilon_{12} - n_{12}^2$ and ϵ_{12} and n_{12} are the dielectric constant and refractive index of the measured solution, respectively. ϵ_1 and n_1 are the dielectric constant and refractive index, respectively, of the solvent. The slope is obtained by extrapolation of the straight line to concentration $C_2 = 0$. [e] All measurements were obtained on sublimed material. The sublimation was carried out either around 170° at 1–2 mm or around 185° at atmospheric pressure. Nelson[7b] obtained the same value for the moment (6.77 D.) on nonsublimed material at room temperature.

Dipole moments were measured in benzene solutions by following the concentration dependence of the dielectric constant[8] and refractive indices.[9] Calculations were based on the methods of Guggenheim[10] and Smith.[11] The contribution of induced and orientation polarization to the total polarization of dichlorobis(acetylacetonato)tin(IV) at 30° is approximately 14 and 86%, respectively, as calculated by using the Debye equation.

The constant value of the dipole moments obtained, with strong evidence for the *cis* (Ia) structure in solution, then suggests that a *cis–cis* (II) equilibrium is most probably the prevailing one in solution. The dipole moment data are in good agreement with the data of Faller and Davison,[4] who have shown by means of temperature-dependent nmr studies that a rapid equilibrium is involved at approximately 90° and that this is most likely the *cis–cis* (II) interconversion of the two enantiomeric forms.

The mean deviation among the obtained moments is ±0.28 D. (Table I). The deviations between

---

[1] Hunter College, The City University of New York, New York, N. Y.

[2] Y. Kawasaki and T. Tanaka, *J. Chem. Phys.*, **43**, 3396 (1965).

[3] J. A. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

[4] J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 182 (1967).

[5] Y. Kawasaki, T. Tanaka, and R. Okawara, *Inorg. Nucl. Chem. Letters*, **2**, 9 (1966).

[6] W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965).

[7] (a) W. H. Nelson, paper presented at 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11–16, 1966; (b) W. H. Nelson, personal discussion, Sept 1966, not published.

[8] The dielectric constants were measured on a capacitance-measuring assembly, Type No. 1610-A, General Radio Co., Concord, Mass.

[9] Refractive indices were measured on an Abbé refractometer.

[10] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[11] J. W. Smith, *ibid.*, **46**, 394 (1950).

individual measurements do not follow a temperature-dependent trend and, therefore, should be considered as experimental errors and not significant in terms of a change in a configurational equilibrium.

In conclusion, the constant value of the dipole moments measured in solution over the given temperature range in addition to published[4] infrared and Raman spectra and high-temperature nmr studies seem to provide strong evidence for a *cis–cis* (II) configurational equilibrium in solution.

CONTRIBUTION FROM THE CHEMISTRY RESEARCH SECTION,
ROCKETDYNE, A DIVISION OF NORTH AMERICAN AVIATION, INC.,
CANOGA PARK, CALIFORNIA 91304

Chlorine Pentafluoride. Preparation and Properties

BY D. PILIPOVICH, W. MAYA, E. A. LAWTON, H. F. BAUER,
D. F. SHEEHAN, N. N. OGIMACHI, R. D. WILSON,
F. C. GUNDERLOY, JR., AND V. E. BEDWELL

Received April 10, 1967

Three communications reporting the synthesis of ClF_5 have appeared.[1-3] This halogen fluoride has been under independent investigation in the Rocketdyne laboratories, and we wish now to report on some of our work in this area. Chlorine pentafluoride was first prepared in low yields in our laboratories by reactions of F_2 with chlorine and chlorine-containing compounds in a glow discharge at −196°. Despite the very small quantities of ClF_5 isolated, we established the fact that Cl_2 and F_2 were sufficient for its formation and inferred its structure from the infrared spectrum subsequently published by Begun, *et al.*[4] Molecular weights determined from vapor density measurements of impure ClF_5 also inferred the composition.

What we believe to be the most useful laboratory preparation of ClF_5 involves the fluorination of an alkali metal chlorotetrafluoride, $MClF_4$. Those examined include $KClF_4$, $RbClF_4$, and $CsClF_4$. Although all salts yielded ClF_5 upon fluorination, the cesium and potassium salts were investigated more extensively in this study. The general reaction for the salt fluorination is

$$MClF_4 + F_2 \longrightarrow MF + ClF_5 \qquad (1)$$

From the above equation it is seen that only one condensable gaseous product should be obtained. This was confirmed repeatedly by experiment; *i.e.*, pure ClF_5 was obtained in these reactions.

The conversions of $MClF_4$ to ClF_5 were variable. Using $KClF_4$, conversions from 1 to 25% have been observed. The lowest conversion was observed at 80°, while at 150° a consistent conversion of 10% was noted. Higher conversions were obtained with $CsClF_4$ and ranged from 25 to 90%. With both salts, however, pure ClF_5 was the only condensable gaseous product.

Chlorine pentafluoride is a typical interhalogen fluoride in that it is a corrosive, highly oxidizing substance. It is colorless in the gas phase, water white in the liquid phase, and freezes to a white solid. Vapor pressures were measured on the range −79.0 to +25° and are fitted to the equation $\log P_{\text{mm}} = 7.2683 - 1137.16/T(°\text{K})$. Measured vapor pressures at the noted temperatures are [T (°C), P (mm)]: −79.2, 16.5; −63.2, 55.0; −50.0, 128.0; −45.3, 166.0; −35, 290.0; −26.2, 453.5; −23.7, 507; −17.9, 634.5; −14.5, 734.5; −0.2, 1293; +24.8, 2855. The normal boiling point is −14.0° and the melting point is −103 ± 4°. The derived Trouton constant of 21.8 shows ClF_5 to be a nonassociated liquid. The density of ClF_5 was measured in the range of −80 to −23°. The density–temperature relationship of d (g/ml) $= 2.696 - (3.08 \times 10^{-3}T(°\text{K}))$ is derived from the measured values (°C, g/ml): −80, 2.100; −57, 2.0361; −23, 1.922.

The thermal stability of ClF_5 is somewhat less than that of ClF_3. The equilibrium

$$ClF_5 \rightleftharpoons ClF_3 + F_2$$

was found to be established fairly readily above 165° and has been studied in detail.[5]

Chlorine pentafluoride was smoothly reduced by burning with ammonia to give a mixture of NH_4Cl and NH_4F. Multiple analyses of the combustion products gave an F/Cl ratio of 4.92. These agreed closely with chromatographic assays, using the technique of Lysyj and Newton,[6] which showed the presence of small quantities of Cl_2. The molecular weight was determined from the vapor density and was found to be 128 (calcd, 130.5).

The high-resolution F^{19} nmr spectrum for ClF_5 has been recorded using a Varian DP-60 spectrometer operating at 56.4 Mc. The spectrum was obtained on a 50 mole % solution of ClF_5 in $CFCl_3$. Two band structures were noted in the nmr spectrum. A strong doublet was recorded at −247 ppm (relative to $CFCl_3$) and a weak quintet at −412 ppm. The coupling constant for the band structures is $J = 130$ cps. The seven-component F^{19} spectrum recorded confirms the C_{4v} symmetry deduced from infrared and Raman studies.[3]

A stable mass-cracking pattern for ClF_5 has been obtained with a CEC 21-103 C mass spectrometer. Observed ions, excluding Cl^{37} isotopes, with the relative abundance were [m/e, ion, abundance (%)]: 111, ClF_4^+, 82.0; 92, ClF_3^+, 18.6; 73, ClF_2^+, 100.0; 54, ClF^+, 21.0; 46, ClF_3^{2+}, 3.5; 37.5, ClF_2^{2+}, 0.5; 35, Cl^+,

---

[1] D. F. Smith, *Science*, **140**, 889 (1963).

[2] E. Gatti, R. L. Krieger, J. E. Sicre, and H. J. Schumacher, *J. Inorg. Nucl. Chem.*, **28**, 655 (1965).

[3] F. P. Gortsens and R. H. Toeniskoetter, *Inorg. Chem.*, **5**, 1925 (1966).

[4] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

[5] H. F. Bauer and D. F. Sheehan, *Inorg. Chem.*, **6**, 1736 (1967).

[6] I. Lysyj and P. R. Newton, *Anal. Chem.*, **35**, 90 (1963).