this reaction product must remain a matter for speculation at the present. Unfortunately, solubility problems prevented an investigation of the nmr of either this substance or of the adduct I above.

Irrespective of the details of the structure, it seems clear that, in the indium case at least, reaction with maleic anhydride is not a satisfactory test of the presence of the diene form of the cyclopentadienyl ligand. Since the activation energy for the Diels–Alder reaction of maleic anhydride and cyclopentadiene is small, it is possible that the reaction with cpIn is evidence of an equilibrium in solution which normally lies strongly to the left. Further work on this

h^5-cpIn ⇌ h^1-cpIn

question is planned.

Acknowledgment. This work was supported by the National Research Council of Canada.

Registry No. cpIn, 34822-89-4; BF_3, 7637-07-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; $B(CH_3)_3$, 593-90-8; cpIn·BF_3, 41375-74-0; cpIn·BCl_3, 41375-75-1; cpIn·BBr_3, 41375-76-2; cpIn·$B(CH_3)_3$, 41375-77-3; $C_4H_2O_3$, 108-31-6; cpIn·$C_4H_2O_3$, 41375-78-4; $C_9H_7O_3In \cdot BCl_3$, 41429-81-6.

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850

Tin and Germanium β-Diketonate Complexes. I. Stereochemistry, Configurational Rearrangements, and Vibrational Spectra of Dihalobis(acetylacetonato)tin(IV) Complexes[1]

RALPH W. JONES, Jr., and ROBERT C. FAY*

Received April 16, 1973

The kinetics of exchange of acetylacetonate methyl groups between the two nonequivalent sites in *cis*-dihalobis(acetylacetonato)tin(IV) complexes, $Sn(acac)_2X_2$ (X = F, Cl, Br, or I), have been determined by nmr line-broadening studies of 1,1,2,2-tetrachloroethane solutions. First-order rate constants (sec^{-1}), extrapolated to 25°, activation energies (kcal/mol), and activation entropies (eu) are respectively as follows: 8.0, 13.9 ± 0.7, −9.8 ± 2.5 (X = F); 0.15, 16.0 ± 0.4, −10.6 ± 1.0 (X = Cl); 0.21, 15.6 ± 0.4, −11.5 ± 1.2 (X = Br); 0.63, 15.7 ± 0.7, −8.6 ± 2.0 (X = I). It is shown that these rearrangements occur by an intramolecular mechanism. The preparation and characterization of pure $Sn(acac)_2F_2$ is described for the first time, and evidence is presented which establishes that this complex exists as the cis geometrical isomer. Infrared frequencies for the $Sn(acac)_2X_2$ complexes are reported in the range 1600–33 cm^{-1}; Sn–X, Sn–O, and other band assignments are given. The spectra suggest that the stereochemistry is cis in the solid state as well as in solution.

Introduction

Dihalobis(acetylacetonato) complexes of the type $M(acac)_2X_2$ are known for all of the group IV metals except Pb(IV). The stereochemistry and configurational rearrangements of these compounds are subjects of considerable interest.

With the exception of $Ti(acac)_2I_2$, which exists as an equilibrium mixture of cis and trans isomers,[2] all of the known Ti(IV),[3-6] Zr(IV),[6-8] and Hf(IV)[6-8] complexes adopt a cis octahedral configuration in solution. These molecules are stereochemically nonrigid, as evidenced by rapid, intramolecular exchange of acetylacetonate methyl groups between the two nonequivalent sites of the cis isomer. Nmr line-broadening studies of $Ti(acac)_2X_2$ (X = F, Cl, Br) in dichloromethane have afforded first-order rate constants for methyl group exchange of 3-69 sec^{-1} at −40° (670-16,000 sec^{-1} at 25°) and activation energies of about 11.5 kcal/mol.[4] The corresponding Zr(IV) and Hf(IV) complexes (X = Cl, Br) are even less rigid; the exchange rate for $Zr(acac)_2Cl_2$ is too fast to measure (>10 sec^{-1}) at −130°.[7]

Although Kawasaki and coworkers proposed for the tin(IV) complexes $Sn(acac)_2X_2$ (X = Cl, Br, I) a distorted trans structure containing somewhat localized double bonds within the chelate rings,[9-12] it is now well established by nmr,[13-15] infrared,[15-16] Raman,[15] and dipole moment[6,17-19] studies that these complexes have a cis structure in solution. Cox, *et al.*,[20] suggested that $Sn(acac)_2F_2$ may be trans; however, details of the preparation and characterization of this complex have not been reported. Smith and Wilkins[14] were unable to prepare the pure compound but observed for the impure product a spin-spin coupling constant $J(Sn–C_\gamma H)$ in the range expected for the cis isomer. No reliable, quantitative kinetic results are available for stereochemical rearrangements of any of these compounds. A limited amount of variable-temperature nmr data has been reported for $Sn(acac)_2Cl_2$;[12,15] however, the published activation energy[12] of 5.4 kcal/mol for

---

[1] Abstracted in part from the Ph.D. thesis of R. W. Jones, Jr., Cornell University, 1971.

[2] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 9, 2048 (1970).

[3] D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).

[4] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 6, 1512 (1967).

[5] D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).

[6] N. Serpone and R. C. Fay, *Inorg. Chem.*, 8, 2379 (1969).

[7] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, 7, 502 (1968).

[8] R. C. Fay and T. J. Pinnavaia, *Inorg. Chem.*, 7, 508 (1968).

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

[10] Y. Kawasaki, R. Ueeda, and T. Tanaka in "International Symposium on Nuclear Magnetic Resonance," Preliminary Report, Tokyo, Sept 1965.

[11] Y. Kawasaki, T. Tanaka, and R. Okawara, *Spectrochim. Acta, Part A*, 22, 1571 (1966).

[12] Y. Kawasaki and T. Tanaka, *Inorg. Nucl. Chem. Lett.*, 3, 13 (1967).

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

[14] J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, 1749 (1966).

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

[16] I. Douek, M. J. Frazer, Z. Goffer, M. Goldstein, B. Rimmer, and H. A. Willis, *Spectrochim. Acta, Part A*, 23, 373 (1967).

[17] M. Cox, J. Lewis, and R. S. Nyholm *J. Chem. Soc.*, 6113 (1964).

[18] W. H. Nelson, *Inorg. Chem.*, 6, 1509 (1967).

[19] V. Doron and C. Fischer, *Inorg. Chem.*, 6, 1917 (1967).

[20] M. Cox, R. J. H. Clark, and H. J. Milledge, *Nature (London)*, 212, 1357 (1966).

exchange of methyl groups is unusually low, and the exchange process has been incorrectly interpreted[12] in terms of configurations having localized double bonds in the acetylacetonate rings.

The present paper reports the preparation and characterization of pure $Sn(acac)_2F_2$ and variable-temperature nmr studies of the complete series of $Sn(acac)_2X_2$ complexes (X = F, Cl, Br, or I). Also reported are infrared spectra in the range 4000–33 cm^{-1}.

Subsequent papers in this series will deal with the stereochemistry and rearrangements of dihalobis(β-diketonato)germanium(IV) complexes, which have recently been shown to exist as both cis and trans isomers.[21] The silicon complex $Si(acac)_2Cl_2$ may also be trans.[22]

Experimental Section

Difluorobis(2,4-pentanedionato)tin(IV). This compound was prepared in 68% yield by reaction of tin(IV) fluoride (2.9 g, 15 mmol) (Research Organic/Inorganic Chemical Corp.) and acetylacetone (3.1 ml, 30 mmol) (Matheson Coleman and Bell; bp 136–140°) in ~100 ml of refluxing dichloromethane. After a reaction time of ~24 hr, unreacted SnF_4 was removed by filtration of the hot solution, and the product was isolated from the filtered mother liquor by addition of hexane. The resulting white powder was recrystallized from dichloromethane–hexane and dried *in vacuo*; mp 225–226°.

Anal. Calcd for $Sn(C_5H_7O_2)_2F_2$: C, 33.84; H, 3.98; F, 10.71; Sn, 33.44; mol wt 355. Found: C, 34.01; H, 4.11; F, 10.90; Sn, 33.30; mol wt 330 (cryoscopic, 0.135 *m* nitrobenzene solution). Additional data: molar conductance 0.092 ohm^{-1} cm^2 mol^{-1} (1.5×10^{-3} *M* nitrobenzene solution, 25°). Pmr (0.15 *M* $CDCl_3$ solution, 37°): τ 4.29 ($C_\gamma H$), 7.82 (CH_3, broad, time-averaged signal), $J(Sn-C_\gamma H)$ 8.0 Hz; $Sn-CH_3$ coupling obscured by line broadening in $CDCl_3$ but $J(Sn-CH_3)$ = 8.6 Hz in CH_2Cl_2. Pmr (saturated benzene solution, 37°): τ 5.01 ($C_\gamma H$), 8.47 (CH_3, time-averaged signal). ^{19}F nmr (0.28 *M* CH_2Cl_2 solution, 31°): 153 ppm relative to an internal reference of $CFCl_3$ (10% by volume), $J(^{117}Sn-F) = 1874 \pm 10$ Hz, $J(^{119}Sn-F) = 1974 \pm 10$ Hz.

$Sn(acac)_2X_2$ Complexes (X = Cl, Br, or I). $Sn(acac)_2Cl_2$ was prepared by reaction of tin(IV) chloride and acetylacetone in chloroform.[23] The resulting white crystals were recrystallized twice from benzene–hexane; mp 203–205°, lit.[23] mp 202°. $Sn(acac)_2Br_2$ was obtained as white crystals by reaction of tin(IV) bromide and copper(II) acetylacetonate in chloroform[24] followed by recrystallization (twice) from ethyl acetate; mp 183–185°, lit.[24] mp 187°. $Sn(acac)_2I_2$ was synthesized in 60% yield by the method of Ueeda, *et al.*;[25] however the reaction time was extended to 18 hr; mp 179–182°, lit.[25] mp 179–180°. *Anal.* Calcd for $Sn(C_5H_7O_2)_2I_2$: C, 21.04; H, 2.48; I, 44.47; Sn, 20.80. Found: C, 21.31; H, 2.56; I, 44.85; Sn, 21.04. The identity and purity of these complexes was further confirmed by comparison with previously published infrared and pmr data.[11,13-15,18]

Dichlorobis(1-phenyl-1,3-butanedionato)tin(IV). This compound was prepared in refluxing chloroform by reaction of tin(IV) chloride and benzoylacetone.[26] Recrystallization from chloroform gave diamond-shaped plates; mp 221–223°, lit.[26] mp 220°.

Anhydrous Conditions. Although β-diketonate complexes of tin(IV) are less sensitive to hydrolysis than the analogous Ti(IV),[4] Zr(IV),[7] and Hf(IV)[7] compounds, they were nevertheless prepared and subsequently handled in a dry nitrogen atmosphere. Solvents used in syntheses and physical measurements were dried by standard methods. Dichloromethane, chloroform, benzene, hexane, and 1,1,2,2-tetrachloroethane were refluxed for at least 24 hr over calcium hydride. Ethyl acetate was distilled from phosphorus pentoxide, and nitrobenzene was purified by a published procedure.[4]

Nmr Line-Broadening Studies of $Sn(acac)_2X_2$ Complexes. Nmr spectra of the acetylacetonate methyl resonances were recorded in the temperature range −10 to +160° using a Varian A-60A or A-60 spectrometer equipped with a V-6040 temperature controller. Prior to a kinetic run, the sweep width (50 Hz) was calibrated by the audiofrequency side-band technique.

The solvent was 1,1,2,2-tetrachloroethane (bp 146°; Eastman Organic Chemicals) which had been dried over and freshly distilled from calcium hydride. This solvent was chosen because of its relatively high boiling point and long liquid range and because of its homologous relationship to dichloromethane, in which the analogous $Ti(acac)_2X_2$ complexes had been studied previously.[4] (Unfortunately, higher coalescence temperatures for the tin complexes precluded use of dichloromethane.) Also, 1,1,2,2-tetrachloroethane has a single, sharp resonance on which one can optimize the magnetic field homogeneity; the resolution of the retuned field at each temperature was of the order of 0.4 Hz. Solutions were sealed *in vacuo* after degassing several times by the freeze–thaw–refreeze method.

The presence of small amounts of acetylacetone was noted in high-temperature spectra of $Sn(acac)_2F_2$ and $Sn(acac)_2I_2$. The diketone probably results from thermal decomposition in solution since the solid complexes are analytically pure. In any case, the presence of the sharp acetylacetone signal does not complicate the spectral analysis.

Strenuous efforts were made to eliminate or minimize the common sources of error discussed by Allerhand, *et al.*[27] Spectra were recorded at slow sweep rates (0.1 Hz/sec) and radiofrequency power levels below saturation. Errors due to instrument instability were reduced by averaging five scans of the spectrum at each temperature. The temperature was determined before and after the five spectra were recorded by measuring the chemical shift between the nonequivalent protons of methanol (low temperatures) or 1,2-ethanediol (high temperatures). Seven minutes was allowed for each sample to equilibrate. By maintaining identical flow rates of nitrogen through the gas flow probe and identical spinning rates at each temperature, it was found that the temperature could be maintained within ±0.2° in the range 0–110°; in general, the scatter in our log *k vs.* $1/T$ plots can be accounted for by temperature fluctuations of <0.5°. Temperatures were calculated from chemical shifts using the equations given by Van Geet.[28-31]

Values of the mean residence time τ for an acetylacetonate methyl group were obtained by comparing the experimental spectra with theoretical spectra calculated using the Gutowsky–Holm total line shape equation.[32] Theoretical spectra were calculated at intervals of 0.005 Hz for an appropriate range of ~140 values of τ. Other input parameters were $\delta\nu$, the observed frequency separation between the two resonances in absence of exchange, and T_2, the transverse relaxation time. $\delta\nu$ was essentially temperature independent. T_2, however, was temperature dependent as evidenced by viscosity broadening in the region of slow exchange.

Following the procedure employed by Fay and Lowry,[4] values of T_2 were estimated from the half-maximum line widths of the methyl resonance of the analogous zirconium complex, *cis*-$Zr(acac)_2Cl_2$.[6-8] This complex and the tin compounds are presumably isostructural, but the line width of *cis*-$Zr(acac)_2Cl_2$ is not affected by exchange broadening because at all accessible temperatures the rate of exchange is fast on the nmr time scale. In the range 8–58°, the line width of the methyl resonance of *cis*-$Zr(acac)_2Cl_2$ in 1,1,2,2-tetrachloroethane (0.278 *M*) can be fit by least squares to the linear equation

$$1/\pi T_2 = -0.0145t + 1.24 \qquad (1)$$

where $1/\pi T_2$ is the full line width at half-maximum amplitude in hertz and t is the temperature in degrees centigrade. The standard

---

[21] (a) T. J. Pinnavaia, L. J. Matienzo, and Y. A. Peters, *Inorg. Chem.*, 9, 993 (1970); (b) R. W. Jones, Jr., Ph.D. Thesis, Cornell University, 1971.

[22] D. W. Thompson, *Inorg. Chem.*, **8**, 2015 (1969).

[23] W. Dilthey, *Ber. Deut. Chem. Ges.*, 36, 923 (1903).

[24] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **125**, 372 (1924).

[25] R. Ueeda, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Organometal. Chem.*, 5, 194 (1966).

[26] W. Dilthey, *J. Prakt. Chem.*, **111**, 147 (1925).

[27] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 88, 3185 (1966).

[28] A. L. Van Geet, *Anal. Chem.*, 40, 2227 (1968); **42**, 679 (1970).

[29] The calibration charts supplied by Varian Associates are in error.[28,30,31] Use of the Varian chart for 1,2-ethanediol does not produce a significant error in the activation parameters determined for $Sn(acac)_2X_2$ (X = Cl, Br, I). However for $Sn(acac)_2F_2$, which was studied in a temperature range requiring use of the methanol "thermometer," use of the Varian chart would introduce errors of −1.6 kcal/mol in the activation energy and −5 eu in the activation entropy.

[30] R. C. Neuman and V. Jonas, *J. Amer. Chem. Soc.*, **90**, 1970 (1968).

[31] O. Yamamoto and M. Yanagisawa, *Anal. Chem.*, **42**, 1463 (1970).

[32] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

error of the fit is ±0.02 Hz. Above 58°, the line width is controlled by the field homogeneity and has a value of ~0.40 Hz.

Kinetic data for $Sn(acac)_2F_2$ and $Sn(acac)_2I_2$ were collected in the temperature region below 58°. For these compounds, the line shape computations were carried through for values of T_2, calculated from eq 1, appropriate to the 10° ranges 10-20°, 20-30°, etc., and a value of τ at each temperature was determined by comparison of the experimental line shape with the theoretical line shape calculated using a value of T_2 applicable to that temperature. For $Sn(acac)_2Cl_2$ and $Sn(acac)_2Br_2$, the kinetic data were collected in the region where T_2 is temperature independent; appropriate values of T_2 were derived from the line widths in the fast-exchange limit (0.41 and 0.40 Hz, respectively).

In the comparison of experimental and theoretical spectra, the following characteristic line shape parameters were used to determine an average value of τ at each temperature: line widths at one-half ($\Delta_{1/2}$) and three-quarters ($\Delta_{3/4}$) maximum amplitude and, below coalescence, $\delta\nu_e$, the frequency separation between the two absorption maxima. Other common line shape parameters, $\Delta_{1/4}$ and r, the ratio of the maximum amplitude to the central minimum, were not employed because the experimental line shape near the base line is modified by the presence of $^{117,119}Sn-CH_3$ coupling satellites; tin-proton coupling was not included in calculating the theoretical spectra.[33] In one case, $Sn(acac)_2F_2$, the τ values derived from $\delta\nu_e$ at the three lowest temperatures (Table I) were ~30% larger than the τ values derived from the line widths. Examination of log k *vs.* $1/T$ plots indicated that these τ values based on $\delta\nu_e$ are anomalous; consequently they were omitted in determining average values of τ.

Infrared Spectra. Infrared spectra of the $Sn(acac)_2X_2$ complexes were recorded in the region 4000-250 cm^{-1} with a Perkin-Elmer 521 grating spectrophotometer. Dichloromethane solutions (5-15 g/100 ml) were studied in 0.1-mm cesium bromide cells; Nujol mulls were supported between cesium iodide plates.

In the region 600-33 cm^{-1}, spectra of benzene solutions (1-4 g/100 ml) and Nujol mulls were obtained with a Beckman IR-11 spectrophotometer. Solutions were contained in high-density polyethylene cells of path lengths 0.5, 1, and 2 mm, and mulls were supported between polyethylene plates.

The Perkin-Elmer and Beckman instruments were calibrated with indene and water vapor, respectively. The estimated uncertainty in reported frequencies is less than ±4 cm^{-1} above 800 cm^{-1} and less than ±2 cm^{-1} below 800 cm^{-1}, where spectra were run on an expanded scale.

Results and Discussion

Characterization and Stereochemistry of $Sn(acac)_2F_2$. Pure $Sn(acac)_2F_2$ does not appear to have been prepared previously. Muetterties[34] noted complex formation between acetylacetone and SnF_4 but gave no further data. Smith and Wilkins[14] isolated an impure, sticky solid whose nmr spectrum suggested the presence of *cis*-$Sn(acac)_2F_2$. Cox, *et al.*,[20] reported that $Sn(acac)_2F_2$ exhibits only one Sn-F infrared stretching frequency (581 cm^{-1}) and suggested that this may indicate that the fluorine atoms are in trans positions.

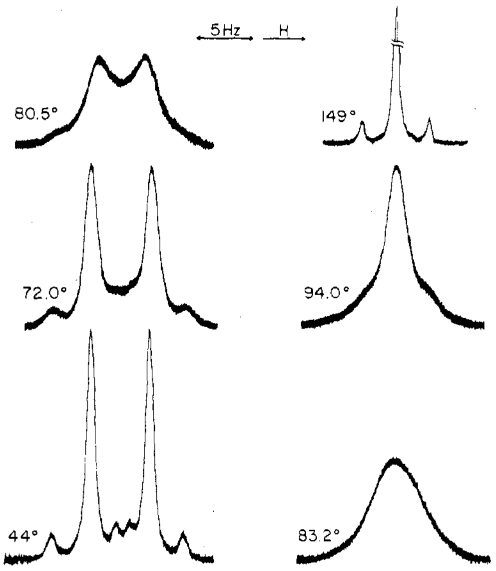

Figure 1. Methyl region of pmr spectra for $Sn(acac)_2Cl_2$ in 1,1,2,2-tetrachloroethane.

The analytically pure $Sn(acac)_2F_2$ prepared in this work was obtained by direct reaction of acetylacetone and SnF_4 in dichloromethane. The compound is monomeric and a nonelectrolyte in nitrobenzene. The following evidence indicates that $Sn(acac)_2F_2$ has the cis configuration in solution: (1) a broad, time-averaged methyl resonance at ambient temperature but two methyl lines of equal intensity at lower temperatures (Table I), (2) two Sn-F stretching frequencies (571 and 586 cm^{-1}) in infrared spectra of dichloromethane solutions (Figure 4 and Table IX), and (3) a dipole moment of 6.1 D in benzene solution.[6] The probable configuration in the solid state is also cis (see section on vibrational spectra below). Thus the stereochemical results for $Sn(acac)_2F_2$ are fully in accord with data for the other $Sn(acac)_2X_2$ complexes;[6,13-19] there is no convincing evidence that any of these compounds exist in the trans configuration. The pmr spectrum of a related benzoylacetonate complex, $Sn(bzac)_2Cl_2$, in 1,1,2,2-tetrachloroethane at 33° exhibits four methyl resonances of approximately equal intensities, consistent with a near-statistical equilibrium mixture of the three geometrical isomers[35] which have chlorine atoms in cis positions.

The ^1H and ^{19}F nmr spectra of $Sn(acac)_2F_2$ exhibit the effects of spin-spin coupling between these nuclei and the more abundant isotopes of tin with spin $^1/_2$, *i.e.*, ^{117}Sn (7.67% abundance) and ^{119}Sn (8.68% abundance). The large values of $J(^{117}Sn-F)$ and $J(^{119}Sn-F)$ (1874 and 1974 Hz) are consistent with direct bonding of fluorine to tin.[36] As was anticipated by Smith and Wilkins,[14] the J values for coupling of $^{117,119}Sn$ to the CH_3 and $C_\gamma H$ protons in $Sn(acac)_2F_2$ are larger than for the other $Sn(acac)_2X_2$ complexes (Table VIII); the coupling constants increase as X varies in the order I < Br < Cl < F, in accord with the relative ability of the halogen atoms to contract the d orbitals of tin.[13]

Rearrangements of $Sn(acac)_2X_2$ Complexes. The methyl region of pmr spectra of the $Sn(acac)_2X_2$ complexes exhibits line broadening owing to rapid exchange of acetylacetonate methyl groups between the two nonequivalent environments of the cis isomer. Representative spectra are presented in Figure 1. Two resonances are observed at low temperatures, and a single, time-averaged resonance is observed at high temperatures. (The weak satellite lines are due to $^{117,119}Sn-CH_3$ coupling.) Characteristic line shape parameters in the coalescence region are given in Tables I-IV along with average values of the lifetime τ, where $\tau = \tau_A/2 = \tau_B/2$ and τ_A and τ_B are mean residence times for an acetylacetonate methyl group in either of the two environments. The τ values were determined by comparing observed spectra of 1,1,2,2-tetrachloroethane solutions with theoretical spectra calculated using the Gutowsky-Holm total line shape equation[32] (see Experimental Section). The concentration independence of the τ values (Table V) demonstrates that the exchange process is first order. Arrhenius activation energies, E_a, and frequency factors, A, were obtained in the usual way from

---

[33] If average values of τ are based on $\Delta_{1/2}$, $\Delta_{3/4}$, $\delta\nu_e$, $\Delta_{1/4}$, and r, rather than on just the first three parameters, the mean errors propagated in the activation parameters for the four $Sn(acac)_2X_2$ complexes are −0.8 kcal/mol in E_a and −2.3 eu in ΔS^*.

[34] E. L. Muetterties, *J. Amer. Chem. Soc.*, **82**, 1082 (1960).

[35] N. Serpone and R. C. Fay, *Inorg. Chem.*, 6, 1835 (1967).

[36] P. A. W. Dean and D. F. Evans, *J. Chem. Soc. A*, 1154 (1968).

Table I. Methyl Pmr Line Shape Parameters and Values of τ for $Sn(acac)_2F_2$[a]

Temp,[b] °C	$\delta\nu_e$,[c] Hz	Line widths,[d] Hz		$10^2\tau$, sec
		$\Delta_{1/2}$	$\Delta_{3/4}$	
9.2	4.74[e]	1.94	1.10	20
13.0	4.56[e]		1.27	15
15.5	4.42[e]		1.43	14
17.2	4.11		1.58	11
19.2	3.98		1.76	10
21.5	3.73		2.04	8.8
24.3	3.18			7.1
26.0	2.81			6.5
31.2		4.85	2.96	4.3
33.3		3.75	2.13	3.3
34.5		3.11	1.82	2.8
38.0		2.52	1.44	2.2
40.4		2.04	1.18	1.9
41.9		1.87	1.09	1.7

$\delta\nu^f = 4.79$ Hz; $T_c{}^g = 28°$

[a] 0.70 *M* in 1,1,2,2-tetrachloroethane. [b] Calculated using the Van Geet equation for methanol. [c] Observed frequency separation. [d] Full line width at designated fraction of maximum amplitude. [e] Not used in determining the average value of τ. [f] Frequency separation in the slow-exchange limit. [g] Coalescence temperature.

Table II. Methyl Pmr Line Shape Parameters[a] and Values of τ for $Sn(acac)_2Cl_2$[b]

Temp,[c] °C	$\delta\nu_e$, Hz	Line widths, Hz		$10^2\tau$, sec
		$\Delta_{1/2}$	$\Delta_{3/4}$	
66.9	5.11	2.30	1.16	12
72.0	4.60		1.62	8.2
74.6	4.14		2.44	6.7
77.3	3.43			5.6
80.5	2.36			4.8
81.7		6.22	4.48	4.4
82.5		5.73	3.73	4.1
83.2		5.60	3.51	4.0
84.9		4.97	2.87	3.5
86.8		4.39	2.54	3.2
88.6		3.74	2.21	2.9
91.3		2.99	1.73	2.4
94.0		2.45	1.43	2.0

$\delta\nu = 5.41$ Hz; $T_c = 82°$

[a] Symbols are defined in Table I. [b] 0.258 *M* in 1,1,2,2-tetrachloroethane. [c] Calculated using the Van Geet equation for 1,2-ethanediol.

Table III. Methyl Pmr Line Shape Parameters[a] and Values of τ for $Sn(acac)_2Br_2$[b]

Temp,[c] °C	$\delta\nu_e$, Hz	Line widths, Hz		$10^2\tau$, sec
		$\Delta_{1/2}$	$\Delta_{3/4}$	
60.7	5.44	1.68	1.03	15
64.2	5.33	1.97	1.14	12
65.2	5.18	2.66	1.29	10
68.8	4.91		1.62	8.3
71.3	4.54		2.28	6.8
74.4	3.97			5.7
77.4	2.40			4.6
79.6		6.41	4.65	4.0
81.3		5.78	3.83	3.9
85.6		4.24	2.48	2.9
87.8		3.20	1.90	2.4
93.0		2.36	1.37	1.8
97.1		2.07	1.23	1.5
102.0		1.50	0.92	1.1

$\delta\nu = 5.63$ Hz; $T_c = 78°$

[a] Symbols are defined in Table I. [b] 0.210 *M* in 1,1,2,2-tetrachloroethane. [c] Calculated using the Van Geet equation for 1,2-ethanediol.

Table IV. Methyl Pmr Line Shape Parameters[a] and Values of τ for $Sn(acac)_2I_2$[b]

Temp,[c] °C	$\delta\nu_e$, Hz	Line widths, Hz		$10^2\tau$, sec
		$\Delta_{1/2}$	$\Delta_{3/4}$	
47.6	5.53	2.14	1.16	13
49.8	5.43	3.07	1.40	10
52.2	5.22		1.67	8.6
53.7	4.96		2.08	7.3
55.6	4.60			6.7
58.3	3.92			5.5
58.6	3.32			4.9
60.0	2.67			4.6
62.7		6.58	4.68	4.2
65.1		5.68	3.56	3.5
66.8		4.86	2.93	3.1
68.8		4.07	2.26	2.6
70.3		3.52	1.97	2.4
73.7		2.67	1.46	1.8

$\delta\nu = 5.83$ Hz; $T_c = 61°$

[a] Symbols are defined in Table I. [b] 0.263 *M* in 1,1,2,2-tetrachloroethane. [c] Calculated using the Van Geet equation for 1,2-ethanediol.

Table V. Concentration Dependence of Lifetimes for Methyl Group Exchange in $Sn(acac)_2X_2$[a]

Compd	Temp, °C	Concn, *M*	$10^2\tau$, sec	Concn, *M*	$10^2\tau$, sec
$Sn(acac)_2F_2$	22.0	0.070	8.4	0.050	8.3
	37.0	0.070	2.4	0.050	2.4
$Sn(acac)_2Cl_2$	81.3	0.513	3.9	0.257	4.0
	93.7	0.513	1.9	0.257	2.0
$Sn(acac)_2Br_2$	71.2	0.402	6.6	0.210	6.6
	86.9	0.402	2.4	0.210	2.5
$Sn(acac)_2I_2$	53.9	0.263	7.3	0.175	7.6
	65.1	0.263	3.5	0.175	3.6

[a] In 1,1,2,2-tetrachloroethane solution.

Table VI. Kinetic Data for Methyl Group Exchange in $Sn(acac)_2X_2$[a] and $Ti(acac)_2X_2$[b] Complexes

	$k_{25°}$, sec^{-1}	E_a, kcal/mol	log *A*	ΔS^*, eu
$Sn(acac)_2F_2$	8.0	13.9 ± 0.7[c]	11.08 ± 0.54	−9.8 ± 2.5
$Sn(acac)_2Cl_2$	1.5×10^{-1}	16.0 ± 0.4	10.92 ± 0.23	−10.6 ± 1.0
$Sn(acac)_2Br_2$	2.1×10^{-1}	15.6 ± 0.4	10.72 ± 0.26	−11.5 ± 1.2
$Sn(acac)_2I_2$	6.3×10^{-1}	15.7 ± 0.7	11.34 ± 0.44	−8.6 ± 2.0
$Ti(acac)_2F_2$	1.6×10^4	11.6 ± 0.5	12.70 ± 0.49	−2.4 ± 2.3
$Ti(acac)_2Cl_2$	6.7×10^2	11.2 ± 0.6	11.03 ± 0.51	−10.0 ± 2.3
$Ti(acac)_2Br_2$	2.3×10^3	11.6 ± 0.4	11.85 ± 0.36	−6.3 ± 1.6

[a] In 1,1,2,2-tetrachloroethane. The temperature dependence of T_2 was taken into account for X = F and I (see Experimental Section). [b] In dichloromethane. The temperature dependence of T_2 was taken into account. Data from ref 4. [c] All errors are random errors estimated at the 95% confidence level.

the least-squares straight line of log *k* *vs.* $1/T$ plots (Figure 2), where $k = (2\tau)^{-1}$ is the first-order rate constant for exchange. Activation entropies, ΔS^*, extrapolated to 25°, were calculated from the relation, $\Delta S^* = R\,[\ln A - \ln (RT/Nh)] - R$. The activation parameters are summarized in Table VI along with extrapolated values of *k* at 25°. Also included in Table VI, for comparison, are kinetic data for the corresponding titanium compounds.

The results for $Sn(acac)_2F_2$ are subject to appreciable systematic error because T_2 is temperature dependent throughout the entire temperature range in which spectra were recorded. This is not a problem for $Sn(acac)_2Cl_2$ and $Sn(acac)_2Br_2$ because, for these complexes, T_2 is temperature independent throughout the coalescence region. $Sn(acac)_2I_2$ is an intermediate case. Systematic errors owing to the temperature dependence of T_2 were minimized by computing theoretical line shapes for a range of T_2's and then comparing the experimental line shape at each temperature with a theoretical line shape computed using a value of T_2 appropriate to that temperature (see Experimental Section). The effect of using a constant value of T_2 throughout the entire temperature range, rather than a variable value, is shown in Figure 3 and Table VII. Use of a fixed value of T_2 produces

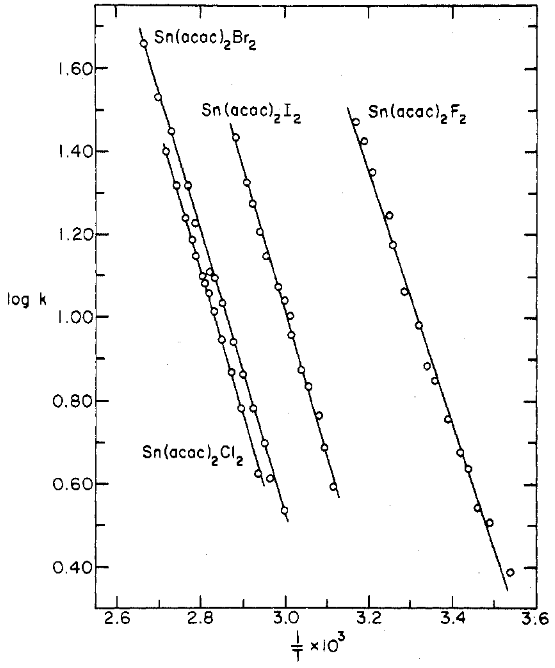

Figure 2. Arrhenius plots for exchange of nonequivalent methyl groups in Sn(acac)$_2$X$_2$ complexes.

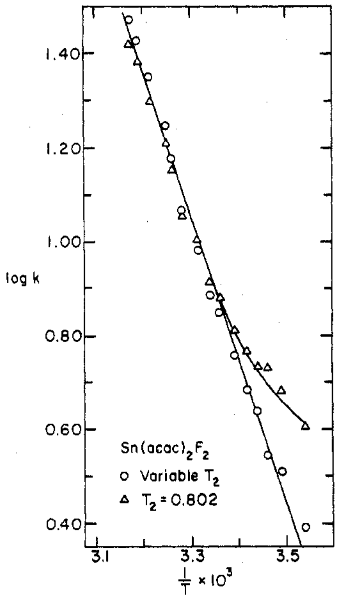

Figure 3. Arrhenius plots for exchange of nonequivalent methyl groups in Sn(acac)$_2$F$_2$. log k values are based on theoretical line shapes calculated assuming (1) a constant value of T_2 = 0.802 sec, the value at the fast-exchange limit (△), and (2) variable values of T_2, appropriate to the temperatures of measurement (○).

curvature in the Arrhenius plots (see Figure 3) with a consequent increase in the "random" errors in E_a and ΔS^* obtained by linear least-squares analysis (compare the errors in Tables VI and VII). It is evident from Table VII that an overestimate of T_2 decreases both E_a and ΔS^*. For Sn(acac)$_2$F$_2$, use of T_2 = 0.802 sec, the value at the fast-exchange limit, would produce very large errors in E_a and ΔS^*, −3.5 kcal/mol and −11 eu, respectively; however, for reasonable estimates of uncertainty in T_2, the systematic errors propagated in E_a and ΔS^* are about ±1 kcal/mol and ±4 eu. For Sn(acac)$_2$I$_2$, the systematic errors are smaller and probably less than the random errors given in Table VI.

The rate of methyl group exchange in Sn(acac)$_2$X$_2$ increases as the halogen varies in the order Cl $\lesssim$ Br < I < F; however, the halogen has only a relatively small effect on the rates. Within experimental uncertainty, the activation parameters are independent of the halogen, except that the activation energy for Sn(acac)$_2$F$_2$ is about 2 kcal/mol lower than for the other Sn(acac)$_2$X$_2$ complexes. It is interesting to compare these results with data for the corresponding titanium compounds.[4] The titanium compounds exhibit a rather similar halogen dependence (Cl < Br < F < I),[2,4] but the tin complexes are considerably more rigid. Rate constants for Sn(acac)$_2$X$_2$ are 10^3-10^4 times smaller than for Ti(acac)$_2$X$_2$, and activation energies are about 4 kcal/mol higher.[37] The activation parameters determined herein for Sn(acac)$_2$Cl$_2$ (Table VI) do not agree with the unusually low values of E_a = 5.4 kcal/mol and log A = 4.3 reported by Kawasaki and Tanaka.[12]

Table VII. Effect of T_2 on Kinetic Data

T_2, sec	Temp, °C a	Temp, °C b	$10^2\tau$, sec	E_a, kcal/mol	ΔS^*, eu
			Sn(acac)$_2$F$_2$		
0.321	17.1	15.5	14	15.2 ± 1.4^c	−5.2 ± 4.5^c
		24.3	7.2		
		34.5	2.6		
		41.9	1.3		
0.371	26.3	15.5	13	14.1 ± 1.3	−9.0 ± 4.4
		24.3	7.1		
		34.5	2.7		
		41.9	1.4		
0.440	35.5	15.5	13	13.0 ± 1.2	−12.8 ± 4.1
		24.3	6.9		
		34.5	2.8		
		41.9	1.5		
0.539	44.8	15.5	12	12.1 ± 1.2	−15.8 ± 4.0
		24.3	6.8		
		34.5	2.8		
		41.9	1.7		
0.802	d	15.5	9.3	10.4 ± 1.1	−21.1 ± 3.7
		24.3	6.6		
		34.5	3.1		
		41.9	1.9		
			Sn(acac)$_2$I$_2$		
0.539	44.8	47.6	13	16.4 ± 0.6	−6.7 ± 1.9
		55.6	6.8		
		66.8	3.0		
0.699	53.9	47.6	12	15.5 ± 0.6	−9.3 ± 1.9
		55.6	6.7		
		66.8	3.1		
0.784	d	47.6	12	15.2 ± 0.6	−10.2 ± 1.9
		55.6	6.6		
		66.8	3.1		

^{a} Temperature at which T_2 was estimated from eq 1. ^{b} Temperature at which spectrum was recorded. ^{c} Random errors; estimated at the 95% confidence level. ^{d} Fast-exchange limit.

Possible mechanisms for configurational rearrangements of dihalobis(β-diketonato)metal complexes have been described in detail in previous papers.[4,35] These include (1) complete dissociation of one diketonate ligand to give a four-coordinate intermediate; (2) dissociation of a halide ion to give a five-coordinate intermediate; (3) rupture of one M-O bond to give a five-coordinate intermediate which has one monodentate diketonate ligand; and (4) twisting mechanisms which effect rearrangement without metal-ligand bond rupture.

---

(37) A small part of this difference may be due to a solvent effect since the Ti(acac)$_2$X$_2$ complexes were studied in dichloromethane and the Sn(acac)$_2$X$_2$ complexes, in 1,1,2,2-tetrachloroethane. However the effect of solvents on the coalescence temperature of Sn(acac)$_2$Cl$_2$[12] suggests that the rate constant ought to change by no more than a factor of 10 on going from dichloromethane to a solvent as closely related as 1,1,2,2-tetrachloroethane.

There is a considerable amount of strong evidence which argues against the intermolecular mechanisms, (1) and (2). Faller and Davison[15] have noted that tin-proton coupling in $Sn(acac)_2Cl_2$ is observed before, during, and after coalescence of the methyl resonances. This is the case for all of the $Sn(acac)_2X_2$ complexes, as is shown by Table VIII, which lists tin-proton coupling constants in the slow- and fast-exchange limits. Observation of tin-proton coupling in the fast-exchange limit implies that a given acetylacetonate ligand remains attached to the same tin atom for a period of time which is long compared with the time scale of methyl group exchange. Further evidence against an acac dissociation mechanism is provided by pmr spectra of equimolar mixtures of $Sn(acac)_2X_2$ and free acetylacetone in 1,1,2,2-tetrachloroethane. In the temperature region of fast exchange (~120°), these spectra show two methyl resonances separated by 0.05-0.13 ppm, a sharp, time-averaged resonance for $Sn(acac)_2X_2$ and a separate, sharp resonance for the enol form of H(acac). The line widths are ~0.5 Hz and show no sign of exchange broadening. These results are in accord with a previous report[38] that the rate of intermolecular acac exchange between $Sn(acac)_2Cl_2$ and H(acac) is too slow to be measured at 105°.

Table VIII. $^{117,119}Sn-^1H$ Coupling Constants (Hz) for $Sn(acac)_2X_2$ in 1,1,2,2-Tetrachloroethane Solution

	Slow exchange		Fast exchange	
Compd	*J*(Sn–CH_3)[a]	*J*(Sn–CγH)[b]	*J*(Sn–CH_3)[c]	*J*(Sn–CγH)[c]
$Sn(acac)_2F_2$	*d*	8.0[h]	7.1	8.4
$Sn(acac)_2Cl_2$	7.2, 6.4[e]	6.2	6.1	6.1
$Sn(acac)_2Br_2$	6.2, 6.0[f]	5.4	5.4	5.2
$Sn(acac)_2I_2$	4.6, 4.6[g]	3.4	4.4	3.4

[a] At the slow-exchange limit, −5 to +10°. [b] At ambient temperature, 37°. [c] At the fast-exchange limit, 105–125°. [d] Satellites are obscured by overlap with central methyl resonances. [e] The first value listed refers to the low-field resonance; the second value, to the high-field resonance. [f] Uncertain due to overlap. [g] Partially obscured by overlap. [h] Intermediate exchange rate for $Sn(acac)_2F_2$ at 37°.

Rearrangement by an intermolecular mechanism involving complete dissociation of a halide ion is ruled out by a study of the pmr spectra of mixtures of two different dihalo complexes. Spectra of equimolar mixtures of $Sn(acac)_2X_2$ and $Sn(acac)_2Y_2$ (X = F, Y = Cl; X = F, Y = Br; X = Cl, Y = I) in 1,1,2,2-tetrachloroethane at the fast-exchange limit exhibit resolution of two of the three time-averaged methyl signals expected for an equilibrium mixture of $Sn(acac)_2X_2$, $Sn(acac)_2Y_2$, and $Sn(acac)_2XY$.[39] If the mechanism of methyl group exchange involved complete dissociation of halide ions, only a single methyl resonance would be observed because of rapid, intermolecular halide exchange. These experiments indicate that the rate of halide exchange is slow compared with the rate of methyl group exchange. Further support for this conclusion is provided by a recent study of the kinetics of ^{36}Cl exchange between tetraethylammonium chloride and $Sn(acac)_2Cl_2$.[40] Exchange is relatively slow and proceeds by a bimolecular mechanism ($k_2 = 1.8 \times 10^{-3}$ l. mol^{-1} sec^{-1} at 15° in $CHCl_3$; the extrapolated value of the first-order rate constant for methyl group exchange at 15° in 1,1,2,2-tetrachloroethane is 6.1×10^{-2} sec^{-1}).

Harrod and Taylor[41] have recently proposed that methyl group exchange in bis(phenoxo)bis(acetylacetonato)titanium(IV) complexes involves formation of a tightly bound ion pair. They suggested that rearrangement could occur by migration of a phenoxide anion across the surface of the resulting five-coordinate, cationic complex, followed by collapse of the ion pair to a neutral six-coordinate species. Applied to the dihalo complexes studied here, this mechanism would permit the rate of methyl group exchange to be faster than the rate of halide exchange if the tight ion pair forms and collapses more rapidly than it dissociates. Sufficient experimental data are not yet available to evaluate Harrod and Taylor's proposal properly. However, we note here that the kinetic data for $Sn(acac)_2X_2$ and $Ti(acac)_2X_2$ (Table VI) are relatively independent of the halogen. An appreciable halogen dependence might be expected for Harrod and Taylor's mechanism since formation of an ion pair involves rupture of an M-X covalent bond; the mean thermochemical Ti-X bond energy in the titanium tetrahalides varies from 71 kcal/mol for X = I to 140 kcal/mol for X = F.[42]

The relative merits of the intramolecular mechanisms (M-O bond rupture and twist mechanisms) will be considered in a later paper in this series. Here we note only two relevant points. (1) The halogen independence of the kinetic data tends to favor a ring-opening mechanism; the size and electronic properties of the halogen would have a direct effect on a twisting process but only a secondary effect on the ease of M-O bond rupture. (2) In the case of dihalobis(benzoylacetonato)titanium(IV) complexes, $Ti(bzac)_2X_2$ (X = F, Cl, Br), twists about a single C_3 axis have been ruled out previously[35] by simultaneous broadening and coalesence of the four methyl resonances of the three *cis*-dihalo isomers. The temperature dependence of the methyl region of the pmr spectrum of $Sn(bzac)_2Cl_2$ is qualitatively similar (T_c = 74°).

Vibrational Spectra. Infrared frequencies for the $Sn(acac)_2X_2$ complexes in solution and in the solid state are listed in Table IX. Solution spectra in the region 620-250 cm^{-1} are presented in Figure 4. Spectra were studied over the frequency range 4000-33 cm^{-1}; however, no bands were found above 1600 cm^{-1}, except for C-H stretching bands, which are not of interest in the present work. The O-H stretching region (3500-3000 cm^{-1}) was carefully examined in order to verify that no water or hydroxyl groups were present.

Kawasaki, *et al.*,[11] and Douek and coworkers[16] have previously investigated some of these complexes (X = Cl, Br, I) in the 4000-400- and 450-80-cm^{-1} regions, respectively. In addition, Faller and Davison[15] have reported infrared and Raman spectra (1400-250 cm^{-1}) for $Sn(acac)_2Cl_2$. Our spectra correspond closely to those of Kawasaki, *et al.*,[11] and Faller and Davison[15] but differ significantly from the spectra of Douek, *et al.*[16] The latter workers have reported many additional bands, some strong, which we have not observed.

---

(38) G. E. Glass and R. S. Tobias, *J. Organometal. Chem.*, 15, 481 (1968).

(39) The resonance of the mixed complex apparently coincides with one of the two sharp but overlapping resonances due to the parent complexes. That the mixed complex is present is indicated by the spectrum of the $Sn(acac)_2Cl_2$-$Sn(acac)_2I_2$ mixture, recorded at ambient temperature after heating to the fast-exchange limit; five of the eight methyl signals expected for a mixture of $Sn(acac)_2Cl_2$, $Sn(acac)_2I_2$, and $Sn(acac)_2ICl$ are resolved. However, the equilibrium $Sn(acac)_2Cl_2 + Sn(acac)_2I_2 \rightleftarrows 2Sn(acac)_2ICl$ appears to be established relatively slowly since the ambient-temperature spectrum, recorded before heating, showed only the four methyl resonances of $Sn(acac)_2Cl_2$ and $Sn(acac)_2I_2$.

(40) J. M. Bull, M. J. Frazer, L. I. B. Haines, and J. Measures, Abstracts, Chemical Society (London) Autumn Meeting, Southampton, 1969, p A14.

(41) J. F. Harrod and K. Taylor, *Chem. Commun.*, 696 (1971).

(42) Computed from enthalpy data in "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1960.

Table IX. Vibrational Frequencies (cm^{-1}) for Sn(acac)$_2$X$_2$ in the Region 1600–33 cm^{-1}

Sn(acac)$_2$F$_2$		Sn(acac)$_2$Cl$_2$		Sn(acac)$_2$Br$_2$		Sn(acac)$_2$I$_2$		Predominant mode[c]
Soln[a]	Nujol[b]	Soln	Nujol	Soln	Nujol	Soln	Nujol	
1575 vs[d]		1575 vs		1572 vs		1570 vs		$\nu_s(\text{C}\underline{\cdots}\text{O})$
1554 vs		1554 vs		1554 vs		1555 vs		
1533 vs		1532 vs		1532 vs		1533 vs		$\nu_{as}(\text{C}\underline{\cdots}\text{C})$
1426 s		1425 s		1425 s		1426 s		CH$_3$ deg def
1365 vs		1362 vs		1362 vs		1360 vs		CH$_3$ sym def
1346 sh		1345 sh		1345 sh		1343 sh		$\nu_{as}(\text{C}\underline{\cdots}\text{O})$
1282 s	1285 s	1282 s	1282 s	1282 s	1280 s	1280 s	1275 s	$\nu_s(\text{C}\underline{\cdots}\text{C})$
			1202 vw					
1194 vw	1200 vw	1193 vw	1195 vw	1194 vw	1196 vw	1192 vw	1193 vw	δ(C–H)
1025 s	1019 s	1025 s	1024 s	1025 s	1020 s	1024 s	1019 s	CH$_3$ rock
937 s	936 s	938 s	936 s	938 s	935 s	935 s	931 s	Complex vibration
							811 s	
801 m	821 s	800 m	809 s	800 m	804 s	800 m	801 s	π(C–H)
688 w	691 m	685 w	684 s	685 w	682 s	679 w	680 s	Ring def
647 w	648 m	647 w	649 m	647 w	646 m	644 w	644 m	$\pi(\text{C}\underline{\cdots}\text{C}\underline{\cdots}\text{C})$
598 s	597 s	590 m	591 s	590 m	590 s	582 m	582 s	Some ν(Sn–O)
			554 w		553 w		554 vw	
463 m	465 s	457 m	461 s	458 m	458 s	448 m	448 m	ν(Sn–O)
420 m	420 s	419 m	422 s	419 m	419 s	416 m	416 s	Ring def ?
	414 sh		416 sh	416 sh	413 sh		411 s	
					333 w			
		283 sh	293 w					
261 sh	266 sh	265 w	260 m		272 sh	269 sh		
						249 s	247 m	
237 sh	221 m	227 m	228 s	233 m	231 s	226 m	215 m	
		193 m	192 s	200 w	196 s			
				179 w	177 w			
	71 m							
586 m	581 s	344 s, b	334 s, b	262 vs	264 s	180 s	185 m	ν(Sn–X)
571 m	563 s						174 m	ν(Sn–X)
247 s	244 s	142 w	134 w					δ(X–Sn–X)

[a] Frequencies above 300 cm^{-1} refer to dichloromethane solutions (7 g/100 ml); frequencies below 300 cm^{-1} refer to benzene solutions (1–4 g/100 ml). [b] In the frequency range 1300–33 cm^{-1}. [c] ν_s, symmetric stretch; ν_{as}, asymmetric stretch; δ, in-plane deformation; π, out-of-plane deformation. [d] s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

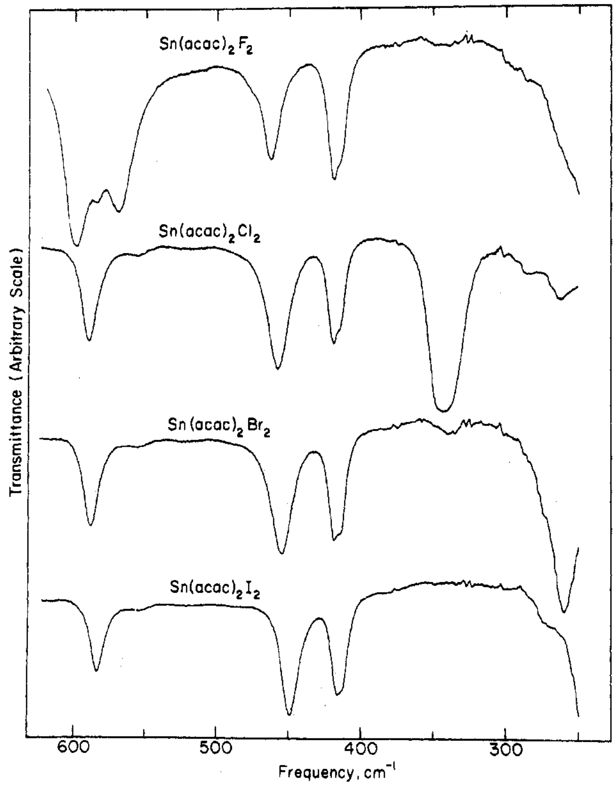

Figure 4. Far-infrared spectra of Sn(acac)$_2$X$_2$ in dichloromethane solution (15 g/100 ml).

The assignments in Table IX are based in large part on previous normal-coordinate treatments of metal acetylacetonates[43,44] and studies of the frequency shifts which occur upon isotopic substitution.[43–47] Assignments for the ligand vibrations follow closely those given earlier[8] for Zr(acac)$_2$X$_2$ and Hf(acac)$_2$X$_2$, except that the 937-cm^{-1} band has now been assigned to a "complex vibration," rather than C-CH$_3$ stretching, on the basis of Junge and Musso's recent studies of ^{13}C-, ^{18}O-, and ^{2}H-labeled Cu(acac)$_2$ and related acetylacetonates.[46] In addition, these labeling studies suggest that the 647-cm^{-1} band is due to an out-of-plane deformation of the $\text{C}\underline{\cdots}\text{C}\underline{\cdots}\text{C}$ portion of the chelate ring.

It is interesting to note that the highest frequency carbonyl band, due to symmetric stretching in a 1:1 (metal-ligand) model, is split into a doublet (1575 and 1554 cm^{-1}). This splitting, which was also observed for the zirconium and hafnium analogs, may result from coupling through the metal atom of the $\nu_s(\text{C}\underline{\cdots}\text{O})$ vibrations of the two chelate rings.

Kawasaki, *et al.*,[11] have assigned the strong band near 450 cm^{-1} to Sn-O stretching and have interpreted the variation in frequency of this band in the series of compounds Sn(acac)$_2$XX′ (X, X′ = alkyl, aryl, and/or halogen) in terms of the inductive effect of X and X′. The 15-cm^{-1} increase in the frequency of this band on going from Sn(acac)$_2$I$_2$ to Sn(acac)$_2$F$_2$ may well be due to an increase in the electron-withdrawing power of the halogen with a consequent in-

---

(43) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 6, 433 (1967), and references therein.

(44) M. M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, 23, 1037 (1967).

(45) S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, 46, 1506 (1967).

(46) H. Junge and H. Musso, *Spectrochim. Acta, Part A*, 24, 1219 (1968).

(47) K. Nakamoto, C. Udovich, and J. Takemoto, *J. Amer. Chem. Soc.*, 92, 3973 (1970).

crease in the strength of the Sn-O bonds. On the other hand, the frequency variation within the series of $Sn(acac)_2X_2$ complexes could result from the variation in mass of the SnX_2 group to which the oxygens are attached. (It is pertinent to note that the frequencies of the 450-cm^{-1} band ($I < Br < Cl < F$) do not correlate with the rates of configurational rearrangement ($Cl < Br < I < F$)). In any case, the halogen-substituent effect does support assignment of the 450-cm^{-1} band to a Sn-O stretching mode rather than an acac ligand vibration. A similar halogen substituent effect on the band occurring at 598-582 cm^{-1} suggests that this normal mode also involves some Sn-O stretching. The frequencies of the 688- and 420-cm^{-1} bands are less dependent on the halogen; ^{18}O- and metal-labeling studies of related compounds suggest that these bands arise from ring deformations involving substantial motion of the oxygens but relatively little metal-oxygen stretching.[45-47]

The assignment of metal-halogen vibrations is evident from a comparison of the spectra in the region below 600 cm^{-1} (see Figure 4 and Table IX). For the cis isomer, both symmetric and asymmetric Sn-X stretching modes are infrared active. These are observed in the spectrum of $Sn(acac)_2F_2$ as unique bands of comparable intensity at 586 and 571 cm^{-1} in solution and at 581 and 563 cm^{-1} in the solid state. In agreement with Douek, *et al.*,[16] we assign the unique, strong bands at 344, 262, and 180 cm^{-1} to Sn-Cl, Sn-Br, and Sn-I stretching modes, respectively. The symmetric and asymmetric components are split by 11 cm^{-1} in the spectrum of solid $Sn(acac)_2I_2$; in general, however, ν_s(Sn-X) and ν_{as}(Sn-X) are not resolved in our spectra when X = Cl, Br, or I. Cox, *et al.*,[20] assigned bands at 334 and 264 cm^{-1} to Sn-Cl stretching in the dichloride, but the latter assignment seems unlikely in view of the small splitting (15-18 cm^{-1}) between the symmetric and asymmetric modes in the difluoride. We believe that the broad band at 344 cm^{-1} (334 cm^{-1} in the solid) results from overlap of the two Sn-Cl stretching modes. Douek, *et al.*,[16] claimed that the second ν(Sn-Cl) can be seen as a shoulder at 338 cm^{-1}, which would make the splitting about 7 cm^{-1}.

The X-Sn-X bending modes, $\nu_5(T_{2g})$, of SnF_6^{2-} and $SnCl_6^{2-}$ have been observed at 252[48] and 158 cm^{-1},[49] respectively. On this basis we assign the strong band of $Sn(acac)_2F_2$ at 247 cm^{-1} to the F-Sn-F bending mode and tentatively assign the 142-cm^{-1} band of $Sn(acac)_2Cl_2$ to the Cl-Sn-Cl bending mode.

The nearly exact correspondence of the solution and solid-state spectra of the $Sn(acac)_2X_2$ complexes indicates that the stereochemistry is cis in the solid state as well as in solution. This is supported by observation of two Sn-X stretching bands in the solid-state spectra of $Sn(acac)_2F_2$ and $Sn(acac)_2I_2$ and by a recent single-crystal X-ray study of $Sn(acac)_2Cl_2$.[50]

Acknowledgments. Support of this research by National Science Foundation Grants GP-16280 and GP-30691X is gratefully acknowledged. We also thank Drs. T. L. Brown and J. A. Ladd for the computer program which was used in the line shape calculations.

Registry No. $Sn(acac)_2F_2$, 25426-91-9; $Sn(acac)_2Cl_2$, 16919-65-6; $Sn(acac)_2Br_2$, 16919-66-7; $Sn(acac)_2I_2$, 16919-67-8; tin(IV) fluoride, 7783-62-2; acetylacetone, 123-54-6.

[48] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 6, 2212 (1967).

[49] I. Wharf and D. F. Shriver, *Inorg. Chem.*, 8, 914 (1969).

[50] E. O. Schlemper, private communication.

Contribution from the Department of Chemistry,
Ithaca College, Ithaca, New York 14850

Aggregation of Nickel(II), Copper(II), and Zinc(II) Derivatives of Water-Soluble Porphyrins

ROBERT F. PASTERNACK,* LYNN FRANCESCONI,[1] DON RAFF,[2] and ESTHER SPIRO

Received February 12, 1973

The solution properties of the nickel(II), copper(II), and zinc(II) derivatives of tetracarboxyphenylporphine (TCPP) and tetra(*N*-methylpyridyl)porphine (TMPyP) have been investigated. At $\mu = 0.1\ M$ and 25°, NiTMPyP, CuTMPyP, ZnTMPyP, and ZnTCPP show no tendency to aggregate. However, under these conditions NiTCPP and CuTCPP dimerize with concentration equilibrium constants of 1.57×10^5 and $1.69 \times 10^5\ M^{-1}$, respectively. The kinetics of the process $2MTCPP \rightleftarrows (MTCPP)_2$ (k_{22}, k_{-22}) have been investigated *via* the temperature-jump technique. For NiTCPP, $k_{22} = 6.2 \times 10^7\ M^{-1}\ sec^{-1}$ and $k_{-22} = 4.0 \times 10^2\ sec^{-1}$; for CuTCPP, $k_{22} = 4.5 \times 10^7\ M^{-1}\ sec^{-1}$ and $k_{-22} = 2.7 \times 10^2\ sec^{-1}$.

Introduction

The chemical and physical properties of metalloporphyrins continue to attract considerable interest because of the vital role some of these species play in biological processes. The porphyrin ligand has a profound influence on the kinetic and thermodynamic properties of the metal center with respect to ternary complex formation and oxidation-reduction behavior.[3] Recent studies have shown that some meso-substituted porphyrins dimerize in aqueous solution;[4,5] the tendency of porphyrins to aggregate is also of considerable biological significance.[6,7]

The properties of water-soluble porphyrins of the meso-substituted variety are dependent on the charge type of the periphery of the molecule. Porphyrins having negative

---

[1] NSF Undergraduate Research Program participant, summer 1972.

[2] In partial fulfillment of the B.A. degree at Ithaca College.

[3] P. Hambright, *Coord. Chem. Rev.*, 6, 247 (1971).

[4] R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Ventura, and L. de C. Hinds, *J. Amer. Chem. Soc.*, 94, 4511 (1972).

[5] R. F. Pasternack, *Ann. N. Y. Acad. Sci.*, in press.

[6] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964.

[7] R. G. Clayton in "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N. Y., 1966.