Contribution from the Departments of Chemistry, Simon Fraser University,
Burnaby 2, British Columbia, Canada, and University of Windsor, Windsor, Ontario N9B 3P4, Canada

Coordination Compounds of Indium. XXIII. Adducts of Cyclopentadienylindium(I) with Boron Trihalides or Trimethylboron

J. G. CONTRERAS and D. G. TUCK*

Received March 28, 1973

Cyclopentadienylindium(I) (cpIn) in chloroform reacts with gaseous BX_3 (X = F, Cl, Br, or CH_3) to yield solid cpIn·BX_3 species, whose structures have been investigated. Vibrational spectroscopy shows that the BX_3 group has the expected trigonal-pyramidal structure. The cyclopentadienyl ligand is in the monohapto (σ-bonded diene) form in the adduct, in marked contrast to the stereochemistry of the parent cpIn.

Introduction

The chemistry of indium(I) has been much less explored than that of the more easily accessible +III state, and the number of compounds presently known is small, and little structural information is available.[1,2] As part of a general study of the lower oxidation states of this element, we have now investigated the possible donor properties of some indium(I) species toward the strongly basic trihalides of boron.

The trihalogenoindate(I) anionic complexes[2] have been shown by vibrational spectroscopy,[1] and supporting force constant calculations,[3] to be isostructural with the trigonal-pyramidal SnX_3^- anions (X = Cl, Br, or I). The interactions of these latter complexes with transition metal ions to give Cl_3Sn-M bonds are well established;[4] by contrast, adduct formation with boron trifluoride is apparently followed by a ligand rearrangement reaction.[5,6] We have found no evidence of complex formation between InX_3^{2-} anions and BF_3, but with the organoindium compound cyclopentadienylindium(I) (cpIn), 1:1 adducts are readily prepared with boron trihalides and trimethylboron. This cyclopentadienyl compound[7] is the only reasonably stable organoindium(I) species presently available, the corresponding methylcyclopentadienyl compound being much more difficult to handle.[8] The analogy between indium(I) and tin(II) species is again useful here, since $Sn(cp)_2$ also forms a 1:1 adduct with BF_3,[9] although we find important differences in the two series of addition compounds.

We have also investigated the interaction between cyclopentadienylindium(I) and the two Lewis acids, chloroform and trifluoroiodomethane, with the aim of determining the basicity of cpIn relative to other donors. Finally, the reaction of both cpIn and cpIn·BX_3 with maleic anhydride has been studied in an attempt to obtain information on the structure of the cyclopentadienyl ring in these two molecules.

Experimental Section

General. Spectroscopic techniques were those described previously.[8] ^1H and ^{19}F nmr spectra were recorded with a Varian A-56/60 spectrometer, operating at frequencies of 60 and 56.4 MHz, respectively.

Indium analysis was by atomic absorption spectroscopy. Boron was determined by a modification of the method described by Taylor.[10]

Preparative. (a) cpIn·BX_3 Adducts. Cyclopentadienylindium(I), prepared by the method of Fischer and Hofmann,[7] was dissolved in freshly distilled dry chloroform, and a small excess of boron trihalide condensed into the vessel *in vacuo*. The mixture was then allowed to warm to room temperature and stirred for approximately 30 min, after which time solvent and unreacted boron trihalide were removed by evaporation. The solid products, which were identified as the appropriate cyclopentadienylindium(I)–boron trihalide (or trimethylboron) adduct, were insoluble in all the common organic solvents (*e.g.*, benzene, carbon, tetrachloride, dichloromethane, chloroform, acetonitrile, nitromethane, and dimethyl sulfoxide) and sensitive to moisture; the ease of hydrolysis, judged qualitatively, was cpIn·BBr_3 > cpIn·BCl_3 > cpIn·$B(CH_3)_3$ > cpIn·BF_3. Analytical and other results for the compounds prepared are given in Table I.

(b) $InCl_3^{2-}$·BX_3 Reaction. The salts Me_2bipy·InX_3 (Me_2bipy = *N,N'*-dimethyl-4,4'-bipyridinium cation; X = Cl, Br, or I) were treated in a similar manner with excess boron trifluoride. After removal of excess BF_3 by pumping, the initial indium(I) compound was recovered unchanged.

(c) Maleic Anhydride Reactions. Maleic anhydride (1 mmol) in dry freshly distilled chloroform was allowed to react with an equimolar quantity of cpIn in chloroform. The solution was stirred for 24 hr at room temperature in a dry atmosphere. The dried yellow-brown solid obtained was shown by analysis to be $C_9H_7O_3In·CHCl_3$ (Calcd: C, 30.2; H, 2.0; In, 29.0. Found: C, 30.1; H, 2.0; In, 28.5). The presence of chloroform in the solid was confirmed by infrared absorption at 2400 (m), 2260 (w), 1485 (s), and 391 cm^{-1} (vw). The stoichiometry $C_9H_7O_3In$ is that expected from a 1:1 Diels–Alder addition of cpIn and maleic anhydride. The compound is insoluble in all the common organic solvents. Infrared absorptions were detected at 3060 (w), 2965 (mw), 2880 (w), 1855 (ms), 1778 (s), 1660 (ms), 1631 (ms), 1360 (mw), 1305 (mw), 1005 (w), 970 (ms), 940 (s), 915 (s), 847 (w), 722 (mw), 675 (w), 665 (mw), and 623 cm^{-1} (m) (plus the chloroform bands noted above). The substance decomposes at 185°, without melting.

In the reaction of maleic anhydride and cpIn·BCl_3, a suspension of the latter in a chloroform solution of the anhydride (1 mmol of each reactant) was again stirred at room temperature for 24 hr. The orange-red solid obtained analyzed as $C_9H_7O_3InBCl_3$, corresponding to the boron trichloride adduct of 7-indiobicyclo[2.2.1]hept-5-ene-1,2-dicarboxylic acid anhydride (Calcd: C, 27.3; H, 1.8; In, 29.1; B, 2.7; Cl, 27.0. Found: C, 27.7; H, 1.8; In, 29.4; B, 2.6; Cl, 26.6), mp 145° dec. This compound is insoluble in all common organic solvents except ether. Infrared absorptions were at 3045 (mw), 2930 (ms), 2880 (ms), 1855 (ms), 1775 (s), 1662 (ms), 1631 (s), 1375 (s, br), 1262 (m), 1002 (w), 970 (mw), 930 (ms), 912 (s), 835 (w), 762 (s), 721 (mw), 675 (w), 665 (w), 622 (mw), 475 (mw), 425 (w), and 325 cm^{-1} (w).

Mass Spectrometry. The mass spectra of the cpIn·BX_3 adducts were recorded on a Hitachi Perkin-Elmer RMU-6D instrument, operating at an exciting voltage of 80 kV and with the inlet temperature shown. In each case, an intense peak was detected at mass 115 (In). Other important peaks (with intensities relative to the In^+ peak) were

---

* Address correspondence to this author at the University of Windsor.

(1) J. G. Contreras, J. S. Poland, and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, in press.

(2) J. G. Contreras and D. G. Tuck, *Chem. Commun.*, 1552 (1971).

(3) J. G. Contreras and D. G. Tuck, *Inorg. Chem.*, 11, 2967 (1972).

(4) J. F. Young, *Advan. Inorg. Chem. Radiochem.*, 11, 92 (1968).

(5) M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Amer. Chem. Soc.*, 88, 1588 (1966).

(6) I. Wharf and D. F. Shriver, *J. Inorg. Nucl. Chem.*, 32, 1831 (1970).

(7) E. O. Fischer and H. P. Hofmann, *Angew. Chem.*, 69, 639 (1957).

(8) J. S. Poland and D. G. Tuck, *J. Organometal. Chem.*, 42, 307 (1972).

(9) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 92, 2577 (1970).

(10) L. H. Taylor, *J. Chem. Soc.*, 820 (1946).

Table I. Analytical Results for cpIn·BX_3 Adducts

			Calcd, %					Found, %				
Compound	Color	Mp, °C	C	H	In	B	X	C	H	In	B	X
cpIn·BF_3	Pale yellow	270 dec			46.4	4.4				46.5	4.6	
cpIn·BCl_3	Orange yellow	190 dec	20.2	1.7	38.6	3.7	35.8	19.9	1.7	38.6	3.7	35.2
cpIn·BBr_3	Dark yellow	286	13.9	1.6	26.7	2.6	55.7	12.3	1.1	26.5	2.6	55.4
cpIn·$B(CH_3)_3$	Pale yellow	164 dec			48.7	4.7				48.3	4.8	

the following. cpIn·BF_3 (160°): 180 (33) (Incp), 126 (21) (InB). cpIn·BCl_3 (200°): 113 (100), 112 (75) (?); 81 (27), 82 (17) (BCl_2); 116 (25), 117 (21), 118 (20) (BCl_3). cpIn·BBr_3 (250°): 275 (100) ($InBr_2$), 203 (52) (InBBr); 137, 139 (48) (?); 171 (33) (BBr_2). cpIn·$B(CH_3)_3$ (25°): 180 (99) (Incp); 41 (20) [$B(CH_3)_2$]. The high temperature required to achieve sufficient vapor pressure for the halide species clearly causes profound molecular decomposition and ligand redistribution before ionization, since only in the case of the trimethylboron compound is $Incp^+$ detected, whereas this ion is the principal mass peak in the spectrum of cyclopentadienylindium(I).[8] The cpIn·$B(CH_3)_3$ compound apparently undergoes simple dissociation into its parent molecules on heating.

Results and Discussion

Interaction of cpIn with $CHCl_3$ and $CF\cdot I$. Abel and his coworkers have shown that the interaction between chloroform and electron pair donors leads to significant changes in both the ^1H nmr resonance[11] and the ν(C-H) [or ν(C-D)] stretching frequency[12] of $CHCl_3$. A solution of cpIn in chloroform (0.8 *M* concentration) had the solvent ^1H resonance at 436 Hz from TMS (*cf.* 434 Hz for the pure solvent, both at ambient temperature). The ν(C-D) frequency of a similar solution of cpIn in $CDCl_3$ was at 2262 cm^{-1}, virtually unchanged from the frequency of pure $CDCl_3$. From these results, we conclude that cpIn is too weak a Lewis base to interact significantly with chloroform. Similar studies were carried out with solutions of cpIn and trifluoroiodomethane, which has also been used as a standard Lewis acid in comparisons of the relative basicities of donor molecules.[13] An important complication in this work was the possible insertion reaction which eventually gives rise to indium monoiodide,[14] but the use of freshly distilled CF_3I prevented this reaction from becoming significant within the time of the measurement. As in the work discussed above, we find that the ^{19}F resonances of the pure CF_3I (−0.2421 KHz from external $CFCl_3$) and of the solution (0.4 *M* cpIn) (−0.2425 KHz) are the same within experimental error.

Table II. B-X Vibrations in Solid cpIn·BX_3 Adducts[a]

Vibrations[b]	X = F	X = Cl	X = Br
ν_{asym}(B-X)	1101, 1065	692, 675	580
ν_{sym}(B-X)	776	375	431
ν_{asym}(BX_3)	521	260	355

[a] Frequencies in cm^{-1}. [b] Approximate description.

Vibrational Spectra of the 1:1 Adducts. (a) Boron Trihalide Moiety. The changes which take place in the vibrational spectra of BX_3 (X = F, Cl, Br, or I) on complex formation, *i.e.*, as the local molecular symmetry of BX_3 changes from D_{3h} to C_{3v}, have been discussed in detail by a number of authors. We follow here the analysis of Swanson and Shriver[15,16] on $CH_3CN\cdot BX_3$ (X = F, Cl, or Br); these authors, who give a number of references to similar work in the literature, have assigned the spectrum of the adducts and have confirmed the assignments by force constant calculations. Such calculations are of considerable importance, in that the potential energy distributions allow identification of those vibrations which are sufficiently pure for meaningful comparison to be made between different adducts. Table II lists the B-X vibrations in cpIn·BX_3, assigned by analogy with the work on the corresponding acetonitrile adducts. Because of the mixing which occurs in the B-X skeletal vibrations, no simple relationships relate the B-X frequencies to the strength of the N-B coordinate bond in a series of BF_3 adducts involving nitrogen donors.[15] Swanson and Shriver do, however, suggest that the frequency separation between ν_{asym} and ν_{sym} in such a series decreases with increasing basicity of the donor. On this basis, the separation of approximately 310 cm^{-1} for the cpIn·BF_3 adduct implies that cpIn is about as strong a donor to BF_3 as is acetonitrile. It does not seem possible to test this conclusion with the results for BCl_3 and BBr_3 because of the lack of suitable results for other donors; the difference $\nu_{asym} - \nu_{sym}$ in fact increases only slightly from cpIn·BF_3 to cpIn·BCl_3.

The spectrum of cpIn·$B(CH_3)_3$ presents a more difficult problem, due to a lack of comparable information on the vibrational spectra of the adduct of trimethylboron. Table II lists the vibrational modes of $B(CH_3)_3$, following Woodward, *et al.*,[17] and our tentative assignments for the analogous modes in cpIn·$B(CH_3)_3$. The frequency shifts are similar to those between BX_3 and cpIn·BX_3. Further work on adducts of $B(CH_3)_3$ is planned.

(b) B-In and cp-In Vibrations. Each of the three boron trihalide adducts prepared has an infrared band at 515 cm^{-1}; in cpIn·$B(CH_3)_3$, this appears at 505 cm^{-1}. We believe this is the stretching mode of the In-B coordinate bond; ν(In-C) for indium-carbon bonds involving simple alkyl groups has been found in the region of 500 cm^{-1}.[18,19] In $In(cp)_3$ and its adducts, ν(In-C) is at ~300 cm^{-1}, and we assign bands at 285 cm^{-1} to this mode in cpIn·BX_3 (X = Cl, Br, or CH_3).

(c) Cyclopentadienylindium Moiety. The infrared spectrum[18] of cpIn shows bands at 3070 (vw), 1430 (w, br), 998 (m), 765 (s), 737 (m), and 720 cm^{-1} (ms). This spectrum is that expected for a pentahapto (centrally σ-bonded) structure, according to Fritz,[20] and thus in agreement with the known structure[21,22] of cpIn. The spectrum of $Incp_3$, on the other hand, is more complex and in agreement with the σ-bonded diene (monohapto) structure for the ligand subsequently demonstrated by X-ray structure analysis.[23]

Those bands in the infrared spectra of the cpIn·BX_3 ad-

---

(11) E. W. Abel, D. A. Armitage, and S. P. Tyfield, *J. Chem. Soc. A*, 555 (1967).

(12) E. W. Abel, D. A. Armitage, and G. R. Willey, *Trans. Faraday Soc.*, 60, 1257 (1964); E. W. Abel, D. A. Armitage, and D. B. Brady, *ibid.*, 62, 3459 (1966).

(13) P. M. Spazianti and V. Gutmann, *Inorg. Chim. Acta*, 5, 273 (1971).

(14) J. G. Contreras and D. G. Tuck, unpublished work.

(15) D. F. Shriver and B. Swanson, *Inorg. Chem.*, **9**, 1406 (1970).

(16) B. Swanson and D. F. Shriver, *Inorg. Chem.*, **10**, 1354 (1971).

(17) L. A. Woodward, J. R. Hall, R. N. Dixon, and N. Sheppard, *Spectrochim. Acta*, **15**, 249 (1959).

(18) H. C. Clark and A. L. Pickard, *J. Organometal. Chem.*, **8**, 427 (1967); **13**, 61 (1968).

(19) J. S. Poland and D. G. Tuck, *J. Organometal. Chem.*, **42**, 315 (1972).

(20) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 240 (1964).

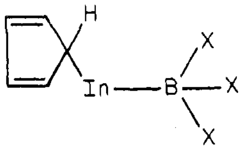
(21) E. Frasson, F. Menegus, and C. Panattoni, *Nature (London)*, **199**, 1087 (1963).

(22) S. Shibata, L. S. Bartell, and R. M. Gavin, *J. Chem. Phys.*, **41**, 717 (1964).

(23) F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *Inorg. Chem.*, **11**, 2832 (1972).

ducts attributed to vibrations of the cyclopentadienyl group are listed in Table III. These spectra are similar to those reported earlier[8] for In(cp)$_3$ and to the spectrum[24] of Hg(cp)$_2$, for which a σ-bonded diene structure is favored. We therefore conclude that the cyclopentadienyl group in cpInBX$_3$ is in the monohapto form.

Structure of the Adducts. The vibrational spectra lead to the formulation of the adducts on the basis of a monomer.



One obvious uncertainty is the magnitude of the C-In-B bond angle. It seems probable from the solubility behavior of these substances that there are appreciable intermolecular interactions between the monomeric units in the solid phase, possibly due to dipole-dipole interactions. An alternative possibility is bonding from the cyclopentadienyl ring of one molecule to the indium of another; such ring-metal interactions have been shown to play an important part in the structure of benzene-AlCl$_3$ and similar adducts.[25]

The change in the mode of In-cp bonding on adduct formation is especially interesting. Cyclopentadienylindium(I) does not undergo an acid-base interaction with CHCl$_3$ and similar species in solution (see above), but does react with stronger Lewis acids such as BX$_3$. Calculations on the energy levels in the cyclopentadienyl radical have shown that the diene form is significantly higher in energy than the symmetrical ground state,[26] and it seems clear that h^1-cpIn must also lie some way above the h^5-cpIn ground state. At the same time, the experimental evidence demonstrates that only in this higher energy structure can sufficient electron donation take place to yield stable adducts with BX$_3$. The total stabilization achieved in forming cpIn·BX$_3$ compensates for the energy required to promote the cyclopentadienyl group into the diene form (and the BX$_3$ group into trigonal-pyramidal symmetry). On the present evidence, cpIn can only act as an electron pair donor if the interaction is sufficiently strong to give access to the diene structure of the ligand. With weaker acids such as chloroform, this is energetically impossible and no acid-base interaction is observed.

One final point is that the cyclopentadienyl ligand apparently favors the monohapto configuration with electropositive main group elements and adopts this structure in indium(III) complexes.[19,23,27] Donation from indium(I) to boron trihalides presumably has the effect of raising the effective positive charge on the metal atom, thus causing the ligand to reorganize into the diene form. It is hoped to discuss the reasons for this effect elsewhere.

Harrison and Zuckerman[9] have prepared the adduct cp$_2$Sn·BF$_3$ analogous to cpIn·BF$_3$. The infrared evidence again demonstrates that the BF$_3$ group has C_{3v} symmetry in this adduct, but these authors conclude that the cyclopentadienyl group is in the pentahapto form in both cp$_2$Sn and the adduct. Mossbauer studies of the tin nucleus show very little change in the tin σ-orbital hybridization on donation and further indicate that the tin lone pair and the cyclopentadienyl rings are at the same relative distance from the tin nucleus in both species. There are therefore significant differences between the cp$_2$Sn and cpIn adducts with BF$_3$, but the reasons for these differences are not immediately clear at present.

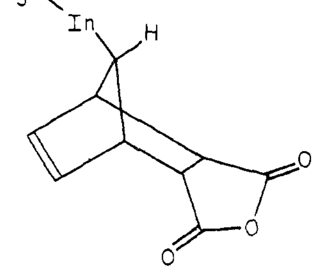
Table III. Vibrations of the Cyclopentadienyl Group in Solid cpIn·BX$_3$ Adducts[a]

X = F	X = Cl	X = Br	X = CH$_3$
3042 w	3040 w	3035 w	3060 m
2958 m		2930 s	2925 m
2855 mw	2880 m, br	2870 s	2855 m
1578 vw	1565 m	1545 ms	1555 s
1305 vw	1305 mw	1297 w	1305 w
1275 m	1263 mw	1252 s	1255 m
1212 vw	1198 mw	1135 s	1215 w
1009 s	1005 mw	1018 s	1005 s
	940 ms	935 m	
	911 ms		
	860 m		888 m
808 m	807 ms		802 ms
758 w	760 mw	786 s, br	758 m
721 ms	718 s	715 m	725 s

[a] Frequencies in cm^{-1}.

Reactions with Maleic Anhydride. Mink, *et al.*,[28] have shown that bis(cyclopentadienyl)mercury undergoes Diels-Alder addition with both maleic anhydride and benzoquinone. In each case, the reaction involves addition of the dione across the diene system of each of the cyclopentadienyl rings, and it has been suggested that this reaction constitutes evidence for the diene structure of the ring.

We have accordingly investigated the reaction of maleic anhydride with cpIn·BCl$_3$ and find that reaction occurs easily to give the product I, identified analytically as the 1:1 Diels-Alder adduct, presumably with the structure



I

The infrared spectrum (see Experimental Section) has strong absorptions at 1778 and 1855 [ν(C=O)], ν(In-B) at 475, and ν(B-Cl) at 675 + 665 and 325 cm^{-1}. These ν(B-Cl) frequencies are slightly lower than those reported in Table II for cpIn·BCl$_3$, presumably because of the change in the mass of the organoindium residue to which the BCl$_3$ group is attached. It is interesting that the cpIn·BCl$_3$ species is significantly stable and that the In→B bond is preserved throughout the Diels-Alder reaction of the ligand.

The diagnostic reliability of this reaction is, however, considerably lessened by the finding that maleic anhydride also reacts with cyclopentadienylindium(I) itself, again yielding a 1:1 product. The infrared spectrum of this substance is almost identical with that obtained from I as far as the vibrations of the organic groups are concerned. The structure of

---

[24] E. Maslowsky and K. Nakamoto, *Inorg. Chem.*, 8, 1108 (1969).

[25] I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1442 (1970), and references cited therein.

[26] See, for example, G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, 3rd ed, Methuen, London, 1968, p 100.

[27] A. F. Berniaz and D. G. Tuck, *J. Organometal. Chem.*, in press.

[28] J. Mink, L. Bursics, and G. Vegh, *J. Organometal. Chem.*, 34, C4 (1972).

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

$h^5\text{-cpIn} \rightleftharpoons h^1\text{-cpIn}$

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 $J(\text{Sn–C}_\gamma\text{H})$ 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).