pathways are allowed on the basis of the line shape analysis: (g) twist mechanisms involving less than *ca.* 50% and from *ca.* 25 to 75% rotation about the real and pseudo C_3 axes of Al(pmhd)$_3$ and Ga(pmhd)$_3$, respectively; (h) bond rupture with formation of SP–axial transition states and products by the primary process; (i) for Al(pmhd)$_3$, bond rupture producing TBP–axial transition states.

The estimate that linkage isomerization of Ga(triac)$_3$ is at least $^1/_{800}$ times as fast as rearrangement of Ga(pmhd)$_3$ is interpreted to mean that the bond rupture path (h) is unlikely for the latter. A similar argument for Al(pmhd)$_3$ is inconclusive and the significant difference in activation entropies and preexponential factors between the two complexes is consistent with the possibility that different mechanisms may be involved. If a bond rupture process were common to the rearrangements of these complexes, the rates would be expected to parallel the average M–O bond energies. The only available bond energies are derived from calorimetric measurements of M(acac)$_3$ complexes. For homolytic fission the mean Al–O and Ga–O bond energies are 63 and 48 kcal/mol.[51] The mean Sc–O bond energy is reported to be 67 kcal/mol.[52] To the extent that these bond energies are accurate and are applicable in the present context, it is seen that the rearrangement rates of M(pmhd)$_3$ do not correlate with them. Ionic size appears to be a more important determinant of rate. Pauling's ionic radii for tripositive Al, Ga, and Sc are 0.50, 0.62, and 0.81 Å, respectively, which is the order of increasing rearrangement rates of M(pmhd)$_3$ complexes. Rearrangement rates in two other series of complexes, M(tfac)$_3$[7] (M = Al, Ga, In) and M(acac)$_2$X$_2$[38,53] (M = Ti, Zr, Hf), appear to follow a similar order. Increased ionic size should decrease steric interactions and facilitate a twist mechanism.

The most important conclusions from the present investigation are presented in the list of excluded and allowed rearrangement mechanisms given above. The arguments just given and the activation parameters in Table IX do not lead to an unambiguous selection of only one of the allowed mechanisms for each complex. The fundamental question as to whether a bond rupture or a twist mechanism is operative cannot, unfortunately, be answered by the results of this study. Investigation of other aluminum complexes, whose properties may permit a clear distinction between twist and bond rupture rearrangement pathways by line shape analysis is under way.[54]

Acknowledgment.—This research was supported by the National Science Foundation under Grant GP-7576X. We thank Dr. R. C. Fay for a preprint of ref 44 prior to its publication, Dr. G. M. Whitesides for valuable discussions, and Mrs. Sandra Eaton for checking rate constant relationships.

[51] R. J. Irving and G. W. Walter, *J. Chem. Soc. A*, 2690 (1969).

[52] J. L. Wood and M. M. Jones, *Inorg. Chem.*, **3**, 1553 (1964).

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

[54] J. R. Hutchison, R. H. Holm, and E. L. Muetterties, work in progress

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AND THE RADIATION LABORATORY,[1] UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA 46556

Mössbauer Spectra of Tin(IV) Complexes of Picolinic and Pyridine-2,6-dicarboxylic Acids

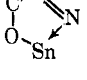
BY DATTA V. NAIK AND COLUMBA CURRAN*

Received June 8, 1970

Mössbauer and infrared spectra have been obtained for a series of tin(IV) complexes containing two picolinate groups, for chloro- and bromotris(picolinato)tin(IV), for di-*n*-butyl(dipicolinato)tin(IV), and for the monohydrates of diphenyl(dipicolinato)tin(IV) and bis(dipicolinato)tin(IV). Quadrupole splittings indicate a trans arrangement of C–Sn–C bonds in all R$_2$Sn(pic)$_2$ and R$_2$Sn(dipic) compounds except diphenylbis(picolinato)tin(IV). A comparison of the isomer shifts of tin(IV) complexes with picolinic acid and 8-hydroxyquinoline reveal a much greater tin s character for trans than for cis C–Sn–C bonds.

Mössbauer spectra of complexes of picolinic acid and pyridine-2,6-dicarboxylic acid (dipicolinic acid) with tin(II) have been reported from this laboratory.[2] Many more varied complexes of tin(IV) with these acids can be prepared and it is of interest to learn something about the electron distribution in these complexes and their configuration from Mössbauer spectra.

It is also of interest to compare tin complexes of picolinic acid with those of 8-hydroxyquinoline. Both sets of complexes contain five-membered



rings. The smaller isomer shift obtained for Sn(ox)$_2$ than for Sn(pic)$_2$[2] suggests that the electrons of the ring O–Sn bond are more effective than those of the COO–Sn bond in shielding the outer unshared tin electrons. The greater variety of tin(IV) complexes affords a more extensive comparison of the O–Sn bonds in these complexes.

[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-736.

[2] M. A. Doskey and C. Curran, *Inorg. Chim. Acta*, **3**, 169 (1969).

TABLE I

INFRARED FREQUENCIES (CM^{-1}) AND MÖSSBAUER PARAMETERS AT 80°K (MM/SEC) WITH A BARIUM STANNATE SOURCE

	% C		% H		OCO stretching						
	Calcd	Found	Calcd	Found	Antisym	Sym	Sn–O	δ	ΔE_Q	Γ_1	Γ_2
$(n\text{-}C_4H_9)_2Sn(pic)_2$	50.00	50.30	5.50	5.72	1666 1624	1348 1383	427	1.45	4.35	1.15	1.20
$(C_2H_3)_2Sn(pic)_2$	46.20	45.41	3.36	3.92	1669	1347		1.18	4.02	1.30	1.27
$(C_6H_5)_2Sn(pic)_2$	55.80	55.19	3.48	3.64	1680	1328	442	0.80	1.94	1.03	1.03
$SnI_2(pic)_2$	23.24	23.39	1.30	1.68	1699	1323	460	0.64	...	1.64	
$SnBr_2(pic)_2$	27.52	28.23	1.53	1.80	1703	1326	465	0.44	...	1.26	
$SnCl_2(pic)_2$	33.20	33.14	1.85	2.15	1704	1326	467	0.31	...	1.42	
$SnBr(pic)_3$	38.20	38.86	2.15	2.44	1692	1332 1346	462	0.18	...	1.46	
$SnCl(pic)_3$	41.50	40.64	2.30	2.37	1691	1333 1348	464	0.15	...	1.61	
$(n\text{-}C_4H_9)_2Sn(dipic)$	45.30	45.56	5.30	5.42	1685	1335		1.46	4.07	1.11	1.16
$(C_6H_5)_2Sn(dipic)\cdot H_2O$	50.00	50.74	3.30	3.72	1692	1332		1.22	3.99	1.10	1.19
$Sn(dipic)_2\cdot H_2O$	36.00	36.82	1.71	1.66	1680	1340		0.20	0.96	1.55	1.53
Na(pic)					*1608*	*1385*					
Na_2dipic					1618	1369					

Experimental Section

Preparation and Purification of Compounds.—Di-*n*-butyltin dichloride, diphenyltin dichloride, divinyltin dichloride, tin(IV) bromide, and tin(IV) iodide were obtained from Alfa Inorganics, Inc. Anhydrous tin(IV) chloride was obtained from J. T. Baker Co. Anhydrous tin(II) bromide was a City Chemical Corp. product. Anhydrous tin(II) chloride and sodium methylate were obtained from Matheson Coleman and Bell, Inc., and dipicolinic acid was from Aldrich Chemical Co. Picolinic acid and tetraethylammonium hydroxide were supplied by Eastman Organic chemicals. The sodium salt of picolinic acid was prepared by mixing methanol solutions of picolinic acid and sodium methylate in a 1:1 mole ratio and evaporating to dryness.

Di-*n*-butyl-, diphenyl-, and diiodobis(picolinato)tin(IV) were prepared by mixing absolute methanol solutions of diorganotin dichloride or tin(IV) iodide and sodium picolinate in a 1:2 ratio. The precipitates obtained in each case were washed with methanol. These and all other compounds were dried under vacuum at 110° unless otherwise indicated. All compounds melted with decomposition. The melting points of the above compounds were 198–200, 280–282, and 222–224°, respectively. An absorption at 170 cm^{-1} in the spectrum of the diiodo compound is attributed to the Sn–I stretching vibration.

Divinylbis(picolinato)tin(IV) was prepared by refluxing a solution of divinyltin dichloride and sodium picolinate in a 1:2 ratio for 4 hr. The clear solution was evaporated to dryness and the residue was extracted with benzene. Evaporation of the benzene solution yielded light yellow crystals which were dried under vacuum at room temperature; mp 200–202°.

Dichloro- and dibromobis(picolinato)tin(IV) were prepared by a method developed by J. F. Lefelhocz in this laboratory. Hot ethanol solutions of tin(II) halide and picolinic acid in a 1:2 ratio were mixed snd stirred overnight exposed to air. The white precipitates obtained were washed with hot absolute ethanol. The dried products, in about 75% yield, had melting points of 271–273 and 262–264°, respectively. Infrared absorptions at 342 cm^{-1} with a shoulder at 360 cm^{-1} and at 222 cm^{-1} with a shoulder at 228 cm^{-1} are attributed to the Sn–Cl and Sn–Br stretching vibrations.

Chloro- and bromotris(picolinato)tin(IV) precipitated after stirring hot methanol solutions of the tin(IV) halide and sodium picolinate in a 1:3 ratio for 1 hr. The white products were washed with methanol; mp 271–273 and 262–264°, respectively. The same products were obtained when the mole ratio of halide to sodium picolinate was 1:2. Equivalent conductances of 2 and 7 cm^2 ohm^{-1} were obtained for these compounds in 0.004 *M* dimethylformamide solutions, compared to 77 cm^2 ohm^{-1} for tetramethylammonium chloride.

***Di-n*-butyl(pyridine-2,6-dicarboxylato)tin(IV), $(n\text{-}C_4H_9)_2$Sn(dipic), and diphenyl(pyridine-2,6-dicarboxylato)tin(IV) monohydrate, $(C_6H_5)_2Sn(dipic)\cdot H_2O$,** precipitated on mixing methanol solutions of the diorganotin dichlorides and $[(C_2H_5)_4N]_2$dipic in a 1:1 ratio. The latter was prepared as a hydrated salt by evaporating a methanol solution of 10% aqueous tetraethylammonium hydroxide and dipicolinic acid in a 2:1 mole ratio. The white products were washed with methanol. As evidenced from infrared spectra, the hydrate did not lose water on heating at 160° for 7 hr. The melting points for these two compounds are 253–255 and 283–285°.

Bis(pyridine-2,6-dicarboxylato)tin(IV) monohydrate was prepared by passing a slow stream of dry air through a refluxing ethanol solution of dipicolinatotin(II)[2] and an excess of dipicolinic acid for 24 hr with stirring. The white precipitate was washed with hot absolute methanol. It did not lose water when heated at 160° for 12 hr and did not melt below 290°.

Infrared and Mössbauer Spectra.—Infrared spectra were obtained in KBr disks using Perkin-Elmer spectrometers, Models 457, 421, and 521. Absorptions attributed to Sn–Br and Sn–I vibrations were obtained with a Beckman RIIC 620 Fourier interferometer spectrometer in polyethylene disks. Mössbauer measurements were obtained with a 1-mCi ^{119m}Sn barium stannate source at room temperature and absorbers at 80°K. The instrumentation and data processing have been described previously.[3] In calibrating, the isomer shift of tin(II) chloride relative to tin(IV) oxide was taken as 4.05 mm/sec;[4] stannic oxide gave an isomer shift of −0.025 mm/sec relative to the barium stannate source. Routine calibrations were made with $(C_4H_9)_2SnCl_2\cdot$*o*-phen, having an isomer shift of 1.57 mm/sec and a quadrupole splitting of 4.08 mm/sec; the latter was shown to be not affected by small changes in sample thickness. The Mössbauer spectrum obtained for di-*n*-butylbis(picolinato)tin(IV) is illustrated in Figure 1. Pertinent infrared data and Mössbauer parameters are listed in Table I. The latter are considered to be accurate to ±0.05 mm/sec with a relative precision of ±0.03 mm/sec.

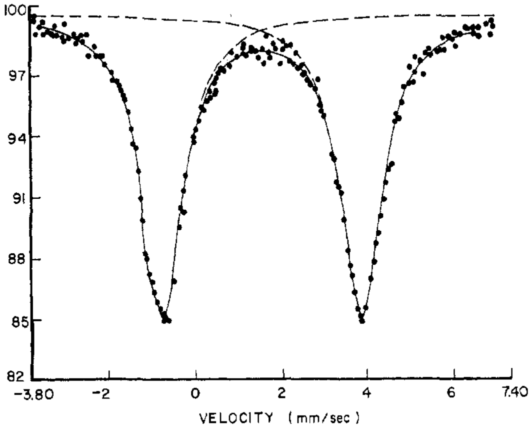


Figure 1.—Mössbauer spectrum of dibutylbis(picolinato)tin(IV).

Discussion of Results

The large quadrupole splittings obtained for $(C_4H_9)_2$-$Sn(pic)_2$ and $(H_2C{=}CH)_2Sn(pic)_2$ indicate a trans ar-

---

(3) M. A. Mullins and C. Curran, *Inorg. Chem.*, **7**, 2584 (1968).

(4) M. A. Mullins and C. Curran, *ibid.*, **6**, 2017 (1967).

rangement of hydrocarbon groups in these compounds, and the relatively low value for $(C_6H_5)_2Sn(pic)_2$ reveals a cis configuration. The difference in configuration for octahedral dialkyl- and diphenyltin(IV) complexes has been reported previously for acetylacetonates,[5] isothiocyanates,[3] dithiocarbamates,[6] and pyridine 1-oxide 2-thiolates.[7] In the event of nearly linear C–Sn–C bonds, the order of splittings, butyl > vinyl, is expected because of the greater tin share of electrons of the tin-carbon bonds in the dibutyl compound.

The C–Sn–C bond angle in crystalline $(CH_3)_2Sn(ox)_2$ is 111°; this compound has a distorted octahedral configuration.[8] The average quadrupole splittings reported by different authors for $(n\text{-}C_4H_9)_2Sn(ox)_2$ and $(C_6H_5)_2Sn(ox)_2$, 2.1 and 1.6 mm/sec, respectively, indicate a C–Sn–C bond angle in each complex closer to 90° than to 180°. These are commonly referred to as cis complexes. The isomer shifts of the bis-picolinato complexes (I_2, 0.64; Br_2, 0.44, Cl_2, 0.31; $(C_6H_5)_2$, 0.80 mm/sec) compare with values for the bisoxinates[9] (I_2, 0.61; Br_2, 0.44; Cl_2, 0.34; $(C_6H_5)_2$, 0.70 mm/sec). These similarities indicate similar polarities for the ring oxygen–tin and COO–Sn bonds. The isomer shift for $(C_4H_9)_2Sn(pic)_2$ is 1.45 mm/sec. Using the same instrument, we have obtained an isomer shift of 0.92 mm/sec for $(C_4H_9)_2Sn(ox)_2$.[3] The difference in these values, 0.5 mm/sec, *indicates a much larger tin s character in trans than in cis C–Sn–C bonds.* We have noted a significantly larger difference in the isomer shifts of octahedral dibutyl- and diphenyltin(IV) compounds when the phenyl groups are cis than when they are trans and have suggested[3] that this may be associated with large C=Sn double-bond character (involving tin 5d orbitals) in *cis*-diphenyltin(IV) complexes. It is now evident that this difference in $\Delta\delta$ is associated with greater tin s character for trans C–Sn–C bonds. Mössbauer data are consistent with the relative ^{119}Sn–CH spin–spin coupling constants, 77.6 and 71.2 cps, reported for $(CH_3)_2Sn(pic)_2$ and $(CH_3)_2Sn(ox)_2$, respectively.[10] The former compound has been shown to be a monomer in bromoform solution.

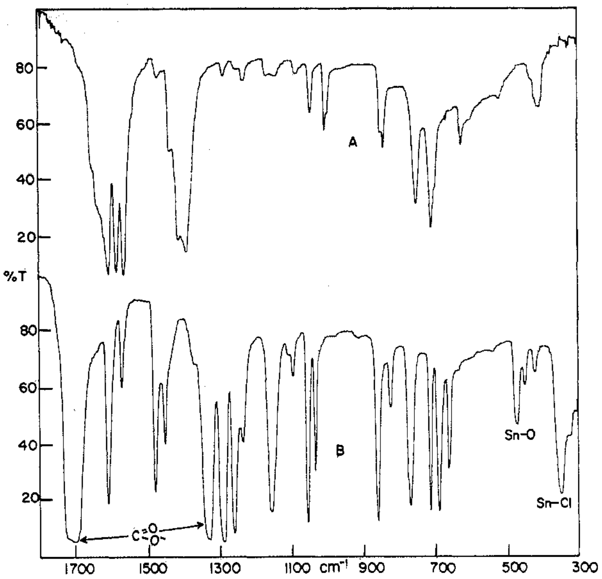


Figure 2.—Infrared spectra in KBr disks: A, sodium picolinate; B, dichlorobis(picolinato)tin(IV).

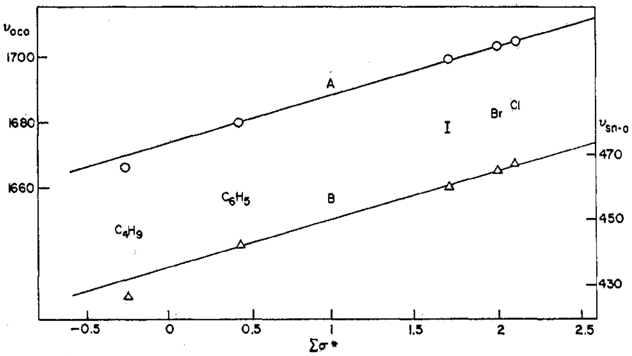
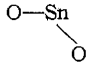


Figure 3.—Variation (cm^{-1}) of ν_{OCO} (antisym), A, and of ν_{Sn-O}, B, with $\Sigma\sigma^*$ for two indicated Y groups in $Y_2Sn(pic)_2$.

The infrared spectrum of $SnCl_2(pic)_2$, Figure 2, is typical of all picolinato complexes except $(C_4H_9)_2Sn(pic)_2$ and $(vinyl)_2Sn(pic)_2$; for these two compounds a coupling between the OCO stretching vibrations complicates the spectra in the 1650- and 1350-cm^{-1} regions. There was no significant change in these spectra from the disks to Nujol mulls. The assignment of Sn–O stretching vibration frequencies, Table I, has been made from a comparison with infrared spectra of $(C_4H_9)_2Sn(benzoate)_2$ and $(C_4H_9)_2Sn(benzoate)_2\cdot o$-phen, which show strong absorptions at 450 and 427 cm^{-1}, respectively, not present in the spectra of sodium benzoate, ethyl benzoate, and $(C_4H_9)_2SnCl_2\cdot o$-phen. The broad absorptions may well be envelopes of unresolved antisymmetric and symmetric Sn–O stretching frequencies; single, broad Sn–O absorptions were also observed for $(C_4H_9)_2Sn(2\text{-SpyO})_2$ and $(C_6H_5)_2Sn(2\text{-SpyO})_2$, which have cis



bonds.[7] Figure 3 reveals that both the antisymmetric OCO and the Sn–O stretching vibration frequencies for the $SnX_2(pic)_2$ and $(C_6H_5)_2Sn(pic)_2$ complexes are linear functions of the Taft $\Sigma\sigma^*$ constants[11] for the phenyl and halogen substituents. The frequencies for the dibutyl complex are observed to fall below these lines. This is consistent with the conclusion from Mössbauer data that the Sn–O bonds in this complex have less tin s character—a bond weakening factor.

The lower isomer shifts obtained for the $SnX(pic)_3$ than for the $SnX_2(pic)_2$ complexes are expected for an increase in coordination number. Seven-coordination is indicated for tin in $SnCl(pic)_3$ by infrared spectra. The OCO absorption at 1691 cm^{-1} and the high-frequency ring vibration at 1603 cm^{-1} (compared to 1583 cm^{-1} for sodium picolinate) indicate three O–Sn and three N–Sn bonds, and the absorption at 335 cm^{-1} is attributed to the Sn–Cl vibration. In the spectrum of $SnBr(pic)_3$ other absorption in the 250-cm^{-1} region pre-

---

(5) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, 390 (1968).

(6) B. W. Fitzsimmons, A. A. Owusu, N. J. Seeley, and A. W. Smith, *J. Chem. Soc. A*, 935 (1970).

(7) D. Petridis, F. P. Mullins, and C. Curran, *Inorg. Chem.*, **9**, 1270 (1970).

(8) E. O. Schlemper, *ibid.*, **6**, 2012 (1967).

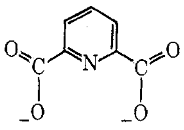
(9) K. M. Ali, D. Cunningham, M. J. Frazer, J. D. Donaldson, and B. J. Senior, *J. Chem. Soc.*, 2836 (1969).

(10) M. M. McGrady and R. S. Tobias, *J. Amer. Chem. Soc.*, **87**, 1909 (1965).

(11) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, pp 591, 595.

vents a definite assignment of the Sn–Br vibration. Seven-coordination for tin in $SnXA_3$, where A is a bidentate ligand, appears to be rather common. The crystal structures for three such compounds have been determined recently: monochloro- and monohydroxotris(tropolinato)tin(IV)[12] and $CH_3Sn(S_2CN(C_2H_5)_2)_3$.[13] The isomer shift for $SnCl(pic)_3$, 0.15 mm/sec, compares with the value 0.11 mm/sec for $SnCl(ox)_3$.[9]

Resonance stabilization is expected to preserve a planar configuration for the dipicolinate anion



and result in its functioning as a tridentate ligand. The crystal structure of Ag(dipic)(dipicH$_2$) reveals this planarity and tridentate function.[14] The high frequencies for the antisymmetric OCO vibrations in the spectra of the three dipicolinato complexes indicate that the carbonyl groups are not involved in chelation or intermolecular CO–Sn bonding. The large quadrupole splittings, 4.07 and 3.99 mm/sec, obtained for $(C_4H_9)_2Sn(dipic)$ and $(C_6H_5)_2Sn(dipic)\cdot H_2O$, respectively, indicate trans C–Sn–C bonds in these compounds. The difference in the isomer shifts for the two compounds is only 0.24 mm/sec, compared to the difference of 0.65 mm/sec between *trans*-$(C_4H_9)_2Sn(pic)_2$ and *cis*-$(C_6H_5)_2Sn(pic)_2$.

The geometry of the ligand and the reluctance of tin for seven-coordination unless forced by chelation suggest that the water molecule in $Sn(dipic)_2\cdot H_2O$ is not directly bonded to tin. The crystal structure of Ag(dipic)(dipicH$_2$) reveals linear N–Ag–N bonds, with the planes of the two ligands intersecting at an angle of 85°. It is expected that the N–Sn–N bond angle in $Sn(dipic)_2\cdot H_2O$ will also be close to 180°. The quadrupole splitting for this compound, 0.96 mm/sec, is probably associated with the maximum in electron density along the N–Sn–N axis. The isomer shift for this compound, 0.20 mm/sec, compares with 0.31 mm/sec for $SnCl_2(pic)_2$. Assuming similar orbital hybridization for these two compounds, the data suggest a greater polarity for the Sn–O than for the Sn–Cl bond.

[12] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3636 (1970).

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

[14] M. G. B. Drew, G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

Contribution from the School of Chemistry,
Rutgers University, New Brunswick, New Jersey 08903

Mössbauer Spectroscopy of Organometallic Compounds. Alkyl- and Aryltin Cyanates and Related Molecules

By K. L. LEUNG[1] and R. H. HERBER*

Received July 13, 1970

A number of organotin cyanates have been prepared and characterized by infrared and Mössbauer spectroscopy with respect to the nature of the NCO group in such molecules. From the Mössbauer results for $Sn(NCO)_6^{2-}$ and related octahedral hexahalogen complexes it is possible to derive a group electronegativity for a nonbridging cyanate group, and this value (9.68 on the Mulliken scale) can be compared to the value obtained from systematics of trimethyltin halides and pseudohalides (9.16). The infrared and Mössbauer data are interpreted in terms of a nonbridging NCO ligand for trialkyltin and dialkyltin cyanates, except for the presence of a weakly bridging group in the case of $(CH_3)_3SnNCO$. In the latter case, both the temperature-dependent Mössbauer resonance-effect magnitude and the presence of the Sn–$(CH_3)_3$ symmetric vibration in the infrared spectrum show that the trimethyltin moiety is nonplanar and that this molecule can be envisioned as having a distorted pyramidal structure with covalent cyanate groups bonded to the metal atom.

I. Introduction

As part of a continuing series of studies of organotin halides and pseudohalides by Mössbauer spectroscopy,[2] a detailed investigation has been undertaken to elucidate the nature of the cyanate[3] ligand in organotin compounds. Although such molecules have been the subject of an extensive literature in recent years, Mössbauer spectroscopy can serve to provide additional information concerning the structure, symmetry, and bonding in these materials and to shed some light on the character of the ligands attached to the heavy-metal atom. Moreover, such spectroscopic measurements can give information concerning the integrity of the molecular structure in solution compared to neat (solid) samples. The present study on organotin cyanates was undertaken with these aims in mind.

II. Experimental Section

The compounds used in the present study (all of which have been reported previously) were prepared by literature methods with only minor modifications. $[(CH_3)_4N]_2Sn(NCO)_6$ and $[(C_2H_5)_4]_2SN(NCO)_6$ were prepared by the method of Forster and Goodgame[4] by allowing the corresponding hexachloro salt to react with AgNCO in acetone. The organotin cyanates were obtained by the reaction between the corresponding organotin halide (chloride or bromide) and silver cyanate in a suitable

---

[1] Henry Rutgers Scholar, 1969–1970. NSF Senior Research Participant, supported in part by Grant 27-1233.

[2] For the preceding paper in this series, see H.-S. Cheng and R. H. Herber, *Inorg. Chem.*, **9**, 1686 (1970).

[3] In this and the subsequent discussion the term *cyanate* has been used for the NCO fragment without implications concerning the details of the bonding of this ligand, although the spectroscopic data for nonbridging NCO moieties clearly point to the formation of metal-to-nitrogen bonds, so that the group in question is, in fact, an *isocyanate* entity in these compounds.

[4] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1286 (1965).