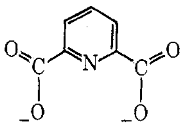
vents a definite assignment of the Sn–Br vibration. Seven-coordination for tin in $SnXA_3$, where A is a bidentate ligand, appears to be rather common. The crystal structures for three such compounds have been determined recently: monochloro- and monohydroxotris(tropolinato)tin(IV)[12] and $CH_3Sn(S_2CN(C_2H_5)_2)_3$.[13]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

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

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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

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[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).

TABLE I

EXPERIMENTAL PARAMETERS FOR THE ORGANOTIN CYANATES DISCUSSED IN THE TEXT

Sample	Mp or bp, °C	IS,[a] mm/sec	QS,[b] mm/sec	ν_a,[c] cm^{-1}
$(CH_3)_3SnNCO$	105–107	1.36	3.31	2220
$(CH_3)_3SnNCO$ in THF		1.25	3.11	
$(C_2H_5)_3SnNCO$	53–54	1.46	3.29	2208
$(C_3H_7)_3SnNCO$	100 (0.03 mm)	1.48	3.33	2214
$(n\text{-}C_4H_9)_3SnNCO$	125–130 (0.2 mm)	1.36	3.19	2189
$(n\text{-}C_4H_9)_3SnNCO$ in THF		1.42	3.15	
$(C_6H_5)_3SnNCO$	73–75	1.30	2.47	2201
$(C_6H_5CH_2)_3SnNCO$	119–120	1.51	2.85	2205
$(CH_3)_2Sn(NCO)_2$		1.29	2.84	2204
$(n\text{-}C_4H_9)_2Sn(NCO)_2$	48–50	1.31	3.15	2194, 2173
$(i\text{-}C_4H_9)_2Sn(NCO)_2$	93–95	1.45	3.51	2202, 2178
$(C_6H_5CH_2)_2Sn(NCO)_2$	142–145	1.12	2.21	2185
$[(CH_3)_4N]_2Sn(NCO)_6$	>350	−0.053	0	2186
$[(C_2H_5)_4N]_2Sn(NCO)_6$	>350	−0.097	0	

[a] With respect to the centroid of the $BaSnO_3$–$BaSnO_3$ spectrum at 294°K. All values ±0.03 mm/sec. [b] All values ±0.05 mm/sec. [c] Ir spectra taken as Nujol mulls (solids) or neat liquids at ~25°.

solvent.[5–9] When possible, the (liquid) bromides were used to facilitate the isolation of the solid product from unreacted starting material. Rigorously dried benzene was used as a reaction medium for the preparation of the trimethyl, triethyl, tripropyl, tributyl, and tribenzyl compounds; ether for the triphenyltin cyanate; petroleum ether (bp 60–90°) for the di-*n*-butyl- and diisobutyltin cyanates; acetonitrile for the dimethyltin compound, and ethanol for the dibenzyltin compound. Products were purified by sublimation (trimethyl, triethyl, and dimethyl), distillation under reduced pressure (tripropyl and tributyl), or recrystallization from petroleum ether (triphenyl, tribenzyl, di-*n*-butyl, and diisobutyl) or ethyl acetate–alcohol mixtures (dibenzyl). The physical properties of all of the compounds obtained by these methods were in good agreement with literature values, except for the melting point of triphenyltin cyanate. The value of this temperature has been reported as 146–148° by Beck and Schuierer,[10] 100–103° by Mufti and Poller,[5b] and 98–99° by Srivastava and Tandon.[11] The product obtained in the present study from the reaction of triphenyltin chloride with silver cyanate in ether and identified as $(C_6H_5)_3Sn(NCO)$ by elemental analyses was found to have a melting point of 73–75°. The product recrystallized from petroleum ether (bp 52–59°) gave a melting point of about 73–74°.

A number of unsuccessful attempts were made to synthesize the elusive compound $Sn(NCO)_4$, which had been the subject of a number of earlier studies. Among the methods tried were: (i) the reaction of $SnCl_4 \cdot 5H_2O$ with AgNCO in a Soxhlet extractor, using benzene as a solvent and allowing the reflux to continue for 48 hr; (ii) the same method using KNCO and acetone under nitrogen; (III) refluxing SnI_4 with AgNCO; (iv) refluxing anhydrous $SnCl_4$ with AgNCO in acetonitrile in a drybox; and (v) refluxing thallous cyanate with anhydrous $SnCl_4$ in acetonitrile–benzene in a drybox. None of these attempts led to the isolation of the tetracyanate, and there is some evidence that reduction of tin to the stannous oxidation state occurred during the synthetic procedure, even under rigorously anhydrous conditions. In the presence of air, a number of hydrolysis products (including hydrated SnO_2) were recovered from the reaction mixture, and it is possible that the $Sn(NCO)_4$, if formed at all, is extremely labile in the presence of air and/or water vapor and that reaction is very rapid under aerobic conditions.

Mössbauer spectra were obtained at 80 ± 2°K using the constant-acceleration type of spectrometer described earlier. The samples were prepared for spectroscopic examination either as powdered solids in a copper sample holder, sandwiched between two layers of aluminum foil, or as neat liquids in a copper sample holder which had been fitted with two 5-mil thermoadhesive Mylar[12] windows, into which the sample could be injected by means of a hypodermic syringe. In a typical spectrum, at least 5 × 10^5 counts were accumulated per channel. Since the resonance-effect magnitude (ϵ) in these samples is typically about 5% or greater at liquid nitrogen temperature, the signal-to-(statistical) noise ratio usually exceeded ~30, although significantly lower values of this ratio were obtained in some of the high-temperature runs (*vide infra*) in which the value of ϵ may be 1% or less.

Calibration of the velocity transducer was effected using a $Pd(^{57}Co)$ source in conjunction with an NBS standard[13] 0.8-mil metallic iron absorber, and a value for the ground-state splitting in metallic iron of 3.9177 mm/sec at 24.1°.[14] Only the inner four lines of the six-line magnetic hyperfine spectrum of metallic iron were used in this calibration, since all of the information pertinent to the present study falls within the limits defined by this portion of the spectrum. All isomer shifts quoted in the present study are with reference to the center of a $BaSnO_3$–$BaSnO_3$ spectrum at room temperature. This reference point—which also defines the zero velocity point of the Doppler motion—is identical, within the quoted experimental error, with that for SnO_2, and consequently all isomer shift data here reported are directly comparable to other data reported with respect to SnO_2.

The temperature dependence of the resonance effect in $(CH_3)_3SnNCO$ was studied using a variable-temperature dewar which could be held within ±2°K over periods of 24–48 hr.[15] Temperature measurements and control in this dewar were effected using a calibrated platinum-resistance thermometer and a proportional controller to monitor the current input to the heater block of the sample holder.

Infrared measurements in the carbonyl region were obtained on a Perkin-Elmer Model 21 or Model 137 double-beam spectrometer, using NaCl optics. High-resolution spectra in the range 650–400 cm^{-1} were obtained on a Perkin-Elmer Model 225 grating spectrometer.

The mass spectrum of $(CH_3)_3SnNCO$ was obtained using a Hitachi Perkin-Elmer RMU-7 double-focusing high-resolution mass spectrometer provided with a heated solid sample inlet system.

III. Results and Discussion

Inasmuch as no definitive examples of oxygen-bonded organotin cyanates have been reported, the question of the metal–ligand interaction (*i.e.*, whether for a nonbridging cyanate group Sn–N or Sn–O bonding occurs) cannot be decided unambiguously on the basis of the spectroscopic evidence alone. However, in the context of the available infrared and structural data[16] on organotin thiocyanates, the observations of the CN asymmetric stretch at ~2200 cm^{-1} in the organotin compounds [except for $(CH_3)_3SnNCO$] reported in Table I,

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(5) (a) H. H. Anderson and J. A. Vesta, *J. Org. Chem.*, **19**, 1300 (1954); (b) A. S. Mufti and R. C. Poller, *J. Chem. Soc.*, 5055 (1965).

(6) J. S. Thayer and D. P. Strommen, *J. Organometal. Chem.*, **5**, 383 (1966).

(7) V. A. Chauzov, O. V. Litvinova, and Yu. I. Baukov, *Zh. Obshch. Khim.*, **36**, 952 (1966).

(8) T. N. Srivastava and S. N. Bhattacharya, *J. Inorg. Nucl. Chem.*, **29**, 1873 (1967).

(9) C. J. Cattanach and E. F. Mooney, *Spectrochim. Acta, Part A*, **24**, 407 (1968).

(10) W. Beck and E. Schuierer, *Chem. Ber.*, **97**, 3517 (1964).

(11) T. N. Srivastava and S. K. Tandon, *Indian J. Appl. Chem.*, **26**, 171 (1963).

(12) Type GT-300, G. T. Schjeldahl Co., Northfield, Minn.

(13) NBS Standard reference material, No. 138.

(14) J. J. Spijkerman, J. R. DeVoe, and J. C. Travis, *Nat. Bur. Stand. (U. S.), Spec. Publ.*, **No. 260-20** (1970).

(15) Janis Model DT-274, Janis Research Co., Stoneham, Mass. 02180. The authors are indebted to Professor R. Axtman and Dr. Y. Hazony for the use of this equipment in the present study.

(16) R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, **22**, 611 (1970); M. Wada and R. Okawara, *ibid.*, **8**, 261 (1967).

and the medium strong band at ~480 cm^{-1} (Figure 5) in $(CH_3)_3SnNCO$ which may be assigned to the NCO bending mode may be taken as indicative of a strong Sn–N bonding interaction. Based on the assumed correctness of this conclusion it is inferred that all of the compounds here reported have, in fact, the *iso*cyanate structure.

The Mössbauer parameters for the compounds in question—as well as other physical parameters—are summarized in Table I, and a typical Mössbauer spectrum is shown in Figure 1. The line widths (fwhm) observed in these spectra are ~0.95–1.20 mm/sec, but since no particular effort was made to control sample thickness, such values can only be used as indirect evidence concerning the absence of unresolved hyperfine interactions. With the exception of the two hexacyanato salts, the observed isomer shifts fall into the range 1.1–1.5 mm/sec with respect to $BaSnO_3$ showing unambiguously that all of the compounds discussed in the present context can be considered formally as derived from Sn(IV) in which the primary hybridization involves the metal 5s and 5p orbitals. All of the organotin cyanates show an appreciable quadrupole splitting at 80°K, and the two resonance lines are readily resolved in the data analysis.

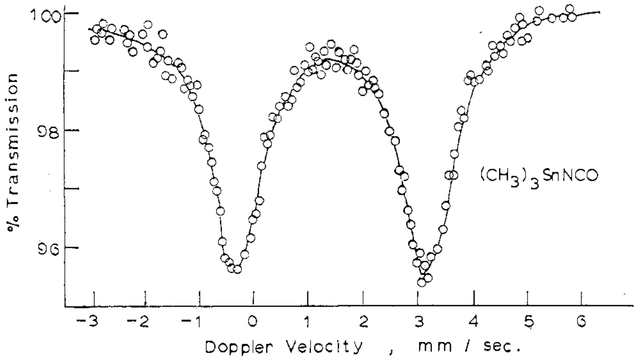

Figure 1.—Mössbauer spectrum of $(CH_3)_3SnNCO$ at 78°K. The Doppler velocity is reported with respect to the center of a $BaSnO_3$–$BaSnO_3$ spectrum at 294°K.

In contrast, as expected, the Mössbauer spectra of $[(CH_3)_4N]_2Sn(NCO)_6$ and $[(C_2H_5)_4N]_2Sn(NCO)_6$ consist of a singlet, in consonance with the octahedral structure of the $Sn(NCO)_6^{2-}$ moiety proposed earlier. From the isomer shift systematics of octahedral hexahalo- and hexapseudohalotin(IV) complexes reported[17] earlier, it is possible to estimate a group electronegativity of the -NCO ligand, using the Mulliken electronegativity scale, calibrated from the data of Politzer[18] and developed in a recent study of mixed-halogen complexes of tin by Clausen and Good.[19] The value so derived is $\chi_{NCO(t)} = 9.68$, and this value must be considered descriptive of the group electronegativity of a terminal (*i.e.*, nonbridging) cyanate group bonded to tin. Ligands of such electronegativities (corresponding to ~3.4 on the Pauling scale) are known to be capable of forming bridging entities when bonded to tin, and a large number of such halogen- and pseudohalogen-bridged compounds—identified on the basis of X-ray diffraction, infrared, or Mössbauer data—have been reported in the literature.[20–24] This bridging behavior leads, of course, to pentacoordinated metal atoms in the case of R_3SnX and hexacoordinated metal atoms in the case of R_2SnX_2.

In this context, the quadrupole splitting which is observed in the dialkyltin dicyanates gives a significant clue to the nature of the NCO group. It has been previously noted[25,26] that for strongly bridging ligands, the quadrupole splitting which is observed for the trans octahedral complexes, R_2SnX_2, was approximately 3.7–4.1 mm/sec for the case R = CH_3. In dimethyltin dithiocyanate, the QS has been reported as 3.87 mm/sec. The crystal structure of this compound has recently been reported[27,28] and is found to consist of linear $(CH_3)_2Sn$ fragments bonded at right angles by linear NCS units. The Sn–N distance is found to be 2.139 (13) Å and the Sn–S distance 3.202 (7) Å.

In contrast, the quadrupole splitting observed in the present study for $(CH_3)_2Sn(NCO)_2$ is 2.84 mm/sec and for $(C_2H_5)_2Sn(NCO)_2$ is 3.15 mm/sec at liquid nitrogen temperature [compared to 3.96 mm/sec for $(C_2H_5)_2Sn(NCS)_2$, 4.65 mm/sec for $(CH_3)_2SnF_2$, and 4.18 mm/sec for $(CH_3)_2Sn[(C_6H_5)_2PO]_2$,[29] all of which have been assigned a trans octahedral structure]. On this basis, it is clear that the NCO ligand does not act as a bridging group in the dialkyltin dicyanates and that the structures of these molecules must be envisioned as being distorted tetrahedra. The field gradient which is observed (giving rise to the quadrupole splittings cited above) arises both from the departure from tetrahedral symmetry and the p-electron asymmetry in the σ-bonding framework of these molecules. The latter effect occurs as a consequence of the formulation[30] that p character will be concentrated in the metal sp^3 orbital involved in bonding to the more electronegative (NCO) ligand and s character in the orbital directed to the more electropositive (R) ligand.

The Mössbauer data for the trialkyl- and triaryltin cyanates summarized in Table I are consistent with the above conclusion that the NCO ligand does not participate in a strong bridging interaction between two adjacent tin atoms. Alcock and Timms[31,32] have recently carried out an X-ray diffraction study of tribenzyltin acetate and tricyclohexyltin acetate and found that these two molecules exhibit trigonal-bipyramidal and distorted tetrahedral configurations, respectively. Since both of these molecules have the same carboxyl moiety involved in the bonding, the most obvious explanation for the bidentate nature of the ligand in one case (R = benzyl) and the monodentate nature of this

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[17] R. H. Herber and H.-S. Cheng, *Inorg. Chem.*, **8**, 2145 (1969).

[18] P. Politzer, *J. Amer. Chem. Soc.*, **91**, 6235 (1969).

[19] C. A. Clausen, III, and M. L. Good, *Inorg. Chem.*, **9**, 817 (1970).

[20] H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 85 (1963); I. R. Beattie, G. P. McQuillan and R. Hulme, *Chem. Ind.* (*London*), 1429 (1962).

[21] H. Kriegsman and S. Pischtschan, *Z. Anorg. Allg. Chem.*, **308**, 212 (1961); **315**, 283 (1962).

[22] R. Okawara and K. Yasuda, *J. Organometal. Chem.*, **1**, 356, 360 (1964).

[23] E. O. Schlemper and D. Britton, *Inorg. Chem.*, **5**, 507 (1966).

[24] R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, **21**, 115 (1970).

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

[26] R. R. Berrett and B. W. Fitzsimmons, *J. Chem. Soc. A*, 1679 (1967).

[27] R. A. Forder and G. M. Sjeldrick, *J. Organometal. Chem.*, **22**, 611 (1970).

[28] D. Britton and Y. M. Chow, *Inorg. Chem.*, in press.

[29] N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc. A*, 1679 (1967).

[30] H. A. Bent. *J. Inorg. Nucl. Chem.*, **19**, 32 (1961); *Chem. Rev.*, **61**, 275 (1961).

[31] N. W. Alcock and R. E. Timms, *J. Chem. Soc.*, 1873 (1968).

[32] N. W. Alcock and R. E. Timms, *ibid.*, 1876 (1968).

ligand in the other (R = cyclohexyl) invokes the differences in the steric requirements of the two organic groups. On this basis it is considered unlikely that the cyanate ligand could act as a bidentate moiety in $(C_6H_5)_3SnNCO$, and this molecule, as well as the related tribenzyltin cyanate for which the quadrupole splitting is 0.38 mm/sec larger (but still much smaller than is normally observed for trigonal-bipyramidal triorganotin compounds), must be considered as having distorted tetrahedral structures, with essentially monodentate cyanate groups present in the molecule.

Bonding in $(CH_3)_3SnNCO$.—The unusual chemical and physical properties of trimethyltin cyanate justify a more extensive study of this molecule by the methods discussed in this investigation. Unlike the higher trialkyl homologs, this compound is a solid at room temperature, with a melting point (105–107°) which appears unusually high for its molecular weight (compare the melting point of $(C_2H_5)_3SnNCO$ of 53–54°). Similar observations have been made for $(CH_3)_3SnF$ and $(CH_3)_3SnCN$, in each case the high lattice energy being associated with a trigonal-bipyramidal configuration in which the bridging ligands effectively form very long two-dimensional polymeric chains. In addition, the antisymmetric stretching frequency of the NCO ligand in $(CH_3)_3SnNCO$ at 2220 cm^{-1} is higher than that observed for the other trialkyltin cyanates, again suggesting that the NCO ligand in this molecule behaves somewhat differently than it does in the homologous longer alkyl chain compounds.

To explore this point further, a number of measurements of the pertinent Mössbauer parameters have been carried out. It has been noted previously that for a series of related tin compounds such as SnX_4,[33,34] SnX_6^{2-},[17,19,35,36] and the phthalocyaninotin dihalides[37,38] there exists a good correlation between the isomer shift observed for the ^{119}Sn resonance and the ligand electronegativity. This is also true for the trimethyltin halides and pseudohalides, as shown in Figure 2. The electronegativities used here are again the Mulliken values for F, Cl, Br, I, and H, while the group electronegativity for OH has been evaluated from the data of O'Rourke and Curran[38] on phthalocyanine dihalide complexes. From the isomer shift value for $(CH_3)_3SnNCO$ at 80°K, this correlation gives a group electronegativity (Mulliken) of 9.16, calculated from the least-squares fit which obeys the relationship[39]

$$IS[(CH_3)_3SnX] = 1.737 - 0.04113\chi_M(L)$$

This value is appreciably smaller than that calculated for the SnX_6^{2-} series [$\chi(NCO) = 9.68$] as discussed above, suggesting that the cyanate ligand in $(CH_3)_3SnNCO$ does not have the same electron configuration in this molecule as it does in the octahedral complex where it must be acting as a unidentate moiety.

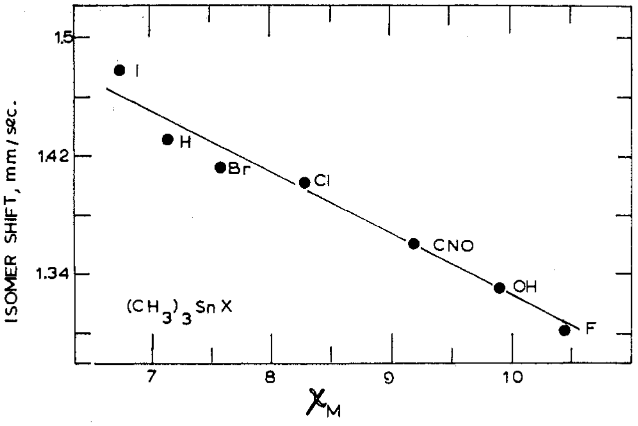

Figure 2.—Isomer shift for trimethyltin halides and pseudohalides as a function of the Mulliken electronegativity of the ligand. The value for the group electronegativity of the OH moiety is taken from the data of ref 38.

To explore the possibility of polymer formation in $(CH_3)_3SnNCO$ further, the Mössbauer spectra of THF solutions of this molecule and of the corresponding *n*-butyl analog have been examined, and the data are included in the summary of Table I. From this table it is noted that the isomer shift and quadrupole splitting changes in going from the neat solid to the (frozen) solution are −0.11 and −0.20 mm/sec, respectively, for the methyl compound and +0.06 and −0.04 mm/sec, respectively, for the *n*-butyl compound. These data suggest that the changes in the nearest-neighbor environment of the metal atom in $(CH_3)_3SnNCO$ in going from the neat solid to the solution are at most very small and that if there is appreciable bridging character of the NCO group in the solid, the donor properties of the solvent—which presumably replaces one of the axial ligand sites in solution—cannot differ significantly from that of the ligand in the solid.

Finally, it is worth examining the temperature dependence of the area under the resonance curve for $(CH_3)_3SnNCO$, since such measurements serve to elucidate the strength of the intermolecular forces in the solid. The area under the resonance curve can be related to the recoil-free fraction, f_a, in the absorber, and this parameter, in turn, is related[40] to the mean-square amplitude of vibration of the ^{119}Sn atom along the molecular symmetry axes.[41] Briefly stated, it has been found that molecules with strong intermolecular bonds, such as the polymeric $(CH_3)_3SnF$, $(CH_3)_2SnF_2$, β-Sn, and SnO_2, etc., all show a resonance effect at room temperature and it is observed that the recoil-free fraction decreases only slowly with increasing temperature. Monomeric organotin compounds such as $(CH_3)_4Sn$, $(C_6H_5)_4Sn$, and $(CH_3)_3SnH$, etc., on the other hand, in which the intermolecular forces are only weak van der Waals forces, show no resonance effect at room temperature and have a large temperature dependence of the recoil-free fraction in the range $78 < T < 300$°K. In this context it should be noted that the

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(33) M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 915 (1964).

(34) V. I. Gol'danskii, *At. Energy Rev.*, **4**, 3 (1963).

(35) A. G. Davies, L. Smith, and P. J. Smith, *J. Organometal. Chem.*, **23**, 135 (1970).

(36) See for example the extensive discussion by V. I. Gol'danskii and E. F. Makarov (Chapter I) and M. Cordey-Hayes (Chapter V) of "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968.

(37) H. A. Stöckler, H. Sano, and R. H. Herber, *J. Chem. Phys.*, **45**, 1182 (1966); **46**, 2020 (1967).

(38) M. O'Rourke and C. Curran, *J. Amer. Chem. Soc.*, **92**, 1501 (1970).

(39) It should be noted that one conspicuous failure of this correlation between isomer shifts and (group) electronegativities is found for the datum point for $(CH_3)_4Sn$ which gives an impossibly large value for the correlated electronegativity of the $-CH_3$ group. This failure cannot be ignored in the application of these systematics.

(40) See for example ref 36 and R. H. Herber "Symposia of the Faraday Society," No. 1, The Faraday Society, London, 1968, p 86.

(41) For a recent discussion of the application of such measurements to $(CH_3)_2SnF_2$ see R. H. Herber and S. Chandra, *J. Chem. Phys.*, in press, and to $(CH_3)_3SnCN$ see R. H. Herber, S. Chandra, and Y. Hazony, *ibid.*, **52**, 6045 (1970).

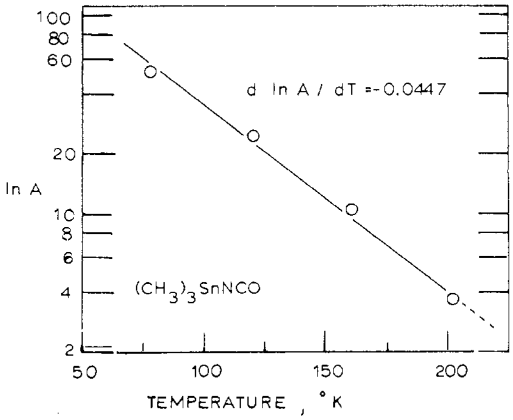

Figure 3.—Temperature dependence of the area under the Mössbauer resonance curve for $(CH_3)_3SnCNO$.

resonance effect in $(CH_3)_3SnNCO$ is not observed at room temperature under conditions where a resonant absorption as small as 0.1% could have readily been detected. To put this result (which by itself can only give qualitative information concerning the strength of intermolecular forces) on a more quantitative basis, the area under the resonance curve for $(CH_3)_3SnNCO$ was determined at four temperatures in the range $78 < T < 202°K$ (Figure 3), and the slope, $d \ln A/dT$, was found to be $-0.0447\ deg^{-1}$. To facilitate comparison with related compounds, the temperature dependence of the area under the resonance curve (normalized to the datum point at 120°K so that the thickness effects cancel) for β-Sn,[42] $(CH_3)_3SnF$, $(CH_3)_3SnNCO$, and $(CH_3)_4Sn$[42] have been summarized in Figure 4. From these data it is readily seen that the intermolecular bonding forces in the cyanate are very much weaker than they are in the three-dimensional polymeric β-Sn and the one-dimensional polymeric $(CH_3)_3SnF$ but somewhat stronger than they are in monomeric $(CH_3)_4Sn$.

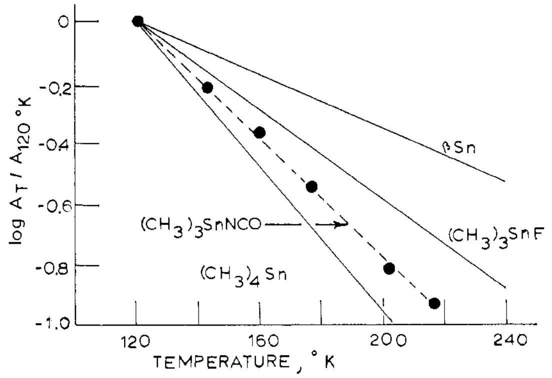

Figure 4.—Temperature dependence of the area under the Mössbauer resonance curve for $(CH_3)_3SnNCO$ and related absorbers. The data have been normalized to the 120°K data point for comparison.

The polymeric nature of solid trimethyltin cyanate is also indicated by the results of the mass spectrometric data obtained by introducing the solid sample in the heated inlet system of the spectrometer. In addition to a relatively weak set of lines at $m/e \sim 206$ (corresponding to the monomer parent molecule M) there is a medium strong set of lines at $m/e \sim 329$ (tentatively assigned to M + Sn) and a weaker set of lines at $m/e \sim 356$ (M + Sn + CO or M + Sn + $2CH_3$), as well as sets at $m/e \sim 299$, 269, and 254, all of which can be presumed to arise from fragments of a linear chain polymer. Moreover, it is interesting to note that the heavy-mass peaks are seen only early in the sampling regimen, again indicative of the relatively weak bridging interaction which is ascribed to the NCO moiety. Extended heating of the sample apparently results in a disruption of the polymer chain to give largely monomer and smaller fragments in the vapor which is sampled by the mass spectrometer analyzer system.

In summary, then, these data suggest a weak bidentate nature of the NCO ligand in the solid trimethyltin compound in which the bridging bond between adjacent $(CH_3)_3Sn$ groups is relatively easily broken and in which the stabilization of the pentacoordinate structure cannot be very pronounced. This interpretation is reinforced by the absence of a temperature-dependent intensity asymmetry of the quadrupole doublet (Gol'danskii–Karyagin effect).[43] Such an effect is especially pronounced when adjacent $(CH_3)_3Sn$ units are tied together by strong bonding forces [*e.g.*, in $(CH_3)_3SnF$ and to a somewhat smaller extent in $(CH_3)_3SnCN$] and is essentially absent when such bridging interactions are weak or absent. The area ratio parameter R,[44] included in the data summarized in Table II, is seen to be temperature independent. Its difference from unity is (presumably) due to a small residual crystal orientation effect which gives rise to a temperature-independent asymmetry in the intensities of the components of the quadrupole split doublet.

Table II

Temperature Dependence Data for $(CH_3)_3SnNCO$

Temp, °K	Area[a]	Log $(A_T/A_{120°K})$	$R = I_+/I_-$[b]
294	*c*	*c*	
202	37.73	−0.818	0.916
160	105.07	−0.373	0.881
120	247.82	0	0.905
78	512.88	0.316	0.933

[a] In arbitrary units; the areas under the resonance curves have been determined both from the graphic displays ($A = \pi\epsilon\Gamma/2$) and from appropriate computer programs, assuming Lorentzian line shapes. [b] The area ratio R has been determined both from the computer data and by gravimetric integration of the graphically displayed data. The two methods give results which are in good agreement with each other and have an estimated error of $\sim\pm 4\%$. [c] No effect observed.

These conclusions are consistent with the infrared data in the 650–400-cm^{-1} region summarized in Figure 5. In this range, in addition to the strong bands at about 550 cm^{-1}, which can be assigned to the Sn–C_3 asymmetric mode, and a band at 610 cm^{-1}, there is an additional medium strong absorption at 517 cm^{-1} which shows up clearly in both the KBr pellet sample (0.83% by weight) and the Nujol mull (CsI plates) sample. On

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(42) The data for β-Sn have been taken from C. Hohenemser, *Phys. Rev.*, **139**, A185 (1965); the data for $(CH_3)_4Sn$ are taken from H. A. Stöckler, H. Sano, and R. H. Herber, *J. Chem. Phys.*, **47**, 1567 (1967).

(43) V. I. Gol'danskii, *et al.*, *Dokl. Akad. Nauk SSSR*, **147**, 127 (1962); *Dokl. Phys. Chem.*, **147**, 766 (1963); S. V. Karyagin, *Dokl. Akad. Nauk SSSR*, **148**, 1102 (1963); *Dokl. Phys. Chem.*, **148**, 110 (1964)].

(44) The parameter R is defined as I_+/I_-, where I_+ and I_- are the areas under the more positive and more negative velocity (with respect to the spectrum centroid) component of the quadrupole doublet, respectively. For further discussion covering the significance of this parameter, see ref 41, 43.

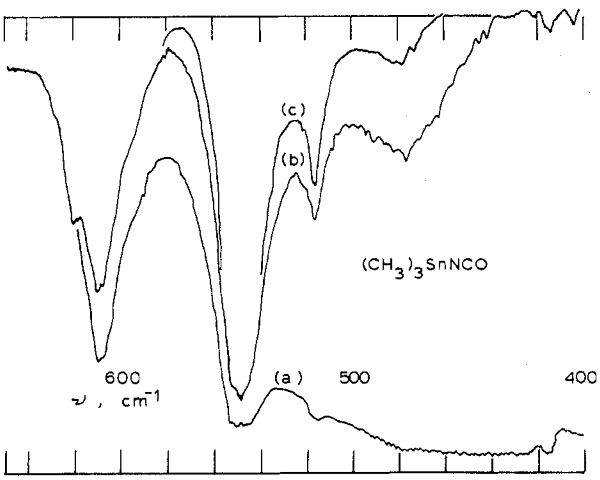

Figure 5.—Portion of the infrared spectrum of $(CH_3)_3SnNCO$ from 650 to 400 cm^{-1}. (a) Nujol mull spectrum using NaCl plates; (b) KBr pellet spectrum; (c) Nujol mull spectrum using CsI plates. The band at ~550 cm^{-1} is due to the Sn–C_3 asymmetric stretch, while that at 517 cm^{-1} is assigned to the Sn–C_3 symmetric mode. All data are at ~40°.

the basis of the infrared spectra of related molecules, such as $[(CH_3)_3Sn]_2SO_4$,[45] $[(CH_3)_3Sn]_2CrO_4$,[45] $[(CH_3)_3Sn]_2SeO_4$,[46] and $[(C_2H_5)_3Sn]_2$,[47] this band can be assigned with some confidence to the $Sn(CH_3)_3$ symmetric vibration. Its presence in the infrared spectrum rules out a planar trimethyltin moiety such as would be expected if the NCO group were acting as a strongly bridging ligand and is in consonance with the formulation of trimethyltin cyanate as having a distorted pyramidal structure with only weakly bridging cyanate moieties.

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[45] H. C. Clark and R. Goel, *Inorg. Chem.*, **4**, 1428 (1965).

[46] J. R. Sams, private communication.

[47] D. H. Lohman, *J. Organometal. Chem.*, **4**, 382 (1965).

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The Electrochemical Oxidation of Bis(π-cyclopentadienyldicarbonyliron)

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Bis(π-cyclopentadienyldicarbonyliron) can be oxidized at carbon and platinum electrodes in acetone, acetonitrile, and dichloromethane using a variety of supporting electrolytes. Three general routes have been used for the preparation of complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ [L = neutral ligand; X = anionic ligand] by electrochemical oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$.

Introduction

It was recently reported[2] that chemical oxidation of bis(π-cyclopentadienyldicarbonyliron) by anhydrous ferric perchlorate in acetone or acetonitrile gives solutions of the corresponding solvento complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)^+$. The reactions involve the oxidative fissioning of the metal–metal bond in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. The overall stoichiometry for both reactions is 2:1 suggesting that the net reaction is

$$2S + 2Fe^{3+} + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \longrightarrow 2Fe^{2+} + 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+$$

where S = acetone or acetonitrile. It was also reported that acetone was easily displaced from the acetone complex by a variety of neutral or anionic ligands giving complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2X$.

Here we report that bis(π-cyclopentadienyldicarbonyliron) can be oxidized electrochemically in a variety of media and that complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ (L = $S(C_2H_5)_2$, $NCCH_3$) and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X^- = Cl^-) can be isolated in good yield either directly or indirectly using electrochemical techniques. The acetone complex has been prepared *in situ* and not isolated as a solid.

Experimental Section

All manipulations were carried out under nitrogen in deaerated solvents. Infrared spectra were obtained in KBr pellets using a Perkin-Elmer 421 spectrophotometer. Ultraviolet–visible spectra were obtained on a Cary 14 spectrophotometer.

A. **Materials.**—Bis(π-cyclopentadienyldicarbonyliron) (Alfa Inorganics) was purified by successive recrystallization from benzene–petroleum ether and dichloromethane–pentane. Ammonium hexafluorophosphate (Alfa Inorganics) was purified by three recrystallizations from acetone–dichloromethane and finally

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[2] E. C. Johnson, T. J. Meyer, and N. Winterton, *Chem. Commun.*, 934 (1970); E. C. Johnson, T. J. Meyer, and N. Winterton, submitted for publication.