$(CH_3)_2C_5H_3NO)]$ can exist in these solutions. It seems, therefore, that steric interaction in *cis*-$TiF_4\cdot[(DMA)(2,6-(CH_3)_2C_5H_3NO)]$ is somewhat less than for the *cis*-$TiF_4\cdot 2(2,6-(CH_3)_2C_5H_3NO)$ structure, as might be expected.

The existence of *trans*-$TiF_4\cdot[(TMU)(4-CH_3C_5H_4NO)]$ when no *trans*-$TiF_4\cdot[(TMU)(4-O_2NC_5H_4NO)]$ could be found might seem puzzling, because the *para*-substituted pyridine 1-oxides should have the same steric requirement. However, it has been suggested that a strongly basic ligand will favor the *trans* isomer.[9] The weakly basic nature of 4-nitropyridine 1-oxide[11] should then favor formation of the *cis* isomer.[9] In fact, this effect was also observed in the study of the adducts of 2-methylpyridine 1-oxide and 2,4-dimethylpyridine 1-oxide. The former donor molecule, which from resonance considerations would be expected to be the weaker donor of the two, formed the $TiF_4\cdot 2D$ complex with a higher *cis*:*trans* ratio (see Table I). At this time it is not known what effect specific solvation may have on the *cis* and *trans* isomers, and there is a lack of quantitative studies. Thus, many questions concerning the factors which determine the $TiF_4\cdot 2$(donor) stereochemistry warrant further study.

Acknowledgment.—The financial support of this work by the U. S. Air Force Material Laboratory is gratefully acknowledged by R. O. R.

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[11] D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

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

Mössbauer Spectroscopy of Organometallic Compounds: Alkyltin Cyanides, Thiocyanates, and Related Molecules

By B. GASSENHEIMER[1] and R. H. HERBER

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Mössbauer, infrared, and nuclear magnetic resonance data are reported for a number of related alkyl- and aryltin thiocyanates and cyanides. From ^{119}Sn isomer shift and quadrupole splitting data it is inferred that the R_3SnCN and R_3SnSCN compounds in the solid state adopt a trigonal-bipyramidal configuration involving a planar R_3Sn moiety linked by bridging bidentate –CN– or –SCN– groups. The quadrupole splittings which are observed arise largely from the C_{3v} symmetry around the metal atom and the difference in donor properties of the equatorial and axial ligands, rather than from p_π–p_π or p_π–d_π interactions. The Mössbauer and infrared data for the $R_2Sn(SCN)_2$ species are consistent with nearly octahedral symmetry around the metal atom in which the two R groups occupy *trans* coordination sites. Mössbauer data for frozen solutions of $(C_4H_9)_2Sn(SCN)_2$ in MHF (glassy matrix) and CH_3CN (crystalline matrix) are interpreted in terms of an octahedral complex structure in which two solvent molecules occupy two of the six (equatorial) coordination sites. Nuclear magnetic resonance data for methyl- and ethyltin compounds can be correlated with ^{119}Sn isomer shift data, an increase in the proton shift from TMS being reflected in an increase in the isomer shift, referred to SnO_2.

I. Introduction

The details concerning the structure and bonding in organotin cyanides and thiocyanates have received considerable attention in the recent literature in an attempt to correlate the structural parameters of such species with their observable physical and chemical properties. Mössbauer effect spectroscopy—used in conjunction with other molecular structure spectroscopic techniques such as nuclear magnetic resonance, infrared, and X-ray diffraction methods—can serve to shed considerable light on these problems, and the present study was undertaken to examine the detailed relationships between the Mössbauer parameters of a number of organotin cyanides and thiocyanates and the structural and bonding parameters determined by other methods.

II. Experimental Section

The compounds examined in the present study were prepared by methods reported in the earlier literature. The organotin thiocyanates were obtained[2] by mixing ethanol solutions of the corresponding organotin bromide or chloride with an ethanolic solution of KSCN, filtering off the insoluble halide, and isolating the organotin thiocyanate from the C_2H_5OH filtrate. The products were purified by recrystallization from benzene [$(CH_3)_3SnSCN$, $(C_6H_5)_3SnSCN$] or from acetonitrile [$R_2Sn(SCN)_2$] or by distillation [$(C_2H_5)_3SnSCN$ and $(C_4H_9)_3SnSCN$] and gave satisfactory elemental analyses[3a] for C, N, H, and S. The organotin cyanides were prepared[3b] by contacting ether solutions of the corresponding alkyltin halide with aqueous solutions of KCN, recovering the crude product from the ether layer, and recrystallizing from benzene.

$Sn(SCN)_4$ was prepared by refluxing an acetonitrile solution containing 0.11 mol of $SnCl_4$ through a Soxhlet extractor containing 0.44 mol of KSCN for 30 hr under nitrogen. The resultant white, hygroscopic solid (which yellows on exposure to air) was analyzed spectrophotometrically using the absorbance of the ferric thiocyanate complex at 480 μ. The observed SCN:Sn

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[1] Senior Research Participant.

[2] D. Seyferth and E. G. Rochow, *J. Am. Chem. Soc.*, **77**, 1302 (1955); M. Wada, M. Nichina, and R. Ikawara, *J. Organometal. Chem.* (Amsterdam), **3**, 70 (1965).

[3] (a) G. I. Robertson, Florham Park, N. J.; (b) W. F. Edgell and C. H. Ward, *J. Am. Chem. Soc.*, **76**, 1169 (1954); see also: D. Seyferth and N. Kahlen, *J. Org. Chem.*, **25**, 809 (1960); J. Lorberth, *Ber.*, **98**, 1201 (1965); G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **6**, 49 (1956).

ratio was 3.62 (theoretical, 4.00), the most likely source of error being partial hydrolysis of the sample prior to weighing.

Infrared spectra were obtained using a Beckman Infracord IR-7 on neat liquids or Nujol mulls of the solid samples. Nmr data were obtained on a Varian A-60 or HA-100 spectrometer at room temperature (except for the experiments on $(CH_3CH_2)_3SnSCN$, *vide infra*), using TMS as an internal standard. Mössbauer spectra were obtained in a liquid nitrogen cooled dewar (sample temperature 80 ± 2°K) using a $Ba^{119}SnO_3$ source as described earlier.[4,5] Velocity calibration was effected using a 0.5-mil natural iron foil. All ^{119}Sn isomer shifts referred to in this paper are with respect to SnO_2[6] at 296°K.

III. Results and Discussion

The Mössbauer parameters for the compounds examined in the present investigation are summarized in Table I. The isomer shift (IS) and quadrupole splitting (QS) were extracted from spectra of the type shown in Figure 1 by the method-of-chords analysis described earlier,[7] from runs in which at least 5×10^5 counts were accumulated per channel (*i.e.*, with a statistical counting error of ±0.14% or less).

TABLE I

MÖSSBAUER PARAMETERS FOR ORGANOTIN CYANIDES AND THIOCYANATES[b]

Compound	No.	Mp, °C	IS,[a] mm/sec	QS,[a] mm/sec	ν(C≡V), cm^{-1}
$(CH_3)_3SnSCN$	**1**	108	1.40	3.77	2081
$(C_2H_5)_3SnSCN$	**2**	33	1.57	3.80	2081
$(C_4H_9)_3SnSCN$	**3**		1.60	3.69	2075
$(C_6H_5)_3SnSCN$	**4**	172	1.35	3.50	2088
$(CH_3)_2Sn(SCN)_2$	**5**	197	1.48	3.87	2081
$(C_2H_5)_2Sn(SCN)_2$	**6**	190	1.56	3.96	2075
$(C_4H_9)_2Sn(SCN)_2$	**7**	142	1.56	3.88	2078
(0.8 *M* in MHF)			1.47 ± 0.05	3.98 ± 0.05	...
(0.8 *M* in CH_3-CN)			1.49 ± 0.05	3.86 ± 0.05	...
$(C_4H_9)Sn(SCN)_3$			1.43	1.46	
$Sn(SCN)_4$			0.56	0	
$(CH_3)_3SnCN$	**8**	182	1.39	3.12	2160
$(C_2H_5)_3SnCN$	**9**	163	1.41	3.19	2160
$(C_4H_9)_3SnCN$	**10**	90	1.37	3.27	2151

[a] All ±0.02 mm/sec, unless otherwise shown. [b] All absorber temperatures are 80 ± 2°K; the source ($BaSnO_3$) temperature is 296 ± 2°K. All isomer shifts are with respect to SnO_2 at room temperature.

(a) **Isomer Shifts.**—The observed isomer shifts which are related to the electron density of the ^{119}Sn nucleus are qualitatively similar to those which have been reported for other organotin compounds. However, the quantitative differences between the isomer shifts for the trialkyltin pseudohalides and the corresponding tetraalkyltins and alkyltin hydrides can be related to the difference in hybridization between these two classes. The isomer shifts for $(CH_3)_4Sn$, $(CH_3)_3SnH$, and $(CH_3)_2SnH_2$, all of which are known to be tetrahedral and are thus described as involving sp^3 hybridization of the tin atom, are 1.23 ± 0.02 mm/sec with respect to SnO_2. The isomer shifts observed in the present study for $(CH_3)_3SnCN$ and $(CH_3)_3SnSCN$ are 1.39 and 1.40 mm/sec, respectively, *i.e.*, shifted to more positive values of 0.16–0.17 mm/sec. The detailed crystal structure of $(CH_3)_3SnCN$ has been reported by Schlemper and Britton,[8] who found this molecule to have a trigonal-bipyramidal structure with $Sn-C(CH_3)$ bond lengths of 2.17 ± 0.03 Å and Sn–C(CN) or Sn–N(CN) bond lengths of 2.48 ± 0.02 Å and the three methyl groups isoplanar with the metal atom. Although these authors ascribe a significant ionic character to the metal–ligand interaction, the hybridization in the σ-bonding framework can be described as being primarily sp^3d. On this basis and the by now well-established[9] fact that for ^{119}Sn $\Delta R/R > 0$, the increase in electron density at the tin nucleus in the trigonal-bipyramidal compounds must be ascribed to the electron delocalization effects (effectively a deshielding) of the 5s electrons in going from sp^3 to sp^3d hybridization. A similar increase in IS is observed in going from $(CH_3CH_2)_4Sn$ (1.33 mm/sec) to $(CH_3CH_2)_3SnCN$ (1.41 mm/sec) and $(CH_3CH_2)_3SnSCN$ (1.57 mm/sec). An essentially identical description can be made in terms of the partial ionic character of the metal–SCN bond if it is assumed that the charge transfer to the ligand involves mainly 5p electrons (see below), thus again effectively deshielding the 5s electrons and giving rise to the increase in the s-electron density at the nucleus.

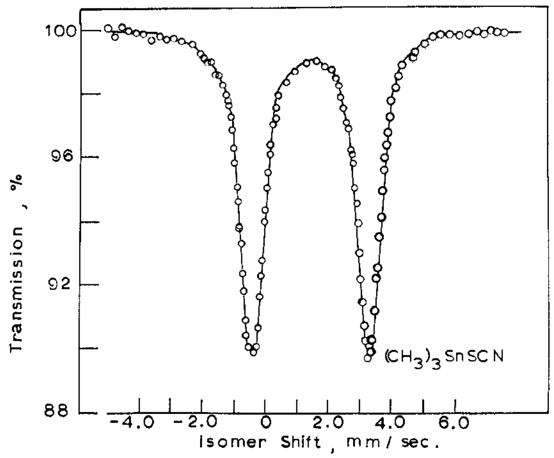

Figure 1.—Mössbauer spectrum of $(C_2H_5)_3Sn$ SCN at 96°K. The isomer shift is with respect to SnO_2. The source used was $Ba^{119m}SnO_3$ at 296°K.

The absence of quadrupole splitting and the small isomer shift (with respect to SnO_2) for $Sn(SCN)_4$ suggest a polymeric octahedral structure for this material in the solid state consistent with its low solubility in nonpolar organic solvents. From isomer shift electro-

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(4) H. Sano and R. H. Herber, *J. Inorg. Nucl. Chem.*, **30**, 409 (1968).

(5) N. Benczer-Koller and R. H. Herber in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter II.

(6) Such shifts are identical with those with respect to $BaSnO_3$, within the experimental error of ±0.035 mm/sec at 296°K.

(7) R. H. Herber, Advances in Chemistry Series, No. 68, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1968, p 6; see also ref 5 therein.

(8) E. O. Schlemper and D. Britton, *Inorg. Chem.*, **5**, 507, 2244 (1966).

(9) (a) J. P. Bocquet, Y. Y. Chu, O. C. Kistner, and M. L. Perlman, *Phys. Rev. Letters*, **17**, 809 (1966). (b) See also the discussion by J. J. Spijkerman in "The Mössbauer Effect and Its Application in Chemistry," Advances in Chemistry Series, No. 68, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1967. (c) V. I. Gol'danskii and E. F. Makarov in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter I. See also the editor's note, p 59, in this reference.

negativity systematics for SnX_4 and R_3SNX (R = CH_3, C_2H_5) the group electronegativity for a bridging SCN group is interpolated to be ~3.15 on the Allred–Rochow scale, but this number may be subject to revision on the basis of more extensive systematic data.

Table II

Methyl and Methylene Proton Chemical Shifts (from TMS) for Ethyltin Halide and Pseudohalide Compounds Discussed in the Text[a]

Compound	δ_{CH_3}	δ_{CH_2}
$(C_2H_5)_3SnCN$	1.33	1.25
$(C_2H_5)_3SnSCN$	1.33	1.33
$(C_2H_5)_2Sn(SCN)$	1.39	1.83
$(C_2H_5)_4Sn$	1.18	0.74
$(C_2H_5)_3SnCl$	1.30	1.30
$(C_2H_5)_2SnCl_2$	1.44	1.79
$(C_2H_5)SnCl_3$	1.55	2.34
$(C_2H_5)_3SnBr$	1.33	1.33
$(C_2H_5)_2SnBr_2$	1.43	1.86
$(C_2H_5)SnBr_3$	1.44	2.43
$(C_2H_5)_3SnI$	1.31	1.31
$(C_2H_5)_2SnI_2$	1.42	2.02

[a] All data refer to CCl_4 solutions at 296°K or have been appropriately corrected.

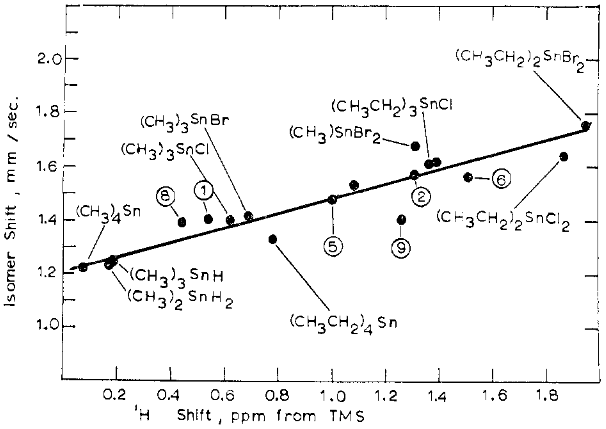

Figure 2.—Correlation between the proton nmr shift (of the α-carbon protons) and the Mössbauer isomer shifts for a number of organotin compounds. The numbers refer to the compound identifications in Table I.

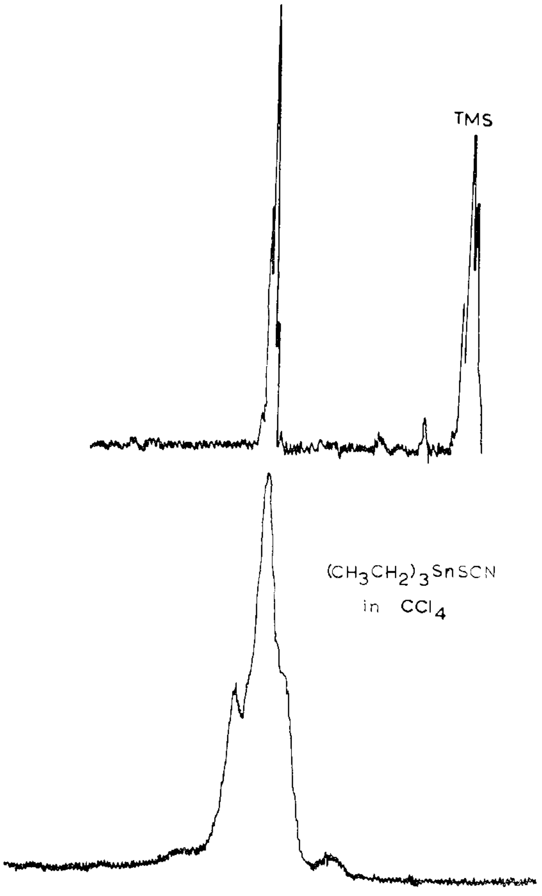

Figure 3.—Proton magnetic resonance spectrum for $(C_2H_5)_3$-$SnSCN$ in CCl_4. The lower curve has been run on an expanded horizontal-sweep scale. Both spectra at 296°K.

(b) Isomer Shift–Nmr Chemical Shift Correlation.—The organotin halides and pseudohalides are, of course, susceptible to proton nuclear magnetic resonance study, and a number of such investigations have been reported.[10,11] Results for the present series of compounds have been collected in Table II in which the chemical shifts (in ppm from TMS) for the methyl protons in a number of methyltin compounds, as well as the methylene proton shifts in a number of ethyltin compounds, are summarized (although nmr data for *n*-propyl and *n*-butyl organotin compounds have been obtained in these laboratories, the spectra are too complex[12] to permit an unambiguous assignment of the resonance peaks at the present time). Both the nmr resonance of the protons on the α carbon and the Mössbauer effect isomer shift will reflect the details of the C–Sn bonding, and hence it is expected that a correlation should exist between these two parameters. That this expectation is indeed correct is evident from the data summarized in Figure 2 which suggests a linear relationship between the two parameters. It is clear (despite the appreciable scatter of the data) that an increase in the proton nmr shift from TMS is reflected in an increase of the isomer shift referred to SnO_2. In this context, it is interesting to make some special comments concerning the nmr spectra of ethyltin halides and pseudohalides. A thoroughly recrystallized sample of $(CH_3CH_2)_3SnSCN$ in CCl_4 showed only a single (albeit asymmetric) nmr resonance (δ 1.33) when examined at 60 MHz (Varian A-60) at room temperature (Figure 3), rather than the expected triplet and quadruplet spectra usually associated with an ethyl moiety. Similar results were observed in acetonitrile solvent (δ 1.29) at room temperature. At 100 MHz (Varian HA-100) the spectrum is sufficiently spread out to permit resolution of the two peaks with an approximate ratio of 2:3, and upon scale expansion the individual lines of the multiplets could be observed (but not identified). The asymmetry of the resonance pattern is not sensitive to temperature changes in the range 220–300°K. These results can be understood on the basis of an accidental degeneracy of the methyl and methylene proton reso-

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[10] L. Verdonck and G. P. van der Kelen, *Bull. Soc. Chim. Belges*, **76**, 258 (1967).

[11] L. Verdonck and G. P. van der Kelen, *Ber. Bunsenges. Physik. Chem.*, **69**, 378 (1965).

[12] R. H. Herber and Y. Goscinny, unpublished results.

nances in $(CH_3CH_2)_3SnSCN$ rather than on the basis of a thermal averaging effect. To test this hypothesis further, a number of related ethyltin halides and pseudohalides have been examined with respect to the position of the methyl and methylene proton resonances. Of the triethyltin compounds, only the cyanide has a sufficiently large difference in proton chemical shifts to permit resolution of the individual multiplets at 60 MHz. These data are summarized in Figure 4 in which the chemical shifts are plotted as a function of the number (n) of halide or pseudohalide groups bonded to the tin atom. It is seen that for the ethyltin halides and ethyltin thiocyanates the position of the methylene proton resonance (which, as expected, varies more sensitively with a change in n than the methyl proton resonance) crosses the position for the methylene resonance when $n \approx 1$. Consequently the nmr spectra of the triethyltin halides and thiocyanate show only a single (asymmetric) proton resonance peak due to the accidental degeneracy of the two multiplets. A similar result has been observed for $(C_2H_5)_{4-n}SnX_n$ (X = Cl, Br, I, or OCH_3) by Verdonck and van der Kelen,[10] who showed that the difference in the resonance frequency ($\nu_A - \nu_B$ in their paper) goes through zero for $n \approx 1$. This phenomenon, which appears to be quite general for triethyltin compounds, should be kept in mind when proton nmr spectra are used for product identification since the spectral pattern observed for $(A_3B_2)_3SnX$ species will appear (at least qualitatively) very similar to related methyltin compounds.

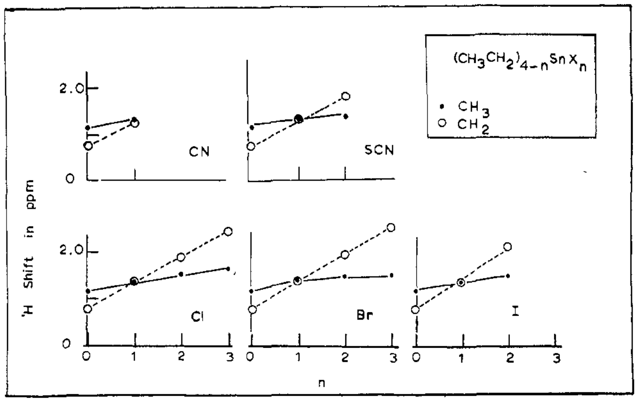

Figure 4.—Variation of proton nmr shifts with the number of halide (or pseudohalide) groups in the series $(CH_3CH_2)_{4-n}SnX_n$. The solid points are the methyl group protons and the open points are the methylene protons. All data are for CCl_4 solutions at 296°K.

(c) **Quadrupole Splitting.**—This parameter, which arises from the interaction between the nuclear quadrupole moment and the gradient of the electrostatic field at the nucleus, is included in the data summarized in Table I. With the exception of $Sn(SCN)_4$, all of the alkyl- and aryltin pseudohalides show a QS which is large compared to the natural line width of the ^{119}Sn resonance, and the two components of the resonance spectrum are readily resolved.

The data for the trialkyltin thiocyanates are compatible with a common trigonal-bipyramidal structure for these molecules. Assuming that the hybridization of the tin atom is appropriately described as being $5s5p^35d$, the major contribution to the field gradient at the metal atom lattice site arises from the C_{3v} symmetry of the molecule. There are, however, two additional effects which must be considered in an evaluation of the QS in such compounds, namely, (a) electronegativity effects on the σ bonds and (b) field gradient contributions from orbital overlaps in the π interactions. The electronegativity effects have been discussed by Bent,[13] who concluded that when both s and p orbitals are involved in the hybridization leading to bonding to two different ligands, s character will be concentrated in the bonds to the more electropositive ligand while p character will be concentrated in the bonds to the more electronegative ligand. In the present context this means that the two axial bonds (to the bridging SCN ligand) will have more p character than the bonds to the three (presumably coplanar) alkyl groups. This change in the bond character from equivalent contributions from all three 5p orbitals to one in which the $5p_z$ (z being defined as the C_{3v} rotational axis) contribution is enhanced will increase the magnitude of the field gradient above that associated with five equivalent metal–ligand bonds of this symmetry. Moreover the involvement of a single 5d orbital in the hybridization scheme will make its own (although considerably smaller) contribution to the field gradient and must be considered in making a quantitative estimate of the total gradient at the metal atom nucleus.

As far as the π-bonding effects are concerned, there are two contributions which must be considered in a discussion of the effects of bridging thiocyanate groups, namely, the interaction with lone-pair electrons on the sulfur atom and the possible involvement of the π-electron distribution in the C–N multiple bond. These two effects can be estimated—at least qualitatively—by consideration of the Mössbauer data for the trialkyltin cyanides (*vide infra*) on the one hand and trialkyltin halides (specifically the chlorides) on the other. The Mössbauer data for this latter group of compounds[14,15] have been summarized in Table III from which the following generalizations can be abstracted. The QS parameter decreases systematically for a given R_3SnX as the size of the halogen increases and decreases from R = ethyl to R = isobutyl as the size of the alkyl group increases. Specifically, it is seen that $QS((C_2H_5)_3SnCl) \approx QS((C_2H_5)_3SnSCN)$ and that this value is significantly larger (by about 0.6 mm/sec) than the splitting observed for the analogous cyanide compounds. In the case of the chlorides, both axial ligands have lone-pair electrons which can overlap with the

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

(14) These data are taken largely from the results obtained by Y. Goscinny in these laboratories, and the authors are indebted to M. Goscinny for permission to quote these results: Y. Goscinny and R. H. Herber, to be submitted for publication.

(15) V. V. Khrapov, Ph.D. Thesis, Institute of Chemical Physics, Moscow, 1965; V. I. Gol'danskii, *et al.*, in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter VI.

Table III

Mössbauer Parameters (mm/sec) for R_3SnX Compounds at Liquid Nitrogen Temperatures

	X									
	F		Cl		Br		I		OH	
R	IS	QS	IS	QS	IS	QS	IS	QS	IS	QS
CH_3	1.24	3.77	1.40	3.47	1.41	3.54	1.49	3.15	1.07	2.71
C_2H_5	1.47	4.00	1.61	3.74	1.61	3.27	1.57	3.13	1.35	3.00
n-C_3H_7	1.44	3.96	1.62	3.61	1.64	3.46	1.59	2.90		
n-C_4H_9	1.37	3.75	1.53	3.40	1.54	3.26	1.47	2.71	1.46	3.21 (?)
i-C_4H_9	1.47	3.82	1.60	3.36	1.60	3.20	1.63	2.73		
C_6H_5	1.18	3.62	1.36	2.51	1.20	2.51	1.19	2.05	1.21	2.70

[a] All values are ±0.05 mm/sec. Data are taken from ref 9c and R. H. Herber and Y. Goscinny, unpublished results.

empty 6p orbitals of the metal atom and thereby contribute to the field gradient at the tin nucleus. In the case of bridging SCN groups, only one nearest neighbor atom (*e.g.*, sulfur) has a lone pair, but the other end of the bridging moiety consists of a carbon–nitrogen multiple bond with a high electron density concentrated in the π orbitals of the ligand. Finally, in the trialkyltin cyanides, in which the bridging group has (formally) no lone pairs, only the carbon–nitrogen multiple-bond π-electron density can contribute to the field gradient at the tin nucleus by means of a π interaction with the empty 6p (or 5d) orbitals on the metal atom. Back-donation from filled 4d metal atom orbitals to empty π^* ligand orbitals, which has an appreciable effect on IS, will make only a small contribution to the field gradient.

From the present data it is apparent that the major contribution to the observed field gradient arises from the C_{3v} symmetry of the molecules and the electronegativity differences of the axial and equatorial ligands and that the π interactions with the metal orbitals—if present at all—make only a very minor contribution to the field gradient at the tin atom lattice site. Essentially the same conclusions were reached in a recent study[16] of $(CH_3)_3SnCl$ and its adducts with various Lewis bases, in which it was noted from both Mössbauer and nmr data that any π-bonding effects are small with respect to their contribution to the total field gradient[17] which is observed at the tin nucleus site.

(d) Bonding Character of the SCN Ligand (R_3SnSCN).—In the foregoing discussion of the trialkyltin thiocyanates it has been assumed that the thiocyanate ligand is an essentially linear bridging moiety involving a tin–sulfur bond at one end and a nitrogen–tin bond at the other. This assumption is based on both infrared and Mössbauer data as summarized in Table I. The characteristic CN stretch in $(CH_3)_3SnCN$ occurs at 2160 cm^{-1} and at essentially the same position in the ethyl and butyl homologs. Since the methyl compound is known to involve linear CN bridging groups, this mode is taken as characteristic of a bidentate linear cyanide bridge. This characteristic frequency is shifted to $\sim$2081 cm^{-1} in the trialkyltin thiocyanate compounds in consonance with the expected electron-withdrawing effects of the sulfur atom. That these frequencies are appropriately assigned to a linear SCN fragment can be inferred from the recent work of Keller, *et al.*,[18] on infrared data for the thiocyanate complexes of palladium in which the ligand can adopt both nitrogen- and sulfur-bonded configurations.

(e) Bonding in $R_2Sn(SCN)_2$ Compounds.—Both the similarity in the CN infrared frequencies to those observed in the trialkyltin thiocyanates and the high melting points observed for the dialkyltin dithiocyanates strongly suggest that the latter are octahedral complexes involving four bridging SCN ligands to neighboring molecular units. The similarity in the isomer shifts observed for R_3SnCN and $R_2Sn(SCN)_2$ support the previously made assumption that the ionicity of the metal–ligand bond resulting from charge transfer from Sn to SCN cannot be significantly different in the compounds which have been examined. It should also be noted that the magnitude of the QS parameter makes it possible to distinguish between the *cis* and *trans* configurations of the R groups in these species. Fitzsimmons, *et al.*,[19,20] in an extension of earlier work on ^{57}Fe Mössbauer spectra, have concluded that for the compounds of the type R_2SnX_4 (X = Cl, O, or N; R = alkyl or aryl), $(QS)_{trans} \approx 2(QS)_{cis}$ and that $(QS)_{trans} \approx 4$ mm sec^{-1}. A similar interpretation has been suggested by Greenwood and Ruddick[21] for the compound $(CH_3)_2Sn[(C_6H_5)_2PO]_2$ (QS = 4.18 mm sec^{-1} at 80°K) to which they assigned a D_{2h} symmetry. On this basis it seems reasonable to conclude that the $R_2Sn(SCN)_2$ compounds listed in Table I all have the two R groups occupying *trans* positions in the octahedral structure.

Finally, it is appropriate to comment briefly on the Mössbauer data for frozen methylhydrofuran (MHF) and acetonitrile solutions of $(C_4H_9)_2Sn(SCN)_2$ (Table I). This compound is essentially insoluble in nonpolar organic solvents such as benzene but quite soluble in polar solvents, suggesting that the six-coordinate structure of the solid is preserved in polar solvents with solvent molecules occupying two of the six coordination sites. The near identity of the Mössbauer parameters for the neat solid and the acetonitrile and MTF solutions is then readily understood in terms of the similar-

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[16] J. C. Hill, R. S. Drago, and R. H. Herber, *J. Am. Chem. Soc.*, in press.

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ity of the bonding properties of the SCN bridging groups in the former and the –C≡N: and $^{\mathrm{C}}_{\mathrm{C}}\!\!>\!\mathrm{O}\!:$ groups in the latter. From the value for the QS it is inferred that the two alkyl groups still occupy *trans*-octahedral positions, but the present data do not permit any conclusions to be drawn concerning the *cis* or *trans* arrangement of the two SCN groups relative to the two solvent molecules. Moreover the observed similarity in the frozen-solution parameters for acetonitrile solutions (crystalline) and MTF solutions (glassy) lends added support to the assumption that the Mössbauer parameters reflect the nature of the metal–ligand bonding rather than structural features imposed by the nature of the surrounding matrix.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Kinetics of Interconversion of Triethylenetetraminenickel(II) and Tetracyanonickelate(II)

BY GERALD B. KOLSKI AND DALE W. MARGERUM[1]

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Fifth-order kinetics are observed in the rate of formation of $Ni(CN)_4^{2-}$ from $Ni(trien)^{2+}$ and cyanide. The reaction is first order in $Ni(trien)^{2+}$ and fourth order in total cyanide ($CN^- + HCN$) from pH 5 to 12. As is the case with the aquonickel ion, HCN is a reactant as well as CN^-. From pH 5 to 7.5 the rate expression for the formation of $Ni(CN)_4^{2-}$ is $k_{2,2}[Ni(trien)^{2+}][CN^-]^2[HCN]^2$, where $k_{2,2} = 4.0 \times 10^{18}\ M^{-4}\ sec^{-1}$. This rate constant is more than twice as large as the corresponding constant for the reaction of CN^- and HCN with $Ni(H_2O)_6^{2+}$. This is extraordinary considering the fact that the strongly coordinated trien molecule must be displaced from nickel, a process which is extremely slow without the assistance of cyanide. At higher pH the reaction becomes fourth order in CN^- with $k_4 = 10^{18}\ M^{-4}\ sec^{-1}$. In the reverse reaction the disappearance of $Ni(CN)_4^{2-}$ in the presence of trien is first order in each reactant, confirming the forward kinetics.

Introduction

The formation of tetracyanonickelate(II) ion from aquonickel ion has recently been shown[2] to be a relatively fast reaction with a fourth-order dependence in total cyanide, where both CN^- and HCN may be reactants. The reaction of aminocarboxylatonickelate complexes (NiL^{2-}) to form $NiL(CN)^{3-}$ also are rapid and can proceed *via* HCN.[3] However, the complete displacement of ethylenediaminetetraacetate ion from nickel is slow and requires only three cyanide ions around nickel in the rate-determining step, followed by rapid addition of a fourth cyanide ion to give tetracyanonickelate(II).[4]

$$\mathrm{Ni(trien)^{2+}} + 4\left[\begin{array}{c}\mathrm{CN^-}\\ \mathrm{H^+}\downarrow\uparrow\\ \mathrm{HCN}\end{array}\right] \rightleftarrows \mathrm{Ni(CN)_4^{2-}} + \left[\begin{array}{c}\mathrm{trien}\\ \mathrm{H^+}\downarrow\uparrow\\ \mathrm{Htrien^+}\\ \mathrm{H^+}\downarrow\uparrow\\ \mathrm{H_2trien^{2+}}\end{array}\right] \qquad (1)$$

In the present work the reaction in eq 1, where trien is triethylenetetramine, is studied in both forward and reverse directions. Once again HCN is found to be an important reactant. The reaction is fourth order in total cyanide in a manner similar to aquonickel rather than following the behavior of the EDTA complex. An astonishing observation is that from pH 5 to 8 the nickel–trien complex reacts faster to form $Ni(CN)_4^{2-}$ than does the aquonickel ion. One reason why this behavior is surprising is that the dissociation of nickel–trien is known to be very slow at pH 4–7,[5] and using formation rate data the half-life calculated for the dis-

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