

Synthesis, Vibrational Spectroscopy, and Mössbauer Effect Study of Tin(II) Complexes of Crown Ethers

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The preparation, characterization, and infrared and ^{119}Sn Mössbauer effect spectra for a number of Sn(II) complexes of cyclic polyethers are discussed. 18-Crown-6 forms a solid reaction product with anhydrous tin(II) chloride and tin(II) thiocyanate which contains two distinct tin sites per molecule. On the basis of isomer shift and quadrupole splitting systematics, the Mössbauer spectrum can be analyzed in terms of a cationic moiety, SnL^+ ($\text{L} = \text{Cl}$ or NCS), bonded to the crown ether, and an anionic moiety, SnL_3^- , present as a gegenion. A very similar structure is postulated for the reaction product between dibenzo-18-crown-6 and tin(II) thiocyanate. By contrast, the reaction product obtained with 18-crown-6 and $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, contains only one tin site per molecule. This tin site is characterized by a sharp singlet Mössbauer spectrum and has an isomer shift which is among the most positive recorded for a tin(II) species. The infrared spectrum of this compound does not indicate the presence of waters of hydration. The temperature dependence of the Mössbauer recoil-free fraction for $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and the tin(II) perchlorate-crown ether complex, as well as for the other products isolated in this study, is presented.

I. Introduction

Since the extensive pioneering studies of Pedersen^{1,2} in 1967, relating to the complexation of a wide variety of cations by the cyclic polyethers called collectively "crown ethers", a large number of investigations have sought to clarify the metal-ligand interactions in such systems. Part of the motivation for these studies was the discovery^{2,3} of the unusual solubilizing properties of the crown ethers, which made it possible to use inorganic reagents—especially oxidants^{4,5} such as MnO_4^- and potassium benzoate—in the presence of organic solvents to bring about reaction of organic species under well-controlled conditions. Moreover, the polyethers have also been investigated as possible model systems for biological reactions^{6,7} and the relationship between their structure and thermodynamic³ and kinetic properties⁸ has been amply documented in the scientific literature.

The first estimate of the size of the "cavity" in typical crown ethers, and more specifically in 18-crown-6, the most extensively studied of these molecules, was based on atomic models and was thought² to be on the order of 4 Å, that is, large enough to accommodate the cation of any uncomplexed metal. Subsequent refinement⁹ of the cavity size estimate reduced the apparent diameter of the cavity in 18-crown-6 to 2.6–3.2 Å, and much of the subsequent discussion of the chemical and physical properties of 18-crown-6 cation systems has focused on the question of the accommodation of the metal ion in the available space, assuming the polyether to adopt an essentially planar configuration.

A large number of mono- and divalent cations have been reported to form stable adducts with 18-crown-6, but surprisingly, there is no report of a complex with tin(II), although the diameter¹⁰ of this ion (2.44 Å) is small enough to be accommodated within the planar ligand. Moreover, size alone clearly is not the sole determining factor with respect to the stability of adduct formation since both larger¹⁰ monovalent cations (e.g., K^+ (2.66 Å) and Rb^+ (2.96 Å)) as well as divalent cations (e.g., Ba^{2+} (2.70 Å) and Pb^{2+} (2.36–2.62 Å)) have been reported^{1,9} to form stable systems with 18-crown-6.

In the present study we report the first detailed data on tin(II)–18-crown-6 complexes, their synthesis and vibrational spectroscopy and their hyperfine parameters and the metal atom dynamics as elucidated by ^{119}Sn Mössbauer effect spectroscopy. In the context of the latter, it has been necessary to study in detail a number of other tin(II) compounds—such as $\text{Sn}(\text{ClO}_4)_2$, $(\text{CH}_3)_4\text{NSnCl}_3$, and SnCl_2 —and data for these systems are presented as well as part of the present investigation.

II. Experimental Section

A. Synthesis. All synthetic manipulations were carried out under dry nitrogen. The crown ethers were obtained commercially. 18-Crown-6 was purified from its acetonitrile complex¹¹ and dibenzo-18-crown-6 was recrystallized from dry methanol and vacuum dried at 25 °C. Spectral grade solvents were used without further purification. $\text{Sn}(\text{SCN})_2$, SnCl_2 , $(\text{CH}_3)_4\text{NSnCl}_3$, $(\text{C}_2\text{H}_5)_4\text{NSnCl}_3$, SnI_2 , and $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ were prepared by literature methods.¹²

18-Crown-6-bis[tin(II) chloride]. Anhydrous SnCl_2 was dissolved in dry methanol (25 mL) and added to a methanol solution of the polyether (1.8 g in 25 mL, 100% excess) at room temperature. The reaction mixture was refluxed with constant stirring under dry N_2 for 2 h and then concentrated to 20 mL. On cooling to 0 °C white needles separated. These were separated by filtration and dried in vacuo over CaSO_4 and had a sharp melting point of 146 °C (uncor). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_6\text{Sn}_2\text{Cl}_4$: C, 22.40; H, 3.76; Sn, 36.89. Found: C, 22.41; H, 3.77; Sn, 35.33. Smaller ratios of crown ether to SnCl_2 gave heterogeneous products which partially melted at temperatures less than 146 °C and are assumed to contain unreacted reagent. Recrystallization of the pure product from dry methanol or ethanol did not change the physical properties of the initially obtained material. The infrared data for 18-crown-6- Sn_2Cl_4 are summarized in Table I. The ^1H NMR spectrum of this compound in deuteriochloroform shows, in addition to a singlet at 3.70 ppm ascribed to uncomplexed 18-crown-6 (3.62 ppm in deuteriochloroform), a sharp singlet at 3.98 ppm relative to Me_4Si .

18-Crown-6-bis[tin(II) thiocyanate]. Tin(II) thiocyanate (0.42 g) and 18-crown-6 (0.49 g) were combined in 30 mL of hot acetonitrile and refluxed for 1 h under dry nitrogen. After cooling for 48 h at 0 °C, the white needles which separated were filtered, dried at 25 °C in vacuo over CaSO_4 , and gave a sharp melting point of 177 °C (uncor). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_6\text{Sn}_2(\text{NCS})_4$: C, 26.18; H, 3.30; N, 7.63; S, 17.47; Sn, 32.34. Found: C, 26.17; H, 3.33; N, 7.90; S, 17.34; Sn, 32.09. Products obtained from methanol and chloroform solutions had identical physical properties with those of the product recovered from CH_3CN . The infrared data for the $[\text{Sn}^{\text{II}}(\text{SCN})_2]_2$ complex are summarized in Table I. The ^1H NMR spectrum of this compound in deuterioacetone gave a singlet resonance at 4.02 ppm relative to Me_4Si .

Dibenzo-18-crown-6-bis[tin(II) thiocyanate]. A solution of the crown ether (0.90 g, 90% excess) in dry CHCl_3 (60 mL) was added to $(\text{SCN})_2\text{Sn}^{\text{II}}$ (0.31 g) and the resulting mixture was refluxed under dry nitrogen for 24 h. At the end of this time a cream white solid had precipitated and was separated by filtration and vacuum dried at room temperature. The product does not have a sharp melting point but decomposes above 190 °C. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6$ - $[\text{Sn}(\text{SCN})_2]_2$: C, 34.73; H, 2.91; N, 6.75; S, 15.45; Sn, 28.60. Found: C, 31.55; H, 2.39; N, 7.26; S, 16.46; Sn, 28.73. The infrared data are summarized in Table I.

18-Crown-6-Sn(ClO₄)₂. Tin(II) perchlorate trihydrate was filtered from its aqueous solution, washed with chloroform, and dissolved in

Table I. Infrared Data for 18-Crown-6 and the Tin(II) Compounds Discussed in the Text^a

18-Crown-6	Dibenzo-18-crown-6	18-Crown-6-Sn ₂ Cl ₄	18-Crown-6-Sn ₂ (NCS) ₄	18-Crown-6-Sn(ClO ₄) ₂	Dibenzo-18-crown-6-Sn ₂ (NCS) ₄
					1380 w
1351 m		1348 s	1350 s	1351 m	
1346 m	1340 m	1337 sh			1325 m
1286 sh, m	1300 m	1282 s	1284 m	1285 m	
1280 m	1260 vs				
1248 m	1240 vs	1244 m	1246 m	1249 m	1245 s
		1240 sh, w			
1234 w		1231 w	1233 w	1235 w	
1228 sh, w					1200 m
1136 sh				1148 sh	
1130 sh	1130 vs	1129 sh, w		1133 sh	1130 s
1106 vs		1109 sh, b	1111 sh, w	1122 sh	1110 w
1091 sh	1070 m	1090 vs, b	1102 sh, w	1102 vs	
	1060 m		1089 vs	1089 sh	1090 s
1057 w	1050 m	1056 sh, w	1055 sh, w	1054 sh	1060 m
	1025 w				1040 w
966 s	995 s	965 s	969 s	964 s	955 s
	935 s	954 sh, w			
	915 w				
	900 w				
844 w				847 sh, w	870 w
					855 w
837 m	815 m	834 s	833 m	839 m	845 w
	810 w	825 sh	825 sh	826 sh	830 w
	780 m	817 sh, w	818 sh, w	638 m	755 m
	775 m			627 m	755 m
	755 s				740 m
	735 s				
	725 s				
528 w		547 w	535 w	529 w	
		535 w	500 w		

^a Symbols: s = strong, m = medium, w = weak, sh = shoulder, b = broad.

~50 mL of dry ether which had been freshly distilled from sodium. To this was added an excess quantity of 18-crown-6 dissolved in ether, and a white precipitate immediately formed and was filtered off. The precipitate was washed with small quantities of dry ether and then dried in vacuo at room temperature. The product decomposes at ~160 °C without melting and is soluble in acetone. The infrared data are summarized in Table I. The ¹H NMR spectrum in deuteriochloroform shows a sharp singlet resonance at 3.87 ppm from Me₄Si. Anal. Calcd for C₁₂H₂₄O₆Sn(ClO₄)₂: C, 24.77; H, 4.13; Cl, 12.19; Sn, 20.40. Found: C, 28.43; H, 5.47; Sn, 14.85; Cl, 10.89. The analytical results (vide infra) suggest the presence of ~25% unreacted 18-crown-6 as an inclusion impurity in the precipitate.

Other Reactions Attempted. No reaction was observed between 18-crown-6 and SnI₂ in CHCl₃ or SnSO₄ in CH₃OH or CH₃CN. Attempts were also made to selectively replace the presumed SnCl₃⁻ anion in 18-crown-6-Sn₂Cl₄ (vide infra) by reacting the complex with saturated solutions of LiBF₄, (C₄H₉)₄NBF₄, or NaB(C₆H₅)₄ in methanol. No reaction was observed in the first two instances while only the sodium salt of 18-crown-6 (mp 176–185 °C) was recovered from the latter.

B. Spectroscopy. The ¹¹⁹Sn Mössbauer effect spectra on all compounds reported in this study were obtained in the appropriate temperature range between liquid nitrogen and room temperature using the constant acceleration transmission spectrometer described earlier.¹³ Periodic spectrometer calibration was effected using the magnetic hyperfine spectrum of metallic iron at room temperature. All isomer shifts are reported with respect to the centroid of a room temperature BaSnO₃ spectrum obtained using the same source as was employed in the sample spectra. Computer reduction of the data was effected using the matrix inversion least-squares fitting program detailed earlier.¹³

Routine infrared spectra were recorded on a Perkin-Elmer Model 225 grating spectrometer on 1% KBr solution or Nujol mulls of the sample compounds. High-resolution (1 cm⁻¹ resolution) infrared spectra were obtained using a Nicolet 7199 series digitized Fourier transform interferometer instrument over the range 4000–200 cm⁻¹ at ambient temperature. For typical spectra (~0.5% in KBr), 250–1000 scans were collected as needed to achieve the desired signal-to-noise ratio. In these spectra—some of which are reproduced below—the absorbance is plotted in the positive vertical direction,

in contrast to conventional practice, and the spectra should be “read” with this inversion in mind.

Proton NMR spectra were obtained on room temperature solutions of the sample compounds in deuterated solvents using a Varian T60 spectrometer with Me₄Si as an internal standard.

Results and Discussion

(a) SnCl₂. The Mössbauer spectrum of anhydrous SnCl₂ consists of a slightly broadened singlet having an isomer shift¹⁴ at 78 K of 4.182 ± 0.006 mm s⁻¹. The line width at 320 K (uncorrected for thickness broadening) is ~1.00 mm s⁻¹ indicating that the quadrupole hyperfine interaction is less than 0.3 mm s⁻¹ and hence unresolvable from the data. The temperature dependence of the isomer shift over the temperature range 78 ≤ T ≤ 320 K is 3.77 × 10⁻⁴ mm s⁻¹ in good agreement with the “classical” slope (3kT/2mc²) of 3.499 × 10⁻⁴ mm s⁻¹ deg⁻¹. The ln (area) vs. temperature plot shows some curvature over the entire temperature range, but a linear least-squares fit yields d ln A/dT = 1.648 × 10⁻² deg⁻¹ (correlation coefficient 0.992) leading to a Mössbauer lattice temperature of ~96 K, assuming the effective vibrating mass to be that of the bare tin ion. This assumption—and thus the calculated Mössbauer lattice temperature—is open to serious reservation since the crystallographic data¹⁵ on SnCl₂ show that the metal atom has three Cl atoms as nearest neighbors in the same plane at distances of 3.22, 3.26, and 3.30 Å, two Cl atoms at distances of 2.78 Å, two Cl atoms at 3.06 Å, and two Cl atoms at 3.86 Å in the planes z = 3/4 and z = -1/4. Thus the structure of Sn(II) chloride may be described as formed from pyramidal SnCl₃ groups sharing three bridging chlorine atoms with six additional near neighbor chlorine contacts. Thus the assumption that the metal atom vibrational motion can be described with reference to a bare Sn(II) ion is clearly an oversimplification of the actual bonding interactions in this solid.

(b) 18-Crown-6-Sn₂Cl₄. The ¹¹⁹Sn Mössbauer spectrum of the tin(II) chloride complex of 18-crown-6 is shown in Figure

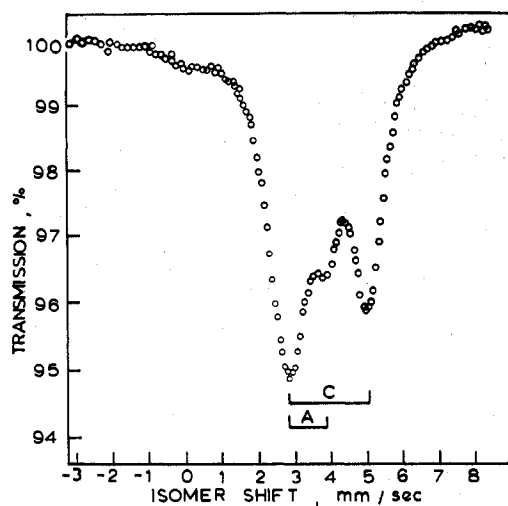


Figure 1. Mössbauer spectrum of 18-crown-6-(SnCl₂)₂ at 78 K. The assignment of the two doublets to the anion (A) and cation (C) of the (presumed) structure is discussed in the text.

1. There are a number of possible ways in which such a spectrum can arise, but from a consideration of both the values of the isomer shift (IS) and quadrupole splitting (QS) hyperfine interaction parameters, as well as the temperature dependence of the line widths (full width at half maximum), the only internally consistent and tenable hypothesis is that the spectrum consists of two quadrupole split doublets. One component of each doublet gives rise to the resonance maximum at $\sim 2.84 \text{ mm s}^{-1}$. The other components are located at ~ 3.83 and $\sim 4.94 \text{ mm s}^{-1}$, respectively. Thus, there are two distinct tin sites per crown ether complex, consistent with the analytical data, each of which gives rise to a resolvable quadrupole hyperfine interaction indicating that the local electronic environment around each metal atom has a symmetry less than cubic (e.g., T_d or O_h). Moreover, the hyperfine interaction parameters for the doublet with the smaller quadrupole splitting (hereafter referred to as the "A" doublet, IS = $3.330 \pm 0.004 \text{ mm s}^{-1}$ and QS = $0.992 \pm 0.009 \text{ mm s}^{-1}$ at 78 K) are very similar to those reported¹⁶ for the SnCl₃⁻ anion (IS = $3.54 \pm 0.06 \text{ mm s}^{-1}$ and QS = $1.00 \pm 0.12 \text{ mm s}^{-1}$ at 77 K). On this basis, the A doublet has been assigned to the SnCl₃⁻ anion for which the primary interaction with the crown ether moiety is an electrostatic one. The doublet with the larger quadrupole splitting (hereafter referred to as the "C" doublet, IS = $3.889 \pm 0.003 \text{ mm s}^{-1}$, QS = $2.109 \pm 0.007 \text{ mm s}^{-1}$ at 78 K) is presumed to arise from an SnCl⁺ cation bonded to the oxygens of the crown ether. These data, as well as the Mössbauer parameters for the other compounds here reported, are summarized in Table II.

The formulation of the crown ether complex as 18-crown-6-SnCl⁺SnCl₃⁻, with two metal atoms per ligand, is similar to the formulations reported earlier of transition-metal complexes with these macrocyclic molecules. Su and Weiher¹⁷ reported the isolation of a cobaltous chloride complex to which they assigned the structure [dicyclohexyl-18-crown-6-Co²⁺][CoCl₄²⁻], while de Vos et al.¹⁸ showed that in the case of NiCl₂, NiBr₂, CoCl₂, CoBr₂, CuCl₂, and CuBr₂, the metal to ligand ratio was always 2:1 regardless of the molar ratio of the reactants. Knöchel et al.¹⁹ on the other hand have prepared a number of 1:1 complexes between polyethers and transition metal and main group halides and nitrates and observed that (in the case of CoCl₂) hydrated salts give rise to 1:1 complexes while the anhydrous salt gives a 2:1 complex by precipitation from solutions of the two reactants on mixing. Bereman and Choi²⁰ have examined the electronic spectrum of the copper analogue of Su and Weiher's complex¹⁷ and

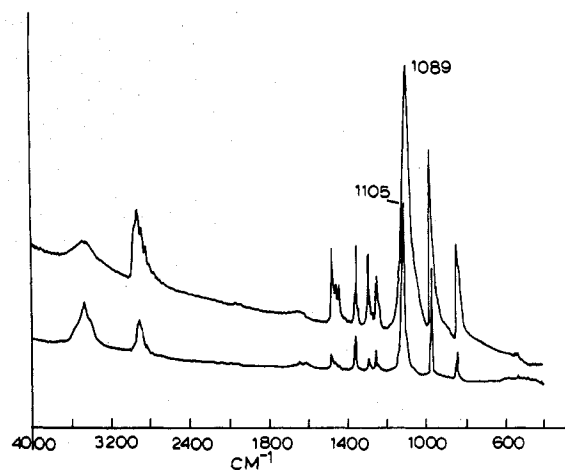


Figure 2. Infrared spectrum of 18-crown-6-(SnCl₂)₂ (top trace) and the uncomplexed polyether (bottom trace). Absorbance (increasing from the origin) is plotted on the ordinate in arbitrary units.

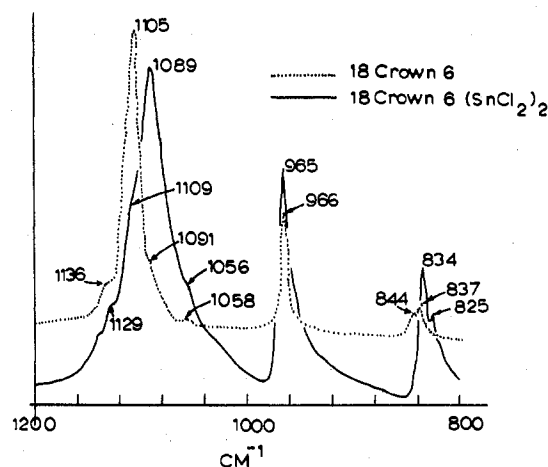


Figure 3. Portion (1200–800 cm⁻¹) of the infrared spectrum of 18-crown-6-(SnCl₂)₂ (solid line) and uncomplexed polyether (dotted line), showing the major shifts which are observed in the C–O–C asymmetric and symmetric modes. The band at $\sim 966 \text{ cm}^{-1}$, assigned to a CH₂ motion, is unaffected by complexation in this molecule.

suggested a structure corresponding to [crown ether Cu²⁺]-[CuBr₄²⁻] on the basis of their spectral and thermochromic observations. The lanthanide complexes of dibenzo-18-crown-6 prepared by King and Heckley²¹ all correspond to a 1:1 formulation according to the extensive analytical data reported by these authors.

The high-resolution infrared spectrum of the 18-crown-6-Sn₂Cl₄ complex is shown in Figure 2 and the 1200–800-cm⁻¹ region in greater detail in Figure 3, together with the corresponding spectra of the uncomplexed crown ether. Although the general features of the two infrared spectra are quite similar, the high-resolution scale expansion feature of the interferometer spectrometer shows clearly the effect of metal ion complexation in the 1200–700-cm⁻¹ region. Of the three strong bands in this region, the 1106-cm⁻¹ band, assigned to the asymmetric COC stretch, is partially red shifted to 1090 cm⁻¹ in the complex, the 965-cm⁻¹ band, assigned to a CH₂ wag or bending motion, is unshifted (966 cm⁻¹ in the complex), and the feature at $\sim 840 \text{ cm}^{-1}$, which is probably due to the COC symmetric motions, shows a more complex change. Specifically with reference to the latter the feature at 844 cm⁻¹ is completely missing in the spectrum of the complex, the more intense absorption at 837 cm⁻¹ is shifted to 834 cm⁻¹ in the complex, and two new features appear in the spectrum at 825 and 817 cm⁻¹. It is also worth noting that the 18-crown-

Table II. Mössbauer Effect Data for the Sn(II) Compounds Discussed in the Text^a

Compd	IS, mm s ⁻¹ , 78 K	QS, mm s ⁻¹ , 78 K	d(IS)/dT, mm s ⁻¹ deg ⁻¹	d ln A/dT, deg ⁻¹	Correl coeff	Temp range for ln A(T) linear fit, K
SnCl ₂	4.182 ± 0.006	~0	-3.77 × 10 ⁻⁴	-1.65 × 10 ⁻²	0.992	78-320
18-Crown-6- Sn ₂ Cl ₄						
(A)	3.300 ± 0.004	0.992 ± 0.009	-2.39 × 10 ⁻⁴	-2.83 × 10 ⁻²	0.992	78-175
(C)	3.889 ± 0.003	2.109 ± 0.007	-5.39 × 10 ⁻⁴	-1.66 × 10 ⁻²	0.999	78-175
Sn(NCS) ₂	3.609 ± 0.002	1.092 ± 0.004	-2.33 × 10 ⁻⁴	-1.35 × 10 ⁻²	0.998	78-200
18-Crown-6- Sn ₂ (NCS) ₄						
(A)	3.262 ± 0.010	1.704 ± 0.010				
(C)	4.141 ± 0.010	1.423 ± 0.010				
Sn(ClO ₄) ₂ ·3H ₂ O	3.752 ± 0.005	1.337 ± 0.007	~0	-9.56 × 10 ⁻³		78-150
18-Crown-6- Sn(ClO ₄) ₂	4.445 ± 0.006	~0	~0	-2.25 × 10 ⁻²	0.999	78-120
Bz ₂ -18-crown-6- Sn ₂ (NCS) ₄						
(A)	3.451 ± 0.013	1.217 ± 0.025				
(C)	3.807 ± 0.010	1.929 ± 0.020				
(CH ₃) ₄ NSnCl ₃	3.258 ± 0.006	1.183 ± 0.011		-3.17 × 10 ⁻²	0.995	78-110
(C ₂ H ₅) ₄ NSnCl ₃	3.416 ± 0.003	1.067 ± 0.006	-2.63 × 10 ⁻⁴	-2.07 × 10 ⁻²	0.999	78-175
(CH ₃) ₄ NSn(NCS) ₃	3.264 ± 0.003	1.451 ± 0.005	-5.24 × 10 ⁻⁴	-2.42 × 10 ⁻²	0.999	78-125

^a All isomer shifts refer to the centroid of a BaSnO₃ spectrum at 295 K, taken with the same source as that used in the data acquisition.

6-Sn₂Cl₄ infrared spectrum shows a shoulder at ~1109 cm⁻¹, nearly coincident with the strong 1106 cm⁻¹ CO stretch in the pure crown ether, consistent with the hypothesis that the metal cation interacts strongly with only two (or three) of the polyether oxygen atoms, leaving the others essentially unaffected. The infrared absorption at 966 cm⁻¹, assigned²² to a CH₂ wag or twist mode, while somewhat broadened in the tin(II) complex, is unaffected by metal ion complexation in the present compound.

The Mössbauer, infrared, and Raman data are not adequate to answer unambiguously the question of the number of oxygen atoms of the polyether which are involved in bonding to the metal atom. In many of its compounds in the solid state, the Sn(II) ion adopts a configuration²³ with three ligands and a lone pair occupying the four vertices of a distorted tetrahedron or with a site symmetry which may be approximated as C_{3v}. It is thus plausible that in the present case, the SnCl⁺ ion is covalently bonded to two oxygens of the ether, with the lone pair occupying a fourth coordination site. It is also possible for the halogen atom to be more extensively involved as a bridging ligand to the anionic tin moiety, as has been suggested²⁰ in the case of 18-crown-6-Cu₂Br₄, but the validity of this alternative can probably only be decided on the basis of a complete single-crystal x-ray diffraction study.

The ¹¹⁹Sn Mössbauer parameters of 18-crown-6-Sn₂Cl₄ were also examined over the temperature range 78 ≤ T ≤ 130 K in order to elucidate the lattice dynamical properties of the two tin sites. Since the two quadrupole doublets are not separately resolved in the spectra, it is necessary to make a simplifying assumption concerning the temperature dependence of the intensity ratio of the two components of the quadrupole split doublet; that is, the possible existence of a Gol'danskii-Karyagin effect²⁴ in the SnCl₃⁻ anion. This assumption can be based on the ¹¹⁹Sn Mössbauer data for (CH₃)₄NSnCl₃ which has been examined over the temperature range 78 ≤ T ≤ 110 K. The spectrum of this compound consists of a well-resolved doublet (IS = 3.258 ± 0.006 mm s⁻¹ and QS = 1.182 ± 0.011 mm s⁻¹ at 78 K). The intensity ratio of the two components, R = A⁺/A⁻ (where A⁺ and A⁻ are the areas of the more positive and more negative velocity peak, respectively) is temperature insensitive and has a value of 0.994 ± 0.063 over the above temperature range. The comparable data for (C₂H₅)₄NSnCl₃ (IS = 3.416 ± 0.003 mm s⁻¹, QS = 1.067 ± 0.006 mm s⁻¹ at 78 K) over the temperature range 78 ≤ T ≤

175 K is R = 0.930 ± 0.063. On this basis, then, it is assumed that R is equal to unity for the SnCl₃⁻ anion and, thus, that the contribution to the total area under resonance peak 1 (Figure 1) due to the lower velocity component of the C doublet is the observed area minus the area under peak 2. Analysis of the intensity ratio of the C component then leads to the observation that again R is temperature insensitive, having a value of 0.973 ± 0.038 over the range 78 ≤ T ≤ 130 K. Thus the tin moiety which is presumably bonded to the crown ether ring does not show evidence for a large vibrational anisotropy over the temperature range in question, in consonance with the general observation that such effects are usually absent in the Mössbauer spectra of tin(II) compounds and in contrast to the large intensity asymmetries which can be observed²⁵ in tin(IV) spectra.

(c) Sn(NCS)₂ and (CH₃)₄NSn(NCS)₃. The Mössbauer spectrum of tin(II) dithiocyanate consists of a well-resolved doublet having an isomer shift of 3.609 ± 0.002 mm s⁻¹ and a quadrupole splitting of 1.092 ± 0.004 mm s⁻¹ at 78 K. These results are only partially in agreement with those of Donaldson and Senior¹⁴ who were not able to resolve the QS hyperfine interaction from their data, although they reported excessively broad (1.8-2.0 mm s⁻¹) resonance lines in their study. The temperature dependence of the isomer shift is d(IS)/dT = -2.33 × 10⁻⁴ mm s⁻¹ and the temperature dependence of the area under the resonance curve is given by d ln A/dT = -1.353 × 10⁻² deg⁻¹ (correlation coefficient 0.998). As was noted above in the discussion of the data for SnCl₂, this latter value cannot be directly converted into an effective lattice temperature due to the uncertainty in the effective mass which contributes to the phonon spectrum. The extensive intermetallic bridging in the solid state by the bidentate thiocyanate groups, as reported by Chamberlain and Moser,¹² leaves undecided the question of the motional moiety in the solid-state structure.

The Mössbauer spectrum of (CH₃)₄NSn(NCS)₃ at liquid nitrogen temperature consists of the expected doublet with an isomer shift of 3.264 ± 0.003 mm s⁻¹ and a quadrupole splitting of 1.451 ± 0.005 mm s⁻¹. The isomer shift is only weakly temperature dependent. The temperature dependence of the area under the resonance curve is given by d ln A/dT = -2.42 × 10⁻² deg⁻¹ (correlation coefficient 0.999). This value is appreciably larger than that observed for Sn(NCS)₂, but very similar to that determined for the anion in the 18-

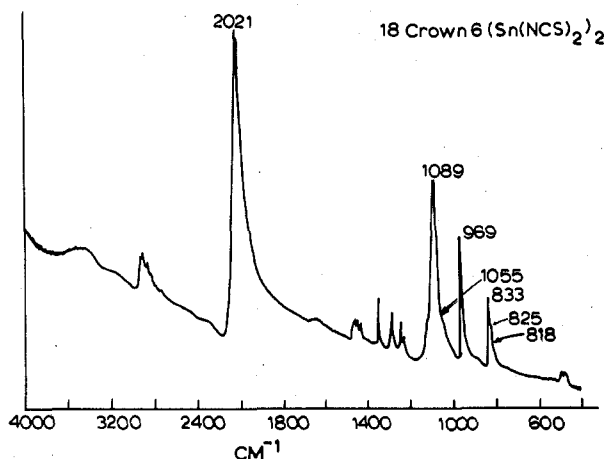


Figure 4. Infrared spectrum of 18-crown-6-(Sn(NCS)₂)₂. Absorbance (increasing from the origin) is plotted on the ordinate in arbitrary units.

crown-6-tin(II) thiocyanate complex (vide infra).

Because the positions of the intense infrared-active bands of the thiocyanate group have considerable diagnostic utility, the vibrational spectra of the thiocyanate compounds discussed in the present work have been examined in some detail. Chamberlain and Moser¹² have reported the infrared spectra of KSCN and Sn(NCS)₂ and concluded from their study that there is almost certainly extensive bridging in the latter, based on the shift of the C-S stretch (749 cm⁻¹ in KSCN) to 780–804 cm⁻¹. Moreover, from the position of this band in Sn(NCS)₂ these authors infer that the primary bonding interaction is between the tin and the nitrogen atom of the ligand and that the latter is bonded to the next tin atom via an extended linear bridging configuration. Finally it is worth noting from the data of Chamberlain and Moser that the CS stretch in (CH₃)₄NSn(NCS)₃ and (C₂H₅)₄NSn(NCS)₃ is observed at 821 cm⁻¹ with little or no evidence for bridging of the N-bonded pseudohalide.

(d) **18-Crown-6-[Sn(NCS)₂]₂**. The infrared spectrum of 18-crown-6-[Sn(NCS)₂]₂ in KBr (Figure 4) shows an intense broad band at 2021 cm⁻¹ (2020 cm⁻¹, broad in Nujol) due to the CN stretch as well as some weak unassigned features at ~500 cm⁻¹. As in the case of the tin(II) chloride complex, the COC asymmetric stretch is red shifted to 1089 cm⁻¹ while the less intense symmetric mode is shifted to 833 cm⁻¹ with shoulders at 825 and 818 cm⁻¹. As in the case of the SnCl₂ complex, the CH₂ mode at 966 cm⁻¹ is essentially unaffected by metal ion bonding. Finally, it is worth noting that the intense band at 1089 cm⁻¹ shows a shoulder at ~1102 cm⁻¹, again suggestive of the presence of ether oxygen atoms uninvolved in the metal ion interaction in the complex. The remainder of the infrared spectrum is very similar to that of 18-crown-6 and shows the characteristic features at 1350 cm⁻¹ (split into a doublet at 1350 and 1340 cm⁻¹ in Nujol), at 1284 cm⁻¹ (1283 cm⁻¹ in Nujol), and at 1246 cm⁻¹ (1245 cm⁻¹ in Nujol). Thus, in this complex there is no evidence for either the blue shift observed by Knöchel et al.¹⁹ or the red shift noted by King and Heckley²¹ for the lanthanide complexes of dibenzo-18-crown-6. From these data it may be inferred that the thiocyanate ligand is N bonded to the metal atom(s) in the crown ether complex (i.e., the ligand is appropriately referred to as acting as an isothiocyanate moiety) with little evidence for a bridging interaction of the ligand.

The ¹¹⁹Sn Mössbauer spectrum of the 18-crown-6-tin(II) thiocyanate reaction product is shown in Figure 5 which again shows the presence of a complex spectrum which can be analyzed in terms of two doublets, consistent with the analytical data which show the presence of two tin atoms per

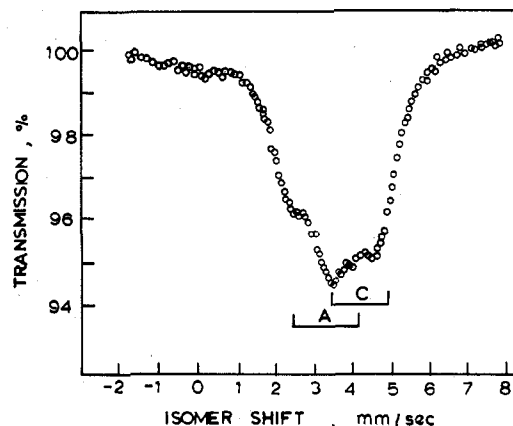


Figure 5. Mössbauer spectrum of 18-crown-6-(Sn(NCS)₂)₂ at 78 K. The assignment of the two doublets to the anion (A) and cation (C) of the (presumed) structure is discussed in the text.

crown ether. The assignment of the doublets is facilitated by the spectral data for (CH₃)₄NSn(NCS)₃ (IS = 3.264 mm s⁻¹, QS = 1.451 mm s⁻¹ at 78 K). Using these values, the doublet consisting of resonance maxima 2 and 4 (Figure 5C) is assigned to the cationic moiety, Sn(NCS)⁺, presumed to be bonded to one or more of the ether oxygens, while resonance maxima 1 and 3 (Figure 5A) are assigned to the anion, Sn(NCS)₃⁻. With this assignment the hyperfine interaction parameters for the cation (IS = 4.141 mm s⁻¹, QS = 1.423 mm s⁻¹) and the anion (IS = 3.262 mm s⁻¹, QS = 1.704 mm s⁻¹) at liquid nitrogen temperature give an internally consistent set of parameters which can be used to describe the bonding interaction in this complex.

For both the SnCl₂ complex and the Sn(NCS)₂ complex with 18-crown-6, the (presumed) cation has a more positive isomer shift than the (presumed) anion, the differences being 0.56 and 0.88 mm s⁻¹ at 78 K, respectively. Since for ¹¹⁹Sn data a more positive isomer shift indicates a larger 5s electron density at the tin nucleus, these data are consistent with the formulation suggested above in which the species bonded to the crown ether is more appropriately characterized as an Sn²⁺ ion than is the gegenanion. This point will be discussed more fully below in connection with the data for the 18-crown-6-tin(II) perchlorate complex.

Due to the overlapping nature of the constituent resonance peaks in the 18-crown-6-Sn₂(NCS)₄ spectrum, it was felt that a detailed temperature dependence study of this molecule was not warranted due to the problems of unique fitting of such spectra. It is, however, appropriate to note that at 78 K, the area ratio of the two doublets—using the assignment outlined above—is 0.97. Making the assumption that at liquid nitrogen temperature the recoil-free fractions (*f* factors) for the two tin sites are not markedly different from each other leads to the confirmation of the formation of this complex with an equal number of tin atoms in each site.

(e) **Sn(ClO₄)₂·3H₂O**. As is true for the majority of other Sn(II) inorganic compounds, the Mössbauer spectrum of this compound at liquid nitrogen temperature consists of a well-defined doublet with an isomer shift of 3.752 ± 0.005 mm s⁻¹ and a quadrupole splitting of 1.337 ± 0.007 mm s⁻¹. The isomer shift is essentially temperature independent in the range 78 ≤ *T* ≤ 300 K having an average value of 3.768 ± 0.006. In contrast, the quadrupole splitting is unusually temperature sensitive, dropping to a value of 1.13 mm s⁻¹ at 300 K, presumably due to thermal expansion—and concomitant strain relaxation of the chain bonding—of the lattice. Consistent with this hypothesis is the observation that the temperature dependence of the area under the resonance curve is not well fitted by a linear regression of the semilogarithmic data,

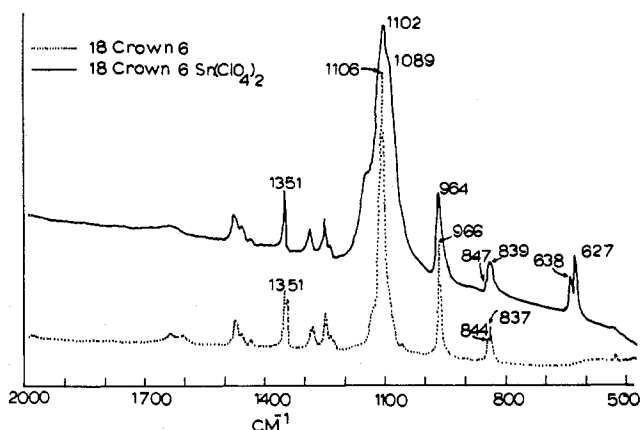


Figure 6. Portion (2000–500 cm^{-1}) of the infrared spectrum of 18-crown-6- $\text{Sn}(\text{ClO}_4)_2$ (solid line) and uncomplexed polyether (dotted line) showing the change in the asymmetric ($\sim 1100 \text{ cm}^{-1}$) and symmetric ($\sim 840 \text{ cm}^{-1}$) C–O–C mode on complexation. The CH_2 mode at $\sim 965 \text{ cm}^{-1}$ is unaffected by complexation in this molecule. The features at 638 and 627 cm^{-1} are due to the ClO_4^- counterion.

although the data in the range $78 \leq T \leq 150 \text{ K}$ give an approximate value of $d \ln A/dT = -9.56 \times 10^{-3} \text{ deg}^{-1}$.

(f) 18-Crown-6- SnClO_4 . The infrared spectrum of the product obtained from the reaction of 18-crown-6 with $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Figure 6) has a number of distinct features, including a medium strong absorption at 638 and 627 cm^{-1} due to the ClO_4^- moiety and the complete absence of absorption bands due to H_2O . In contrast to the other 18-crown-6-tin(II) compounds examined in the present study, the most intense infrared absorption due to the asymmetric COC mode remains essentially unshifted (1102 cm^{-1}), although this band is significantly broadened and shows a shoulder at 1089 cm^{-1} similar to the position of the most intense absorptions in the SnCl_2 and $\text{Sn}(\text{NCS})_2$ complexes. Again, the 964- cm^{-1} band is unaffected by complexation while the symmetric COC mode shows a maximum at 839 cm^{-1} with shoulders at 847, 834, and 826 cm^{-1} .

The 78 K Mössbauer spectrum for this product is shown in Figure 7, and—in contrast to the spectra of the other crown ether complexes examined in this study and, in fact, to most other Sn(II) compounds—consists of a singlet resonance peak with an isomer shift of $4.445 \pm 0.006 \text{ mm s}^{-1}$. It is also worth noting that the full widths at half maximum (0.88 mm s^{-1} at 78 K and 0.82 mm s^{-1} at 140 K), uncorrected for thickness broadening, are among the narrowest observed for inorganic or organometallic compounds of tin and indicate an almost ideal cubic symmetry for the charge distribution around the metal ion.

Although the limited analytical data for this sample are far from satisfactory (two samples exploded during analysis for tin; oxygen cannot be adequately determined in the presence of heavy metals²⁶), both the available results and the Mössbauer effect data indicate the presence of a single tin site in this complex. This observation is particularly tantalizing in view of the observations of Knöchel et al.¹⁹ (vide supra), who noted in their study of heavy-metal complexation by polyethers that hydrated salts gave 1:1 complexes, while anhydrous salts (specifically CoCl_2) gave rise to 2:1 complexes of metal to ligand. In the present study, this observation appears to be confirmed in the sense that the anhydrous tin(II) salts used as reactants have yielded 2:1 complexes while $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ results in a 1:1 complex, which, incidentally, is free of waters of hydration as judged from the infrared data.

There have been numerous estimates reported for the isomer shift, relative to SnO_2 or BaSnO_3 , appropriate to a bare tin(II) ion. Lees and Flinn,²⁷ from their systematic study of isomer shifts of Sn^{2+} compounds suggested a value of 4.76 mm s^{-1} ,

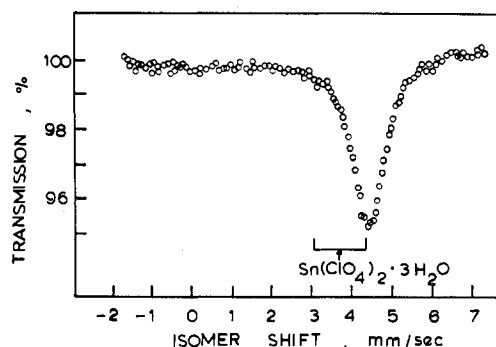


Figure 7. Mössbauer effect spectrum of 18-crown-6- $\text{Sn}(\text{ClO}_4)_2$ at 78 K showing the sharp single line resonance discussed in the text. The line positions for the $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ doublet at 78 K, obtained using the same source, are indicated below the data curve. The isomer shift of the tin(II) ion in 18-crown-6- $\text{Sn}(\text{ClO}_4)_2$ is more positive by 0.69 mm s^{-1} at 78 K than that in $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$.

but this value is open to some question since the assumption implicit in their analysis that there is no sp hybridization in the compounds examined is probably not valid. Donaldson and Senior¹⁴ have suggested a more positive IS value for Sn^{2+} , but this is based on a very long extrapolation of the electronegativity data of Hinze and Jaffe.²⁸ The most positive experimental values which have been reported are $4.67 \pm 0.04 \text{ mm s}^{-1}$ for 3- Sn -1,2- $\text{B}_9\text{C}_2\text{H}_{11}$ at 77 K by Rudolph and Chowdhry²⁹ and the value of $4.18 \pm 0.02 \text{ mm s}^{-1}$ observed for anhydrous SnCl_2 at liquid nitrogen temperature.³⁰ Thus the very large positive isomer shift observed in the spectrum of the tin(II) perchlorate crown ether complex is indicative of an almost “bare” stannous ion held to the crown ether by bonding forces which are assumed to be principally of an ionic (electrostatic) nature.

Formulating the electron configuration of this ion as $[\text{Kr}] 5s^2 4d^{10}$ would, of course, lead to a spherically symmetric charge distribution around the metal ion, and hence to the absence of a field gradient and the concomitant absence of a quadrupole hyperfine interaction as evident from the Mössbauer spectrum.

It should, however, be noted that despite a minimal covalent bonding interaction between the metal ion and the crown ether, the presence of the tin(II) perchlorate does give rise to small changes in the NMR and vibrational spectra of the ether moiety. The ^1H NMR spectrum of the compound in deuterioacetone shows the presence of a sharp singlet resonance at 3.87 ppm from Me_4Si ; that is, the protons are shifted ~ 0.25 ppm downfield from the uncomplexed crown ether value.³¹

The temperature dependence of the area under the Mössbauer resonance curve is summarized graphically in Figure 8 for both $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and the polyether complex. The data in the temperature range $78 \leq T \leq 120 \text{ K}$ for the latter are well fit by a linear regression of the form $\ln A = a + bT$ and yields $d \ln A/dT = 2.254 \times 10^{-2} \text{ deg}^{-1}$ with a correlation coefficient of 0.999. At temperatures above 125 K, there is considerable curvature in the $\ln A$ vs. T data, indicative of appreciable anharmonicity in the motion of the tin ion within its potential energy well. Due to the absence of a quadrupole hyperfine interaction in the Mössbauer spectrum of this compound and the lack of large (orientable) single crystals, the elucidation of the vibrational anisotropy (if any) in this tin(II) species, which was part of the original motivation for this study, cannot be pursued by presently available techniques.

(g) Bz_2 -18-crown-6- $\text{Sn}_2(\text{NCS})_4$. The Mössbauer spectrum of the product obtained from the reaction between dibenzo-18-crown-6 and $\text{Sn}(\text{NCS})_2$ consists of three resonance maxima, similar to the spectra observed for 18-crown-6- $(\text{SnCl}_2)_2$ and

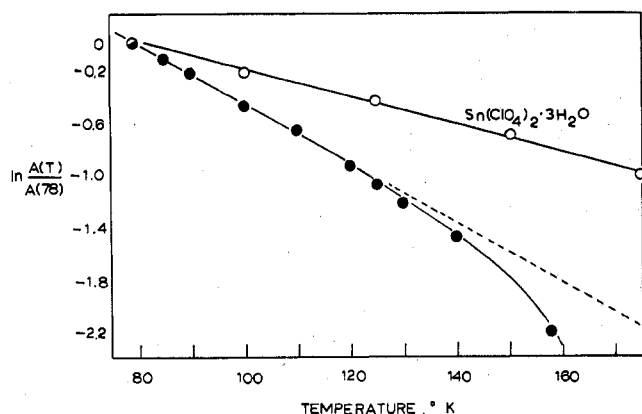


Figure 8. Temperature dependence of the area under resonance curve (normalized to the 78 K value to facilitate intersample comparison) for $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (top trace) and 18-crown-6- $\text{Sn}(\text{ClO}_4)_2$ (bottom trace). The curvature evident in the latter at temperatures above ~ 125 K is due to motional anharmonicity and is also observed in tin(II) chloride trihydrate at temperatures above ~ 200 K.

18-crown-6- $\text{Sn}_2(\text{NCS})_4$. The proposed analysis of this spectrum is similar to the one suggested above for the latter compound, and leads to an $\text{IS} = 3.807 \pm 0.010 \text{ mm s}^{-1}$ and $\text{QS} = 1.929 \pm 0.020 \text{ mm s}^{-1}$ for the (presumed) cationic moiety (e.g., $\text{Sn}(\text{NCS})^+$) and an $\text{IS} = 3.451 \pm 0.013 \text{ mm s}^{-1}$ and $\text{QS} = 1.217 \pm 0.025 \text{ mm s}^{-1}$ for the anionic counterion (e.g., $\text{Sn}(\text{NCS})_3^-$) at 78 K. It should be noted, however, that in the case of the dibenzo crown ether complex the difference in isomer shift between the A tin site and the C tin site is only 0.36 mm s^{-1} compared to a difference of 0.88 mm s^{-1} in the case of 18-crown-6- $\text{Sn}_2(\text{NCS})_4$ at 78 K and that the hyperfine parameters of the A site are not in good agreement with the parameters determined for the tetramethylammonium salt of $\text{Sn}(\text{NCS})_3^-$. These observations indicate that the binding of the two types of tin atoms in the dibenzo-18-crown-6 complex may be qualitatively different from that in the nonaromatic side chain complex, as is also suggested by the changes in the infrared spectrum of dibenzo-18-crown-6 on complexation with $\text{Sn}(\text{NCS})_2$ (see Table I). It is clear that further detailed structural data on this complex are required before a more definite description of its configuration can be given.

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Registry No. SnCl_2 , 7772-99-8; 18-crown-6- Sn_2Cl_4 , 65415-36-3; $\text{Sn}(\text{NCS})_2$, 3602-20-8; 18-crown-6- $\text{Sn}_2(\text{NCS})_4$, 65415-34-1; $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, 21107-46-0; 18-crown-6- $\text{Sn}(\text{ClO}_4)_2$, 65415-32-9; Bz_2 -18-crown-6- $\text{Sn}_2(\text{NCS})_4$, 65516-93-0; $(\text{CH}_3)_4\text{NSnCl}_3$, 14877-00-0; $(\text{C}_2\text{H}_5)_4\text{NSnCl}_3$, 7781-71-7; $(\text{CH}_3)_4\text{NSn}(\text{NCS})_3$, 22728-79-6.

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