

= 73.3 ± 0.4 (one standard deviation) kJ mol^{-1} and $T = 385.3$ K (95% confidence interval 394.7–375.9 K). There is some randomness in the variation of ΔH^\ddagger and ΔS^\ddagger characterizing the $[\text{Sc}(\text{tmu})_6]^{3+}/\text{tmu}$ system in CD_3NO_2 solution with change in the concentration of the exchanging species, but in CD_3CN solution both parameters decrease systematically with decrease in the concentrations of the exchanging species.⁵ The $[\text{Sc}(\text{tmp})_6]^{3+}/\text{tmp}$ system in CD_3CN is also characterized by a systematic variation of ΔH^\ddagger and ΔS^\ddagger with change in concentration.² It is possible that to some extent experimental error produces an internal $\Delta H^\ddagger/\Delta S^\ddagger$ compensation, which results in an apparent isokinetic relationship for the first system, but the systematic $\Delta H^\ddagger/\Delta S^\ddagger$ variation of the latter two systems may reflect changes occurring in the environment outside the first coordination sphere as the concentrations of the exchanging species are varied.²⁷

A statistical method of assessing the significance of the linearity of isokinetic plots has been proposed in the literature²⁸ according to which this linearity may be attributed to chemical origins with 95% certainly if the harmonic mean of the experimental temperatures, T_{hm} , lies outside the 95% confidence interval for T (the slope of the $\Delta H^\ddagger/\Delta S^\ddagger$ plot) derived through linear regression. Since the lower 95% confidence limit of T is 375.9 K, which is greater than the highest temperature examined (370 K), it is clear that the position of a given system in the scandium(III) isokinetic plot may be attributed in part at least to chemical origins.

Six-coordinate scandium(III) and magnesium(II) are characterized by effective ionic radii²⁹ of 0.745 and 0.72 Å, respectively, and thus a comparison of their ligand-exchange parameters should reflect the differing formal charges to a significant extent. Ligand-exchange data for magnesium-

(II),³⁰⁻³⁶ which are thought to characterize D mechanisms, also exhibit a linear relationship between ΔH^\ddagger and ΔS^\ddagger (Figure 3) for which $\Delta G^\ddagger = 41.9 \pm 0.4$ kJ mol^{-1} , $T = 252.8$ K (262.4, 243.2 K), and $T_{\text{hm}} = 223.9$ K. (The reason for the $[\text{Mg}(\text{MeOH})_6]^{2+}$ point lying considerably off the isokinetic line is not understood, and it has been excluded from the linear regression analysis.) The difference in ΔG^\ddagger for scandium(III) and magnesium(II) suggests that the magnitude of the surface charge density exerts a major influence on the magnitude of ΔG^\ddagger for D ligand-exchange processes. In agreement with this supposition $\Delta G^\ddagger \sim 69.5$ kJ mol^{-1} ($T \sim 410$ K), derived from a recent compilation³⁷ of data for ligand exchange on six-coordinate aluminum(III), is closer to the scandium(III) value than to the magnesium(II) value. However, these data also reflect the approximate nature of the relationship between ΔG^\ddagger and surface charge density; if this relationship was exact, the smaller aluminum(III) center (ionic radius = 0.53 Å),²⁹ should produce a significantly greater ΔG^\ddagger value than does scandium(III). While the three metal ions considered all possess electronic dispositions that are not readily polarized, it is nevertheless to be expected that differences in bonding will be superimposed upon the metal ion–ligand dipole interaction. The close proximity to the linear regression line of the data arising from ligand exchange on scandium(III) proceeding through an A mechanism (Figure 3) suggests that surface charge density is a significant determinant for ΔH^\ddagger and ΔS^\ddagger for this mechanism also.

Acknowledgment. We thank the Australian Research Grants Committee for supporting this study.

Registry No. $[\text{Sc}(\text{nma})_6](\text{ClO}_4)_3$, 78199-04-9; $[\text{Sc}(\text{nmf})_6](\text{ClO}_4)_3$, 78199-06-1; $[\text{Sc}(\text{dea})_6](\text{ClO}_4)_3$, 78217-04-6; $[\text{Sc}(\text{def})_6](\text{ClO}_4)_3$, 78199-08-3; $[\text{Sc}(\text{npa})_6](\text{ClO}_4)_3$, 78199-10-7; $[\text{Sc}(\text{dbf})_6](\text{ClO}_4)_3$, 78199-12-9; $[\text{Sc}(\text{tso})_6](\text{ClO}_4)_3$, 78199-14-1.

Supplementary Material Available: Table III listing k_{ex} values and experimental temperatures used in the derivation of the kinetic parameters for the dea and nma systems given in Table II (3 pages). Ordering information is given on any current masthead page.

- (27) It should be noted that the variation in k_{ex} at the midpoint of the experimental temperature range and the free ligand concentration variation are respectively 1.7- and 63-fold for $[\text{Sc}(\text{tmu})_6]^{3+}/\text{tmu}/\text{CD}_3\text{NO}_2$, 1.2- and 5-fold for $[\text{Sc}(\text{tmu})_6]^{3+}/\text{tmu}/\text{CD}_3\text{CN}$, and 2- and 100-fold for $[\text{Sc}(\text{tmp})_6]^{3+}/\text{tmp}/\text{CD}_3\text{CN}$, consistent with ligand exchange proceeding predominantly through a D mechanism. In contrast k_{ex} ($=1/\tau_c$) increases greatly and systematically with increase in the free ligand concentration for those systems characterized by an A mechanism²⁴ or the simultaneous operation of D and A mechanisms^{4,5} as seen in Figure 2. Thus if the k_{ex} variations observed in the three systems above are taken as a measure of environmental effects, the influence of these effects upon the kinetic parameters derived for those systems undergoing ligand exchange through A or simultaneous D and A mechanisms is likely to be small.
- (28) R. R. Krug, W. G. Hunter, and R. A. Grieger, *J. Phys. Chem.*, **80**, 2335 (1976).
- (29) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **B25**, 925 (1969); **B26**, 1046 (1970).

- (30) J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).
- (31) S. Nakamura and S. Meiboom, *J. Am. Chem. Soc.*, **89**, 1765 (1967).
- (32) T. D. Alger, *J. Am. Chem. Soc.*, **91**, 2220 (1969).
- (33) F. L. Dickert, *Ber. Bunsenges. Phys. Chem.*, **83**, 593 (1979).
- (34) D. L. Pisaniello and S. F. Lincoln, *Aust. J. Chem.*, **32**, 715 (1979).
- (35) D. L. Pisaniello, S. F. Lincoln, and E. H. Williams, *Inorg. Chim. Acta*, **31**, 237 (1978).
- (36) S. F. Lincoln, D. L. Pisaniello, T. M. Spotswood, and M. N. Tkaczuk, *Aust. J. Chem.*, **34**, 283 (1981).
- (37) A. E. Merbach, P. Moore, O. W. Howarth, and C. H. McAteer, *Inorg. Chim. Acta*, **39**, 129 (1980).

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Synthesis, Vibrational Spectroscopy, and Mössbauer-Effect Study of Tin(II) Complexes of 15-Crown-5

ROLFE H. HERBER* and GILBERT CARRASQUILLO

Received February 10, 1981

Three new complexes of the polyether 15-crown-5 and stannous salts have been prepared and characterized by elemental analysis and infrared and ¹¹⁹Sn Mössbauer-effect spectroscopy. With tin(II) chloride and thiocyanate, 2:3 complexes are formed that contain two different kinds of metal atoms in the ratio 2:1. One of the metal atoms interacts directly with the crown ether ligands while the other metal atoms are present as anionic counterions in the structure. With tin(II) perchlorate, the crown ether forms a 2:1 complex with a unique Sn²⁺ ion in the structure. The ¹¹⁹Sn Mössbauer isomer shift due to this metal ion is among the most positive (at 78 K) so far reported and can be characterized as a "bare" stannous ion sandwiched between two ring polyether moieties. The lattice dynamics of these complexes (as probed by the tin Mössbauer resonance) and the infrared spectra of these new complexes are discussed.

In an earlier study,¹ we have reported the synthesis, vibrational spectroscopy, and ¹¹⁹Sn Mössbauer-effect parameters

for a number of the complexes formed between stannous salts and the macrocyclic ethers 18-crown-6 and dibenzo-18-

Table I. ^{119}Sn Mössbauer-Effect Data for the Sn(II) Compounds Discussed in the Text^a

compd	IS(78 K), mm s ⁻¹	QS(78 K), mm s ⁻¹	$10^2 d[\ln[A(T)/A(78)]/dT, \text{K}^{-1}$	
SnCl ₂	4.182 ± 0.006	~0	-1.65	ref 1
Sn(SCN) ₂	3.609 ± 0.002	1.092 ± 0.004	-1.35	ref 1
Sn(ClO ₄) ₂ ·3H ₂ O	3.752 ± 0.005	1.337 ± 0.007	-0.96	ref 1
(15Cr5) ₂ (SnCl ₂) ₃ (A)	3.43 ± 0.05	1.16 ± 0.02	-1.82	78 < T < 150 K
(15Cr5) ₂ (SnCl ₂) ₃ (C)	4.59 ± 0.05	~0	-1.36	78 < T < 150 K
(15Cr5) ₂ Sn(ClO ₄) ₂	4.53 ± 0.01	~0	-2.83	78 < T < 120 K
(15Cr5) ₂ [Sn(SCN) ₂] ₃ (A)	3.43 ± 0.03	1.16 ± 0.03	-2.04	81 < T < 120 K
(15Cr5) ₂ [Sn(SCN) ₂] ₃ (C)	4.54 ± 0.03	~0	-2.06	81 < T < 120 K

^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. The temperature ranges refer to the temperature dependence of the area under the resonance curve data.

crown-6. In this connection it was pointed out that the size of the polyether cavity is large enough to accommodate the bare metal ion and that the stoichiometry of the products, which are obtained from alcohol solutions of the reactants, is dependent on the chemical nature of the anion of the Sn²⁺ salt.

Bünzli et al.² have pointed out in connection with an extensive study of crown ether complexes of the lanthanides that for 18-crown-6 both 1:1 (La to Nd) and 4:3 (La to Gd) complexes could be obtained, while for 15-crown-5, only 1:1 complexes with the rare earths were isolated. In a subsequent detailed study of Pr(III) complexes of 15-crown-5 and 18-crown-6, Bünzli et al.^{3,4} have described the analytical data, infrared spectra, and magnetic susceptibilities of a series of praseodymium complexes with different anions and note that with both ligands, 1:1 complexes are isolated from CH₃CN or CH₃CH-CH₃OH solutions. With the still smaller ligand 12-crown-4, the lanthanide nitrates yield 1:1 complexes while 1:2 complexes have been reported for Pr(ClO₄)₃ complexes of 15-crown-5 and 12-crown-4. The thermodynamics of the formation of uni- and bivalent cation complexes has been reported by Izatt et al.,^{5,6} who point out that the marked selectivity toward these cations shown by 18-crown-6 is not found for the smaller cyclic polyether, and only NH₄⁺ forms a more stable complex with 15-crown-5 than with 18-crown-6, presumably because the larger cations (K⁺, Rb⁺) are too large to be effectively accommodated in the ring cavity. It should be noted, however, that these results pertain to aqueous solutions of the reactants.

In the present study a number of Sn²⁺ complexes of 15-crown-5 have been prepared and characterized by infrared and ^{119}Sn Mössbauer-effect spectroscopy.

Experimental Section

(a) **Synthesis of Complexes.** (15Cr5)₂(SnCl₂)₃ (Cr = crown) was prepared by dissolving 1.0 g (4.5 mmol) of 15-crown-5⁷ and 2.05 g (9.08 mmol) of SnCl₂·2H₂O in two separate 10-mL aliquots of carefully degassed methanol and mixing at room temperature. The volume of the clear solution was reduced by a factor of 2, and the crystals that formed overnight were collected by filtration, washed with a small quantity of degassed methanol, dried under vacuum, and stored under vacuum over CaSO₄. A second crop was obtained by reducing the above filtrate volume; mp (uncorrected) 152 °C. Anal.⁸ Calcd for C₂₀H₄₀O₁₀Sn₃Cl₆: C, 23.80; H, 3.99; Sn, 35.28; Cl, 21.08.

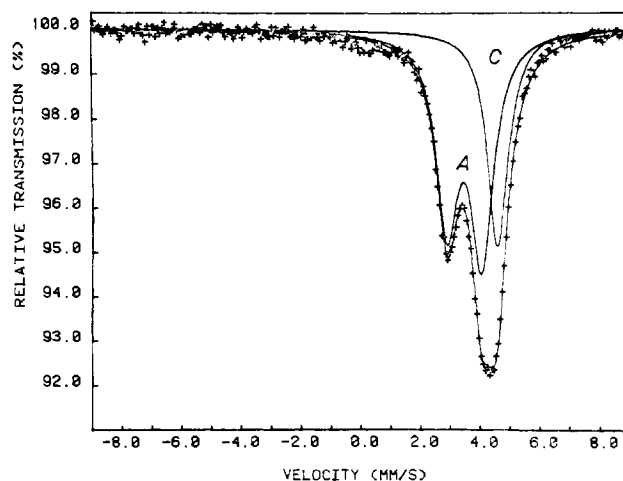


Figure 1. ^{119}Sn Mössbauer-effect spectrum of (15-crown-5)₂(SnCl₂)₃ at 80 K with a CaSnO₃ source at 295 K. The broad resonance at ~4.3 mm s⁻¹ has been computer revolved into two resonance absorptions as shown. The isomer shift scale is with respect to the resonance maximum of a room-temperature BaSnO₃ spectrum taken with the same source.

Found: C, 23.98; H, 3.81; Sn, 35.16; Cl, 21.65. (15Cr5)₂Sn(ClO₄)₂ was prepared similarly from 0.25 g (1.14 mmol) of 15-crown-5 and 0.84 g (2.26 mmol) of Sn(ClO₄)₂·3H₂O. The white crystalline product that is formed does not have a sharp melting point but decomposes above ~140 °C. Anal. Calcd for C₂₀H₄₀O₁₀SnCl₂: C, 31.69; H, 5.32; Sn, 15.66; Cl, 9.35. Found: C, 31.11; H, 5.31; Sn, 15.11; Cl, 9.56. (15Cr5)₂[Sn(SCN)₂]₃ was prepared similarly with use of 1.05 g (4.7 mmol) of 15-crown-5 and 1.11 g (4.72 mmol) of Sn(SCN)₂. In this case a white precipitate was formed immediately. The methanol solution was heated gently to dissolve the solid and then allowed to cool slowly to room temperature, which afforded a crop of large crystals that were separated by filtration and washed with degassed methanol. A further crop was obtained on cooling the filtrate to 0 °C. The product was stored over CaSO₄ under vacuum; mp 164 °C. Anal. Calcd for C₂₆H₄₀O₁₀Sn₃S₆N₆: C, 27.27; H, 3.52; N, 7.34. Found: C, 26.22; H, 3.41; N, 6.71. The same reaction run with a metal to crown ether ratio of 2:1 afforded an identical product, with the following analytical data: 28.27% C, 3.46% H, 7.60% N, and a mixture melting point with the product of the 1:1 reaction of 162 °C. Variation of the reactant ratios was not attempted in the case of the other reactions described above.

(b) **Infrared Spectra.** These were recorded on 1% KBr pellets or Nujol mull samples with use of a Perkin-Elmer 283 spectrometer under microprocessor control. There was no significant difference⁹ in the results obtained by the two dispersion techniques. Spectra of neat 15-crown-5 were obtained with use of NaCl plates.

(c) **^{119}Sn Mössbauer-Effect Spectra.** The details of the constant-acceleration spectrometer and its velocity calibration have been described earlier.¹⁰ Data reduction was effected with use of a matrix

(1) R. H. Herber and A. E. Smelkinson, *Inorg. Chem.*, **17**, 1023 (1978).

(2) J.-C. G. Bünzli and D. Wessner, *Helv. Chim. Acta*, **61**, 1454 (1978).

(3) J.-C. G. Bünzli, D. Wessner, and H. T. T. Oanh, *Inorg. Chim. Acta*, **32**, L33 (1979).

(4) J.-C. G. Bünzli and D. Wessner, *Inorg. Chim. Acta*, **44**, L55 (1980).

(5) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7620 (1976).

(6) R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7626 (1976).

(7) Aldrich Chemical Co., Milwaukee, Wis. 53233.

(8) Galbraith Analytical Laboratories, Inc., Knoxville, Tenn. 37921.

(9) We are indebted to Dr. Bünzli for calling this possibility to our attention.
(10) A. J. Rein and R. H. Herber, *J. Chem. Phys.*, **63**, 1021 (1975), and references therein.¹

inversion least-squares fitting program suitably modified to run on the Rutgers University IBM 370/168 computer. All isomer shifts are reported with respect to the center of a room-temperature (295 ± 2 K) BaSnO_3 reference spectrum. It was noted in some of the preliminary experiments that the crown ether complexes of stannous halides and pseudohalides react with the aluminum foil normally used to confine the samples in the copper sample holders and to ensure thermal homogeneity across the samples. To avoid this problem, we sandwiched powdered samples between layers of plastic wrap (3.64 mg cm^{-2}) and covered this sample again with aluminum foil (4.43 mg cm^{-2}) to reduce thermal gradients. Under these conditions, no chemical degradation of any of the samples was observed.

Results and Discussion

(a) $(15\text{Cr5})_2(\text{SnCl}_2)_3$. A representative ^{119}Sn Mössbauer spectrum of the complex formed between 15Cr5 and stannous chloride is shown in Figure 1. This asymmetric resonance pattern can be deconvoluted into a singlet (C) and a doublet (A), for which the calculated parameters are summarized in Table I. The doublet (A) at 80 K has an isomer shift (IS) of $3.43 \pm 0.05 \text{ mm s}^{-1}$ and a quadrupole splitting (QS) of $1.16 \pm 0.02 \text{ mm s}^{-1}$. The singlet resonance (C) has an isomer shift of $4.59 \pm 0.05 \text{ mm s}^{-1}$. The line widths extracted from the least-squares matrix inversion computer program for all three lines are 0.89 mm s^{-1} . The ratio of the areas under the A doublet to the C singlet at 80 K is 1.85. It is, of course, possible to deconvolute the spectrum shown in Figure 1 in another way, that is, by assigning the two outside peaks to the A doublet and the middle resonance peak to the C singlet. Such an assignment, however, leads to an unreasonably large quadrupole hyperfine interaction ($\sim 1.6 \text{ mm s}^{-1}$ at 78 K) compared to the reference compounds $(\text{CH}_3)_4\text{SnCl}_3$ and $(\text{C}_2\text{H}_5)_4\text{NSnCl}_3$, discussed earlier.¹ While the assignment implied in Figure 1 cannot be made with complete certainty, the internal consistency of the data suggests that this is the preferred interpretation of the present results.

Moreover, these results are readily understood in terms of a proposed structure for the 2:3 complex in which the singlet resonance is ascribed to a "bare" Sn^{2+} ion sandwiched between two 15Cr5 ligands and the doublet resonance arises from two SnCl_3^- anions present as gegencounterions in the matrix. This interpretation is consistent with the earlier assignment¹ of the resonance spectra of $(18\text{Cr6})(\text{SnCl}_2)_2$ and $(18\text{Cr6})\text{Sn}(\text{ClO}_4)_2$ and the corresponding calibration data on $(\text{C}_2\text{H}_5)_4\text{NSnCl}_3$. The very large positive isomer shift of the cation site C is close to the value of $4.67 \pm 0.04 \text{ mm s}^{-1}$ for 3-Sn-1,2- $\text{B}_9\text{C}_2\text{H}_{11}$ at 77 K reported by Rudolph and Chowdhry¹¹ and corresponds to an essentially "bare" Sn^{2+} with an electron configuration $[\text{Kr}] 5s^2 4d^{10}$. From the line width and isomer shift of this resonance it is clear that there is effectively no distortion from spherical symmetry of the electronic charge distribution around the cation, which is sandwiched between two 15Cr5 cyclic ligands. The chemical interaction between the polyether and the ligand must be envisioned as essentially purely electrostatic, with little or no covalency in the metal to ligand bond.

Using the assignments of the ^{119}Sn Mössbauer resonance spectrum (Figure 1) discussed above, it is possible to calculate the temperature dependence of the area under the resonance curve—and hence a Mössbauer lattice temperature—for the two kinds of tin atoms present in this compound. The resulting data are summarized graphically in Figure 2. The two slopes $-d \ln [A(T)/A(78)]/dT$ are respectively $-1.82 \times 10^{-2} \text{ K}^{-1}$ and $-1.36 \times 10^{-2} \text{ K}^{-1}$. Making the assumption¹ that the effective mass that describes the temperature dependence of the area under the Mössbauer resonance curve is that of a "bare" $\text{Sn}(\text{II})$ ion leads to a relationship of the form $\theta_M = 1.338 \times 10(-d \ln A/dT)^{-1/2}$ from which the Mössbauer lattice temperatures for the two sites are 99 K (anion site) and 114 K (cation site).

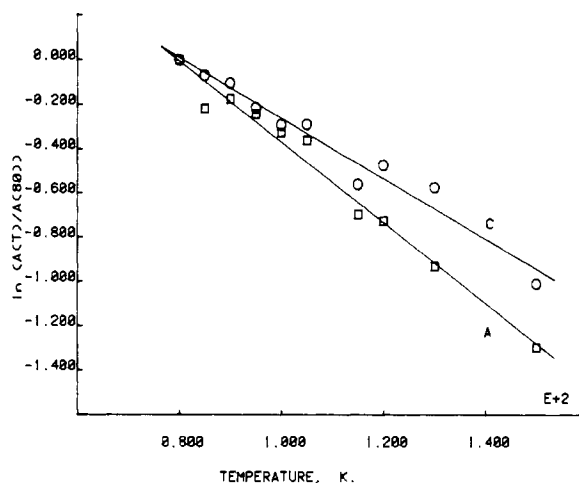


Figure 2. Temperature dependence of the area under the resonance curve for the cation singlet (C, circles) and the anion doublet (A, squares) of the ^{119}Sn Mössbauer spectra of $(15\text{Cr5})_2(\text{SnCl}_2)_3$. The straight lines are linear least-squares fits to the data and have correlation coefficients (10 points) of 0.982 and 0.989, respectively.

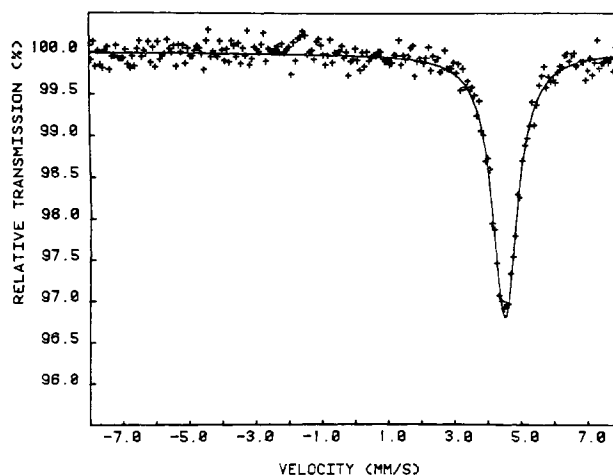


Figure 3. ^{119}Sn Mössbauer-effect spectrum of $(15\text{-crown-5})_2\text{Sn}(\text{ClO}_4)_2$ at 78 K.

For comparison, the corresponding value¹ for SnCl_2 is ~ 96 K and for $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ it is ~ 89 K. As noted previously, a serious weakness in this analysis arises from the use of the "bare" atom effective mass in the calculation of a Mössbauer lattice temperature, since covalency effects normally play a significant role in the lattice dynamical behavior of solids of the type here under discussion. However, in the absence of second-order Doppler shift data, no experimental estimate of a more appropriate effective vibrating mass can be calculated from the available data, and the above cited lattice temperatures should be regarded in relative terms only. It is, however, interesting to note that the cation site metal atom has the higher value of θ_M , in consonance with the sandwich structure inferred above.

(b) $(15\text{Cr5})_2\text{Sn}(\text{ClO}_4)_2$. In contrast to the ^{119}Sn Mössbauer spectrum of the 15Cr5 stannous chloride complex discussed above, the spectrum of the complex with stannous perchlorate consists of a sharp singlet resonance at an isomer shift of $4.53 \pm 0.01 \text{ mm s}^{-1}$ at 78 K (Figure 3). In consonance with the earlier interpretation,¹ this resonance line is assigned to a "bare" Sn^{2+} ion sandwich between two 15Cr5 ligands. The perchlorate anions provide the requisite anionic gegenions needed to stabilize the structure. The temperature dependence of the isomer shift, $d(\text{IS})/dT$, corresponds to $-4.58 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$. This value is about 30% larger than the "classical"

(11) R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, **13**, 248 (1974).

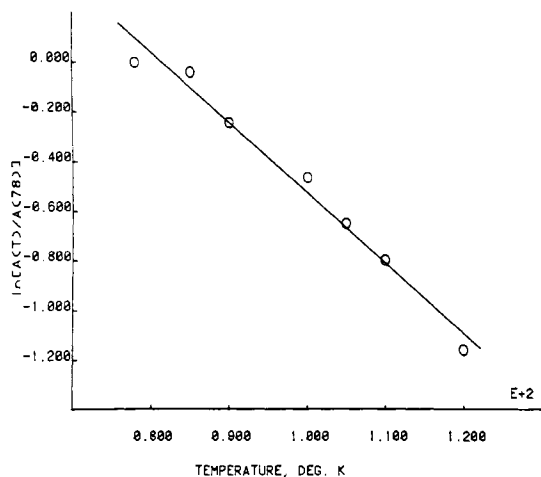


Figure 4. Temperature dependence of the area under the ^{119}Sn Mössbauer resonance curve for $(15\text{-crown-5})_2\text{Sn}(\text{ClO}_4)_2$ (see Figure 3). The straight line is a least-squares fit to the data, and the correlation coefficient (7 points) is 0.990.

free atom slope ($3kT/2mc^2$) of $-3.499 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ and reflects the influence on the vibrating effective mass of the two polyether ligands sandwiching the metal ion. The temperature dependence of the recoil-free fraction for a thin Mössbauer absorber can be equated to the temperature dependence of the area under the resonance curve in the high-temperature limit. For the $^{15}\text{Cr5 Sn}(\text{ClO}_4)_2$ complex, this temperature dependence (Figure 4) is given by $d \ln A/dT = -2.827 \times 10^{-2} \text{ K}^{-1}$ over the temperature range $78 \leq T \leq 120 \text{ K}$, with a correlation coefficient of 0.990 for the seven data points. This temperature dependence is comparable to that observed for the $^{18}\text{Cr6} [\text{Sn}(\text{ClO}_4)_2]$ complex ($-2.25 \times 10^{-2} \text{ K}^{-1}$) over the same temperature range and is significantly larger than that reported for the cationic tin site in $^{18}\text{Cr6} (\text{SnCl}_2)_2$ or the corresponding data for $\text{Sn}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, suggesting that the mean square amplitude of vibration has a larger temperature dependence in the "bare ion" sandwich configuration than in the presence of a strong (covalent) metal atom-to-ligand bonding interaction. In the case of stannic compounds, in which the tin atom is part of an extended covalent network structure—as, for example, in SnS_2 and SnSe_2 — $d \ln A/dT$ is typically¹² on the order of $-0.5 \times 10^{-2} \text{ K}^{-1}$.

Finally, in the context of the present discussion, it is worth noting that the tin isomer shift in $(^{15}\text{Cr5})_2\text{Sn}(\text{ClO}_4)_2$ and the resonance ascribed to the cation site in $(^{15}\text{Cr5})_2(\text{SnCl}_2)_3$ are among the most positive noted for any stannous ion electron configuration.¹³ In a recent discussion of the electronic properties of CsSn , Bates et al.¹⁴ point out that the 5s electron density in intermetallic compounds can be estimated from ^{119}Sn Mössbauer isomer shifts, in consonance with the earlier discussion pertaining to $\text{Sn}(\text{II})$ and $\text{Sn}(\text{IV})$ compounds by Lees and Flinn.¹⁵ From such systematics, the extrapolated isomer shift for a tin site in which the 5s electron density corresponds to two, together with sufficient 5p electron density to account for the bond hybridization, is $\sim 3.96 \text{ mm s}^{-1}$. The present data for a "bare" Sn^{2+} ion can be accounted for in terms of the shielding effect of the 5p electrons, which reduce the effective 5s electron density at the tin nucleus in the case of the intermetallics and the stannous compounds considered in the

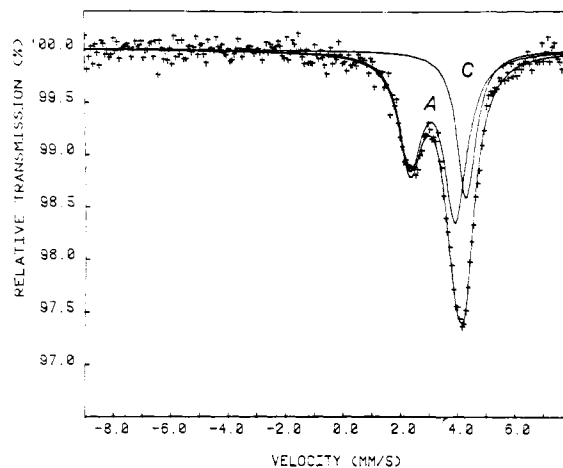


Figure 5. ^{119}Sn Mössbauer-effect spectrum of $(15\text{-crown-5})_2[\text{Sn}(\text{SCN})_2]_3$ at 81 K.

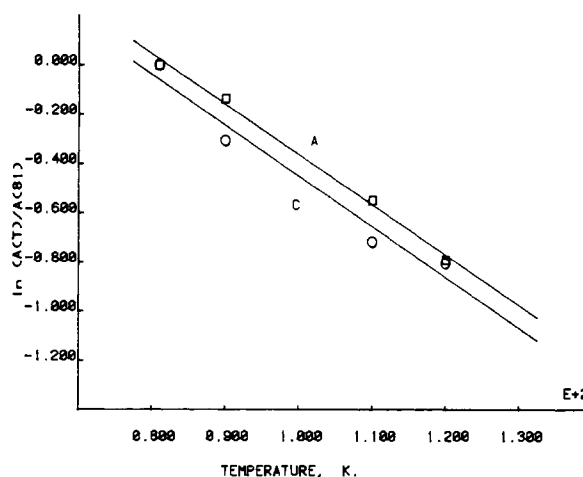


Figure 6. Temperature dependence of the area under the resonance curve for the cation singlet (C, circles) and the anion doublet (A, squares) of the ^{119}Sn Mössbauer spectra of $(^{15}\text{Cr5})_2[\text{Sn}(\text{SCN})_2]_3$. The two straight lines are linear least-squares fits to the data and have correlation coefficients (4 points) of 0.99 and 0.98, respectively.

systematics of Lees and Flinn.¹⁵ This shielding effect amounts to an isomer shift difference of about 0.5 s^{-1} when the 5p population is on the order of 3.

(c) $(^{15}\text{Cr5})_2[\text{Sn}(\text{SCN})_2]_3$. The ^{119}Sn Mössbauer spectrum of the reaction product between the polyether and anhydrous stannous thiocyanate (Figure 5) is qualitatively similar to that observed for the reaction product with stannous chloride, and the numerical data extracted from such spectra are summarized in Table I. In contrast to the complex formed with $^{18}\text{Cr6}$, the spectrum due to the $^{15}\text{Cr5}$ 2:3 complex can be deconvoluted into a singlet (C) and a doublet (A). The latter resonance is assigned to the $\text{Sn}(\text{SCN})_3^-$ anion on the basis of isomer shift and quadrupole splitting systematics.^{1,16} It should be noted, parenthetically, that the assignment implied in Figure 5 is only one of several possibilities. However, the assignment of the two outermost lines as a doublet to the anion, and the resonance line at $\sim 4.0 \text{ mm s}^{-1}$ to the cation singlet, leads both to isomer shift inconsistencies as well as to an area ratio that is untenable with respect to the presence of three tin atoms per formula unit. The assumptions made in the interpretation offered here is that the recoil-free fractions of the doublet and of the singlet are nearly the same at liquid nitrogen temperature. No prior constraints (intensity, line width or position)

(12) R. H. Herber, A. E. Smelkinson, M. J. Sienko, and L. F. Schneemyer, *J. Chem. Phys.*, **68**, 3705 (1978).

(13) P. A. Flinn in "Mössbauer Isomer Shifts", G. K. Shenoy and F. E. Wagner, Eds., North-Holland Publishing Co., Amsterdam, 1978, p 593ff.

(14) C. W. Bates, Jr., P. M. Th. M. van Attekum, G. K. Wertheim, and D. N. E. Buchanan, *Phys. Rev. B: Condens. Matter*, **B22**, 3968 (1980).

(15) J. K. Lees and P. A. Flinn, *J. Chem. Phys.*, **48**, 882 (1968).

(16) J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, 1796 (1966); see however J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, **29**, 2191 (1967).

Table II. Summary of Infrared Data for 15-Crown-5 (Neat, NaCl Plates) and the Stannous Complexes Discussed in the Text^a

15-crown-5	(15Cr5) ₂ ⁻ (SnCl ₂) ₃	(15Cr5) ₂ ⁻ [Sn(SCN) ₂] ₃	(15Cr5) ₂ ⁻ Sn(ClO ₄) ₂
2860 vs	2910 s 2867 s	2910 m 2867 m 2010 vs (CN)	2915 s, b 2871 m
1448 m	1454 m, b	1441 m, b	1447 m, b
1356 s	1351 s	1349 m	1354 m
1293 m, b	1300 s	1295 m	1302 m
1252 m	1245 s	1242 m	1246 ms
1128 s (COC)	1114 m	1115 s	1119
	1084 vs	1982 s	1087 s, b
	1035 m	1030 m	1039
983 m	940 s	947 s	946 s
938 s, b (CH ₂)			
855 m	855 s 816 m	855 s 816 m	855 s 816 s, b 630 w, sh 621 s (Cl-O)

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

have been imposed in fitting the spectral data as implied in Table I.

The singlet (C) is again assumed to arise from a "bare" Sn²⁺ cation sandwiched between two 15Cr5 ligands, consistent with the isomer shift data referred to in the discussion of the chloro and perchlorate compounds above. The ratio of the (A) doublet to the (C) singlet areas is 2.1:1 at 81 K, consistent with the observed stoichiometry and the structure for the complex, which is presumed to consist of a (15Cr5)₂Sn²⁺ sandwich and two Sn(SCN)₃⁻ counterions in the solid state.

Finally, in connection with these results, it should be noted that the temperature dependence of the logarithm of the area under the resonance curve (reflecting the recoil-free fraction) for the C and A resonances in (15Cr5)₂[Sn(SCN)₂]₃, while identical within experimental error, are larger than the respective values for the chloro complex and smaller than the value for the perchlorate complex (see Table I). In these compounds, in which relatively strong bonding interactions between ionically interacting species as well as within each charged moiety can be presumed to occur, the simple relationships that have been suggested earlier¹⁷ as describing the

lattice dynamics of purely covalent solids are no longer applicable. It seems clear from the present data that the motions of the metal atoms in these solids are not simply related to the formula weights of the chemical species present, but reflect the detailed bonding and geometry of the participating ligands as well.

The infrared spectra of the 15Cr5 stannous complexes prepared in this study are summarized in Table II and support the existence of a direct bonding interaction between the metal ion and the crown ether as discussed above. It had been noted¹ in the earlier study of the corresponding 18Cr6 complexes that the asymmetric COC stretch is shifted from 1106 cm⁻¹ in the free ligand to ~1089 cm⁻¹ in the stannous chloride compound. This shift has also been reported by Bünzli and Wessner² in the complexes formed by the lighter lanthanoid nitrates with 18Cr6. In 15Cr5, the corresponding absorption is observed at 1128 cm⁻¹ in the free ligand. This band is shifted to 1114–1119 cm⁻¹ in the stannous complexes here reported. This red shift of 9–14 cm⁻¹ is similar to those reported for the 1:1 complexes of 15Cr5 and the lighter lanthanoids by Bünzli and Wessner, and in the La(III) complexes of benzo 15Cr5 as studied by King and Heckley,¹⁸ but only half to one fourth as large. Similar shifts have been reported by Bünzli et al.³ in their study of Pr(III) complexes of 15Cr5; however, the characteristic blue shift (by 15–20 cm⁻¹) of the band, which is observed at 855 cm⁻¹ in the free ligand, has not been observed in the stannous complexes of this crown ether.

Acknowledgment. This work has been generously supported by the National Science Foundation under Grant DMR 7808615A02 and by a grant for computing services from the Center for Computer and Information Services, Rutgers University. The authors are indebted to Mr. T. K. McGuire for assistance with the computational aspects involved in this research, and to Mr. Mark Tellefsen for some of the preliminary synthetic studies. This work was taken in part from the Senior Research Thesis of G.C. submitted to Rutgers University, May 1980. Finally, the authors would like to acknowledge their indebtedness to Drs. T. Vieggers and J. Trooster, who wrote the SPECTRA computer program used in this work, and in particular to the late Dr. Trosster for his unflinching willingness to assist in the Mössbauer studies carried out in these laboratories.

Registry No. (15Cr5)₂(SnCl₂)₃, 78716-12-8; (15Cr5)₂Sn(ClO₄)₂, 78716-13-9; (15Cr5)₂[Sn(SCN)₂]₃, 78716-14-0; 15-crown-5, 33100-27-5.

(17) Y. Hazony and R. H. Herber, *J. Phys. (Orsay, Fr.)* **66**, 131 (1974); R. H. Herber, J. Fischer, and Y. Hazony, *J. Chem. Phys.*, **58**, 5185 (1973); Y. Hazony and R. H. Herber in "Mössbauer Effect Methodology", Vol. 8, I. Gruverman, Ed., Plenum Press, New York, 1973.

(18) R. B. King and P. R. Heckley, *J. Am. Chem. Soc.*, **96**, 3118 (1974).