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Vibrational Frequencies and Intramolecular Forces in Anionic Tin–Halogen Complexes and Related Species

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Far-infrared and Raman spectra are reported for solids containing the SnX_6^{2-} (X = Cl, Br, I) and SnX_3^- (X = F, Cl, Br, I) ions in combination with large monopositive cations. These results include the first complete report of infrared- and Raman-active fundamentals for SnF_3^-, SnI_3^-, and SnI_6^{2-}. Normal-coordinate vibrational analysis was performed for these complexes and for SnX_4 (X = Cl, Br, I) under a uniform set of approximations. For a series of compounds containing the same halide it is found that the primary stretching force constants are approximately proportional to the metal oxidation state divided by the coordination number. Theoretical values for the force constants were calculated using an ionic model. These reproduce the reduction in force constant which is observed upon going from SnX_4 to SnX_6^{2-}.

Introduction

This report concerns the influence of oxidation state and coordination number on vibrational frequencies and force constants. While the literature contains many incidental observations on this topic, there are few systematic investigations. Qualitatively, it is known that metal halogen frequencies decrease with decreasing oxidation state of the central metal and also usually decrease upon an increase in the coordination number.[2–4] In a quantitative study, Siebert has shown that for a binary halide and its corresponding anionic halogeno complex, the primary stretching force constant is approximately inversely proportional to the coordination number of the central atom.[5]

Before the present work, all of the infrared- and Raman-active fundamentals had been observed and assigned for SnX_3^- (X = Cl, Br) and SnX_6^{2-} (X = F, Cl, Br). However, the condition of the samples studied varied from ether solutions to solids containing small cations. Therefore, it was necessary to redetermine these frequencies under uniform conditions (solids containing large monopositive cations) and to investigate analogous salts of SnF_3^-, SnI_3^-, and SnI_6^{2-}, for which literature data were either fragmentary or nonexistent.

Experimental Section

Far-infrared spectra were recorded on a Beckman IR-11 which was modified by the addition of a photoelectric demodulation system and a dimmer switch on the Golay lamp which greatly extended the life of the detector. Calibration of the instrument was occasionally checked with atmospheric water bands and the instrument was found to be within ±0.5 cm^{-1} of the reported band positions.[6] All samples were observed as Nujol mulls between high-density polyethylene plates.

The Raman spectrometer consists of a SPEX 1400 double monochromator and a SPEX 1430 sample illuminator. The source is a 50-mW Spectra-Physics He-Ne laser, Model 125. Photon counting detection is employed *via* an ITT FW-130 photomultiplier maintained at *ca.* −10° by a thermoelectric cooler (Products for Research Inc.). Amplification and derivative discrimination of the signal is provided by an ORTEC 260 Time Pickoff in conjunction with a 403A Time Pickoff Control. The resulting pulses are modified and amplified by a holding amplifier and filter designed by R. J. Loyd. The signal is displayed on a Leeds and Northrup Type H strip chart recorder. Most samples were observed as solid 0.5-in. diameter pellets. However, $[(C_6H_5)_4As][SnI_3]$ was air sensitive and was handled in nitrogen-filled all-glass cells. After each run the position of the 6328.17-Å laser line was observed to calibrate the wavelength pipping signal. From an observation of the 6351.87-Å Ne line it is estimated that band positions for sharp Raman lines are determined to within ±0.14 Å. Over the frequency range for the compounds in this study the error is *ca.* ±1 cm^{-1} for Raman shifts.

X-Ray powder patterns were determined with a 114-mm diameter Debye–Scherrer camera using nickel-filtered Cu Kα radiation. Film shrinkage corrections were applied by use of added alkali halide calibrants in the samples.

Preparations.—All solutions of iodide complexes and tribromostannate(II) solutions were manipulated under nitrogen by use of Schlenk techniques and glove bags.[7] The solid triiodostannate(II) complexes were oxygen sensitive and were stored under nitrogen in sealed ampoules. Carbon, hydrogen, and nitrogen analyses were performed by Miss Hilda Beck of this department. Cl, Br, and I were determined gravimetrically as silver halide. Tin and fluoride analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

$[(CH_3)_4N]_2[SnCl_6]$ and $[(CH_3)_4N]_2[SnBr_6]$ were prepared by adding the stannic halide to aqueous acid solutions of the tetramethylammonium halide, to give white and orange-yellow products, respectively.

$[(C_2H_5)_4N]_2[SnCl_6]$ and $[(C_2H_5)_4N]_2[SnBr_6]$ were precipitated by mixing ethanol solutions of stannic halide and tetraethylammonium halide. The bromide complex was yellow in this case.

The above compounds gave C, H, N, and Cl or Br analyses close to theoretical.

$[(C_2H_5)_4N]_2[SnI_6]$ and $[(n\text{-}C_3H_7)_4N]_2[SnI_6]$.—Stannic iodide

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[1] Alfred P. Sloan Fellow

[2] R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

[3] D. M. Adams, "Metal–Ligand and Related Vibrations," Edward Arnold Ltd., London, 1968, pp 46–79.

[4] Exceptions to the decrease in frequency upon increase in coordination number are known when the central metal serves as an electron donor: D. F. Shriver and M. P. Johnson, *Inorg. Chem.*, **6**, 1265 (1967).

[5] H. Siebert, *Z. Anorg. Allgem. Chem.*, **274**, 34 (1953).

[6] K. N. Rao, C. J. Humphreys, and D. H. Rank, "Wavelength Standards in the Infrared," Academic Press, New York, N. Y., 1966, p 145.

[7] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, Chapters 7 and 8.

(4.70 g) in chloroform (50 ml) was added to excess tetraethylammonium iodide (4 g) in chloroform (150 ml) to yield a dark maroon precipitate of tetraethylammonium hexaiodostannate, yield ~91%. *Anal.* Calcd for $C_{16}H_{40}I_6N_2Sn$: C, 16 85; H, 3.53; N, 2.46; I, 66.76. Found: C, 16.88, 16:88; H, 3.40, 3.42; N, 2.48, 2.58; I, 66.30. A similar preparation using tetra-*n*-propylammonium iodide gave the dark maroon hexaiodostannate(IV) complex. *Anal.* Calcd for $C_{24}H_{56}I_6N_2Sn$: C, 23.01; H, 4.56; N, 2.24; I, 60.78. Found: C, 23.01, 23.01; H, 4.42, 4.38; N, 2.17, 2.24; I, 59.67.

$[(C_6H_5)_4As][SnCl_3]$.—The preparation and analysis of this sample are described elsewhere.[8]

$[(C_6H_5)_4P][SnCl_3]$ was prepared in the same manner as **$[(C_6H_5)_4As][SnCl_3]$** to give a white product. *Anal.* Calcd for $C_{24}H_{20}Cl_3PSn$: C, 51.07; H, 3.57; Cl, 18.84. Found: C, 50.70, 50.65; H, 3.41, 3.47; Cl, 18.97.

$[(C_6H_5)_4As][SnBr_3]$.—A solution of tetraphenylarsonium carbonate (prepared from tetraphenylarsonium chloride and silver carbonate) was slowly added, while stirring, to a solution of stannous bromide in 3 *M* hydrobromic acid. The light yellow tribromostannate(II) was filtered off and air dried. *Anal.* Calcd for $C_{24}H_{20}AsBr_3Sn$: C, 38.86; H, 2.72; Br, 32.32. Found: C, 38.31, 38.38; H, 2.76, 2.58; Br, 32.51.

$[(C_6H_5)_4As][SnI_3]$.—Stannous chloride (1.0 g) was dissolved in boiling 3 *M* hydriodic acid (100 ml). Tetraphenylarsonium chloride (2.09 g) was slowly added to the hot stirred solution. After 30 min the deep yellow triiodostannate(II) was filtered off, washed with degassed ethanol, and dried *in vacuo. Anal.* Calcd for $C_{24}H_{20}AsI_3Sn$: C, 32.66; H, 2.28; I, 43.13. Found: C, 32.22, 32.26; H, 2.00, 2.00; I, 42.53.

$[(C_6H_5)_4As][SnF_3]$ and **$[(C_6H_5)_4P][SnF_3]$.**—Procedures using adaptions of the above methods were unsuccessful owing to the high solubility of the SnF_3^- complex even in strong hydrofluoric acid solutions. Addition of ethanol or ether invariably gave stannous fluoride as the least soluble component in the system. Finally, the solubility of the salts of these cations in methylene chloride was used as the basis of an extraction procedure.

Tetramethylammonium fluoride (2 g) and stannous fluoride (2.4 g) were dissolved in a filtered solution of tetraphenylarsonium carbonate prepared by boiling tetraphenylarsonium chloride (2.09 g) in water (50 ml) with a large excess of silver carbonate. The mixture was extracted with methylene chloride (ten 30-ml portions), the combined extracts were evaporated to *ca.* 20 ml, and the product was precipitated with a large amount of pentane. The crude material contained some $[(C_6H_5)_4As]F$ and was dissolved in fresh, concentrated aqueous stannous fluoride solution. The mixture was extracted as above, and addition of pentane to the concentrated extracts gave white tetraphenylarsonium trifluorostannate(II). *Anal.* Calcd for $C_{24}H_{20}AsF_3Sn$: C, 51.47; H, 3.60; Sn, 21.19; F, 10.18. Found: C, 51.36, 51.36; H, 3.58, 3.54; Sn, 19.92; F, 9.50.

A procedure analogous to that used for $[(C_6H_5)_4As][SnF_3]$ gave white tetraphenylphosphonium trifluorostannate(II).[9] *Anal.* Calcd for $C_{24}H_{20}F_3PSn$: C, 55.96; H, 3.91; Sn, 23.04; F, 11.07. Found: C, 55 67, 55.53; H, 3 92, 3.82; Sn, 21.25; F, 10.58.

***trans*-$[Co(en)_2(NO_2)_2][SnCl_3]$.**—A hot aqueous solution (50 ml) of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ (3.33 g) and potassium chloride (1.5 g) was added to one of stannous chloride dihydrate (2.25 g) and KCl (1.5 g). The mixture was cooled in ice and the yellow crystals of *trans*-dinitrobis(ethylenediamine)cobalt(III) trichlorostannate(II) were filtered off, washed with methanol and ether, and air dried. *Anal.* Calcd for $C_4H_{16}Cl_3CoN_6O_4Sn$: C, 9.68; H, 3.25; N, 16.94; Cl, 21.44. Found: C, 9.77, 9.52; H, 3.04, 2.97; N, 16.58, 16.48; Cl, 21.08.

***trans*-$[Co(en)_2(NO_2)_2][SnI_3]$.**—Fresh stannous iodide hydrate (prepared by adding stannous chloride (1.90 g) to excess potassium iodide in water (20 ml)) was added with stirring to an ice-cold aqueous solution (150 ml) of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ (3.33 g) and potassium iodide (1.7 g). The mixture was stirred for 3 hr at 0° and allowed to settle. The supernatant liquor was decanted, and the yellow product was washed with ice-cold degassed water and methanol and then filtered off under nitrogen. The compound was further washed with degassed methanol and ether and dried *in vacuo. Anal.* Calcd for $C_4H_{16}CoI_3N_6O_4Sn$: C, 6.24; H, 2.09; N, 10.91; I, 49.41. Found: C, 6.09, 6.09; H, 2.21, 2.16; N, 10.36, 10.18; I, 48.24.

Results and Discussion

Assignments and Band Positions.—There is an extensive literature on the vibrational spectra of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ which is summarized in Table I along with results of the present study. No disagreement exists over the assignment of the infrared-active fundamentals (ν_3 and ν_4) and Raman-active fundamentals (ν_1, ν_2, and ν_5); however, the agreement between the exact band positions for the same substance is only fair.

The infrared bands of SnI_6^{2-} have been reported for the cesium and tetraethylammonium salts (Table I). In fair agreement with these reports, we assign ν_3 to the 161-cm^{-1} band of $[(C_2H_5)_4N]_2[SnI_6]$ and ν_4 to a weak band at 84 cm^{-1}. A shoulder at 93 cm^{-1} in the latter region is unassigned. Because tetramethylammonium salts generally contain a lattice mode in this region, the salt of this cation was not investigated. The Raman lines assigned to fundamentals ν_1, ν_2, and ν_5 (Figure 1B) display the characteristic strong–weak–medium intensity pattern for an MX_6 species. As shown in Figure 1A, Raman bands are also observed at 244, 182, and 138 (sh) cm^{-1}. The first of these corresponds to $2\nu_1$ and the second to $2\nu_2$. However, the shoulder at 138 cm^{-1} does not agree well with $2\nu_5$ and it may represent an overtone or combination involving lattice modes.

An X-ray structure determination on $KSnCl_3 \cdot KCl \cdot H_2O$ has demonstrated the presence of an $SnCl_3^-$ complex as a slightly distorted trigonal pyramid.[10] Furthermore, the Raman solution spectra of $SnCl_3^-$ and $SnBr_3^-$ are characteristic of a pyramidal XY_3 species.[11] These observations agree with the stereochemical activity of the lone electron pair on Sn(II) which is observed with most, but not all, stannous compounds.[12] Accordingly, the SnX_3^- spectra are interpreted in terms of regular or distorted pyramidal species depending on the details of each spectrum.

Results from both infrared and Raman spectra for $[(C_6H_5)_4As][SnX_3]$ compounds together with appropriate literature data are shown in Table II. For an XY_3 system with C_{3v} symmetry, four fundamentals, ν_1 and ν_2 (A_1), ν_3 and ν_4 (E) are expected, all infrared and Raman active. While the tetraphenylarsonium cation has no significant interfering absorptions in the infrared region of interest (50–350 cm^{-1}), several large cation

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[8] I. Wharf and D. F. Shriver, to be submitted for publication.

[9] H. F. Holtzclaw, D. P. Sheetz, and B. D. McCarthy, *Inorg. Syn.*, **4**, 176 (1953).

[10] D. Gredenic and B. Kamenar, *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962).

[11] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 402 (1962).

[12] J. D. Donaldson, *Progr. Inorg. Chem.*, **8**, 287 (1967).

TABLE I

VIBRATIONAL FREQUENCIES (cm^{-1}) OF HEXAHALOSTANNATE(IV) IONS

Compound	State	ν_1	ν_2	ν_3	ν_4	ν_5	$\nu_4 + \nu_5$
$[(CH_3)_4N]_2[SnCl_6]$[a]	Solid	312 vs	235 w, br	309 vs	168 s	165 s	. . .
$[(C_2H_5)_4N]_2[SnCl_6]$[a]	Solid	310 s	234 w, br	303 s	166 s	158 s	314 s
$[(C_2H_5)_4N]_2[SnCl_6]$[b]	Solid			295	161		310
$[(C_2H_5)_4N]_2[SnCl_6]$[c]	Solid	305.5	. . .	318, 276	161	. . .	
Cs_2SnCl_6[c]	Solid	309	243	310	171	165	
$[NH_4]_2[SnCl_6]$[c]	Solid	317	250	310	180	179	
K_2SnCl_6[c]	Solid	323	249	314	174	184	
$[NH_4]_2[SnCl_6]$[d]	Solid	. . .	. . .	313	177	. . .	
K_2SnCl_6[d]	Solid	. . .	. . .	318	174	. . .	
Cs_2SnCl_6[e]	Solid	. . .	. . .	309	172	. . .	
$[NH_4]_2[SnCl_6]$[e]		318	238	318	178	169	
K_2SnCl_6[e]		311	235	325	172	165	
$[(C_2H_5)_4N]_2[SnCl_6]$[f]	CH_3NO_2 soln	. . .	. . .	300	. . .	. . .	
$SnCl_6^{2-}$ [g]	Aq soln	311	229	. . .	. . .	158	
$[(CH_3)_4N]_2[SnBr_6]$[a]	Solid	181 vs	137 m	213 s	116 m	108 s	
$[(C_2H_5)_4N]_2[SnBr_6]$[a]	Solid	185 s	136 w	215 vs	114 s	103 m	
$[(C_2H_5)_4N]_2[SnBr_6]$[b]	Solid	. . .	. . .	206	110		
$[(C_2H_5)_4N]_2[SnBr_6]$[i]	Solid	182	135	203	111	101	
$[NH_4]_2[SnBr_6]$[d]	Solid			217	122		
K_2SnBr_6[d]	Solid			220	117		
$[NH_4]_2[SnBr_6]$[e]	Solid			227	120		
Cs_2SnBr_6[e]	Solid			222	118		
K_2SnBr_6[e]	Solid			224	118		
K_2SnBr_6[h]	Solid			232			
Cs_2SnBr_6[h]	Solid			215			
$SnBr_6^{2-}$ [g]	Aq soln	184	140			101	
$[(C_2H_5)_4N]_2[SnI_6]$[a]	Solid	122 s	93 w	161 s	(93 sh) 84 w	78 sh	
$[(C_3H_7)_4N]_2[SnI_6]$[a]	Solid	114 s	. . .	159 vs	81 w	83 m	
Cs_2SnI_6[d]	Solid			165	86		
$[(C_2H_5)_4N]_2[SnI_6]$[i]	Solid			156	90 sh 79 m		

[a] This work. [b] J. A. Creighton and J. H. S. Green, *J. Chem. Soc., A*, 808 (1968). [c] D. M. Adams and D. M. Morris, *ibid.*, 1669 (1967). [d] N. N. Greenwood and B. P. Straughan, *ibid.*, 962 (1966). [e] J-P. Matthieu and M. Debeau, *Compt. Rend.*, **260**, 5229 (1965); Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz, 1966, p 157. [f] I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc., A*, 712 (1967). [g] L. A. Woodward and L. E. Anderson, *ibid.*, 1284 (1957). [h] D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *ibid.*, 100 (1967). [i] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968).

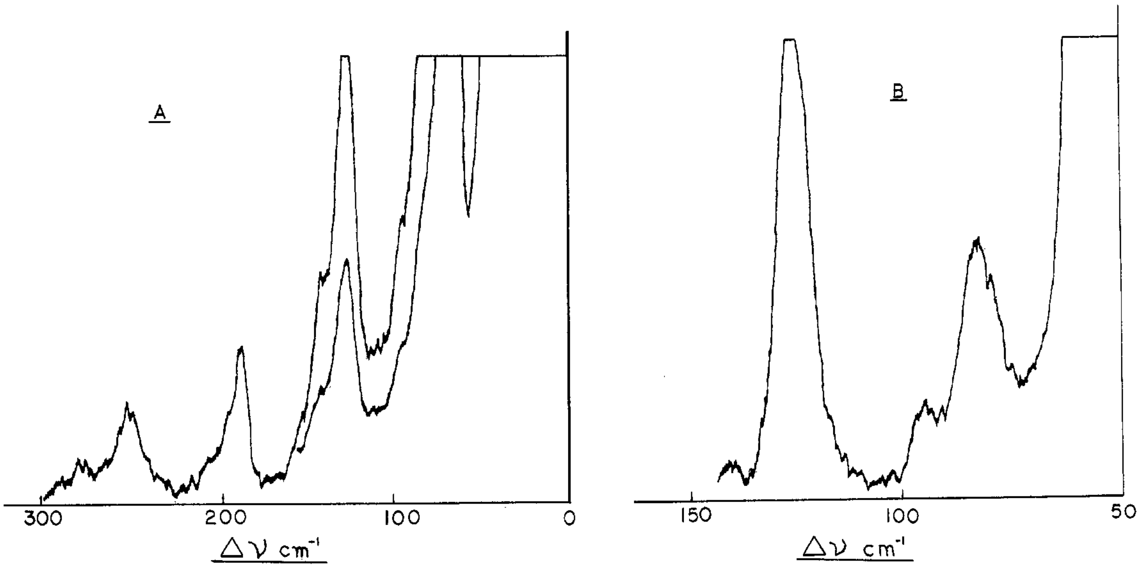

Figure 1.—Raman spectrum of $[(C_2H_5)_4N]_2[SnI_6]$: (A) scan showing ν_1 and overtones, $2\nu_1$ and $2\nu_2$; (B) expanded scan showing ν_1, ν_2, and ν_5.

TABLE II

VIBRATIONAL FREQUENCIES (CM^{-1}) OF TRIHALOSTANNATE(II) IONS

C_{3v} Symmetry

Compound	State	Method	ν_1	ν_2	ν_3	ν_4
$[(C_6H_5)_4As][SnCl_3]$[a]	Solid	Ir	291 s	133 w	258 vs	110 vw
		Raman	288 vw	130 sh	259 vw	105 vs
$[(C_6H_5)_4P][SnCl_3]$[a]	Solid	Ir	292 s	....	258 vs	....
$[Co(en)_2(NO_2)_2][SnCl_3]$[a]	Solid	Ir	294 s	130 wsh	252 vs	110 vw
$SnCl_3^-$[b]	$(C_2H_5)_2O$ soln	Raman	297	128	256	103
$SnBr_3^-$[b]	$(C_2H_5)_2O$ soln	Raman	211	83	181	65
$[(C_6H_5)_4As][SnF_3]$[a]	Solid	Ir	520 m	280 w		224 s
$[(C_6H_5)_4P][SnF_3]$[a]	Solid	Ir		280 w	478	224 s

C_s Symmetry

Compound	State	Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$[(C_6H_5)_4As][SnBr_3]$[a]	Solid	Ir	201 s	176 vs	86 w	65 w	183 vs	65 w
		Raman	202 w	176 w	97 vs	73 vs	186 m	73 vs
$[(C_6H_5)_4As][SnI_3]$[a]	Solid	Ir	151 s	124 s	65 vw	....	143 s	....
		Raman	152 m	128 m	60 vs?	50 vs?	137 s	50 vs?
$[Co(en)_2(NO_2)_2][SnI_3]$[a]	Solid	Ir	149 s	123 s	....	....	132 m 137 sh	....

[a] This work. [b] Reference 11.

bands are observed in the Raman spectra. All three compounds $[(C_6H_5)_4As][SnX_3]$ (X = Cl, Br, I) have bands at *ca.* 236 and 247 cm^{-1}, while nearer to the exciting line very strong Raman emissions are observed. $[(C_6H_5)_4As][SnCl_3]$ has a very strong band merging with the exciting line below 100 cm^{-1}, while $[C_6H_5)_4As][SnBr_3]$ has very strong bands at 73 and 97 $\text{cm}^{-1}$and $[(C_6H_5)_4As][SnI_3]$ has strong bands at 50 and 60 cm^{-1}. Interestingly, the intensities of bands in the Raman spectra of SnX_3^- species are somewhat less than those of the equivalent SnX_6^{2-}.

The data for $[(C_6H_5)_4As][SnCl_3]$ require no further comment, except that variation of a large cation has little effect on the frequencies. However, the assignments for the trifluorostannate(II) ion differ from those proposed for the spectra of alkali metal salts of this anion. From an early investigation[13] of the Raman and infrared spectra of NH_4SnF_3, the assignments made were ν_s(Sn–F) 552 cm^{-1} and ν_{as}(Sn–F) 478 cm^{-1}. Since this report, Donaldson, *et al.*, have published vibrational data for a large number of alkali and alkaline earth trifluorostannates(II).[14,15] A very large variation with cation was noted and in nearly all cases an additional band at $\sim$400 cm^{-1} was observed. The assignments, made by extrapolation from the literature values for SnX_3^- (X = Cl, Br), were ν_1 $\sim$430–480 and ν_3 $\sim$370–410 cm^{-1}, while the higher frequency shoulder at 490–530 cm^{-1} was assigned to $\nu_3 + \nu_4$, of a regular pyramidal SnF_3^- species.[14,15] However, it is possible that these metal salts do not contain discrete trifluorostannate ions.[16]

The infrared spectra of the large-cation-containing compounds considered here, $[(C_6H_5)_4As][SnF_3]$ and $[(C_6H_5)_4P][SnF_3]$, show only two sharp peaks in the tin–fluorine stretching region. In order to observe these, it was necessary so use two cations, because cation bands obscure one or other of the peaks in each case (Figure 2). It is unlikely that exchange of $(C_6H_5)_4P^+$ for $(C_6H_5)_4As^+$, where both can be assumed to have very similar dimensions, will cause large variation in the Sn–F stretching vibrations. Very little difference is noted between the values for the Sn–Cl stretch vibrations for $[(C_6H_5)_4As][SnCl_3]$ and $[(C_6H_5)_4P][SnCl_3]$. Assignments were made by analogy with the $SnCl_3^-$ and $SnBr_3^-$ systems.

Both the infrared and the Raman spectra of $[(C_6H_5)_4As][SnBr_3]$ and $[(C_6H_5)_4As][SnI_3]$ (Figures 3 and 4) show three bands in the Sn–X stretching region instead of the expected two. Otherwise, the $SnBr_3^-$ bands fall in nearly identical regions for either the solid or the solution, which indicates the coordination number of tin is unchanged in the solid. The obvious interpretation is that the degeneracy of ν_3 has been lifted by low site symmetry. The assignments presented in Table II are based on the simple assumption of C_s symmetry which leads to six fundamentals—ν_1, ν_2, ν_3, and ν_4 of species A′ and ν_5 and ν_6 of species A″.

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(13) H. Kriegsmann and G. Kessler, *Z. Anorg. Allgem. Chem.*, **318**, 227 (1962)

(14) J. D. Donaldson, J. F. Knifton, J. O'Donoghue, and S. D. Ross, *Spectrochim. Acta*, **22**, 1173 (1966).

(15) J. D. Donaldson and B. J. Senior, *J. Chem. Soc., A*, 1821 (1967).

(16) An X-ray diffraction investigation (A. N. Christensen and S. E Rasmussen, *Acta Chem. Scand.*, **19**, 421 (1965)) of a related compound, $CsGeCl_3$, shows it to have an essentially ionic structure of the rhombohedral distorted perovskite type, with each Ge^{2+} ion in a distorted octahedron of six Cl^- ions. The Ge–Cl distances are 2.31 (3) and 3.13 (3) Å and the distortion is caused by a displacement of the germanium(II) ion from the center of symmetry and not by a change in the chloride lattice. Above 155° the compound assumes an ideal perovskite form with 6 identical Ge-Cl distances (2.74 Å). Stannous fluoride also occurs in two mainly ionic forms, one with a monoclinic rutile structure, while a second form has an orthorhombic lattice with the tin(II) ion surrounded by a distorted octahedron of fluoride ions, with Sn–F distances of 2.15 (2), 2.45 (1), and >2.80 Å.[12] Many double fluorides of the form $M^IM^{II}F_3$, in fact, show broad bands in the metal–fluorine stretching region, but it has not been proposed that these compounds contain distinct $M^{II}F_3^-$ species: R. D. Peacock and D. W. A. Sharpe, *J. Chem. Soc.*, 2762 (1959). NOTE ADDED IN PROOF.—Our proposal is borne out by recent X-ray structural studies (G. Bergerhoff and L. Goost, Proceedings of the 11th International Conference on Coordination Chemistry, Haifa, Israel, 1966, p 273).

TABLE III

X-RAY POWDER DATA (*d* SPACINGS, Å)

$[(C_6H_5)_4P][SnF_3]$	$[(C_6H_5)_4As][SnF_3]$	$[(C_6H_5)_4As][SnCl_3]$	$[(C_6H_5)_4As][SnBr_3]$	$[(C_6H_5)_4As][SnI_3]$
8.78 w				11.55 w
7.50 vw	7.59 vw	7.48 m	7.44 w	8.19 vw
6.84 vw	6.89 vw	6.82 m	6.82 w	6.99 vvw
6.21 vs	6.24 vs	6.43 m	6.25 w	5.10 vvw
4.84 vw	4.85 vw	6.09 w	4.85 w	4.03 m
4.38 vs	4.40 vs	4.89 s	4.42 vw	3.49 m
3.89 m	3.96 w	4.56 w	3.81 m	2.48 s
3.57 s	3.62 s	4.37 w	3.30 s	2.17 m
3.33 m	3.28 m	3.89 m	2.33 s	1.62 m
3.08 m	3.12 m	3.73 vw	1.99 m	1.57 s
2.75 m	2.80 m	3.59 vw	1.51 w	1.44 s
2.64 m	2.64 m	3.34 w	1.47 s	1.36 m
2.33 vs	2.32 vs	3.24 w	1.35 m	
2.25 vw	2.27 vs	2.82 vs	1.27 w	
2.17 vw	2.21 vw	2.00 vs		
2.01 vs	2.17 vw	1.26 m		
1.42 s	2.02 vs	1.15 m		
1.21 m	1.59 vw			
	1.43 vs			
	1.22 s			

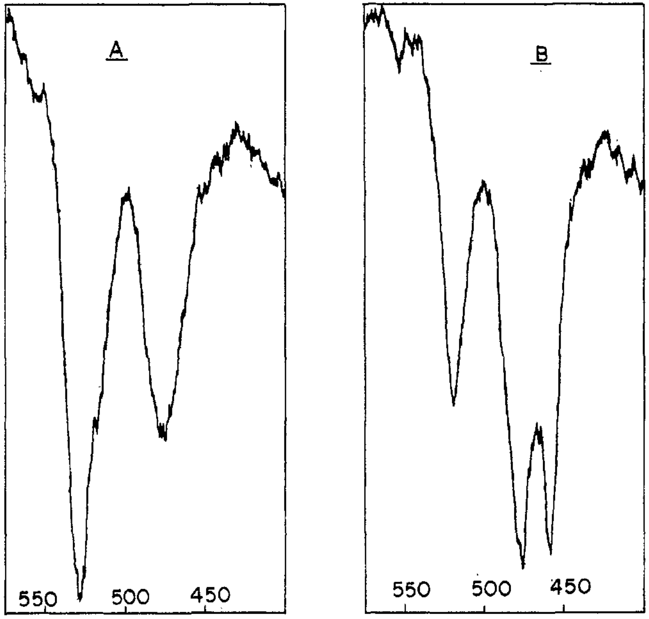

Figure 2.—Infrared spectra (400–575 cm^{-1}) of (A) $[(C_6H_5)_4P][SnF_3]$ and (B) $[(C_6H_5)_4As][SnF_3]$.

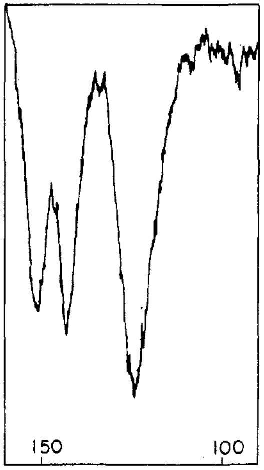

Figure 3.—Infrared spectrum (90–160 cm^{-1}) of $[(C_6H_5)_4As][SnI_3]$.

Another peculiarity is the lack of coincidence between many of the infrared and Raman bands (Table II). It is possible that factor group coupling is responsible for those disparities, which lie outside the ±1-cm^{-1} accuracy of the measurements.

X-Ray Data.—In view of the structural questions raised by the spectral data it appeared advisable to see if the $SnBr_3^-$ and SnI_3^- salts have different crystal classes from the other salts. Accordingly, X-ray powder diffraction data were obtained (Table III). As expected, these data indicate that $[(C_6H_5)_4P][SnF_3]$ and $[(C_6H_5)_4As][SnF_3]$ are isomorphous, with the latter having the larger unit cell. The only other apparent isomorphism occurs between $[(C_6H_5)_4As][SnBr_3]$ and $[(C_6H_5)_4As][SnI_3]$. The implication is that the two anions are isostructural which agrees with the similarities in their spectra.

Force Constants.—Since the number of force constants in a general valence force field potential exceeds the number of observables for the halostannates, some restrictions must be imposed on the potential. In the past a modified Urey–Bradley force field has been used with success in fitting frequencies of some of the complexes considered here and related molecules.[17–21]

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[17] T. Shimanouchi, *Pure Appl. Chem.*, **7,** 131 (1963).

[18] J. Hirashi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta,* **20,** 819 (1964).

[19] D. M. Adams and D. M. Morris, *J. Chem. Soc., A,* 1669 (1967).

[20] Y. Mokai and K. Mori, *Bull. Chem. Soc. Japan,* **37,** 1489 (1964).

[21] M. P. Johnson and J. F. Jackovitz, unpublished calculations on $SnCl_3^-$ and $GeCl_3^-$, Northwestern University, 1967.

TABLE IV

FORCE CONSTANTS (MDYN Å^{-1}) CALCULATED FOR $[(C_6H_5)_4As][SnCl_3]$ WITH DIFFERENT APPROXIMATIONS FOR $f_{r\alpha}$

Approx	f_r	f_{rr}	f_α	$f_{\alpha\alpha}$	$f_{r\alpha}$	ν_1	ν_2	ν_3	ν_4
$f_{r\alpha} = f_{rr}$	1.220	0.130	0.135	0.012	0.130	292	132	258	109
$f_{r\alpha} = f_\alpha$	1.220	0.130	0.140	0.014	0.140	292	133	258	110
$f_{r\alpha} = 0$	1.140	0.090	0.120	0.008	0.000	292	137	258	110
$f_{r\alpha} = {}^1/_2 f_\alpha$	1.190	0.119	0.120	0.006	0.060	292	135	257	110
						Obsd values (ir)			
						291	133	258	110

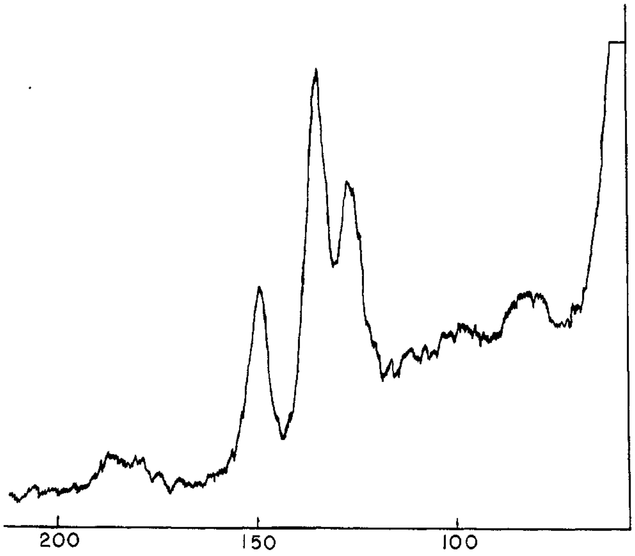

Figure 4.—Raman spectrum (<100–200 cm^{-1}) of $[(C_6H_5)_4As]$-$[SnI_3]$.

However, the additional interaction terms are essentially GVFF parameters and detract from the physical meaning which can be attached to the UBFF model.

Following usual practice it was assumed that force constants associated with stretch–bend and bend–bend interactions are zero if the two internal coordinates do not share a common bond. Thus, for the three types of molecules considered here, the potential functions take the forms: for SnX_6^{2-}

$$2V = 6f_r(\Delta r)^2 + 24f^\alpha{}_{rr}(\Delta r_i)(\Delta r_j) + 6f^\beta{}_{rr}(\Delta r_i)(\Delta r_j) + 12r^2f_\alpha(\Delta\alpha)^2 + 48r^2f^\alpha{}_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 24r^2f^\beta{}_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 24rf_{r\alpha}(\Delta r)(\Delta\alpha)$$

for SnX_4

$$2V = 4f_r(\Delta r)^2 + 12f_{rr}(\Delta r_i)(\Delta r_j) + 6r^2f_\alpha(\Delta\alpha)^2 + 24r^2f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 12rf_{r\alpha}(\Delta r)(\Delta\alpha)$$

and for SnX_3^-

$$2V = 3f_r(\Delta r)^2 + 6f_{rr}(\Delta r_i)(\Delta r_j) + 3r^2f_\alpha(\Delta\alpha)^2 + 6r^2f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 6rf_{r\alpha}(\Delta r)(\Delta\alpha)$$

where $f_{r\alpha}$ refers in all cases to an interaction involving an angle and one of the bonds enolosing it. For the octahedral XY_6 molecule, $f^\alpha{}_{rr}$ represents the interaction between two perpendicular bonds, while $f^\beta{}_{rr}$ accounts for the interaction between two in-line bonds. Similarly, $f^\alpha{}_{\alpha\alpha}$ refers to the interaction between two angles at 90° with a common edge, while $f^\beta{}_{\alpha\alpha}$ represents two "in-plane" angles with a common edge. All other terms have their usual meaning. It is evident that there are still more force constants than frequencies available for the calculations and more approximations must be made. Only for gaseous molecules, where vibrational–rotational structure yields additional data,[22,23] can this be avoided.

Many GVFF treatments of MX_3 systems which have been published[24] have used $f_{r\alpha} = 0$, while recently $f_{r\alpha} = f_\alpha$ was proposed[14] to yield a closer fit to the observed data. This approximation was adopted at first but in the course of the work it became clear that it could not be applied equally well to all three systems under consideration (SnX_3^-, SnX_4, SnX_6^{2-}), and a similar approximation, $f_{r\alpha} = f_{rr}$, was used instead. Where gas-phase data are available,[23] it is found that this approximation is more consistent with these independently obtained force constants. Force constants calculated for $[(C_6H_5)_4As][SnCl_3]$, with differing assumptions for $f_{r\alpha}$, are shown in Table IV. It is evident that several approximations can be used for MX_3 systems and analyses involving nonzero values for $f_{r\alpha}$ give similar values for the primary stretching force constant.

Several GVFF analyses of octahedral MX_6 systems have been published[22,25,26] and various approximations have been suggested. That used here, $f_{r\alpha} = f_{rr}$, is closely supported when additional data from vibrational–rotational spectra[22] can be used and also follows the MUBFF model used successfully on XY_6 systems.[18,19] For SnX_6^{2-} calculations the second assumption invoked was $f^\alpha{}_{\alpha\alpha} = f^\beta{}_{\alpha\alpha}$. Both of these parameters are small and the above approximation is perhaps more realistic than assuming one or the other is zero as has been done previously. The same approximation, $f_{r\alpha} = f_{rr}$, was used for SnX_4 calculations. Where Coriolis coupling

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(22) S. Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967); *J. Chem. Phys.*, **44**, 3353 (1966).

(23) O. Brieux de Mandirola, *J. Mol. Struct.*, **1**, 203 (1968), and references therein.

(24) L. Doyenette, *J. Chem. Phys.*, **58**, 487 (1961); E. G. Claeys and G. P. Van der Kelen, *Spectrochim. Acta*, **22**, 2095 (1966); T. R. Manley and D. A. Williams, *ibid.*, **21**, 1773 (1965).

(25) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967), and references therein.

(26) I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc.*, *A*, 712 (1967).

TABLE V

FORCE CONSTANTS FOR SnX_6^{2-} IONS

	f_r	f^{α}_{rr}	f^{β}_{rr}	f_{α}	$f_{\alpha\alpha}$	$f_{r\alpha}$	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
SnF_6^{2-}	2.900	0.225	0.020	0.272	0.055	0.225	584	470	556	301	241	170
									Obsd[a]			
(d = 2.07 Å)							585	470	556	300[b]	241	...
$SnCl_6^{2-}$	1.435	0.141	−0.013	0.159	0.015	0.141	311	235	303	166	158	112
									Obsd[c]			
(d = 2.42 Å)							310	234	303	116	158	...
$SnBr_6^{2-}$	1.200	0.122	−0.080	0.136	0.006	0.122	185	136	215	113	103	73
									Obsd[c]			
(d =2.61 Å)							185	136	215	114	103	...
SnI_6^{2-}	0.820	0.079	−0.020	0.112	0.000	0.079	122	93	161	84	77	55
									Obsd[c]			
(d = 2.85 Å)							122	93	161	84	78	...

[a] P A. W. Dean and D. F. Evans, *J. Chem. Soc., A*, 698 (1968). [b] Reference 25. [c] This work; $[(C_2H_5)_4N]_2[SnX_6]$ salts.

TABLE VI

FORCE CONSTANTS FOR SnX_3^- IONS

						C_{3v}			
	f_r	f_{rr}	f_{α}	$f_{\alpha\alpha}$	$f_{r\alpha}$	ν_1	ν_2	ν_3	ν_4
SnF_3^-	2.380	0.160	0.035	0.033	0.160	520	280	477	224
							Obsd[a]		
(d = 2.22 Å)						520	280	478[b]	224
$SnCl_3^-$	1.220	0.130	0.135	0.012	0.130	292	132	258	109
							Obsd[a]		
(d = 2.57 Å)						291	133	258	110

									C_s			
	f'_r	f_r	f_{rr}	f_{α}	$f_{\alpha\alpha}$	$f_{r\alpha}$	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$SnBr_3$	1.050	1.160	0.140	0.110	0.011	0.140	200	175	86	66	183	66
									Obsd[a]			
(d' = 2.78 Å, d = 2.69 Å)							201	176	86	65	183	65
	1.055	1.175	0.136	0.127	0.012	0.136	202	176	97	73	185	73
									Obsd[c]			
							202	176	97	73	186	73
SnI_3^-	0.700	0.910	0.093	0.074	0.008	0.093	150	125	64	45	144	45
									Obsd[a]			
(d' = 2.98 Å, d = 2.88 Å)							151	124	65	..	143	..
	0.820	0.950	0.155	0.108	0.008	0.155	152	128	60	51	138	52
									Obsd[c]			
							152	128	60	50	137	50
	0.761	0.947	0.134	0.100	0.008	0.134	151	125	65	51	141	52
									Obsd[d]			
							151	126	65	..	140	..

[a] $[(C_6H_5)_4As][SnX_3]$, ir spectrum. [b] $[(C_6H_5)_4P][SnF_3]$. [c] $[(C_6H_5)_4As][SnX_3]$, Raman values. [d] $[(C_6H_5)_4As][SnI_3]$, average of Raman and ir values.

constants have been used,[27,28] these two force constants often have values of the same order of magnitude.

Calculations were carried out using computer programs written by Schachtschneider.[29] Literature values of bond lengths were used wherever possible for the SnX_6^{2-} and SnX_4 systems. Solution vibrational data were used for the SnF_6^{2-} calculation and an extrapolated Sn–F bond length was employed. For the $SnCl_3^-$ system, the weighted average of the experimental tin–chlorine bond lengths[10] was used and then Sn–X distances for the undistorted SnF_3^- and $SnBr_3^-$ ions were estimated from that. The ratio of the long and short Sn–X bonds in the distorted $SnBr_3^-$

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(27) I. W. Levin and S. Abramowitz, *J. Chem. Phys.*, **44**, 2562 (1966).

(28) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, *J. Mol. Spectry.*, **19**, 78 (1966).

(29) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules," Parts V and VI, Technical Reports No. 231-64 and 53-65, Shell Development Co., Emeryville, Calif., 1964 and 1965.

TABLE VII

FORCE CONSTANTS FOR SnX_4 MOLECULES

	f_r	f_{rr}	f_α	$f_{\alpha\alpha}$	$f_{r\alpha}$	ν_1	ν_2	ν_3	ν_4
$SnCl_4$	2.555	0.078	0.115	0.018	0.078	368	107	402	132
						Obsd[a]			
(d = 2.30 Å)						368	106	403	131
$SnBr_4$	2.100	0.065	0.093	0.015	0.065	221	63	280	88
						Obsd[a]			
(d = 2.44 Å)						220	64	279	88
SnI_4	1.549	0.049	0.070	0.007	0.049	150	47	216	64
						Obsd[a]			
(d = 2.64 Å)						149	47	216	63

[a] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y., 1963, p 106.

and SnI_3^- ions was taken to be that found in $KSnCl_3 \cdot KCl \cdot H_2O$.[10] For the SnX_3^- ions an X–Sn–X angle of 90° was used in all cases, since this is close to the average angle in $KSnCl_3 \cdot KCl \cdot H_2O$.[10] Results of the calculations are shown in Tables V–VII. Values of the fundamental frequencies were matched to within ±1 cm^{-1} of the observed values which corresponds to the expected reliability of the data.

For $SnBr_3^-$ and SnI_3^- two primary stretching force constants were necessary to account for the additional band observed, giving a potential of the form

$$2V = f'_r(\Delta r')^2 + 2f_r(\Delta r)^2 + 6f_{rr}(\Delta r_i)(\Delta r_j) + 3r^2f_\alpha(\Delta\alpha)^2 + 6r^2f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 6rf_{r\alpha}(\Delta r)(\Delta\alpha)$$

(f'_r and f_r are force constants for the long and short Sn–X bonds, respectively; otherwise, the potential is the same as that for SnF_3^- and $SnCl_3^-$.) In order to check the assignment made here for the $SnBr_3^-$ bands, an analysis of an alternate assignment, ν_2 183 cm^{-1} and ν_5 176 cm^{-1}, was carried out. To obtain a fit, it was necessary to use a larger force constant for the long bond than for the short bond (f'_r = 1.23, f_r = 1.07) which is physically unreasonable. The SnI_3^- system gave some difficulty in interpretation. The two pairs of values for ν_2 and ν_5 (ir and Raman) are too divergent to represent with certainty the unperturbed vibrations. Therefore, the averages of the Raman and ir values for ν_2 and ν_5 were used as being more representative of these frequencies in the "isolated" SnI_3^- system.

Discussion

Trends in Force Constants and Frequencies.—The similarity of stretching frequencies and more particularly primary stretching force constants for $Sn^{IV}X_6^{2-}$ and $Sn^{II}X_3^-$ (X = F, Cl, Br, I) implies that *the SnX force constant is proportional to the ratio of the oxidation state (or ionic charge) of the central metal atom divided by the coordination number.* As a test of this generalization we note in Table VIII that the ratio of stretching force constants for SnX_3^- to SnX_4 varies from 0.48 to 0.59 with an average value of 0.54. If we define Ω = oxidation state/coordination number, then $\Omega(SnX_3^-)/\Omega(SnX_4)$ = 0.67. Similarly the force constant ratio for SnX_6^{2-} to SnX_4 averages 0.56 which compares with 0.67 for the corresponding Ω ratio. In the comparison of SnX_3^- to SnX_6^{2-} the force constant ratio varies from 0.82 to 1.11 with an average value of 0.94, while the Ω ratio is 1.0. It is apparent that this empirical generalization is fairly good. However, deviations are not random. There is a slight tendency for the oxidation state to be more influential than the coordination number. This tendency is most noticeable in the order F > Cl > Br > I.

TABLE VIII

COMPARISON OF STRETCHING FORCE CONSTANTS FOR SnX_4, SnX_3^- AND SnX_6^{2-} SYSTEMS

	$Sn^{IV}X_4$	$Sn^{II}X_3^-$		$Sn^{IV}X_6^{2-}$		
X^-	f_{SnX_4}	$f_{SnX_3^-}$	$f_{SnX_3^-}/f_{SnX_4}$	$f_{SnX_6^{2-}}$	$f_{SnX_6^{2-}}/f_{SnX_4}$	$f_{SnX_3^-}/f_{SnX_6^{2-}}$
F^-	...	2.380	...	2.900	...	0.82
Cl^-	2.555	1.220	0.48	1.435	0.56	0.85
Br^- [a]	2.100	1.120 (ir)	0.53	1.200	0.57	0.93
		1.135 (R)	0.54			0.95
I^- [a]	1.549	0.840 (ir)	0.54			1.02
		0.907 (R)	0.59	0.820	0.53	1.11

[a] $f_{SnX_3^-}$ values are weighted averages of the f_r values for the two different bonds for the $SnBr_3^-$ and SnI_3^- systems.

For simple polyhedral molecules in which there is slight interaction between stretching and bending coordinates, the square of the average stretching frequency (weighted according to degeneracy) is representative of the stretching force constant.[30] For the SnX_3^-, SnX_4, and SnX_6^{2-} species the eigenvectors and potential energy distributions (Table IX) indicate the stretching vibrations are fairly pure. Accordingly, a plot of ν_{av}^2 *vs.* Ω was constructed (Figure 5). In addition to SnX_3^-, SnX_4, and SnX_6^{2-}, the $SnCl_5^-$ and $SnBr_5^-$ complexes (for which accurate vibrational analyses are unavailable) follow the correlation.

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(30) W. J. Lehman, *J. Mol. Spectry.*, **7**, 261 (1961).

TABLE IX

EIGENVECTORS FOR SnX_3^- IONS

SnF_3^- and $SnCl_3^-$, C_{3v} symmetry

Symmetry coordinates

$$\left.\begin{aligned} S_1 &= \Delta r_1 + \Delta r_2 + \Delta r_3 \\ S_2 &= \Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} \end{aligned}\right\}A_1$$

$$\left.\begin{aligned} S_{3a} &= 2\Delta r_1 - \Delta r_2 - \Delta r_3 \\ S_{3b} &= \Delta r_2 - \Delta r_3 \end{aligned}\right\}E$$

$$\left.\begin{aligned} S_{4a} &= 2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31} \\ S_{4b} &= \Delta\alpha_{31} - \Delta\alpha_{12} \end{aligned}\right\}E$$

	$SnCl_3^-$	
	Eigenvectors, % S_n	PED, % f
ν_1	100% S_1	81% f_r + 17% f_{rr}
ν_2	16% S_1 + 84 % S_2	46% f_α + 31% $f_{r\alpha}$ + 12% f_r
ν_3	100% S_3	90% f_r
ν_4	8% S_3 + 92% S_4	69% f_α + 16% $f_{r\alpha}$

	SnF_3^-	
	Eigenvectors, % S_n	PED, % f
ν_1	100% S_1	88% f_r
ν_2	6% S_1 + 94% S_2	63% f_r + 16% $f_{r\alpha}$ + 14% f_{rr}
ν_3	100% S_3	94% f_r
ν_4	2% S_3 + 98% S_4	82% f_α + 9% $f_{\alpha\alpha}$

$SnBr_3^-$ and SnI_3^-, C_s symmetry

Symmetry coordinates[a]

$$\left.\begin{aligned} S_1 &= \Delta r_1' + \Delta r_2 + \Delta r_3 \\ S_2 &= \Delta\alpha_{12} + \Delta\alpha_{23}' + \Delta\alpha_{31} \\ S_3 &= 2\Delta r_1' - \Delta r_2 - \Delta r_3 \\ S_4 &= 2\Delta\alpha_{23}' - \Delta\alpha_{12} - \Delta\alpha_{31} \end{aligned}\right\}A'$$

$$\left.\begin{aligned} S_5 &= \Delta r_2 - \Delta r_3 \\ S_6 &= \Delta\alpha_{31} - \Delta\alpha_{12} \end{aligned}\right\}A''$$

	$SnBr_3^-$	
	Eigenvectors, % S_n	PED, % f
ν_1	94% S_1 + 2% S_2 + 4% S_3	61% f_r + 16% f_{rr} + 12% $f_{r\alpha}$
ν_2	3% S_1 + 96% S_3 + 1% S_4	69% f_r' + 16% f_r
ν_3	19% S_1 + 81% S_2	40% f_α + 36% $f_{r\alpha}$ + 8% $f_{\alpha\alpha}$
ν_4	11% S_3 + 89% S_4	62% f_α + 21% $f_{r\alpha}$ + 8% f_{rr}
ν_5	99% S_5 + 1% S_6	85% f_r + 10% f_{rr}
ν_6	10% S_5 + 90% S_6	64% f_α + 19% $f_{r\alpha}$ + 10% f_r

	SnI_3^-	
	Eigenvectors, % S_n	PED, % f
ν_1	77% S_1 + 5% S_2 + 18% S_3	67% f_r + 18% $f_{r\alpha}$
ν_2	17% S_1 + 1% S_2 + 81% S_3 + 1% S_4	78% f_r' + 11% $f_{r\alpha}$
ν_3	14% S_1 + 85% S_2 + 1% S_3	46% f_α + 32% $f_{r\alpha}$ + 10% $f_{\alpha\alpha}$
ν_4	9% S_3 + 91% S_4	66% f_α + 18% $f_{r\alpha}$ + 7% $f_{\alpha\alpha}$
ν_5	98% S_5 + 2% S_6	83% f_r + 9% f_{rr}
ν_6	6% S_5 + 94% S_6	70% f_α + 15% $f_{r\alpha}$ + 8% $f_{\alpha\alpha}$

[a] r_1' is the longer bond and α_{23}' is the angle opposite it.

Figure 5 may be used to predict an average stretching frequency of *ca.* 165 cm^{-1} for the unknown complex SnI_5^{2-}. Similarly the average vibrational frequencies of monomeric $SnCl_2$, $SnBr_2$, and SnI_2 are predicted to be 400, 265, and 200 cm^{-1}, respectively. While another estimate of these frequencies has been made (402, 286, and 236 cm^{-1}, respectively),[31] experimental data are lacking.

As an incidental observation we note that the relationship $f^{\alpha}_{rr} \approx {}^1/_{10}f_r$ holds for the SnX_6^{2-} species (X = Cl, Br, and I). It turns out that a constant ratio for these force constants is related to the observation that $(\nu_1 - \nu_2)/\nu_1$ is about constant for $SnCl_6^{2-}$ and $SnBr_6^{2-}$.[32] The diagonal F matrix elements for the GVFF potential are $F_{11}(A_{1g}) = f_r + 4f_{rr} + f'_{rr}$ and $F(E_g) = f_r - 2f_{rr} + f'_{rr}$. If $(\nu_1 - \nu_2)/\nu_1$ is constant, $(\nu_1^2 - \nu_2^2)/\nu_1^2$ is too. Therefore, neglecting stretch-bend interactions, which the complete analysis shows to be small, we write $[F_{11}(A_{1g}) - F(E_g)]/F_{11}(A_{1g}) \approx -6f_{rr}/f_r$ where f_{rr} and f_{rr}' are neglected in the denominator owing to their smallness relative to f_r.

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(31) L. Brewer, G. R. Somayajula, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).

(32) L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, **17**, 594 (1961). The present work shows that the constancy of this frequency ratio extends to SnI_6^{2-}.

Calculation of Force Constants from an Ionic Model.—The foregoing correlations, which concentrate on the ratio of the oxidation state to coordination number, suggest that the tin–halogen force constant may be determined by a competition between metal–halogen ionic attractions and halogen–halogen ionic repulsions. This idea prompted the calculation of force constants by means of a potential which includes point-charge and induced-dipole terms. Several applications of an ionic model to the calculation of MX and MX_2 frequencies have been published,[33] and a point-charge model has been used with success in calculating force constants for $ZnCl_4^{2-}$ and $ZnBr_4^{2-}$.[34]

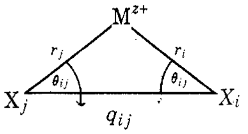
In the present case the point-charge and induced-dipole potential energy terms are those given by Garrick;[35] in addition, nonelectrostatic interactions of the Lennard-Jones type[36] are included. The calculation was performed for SnX_4 and SnX_6^{2-} but not SnX_3^- because the latter pyramidal complex would require an arbitrary introduction of additional terms to achieve an equilibrium condition. The resulting potential for an M^{z+} cation surrounded by n X^- anions is

$$V = -\sum_{i=1}^{n}\frac{ze^2}{r_i} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{e^2}{q_{ij}} - \sum_{i=1}^{n}\frac{ze\mu_i}{r_i^2} +$$

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\mu e\cos\theta_{ij}}{q^2_{ij}} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\mu^2}{q^3_{ij}}(1+\cos^2\theta_{ij}) + \frac{n\mu^2_i}{2\alpha} +$$

$$\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}4\epsilon\left\{\left(\frac{\sigma_{xx}}{q_{ij}}\right)^{12} - \left(\frac{\sigma_{xx}}{q_{ij}}\right)^{6}\right\} + \sum_{i=1}^{n}\frac{A}{r^n}$$

Double summations are for $i \neq j$ with r_i, q_{ij}, and θ_{ij} given by



Note $r_i = r_j$.

The dipole induced in each anion, μ_i, is

$$\mu_i = \alpha E = \frac{\alpha e\{zr_i^{-2} - \sum_{j\neq i} q_{ij}^{-2}\}}{1 + \alpha\sum_{j\neq 1}(1+\cos^2\theta_{ij})q_{ij}^{-3}}$$

where α is the polarizability of anion X.

The first two terms in the potential energy expression represent point-charge interactions followed by two terms accounting for the point-charge–induced-dipole energy. The fifth and sixth terms account for the dipole–dipole repulsions and the energy required to form these dipoles. The latter is a constant and vanishes on differentiation. Next comes the nonelectrostatic interaction between the halide ions, represented by a Lennard-Jones potential,[36] and finally an empirical repulsion term, A/r^n, for the metal–anion interactions, which is necessary for molecular stability. Differentiation with respect to r_i, along with the condition for equilibrium $\partial V/\partial r = 0$, allows the evaluation of A. A second differentiation yields the stretching force constants: for MX_4 (tetrahedral) $\theta_{12} = 35° 16'$

$$f_r = \frac{\partial^2 V}{\partial r_1^2} = -\frac{2ze^2}{r_1^3} + \frac{6e^2\cos^2\theta_{12}}{q_{12}^2} - \frac{6ze\mu_i}{r_1^4} + \frac{36e\mu_i\cos^3\theta}{q_{12}^4} + \frac{36\mu_i^2(1+\cos^2\theta_{12})\cos^2\theta_{12}}{q_{12}^5} + 12\epsilon_{xx}\left\{\frac{156\sigma_{xx}^{12}}{q_{12}^{14}} - \frac{42\sigma_{xx}^{6}}{q_{12}^{8}}\right\}\cos^2\theta_{12} + \frac{(n+1)B}{r_1}$$

$$f_{rr} = \frac{\partial^2 V}{\partial r_1\partial r_2} = \frac{2e^2\cos^2\theta_{12}}{q_{12}^3} + \frac{12e\mu_i\cos^3\theta_{12}}{q_{12}^4} + \frac{12\mu_i^2(1+\cos^2\theta_{12})\cos^2\theta_{12}}{q_{12}^5} + 4\epsilon_{xx}\left\{\frac{156\sigma_{xx}^{12}}{q_{12}^{14}} - \frac{42\sigma_{xx}^{6}}{q_{12}^{8}}\right\}\cos^2\theta_{12}$$

and for MX_6 (octahedral) $\theta_{12} = 45°$ and $\theta_{16} = 0°$

$$f_r = \frac{\partial^2 V}{\partial r_1^2} = -\frac{2ze^2}{r_1^3} + \frac{8e^2\cos^2\theta_{12}}{q_{12}^2} + \frac{2e^2\cos^2\theta_{16}}{q_{16}^3} - \frac{6ze\mu_i}{r_1^4} + \frac{48e\mu_i\cos^3\theta_{12}}{q_{12}^4} + \frac{12e\mu_i\cos^3\theta_{16}}{q_{16}^4} + \frac{48\mu_i^2(1+\cos^2\theta_{12})\cos^2\theta_{12}}{q_{12}^5} + \frac{12\mu_i^2(1+\cos^2\theta_{16})\cos^2\theta_{16}}{q_{16}^5} + 16\epsilon_{xx}\left\{\frac{156\sigma_{xx}^{12}}{q_{12}^{14}} - \frac{42\sigma_{xx}^{6}}{q_{12}^{8}}\right\}\cos^2\theta_{12} + 4\epsilon_{xx}\left\{\frac{156\sigma_{xx}^{12}}{q_{16}^{14}} - \frac{42\sigma_{xx}^{6}}{q_{16}^{8}}\right\}\cos^2\theta_{16} + \frac{(n+1)B}{r_1}$$

$$f_{rr}^{\alpha} = \frac{\partial^2 V}{\partial r_1\partial r_2} = \frac{2e^2\cos^2\theta_{12}}{q_{12}^3} + \frac{12e\mu_i\cos^3\theta_{12}}{q_{12}^4} + \frac{12\mu_i^2(1+\cos^3\theta_{12})\cos^2\theta_{12}}{q_{12}^5} + 4\epsilon_{xx}\left\{\frac{156\sigma_{xx}^{12}}{q_{12}^{14}} - \frac{42\sigma^{6}}{q_{12}^{8}}\right\}\cos^2\theta_{12}$$

$$f_{rr}^{\beta} = \frac{\partial^2 V}{\partial r_1\partial r_6} = \frac{2e^2\cos^2\theta_{16}}{q_{12}^3} + \frac{12e\mu_i\cos^3\theta_{16}}{q_{16}^4} + \frac{12\mu_i^2(1+\cos^2\theta_{16})\cos^2\theta_{16}}{q_{16}^5} + 4\epsilon_{xx}\left\{\frac{156\sigma_{xx}^{12}}{q_{16}^{14}} - \frac{42\sigma_{xx}^{6}}{q_{18}^{8}}\right\}\cos^2\theta_{16}$$

where

$$B = \frac{nA}{r^{n+1}} = \frac{4n\sigma^6\epsilon_{SnX}}{r_1^{n+1}}\left\{\frac{12\sigma^6}{r_1^{13}} - \frac{6}{r_1^7}\right\}$$

The parameters used are given in Table X. Literature values are used for bond lengths (r) and polarizabilities (α). For the nonelectrostatic interactions between the anions, σ_{xx} was extrapolated from the adjacent inert-gas values and inert-gas values were used for ϵ_{xx}. The numbering of the bonds, r, is irrelevant for the tetrahedral SnX_4 system, while for SnX_6^{2-}, the IUPAC convention was used with bonds r_1 and r_6 *trans* to each other.

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TABLE X

PARAMETERS USED IN IONIC MODEL CALCULATIONS

Anion	α,[a] Å^3	$10^{16}\epsilon_0$,[b] ergs molecule	σ_0,[b] Å	r_0(X),[c] Å	r_x(X$^-$),[c] Å	d(Sn–X), Å: SnX_6^{2-}	d(Sn–X), Å: SnX_4
F^-	1.049	48.9	2.794	1.60	1.294	2.070[e]	....
Cl^-	3.681	166.2	3.422	1.92	1.811	2.42[d]	2.30[f]
Br^-	4.805	238.8	3.602	1.97	1.973	2.61[d]	2.44[g]
I^-	7.162	306.4	4.039	2.18	2.228	2.85[d]	2.64[g]

[a] L. Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927). [b] Reference 36, p 1110. [c] r_0(X) stands for the radius of the isoelectronic rare gas, r_x(X$^-$) is that of the halide. E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed, Pergamon Press, Ltd., London, 1961, p 24. [d] "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1955, p M40; Supplement No. 18, 1956–1959, p M22s. [e] Extrapolated from data in *d*. [f] F. O. Brockway, *Rev. Mod. Phys.*, **8**, 260 (1936). [g] M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 391 (1941).

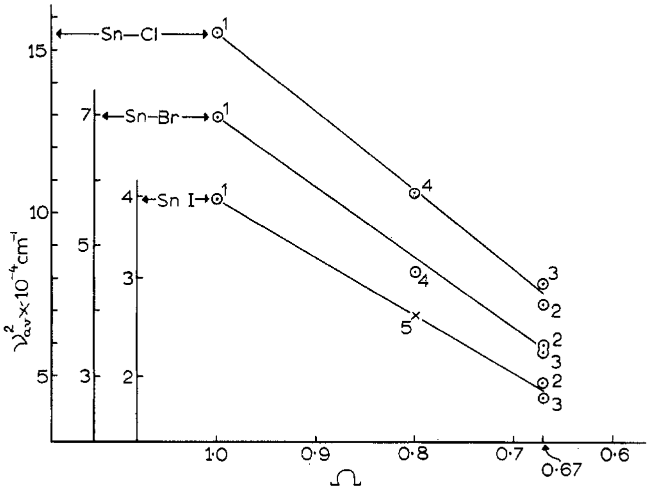

Figure 5.—Variation of weighted-average tin–halogen stretching frequency, $[\nu_{av}(Sn–X)]^2$, with the ratio Ω = oxidation state/coordination number: (1) SnX_4, data from K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 106; (2) SnX_6^-, this work; (3) $SnCl_6^{2-}$, this work; (4) $SnCl_5^-$, ref 26; $SnBr_5^-$, J. A. Creighton and J. H. S. Green, *J. Chem. Soc., A*, 808 (1968); (5) estimate for SnI_5^-.

Theoretical Force Constants.—The calculated force constants are presented in Tables XI and XII. From the first of these tables it is clear that a rather low value is required for the repulsive exponent, *n*, in the Sn–X repulsion term A/r^n. Clearly a value of *n* between 4 and 5 is necessary to fit the experimental force constants rather than 9–12 which is the expected range based on compressibility data for corresponding rare gases. It is probable that the lower values of *n* result from the influence of covalent bonding on this parameter. This is borne out in a general way by nuclear quadrupole resonance.

TABLE XI

PRIMARY FORCE CONSTANTS

X^-	$f_r(SnX_4)$: $n = 12$	$n = 9$	$n = 5$	$n = 4$	n_{exptl}[b]	i[c,d]	$f_r(SnX_6^{2-})$: $n = 12$	$n = 9$	$n = 5$	$n = 4$	n_{exptl}[b]	i[c,e]
F^-	...	...	...	...	...	...	7.748	5.406	3.065[a]	2.284[a]	5.79	...
Cl^-	11.053	7.657	3.129	1.997	4.49	0.48	5.347	3.715	1.538	0.994	4.81	0.66
Br^-	9.697	6.731	2.775	1.786	4.32	...	4.232	2.946	1.231	0.802	4.93	0.60
I^-	7.837	4.878	2.212	1.408	4.18	0.29	3.205	2.254	0.986	0.669	4.48	0.55

[a] Calculated using $n = 6$ and $n = 5$, respectively. [b] Value of *n* in A/r^n term necessary to give f_r value derived from experimental data. [c] Apparent ionic character derived from nqr data. [d] Calculated from results for $SnCl_4$ (R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953)) and SnI_4 ((R. Livingston and H. Zeldes, *Phys. Rev.*, **90**, 609 (1953)). [e] Reference 37.

TABLE XII

RATIO $f_r(SnX_6^{2-})/f_r(SnX_4)$

Anion	$f_r(SnX_4)$exptl	$f_r(SnX_6^{2-})$calcd[a]	$f_r(SnX_6^{2-})$exptl	$\frac{f(SnX_6^{2-})\text{calcd}}{f(SnX_4)\text{exptl}}$	$\frac{f(SnX_6^{2-})\text{exptl}}{f(SnX_4)\text{exptl}}$
Cl	2.555	1.263	1.435	0.49	0.56
Br	2.100	0.938	1.200	0.45	0.57
I	1.549	0.725	0.820	0.47	0.53

[a] Calculated using values of n_{exptl} derived from SnX_4 force constants (Table XI).

Nqr studies of hexahalostannates[37] have shown *ca.* 60% ionic character (Table XI). Similar calculations for the SnX_4 species, using literature data, indicate that the ionic character ranges from 48% for $SnCl_4$ to 29% for SnI_4. It will be noted in Table XI that there is a correlation between lower percentage ionic character and lower exponent values. Interestingly, the less sophisticated point-charge model does not require a reduction in the repulsive exponent for either of the tin complexes studied here or for ZnX_4^{2-} complexes.[34]

The stretch–stretch interaction force constants, which are independent of *n*, are of the right magnitude but

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(37) M. Kubo and D. Nakamura, *Advan. Inorg. Chem. Radiochem.*, **8**, 268 (1968).

do not reproduce the observed trends, other than $f^{\alpha}_{rr} > f^{\beta}_{rr}$ for octahedral complexes.

Adjustment of the repulsive exponent was necessary to obtain agreement with experiment, so the n values determined from known force constants of SnX_4 molecules were employed in the calculation of $SnX_6{}^{2-}$ force constants. This procedure resulted in fairly good agreement between observed and calculated force constants for $SnX_6{}^{2-}$ (Table XII). Similarly, the ratio of calculated force constants for $SnX_6{}^{2-}$ to SnX_4 averages 0.47, which compares favorably with the observed ratio of 0.55 (averaged for X = Cl, Br, and I). In fact, this ratio of force constants is not very sensitive to the repulsive exponent, since a value of 12 for n leads to a calculated average force constant ratio of 0.44. We conclude that an ionic model effectively reproduces the reduction in stretching force constant upon an increase in coordination number.

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Direct Characterization of the Mixed Complexes of Gallium(III) with N,N-Dimethylformamide and 2,4-Pentanedione. Proton Magnetic Resonance Study of First Coordination Sphere Stiochiometry and Kinetics of Ligand Exchange[1a]

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At temperatures below 40° the proton nmr signals of N,N-dimethylformamide (DMF) in the first coordination sphere of Ga(III) can be distinguished. From relative intensities of these signals, a primary solvation number of 6 can be calculated for Ga(III). From the temperature dependence of the proton relaxation rates, the solvent (DMF) exchange parameters k_1 (sec^{-1} at 25°), $\Delta H^{\ddagger}$ (kcal/mol), and $\Delta S^{\ddagger}$ (eu) were calculated to be 1.7, 14.6, and −8.3, respectively. Proton nmr spectra of solutions of $Ga(DMF)_6{}^{3+}$ and tris(2,4-pentanedionato)gallium(III) $[Ga(acac)_3]$ were used to characterize the complexes $Ga(acac)(DMF)_4{}^{2+}$ and $Ga(acac)_2(DMF)_2{}^{+}$. Thermodynamic parameters were obtained from the temperature dependence of the equilibria among these species. Gallium-71 nmr spectra of $Ga(DMF)_6{}^{3+}$ are reported. Data from this study are compared with those obtained for the analogous Al(III) and Be(II) complexes.

Introduction

Recently it has been shown that nuclear magnetic resonance (nmr) techniques can provide detailed information about the structure and lability of the coordination compounds of diamagnetic cations having d^0 and d^{10} electronic configurations.[2-15] The techniques are of special interest because the properties of the cations preclude a direct study of their complexes with most of the conventional experimental techniques. Simple solvent complexes that have been characterized *directly* using nmr methods include $Al(OH_2)_6{}^{3+}$,[2a,4,11] $Ga(OH_2)_6{}^{3+}$,[2a,8,9,11] $Be(OH_2)_4{}^{2+}$,[2a,4] $Mg(OH_2)_6{}^{2+}$,[13,14] $Mg(CH_3OH)_6{}^{2+}$,[12,14] $Mg(CH_3OH)_n(H_2O)_{6-n}{}^{2+}$,[3] $Al(DMSO)_6{}^{3+}$,[6] $Al(DMF)_6{}^{3+}$,[7] and $Be(DMF)_4{}^{2+}$.[10] (DMSO represents dimethyl sulfoxide and DMF represents N,N-dimethylformamide.)

We are particularly interested in kinetic and thermodynamic ligand–ligand interactions in mixed complexes

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[1] (a) Part of this work was abstracted from the Ph.D. thesis of W. G. Movius, Pennsylvania State University, 1968, and was supported in part by the U. S. Atomic Energy Commission. (b) Address correspondence to this author at the Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544.

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