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Carbonium Ion Salts. XIII. Stable Triarylcarbonium Pentahalostannate(IV) Salts¹

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Certain triarylmethyl halides form stable 1:1 adducts with stannic halide; facile hydride-transfer reactions, electronic spectra, and a combination of X-ray, infrared, and Mössbauer effect data demonstrate that these are salts of triarylcarbonium ions and monomeric trigonal-bipyramidal pentahalostannate(IV) ions. The formation of these salts is not kinetically controlled, as the stoichiometry of the solid is not changed by use of excess halide, equilibration in strongly ionizing solvents, or preparation from preformed hexahalostannate(IV) ions. Variable-temperature nmr equilibrium measurements of the ionization of triphenylmethyl chloride by pentachlorostannate(IV) ion in methylene chloride yield the values $\Delta G^\circ = 1.85$ kcal/mol, $\Delta H^\circ = -9.56$ kcal/mol, and $\Delta S^\circ = -38.6$ eu at 25° for this reaction and allow the prediction of the stability of other triarylcarbonium ion pentachlorostannate(IV) salts. The preparations and interconversions of a number of such salts and their bromide analogs are described.

Introduction

Almost without exception, stable, isolable five-coordinate tin(IV) compounds can be classified as complexes between stannic halides and organic bases³ or anion-bridged salts of the triphenyl- or trimethyltin(IV) cation.⁴ The unusual stoichiometry of these compounds may result from the bulk of the organic ligands and from intrinsic stability of the planar trialkyltin cation, since with simple ligands such as halide tin(IV) normally assumes the six-coordinate sp^3d^2 configuration.⁵ Compounds of the type $R_4N^+SnCl_5^-$ have been prepared recently,^{6,7} and the anion in these salts has tentatively been assigned the trigonal-bipyramidal sp^3d con-

figuration from infrared data; however, the preparation of such salts requires the careful addition of tetraalkylammonium halide to excess stannic halide in nondissociating solvents, since with excess halide or on equilibration in polar solvents, the hexachlorostannate(IV) salts are formed. The first clearly established compound in which the pentachlorostannate(IV) ion forms preferentially in the presence of excess available halide is 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate(IV);⁸ the anion in this salt has been shown by X-ray single-crystal analysis⁹ to be a trigonal-bipyramidal $SnCl_5^-$ ion.

Another—and much more readily available—apparent example of a stable pentachlorostannate(IV) is the 1:1 adduct of triphenylmethyl chloride and stannic chloride. In spite of recent interest in five-coordinate tin(IV) species, this compound has not been examined as an example of such coordination, even though reports of its preparation and properties have been in the literature for nearly seven decades.¹⁰ The analogous bromide compound has also been prepared;¹¹ however, neither hexahalostannate(IV) salt has been reported. The primary ionization of triphenylmethyl chloride by stannic chloride in acetonitrile is followed by a second ionization to give the $SnCl_6^{2-}$ ion;¹² however, the coexistence of solvated ions in solution does not show whether a salt of the ions would be stable in the crystalline solid.

The work reported herein was carried out to answer the following questions: (1) Are the 1:1 adducts of triphenylmethyl halides with stannic halides true salts, and if so, what are the structures of the complex anions? (2) Does the unusual stoichiometry of these compounds result from kinetic control under the conditions of preparation, and if so, can the expected hexahalostannate(IV) salts be prepared by changing those condi-

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tions? (3) If the formation of the 1:1 adducts is equilibrium controlled, what are the structural or energetic features of the cation that give rise to this unusual stoichiometry? (4) Can other stable carbonium ion pentahalostannate(IV) salts be prepared.

Experimental Section

Methylene chloride,¹³ cyclohexane,¹³ cycloheptatriene,¹⁴ and triphenylcarbinol¹⁴ were purified and dried as previously reported. Fisher reagent grade benzene was stored over calcium hydride and transferred by pipet. Eastman Kodak White Label acetic and propanoic anhydrides and acetyl chloride and bromide were distilled before use. Baker and Adamson reagent grade stannic chloride and A. D. McKay Co. stannic bromide were distilled from phosphorus pentoxide in an all-glass apparatus under dry nitrogen and stored in the glove box. Matheson anhydrous sulfur dioxide, hydrogen chloride, and hydrogen bromide were used without further treatment. Baker and Adamson 96% sulfuric acid was used for spectral analysis; spectra were recorded on the Cary Model 13 spectrophotometer in silica cells. All reactions involving sensitive species were carried out in a glove box; the atmosphere was cycled constantly over fresh phosphorus pentoxide.

Reactions of Triphenylmethyl Chloride with Stannic Chloride.

A. 1:1 in Cyclohexane.—Stannic chloride (2.16 g, 8.32 mmol) was added dropwise with swirling to a water-white solution of triphenylmethyl chloride,¹⁵ mp 111–112° (2.064 g, 7.43 mmol), in cyclohexane (35 ml) to afford an instantaneous brilliant yellow precipitate which occluded stannic chloride. After the mixture was stirred overnight, the flask contained a free-flowing yellow powder; at no time did any color appear in the solvent. The solvent was decanted and the powder was washed with two 40-ml portions of cyclohexane and dried *in vacuo* to yield 86.3% triphenylcarbonium pentachlorostannate(IV) (3.40 g, 6.40 mmol) as yellow microcrystals, mp 167–168°. Electronic spectrum: 96% sulfuric acid,^{16,17} λ_{\max} 404 and 432 nm (ϵ 38,400); methylene chloride, λ_{\max} 407 and 432 nm. *Anal.* Calcd for $C_{19}H_{15}SnCl_5$: $(C_6H_5)_3C^+$, 45.05; Cl, 32.87. Found: $(C_6H_5)_3C^+$, 45.0; Cl, 33.17.

B. 2:1 in Cyclohexane.—A reaction run as above using stannic chloride (0.366 g, 1.41 mmol) and triphenylmethyl chloride (0.782 g, 2.81 mmol) in cyclohexane (15 ml) afforded a yellow precipitate and a water-white solution; work-up gave 75.3% triphenylcarbonium pentachlorostannate(IV) (0.542 g, 1.01 mmol) as yellow microcrystals, mp 167°. *Anal.* Found for $C_{19}H_{15}SnCl_5$: $(C_6H_5)_3C^+$, 45.9.

C. 1:1 in Methylene Chloride.—Stannic chloride (2.10 g, 8.07 mmol) was added dropwise with swirling to a pale yellow solution of triphenylmethyl chloride (1.97 g, 7.09 mmol) in methylene chloride (10 ml); the solution immediately became deep red-orange. Addition of cyclohexane (20 ml) gave a copious yellow precipitate and a water-white solution; the solvent was decanted and the solid was washed with three 20-ml portions of cyclohexane and dried *in vacuo* to yield 100% triphenylcarbonium pentachlorostannate(IV) (3.83 g, 7.09 mmol) as yellow microcrystals, mp 168°. *Anal.* Found for $C_{19}H_{15}SnCl_5$: $(C_6H_5)_3C^+$, 45.3.

D. 2:1 in Methylene Chloride.—A reaction run as above using stannic chloride (0.860 g, 3.29 mmol) and triphenylmethyl chloride (1.84 g, 6.59 mmol) afforded 94.0% triphenylcarbonium pentachlorostannate(IV) (1.67 g, 3.09 mmol) as yellow needles, mp 167–168°. *Anal.* Found for $C_{19}H_{15}SnCl_5$: $(C_6H_5)_3C^+$, 45.7.

E. 2:1 in Liquid Sulfur Dioxide.—A mixture of triphenylmethyl chloride (1.041 g, 3.76 mmol) and liquid sulfur dioxide

(70 ml) was warmed to the boiling point of sulfur dioxide (*caution!* vigorous magnetic stirring is necessary to prevent hazardous bumping of sulfur dioxide) to give a deep yellow solution, and stannic chloride (0.490 g, 1.88 mmol) was added by syringe (serum cap); the system was at all times protected from the atmosphere. The resulting dark red-brown solution was evaporated to dryness, which left a mixture of discrete white and yellow crystals; washing with cyclohexane (100 ml) removed all white material and left 100% triphenylcarbonium pentachlorostannate(IV) (1.021 g, 1.89 mmol) as yellow microcrystals, mp 167–168°. *Anal.* Found for $C_{19}H_{15}SnCl_5$: $(C_6H_5)_3C^+$, 45.4. Evaporation of the cyclohexane afforded triphenylmethyl chloride.

Triphenylcarbonium Pentabromostannate(IV).—Stannic bromide (5.60 g, 12.8 mmol) was added to a solution of triphenylmethyl bromide,¹⁵ mp 151–152° (4.03 g, 12.5 mmol), in methylene chloride (25 ml) to give a red-orange solution; slow addition of cyclohexane gave orange crystals which were dried *in vacuo* to yield 91.2% triphenylcarbonium pentabromostannate(IV) (8.70 g, 11.4 mmol) as orange prisms. *Anal.* Calcd for $C_{19}H_{15}SnBr_5$: $(C_6H_5)_3C^+$, 31.95. Found: $(C_6H_5)_3C^+$, 31.1.

Reactions of Triphenylcarbonium Pentahalostannate(IV) Salts with Cycloheptatriene.

A. Tropenylum Hexachlorostannate(IV).—Cycloheptatriene (0.180 g, 1.76 mmol) was added to an orange solution of triphenylcarbonium pentachlorostannate(IV) (0.455 g, 0.843 mmol) in methylene chloride (10 ml); the solution lightened and a heavy cream-colored precipitate formed. This was washed with two 15-ml portions of cyclohexane and dried *in vacuo* to yield 0.2454 g of solid which contained 30.8% tropenylum ion by spectral analysis¹⁸ and thus contained a 98.7% yield of tropenylum ion (0.0757 g, 0.831 g-ion) and excess stannic chloride;¹⁹ this material was recrystallized from 12 *N* hydrochloric acid to give clear plates of tropenylum hexachlorostannate(IV), mp 257° (lit.¹³ mp 256–257°). *Anal.* Calcd for $C_{14}H_{14}SnCl_6$: $C_7H_7^+$, 35.48. Found: $C_7H_7^+$, 35.5.

The combined mother liquor and washings were evaporated to dryness and leached with boiling pentane, and the pentane was clarified by filtration through alumina. Evaporation of the pentane gave 79.8% triphenylmethane (0.164 g, 0.673 mmol) as white needles, mp 94.5–95°. The presence of stannic chloride in the mother liquor and washings was shown by copious fuming and the formation of stannic hydroxide when exposed to the atmosphere.

A qualitative reaction as above in acetonitrile followed by ether precipitation afforded tropenylum hexachlorostannate(IV) as an off-white powder. *Anal.* Found for $C_{14}H_{14}SnCl_6$: $C_7H_7^+$, 35.6.

B. Tropenylum Hexabromostannate(IV).—Cycloheptatriene (0.117 g, 1.13 mmol) was added to a solution of triphenylcarbonium pentabromostannate(IV) (0.85 g, 1.12 mmol) in methylene chloride (4 ml) to give an immediate cream-colored precipitate; this was washed with two 10-ml portions of methylene chloride and dried *in vacuo* to yield 100% tropenylum hexabromostannate(IV) (0.44 g, 0.56 mmol) as light yellow crystals.^{20,21} *Anal.* Calcd for $C_{14}H_{14}SnBr_6$: Br, 61.44. Found: Br, 61.19.

Reactions of Triphenylcarbinol with Hexahalostannic Acids.

A. Hexachlorostannic Acid Hexahydrate.²²—Stannic chloride (10.0 g, 38.4 mmol) was placed in a flask fitted with a dropping funnel, a gas delivery tube, and a condenser, and the apparatus was purged with dry nitrogen. The flask was cooled in an ice bath and 12 *N* hydrochloric acid (5.5 ml) was added dropwise with swirling; after addition was complete, hydrogen chloride gas was bubbled through the stirred solution for 1 hr to yield 88.5% hexachlorostannic acid hexahydrate (15.0 g, 34.0 mmol) as mushy white crystals, mp 19–20° (lit.²² mp 19.2°).

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(14) The infrared spectrum of this material showed a slightly perturbed hexachlorostannate(IV) ion spectrum (*vide infra*) but not the spectrum of the pentachlorostannate(IV) ion.

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TABLE I
 METHYL-SUBSTITUTED TRIARYLCARBONIUM HALOSTANNATE(IV) SALTS

Triarylcation ion	Anion	Mp, °C	Per cent yield	Anal, %							
				Calcd				Found			
				C	H	Sn	X	C	H	Sn	X
<i>p</i> -Tolyldiphenyl	SnCl ₅ ⁻	131-133	94.5	43.41	3.10	21.45	32.04	43.40	3.40	21.22	31.98
Di- <i>p</i> -tolylphenyl	SnCl ₅ ⁻	120-123	89.2	44.45	3.38	20.92	31.25	44.20	3.54	21.05	31.05
Tri- <i>p</i> -tolyl	SnCl ₅ ⁻	152-155	98	45.45	3.64	20.42	30.49	45.29	3.79	20.66	30.26
Di- <i>p</i> -tolylphenyl ^a	SnCl ₆ ²⁻	149-150	82.5	57.70	4.38	13.58	24.34	55.30	4.36	16.14	24.04
Tri- <i>p</i> -tolyl	SnCl ₆ ²⁻	186-187	90	58.57	4.69	13.16	23.58	57.86	4.70	12.75	23.74
<i>p</i> -Tolyldiphenyl	SnBr ₅ ⁻	122-123	97	30.97	2.21	15.30	51.51	30.80	2.31	15.59	51.30
Di- <i>p</i> -tolylphenyl	SnBr ₅ ⁻	132-133	94	31.94	2.42	15.03	50.60	31.78	2.61	15.13	50.48
Tri- <i>p</i> -tolyl	SnBr ₆ ²⁻	200-201	86	45.20	3.62	10.15	41.02	45.00	3.87	9.91	40.85
Di- <i>p</i> -tolylphenyl	SnBr ₆ ²⁻	163-165	50.4	44.21	3.36	10.40	42.02	44.14	3.36	10.49	42.01

^a Did not give satisfactory analysis; presence of SnCl₆²⁻ confirmed by infrared spectrum.

B. Hexabromostannic Acid Octahydrate.—A similar reaction to that above using stannic bromide (3.34 g, 7.62 mmol), 48% hydrobromic acid (1.6 ml), and hydrogen bromide gas gave a quantitative yield of hexabromostannic acid octahydrate (6.29 g, 8.4 mmol) containing some excess hydrogen bromide, mp 26-30° (lit.²³ mp 27°).

C. Triphenylcarbonium Pentachlorostannate(IV).—Hexachlorostannic acid hexahydrate (3.37 g, 7.63 mmol) was added to a chilled solution of triphenylcarbinol (1.01 g, 3.88 mmol) in propanoic anhydride (12 ml) (*caution!* slow addition is necessary to prevent bumping) and cyclohexane was added to the resulting orange solution until precipitation had ceased. The solid was washed with four 25-ml portions of cyclohexane and dried *in vacuo* to yield 98.5% triphenylcarbonium pentachlorostannate(IV) (2.06 g, 3.82 mmol) as yellow needles, mp 168-169°. *Anal.* Found for C₁₈H₁₅SnCl₅: (C₆H₅)₃C⁺, 45.2.

D. Triphenylcarbonium Pentabromostannate(IV).—A similar reaction to that above using hexabromostannic acid octahydrate (5.70 g, 7.60 mmol) and triphenylcarbinol (4.48 g, 17.3 mmol) in acetic anhydride (25 ml) yielded 85.7% triphenylcarbonium pentabromostannate(IV) containing excess stannic bromide (4.94 g, 6.50 mmol). *Anal.* Found for C₁₈H₁₅SnBr₅: (C₆H₅)₃C⁺, 27.6.

E. Tropenylum Hexachlorostannate(IV).—A similar reaction to that above using hexachlorostannic acid hexahydrate (2.81 g, 6.36 mmol) and tropanyl methyl ether (1.15 g, 9.46 mmol) in acetic anhydride (10 ml) yielded 76.5% tropanyl hexachlorostannate(IV) (1.86 g, 3.63 mmol) as white crystals, mp 257°. *Anal.* Found for C₁₄H₁₄SnCl₆: C₇H₇⁺, 35.5.

Tetramethylammonium Salts. A. Hexachlorostannate(IV).—Eastman Kodak White Label tetramethylammonium chloride (twice recrystallized from ethanol; 3.90 g, 35.8 mmol) and Baker and Adamson reagent grade stannic chloride pentahydrate (6.30 g, 17.9 mmol) were dissolved in the minimum amount of boiling 12 *N* hydrochloric acid and the solution was cooled to yield white prisms of tetramethylammonium hexachlorostannate(IV), which were dried *in vacuo* over sodium hydroxide. *Anal.* Calcd for C₈H₂₄N₂SnCl₆: C, 20.02; H, 5.04; Cl, 44.34. Found:²⁴ C, 19.63; H, 5.03; Cl, 44.00.

B. Hexabromostannate(IV).—Eastman Kodak White Label tetramethylammonium bromide (twice recrystallized from ethanol; 11.7 g, 75 mmol) was added to a solution prepared by dissolving stannic bromide (16.7 g, 38 mmol) in chilled 48% hydrobromic acid (50 ml). The mixture was heated to 100° and 48% hydrobromic acid was added at that temperature until solution was complete. On cooling the solution deposited yellow cubes of tetramethylammonium hexabromostannate(IV) which were dried *in vacuo* over sodium hydroxide. *Anal.* Calcd for C₈H₂₄N₂SnBr₆: C, 12.87; H, 3.24; Br, 64.23. Found:²⁴ C, 13.07; H, 3.42; Br, 64.23.

Preparation of Other Triarylcation Halostannate(IV) Salts. A. Starting Materials.—*p*-Tolyldiphenylmethyl alcohol²⁵

and chloride,²⁵ di-*p*-tolylphenylmethyl alcohol²⁶ and chloride,²⁶ and tri-*p*-tolylmethyl alcohol,²⁷ chloride,²⁷ and bromide²⁸ were prepared by reported routes.

A solution of di-*p*-tolylphenylcarbinol (20.0 g, 70 mmol) in acetyl bromide (50 ml) was heated at reflux for 1.5 hr. Removal of solvent *in vacuo* gave a crystalline solid which was recrystallized twice from dry ligroin (bp 60-80°) to yield 75% di-*p*-tolylphenylmethyl bromide (18.3 g, 52.5 mmol) as white cubes, mp 121.5-123°. *Anal.* Calcd for C₂₁H₁₉Br: C, 71.78; H, 5.45; Br, 22.76. Found:²⁹ C, 71.84; H, 5.40; Br, 22.95.

An analogous preparation gave an 80% yield of *p*-tolyldiphenylmethyl bromide as white crystals, mp 97-98°. *Anal.* Calcd for C₂₀H₁₇Br: C, 71.22; H, 5.08; Br, 23.69. Found:²⁹ C, 71.21; H, 5.04; Br, 23.87.

B. Triarylcation Pentahalostannate(IV) Salts.—These compounds were conveniently prepared by addition of a calculated excess of the appropriate stannic halide to a rapidly stirred solution of the triarylmethyl halide in a minimum amount of benzene; ligroin was added if necessary to complete precipitation. The brilliant yellow (chloride) or orange (bromide) pentahalostannate(IV) salts were separated by filtration on fritted glass, washed on the filter with a small quantity of ligroin, and dried in a nitrogen atmosphere. Properties and analyses of these salts are given in Table I.

C. Triarylcation Hexahalostannate(IV) Salts.—Equivalent quantities of the appropriate triarylcation pentahalostannate(IV) and triarylmethyl halide dissolved in the minimum amount of methylene chloride were mixed with rapid stirring. After being stirred for 30 min, the precipitates were separated by filtration on fritted glass, washed on the filter with ligroin, and dried in a nitrogen atmosphere. Properties and analyses of these salts are given in Table I. Triphenylcarbonium and *p*-tolyldiphenylcarbonium hexahalostannate(IV) salts could not be formed by this method.

Conversion of Triarylcation Hexahalostannate(IV) Salts to Pentahalostannate(IV) Salts.—For example, a slurry of di-*p*-tolylphenylcarbonium hexabromostannate(IV) (0.200 g, 0.175 mmol) in methylene chloride (1 ml) was added to a calculated excess of stannic bromide in methylene chloride (5 ml) to give a dark green solution; this was stirred for a few minutes and then diluted with ligroin to give an orange precipitate. The solid was filtered on fritted glass, washed with ligroin, and dried *in vacuo* to yield 91.5% di-*p*-tolylphenylcarbonium pentabromostannate(IV) as yellow crystals, mp 130.5-132°.

In analogous reactions *p*-tolyldiphenylcarbonium hexachlorostannate(IV) and hexabromostannate(IV) and tri-*p*-tolylcarbonium hexabromostannate(IV) gave the corresponding pentahalostannate(IV) salts.

Nuclear Magnetic Resonance Spectra. Thermodynamics of the Ionization of Triphenylmethyl Chloride by Pentachlorostannate-

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(29) Analysis by Galbraith Laboratories, Inc.

(IV) Ion.—Spectra were recorded with a Varian A56-60 spectrometer equipped with a variable-temperature probe. In methylene chloride the phenyl protons of triphenylmethyl chloride show a singlet ^1H nmr spectrum at δ 7.20 (TMS) while those of triphenylcarbonium pentachlorostannate(IV) show the characteristic multiplet ^1H nmr spectrum of the triphenylcarbonium ion^{30,31} at δ 7.60–8.40 (TMS); neither spectrum shows any change in the range of -40 to 60° . The nmr spectra of solutions containing both species exhibit separate cation and covalent spectra up to -30° ; above this point the rate of chloride ion exchange between carbonium ion and covalent halide³² becomes significant on the nmr time scale.

Triphenylmethyl chloride (0.0694 g, 0.25 mmol) and triphenylcarbonium pentachlorostannate(IV) (0.135 g, 0.25 mmol) were dissolved in methylene chloride (1.5 ml) and the nmr spectrum of the solution was recorded at intervals from -60 to -30° . The equilibrium composition of the solution was determined at each temperature by integration of the covalent and cationic signals; these values are shown in Table II. These data were fitted by least-squares treatment to a line of the form $\ln K = (a/T) + b$ (Figure 1) to give the following values for the thermodynamic functions at 25° : $\Delta G^\circ = 1.85$ kcal/mol; $\Delta H^\circ = -9.56$ kcal/mol; $\Delta S^\circ = -38.6$ eu.

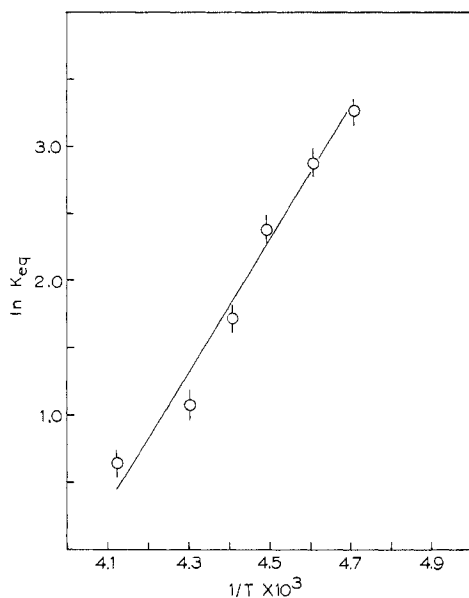


Figure 1.—Plot of $\ln K$ against $1/T$ for the ionization of triphenylmethyl chloride by stannic chloride in methylene chloride solvent.

Mössbauer Effect in Halostannate(IV) Anions.—The Dow spectrometer is a constant-acceleration type using a 512-channel multiscaler for spectrum storage. The basic design is that of Ruegg, *et al.*,³³ modified to fit local needs. The γ -ray source is a long-lived (245-day) isomeric level of $\text{Pd}_{311}^{119}\text{Sn}$ which decays by internal conversion of the first excited state of ^{119}Sn and then to the ground state by emission of a 23.8-keV γ ray. A Doppler shift energy variation of about 10^{-6} eV (1 cm/sec) is produced by mounting the source on a loudspeaker voice coil. The sample is mounted in a dewar flask in which the temperature can be varied from 4.2°K to above room temperature; the boiling point of liquid nitrogen, 78°K , is favored for routine measurements. The velocity scale was calibrated by use of National Bureau of Standards

(30) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).

(31) D. G. Farnum, *J. Am. Chem. Soc.*, **86**, 934 (1964).

(32) H. H. Freedman, A. E. Young, and V. R. Sandel, *ibid.*, **86**, 4722 (1964).

(33) F. C. Ruegg, J. J. Spijkerman, and J. R. DeVoe, *Rev. Sci. Instr.*, **36**, 1018 (1965).

TABLE II
EQUILIBRIUM CONSTANTS FOR THE IONIZATION
OF TRIPHENYLMETHYL CHLORIDE BY STANNIC CHLORIDE^a

Temp, °K	Cation integ	Anion integ	K_{eq}
242.5	11.80	7.90	1.88
232.5	13.83	8.04	2.95
227.0	14.85	6.87	5.57
222.5	13.38	4.67	10.9
217.0	13.63	3.80	17.8
212.5	15.36	3.62	25.9

^a In methylene chloride solvent.

Material No. 725, sodium nitroprusside, used with a cobalt-57 source and the iron-57 Mössbauer effect.

Samples of ammonium and potassium hexachlorostannate(IV) salts were supplied by J. C. Evans, Chemical Physics Research Laboratory, Dow Chemical Co.; the preparations of other materials are given above. Isomer shifts and quadrupole splittings are listed in Tables III and IV; a representative spectrum is shown in Figure 2.

Infrared Spectra.—Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer in Nujol mulls using cesium bromide or polyethylene plates; Nujol for mulls was dried by solution in pentane, treatment with Linde 4A Molecular Sieves, and removal of pentane *in vacuo* in the glove box. A sample of 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate(IV) was generously furnished by H. H. Freedman. Principal Sn-Cl stretching frequencies are listed in Table V.

Results and Discussion

There is no doubt that triphenylcarbonium pentachlorostannate(IV) is a salt containing the triphenylcarbonium cation: Sharp and Sheppard^{10e} have interpreted the infrared spectrum in terms of a salt, and we find that the electronic and nmr spectra of this material are identical with those reported for the triphenylcarbonium ion.^{17,30,31} Further confirmation of this is given by facile hydride exchange with cycloheptatriene in methylene chloride to give tropenylium salts and triphenylmethane. Only ionic triphenylcarbonium salts react with cycloheptatriene in this solvent;^{17,34} covalent triphenylmethyl derivatives do not react.³⁵ This criterion also establishes triphenylcarbonium pentabromostannate(IV) as ionic; however, when a sample of this compound is washed repeatedly with cyclohexane, the per cent cation in the sample is reduced and triphenylmethyl bromide can be isolated from the washings. This facile dissociation of the complex salt is not observed with the pentachlorostannate(IV).³⁶

The identity of the anions in the chlorostannate(IV) salts has been confirmed by infrared spectral comparison to species of known crystallographic structure. The anion in triphenylcarbonium pentachlorostannate(IV) gives an infrared spectrum in the Sn-Cl region³⁷ (Figure 3) identical with that of the anion in 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate.

(34) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(35) H. J. Dauben, Jr., and L. R. Honnen, unpublished work in Ph.D. thesis of L. R. H., University of Washington, 1962.

(36) The nmr spectrum of triphenylcarbonium pentabromostannate(IV) in methylene chloride at -40° shows only triphenylcarbonium ion; however, at 60° resonance is shifted upfield indicating dissociation of the anion and concurrent formation of triphenylmethyl bromide, which is in equilibrium with the cation.

(37) The cation shows no significant absorptions in this region.

TABLE III

Cation	TIN-199 MÖSSBAUER EFFECT ISOMER SHIFTS ^{a-c}			
	SnCl ₅ ⁻	SnBr ₅ ⁻	SnCl ₆ ²⁻	SnBr ₆ ²⁻
Ammonium			-1.051 (0.008) ^d	
Potassium			-1.014 (0.007)	
Tropenylum			-1.020 (0.007)	-0.660 (0.009)
Tetramethylammonium			-1.022 (0.008)	-0.683 (0.008)
Triphenylcarbonium	-0.890 (0.023)	-0.532 (0.008)		
<i>p</i> -Tolyldiphenylcarbonium	-1.051 (0.023)	-0.536 (0.008)		
Di- <i>p</i> -tolylphenylcarbonium	-0.919 (0.012)	-0.587 (0.007)	-1.020 (0.007)	-0.665 (0.008)
Tri- <i>p</i> -tolylcarbonium	-0.997 (0.008)		-1.017 (0.007)	-0.677 (0.007)

^a At 78°K unless noted; units are mm/sec (\pm experimental uncertainty). Isomer shifts are measured with respect to the source, Pd₃^{119m}Sn, held at room temperature. ^b The experimental uncertainty includes our best evaluation of errors in calibration and in determination of the isomer shifts as well as the statistical uncertainty in the determination of the line position. ^c Some comparison compounds include: β -Sn (white), 1.015 (0.007); SnCl₄ (anhydrous), 0.693 (0.007); SnO₂ (very broad), -1.52 (0.02); tetraphenyltin, -0.260 (0.008); Mg₂Sn, 0.347 (0.007). ^d At room temperature.

TABLE IV

TIN-119 MÖSSBAUER EFFECT QUADRUPOLE SPLITTING AT 78°K^a

Cation	Anion	Splitting, mm/sec
Triphenylcarbonium	SnCl ₅ ⁻	0.460 (0.023)
<i>p</i> -Tolyldiphenylcarbonium	SnCl ₅ ⁻	0.671 (0.023)
Di- <i>p</i> -tolylphenylcarbonium	SnCl ₅ ⁻	Yes, small
Tri- <i>p</i> -tolylcarbonium	SnCl ₅ ⁻	Yes, small
Di- <i>p</i> -tolylphenylcarbonium	SnBr ₅ ⁻	Yes, very small

^a All other compounds tested did not show detectable splitting.

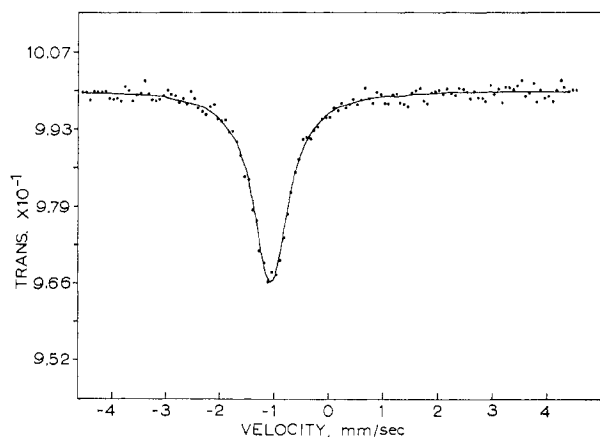


Figure 2.—Mössbauer effect spectrum of tin-119 in ammonium hexachlorostannate(IV) at room temperature. The source is Pd₃^{119m}Sn also at room temperature.

TABLE V

Sn-Cl STRETCHING BANDS OF CHLOROSTANNATE(IV) SALTS

Cation	Anion	Doublet, cm ⁻¹	Singlet, cm ⁻¹
Tetramethylammonium	SnCl ₆ ²⁻		286
Tropenylum	SnCl ₆ ²⁻		286
Di- <i>p</i> -tolylphenylcarbonium	SnCl ₆ ²⁻		290
Tri- <i>p</i> -tolylcarbonium	SnCl ₆ ²⁻		289
3-Chloro-1,2,3,4-tetra-phenylcyclobutenium	SnCl ₅ ⁻	354 320	
Triphenylcarbonium	SnCl ₅ ⁻	354 324	
<i>p</i> -Tolyldiphenylcarbonium	SnCl ₅ ⁻	353 322	
Di- <i>p</i> -tolylphenylcarbonium	SnCl ₅ ⁻	353 322	
Tri- <i>p</i> -tolylcarbonium	SnCl ₅ ⁻	349 318	

(IV), which has been shown to possess the monomeric sp³d trigonal-bipyramidal structure,⁹ and the other pentachlorostannate(IV) salts have extremely similar spectra. The main feature of these spectra is a pair of strong peaks in the region of 354 and 320 cm⁻¹ (Table

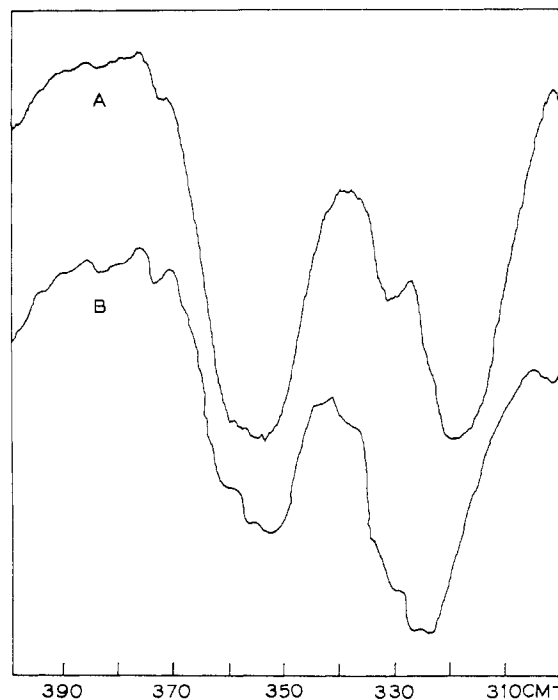


Figure 3.—Comparison of the Sn-Cl stretching bands of (A) 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate(IV) and (B) triphenylcarbonium pentachlorostannate(IV).

V); in comparison, the anion in tetramethylammonium hexachlorostannate(IV), which is known to possess the sp³d² octahedral structure,^{38,39} shows a single sharp band at 286 cm⁻¹, and the other hexachlorostannate(IV) salts show similar spectra (Table V). This correlation with known structure confirms the recent assignments^{6,7} made for tetraalkylammonium pentachlorostannate(IV) salts.

Further information on the halostannate(IV) ions is given by the Mössbauer effect⁴⁰ studies. The ¹¹⁹Sn isotope is stable with respect to nuclear decay and composes about 8% of natural tin. The ground state has a nuclear spin of 1/2 \hbar and a magnetic moment of -1.046 nuclear magnetons, while the first excited state, at 23.8

(38) R. G. Dickinson, *J. Am. Chem. Soc.*, **44**, 276 (1922).

(39) R. W. G. Wyckoff and R. B. Cory, *Am. J. Sci.*, **18**, 437 (1929).

(40) (a) V. I. Gol'danskii, "The Moessbauer Effect and its Applications in Chemistry," Consultant's Bureau, Plenum Pub. Corp., New York, N. Y., 1964; (b) G. K. Wertheim, "Moessbauer Effect: Principles and Applications," Academic Press, New York, N. Y., 1964; (c) H. Frauenfelder, "The Moessbauer Effect," W. A. Benjamin, Inc., New York, N. Y., 1963.

keV, has a spin of $3/2\hbar$, a magnetic moment of 0.76 nuclear magneton, and an electric quadrupole moment of $-0.07 \times 10^{-24} \text{ cm}^2$.⁴¹ Thus both the ground and first excited states can be split by either crystalline or external magnetic fields of 10–20 kG, and the excited state can also be split by interaction of the electric quadrupole moment with electric field gradients due to charge distribution in the lattice or the chemical bonds. The nuclear charge can also interact with s electrons to give a monopole shift (isomer shift) of the energy levels. None of the materials discussed herein has magnetic fields but could show isomer shifts, quadrupole splitting, and lattice vibration characteristics.

The isomer shifts are listed in Table III and shown in Figure 4. Each of the anions has a characteristic range of isomer shifts for the various cations which is—with the exception of the pentachlorostannate(IV) anions—relatively small compared with the line width ($\Gamma_{\text{obsd}} = 0.90 \text{ mm/sec}$) and—with the same exception—the isomer shift ranges are well separated. It is possible to distinguish easily among SnBr_5^- , SnBr_6^{2-} , and SnCl_5^{2-} ions by isomer shift; however, in some cases SnCl_5^{2-} could be confused with SnCl_6^{2-} if only the isomer shift is considered. Examination of Figure 4 shows that the isomer shift change between stannic halide and hexahalostannate(IV) ion is about the same in the chloride and bromide cases. The isomer shifts of the pentabromostannate(IV) salts are grouped close to an arbitrary line connecting the shift of stannic bromide with the average shift of the hexabromostannate(IV) ions; however, in the chloride case the shifts lie below such a line and are scattered, with the triphenylcarbonium ion salt lying closest to the line. The change in isomer shift with coordination number in the bromide case shows a regular loss in electron density at the nucleus with change in hybridization from sp^3 through sp^3d to sp^3d^2 . This presumably arises from a loss of 5s electrons with hybridization change; however, a full evaluation of the effects of geometry, bond distance, shielding parameters, and delocalization, as well as examination of similar systems, would need to be carried out before the origin of the isomer shift could be firmly established.

The quadrupole splittings (Table IV) are generally zero, except in the case of the pentachlorostannate(IV) salts which show some small quadrupole splitting, possibly due to a slight distortion of the Cl_5^- cage, by an unsymmetric lattice contribution or by microscopic crystal effects such as twinning. The quadrupole splitting, taken with the isomer shift data, allows the positive identification of any of these anions by Mössbauer effect studies, since all of the pentachlorostannate(IV) salts show some splitting, and none of the hexachlorostannate(IV) salts shows any splitting.

In hydrocarbon solvent—in which previously reported preparations¹⁰ of triphenylcarbonium pentachlorostannate(IV) have been carried out—the initial ionization of triphenylmethyl chloride by stannic chloride is followed by immediate precipitation; we find

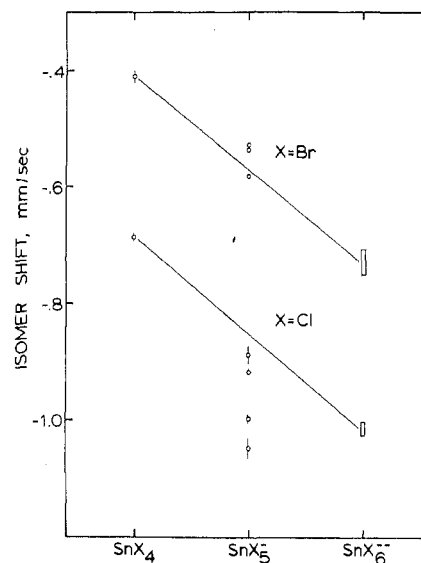


Figure 4.—The ^{119}Sn Mössbauer effect isomer shifts of halo-stannate(IV) salts; see Table III for identification of points.

that no trace of cation color can be observed in the solvent cyclohexane. The stoichiometry of this salt could thus arise from rapid precipitation of intimate ion pairs, which would not allow equilibration to the hexachlorostannate(IV). We find, however, that the nature of the product is not affected by preparation and equilibration in methylene chloride, in which triphenylcarbonium salts are soluble and ionized,^{42,43} or sulfur dioxide, in which triphenylmethyl chloride is largely ionized and partially dissociated^{10c,44} and in which triphenylcarbonium salts are completely dissociated.⁴⁵ There is no barrier to formation of the hexachlorostannate(IV) ion in these solutions, as shown by hydride exchange to yield tropenylium hexachlorostannate(IV) and stannic chloride and by the observations of Gutmann, *et al.*¹² Furthermore, generation of the carbonium ion in the presence of preformed hexachlorostannate(IV) ions by treatment of triphenylcarbinol with hexachlorostannic acid yields only triphenylcarbonium pentachlorostannate(IV), whereas similar treatment of tropenyl methyl ether readily affords tropenylium hexachlorostannate(IV). Thus the formation of triphenylcarbonium pentachlorostannate(IV)—and, from similar arguments, the pentabromostannate(IV)—does not result from kinetic control; the identity of these species is lost in solution, but in the solid state the five-coordinate tin salt is thermodynamically more stable than the six-coordinate salt.

This suggests that the triphenylcarbonium ion is a stronger Lewis acid than the pentachlorostannate(IV) anion and competes favorably with the anion for a chloride ion. Our equilibrium nmr studies in methylene chloride indicate that this is not the case; the ionization of triphenylmethyl chloride by pentachlorostannate-

(42) In a medium of this dielectric constant the salts exist primarily as ion pairs;⁴³ however, the rapidity of hydride exchange with cycloheptatriene indicates that the ionic species are readily accessible to chemical interactions.

(43) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956), and references therein.

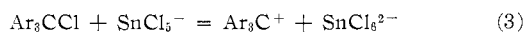
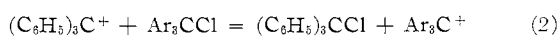
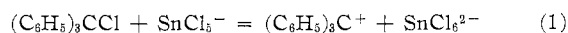
(44) N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5530 (1951).

(45) (a) K. Ziegler and H. Wollschrit, *Ann.*, **479**, 90 (1930); (b) N. N. Lichtin and P. Pappas, *Trans. N. Y. Acad. Sci.*, **20**, 143 (1957).

(41) A. H. Muir, Jr., K. J. Ando, and H. M. Coogan, "Mössbauer Effect Data Index, 1958–1965," Interscience Publishers, New York, N. Y., 1966.

(IV) ion has a negative enthalpy (-11.9 kcal/mol). The entropy term for the ionization, however, is also large and negative (-48.8 eu); above about -25° the contribution of the $T\Delta S$ term overcomes the favorable enthalpy term, and the free energy of ionization becomes positive. Thus the stability of triphenylcarbonium pentachlorostannate(IV) arises from a rather delicate balance of factors; the energy required to ionize triphenylmethyl chloride reduces the enthalpy of hexahalostannate(IV) formation, and the negative entropy of the ionogenic reaction becomes dominant. With a simple halide—such as a tetraalkylammonium halide—there is no comparable ionization energy; entropy comparisons are harder to make, but if we consider the *reverse* reaction of formation of halide and pentachlorostannate(IV) from the hexachlorostannate(IV), it is likely that the molecule-forming reaction in the triarylcarbonium case would have the more positive entropy.⁴⁶

Consideration of the equations



(46) This discussion is based on solution measurements; however, the use of these data to predict successfully the stability of other salts (*vide infra*) makes extension to the solid state reasonable.

shows that (3) is the summation of (1) and (2), and thus $\Delta G^\circ(3) = \Delta G^\circ(1) + \Delta G^\circ(2)$. For a triarylmethyl chloride (Ar_3CCl) to react with stannic chloride to form a stable hexachlorostannate(IV) salt, $\Delta G^\circ(2)$ must be negative and at least as large numerically as $\Delta G^\circ(1)$, which from this work is $+1.85$ kcal/mol. Young, Sandel, and Freedman⁴⁷ have determined $\Delta G^\circ(2)$ for a variety of triarylmethyl chlorides. Their values of $\Delta G^\circ(2)$ for *p*-tolylidiphenylmethyl chloride (-1.6 kcal/mol), di-*p*-tolylphenylmethyl chloride (-3.2 kcal/mol), and tri-*p*-tolylmethyl chloride (-4.6 kcal/mol) suggest that the former would not react with stannic chloride to form a stable hexachlorostannate(IV) salt even in the presence of excess *p*-tolylidiphenylmethyl chloride, while the latter two chlorides should form stable hexachlorostannate(IV) salts. These predictions are confirmed by experiment. In addition, it is clear why 1,2-dichloro-1,2,3,4-tetraphenylcyclobutene ($\Delta G^\circ(2) = 1.8$ kcal/mol) forms a stable pentachlorostannate(IV) salt.^{48,49}

Acknowledgment.—We wish to thank Sharon Alderman and Alan A. MacDonald, who carried out many of these reactions.

(47) A. E. Young, V. R. Sandel, and H. H. Freedman, *J. Am. Chem. Soc.*, **88**, 4532 (1966).

(48) There is a tacit assumption in this discussion that $\Delta H^\circ(L)$ ⁴⁹ for the formation of these complexes is similar; since structural differences are small, this would appear to be reasonable.

(49) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, *ibid.*, **87**, 1700 (1965).

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The Preparation and Structural Characterization of Trirubidium Octachlorodimolybdenum. A Binuclear Structure with Strong Metal–Metal Bonding¹

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The compounds $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ have been isolated and structurally characterized. The green-yellow crystals in solids are obtained by treatment of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with deoxygenated 12 *N* HCl at 60° , followed by addition of RbCl or CsCl and cooling to 0° . The cesium compound is obtained in practically quantitative yield. These compounds can be converted electrochemically into $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ in excellent yields; we believe this is the best way to prepare the latter compounds. $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ appear virtually certain to be isostructural. The structure of $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ has been solved and refined: space group $P62c$; $a = 7.190$ (5) Å, $c = 16.662$ (10) Å at 24° ; $d_{\text{calcd}}(Z = 2) = 3.26$ g cm⁻³; $d_{\text{obsd}} = 3.23 \pm 0.04$ g cm⁻³. The structure consists of Rb^+ ions and discrete $\text{Mo}_2\text{Cl}_8^{3-}$ ions. The latter are not related structurally to the $\text{Mo}_2\text{Cl}_8^{4-}$ ion but may be described as Mo_2Cl_8 groups of the biocahedron ($\text{W}_2\text{Cl}_8^{3-}$) type in which one-third of the bridging Cl atoms are missing. These defective binuclear entities are then rotationally disordered in the crystal. The Mo–Mo distance, 2.38 (1) Å, as well as the squashing together of the two octahedra, shows that there is strong metal–metal bonding, though not so strong as in $\text{Mo}_2\text{Cl}_8^{4-}$ (Mo–Mo = 2.14 Å).

Introduction

In this paper we present the second of a series of reports on the chemical and structural properties of low-valent molybdenum compounds which can be obtained

by treatment of dimolybdenum tetraacetate with mineral acids. The previous paper³ described the structural characterization of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$, a compound containing the $\text{Mo}_2\text{Cl}_8^{4-}$ ion, which has a D_{4h} non-bridged structure (Mo–Mo = 2.14 Å), comparable to that of $\text{Re}_2\text{Cl}_8^{2-}$, with which it is isoelectronic.

(1) Supported by the U. S. Atomic Energy Commission.

(2) Fellow of the Samuel Rubin Foundation. On leave from The University of Ljubljana, Ljubljana, Yugoslavia.

(3) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).