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Tin-119 Mossbauer Spectra of Methyltin(IV) Nitrates and Their Adducts

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^{119}Sn Mossbauer spectra are reported for $(CH_3)_xSn(NO_3)_{4-x}$ (x = 0–3) and for some adducts with pyridine and 2,2′-bipyridyl. The new compounds $(CH_3)_2Sn(NO_3)_2(py)_2$ (py = pyridine), $(CH_3)_2Sn(NO_3)_2(bipy)$ (bipy = 3,3′-bipyridyl), $(CH_3)_3SnNO_3(py)$, $(CH_3)_3SnNO_3(bipy)_{0.5}$, $CH_3Sn(NO_3)_3(bipy)$, $Sn(NO_3)_4(bipy)$, $Cs_2Sn(NO_3)_6$, and $[(C_2H_5)_4N]_2Sn(NO_3)_6$ are described. Vibrational data for the adducts together with ^{119}Sn Mossbauer spectra are used to suggest likely molecular structures.

Introduction

The synthesis of $CH_3Sn(NO_3)_3$[3] has completed the characterization of the series of compounds $(CH_3)_xSn(NO_3)_{4-x}$ (x = 0–3). These volatile tin(IV)–nitrato species are of considerable interest in the context of Mossbauer spectroscopy since single-crystal X-ray diffraction studies have recently been completed for $Sn(NO_3)_4$,[4] $CH_3Sn(NO_3)_3$,[5] and $(CH_3)_3SnNO_3$.[6] The interpretation of Mossbauer parameters for organotin(IV) compounds has in the past been severely hampered by the lack of X-ray crystallographic data. Indeed empirical correlations of Mossbauer isomer shifts (δ) and quadrupole splittings (Δ) have often led to erroneous structural predictions.[7] The emergence of a point charge model and molecular orbital models has however put the interpretation of Δ data on a firmer base.[8] Progress has also been made toward an understanding of isomer shifts in SnX_4L_n (X = anionic ligand, L = neutral donor, n = 0–4) and organotin (IV) compounds.[9,10]

We describe herein the synthesis and characterization of a number of 2,2′-bipyridyl and pyridine adducts of $(CH_3)_xSn(NO_3)_{4-x}$ (x = 1–3) and $Sn(NO_3)_4$. The ^{119}Sn Mossbauer spectra of the organotin(IV) nitrates are discussed in the light of X-ray structural information. Mossbauer parameters together with infrared and Raman spectra are then used to suggest probable solid-state structures for the adducts.

Experimental Section

$Sn(NO_3)_4$,[11] $CH_3Sn(NO_3)_3$,[3] $(CH_3)_2Sn(NO_3)_2$,[12] and $(CH_3)_3Sn(NO_3)$[13] were synthesized by literature methods. The complexes $Sn(NO_3)_4(py)_2$[11] and $CH_3Sn(NO_3)_3(py)_2$[3] (py = pyridine) have also been described.

Preparation of New Adducts. All manipulations involving the very moisture-sensitive tin(IV)–nitrato species were carried out in a drybox. Solvents were rigorously dried prior to use.

$(CH_3)_2Sn(NO_3)_2(py)_2$. Pyridine (7.0 ml, 0.087 mol) was added to a suspension of dimethyltin dinitrate (1.98 g, 0.0073 mol) in chloroform (15 ml). The colorless solution yielded a white solution. Precipitation was completed by addition of n-hexane (5 ml). The product was dried *in vacuo*.

Anal. Calcd for $(CH_3)_2Sn(NO_3)_2(py)_2$: C, 33.44; H, 3.74; N, 13.00. Found: C, 32.40; H, 3.66; N, 12.99.

$(CH_3)_3SnNO_3(py)$. Pyridine (8.0 ml, 0.099 mol) was added to a suspension of trimethyltin nitrate (0.794 g, 0.0035 mol) in chloroform (15 ml). The colorless solution yielded, after removal of solvent and excess pyridine, a colorless oil. Crystallization was effected by stirring for 12 hr with n-hexane.

Anal. Calcd for $(CH_3)_3SnNO_3(py)$: C, 31.51; H, 4.63; N, 9.19. Found: C, 31.28; H, 4.60; N, 9.34.

$Sn(NO_3)_4(bipy)$, $CH_3Sn(NO_3)_3(bipy)$, $(CH_3)_2Sn(NO_3)_2(bipy)$, and $(CH_3)_3SnNO_3(bipy)_{0.5}$. These complexes were all prepared in a similar manner, given below for $Sn(NO_3)_4(bipy)$.

2,2′-Bipyridyl (1.01 g, 0.00647 mol) in chloroform (10 ml) was added to a solution containing tin tetranitrate (2.10 g, 0.00573 mol) in chloroform (15 ml). The light yellow precipitate was recovered by filtration, washed with cold chloroform and hexane, and then dried *in vacuo*.

Anal. Calcd for $Sn(NO_3)_4(bipy)$: C, 22.97; H, 1.54; N, 16.07. Found: C, 22.88; H, 2.18; N, 15.90. Calcd for $CH_3Sn(NO_3)_3(bipy)$: C, 27.76; H, 2.33; N, 14.72. Found: C, 27.78; H, 1.94; N, 14.12. Calcd for $(CH_3)_2Sn(NO_3)_2(bipy)$: C, 33.60; H, 3.29; N, 13.06. Found: C, 33.66; H, 3.07; N, 13.09. Calcd for $(CH_3)_3SnNO_3(bipy)_{0.5}$: C, 31.62; H, 4.31; N, 9.22. Found: C, 30.75; H, 3.67; N, 11.98.

$Cs_2Sn(NO_3)_6$ and $[(C_2H_5)_4N]_2Sn(NO_3)_6$. The salts Cs_2SnCl_6 and $[(C_2H_5)_4N]_2SnCl_6$ were prepared according to the literature.[14] Cs_2SnCl_6 (3.93 g, 0.00658 mol) was added to a solution of dinitrogen pentoxide (19 g, 0.18 mol) in carbon tetrachloride (40 ml). The mixture was stirred for 3–4 hr and excess pentoxide and solvent were removed *in vacuo*. The product was washed with hexane and dried *in vacuo*. $[(C_2H_5)_4N]_2Sn(NO_3)_6$ was similarly prepared.

Anal. Calcd for $Cs_2Sn(NO_3)_6$: NO_3^-, 49.2. Found: NO_3^-, 48.7. Calcd for $[(C_2H_5)_4N]_2Sn(NO_3)_6$: C, 25.58; NO_3^-, 49.52. Found: C, 25.17; NO_3^-, 48.9.

Microanalyses. Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Microanalytical Laboratories. For very hygroscopic compounds carbon was determined by Van Slyke oxidation.[3] Nitrate ion was determined as nitron nitrate.

Physical Measurements. Infrared spectra were recorded using a Beckman IR12 spectrophotometer. Solid-state infrared spectra were obtained on Nujol and Halocarbon mulls between KRS-5 or silver chloride plates. Raman spectra were obtained on crystalline solids using a Spex Raman instrument and the red line of a krypton laser. Frequencies are accurate to ±2 cm^{-1}.

The Mossbauer apparatus had been previously described in detail.[15] Samples were examined both as Fluorolube mulls and as solid

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[3] J. R. Ferraro, D. Potts, and A. Walker, *Can. J. Chem.*, **48**, 711 (1970).

[4] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc. A*, 1959 (1967).

[5] A. Walker, D. Potts, G. S. Brownlee, S. C. Nyburg, and T. J. Szymanski, *Chem. Commun.*, 1073 (1971).

[6] P. Au, M.Sc. Thesis, University of Western Ontario, London, Ontario, Canada; H. C. Clark, private communication.

[7] Discussion of some erroneous structural conclusions by other workers can be found in (a) R. E. B. Garrod, R. H. Platt, and J. R. Sams, *Inorg. Chem.*, 10, 424 (1971); (b) R. H. Platt, *J. Organometal. Chem.*, 24, C23 (1970).

[8] (a) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970); (b) R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969); (c) R. L. Collins and J. C. Travis, "Mossbauer Effect Methodology," Vol. 3, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, p 123; (d) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc. A*, 143 (1969); (e) M. G. Clark, A. G. Maddock, and R. H. Platt, *J. Chem. Soc., Dalton Trans.*, 281 (1972).

[9] A. J. Carty and H. D. Sharma, "Mossbauer Effect Methodology," Vol. 7, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1971, p 167.

[10] (a) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 589 (1970), and references therein; (b) G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, *J. Chem. Soc., Dalton Trans.*, 2025 (1972).

[11] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

[12] C. C. Addison, W. B. Simpson, and A. Walker, *J. Chem. Soc.*, 2360 (1964).

[13] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

[14] G. W. A. Fowles and D. Nicholls, *J. Inorg. Nucl. Chem.*, 18, 130 (1961).

[15] A. J. Carty, T. Hinsberger, L. Mihichuk, and H. D. Sharma, *Inorg. Chem.*, 9, 2573 (1970).

pressed pellets. No significant differences in Mossbauer parameters were noted using the different sampling techniques. In all cases samples were prepared and mounted in a Vacuum Atmospheres Corp. Dri-Lab. Compounds were sealed inside a Mossbauer sample holder fitted with double windows of aluminum foil and polyethylene to prevent ingress of moisture during the Mossbauer measurements. Spectra were recorded with the source ($Ba^{119m}SnO_3$) at room temperature and the absorber at 80°K. The Doppler velocity scale was calibrated against the quadrupole splitting of a nitroprusside absorber and all isomer shift values are quoted relative to an SnO_2 absorber. Spectral data were analyzed by an iterative least-squares curve fitting program assuming Lorentzian line shapes but without further constraints. Spectra of $Sn(NO_3)_4$, $Sn(NO_3)_4(py)_2$, and $Sn(NO_3)_4(bipy)$ consisted of broad single lines implying the presence of unresolved quadrupole splitting. These spectra were simulated by two Lorentzian lines of equal half-widths. Mossbauer isomer shifts, quadrupole splittings, and peak widths at half-height are tabulated in Table I. The parameters are considered to be accurate to ±0.05 mm sec^{-1} with a relative precision of ±0.02 mm sec^{-1}.

Results and Discussion

A. Tin Tetranitrate and the Complexes $[(C_2H_5)_4N]_2Sn(NO_3)_6$, $Cs_2[Sn(NO_3)]_6$, $Sn(NO_3)_4(py)_2$, $Sn(NO_3)_4(bipy)$.

The X-ray crystal and molecular structure determination of $Sn(NO_3)_4$ shows a molecule approximating to D_{2d} symmetry with four symmetrically bidentate nitrate groups completing a dodecahedral arrangement of oxygen atoms around the tin atom.[4] This noncubic arrangement of ligands around tin might be expected to give rise to an electric field gradient and consequently a quadrupole splitting in the Mossbauer spectrum of ^{119}Sn. The observed spectrum at 78° however shows a single broad resonance with an isomer shift δ of −0.04 mm/sec, relative to SnO_2 (Table I). Resolution of the resonance into two Lorentzian lines yields an approximate Δ value of 0.4 mm sec^{-1}. An alternative view of the molecular structure of $Sn(NO_3)_4$ considers two oxygen atoms of a bidentate nitrate group occupying only one coordination position to give a slightly distorted tetrahedral configuration at the tin atom. This latter model serves to emphasize the relatively small electric field gradient expected at the tin nucleus in $Sn(NO_3)_4$ although a more detailed analysis of isomer shifts (*vide infra*) is inconsistent with sp^3 hybridization of tin.

Table I. Mossbauer Parameters for Tin(IV)-Nitrato Species

Compd	δ, mm sec^{-1}	Δ, mm sec^{-1}	δ_{calcd},[a] mm sec^{-1}	Γ,[b] mm sec^{-1}		
$Sn(NO_3)_4$	−0.04	0.40	−0.03	0.84		0.84
$Cs_2Sn(NO_3)_6$	0.12		0.11		0.82	
$[(C_2H_5)_4N]_2Sn(NO_3)_6$	0.12		0.11		0.82	
$Sn(NO_3)_4(py)_2$	0.24	0.67	0.24	0.81		0.81
$Sn(NO_3)_4(bipy)$	0.18	0.43	0.18	0.82		0.82
$(CH_3)_3SnNO_3$	1.44 1.44	4.15 4.14[d]		0.90		0.90
$(CH_3)_3Sn(NO_3)(py)$	1.44	4.20		0.91		0.93
$(CH_3)_3Sn(NO_3)(bipy)_{0.5}$	1.51	4.60		0.86		0.89
$(CH_3)_2Sn(NO_3)_2$	1.56 1.62	4.20 4.13[c]		0.90		0.92
$(CH_3)_2Sn(NO_3)(OH)$	1.28	3.52[d]				
$(CH_3)_2Sn(NO_3)_2(py)_2$	1.48	4.48		0.85		0.85
$(CH_3)_2Sn(NO_3)_2(bipy)$	1.47	4.56		0.75		0.78
$CH_3Sn(NO_3)_3$	0.94	2.35		0.65		0.67
$CH_3Sn(NO_3)_3(py)_2$	0.90	2.40		0.81		0.83
$CH_3Sn(NO_3)_3(bipy)$	0.86	2.19		0.76		0.72

[a] Calculated from eq 2. [b] Line width at half-height. [c] P. J. Smith, *Organometal. Chem. Rev., Sect. A*, 5, 373 (1970). [d] M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nucl. Chem.*, **29**, 1177 (1976).

Several papers have now appeared illustrating an approximately linear relationship between δ and the electronegativity of the coordinating ligands. Both Pauling[16,17] and Mulliken[18,19] electronegativity values have been employed. Recently these correlations have met with criticism with respect to the choice of the values of electronegativity.[20] A more general treatment yields the following equation relating isomer shifts to an operational parameter μ[21] derived from SnX_4, R_4Sn, and SnX_6^{2-} compounds

$$\delta = (0.43 \pm 0.005)(\mu_i - \mu_{Sn}) + 2.10 \qquad (1)$$

μ_i and μ_{Sn} are operational parameters for ligands and the tin atom derived from the experimental values of δ for tin compounds having T_d symmetry at the tin atom on an arbitrary scale with $\mu_F = 10$ and $\mu_{Sn} = 5$ (gray tin). A detailed description can be found elsewhere.[9] It is, however, worth mentioning that the orbital populations and hence s-electron densities are dependent on the nature of the hybrid orbitals involved in forming Sn-L bonds. It has been shown that the population of a tin orbital is related to $\mu_{Sn} - \mu_L$ and the value of μ_{Sn} is dependent on the nature of the hybrid orbital at the tin atom.[9] In compounds where *ideal hybrid* orbitals are involved, δ is given by

$$\delta = -(0.43 \pm 0.005)\mu_L + 4.25 \text{ for } N = 4 \qquad (2a)$$

$$+ 4.06 \text{ for } N = 5 \qquad (2b)$$

$$+ 3.95 \text{ for } N = 6 \qquad (2c)$$

$$+ 3.89 \text{ for } N = 7 \qquad (2d)$$

$$+ 3.84 \text{ for } N = 8 \qquad (2e)$$

These equations can be used to calculate approximate values of isomer shift provided values μ_L are available. For example, employing the measured δ values for $[(CH_3)_4N]_2SnX_6$ ($X = F$, $\delta = -0.40$ mm sec^{-1}; $X = Cl$, $\delta = 0.50$ mm sec^{-1}; $X = Br$, $\delta = 0.74$ mm sec^{-1}; $X = I$, $\delta = 1.25$ mm sec^{-1} [10,18,22]) μ_L values of 10, 7.95, 7.25, and 6.39, respectively, are obtained from eq 2c. Alternatively μ_L values of 7.95, 7.25, and 6.39, respectively, for Cl, Br, and I are obtained from the accurately known isomer shifts of the tetrahalides. These values of μ_L have been used successfully to estimate isomer shifts for a wide range of halo complexes of tin and more importantly to predict the coordination number and stereochemistry of the tin atom in a complex from a measured isomer shift.[9]

As pointed out below the chemical properties and vibrational spectra of $Cs_2Sn(NO_3)_6$ and $[(C_2H_5)_4N]_2Sn(NO_3)_6$ are consistent with the presence of unidentate nitrate. From eq 2c and the measured isomer shift of 0.12 mm sec^{-1}, we obtain $\mu_L = 9.0 \pm 0.1$ for one oxygen atom of a unidentate nitrate ion. This value is well within the range of μ_L values for oxygen donor ligands, typical extremes being $\mu_{OPCl_3} = 9.9$ (from *cis*-$SnCl_4(POCl_3)_2$ [7,23]) and $\mu_{OCH_3} = 8.9$ (from $(CH_3)_xSn(OCH_3)_{4-x}$).[24] Two alternative ways of applying

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[16] V. I. Goldanskii, *At. Energy Rev.*, 4, 3 (1963).

[17] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 4, 589 (1970).

[18] C. A. Clausen, II, and M. L. Good, *Inorg. Chem.*, 9, 817 (1970).

[19] H. S. Cheng and R. H. Herber, *Inorg. Chem.*, 10, 1315 (1971); K. L. Leung and R. H. Herber, *ibid.*, 10, 1020 (1971).

[20] J. E. Huheey and J. C. Watts, *Inorg. Chem.*, 10, 1553 (1971).

[21] For limited series of compounds μ_i is related to the Mulliken electronegativity of the donor atom.[7] However, the intrinsic bond-forming capacity (σ-donor, π-acceptor abilities; softness or hardness) of a ligand to Sn(IV) depends on a number of factors other than electronegativity; hence μ_i derived from the isomer shift is an empirical parameter which is not a simple function of electronegativity.

[22] A. G. Davies, L. Smith, and P. J. Smith, *J. Organometal. Chem.*, 23, 135 (1970).

[23] P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 9, 740 (1970).

[24] R. H. Herber, *Tech. Rep. Ser., Int. At. Energy Ag.*, No. 50, 127 (1966).

Table II. Vibrational Spectra of $Cs_2Sn(NO_3)_6$ and $[(C_2H_5)_4N]_2Sn(NO_3)_6$ (cm^{-1})[a]

$Cs_2Sn(NO_3)_6$		$[(C_2H_5)_4N]_2Sn(NO_3)_6$[b]		
Infrared (solid)	Raman (solid)	Infrared (solid)	Raman (solid)	Assignment
1660 sh		1660 m, sh		
	1575 sh			Asym NO_2 str
1550 s, vbr	1559 m, sp	1570 s, br	1564 w	
	1549 m, sp	1545 s, br	1546 m, sp	
1285 s, vbr	1331 s, sp	1280 s, br	1326 s, sp	Sym NO_2 str
975 sh		969 s, br	1010 s, sp	N–O str
955 s, br	1005 s, sp		1005 sh	
795 sh		790 m, sp[c]		NO_3 out-of-plane rock
790 m, sp				
755 m, sp	758 s, sp	759 m, sp	745 m, sp	Sym NO_2 bend
748 sh				
708 m, sp	715 w	710 w	715 w	Asym NO_2 bend
699 m, sp	695 w	699 m, sp	698 w	
350 s, br	329 s, sp	350 s, br	320 s, sp	Sn–O str
220 w		220 m, br	220 w	

[a] Key: s, strong; m, medium; w, weak; sh, shoulder; sp, sharp; v, very; br, broad. [b] Bands due to cation omitted. [c] Combined with band from cation.

this μ_L value to $Sn(NO_3)_4$ must be considered. First, assuming eight-coordination of tin and the use of eight tin orbitals (eq 2e) a δ value of -0.03 mm sec^{-1} is calculated. This of course assumes an equal contribution from eight oxygen atoms of four bidentate nitrate groups. Alternatively it could be assumed that a bidentate nitrate ion occupies only one coordination site with sp^3 hybrid orbitals of tin being used in bonding. In this case application of the appropriate equation (eq 2a) yields a value of $\delta = 0.38$ mm sec^{-1}. The observed isomer shift is only consistent with the former interpretation. It may be pointed out however that for $Sn(SpyO)_4$ (SpyO = anion of pyridine *N*-oxide 2-thiol),[25] a δ value of 0.80 and $\Delta = 0.0$ mm sec^{-1} agree with sp^3 hybridization at the tin atom.

The anionic complexes $Cs_2Sn(NO_3)_6$ and $[(C_2H_5)_4N]_2Sn(NO_3)_6$ are hygroscopic white solids which, in contrast to the parent $Sn(NO_3)_4$,[11] exhibit no reactivity toward acetone, Nujol, or diethyl ether. The molar conductivity of $[(C_2H_5)_4N]_2Sn(NO_3)_6$ in acetonitrile at 25° varies from 291 ohm^{-1} cm^2 at 8.55×10^{-3} *M* to 324 ohm^{-1} cm^2 at 2.22×10^{-3} *M*, behavior typical of a 2:1 electrolyte in this solvent.[26] The uv spectrum of the compound in acetonitrile exhibits a shoulder on the band associated with the nitrate ion $\pi^* \leftarrow n_p$ transition, indicative of considerable tin–nitrate interaction.[3,12] The vibrational spectra of $Cs_2Sn(NO_3)_6$ and $[(C_2H_5)_4N]_2Sn(NO_3)_6$ are given in Table II. Infrared spectroscopy alone cannot in general be used to differentiate mono- and bidentate nitrato groups. An analysis of the Raman spectrum of a complex may however be more rewarding. The predicted sequence of polarized and depolarized lines in the Raman spectra of uni- and bidentate nitrate groups differ, when C_{2v} symmetry is assumed for the metal nitrate ion model.[27] The sequence of polarization patterns for the N-O stretching modes of unidentate nitrate in decreasing order of frequency are B_1(d), A_1(p), A_1(p) while for bidentate bonding the order is A_1(p), B_1(d), A_1(p). Unfortunately this criterion is not universally applicable owing to the insolubility of many coordination compounds in solvents suitable for polarization measurements. In practice, Raman measurements on a wide range of solid nitrate complexes have indicated that the sequence of Raman intensities of the highest frequency nitrate fundamentals can be used reliably to predict the mode of nitrate coordination.[28,29]

Table III. Relative Raman Intensities for N–O Stretching Bands in Various Nitrato Species

Compd	Band I	II	III	Structure	Ref
	Increasing freq →				
HNO_3	w	vs	s	Unidentate	*a*
$Au(NO_3)_4^-$	w	s	s	Unidentate	*b*
$Pd(NO_3)_4^{2-}$	w	s	vs	Unidentate	*b*
CH_3HgNO_3	m	m	s	Unidentate	*c*
$Ti(NO_3)_4$	vs	w	m	Bidentate	*d*
$Sn(NO_3)_4$	vs	w	m	Bidentate	*d*
$Ce(NO_3)_6^{2-}$	s	w	s	Bidentate	*b, e*
$Mn(NO_3)_4^{2-}$	m	w	vs	Bidentate	*f*
$CH_3Sn(NO_3)_3$	m	w	s	Bidentate	*g*
$(CH_3)_2Sn(NO_3)_2$	m	w	s	Bidentate	*g*
$(CH_3)_3SnNO_3$	m	w	s	Bidentate	*g*
$Cs_2Sn(NO_3)_6$	m	s	s	Monodentate	*g*
$[(C_2H_5)_4N]_2Sn(NO_3)_6$	m	s	s	Monodentate	*g*
$Sn(NO_3)_4(py)_2$	m	s	m	Unidentate	*g*

[a] G. G. McGraw, D. L. Bemitt, and I. C. Hisatsune, *J. Chem. Phys.*, 42, 238 (1965); L. R. Maxwell and V. M. Mosley, *ibid.*, 8, 738 (1940). [b] References 27 and 28. [c] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 58, 1495 (1962). [d] C. C. Addison, D. W. Amos, D. Sutton, and W. H. H. Hoyle, *J. Chem. Soc. A*, 808 (1967). [e] T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, 7, 715 (1968). [f] N. Logan and A. Morris, unpublished results; J. Drummond and J. S. Wood, *J. Chem. Soc. A*, 226 (1970). [g] This work.

For convenience we have listed in Table III the Raman intensities of the three highest nitrate fundamental vibrations of the complexes described herein for which data were obtainable. Some representative patterns for compounds of known structure are also included. For unidentate nitrato species band II (NO_2 symmetric stretch) is medium to strong and by no means the least intense of the three bands. For bidentate nitrato groups however band II (now the NO_2 asymmetric stretch) is weak and without exception the weakest of the three bands. Furthermore band I in the latter case is generally strong. Utilizing this criterion the complexes $Cs_2Sn(NO_3)_6$ and $[(C_2H_5)_4N]_2Sn(NO_3)_6$ contain unidentate groups and hence six-coordinate tin. This is entirely consistent with the change in chemical reactivity from $Sn(NO_3)_4$ to the anions.[3,29]

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(25) D. Petridis, F. P. Mullins, and C. Curran, *Inorg. Chem.*, 9, 1270 (1970).

(26) D. S. Bems and R. M. Fuoss, *J. Amer. Chem. Soc.*, 83, 132 (1961).

(27) R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 5, 1308 (1966).

(28) (a) G. S. Brownlee, Ph.D. Thesis, University of Nottingham, 1969; (b) C. C. Addison, G. S. Brownlee, and N. Logan, *J. Chem. Soc., Dalton Trans.*, 1440 (1972).

(29) C. D. Garner, C. C. Addison, N. Logan, and S. C. Wallwork, *Quart. Rev., Chem. Soc.*, 25, 289 (1971).

Table IV. Nitrate Bands in the Solid-State Spectra of Pyridine and 2,2′-Bipyridyl Adducts of Nitrato–Tin(IV) Species (cm^{-1})

	Assignment				
Compd	Asym NO_2 str	Sym NO_2 str	N–O str	NO_3 out-of-plane rock	NO_2 bend
$Sn(NO_3)_4(py)_2$	1545 s, br	1280 s, br	950 s, br	790 m, sp	758 s, sp 605 m, sp
$CH_3Sn(NO_3)_3(py)_2$	1510 s, br	1275 s, br	970 s, br	795 m, sp	732 m, sp 608 w
$(CH_3)_2Sn(NO_3)_2(py)_2$	1480 s, br	1285 s, br	1000 s, br	818 sh 805 m, br	731 sh 725 m, sp
$(CH_3)_3SnNO_3(py)$	1465 s, br	1290 s, br	1011 s, sp	821 sh	718 m, sp
$Sn(NO_3)_4(bipy)$	1550 s, br	1290 s 1275 s	970 sh 950 s, sp	791 m, sp 785 m, sp	752 m, sp 742 m, sp 700 m, sp
$CH_3Sn(NO_3)_3(bipy)$	1540 s, sp 1512 s, sp	1305 m, sp 1280 s, sp	991 s, sp 965 s, sp	795 m, br	735 m, sp
$(CH_3)_2Sn(NO_3)_2(bipy)$	1470 s, sp	1292 s, sp 1280 s, sp	1010 s, sp	812 m, sp	735 m, sp
$(CH_3)_3SnNO_3(bipy)_{0.5}$	1470 s, br	1285 s, br	1015 s, sp	815 m, sp	735 m, sp

Table V. Vibrational Spectrum of $(CH_3)_3SnNO_3$ (cm^{-1})

Infrared (solid)	Raman (solid)	Assignment
1484 s, br	1528 m 1489 m, br	Terminal N=O str
1405 w, sh	1402 w	Asym CH_3 def
1282 sh 1270 s	1298 w 1263 w	Asym NO_2 str
1211 s, sp 1200 sh	1213 m, sp 1195 m, sp	Sym CH_3 def
1032 s, sp	1032 s, sp	Sym NO_2 str
809 m, sh		NO_3 out-of-plane rock
785 m, br		CH_3 rock
728 m, sp	735 w	NO_2 bend
559 m, sp	557 m, sp 551 sh	Degen Sn–C_2 str
520 vvw	523 vs, sp	Sym Sn–C str
220 m, br	220 m, br	Sn–O str

The Mossbauer spectra of both anionic complexes yield identical isomer shifts and no quadrupole splittings (Table I). The δ values are more positive than in $Sn(NO_3)_4$ consistent with a decrease in coordination number from 8 to 6 and a higher $\bar{s}$ electron density at the tin nucleus.[30] Although $\mu_{NO_3^-}$ was calculated initially from δ for $Sn(NO_3)_6^{2-}$, the internal consistency of the eq 2a–e can be seen from the fact that an isomer shift of 0.12 mm sec^{-1} is in good agreement with that calculated for $Sn(NO_3)_6^{2-}$ from eq 2c using -0.04 mm sec^{-1} for $Sn(NO_3)_4$ and $\mu_{NO_3^-}$ obtained from eq 2e assuming eight-coordination of tin in $Sn(NO_3)_4$. Both anions show zero quadrupole splitting as expected for a cubic environment at the Sn atom.

The compound $Sn(NO_3)_4(py)_2$ exhibits a Raman spectrum with the intensity pattern (m, s, m) of nitrato bands characteristic of unidentate bonding (Table III). The infrared spectrum (Table IV) is closely similar to that of the 2,2′-bipyridyl adduct, for which Raman data could not be obtained owing to fluorescence. Assignments have been made on the basis of unidentate nitrate coordination in both cases.

Mossbauer isomer shifts for both compounds (Table I) agree with six-coordination of tin in both compounds. The isomer shifts of both compounds are more positive than in $Sn(NO_3)_4$. Utilizing μ_L values of 9 ± 0.1 for nitrate and 8.27 for a pyridine nitrogen (calculated from eq 1 using δ = 0.51 mm sec^{-1} for $SnCl_4(py)_2$ and δ = 0.74 mm sec^{-1} for $SnBr_4(py)_2$[31]), an isomer shift of 0.24 mm sec^{-1} is obtained for six-coordinate $Sn(NO_3)_4(py)_2$. A similar calculation gives δ = 0.20 mm sec^{-1} for $Sn(NO_3)_4(bipy)$. By comparison isomer shifts of <0.0 mm sec^{-1} are predicted for structures having four bidentate nitrates and two nitrogen donors. Small quadrupole splittings were observed for both compounds. The small Δ values for the nitrates are consistent with differences in the values of electronegativity of NO_3^- and the ligand.

B. Trimethyltin Nitrate and the Complexes $(CH_3)_3Sn(NO_3)(py)$ and $(CH_3)_3Sn(NO_3)(bipy)_{0.5}$. The molecular structures of $(CH_3)_3SnNO_3$ and the monohydrate $(CH_3)_3Sn(NO_3)H_2O$ have been the subject of considerable conjecture. Infrared studies on the original compound[32] were interpreted in terms of a pseudo-tetrahedral structure containing unidentate nitrate groups. In a later paper by the same authors[33] the structure $[(CH_3)_3SnH_2O]NO_3$ was proposed for the monohydrate on the basis of ionic nitrate bands in the infrared spectrum. Reinterpretation of the infrared spectrum of the anhydrous material led to the conclusion that bridging nitrate groups conferred a five-coordinate stereochemistry on the tin atom, the trimethyltin fragment being planar.[33] Okawara and coworkers also favored a polymeric structure for $(CH_3)_3SnNO_3$ but suggested that the monohydrate contained bridging nitrate groups with the water molecule completing a six-coordinate stereochemistry at the tin atom.[34] A number of X-ray studies on compounds of the type R_3SnX (X = F,[35] NCS,[36] CN,[37] $^1/_2N_2C$[38]) confirm that the stereochemistry around tin is approximately trigonal bipyramidal with bridging X groups and planar trimethyltin moieties. An unpublished X-ray study of $(CH_3)_3SnNO_3$[6] indicates a similar structure, with, however, a slight distortion of the $(CH_3)_3Sn$ unit from planarity and nonequivalent Sn–O bond lengths (2.28 and 2.45 Å). Our infrared data for $(CH_3)_3SnNO_3$ (Table V) are in essential agreement with the work of Clark but differ from the results of Okawara[35] in that a weak band due to ν(Sn–C) is observed at 520 cm^{-1}. This indicates a departure of the $Sn(CH_3)_3$ unit from planarity, similar to that found in $(CH_3)_3SnF$.[36] Interestingly ν(Sn–O)

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(30) If the tin atom was 12-coordinate in the $Sn(NO_3)_6^{2-}$ ion, an isomer shift lower than that in $Sn(NO_3)_4$ would be expected since δ generally decreases with increasing coordination number for the same ligand atom. See ref 9 and G. M. Bancroft and R. H. Platt, *Advan. Inorg. Chem. Radiochem.*, **15**, 59 (1972).

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(33) H. C. Clark, R. J. O'Brien, and A. L. Pickard, *J. Organometal. Chem.*, **4**, 43 (1965).

(34) K. Yasuda and R. Okawara, *J. Organometal. Chem.*, **3**, 76 (1965).

(35) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc., London*, **85**, (1963).

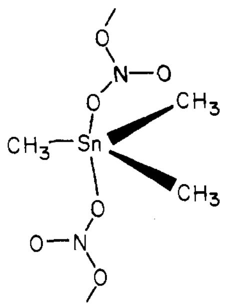
(36) R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, **21**, 115 (1970).

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

(38) R. A. Forder and G. M. Sheldrick, *Chem. Commun.*, 1023 (1970).

in $(CH_3)_3SnNO_3$ occurs at 202 cm^{-1} in the infrared spectrum of the solid but moves to 302 cm^{-1} in dichloromethane solution while ν(Sn–C) increases in intensity considerably in solution. These changes are possibly consistent with breakdown of a polymeric nitrate-bridged species to give a pseudo-tetrahedral structure with a nonplanar $(CH_3)_3Sn$ grouping in solution. We cannot however rule out the participation of a solvent molecule in the tin coordination sphere nor the possibility of chelating bidentate nitrate coordination in a five-coordinate tin environment in solution.

The Raman spectrum of solid $(CH_3)_3SnNO_3$ (Table V) is indicative of bidentate nitrate coordination. It does not seem unreasonable to expect a bridging bidentate nitrate to exhibit a similar intensity pattern in the Raman spectrum to that found for the chelating bidentate ligand. The spectroscopic data are thus in basic agreement with a polymeric nitrate-bridged five-coordinate tin structure (I) in the solid state.



I

The Mossbauer spectrum of $(CH_3)_3SnNO_3$ consists of a quadrupole-split doublet. Parameters extracted from the spectrum are in essential agreement with previous work on this compound.[39] A comparison with Mossbauer data for other $(CH_3)_3SnX$ compounds of known structure,[40] $(CH_3)_3SnNCS$, $(CH_3)_3SnCN$, $(CH_3)_3SnCl$, and $(CH_3)_3SnF$, suggests that Δ is relatively independent of the bridging group X in the compounds.[8] It is now widely accepted[41] that in such systems $\bar{s}$ character is concentrated in Sn–C bonds, and the hybridization of the tin atom is mainly sp^2, with the remaining two axial ligands being bonded *via* Sn 5p or 5pd orbitals, with a small residual amount of $\bar{s}$ character used by tin in the shorter Sn–O bond. In such systems δ does not change appreciably from compound to compound since the s-electron density at the tin nucleus is due to the population of sp^2 orbitals in forming Sn–C bonds and hence is a rather insensitive function of the 5p (or d) orbital populations. In turn the population of the tin 5p or 5pd orbitals will depend on the electronegativity of the coordinated axial ligands X in $(CH_3)_3SnX$.

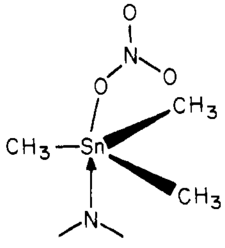
Table VI. Far-Infrared Spectra (600–200 cm^{-1}) of Pyridine and 2,2′-Bipyridyl Adducts[a]

	Assignment	
Compd	Sn–C str	Sn–O str
$Sn(NO_3)_4(py)_2$		349 m, sh, 340 m, sh, 335 m, br, 328 m, sh
$(CH_3)Sn(NO_3)_3(py)_2$	543 w	302 s, br
$(CH_3)_2Sn(NO_3)_2(py)_2$	585 m, sp, 520 vw	280 w, 245 m, br
$(CH_3)_3SnNO_3(py)$	549 s, sp, 515 vw	227 m, br
$Sn(NO_3)_4(bipy)$		338 s, br
$(CH_3)Sn(NO_3)_3(bipy)$	552 w	295 s, vbr
$(CH_3)_2Sn(NO_3)_2(bipy)$	594 m, sp	234 m, sp
$(CH_3)_3SnNO_3(bipy)_{0.5}$	597 m, sp	230 m

[a] Bands due to pyridine and 2,2′-bipyridyl not included.

Only the monoaddition compounds $(CH_3)_3SnNO_3(py)$ and $(CH_3)_3SnNO_3(bipy)_{0.5}$ were isolated from the reaction of $(CH_3)_3SnNO_3$ with the ligands. Raman spectra were not obtainable for these compounds owing to severe decomposition by the laser beam. In Tables IV and VI we summarize infrared and far-infrared assignments for pyridine and 2,2′-bipyridyl adducts of methyltin nitrates. While these data cannot be used to predict per se the mode of nitrate bonding, Raman results for $Sn(NO_3)_6{}^{2-}$, $Sn(NO_3)_4(py)_2$, and the anions $(CH_3)_xSn(NO_3)_{6-x}{}^{2-}$ ($x = 1, 2$)[42] indicate only monodentate nitrate groups. For convenience therefore we have assigned the nitrate bands in Table IV on the basis of the monodentate formalism. There is no evidence for the presence of ionic nitrate in any of these complexes including the $(CH_3)_3SnNO_3$ adducts. It is noteworthy that successive replacement of nitrate groups by methyl groups in the adducts $Me_xSn(NO_3)_{4-x}$ (Tables IV and VI) results in the following spectral changes: (a) a decrease in frequency of the asymmetric NO_2 stretching vibration, (b) an increase in the frequency of the N–O stretching vibration, and (c) a decrease in the frequency separation between the NO_2 asymmetric and symmetric stretches. These observations are the result of changes in $\bar{s}$ character in Sn–O bonds. It is known that a decrease in $\bar{s}$ character causes an increase in the ionicity of Sn–O bonds. A similar trend is observed in SnX_4, $SnX_6{}^{2-}$, R_2SnX_2, and $R_2SnX_4{}^{2-}$ compounds.

The Mossbauer spectra of the two adducts $(CH_3)_3SnNO_3(py)$ and $(CH_3)_3SnNO_3(bipy)_{0.5}$ yield isomer shifts and quadrupole splittings remarkably similar to those of the parent compound. There is thus little doubt that these complexes are five-coordinate tin species of type II. Substitution of a nitrate oxygen atom for a pyridine ring nitrogen changes neither δ nor Δ significantly.



II

C. Dimethyltin Dinitrate and the Complexes $(CH_3)_2Sn(NO_3)_2(py)_2$ and $(CH_3)_2Sn(NO_3)_2(bipy)$. Previous work on the dinitrate led to the suggestion of a tetrahedral tin compound having unidentate nitrate groups.[10] However, the solid-state Raman spectrum (Table VII) is more indicative of bridging or bidentate nitrato coordination, the intensity pattern (m, w, s) for the higher frequency nitrate modes closely resembling that of $(CH_3)_3SnNO_3$. The Mossbauer isomer shift for $(CH_3)_2Sn(NO_3)_2$ is 0.12 mm sec^{-1} higher than δ for the mononitrate but differs little from the reported shifts of $(CH_3)_2SnCl_2$ and $(CH_3)_2Sn(NCS)_2$ which are known[43,44] to have polymeric structures. While the stereo-

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(40) For a complete compilation see P. J. Smith, *Organometal. Chem. Rev., Sect. A*, 5, 373 (1970).

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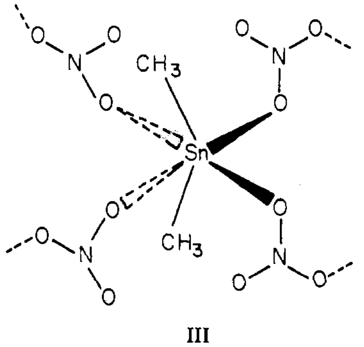
(43) A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. A*, 2862 (1970).

Table VII. Solid-State Vibrational Spectrum of $(CH_3)_2Sn(NO_3)_2$ (cm^{-1})

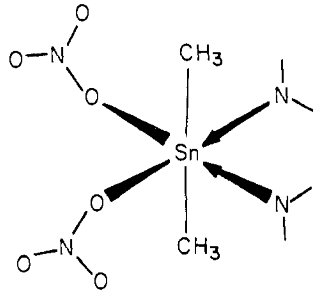
Infrared (solid)	Raman (solid)	Assignment
1600 w	1595 w	
1555 s, sp	1550 m, sp	Terminal N=O str
1536 s, sp	1523 m, sp	
1405 w	1400 vw	Asym CH_3 def
1285 s, sp	1294 w	Asym NO_2 str
1255 s, sp	1282 w	
1215 sh	1210 s, sp	Sym CH_3 def
1209 m, sp	1200 w, sh	
1010 sh	1006 s, sp	Sym NO_2 str
998 s, sp	991 w	
815 sh		NO_3 out-of-plane rock
803 s, sp		
759 s, sp	758 m, br	CH_3 rock
710 w	703 w	NO_2 bend
700 w	695 w	
588 m, sp	586 m, sp	Asym Sn-C_2 str
528 w	531 vs, sp	Sym Sn-C_2 str
283 s, sp	280 s, sp	Sn-O str
209 m	210 m, br	

chemistry around the tin atom in these compounds could be described as a severely distorted octahedron with C-Sn-C angles of 123.3 and 145.9° for the chloride and isothiocyanate, respectively, two of the Sn-X (X = Cl, NCS) interactions are weak. Indeed the arrangement of the four strong bonds around the tin atom can be described as distorted tetrahedral. The bond lengths of the four strong bonds together with the bond angles suggest that although some $\bar{s}$ character is present in all four bonds this is partitioned between the two Sn-C and two Sn-X bonds with the Sn-C bond having the larger amount of $\bar{s}$ character. It appears from the Mossbauer parameters that $(CH_3)_2Sn(NO_3)_2$ is structurally analogous to $(CH_3)_2SnCl_2$ and $(CH_3)_2Sn(NCS)_2$ and not with $(CH_3)_2SnF_2$ and $(CH_3)_2Sn(SO_3F)_2$. In the latter compounds four equivalent Sn-X (X = F, SO_3F) bonds are formed using s-p-d hybrid orbitals, and consequently high values of 4.56 mm sec^{-1} for $(CH_3)_2SnF_2$ and 5.41 mm sec^{-1} for $(CH_3)_2Sn(SO_3F)_2$ are observed.[40] We therefore favor either a monomeric structure having two strong and two weak bonds or a polymeric structure (III) for $(CH_3)_2Sn(NO_3)_2$. A polymeric structure is consistent with the Raman data and relatively low volatility compared to the monomeric species $CH_3Sn(NO_3)_3$ and $Sn(NO_3)_4$ (*vide infra*), but the Mossbauer data cannot distinguish the two possibilities.



III

The Mossbauer spectra of $(CH_3)_2Sn(NO_3)_2(py)_2$ and $(CH_3)_2Sn(NO_3)_2(bipy)$ exhibit marginally lower isomer shifts and higher quadrupole splittings than $(CH_3)_2Sn(NO_3)_2$. The isomer shifts are comparable to previously reported values for $(CH_3)_2SnCl_2(DMSO)_2$ (δ = 1.40, Δ = 4.16) and $(CH_3)_2SnCl_2(pyO)_2$ (δ = 1.42, Δ = 3.96) which have *trans*-dimethyl configurations.[45,46] The relatively small effect of the configuration of the $SnCl_2L_2$ fragment on Mossbauer parameters can be seen from the above examples; in the DMSO derivative the two Cl atoms are cis whereas in the pyridine *N*-oxide compound the chlorine atoms have the trans configuration. We suggest however, that both adducts of $(CH_3)_2Sn(NO_3)_2$ have the same stereochemistry (IV). Our data thus infer a conversion of asymmetrical or bridging bidentate nitrate to monodentate nitrate on reaction with the nitrogen bases.



IV

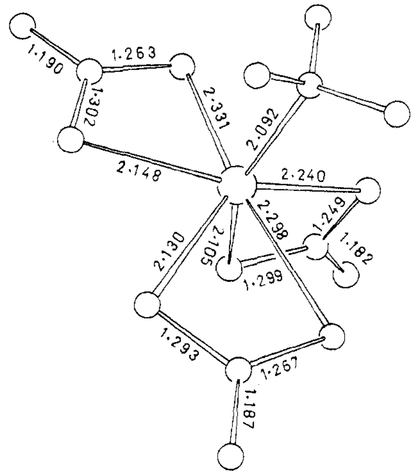


Figure 1. Molecular structure of $CH_3Sn(NO_3)_3$. Some relevant bond lengths (Å) are shown.

D. Methyltin Trinitrate and the Complexes $CH_3Sn(NO_3)_3(py)_2$ and $CH_3Sn(NO_3)_3(bipy)$. Vibrational data for $CH_3Sn(NO_3)_3$ have been discussed in some detail elsewhere.[3] The X-ray structure of this compound has recently been completed[5] confirming the proposed seven-coordination of tin and the presence of three bidentate chelating nitrate groups first suggested from Raman intensity data and physical and chemical properties. The structure is shown in Figure 1. The Mossbauer isomer shift (Table I) is considerably lower than for the dimethyl and trimethyl compounds or the corresponding $RSnX_3$ compounds. This can be attributed to an increase in coordination number. A slight drop in isomer shift occurs on formation of the adducts $CH_3Sn(NO_3)_3(py)_2$ and $(CH_3)Sn(NO_3)_3(bipy)$. These complexes differ markedly from the parent in exhibiting no volatility nor reactivity towards Nujol or ethers. Similar behavioral changes have been accounted for in terms of a change from bidentate chelating nitrate bonding to unidentate bonding.[3] The changes in the infrared spectra of the nitrate groups on reaction of $CH_3Sn(NO_3)_3$ with pyridine are also consistent with

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(44) (a) Y. M. Chow, *Inorg. Chem.*, 9, 794 (1970); (b) R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, 22, 611 (1970).

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the bi-unidentate transformation. The isomer shift would be expected to *increase* for a unit drop in coordination number if the same ligands were involved. The observed decrease in δ possibly reflects a general weakening in the tin-ligand bonds on addition of two molecules of nitrogen donor due to steric crowding.[47]

(47) Note Added in Proof. Since this paper was written, the X-ray crystal structure of $(CH_3)_2Sn(NO_3)_2$ has been completed [J. Hilton, E. K. Nunn, and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 173 (1973)]. The molecule contains asymmetrically nonbridging bidentate nitrate groups.

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Registry No. $Sn(NO_3)_4$, 12372-55-3; $Cs_2Sn(NO_3)_6$, 18723-50-7; $[(C_2H_5)_4N]_2Sn(NO_3)_6$, 51020-80-5; $Sn(NO_3)_4(py)_2$, 17500-58-2; $Sn(NO_3)_4(bipy)$, 50883-35-7; $(CH_3)_3SnNO_3$, 50830-71-2; $(CH_3)_3Sn(NO_3)(py)$, 50978-02-4; $(CH_3)_3Sn(NO_3)(bipy)_{0.5}$, 51016-06-9; $(CH_3)_2Sn(NO_3)_2$, 50830-72-3; $(CH_3)_2Sn(NO_3)_2(py)_2$, 50830-92-7; $(CH_3)_2Sn(NO_3)_2(bipy)$, 50830-93-8; $CH_3Sn(NO_3)_3$, 26284-61-7; $CH_3Sn(NO_3)_3(py)_2$, 50830-94-9; $CH_3Sn(NO_3)_3(bipy)$, 50830-95-0; ^{119}Sn, 14314-35-3.

Contribution from the Department of Chemistry, University of California,
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Correlation of Core Electron Binding Energies with Charge Distributions for Compounds of Carbon, Silicon, and Germanium

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Core electron binding energies for analogous compounds of carbon, silicon, and germanium have been measured by X-ray photoelectron spectroscopy in the gas phase. The chemical shifts have been correlated by the electrostatic potential equation using charge distributions from extended Huckel theory, CNDO/2, and an electronegativity equalization method. The data can be rationalized without any consideration of $p\pi \rightarrow d\pi$ bonding in the silicon and germanium compounds.

The chemical shift associated with atomic core electron binding energies[1] is an electrostatic effect associated with the coulombic potential at the nucleus of the core-ionized atom or, more exactly, at the hole site itself.[2,3] These shifts are usually interpreted, using Koopmans' theorem, in terms of ground-state electronic distributions.[4-6] We have measured the core binding energies for analogous carbon, silicon, and germanium compounds and have correlated the chemical shifts with changes in the calculated charge distributions of the compounds. A principal aim of the work was to determine whether the valence-shell d orbitals of silicon and germanium are important in determining the charge distributions in compounds of these elements. Morgan and Van Wazer[7] have studied the binding energies of carbon, silicon, and germanium in solids. Because of the solid-state problems of work function, charging, and surface impurities and the difficulty of accounting for the Madelung potential in solids, we have restricted our study to compounds in the gas phase.

Experimental Section

Materials. The carbon compounds were obtained from commercial sources and were used as received. The CH_4, C_2H_6, $(CH_3)_2O$, CF_4, CH_3Cl, and CH_3Br were obtained from the Matheson Co.; research grade $C(CH_3)_4$ was obtained from the Phillips Petroleum Co., analytical reagent grade CCl_4 was obtained from Mallinckrodt Chemical Works, and CBr_4 was obtained from the Eastman Kodak Co.

Silane was prepared by the reaction of $SiCl_4$ with $LiAlH_4$;[8] the infrared spectrum agreed with the literature.[6] Methylsilane was prepared by treating $SiCl_3CH_3$ with $LiAlH_4$ using a procedure similar to that used for SiH_4. The vapor pressure[9] (190 Torr at −83.6°) and infrared spectrum[10] agreed with the literature. A sample of Matheson Coleman and Bell practical grade $Si(CH_3)_4$ was used and was found to be pure by infrared spectrometry.[11] Disiloxane was prepared by the hydrolysis of SiH_3Cl and was purified by vacuum distillation. Its vapor pressure[9] (15 Torr at −83.6°) and infrared spectrum[12] agreed with the literature. Silicon tetrafluoride was prepared by pyrolysis of $BaSiF_6$;[13] the infrared spectrum agreed with the literature.[14] Silyl chloride was prepared by the reaction of SiH_4 and AgCl;[15] its vapor pressure[9] (39 Torr at −83.6°) and infrared spectrum[16] agreed with the literature values. Silicon tetrachloride (99.8%, from Matheson Coleman and Bell) was vacuum distilled and checked for purity by infrared spectrometry.[17] Silyl bromide was prepared by treating SiH_3Cl with excess HBr;[18] its vapor pressure[9] (82 Torr at −45.2°) and

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(11) The Coblentz Society, "Evaluated Infrared Reference Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1969, No. 5596.

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