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Registry No. 5-Cl-2,4-$C_2B_5H_6$, 28347-92-4; 5,6-Cl_2-2,4-$C_2B_5H_5$, 71849-86-0; 2-Cl-1,6-$C_2B_4H_5$, 33616-59-0; 2,4-Cl_2-1,6-$C_2B_4H_4$, 71849-87-1; 3-Cl-2,4-$C_2B_5H_6$, 28347-93-5; 1-Cl-2,4-$C_2B_5H_6$, 28347-69-5; 1,5-Cl_2-$C_2B_5H_5$, 71849-88-2; 1,3-Cl_2-$C_2B_5H_5$, 71849-89-3; 3,5-Cl_2-$C_2B_5H_5$, 71849-90-6; 1,7-Cl_2-$C_2B_5H_5$, 71849-91-7; 2,4-$C_2B_5H_7$, 20693-69-0; 1,6-$C_2B_4H_6$, 20693-67-8; CH_3BCl_2, 7318-78-7; $Cl_2BCH_2BCl_2$, 40710-68-7; BCl_3, 10294-34-5.

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Donor and Acceptor Behavior of Divalent Tin Compounds

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Reactions of some tin(II) halide–donor adducts with trifluoroborane produce complexes which contain BF_3, a tin(II) halide, and a donor in a 1:1:1 formulation. Mössbauer and multinuclear (^1H, ^{11}B, ^{19}F, and ^{119}Sn) NMR spectra support a diadduct structure for the products wherein the trifluoroborane moiety is coordinated directly to the tin atom to which the donor molecule also remains coordinated. The proposed structure in the trimethylamine diadduct, $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$, is indicated by a large increase in the isomer shift and decrease in the quadrupole splitting as compared to those of $SnX_2 \cdot N(CH_3)_3$ and by an unusual low-field shift of the ^{11}B NMR signal. Alternative product formulations arising from a Lewis acid displacement reaction or insertion of the tin(II) moiety into a B–F bond were rejected on the basis of the products' spectral characteristics. Other diadducts prepared were $BF_3 \cdot SnX_2 \cdot OS(CH_3)_2$, $BF_3 \cdot SnX_2 \cdot$TMED (TMED = *N,N,N′,N′*-tetramethylethylenediamine), and $BF_3 \cdot SnX_2 \cdot$DP (DP = dipyridyl) (X = Cl, Br, I). The TMED and DP species appeared to adopt chelating structures in the diadducts. Isomeric diadducts $BF_3 \cdot$TMED$\cdot SnX_2$ and $BF_3 \cdot$DP$\cdot SnX_2$, structures in which the acceptor and donor coordinate to separate nitrogens of the ligands, were prepared and proved to be different compounds than those where the divalent tin halide exhibits simultaneous acceptor and donor behavior.

Introduction

Previous work in this laboratory[1-3] has considered the acceptor and donor functions of divalent tin[4] in terms of both $SnX_2 \cdot$donor and $SnR_2 \cdot$acceptor complexes. The spectroscopic properties and thermodynamic stabilities of several such adducts have been determined. Through these investigations and those of other workers (vide infra), it has been shown that the divalent tin compounds with electron-withdrawing substituents act as Lewis acids forming adducts such as $SnCl_2 \cdot N(CH_3)_3$ while those with less electron-withdrawing substituents act as Lewis bases forming adducts such as $BF_3 \cdot Sn[N(CH_3)_2]_2$. The purpose of the present work was to determine whether stable diadducts, wherein tin exercises its donor and acceptor functionalities simultaneously, could be prepared. In principle, species such as $PtCl_2(SnCl_3)_2^{2-}$ [5] and $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot NC_5H_5$[6-8] fulfill this requirement; however, we felt it was important to investigate complexes between tin(II) halide–amine adducts and trifluoroborane in search of structurally analogous diadducts in which the bonding to tin might be more clearly defined.

Experimental Section

A. Equipment and Materials. All reactions were carried out either under flowing dry nitrogen or by using vacuum techniques; a LabConCo glovebox was used for transfer of nonvolatile air-sensitive materials. Tin(II) halide adducts were found to be very air sensitive. ^1H NMR spectra were obtained on a Varian T-60 instrument at 60 MHz (accuracy ±0.02 ppm). A Varian Model XL-100-15 with Nicolet 1080 data system and NT-440 Mona multinuclear accessory was employed in the pulse Fourier transform mode to obtain ^{11}B spectra at 32.1 MHz and ^{119}Sn spectra at 37.28 MHz (accuracy ±0.2 ppm) while a Varian 4412 probe was used for ^{19}F spectra at 94.1 MHz.

Table I. ^1H NMR Parameters of Trimethylamine Adducts[a]

compd	$\delta(CH_3)$[b]	compd	$\delta(CH_3)$[b]
$BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$	1.77	$SnBr_2 \cdot N(CH_3)_3$	1.75[c]
$BF_3 \cdot SnBr_2 \cdot N(CH_3)_3$	1.73	$SnI_2 \cdot N(CH_3)_3$	1.70[c]
$BF_3 \cdot SnI_2 \cdot N(CH_3)_3$	1.67	$F_3B \cdot N(CH_3)_3$	1.97[d]
$SnCl_2 \cdot N(CH_3)_3$	1.81[c]	$(CH_3)_3N$	1.91

[a] Solvent, aniline. [b] ±0.02 ppm. [c] Reference 2. [d] Broad multiplet.

Table II. ^{119}Sn NMR Parameters of Adducts of Divalent Tin Halides[a]

compd	δ[b]	fwhh, Hz
$SnCl_2 \cdot N(CH_3)_3$	111.8	27.5
$SnCl_2 \cdot Me_2SO$	369.5	59.8
$SnBr_2 \cdot Me_2SO$	833.2	479.0
$SnI_2 \cdot Me_2SO$	684.2	439.0
$SnF_2 \cdot Me_2SO$	−56.9	78.7
$SnCl_2 \cdot Py$	294.0	35.9
$BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$	332.8	24.9
$BF_3 \cdot SnCl_2 \cdot Me_2SO$	416.1	99.8
$BF_3 \cdot SnBr_2 \cdot Me_2SO$	881.0	279.0
$BF_3 \cdot SnI_2 \cdot Me_2SO$	625.1	431.0
$BF_3 \cdot SnF_2 \cdot Me_2SO$	not found	
$BF_3 \cdot SnCl_2 \cdot Py$	303.7	32.5

[a] Saturated solutions in dimethyl sulfoxide; all spectra are broad, unresolved multiplets. [b] ±0.2 ppm; referred to external $Sn(CH_3)_4$.

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Table III. ^1H NMR Parameters of *N,N,N′,N′*-Tetramethylethylenediamine (TMED) Adducts[a]

compd	δ(CH_2)[b]	δ(CH_3)
$SnCl_2\cdot TMED$	2.18	1.86
$BF_3\cdot SnCl_2\cdot TMED$	2.23	1.86
$SnBr_2\cdot TMED$	2.06	1.81
$BF_3\cdot SnBr_2\cdot TMED$	2.17	1.84
$SnI_2\cdot TMED$	1.93	1.79
$BF_3\cdot SnI_2\cdot TMED$	2.00	1.80
$BF_3\cdot TMED$	1.99[c]	1.81[c]
$BF_3\cdot TMED\cdot SnCl_2$	2.04[d]	1.82
TMED	2.25	2.04

[a] Saturated solutions in aniline. [b] ±0.02 ppm. [c] Doublet; the average shift is reported. [d] Broad.

Table IV. ^1H NMR Parameters of Dipyridyl Adducts[a]

	H(3)		H(6)		H(5)		H(4)	
compd	δ[b]	J,[c] Hz	δ	J,[d] Hz	δ	J,[e] Hz	δ	J,[f] Hz
dipyridyl	8.69	2.5	8.41	3.9	7.92	3.8	7.37	3.2
$SnCl_2\cdot DP$	8.67	3.0	8.37	4.5	7.91	4.2	7.43	3.0
$BF_3\cdot SnCl_2\cdot DP$	8.77	2.6	8.50	4.0	8.10	4.1	7.60	3.1
$SnBr_2\cdot DP$	8.72	2.8	8.42	3.7	7.95	3.9	7.47	3.3
$BF_3\cdot SnBr_2\cdot DP$	8.81	2.8	8.55	4.3	8.17	3.9	7.67	3.1
$SnI_2\cdot DP$	8.77	2.7	8.47	4.0	8.07	4.0	7.56	3.2
$BF_3\cdot SnI_2\cdot DP$	8.89	2.8	8.64	4.0	8.23	4.0	7.80	3.2
$BF_3\cdot DP$	8.96	2.6	8.73	4.0	8.47	3.9	7.93	3.1
$BF_3\cdot DP\cdot SnCl_2$	8.87	2.8	8.63	4.0	8.32	3.8	7.79	3.8

[a] Solvent, Me_2SO. [b] ±0.02 ppm. [c] Doublet. [d] Doublet. [e] Triplet. [f] Triplet.

Table V. Mössbauer Parameters of Some Tin(II) Halide Adducts[a]

compd	isomer shift, mm s^{-1}	ΔEq, mm s^{-1}
$SnCl_2\cdot N(CH_3)_3$	3.05	1.78[b]
$BF_3\cdot SnCl_2\cdot N(CH_3)_3$	3.87	~0[c]
$SnCl_2\cdot (CH_3)_2SO$	3.32	1.37
$BF_3\cdot SnCl_2\cdot (CH_3)_2SO$	3.99	~0[d]
$SnCl_2\cdot DP$	3.50	1.12[b]
$BF_3\cdot SnCl_2\cdot DP$	3.47	1.34[b]
$SnCl_2\cdot TMED$	3.21	1.02
$BF_3\cdot SnCl_2\cdot TMED$	3.36	1.39[b]
$BF_3\cdot TMED\cdot SnCl_2$	3.91	~0[e]
$BF_3\cdot DP\cdot SnCl_2$	3.93	~0[f]

[a] Precision of parameters ±0.05 mm s^{-1}; absorber temperature 103 K; source, $BaSnO_3$, temperature 25 °C. [b] Peak asymmetry. [c] Fwhh 1.55 mm s^{-1}. [d] Fwhh 1.48 mm s^{-1}. [e] Fwhh 1.82 mm s^{-1}. [f] Fwhh 1.56 mm s^{-1}.

Positive δ values for all spectra indicate shifts downfield from the noted reference standards. Proton chemical shifts are given in Tables I (trimethylamine adducts), III (tetramethylethylenediamine adducts), and IV (dipyridyl adducts). Table II contains ^{119}Sn NMR parameters for several adducts and diadducts. X-ray powder diffraction patterns were obtained by using a Debye-Scherrer camera of 114.6 mm diameter with a copper target source tube fitted with a nickel filter, producing Cu Kα radiation. Melting points were determined on a Thomas Hoover melting point apparatus using glass capillaries sealed with wax. Mössbauer spectra were obtained by using an Austin Science Associates constant acceleration instrument with a New England Nuclear $BaSnO_3$ source at 25 °C. Powder samples were mounted between Mylar sheets on a liquid nitrogen cooled sample holder in an evacuated chamber. The temperature indicated by a thermocouple attached to the holder was 103 K during data collection. An Austin Science Associate laser interferometer attachment was employed for velocity calibration and velocity channels were multiplexed with data channels in a Tracor Northern multichannel analyzer. Collected data were output to an Altair 8800B microcomputer where analysis was carried out with the aid of a North Star Floating Point Board. Spectral parameters were printed on a Teletype while experimental and theoretical spectra were plotted on a Houston Instruments xy recorder interfaced to the microcomputer. Mössbauer parameters for adducts and diadducts are listed in Table V. IR spectra in KBr disks were obtained by using a Beckman Model 4250 spectrophotometer. The IR bands are listed in Table VI.

Benzene and *n*-pentane were nanograde from Mallinckrodt. Ethyl ether (Mallinckrodt) was treated to remove peroxides and distilled before use. Trifluoroborane and trimethylamine were obtained from Matheson in lecture cylinders. 2,2′-Dipyridyl was also obtained from Matheson while *N,N,N′,N′*-tetramethylethylenediamine and dimethyl sulfoxide were reagent grade from Aldrich and were distilled from barium oxide before use. Anhydrous tin(II) halides were prepared fresh in this laboratory.[2]

B. Analytical Methods. Chlorine, bromine, and iodine were determined as halides by potentiometric titration with standard silver nitrate solution after the samples had been treated with dilute sulfuric acid. Tin (10-mg sample) was determined gravimetrically as SnO_2 after repeated oxidation with 4-mL portions of concentrated HNO_3 and heating to red heat in a Vycor vessel to constant mass. Boron analyses were carried out by digesting a mixture of the sample (containing about 3 mmol of boron) with 0.2 g of $CaCl_2$ with concentrated HNO_3. The acid was added through a 36-in. condenser into a 50-mL flask containing the sample mixture. The flask was heated to 200 °C and maintained until all the nitrogen dioxide was driven off, after which 20 mL of water was added and the mixture digested at boiling for 15 min. After being cooled, the solution was diluted to give 2 mg of B/100 mL and the pH was adjusted to 7.4. Mannitol (8 g/100 mL) was then added and the solution titrated back to a pH of 7.14 with standard NaOH solution from which the boron content was determined. Nitrogen determinations were made by using a Coleman Model 29 nitrogen analyzer.

C. Syntheses of Trifluoroborane–Tin(II) Halide–Trimethylamine Diadducts. 1. Trifluoroborane–Tin(II) Chloride–Trimethylamine, $BF_3\cdot SnCl_2\cdot N(CH_3)_3$. The tin(II) halide–trimethylamine adducts were prepared and isolated and then treated with trifluoroborane.

(a) Formation of Tin(II) Chloride–Trimethylamine, $SnCl_2\cdot N(CH_3)_3$. The literature synthesis[2] of $SnCl_2\cdot N(CH_3)_3$ was modified by changing the solvent from *p*-dioxane to ethyl ether. In a typical preparation, 7.58 g (40 mmol) of anhydrous $SnCl_2$ was weighed into a flask which was connected to the vacuum line via a Teflon valve adaptor. Approximately 50 mL of anhydrous, peroxide-free $(C_2H_5)_2O$ and exactly 40 mmol of $(CH_3)_3N$ were condensed into the reaction vessel. After the mixture reached room temperature, it was stirred for 72 h and then filtered and washed with ether giving a slightly yellow product. The physical constants of the product were the same as those reported earlier.[2]

(b) Preparation of Trifluoroborane–Tin(II) Chloride–Trimethylamine, $BF_3\cdot SnCl_2\cdot N(CH_3)_3$. A 7.5-g (30 mmol) portion of freshly prepared $SnCl_2\cdot N(CH_3)_3$ was transferred to a flask and placed on the vacuum line. The vessel was evacuated and approximately 50 mL of ethyl ether was condensed into the flask, followed by a 30-mmol quantity of BF_3. After being warmed to room temperature, the mixture was stirred for 4 days, filtered, and washed with ether. The product was a pale yellow solid, yield 8.8 g (93%) (mp 123–130 °C dec). Anal. Calcd for $C_3H_9BCl_2F_3NSn$: Sn, 37.51; B, 3.41; N, 4.42; Cl, 22.44. Found: Sn, 37.7; B, 3.34; N, 4.25; Cl, 22.4. The ^1H NMR spectrum of a mixture of this compound with $F_3B\cdot N(CH_3)_3$ in aniline solution is displayed in Figure 1. The *d* spacings in the X-ray powder diffraction pattern were as follows [*d*, Å (intensity)]: 6.21 (vvs), 5.55 (s), 4.68 (m), 4.59 (m), 4.38 (vvs, b), 4.10 (w), 3.93 (m), 3.60 (s), 3.53 (s), 3.42 (m), 3.08 (s), 2.94 (s), 2.77 (vs), 2.64 (m), 2.57 (w), 2.51 (m), 2.25 (w), 2.19 (m, b), 2.11 (m), 2.05 (m), 1.94 (w), 1.92 (vw), 1.87 (vw), 1.84 (vw), 1.78 (w), 1.72 (m). The ^{11}B NMR spectrum of this compound in dimethyl sulfoxide (Me_2SO) solution consisted of a broad complex peak at δ 19.4 (referred to external $BF_3\cdot O(C_2H_5)_2$) with full width at half height (fwhh) of 305 Hz. The ^{19}F NMR spectrum of the product in Me_2SO solution consisted of a quartet centered upfield 84.86 ppm (J = 16.2 Hz) from external CF_3COOH. For comparison, the ^{19}F NMR spectrum of $F_3B\cdot N(CH_3)_3$ in Me_2SO solution appeared as a similar 1:1:1:1 quartet centered at +64.48 ppm (J = 15.38 Hz).

2. Trifluoroborane–Tin(II) Bromide–Trimethylamine, $BF_3\cdot SnBr_2\cdot N(CH_3)_3$. Tin(II) bromide–trimethylamine, $SnBr_2\cdot N(CH_3)_3$ was prepared as reported previously.[2] The procedure and solvent employed for the addition of BF_3 to this intermediate were the same as that described for the chloride compound. The product, $BF_3\cdot SnBr_2\cdot N(CH_3)_3$, was a white hygroscopic solid, mp 150–155 °C dec.

3. Trifluoroborane–Tin(II) Iodide–Trimethylamine, $BF_3\cdot SnI_2\cdot N(CH_3)_3$. Tin(II) iodide–trimethylamine, $SnI_2\cdot N(CH_3)_3$, was prepared

Table VI

IR Bands of Simple Adducts[a]

$SnCl_2 \cdot OS(CH_3)_2$	$BF_3 \cdot OS(CH_3)_2$[b]	$SnCl_2 \cdot TMED$[c]	$SnBr_2 \cdot TMED$	$SnI_2 \cdot TMED$	$BF_3 \cdot TMED$	$SnCl_2 \cdot DP$[d]	$SnBr_2 \cdot DP$	$SnI_2 \cdot DP$	$BF_3 \cdot DP$
3020 s	3010 m	3020 m	3020 m	3020 m	3010 w	3070 m	3100 m	3070 m	3240 s
2920 s	2932 w	2940 m	2910 s, b	2900 s, b	2900 sb	3030 m	3060 m	3030 m	3190 s
1630 vw, b	1410 wb	2640 vs	2850 w	2832 m	2830 w	2430 vw	2280 vw	2270 vw	3100 m
1430 s	1370 wb	2600 vs	2620 s, b	2760 w	2560 sb	1613 s	1603 s	1600 s	3050 w
1403 s	1333 w	2580 vs	2560 m	2660 vs, b	2450 s	1603 s	1570 m	1590 s	2360 vw
1322 m	1170–1100	2530 w	2450 s	2580 s	1450 s	1578 m, b	1500 vw	1556 m	2270 vw
1300 w	vvs, overlap	2480 vs	1635 vw, b	2460 s	1415 s	1500 m	1475 m	1525 m	1642 s, b
985 s	1060 vs	1490 s	1485 s	2360 w	1375 m	1480 s	1445 vs	1490 w	1620 s
945 h	1010 s	1475 s	1465 s	1650 vw, b	1280 w	1450 vs	1323 s	1475 m	1615 s
920 vs, b	955 s	1460 m	1415 w	1483 s	1130–1075–	1420 m	1250 m	1450 vs	1595 s
890 sh	875 sb	1421 w	1397 m	1470 s	1025–910	1320 s	1220 w	1320 m	1580 sh
720 w	720 s	1400 w	1280 m	1420 m	s, overlap	1250 s	1150 m	1250 m	1543 s
680 w	685 m	1290 m	1154 m	1405 m	865 m	1220 sh	1110 w	1220 w	1480 s
440 s, b	670 w	1160 m	1122 w	1210 w	788 m	1178 m	1065 w	1155 w	1468 s
340 m	570 w	1130 w	997 s	1158 m	685 w	1158 s	1030 s	1100 vw	1442 s
320 m	340 mb	1005 s	975 s	1130 vw	510 vw	1105 vw	770 s	1065 vw	1380 m
	310 m	980 s	787 w	1000 s	416 s	1065 w	725 m	1040 sh	1320 s
		795 w	550 m	978 s	395 s	1035 m	640 w	1025 s	1285 s
		550 mb	520 m	830 w	345 m	1020 s	415 m	900 vw	1245 s
		520 m	470 w	790 m		990 vw	325 m	765 s	1180 s
		470 w		550 m		775 s		725 w	1160 s
				520 m		726 m		640 w	1120–1050–1025
				460 w		655 w, b		420 m	vs, overlap
						646 wb		330 m	1000 s
						415 m			930 m
						352 mb			900 w
									775 s, b
									730 m
									650 m, b
									615 m, b
									530 m
									470 m
									450 m

IR Bands of Diadducts, $BF_3 \cdot SnX_2 \cdot D$[a]

D, X									
$(CH_3)_3N$, Cl	$(CH_3)_3N$, Br	$(CH_3)_3N$, I	$(CH_3)_2SO$, Cl	TMED, Cl	TMED, Br	TMED, I	DP, Cl	DP, Br	DP, I
3170 s	3160 s	3142 s	3020 s	3025 m	3019 m	3020 m	3210 m, b	3210 m	3200 s, b
2970 w	2980 w	2962 s	2930 s	2980 s, b	2980 s, b	2920 s, b	3100 w	3170 m	3070 m
2720 s	2750 m	2740 s	2310 vw	2630 s	2730 m	2840 w	2330 vw	3080 w	3040 m
2485 w	2490 w	2470 w	2250 vw	2580 s	2640 s, b	2660 vs, b	1603 s	3060 w	1600 s
1635 vw, b	1648 w, b	1640 w	1622 w	2460 s	2590 s	2590 s	1595 w	2270 vw	1570 w
1483 s	1487 s	1480 s	1590 vw	2420 vw	2460 m	2450 s	1580 w	1600 s	1530 vw
1470 s	1475 vs	1470 s	1475 s, sh	1620 w, b	2360 w	2360 w	1535 w	1595 s	1500 w
1420 m	1425 s	1420 m	1455 s, b	1482 s	2340 w	1650 w, b	1500 w	1560 w	1474 m
1382 m	1385 m	1385 m	1427 s	1472 s	1560 s, b	1484 m	1480 s	1524 w	1450 s
1310 m	1315 m	1300 m	1415 s	1460 s	1492 m	1470 s	1450 vs	1500 m	1320 m
1260 w	1262 m	1258 m	1400 s	1410 m	1470 s	1460 s	1325 m	1480 s	1250 m
1140–1070–	1170–1090–	1145–1065	1330 w	1386 w	1463 s	1414 m	1255 w	1455 vs	1160 sh
1035 vs, b	1032 vs, b	1035 vs, b	1307 m	1315 w	1400 w	1400 m	1220 vw	1330 s	1110–1070–
overlap	overlap	overlap	1200 m	1285 m	1290 w	1285 m	1180 m	1285 w	1035 vs,
985 s	990 s	985 s	1100–1070–	1200 m	1125–1080–	1265 m	1165 m	1255 m	overlap
820 vw	918 vw	800 vw	1030 vvs,	1130–1080–	1035 vs,	1130–1080–	1125–1070–	1160 sh	1000 sh
690 w	815 vw	563 m	overlap	1050–1030	overlap	1040 s,	1035 vs,	1125–1070–	764 s
550 m	570 m	530 m, b	990 s	s, overlap	1005 m	overlap	overlap	1035 s,	720 w
530 m, b	535 m, b	450 vw	920 vs, b	996 s	980 s	998 s	1020 s	overlap	645 w
460 vw	350 w	310 vw	800 w	980 s	790 vw	975 s	775 s	770 s	540 w, b
310 m	330 w		770 w	790 w	565–540–	950 w	650–640–	723 m	415 w
			725 w	565–520–	520 m,	920 w	620 w,	640	295
			650 vw	525 m,	overlap	870 w	overlap	540 w, b	
			540 m	overlap	325 m, b	808 w	555–540–	415 m	
			530 m	325 m, b	300 m	790 m	530 w,	298 m	
			480 s	300 m		560 m, b	overlap		
			425 m			510 s, b	420 m		
			340–325–			460 w	325 mb		
			305 s,			340 w			
			overlap			300 m			

Table VI (*Continued*)

IR Bands of Isomeric Diadducts, $BF_3 \cdot D \cdot SnX_2$[a]

D, X									
TMED, Cl	TMED, Cl	TMED, Cl	TMED, Cl	TMED, Cl	DP, Cl	DP, Cl	DP, Cl	DP, Cl	DP, Cl
3090 w	2460 m	1300 m	990 s	690 w	3220 s	1610 s	1415 sh	1110–1080–1040 vs, overlap	650 w, b
3030 m	1630 w, b	1140–1110–1020 vs, overlap	970 s	520 m, b	3170 s	1595 s	1325 m		
2970 s, b	1470 s, b		915 s	390 m	3100 sh	1575 w	1312 sh	930 w	605 w
2720 s	1410 m		865 m	350 w	3060 sh	1535 s	1284 w	810 w	530 w, b
2650 m, b	1355 m		790 w		2350 vw	1505 s	1255 m	775 s	450 w, b
					2270 vw	1485 s	1200 m	720 m	420 w, b
					1640 sh	1450 s	1160 s		340–320 m, overlap
					1625 s	1435 s			

[a] cm^{-1}. [b] CH_3CN solution. [c] Tetramethylethylenediamine. [d] Dipyridyl.

as reported previously.[2] The procedure and solvent used for the addition of BF_3 to this intermediate were the same as that described for the chloride compound. The final product, $BF_3 \cdot SnI_2 \cdot N(CH_3)_3$, was an orange solid, mp 220–228 °C dec, which changed to gray after a few minutes in air.

D. Synthesis of Trifluoroborane–Tin(II) Chloride–Dimethyl Sulfoxide, $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$. 1. Trifluoroborane–Tin(II) Chloride–Dimethyl Sulfoxide, $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$. (a) Preparation of Tin(II) Chloride–Dimethyl Sulfoxide, $SnCl_2 \cdot OS(CH_3)_2$. A 3.8-g (20 mmol) quantity of anhydrous $SnCl_2$ was placed in a flask and an equimolar quantity of dimethyl sulfoxide, distilled from barium oxide, was transferred into the flask, after which the reaction took place with the evolution of heat. Later, the flask was warmed in boiling water and shaken for 1 h during which time the reaction mixture appeared as a clear liquid which, when cooled, formed colorless needle crystals. The flask and the product were reheated and shaken for another hour to ensure completion of the reaction. The product melted at 81–83 °C. Anal. Calcd for $C_2H_6Cl_2OSSn$: Sn, 44.33; Cl, 26.48. Found: Sn, 44.39; Cl, 26.52. The ^1H NMR spectrum of the product in benzene solution consisted of one sharp peak at δ 1.85; in pyridine the peak shifted to δ 2.05. The chemical shift of Me_2SO was δ 2.30 in pyridine solution. The product was also prepared by a second method[9] whereby $SnCl_2$ was stirred in benzene and an equimolar quantity of Me_2SO was added to the mixture. The flask was stirred for 48 h giving a finely divided white solid product with identical IR and NMR spectra.

(b) Preparation of Trifluoroborane–Tin(II) Chloride–Dimethyl Sulfoxide, $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$. A 4.0-g (15 mmol) quantity of freshly prepared $SnCl_2 \cdot OS(CH_3)_2$ was weighed into a flask along with 60 mL of benzene. On the vacuum line, 15 mmol of BF_3 was condensed into the flask and the reaction mixture was stirred for 48 h. The product, a hygroscopic white solid, insoluble in benzene, was filtered, washed once with benzene, and dried under vacuum. It began to melt at 117 °C and decomposed through 130 °C. Anal. Calcd for $C_2H_6BCl_2F_3OSSn$: Sn, 35.37; Cl, 21.13; B, 3.22. Found: Sn, 35.5; Cl, 21.1; B, 3.08. The ^1H NMR spectrum of the diadduct in pyridine solution consisted of one sharp peak at δ 1.77. The ^1H NMR spectrum of $BF_3 \cdot OS(CH_3)_2$ in pyridine solution consisted of a singlet with a chemical shift the same as that of pure Me_2SO in pyridine indicating a displacement had occurred. (The preparation of $BF_3 \cdot OS(CH_3)_2$ is described in the following section.) When aniline was employed as the solvent, the observed chemical shifts were as follows: $BF_3 \cdot OS(CH_3)_2$, δ 2.27; $(CH_3)_2SO$, δ 2.12; $SnCl_2 \cdot OS(CH_3)_2$, δ 1.90; $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$, δ 1.84. The ^{19}F resonance of $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$ in Me_2SO solution was found at +69.4 ppm, while that of $BF_3 \cdot OS(CH_3)_2$ occurred at +71.5 ppm.

(c) Preparation of Trifluoroborane–Dimethyl Sulfoxide, $BF_3 \cdot OS(CH_3)_2$. A 2.55-mL (20 mmol) quantity of trifluoroborane–ethyl ether complex was added to a flask containing 20 mL of pentane. While the mixture was stirred, 20 mmol of dimethyl sulfoxide was added, immediately forming a precipitate. Stirring was continued for 20 min and the reaction mixture was filtered, washed once with pentane, and dried under vacuum, giving a white, hygroscopic solid, mp 51–52 °C. This compound has been previously prepared by Foret et al.,[10] who reported its IR and Raman spectra.

(d) ^{119}Sn NMR Spectra of the Tin(II) Halide–Dimethyl Sulfoxide and Trifluoroborane–Tin(II) Halide–Dimethyl Sulfoxide Compounds. The compounds $SnCl_2 \cdot OS(CH_3)_2$ and $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$ were dissolved in Me_2SO to form saturated solutions. The ^{119}Sn spectra reported in the previous sections were obtained by using these solutions. The other tin(II) halide–Me_2SO compounds were not isolated; ^{119}Sn spectra were first obtained on saturated solutions in Me_2SO after which an equimolar quantity of BF_3 (with respect to the tin) was condensed into each solution and the product was stirred for 24 h. Then, ^{119}Sn NMR spectra were run again and the spectral parameters are listed in Table II along with those of the pyridine adducts which were obtained by the same technique using saturated pyridine solutions.

E. Syntheses of Trifluoroborane–Tin(II) Halide–Tetramethylethylenediamine Adducts. 1. Trifluoroborane–Tin(II) Chloride–Tetramethylethylenediamine, $BF_3 \cdot SnCl_2 \cdot TMED$. (a) Preparation of Tin(II) Chloride–Tetramethylethylenediamine, $SnCl_2 \cdot TMED$. A quantity, 7.58 g (40 mmol), of anhydrous $SnCl_2$ was placed in a flask with a side arm fitted with a septum. About 80 mL of anhydrous ethyl ether was added to the flask and stirring begun. Then, 5.83 mL (40 mmol) of TMED was added to the mixture, the flask was closed, and its contents were stirred for 72 h at 25 °C. The reaction mixture was filtered, washed with ether, and dried under dynamic vacuum giving a white solid (yield 11.5 g, 94%; mp 229–230 °C). Anal. Calcd for $C_6H_{16}Cl_2N_2Sn$: Sn, 38.81; Cl, 23.22; N, 9.16. Found: Sn, 39.2; Cl, 22.7; N, 8.8.

(b) Preparation of Trifluoroborane–Tin(II) Chloride–Tetramethylethylenediamine, $BF_3 \cdot SnCl_2 \cdot TMED$. A 9.2-g (30 mmol) portion of freshly prepared $SnCl_2 \cdot TMED$ was placed in a reaction vessel which was fitted with a side arm containing a septum through which 80 mL of anhydrous ethyl ether was added followed by 3.80 mL (30 mmol) of trifluoroborane–ethyl ether, after which the reaction mixture was stirred for 96 h. The contents were then filtered and washed with ether giving the product as a pale yellow solid (yield 10.1 g (90%); mp 224–229 °C). Anal. Calcd for $C_6H_{16}BCl_2F_3N_2Sn$: Sn, 31.76; B, 2.89; Cl, 19.0; N, 7.49. Found: Sn, 31.0; B, 3.0; Cl, 18.7; N, 7.2. The ^{11}B NMR spectrum in Me_2SO solution consisted of a broad, complex peak at δ +21.1 ppm (fwhh 280 Hz). The *d* spacings in the X-ray powder diffraction pattern were [*d*, Å (intensity)]: 6.04 (m), 5.11 (w), 4.78 (w), 4.58 (m), 4.41 (m), 3.89 (m), 3.69 (mb), 3.52 (w), 3.42 (w), 3.17 (s), 3.04 (m), 2.93 (m), 2.84 (m), 2.74 (w), 2.67 (w), 2.57 (w), 2.45 (wb), 2.31 (w), 2.20 (s), 2.09 (vw), 1.99 (m), 1.91 (m), 1.81 (w), 1.73 (vw), 1.69 (w), 1.58 (w).

2. Trifluoroborane–Tin(II) Bromide–Tetramethylethylenediamine, $BF_3 \cdot SnBr_2 \cdot TMED$. The procedure and solvent employed to prepare this compound were the same as that used for the chloride compound with anhydrous $SnBr_2$ used as the starting material. The intermediate product, $SnBr_2 \cdot TMED$, was a pale yellow solid (mp 245–246 °C). The product, $BF_3 \cdot SnBr_2 \cdot TMED$, was a white solid (mp 180–185 °C).

3. Trifluoroborane–Tin(II) Iodide–Tetramethylethylenediamine, $BF_3 \cdot SnI_2 \cdot TMED$. By use of the above procedure, anhydrous SnI_2 was used to prepare $SnI_2 \cdot TMED$, a yellow solid (mp 228–230 °C dec). The final product, $BF_3 \cdot SnI_2 \cdot TMED$, was an orange solid (mp 207–210 °C dec).

4. Preparation of Related Compounds. (a) Trifluoroborane–Tetramethylethylenediamine, $BF_3 \cdot TMED$. A 1.46-mL (10 mmol) quantity of *N,N,N′,N′*-tetramethylethylenediamine was dissolved in 30 mL of anhydrous ethyl ether and an equimolar quantity of trifluoroborane–ethyl ether was added to the flask which was closed and

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(10) M. T. Foret, M. Tranquille, and M. Fouassier, *Spectrochim. Acta, Part A*, **26a**, 1777 (1970).

the contents were stirred 18 h. The ether was then removed by vapor transfer leaving the product as a slightly yellow solid (mp 85 °C).

(b) Trifluoroborane–Tin(II) Chloride–Tetramethylethylenediamine, BF_3·TMED·$SnCl_2$. A 1.9-g (10 mmol) quantity of anhydrous $SnCl_2$ was reacted with an equimolar quantity of trifluoroborane–tetramethylethylenediamine in 30 mL of anhydrous benzene. The mixture was stirred 72 h and then the product (mp 165–172 °C) was filtered from the reaction mixture and washed with benzene. It was assumed that this synthetic approach would lead to a product having BF_3 coordinated to one TMED nitrogen and $SnCl_2$ to the other; however, this structure was not directly proved.

F. Syntheses of Trifluoroborane–Tin(II) Halide–Dipyridyl Adducts. 1. Trifluoroborane–Tin(II) Chloride–Dipyridyl, BF_3·$SnCl_2$·DP. The preparation of this compound was carried out in two steps. First, 2,2′-dipyridyl was reacted with the tin(II) halide forming the 1:1 adduct, which was then treated with trifluoroborane.

(a) Preparation of Tin(II) Chloride–Dipyridyl, $SnCl_2$·DP. A quantity of 7.58 g (40 mmol) of anhydrous $SnCl_2$ and 80 mL of anhydrous ethyl ether were combined and then a 6.25-g (40 mmol) portion of 2,2′-dipyridyl was added to the reaction vessel and the contents were stirred for 72 h. The product, a yellow solid, was filtered from the reaction mixture, washed once with ether, and dried under vacuum. The yield was 13.3 g (96%) (mp 210–211 °C). Anal. Calcd for $C_{10}H_8Cl_2N_2Sn$: Sn, 34.32; N, 8.10; Cl, 20.51. Found: Sn, 34.9; N, 7.9; Cl, 20.4. The ^1H NMR spectrum of the product in Me_2SO solution (Figure 3) closely resembled the spectrum of 2,2′-dipyridyl (Figure 3) and the chemical shifts are listed in Table IV.

(b) Preparation of Trifluoroborane–Tin(II) Chloride–Dipyridyl, BF_3·$SnCl_2$·DP. A quantity, 10.4 g (30 mmol), of freshly prepared $SnCl_2$·DP and 80 mL of ethyl ether were placed in a flask into which was transferred an equimolar quantity of trifluoroborane–ethyl ether and the mixture was then stirred for 36 h during which time the color changed from yellow to white. The solid product was separated by filtration and dried under vacuum (yield, 11.4 g (92%); mp 156–160 °C dec). Anal. Calcd for $C_{10}H_8BCl_2F_3N_2Sn$: Sn, 28.69; B, 2.61; N, 6.77; Cl, 17.17. Found: Sn, 29.8; B, 2.59; N, 6.74; Cl, 17.1. The ^1H NMR spectrum of the product in Me_2SO solution resembled dipyridyl. The ^{11}B NMR spectrum of the product in Me_2SO solution consisted of a broad complex peak at δ +20.7 (fwhh 254 Hz). The *d* spacings in the X-ray powder diffraction pattern were as follows: [*d*, Å (intensity)]: 9.53 (vs), 7.61 (vs), 6.85 (s), 6.01 (vvs, b), 5.47 (w), 5.15 (s), 4.76 (vw), 4.49 (s), 4.26 (m), 3.98 (m), 3.81 (s), 3.65 (w), 3.54 (vw), 3.43 (s), 3.10 (vw), 2.97 (s), 2.86 (vw), 2.63 (m), 2.57 (w), 2.50 (w), 2.44 (vw), 2.37 (m), 2.29 (w), 2.21 (w), 2.15 (w).

2. Trifluoroborane–Tin(II) Bromide–Dipyridyl, BF_3·$SnBr_2$·DP. The procedure and solvent for the preparation of this compound were the same as those described in the foregoing section with anhydrous $SnBr_2$ used as the starting material. The intermediate product, $SnBr_2$·DP, was a deep yellow solid (mp 253–254 °C). BF_3·$SnBr_2$·DP was obtained by treating freshly prepared $SnBr_2$·DP with an equimolar portion of trifluoroborane etherate. The product was a bright yellow solid (mp 178–185 °C).

3. Trifluoroborane–Tin(II) Iodide–Dipyridyl, BF_3·SnI_2·DP. By use of anhydrous SnI_2, and the procedures and solvent indicated in the previous section, SnI_2·DP and BF_3·SnI_2·DP were prepared. The intermediate product, SnI_2·DP, was a deep brown solid (mp 302–303 °C). The final product, BF_3·SnI_2·DP, was a red solid (mp 239–240 °C dec).

4. Preparation of Related Compounds. (a) Trifluoroborane–Dipyridyl, BF_3·DP. Equimolar amounts (10 mmol) of 2,2′-dipyridyl and trifluoroborane–ethyl etherate were combined in ethyl ether and stirred 24 h, and the solvent was removed in vacuo. The product, BF_3·DP, was a white solid (mp 115 °C).

(b) Trifluoroborane–Dipyridyl–Tin(II) Chloride, BF_3·DP·$SnCl_2$. A 1.9-g (10 mmol) quantity of anhydrous $SnCl_2$ was combined with an equimolar quantity of trifluoroborane–dipyridyl in 30 mL of benzene. The mixture was stirred for 72 h, filtered, washed with ether, and dried under vacuum. The product was a pale yellow solid (mp 135–140 °C). It was expected that the product obtained by this approach would have BF_3 and $SnCl_2$ individually coordinated to the dipyridyl nitrogens.

Discussion

That tin(II) halides form stable adducts with nitrogen and oxygen donors has been conclusively demonstrated.[4] Heats of reaction[3] of SnX_2 (X = F, Cl, Br, I) compounds in Me_2SO solution with equimolar quantities of triethylamine ranged from −8.7 to −11.9 kcal mol^{-1}. Enthalpies of gas-phase dissociation of $SnX_2 \cdot n(N(CH_3)_3)$ (n = 1, 2; X = Cl, Br, I) adducts were of the same general magnitude and exhibited the same order of adduct stability with respect to variation of the halogen substituent.[2] Such SnX_2 adducts with amine donors are regarded as moderate to weak *nv*-type complexes (*n* indicating a lone pair donor function and *v* indicating a vacant metal valence orbital serves as the acceptor site).

The fact that divalent tin has an unshared electron pair in its valence shell indicates a potential donor functionality but, in practice, only a few instances have been reported where such tin compounds form stable adducts with main group Lewis acids.[11,12] One factor which influences the stability of potential SnX_2·acceptor adducts is the ionization potential of the tin lone pair. Measurements by He I PES of about 10.37[13,14] eV have been reported for the highest occupied MO in $SnCl_2$ although disagreement exists as to the assignment of that orbital. One investigation[13] included a supporting CNDO calculation yielding an energy of 10.72 eV for the highest orbital, 4a1, described as a hybridized tin lone pair orbital. The corresponding orbital in $SnBr_2$ was observed at 9.87 eV and predicted by the CNDO calculation to be 10.39 eV. These values are of similar magnitude to the lone pair ionization energies of donors such as ammonia (10.85 eV),[15] providing some indication of potential donor capability. A fuller assessment of the energetics of donor–acceptor bond formation, however, would necessitate consideration of other factors including S_{da}, the overlap integral between the tin donor orbital and a given acceptor orbital.[16] The diffuseness and poor directional character of the tin donor orbital, a hybrid of 5s and 5p atomic orbitals, mitigates against effective overlap and strong covalent donor–acceptor bonding. It was therefore expected that divalent tin halides would behave as weak donors at best; however, Coulombic forces could be important and little information relevant to this general question was available. Previous work in this laboratory involving the reaction of trifluoroborane with tin(II) chloride in ether solvents found no indication of stable adducts.

The established ability of trihalostannate species, SnX_3^-, to serve as ligands in transition metal complexes,[4] contrasted with the parent tin(II) halides which form few such complexes, suggested that SnX_2 adducts with neutral donors such as amines might also exhibit enhanced donor capabilities compared to SnX_2 compounds.

Perhaps the closest approximation to this type of behavior is found in compounds of the form $R_2SnM(CO)_n$·B (R = t-C_4H_9; M = Cr [n = 5], Fe [n = 4]; B = THF, Me_2SO, py).[6-8] Formally stannylene compounds, these species could only be isolated with 1 mol of donor (B) per formula which was shown by X-ray crystallography[7] to be bonded to the tin atom in $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot NC_5H_5$. An ESCA and Mössbauer investigation[8] concluded that the tin should be regarded as Sn(IV) represented by the valence structures a–c. The alternate formulations d and e, with essentially divalent tin acting as an acceptor toward donor B and a donor toward the metal carbonyl were believed to be less satisfactory descriptions.

Mono(trimethylamine) adducts of SnX_2 (X = Cl, Br, I)

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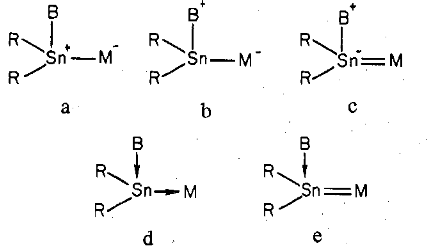


were prepared by a modification of our previously reported procedure.[2] The amine adducts were combined with equimolar quantities of trifluoroborane in diethyl ether to form $BF_3\cdot SnX_2\cdot N(CH_3)_3$ (X = Cl, Br, I) diadducts. The formula of the chloro compound was confirmed by elemental analyses. The Mössbauer spectrum of the tin(II) chloride diadduct, at 103 K consists of a single peak at an isomer shift of 3.87 mm s^{-1} (fwhh 1.55 mm s^{-1}) with respect to $BaSnO_3$. At the same temperature the Mössbauer spectrum of $SnCl_2\cdot N(CH_3)_3$ consists of an asymmetric doublet with an isomer shift of 3.05 mm s^{-1} and a quadrupole splitting of 1.78 mm s^{-1}. Earlier, we reported[2] the isomer shift of $SnCl_2\cdot N(CH_3)_3$ at 25 °C as 2.53 mm s^{-1} with no observable quadrupole splitting. We believe the differences in the observed Mössbauer parameters are attributable to temperature effects which we have also noted in the spectra of other adducts. The isomer shift of $SnCl_2$ has been reported[17] to be 4.07 mm s^{-1} with no observable quadrupole splitting. The Mössbauer spectral parameters indicate that the diadduct $BF_3\cdot SnCl_2\cdot N(CH_3)_3$ is a unique compound in the solid phase, being neither $SnCl_2\cdot N(CH_3)_3$ with BF_3 physically adsorbed in the solid lattice nor a physical mixture of $BF_3\cdot N(CH_3)_3$ and $SnCl_2$ (the expected products of an acid displacement reaction). This is an important point because consideration of the relative acceptor capabilities of $SnCl_2$ and BF_3 suggests that $BF_3\cdot N(CH_3)_3$ and $SnCl_2$ might be the thermodynamically favored products of the reaction. The fact that the diadduct was found instead was interesting in view of the relative weakness[2,3] and assumed lability of $SnCl_2$ adducts, prompting us to investigate analogous adducts of other donors and to extend the investigation to the solution behavior of the diadducts via their NMR spectra.

The ^1H NMR spectra of the $SnX_2\cdot N(CH_3)_3$ and $BF_3\cdot SnX_2\cdot N(CH_3)_3$ (X = Cl, Br, I) compounds in saturated aniline solution are listed in Table I. Strong donor solvents such as pyridine were found to displace BF_3 from the diadducts forming $SnCl_2\cdot N(CH_3)_3$ identified by its ^1H chemical shift. Aniline and dimethyl sulfoxide were the only solvents found which dissolved the compounds without showing evidence of displacing BF_3. The proton resonances of all the adducts and diadducts consisted of singlets. In each case, formation of the diadduct resulted in a small upfield shift of $\delta(CH_3)$ but, since the concentration dependence of the chemical shifts has not been determined, no particular significance can be ascribed to these small shifts. The $\delta(CH_3)$ value for $BF_3\cdot N(CH_3)_3$ in aniline solution is 1.97, which is significantly different than the observed shifts of any of the $BF_3\cdot SnX_2\cdot N(CH_3)_3$ adducts in the same solvent. In order to determine whether dynamic exchange processes were causing averaging of shift values, we prepared a solution containing $BF_3\cdot N(CH_3)_3$ and $BF_3\cdot SnCl_2\cdot N(CH_3)_3$, the NMR spectrum of which (35 °C) showed individual resonances for each species (Figure 1) at substantially the same chemical shifts as listed in Table I. (Adding $SnCl_2$ to a solution of $BF_3\cdot N(CH_3)_3$ in aniline resulted in no apparent change in the ^1H spectrum of the latter.)

The ^{11}B NMR spectrum of $BF_3\cdot SnCl_2\cdot N(CH_3)_3$ in saturated Me_2SO solution consisted of a broad unresolved multiplet (fwhh 305 Hz) at δ 19.4 referred to external $BF_3\cdot O(C_2H_5)_2$. This shift is noteworthy, being substantially downfield from other BF_3 adducts[18] and very similar to those assigned[19] to the tin-coordinated BF_3 in the adducts $(BF_3)_3Sn(NR_2)_2$ (R = CH_3, C_2H_5). The complexity and broad profile of the resonance obscures any identifiable coupling patterns, including the expected quartet structure of BF_3 adducts. The ^{19}F spectrum, on the other hand, showed the expected 1:1:1:1 quartet profile in the resonance appearing 84.9 ppm upfield from external CF_3COOH which may be compared to 64.5 ppm ($J_{^{19}F-^{11}B}$ = 15.4 Hz) for $BF_3\cdot N(CH_3)_3$ in the same solvent.

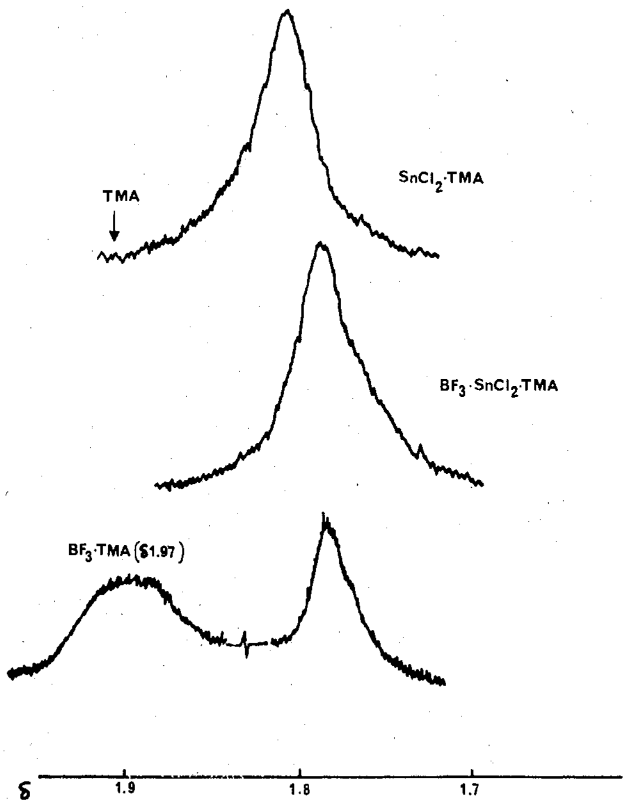
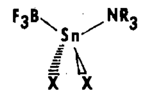


Figure 1. ^1H NMR spectra of trimethylamine adducts.

The ^{119}Sn resonances of $SnCl_2\cdot N(CH_3)_3$ and $BF_3\cdot SnCl_2\cdot N(CH_3)_3$ were broad peaks centered at δ −111.8 and 332.8 (referenced to external $Sn(CH_3)_4$), respectively. We have observed very large concentration shifts in the ^{119}Sn NMR spectra of divalent tin species so the large difference observed above may, in some measure, reflect concentration effects. (Both samples were saturated Me_2SO solutions, but the concentrations were probably different.)

We conclude from the NMR results that the mono- and diadducts are distinct compounds in solution. Moreover, the pronounced ^{119}Sn NMR spectral shifts, the unusual low-field ^{11}B shift, and the large changes in the ^{119}Sn Mössbauer isomer shift and quadrupole splitting suggest the following structure for the diadducts.



The anomalous ^{11}B shift may result from a neighborhood anisotropic effect associated with the electron cloud of the tin atom. Bonded to both a donor and an acceptor, the tin appears to experience nearly compensating shifts of electron density judging by the fact that the ^{119}Sn isomer shift decreases by

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about 1 mm s^{-1} when the trimethylamine adduct of $SnCl_2$ is formed and then increases by over 0.8 mm s^{-1} when BF_3 is added. The isomer shift of the diadduct remains within the accepted range for divalent tin[4] and, characteristic of divalent tin compounds, $BF_3{\cdot}SnCl_2{\cdot}N(CH_3)_3$ reduces aqueous $AgNO_3$, although slowly.

Strong absorptions near 1140, 1070, and 1035 cm^{-1} in the IR spectrum of the diadduct represent BF_3 modes.[20,21] Small shifts of $\nu(CH_3)$ from 3160 cm^{-1} in $SnCl_2{\cdot}N(CH_3)_3$ to 3170 cm^{-1} in the diadduct and of $\delta(CH_3)$ from 1470 in $SnCl_2{\cdot}N(CH_3)_3$ to 1483 cm^{-1} in the diadduct seem to reflect the inductive effect of the coordinated BF_3. A band at 562 cm^{-1}, previously assigned[2] as the Sn–N stretch in $SnCl_2{\cdot}N(CH_3)_3$, shifts down to 550 cm^{-1} in $BF_3{\cdot}SnCl_2{\cdot}N(CH_3)_3$. Another band at 530 cm^{-1} in the spectrum of the latter is tentatively assigned as the Sn–B stretch and the band at 310 cm^{-1} appears to represent a Sn–Cl mode.[9,22–24] The features of the IR spectra of the diadducts appear to be consistent with the proposed structure.

An earlier calorimetric study showed that tin(II) halides dissolved in dimethyl sulfoxide react exothermically with triethylamine,[3] suggesting that Me_2SO is a weaker donor than amines toward these compounds. Nevertheless stable $SnX_2{\cdot}OS(CH_3)_2$ adducts have been reported for both the fluoride[25] and the chloride.[26] In this investigation $SnCl_2{\cdot}OS(CH_3)_2$ was treated with BF_3 in diethyl ether yielding the diadduct $BF_3{\cdot}SnCl_2{\cdot}OS(CH_3)_2$. Spectroscopic parameters were determined for this product in order to establish whether its structure is analogous to that of the trimethylamine adduct. The Mössbauer spectrum of $SnCl_2{\cdot}OS(CH_3)_2$ at 103 K consisted of a doublet, quadrupole splitting 1.37 mm s^{-1}, centered at 3.32 mm s^{-1}, while that of the diadduct consisted of a single broad peak (fwhh 1.48 mm s^{-1}) at 3.99 mm s^{-1}. Again, the isomer shift decreases upon forming the mono adduct with Me_2SO and then increases when the diadduct with BF_3 is formed, closely paralleling the changes in the spectra of the trimethylamine adducts.

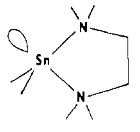
In aniline solution, ^1H chemical shifts observed for $(CH_3)_2SO$, $BF_3{\cdot}OS(CH_3)_2$, $SnCl_2{\cdot}OS(CH_3)_2$, and $BF_3{\cdot}SnCl_2{\cdot}OS(CH_3)_2$ were δ 2.12, 2.27, 1.90, and 1.84, respectively. The upfield shift of the diadduct appears to preclude the possibility of that resonance arising from exchange averaging between $SnCl_2{\cdot}OS(CH_3)_2$ and $BF_3{\cdot}OS(CH_3)_2$. Coordinating BF_3 directly to Me_2SO results in the expected downfield shift of the methyl proton resonance whereas coordination of $SnCl_2$ causes an upfield shift and further coordination of BF_3 to the $SnCl_2{\cdot}OS(CH_3)_2$ results in a small, but significant, additional upfield shift of the resonance of the same protons. It is not especially profitable to speculate on the reasons for the different coordination shift directions but the NMR parameters appear to be reasonable for the proposed structure with BF_3 and Me_2SO separately coordinated to the tin.

The ^{19}F chemical shifts of $BF_3{\cdot}OS(CH_3)_2$ and $BF_3{\cdot}SnCl_2{\cdot}OS(CH_3)_2$ in Me_2SO solution were δ −71.5 and −69.4. Although the shift difference is small, the two signals were distinguishable in mixed solution, indicating that exchange processes, if any, were too slow to be observed at 35 °C. The ^{119}Sn chemical shifts of $SnCl_2{\cdot}OS(CH_3)_2$ and $BF_3{\cdot}SnCl_2{\cdot}OS(CH_3)_2$ in Me_2SO solution were δ −370 and −416, respectively, giving further evidence of the significant difference in the tin environments of the two adducts.

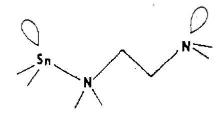
A sharp band at 440 cm^{-1} in the IR spectrum of $SnCl_2{\cdot}OS(CH_3)_2$, absent in that of Me_2SO, was assigned to the Sn–O stretching mode. This band appeared to shift to 480 cm^{-1} in the spectrum of $BF_3{\cdot}SnCl_2{\cdot}OS(CH_3)_2$. Clark and Goel[27] assigned bands at 437 and 415 cm^{-1} in the spectra of $(CH_3)_2SnSO_4{\cdot}OS(CH_3)_2$ and $(CH_3)_2SnCl_2{\cdot}(OS(CH_3)_2)_2$, respectively, to ν(Sn–O). Tanaka[28] assigned aborptions at 482 and 477 cm^{-1} in the spectrum of $SnCl_4{\cdot}(OS(CH_3)_2)_2$ to Sn–O stretching modes.

A band which appears at 530 cm^{-1} in the spectrum of the diadduct is tentatively assigned to ν(Sn-B). Bands associated with the BF_3 group which appear in the 1170–1100-cm^{-1} range in the spectrum of $BF_3{\cdot}OS(CH_3)_2$ shift to 1110–1030 cm^{-1} in the spectrum of the diadduct. The ν(S=O) band which appears at 1045 cm^{-1} in free Me_2SO shifts down to 920 cm^{-1} in the spectrum of $SnCl_2{\cdot}OS(CH_3)_2$. In the diadduct ν(Sn–O) is 920 cm^{-1}, unchanged from its value in the monoadduct, confirming that the Sn–O link remains intact in the diadduct and that BF_3 is not coordinated to the oxygen or to the sulfur of Me_2SO in that adduct. Thus, IR spectra appear to support the proposed structural assignment.

Only a few examples of complexes of tin(II) halides with potentially chelating amines have been reported[1,29,30] and, to our knowledge, structures of such complexes have yet to be determined. We anticipated that a chelate$\cdot SnX_2$ complex might exhibit greater stability and less oxidative sensitivity than complexes with monodenate donors. The 1:1 complex of $SnCl_2$ with *N,N,N′,N′*-tetramethylethylenediamine (TMED) was prepared and found to be unaffected by short exposures to air in sharp contrast to $SnX_2{\cdot}2(CH_3)_3N$ adducts.[2] The ^1H NMR spectrum of $SnCl_2{\cdot}$TMED in aniline solution consists of two singlet resonances at 1.86 and 2.18, both upfield of the corresponding resonances of TMED in aniline (Table III). The 1:1 adduct between trifluoroborane and TMED exhibited methyl and methylene resonances in the same solvent which were split into doublets, indicating that $BF_3{\cdot}N(CH_3)_2CH_2CH_2N(CH_3)_2$ is the structure of the product. Gatti and Wartik[31] reported that TMED$\cdot BH_3$ spontaneously disproportionated to TMED and TMED$\cdot 2BH_3$ at 25 °C, but no such behavior was apparent for the trifluoroborane adduct. The single methyl and methylene environments in $SnCl_2{\cdot}$TMED suggest that the ligand is chelated and that rapid inversion is occurring around the nitrogen atoms or, possibly, that a rapid ligand exchange in solution is averaging the chemical shifts. The small value of the quadrupole splitting, 1.02 mm s^{-1}, falls closer to the range observed for SnX_2 monoadducts with nitrogen chelating donors,[9,32,33] 1.03–1.12 mm s^{-1}, than it does to that observed for SnX_2 monoadducts with tertiary amines,[34] 1.48–1.78 mm s^{-1}. On the basis of this evidence we concluded that the structure of $SnCl_2{\cdot}$TMED is represented by Ia rather than Ib which is analogous to the structure of $BF_3{\cdot}$TMED.



Ia



Ib

The product of the reaction of Ia, $SnCl_2{\cdot}$TMED, and 1 equiv

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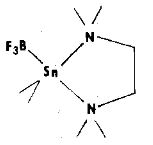
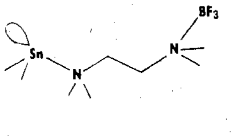
of BF_3 could have a structure such as IIa with the Lewis acid coordinated to the tin donor site or, plausibly, it could result in an acid displacement reaction forming the N,N′-diadduct, IIb. The ^1H NMR spectrum of $BF_3·SnCl_2·TMED$ consists of two singlets at 2.23 and 1.86, the former being shifted slightly downfield from its position in $SnCl_2·TMED$ (Table III) and the latter being unchanged. Broadening of the methylene resonance, which appears to be characteristic of ethylamine moieties to which BF_3 is coordinated, was not visible in the spectrum of $BF_3·SnCl_2·TMED$.



IIa



IIb

For comparison purposes, the isomeric compound $BF_3·TMED·SnCl_2$ (IIb) was prepared by combining $BF_3·TMED$ with an equimolar quantity of $SnCl_2$. The ^1H NMR spectrum of this compound also consisted of two resonances, centered at 2.04 and 1.82, but the former is substantially broadened (Figure 2), as expected, and both appear closer to the shifts observed for $BF_3·TMED$ (Table III). Thus, the ^1H spectra appear to be consistent with the proposed structures for $BF_3·SnCl_2·TMED$ and its structural isomer $BF_3·TMED·SnCl_2$.

The Mössbauer spectrum of $BF_3·SnCl_2·TMED$ consists of an asymmetric doublet centered at +3.36 mm s^{-1} with a quadrupole splitting of 1.39 mm s^{-1}, both of which parameters are notably larger than those of $SnCl_2·TMED$. In contrast, the isomeric product exhibits a single broad (fwhh 1.82 mm s^{-1}) absorption at 3.91 mm s^{-1}.

The ^{11}B NMR spectrum of $BF_3·SnCl_2·TMED$ in Me_2SO solution appeared as a broad singlet at δ 21.1 giving evidence of possible fine structure. The magnitude and direction of the shift compare closely with those previous adducts assigned to have BF_3 coordinated directly to tin.

The IR spectrum of $BF_3·SnCl_2·TMED$ contains bands in the range 1130–1030 cm^{-1} ascribable to coordinated BF_3 modes but no absorptions in the range 720–650 cm^{-1} where the B–N stretch may be expected. The spectra of $BF_3·TMED$ and $BF_3·TMED·SnCl_2$ show peaks at 685 and 690 cm^{-1}, respectively, which we tentatively assign as ν(B–N). The latter spectrum also contains a band at 520 cm^{-1} which appears to represent the Sn–N stretching mode. Bands at 550 and 520 cm^{-1} in the spectrum of $BF_3·SnCl_2·TMED$ were taken to represent $Sn–N_2$ modes, although the Sn–B mode may be expected to appear in the same range, making assignments of both those modes in the $BF_3·SnX_2·TMED$ (X = Cl, Br, I) diadducts uncertain.

The ^1H NMR data for $SnX_2·TMED$ and $BF_3·SnX_2·TMED$ (X = Br, I) (Table III) parallel those described for the $SnCl_2$ adducts. In each case, two singlets are observed which shift slightly to lower field upon forming the diadduct. The small magnitude of these coordination shifts seems consistent with the proposal of BF_3 binding to the tin, somewhat remote from the protons in question.

The adduct $SnCl_2·DP$ has been reported by other workers.[29,34] Fowles and Khan[34] investigated the IR spectrum of $SnCl_2·DP$ and related adducts concluding that the complexes are polymeric with halogen bridges in the solid state. Solution conductivity measurements of tin(II) halide complexes with various bases[1,34] in polar solvents show them to be nonelectrolytes, suggesting that donor solvent molecules simply replace bridging halogen in the tin coordination sphere during solvation.

Fowles and Khan[34] reported the far-IR spectrum of $SnCl_2·DP$ and features of the 4000–450-cm^{-1} spectrum although no tabulation of the latter bands appeared. These investigators concluded that the dipyridyl ligand is a bidentate donor in the complex but did not rule out the possibility of its acting in a bridging rather than a chelating fashion. The bands we observed in the spectrum of $SnCl_2·DP$ closely matched those reported earlier but we have not attempted a further analysis of the IR spectra of either the $SnX_2·DP$ or $BF_3·SnX_2·DP$ adducts.

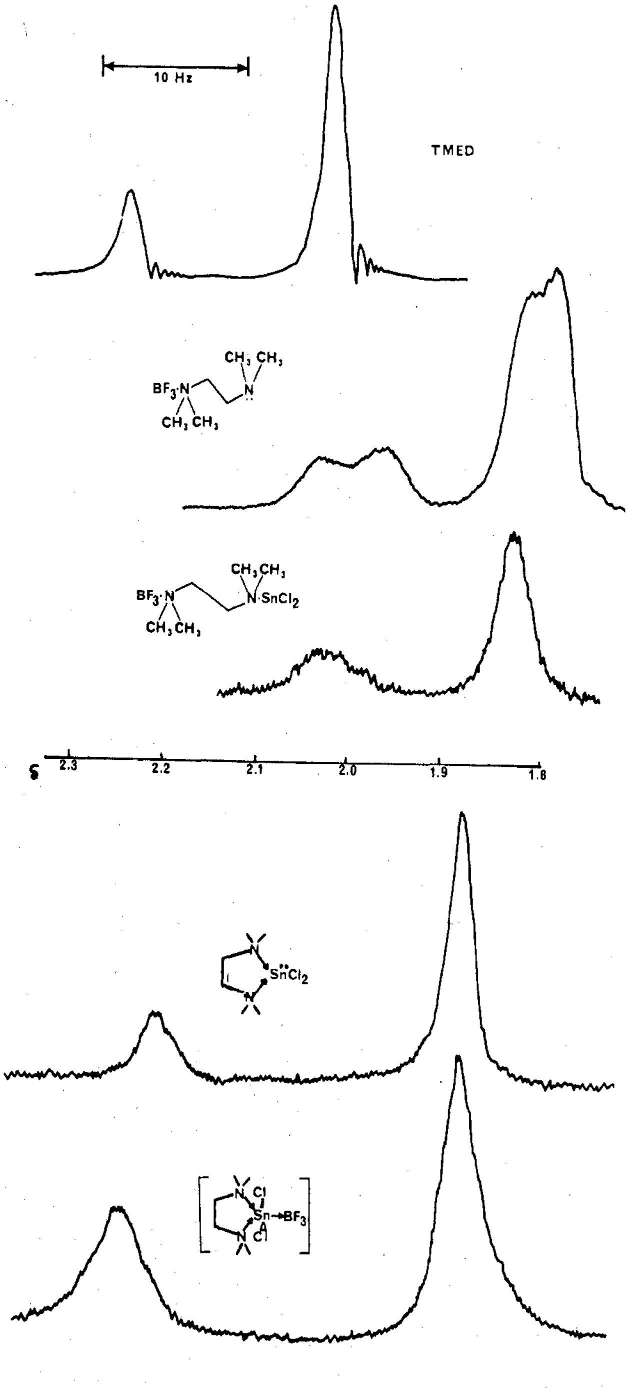


Figure 2. ^1H NMR spectra of TMED adducts: TMED, $BF_3·TMED$, $BF_3·TMED·SnCl_2$, $SnCl_2·TMED$, and $BF_3·SnCl_2·TMED$.

The ^1H NMR spectra of DP and its tin(II) halide adducts were obtained (Table IV and Figure 3). In the former, the order of chemical shifts is H(3) < H(6) < H(5) < H(4) and, when DP is coordinated to the electrophiles $SnCl_2$ and BF_3, the range of the shifts is compressed somewhat and shifted upfield in the case of $SnCl_2·DP$ and downfield in $BF_3·DP$;

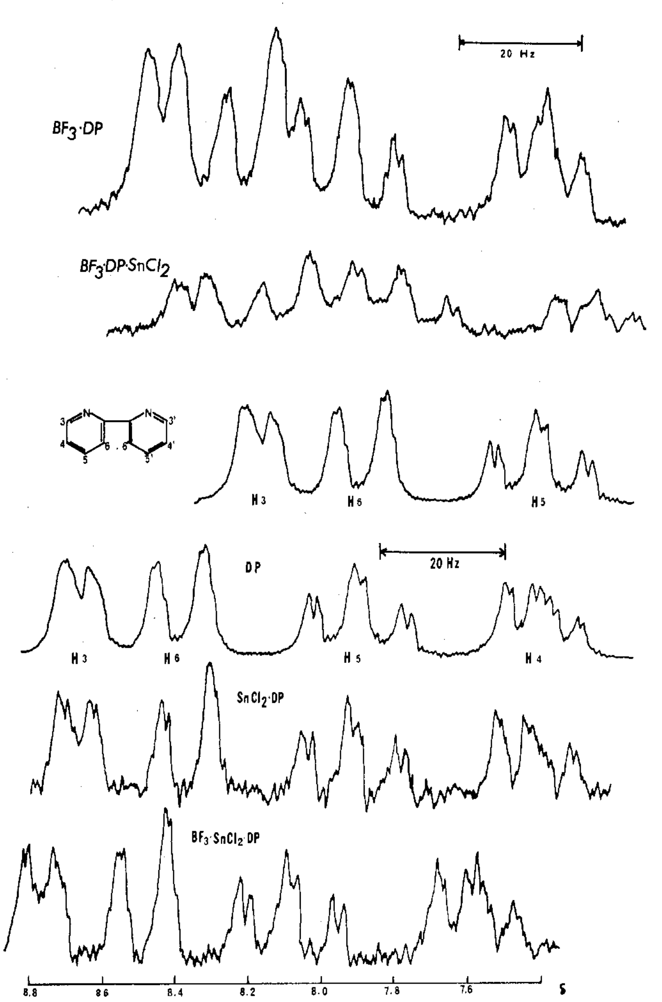
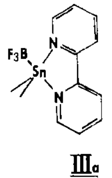


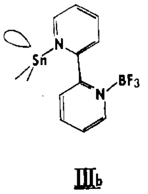
Figure 3. ^1H NMR spectra of dipyridyl adducts: BF_3·DP, BF_3·DP·$SnCl_2$, DP, DP, $SnCl_2$·DP, and BF_3·$SnCl_2$·DP.

however, the general pattern of doublets and triplets remains recognizable. The effect of adding BF_3 to $SnCl_2$·DP is to cause a small downfield shift of the pattern (Figure 3) without appreciably changing the profile. The spectrum of the isomeric compound BF_3·DP·$SnCl_2$, prepared by addition of $SnCl_2$ to an equimolar quantity of BF_3·DP, exhibits a markedly broader profile, perhaps attributable to the unequal electronic influences of the BF_3 and $SnCl_2$ acceptors, the range of which is downfield from that of BF_3·$SnCl_2$·DP but slightly upfield of BF_3·DP. The ^{11}B NMR spectrum of BF_3·$SnCl_2$·DP in Me_2SO solution consisted of a complex, unresolved multiplet at δ +20.7.

We believe that these spectra are consistent with the structural assignments IIIa for BF_3·$SnCl_2$·DP and IIIb for the isomeric BF_3·DP·$SnCl_2$. Additional studies are planned to determine whether and under what conditions interconversion of isomers might occur.



IIIa



IIIb

It is interesting to note that $SnCl_2$·DP is a bright yellow solid, possible as a result of an ultraviolet absorption of the complex tailing into the visible. Fowles and Khan[34] obtained the UV spectra of SnX_2·DP (X = Cl, Br, I) adducts and attributed the lowest energy bands to promotion of a metal s electron into a p orbital ($^1P_1 \leftarrow {}^1S_0$ and $^3P_1 \leftarrow {}^1S_0$). The BF_3 diadduct is a white solid perhaps because coordination of the BF_3 to the tin lone pair stabilizes the s electrons shifting the corresponding UV absorption to higher energy. The isomeric compound, BF_3·DP·$SnCl_2$, is yellow in accordance with this crude rational. Also, $SnBr_2$·DP and SnI_2·DP were found to be deep yellow and dark brown solids while BF_3·$SnBr_2$·DP and BF_3·SnI_2·DP were bright yellow and red, respectively.

Thus, tin(II) halide adducts with the monodentate ligands trimethylamine and dimethyl sulfoxide and with the bidentate, apparently chelating, ligands *N,N,N′,N′*-tetramethylethylenediamine and 2,2′-dipyridyl appear to function as donors via the lone pair on divalent tin toward trifluoroborane.

The isomer shifts of the BF_3·SnX_2·donor compounds (Table V) all lie above +3.36 mm s^{-1}, clearly indicative of tin(II).[35] This is in sharp contrast to the isomer shift (IS) values of the $R_2SnM(CO)_n$·donor compounds[6-8] which fall in the Sn(IV) region (and much more closely resemble the IS reported for $(\eta^5\text{-}C_5H_5)_2Sn{\cdot}BF_3$[11]). We believe that the two types of compounds are structural analogues with BF_3 playing the same role as the metal carbonyl fragment. Evidently the disparate IS values are primarily a consequence of the difference in the $Sn\text{–}BF_3$ (σ) and the $Sn\text{–}M(CO)_n$ (σ + π) bonding interactions. Harrison and Zuckerman[36] have accounted in a qualitative way for the relative IS magnitudes in several classes of tin(II) compounds and adducts. They attributed the unexpectedly small IS values (and large quadrupole splittings) of $R_2Sn{\cdot}M(CO)_n$·donor compounds to shielding effects resulting from populating non-s atomic orbitals on tin by donation from the nucleophile and by π back-donation to the tin from the transition metal carbonyl fragment. Accepting this as a reasonable analysis, we conclude that the much larger IS values (and smaller quadrupole splittings) or our BF_3·SnX_2·donor compounds reflect the absence of a π back-donation in the BF_3–Sn link since similar Sn–donor groups are present in both.

As mentioned earlier, trihalostannate species, SnX_3^-, which can be regarded as complexes between SnX_2 acceptors and X^- donors, form numerous complexes with transition metal Lewis acids.[4] In such complexes, $SnCl_3^-$, for example, is believed to function as a σ donor via the tin lone pair and as a π acceptor through the Sn 5d orbitals. In BF_3·SnX_2·ligand complexes the π component of the bonding is probably minimal but BF_3 is a strong σ acceptor which, taken in the context of the enhanced donor capability of the tin resulting from the charge density flow from the ligand, accounts in some measure for the stability of the diadduct.

A final point of interest is that Wharf and Shriver[20] observed chloride ion abstraction in the reaction of tetraphenylarsonium trichlorostannate(II) with trifluoroborane:

$$(C_6H_5)_4As^+SnCl_3^- + BF_3 \xrightarrow{CH_2Cl_2} (C_6H_5)_4As^+BF_3Cl^- + SnCl_2$$

The reaction had originally been reported[37] to yield the species $(C_6H_5)_4As^+Cl_3SnBF_3^-$, containing a trihalostannate–trifluoroborane adduct. It was concluded that $SnCl_3^-$ is a weak donor (toward BF_3) and that halide abstraction is favored instead of simple adduct formation. We could ask then why the BF_3·SnX_2·ligand complexes were observed in this investigation rather than SnX_2 + BF_3·ligand products which might have been expected from the results of the above investigation. The only clear difference between the complexes is that charged products are formed in the former case so that lattice

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energy considerations may be important. It is also possible, however, that the diadducts are kinetic products and that the rate of conversion to the thermodynamic products is small under the conditions of the experiment. We plan further studies of this question.

Acknowledgment. The authors gratefully acknowledge the support of this investigation by The Robert A. Welch Foundation under Grant E-439. We are indebted to a reviewer for suggesting the comparison between our compounds and the $R_2SnM(CO)_n$·donor species described in ref 6–8. Special thanks go to Professor Mary Good for providing pertinent results prior to publication.

Registry No. $BF_3·SnCl_2·N(CH_3)_3$, 71928-91-1; $BF_3·SnBr_2·N(CH_3)_3$, 71974-94-2; $BF_3·SnI_2·N(CH_3)_3$, 71928-92-2; $BF_3·SnCl_2·OS(CH_3)_2$, 71928-93-3; $BF_3·SnCl_2$·TMED, 71928-94-4; $BF_3·SnBr_2$·TMED, 71928-95-5; $BF_3·SnI_2$·TMED, 71928-96-6; BF_3·TMED·$SnCl_2$, 71928-98-8; $BF_3·SnCl_2$·DP, 71928-99-9; $BF_3·SnBr_2$·DP, 71929-00-5; $BF_3·SnI_2$·DP, 71928-85-3; BF_3·DP·$SnCl_2$, 71928-87-5; $SnCl_2·N(CH_3)_3$, 63528-08-5; $SnBr_2·N(CH_3)_3$, 63528-09-6; $SnI_2·N(CH_3)_3$, 63528-10-9; $SnCl_2·OS(CH_3)_2$, 30822-84-5; $SnCl_2$·TMED, 71928-88-6; $SnBr_2$·TMED, 71928-89-7; SnI_2·TMED, 71928-90-0; $SnCl_2$·DP, 14872-79-8; $SnBr_2$·DP, 31806-30-1; SnI_2·DP, 46389-53-1; BF_3·DP, 71913-06-9; $BF_3·OS(CH_3)_2$, 865-41-8; $(CH_3)_2SO$, 67-68-5; $BF_3·O(CH_2CH_3)_2$, 60-29-7; TMED, 110-18-9; 2,2′-dipyridyl, 366-18-7; $BF_3·N(CH_3)_3$, 420-20-2; $(CH_3)_3N$, 75-50-3; $SnBr_2·Me_2SO$, 71928-78-4; $SnI_2·Me_2SO$, 71928-79-5; $SnF_2·Me_2SO$, 26586-93-6; $SnCl_2$·py, 14872-78-7; $BF_3·SnBr_2·Me_2SO$, 71928-80-8; $BF_3·SnI_2·Me_2SO$, 71928-81-9; $BF_3·SnCl_2$·py, 71974-96-4; BF_3·TMED, 71963-95-6; BF_3, 7637-07-2.

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Gold(III) Fluorosulfate as Fluorosulfate Ion Acceptor. 2.[1] Compounds Containing Halogen and Halogeno(fluorosulfato) Cations

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Gold(III) fluorosulfate, $Au(SO_3F)_3$, is an excellent fluorosulfate ion acceptor, giving the tetrakis(fluorosulfato)aurate(III) ion, $[Au(SO_3F)_4]^-$. This ability is exploited in the synthesis of a number of $[Au(SO_3F)_4]^-$ complexes containing the cations Br_3^+, Br_5^+, $[Br(SO_3F)_2]^+$, and $[I(SO_3F)_2]^+$. All compounds are characterized by their vibrational spectra.

Introduction

We have recently found gold(III) fluorosulfate, $Au(SO_3F)_3$, to be a very good fluorosulfate ion acceptor,[1] forming readily the tetrakis(fluorosulfato)aurate(III) anion. Salts of the type $M[Au(SO_3F)_4]$, with $M^+ = Li^+, K^+, Cs^+, NO^+$, or ClO_2^+, are readily synthesized and characterized by their vibrational spectra; and the acid $H[Au(SO_3F)_4]$, formed when $Au(SO_3F)_3$ is dissolved in fluorosulfuric acid, is able to protonate HSO_3F.[1]

This strong tendency to form the $[Au(SO_3F)_4]^-$ ion and the high thermal stability of the salts suggest that SO_3F^- abstraction from halogen tris(fluorosulfates) such as $I(SO_3F)_3$ and $Br(SO_3F)_3$ should be feasible, and stable reaction products may be obtainable. Support for this view comes from the original synthesis of $Au(SO_3F)_3$,[2] by oxidation of gold with an excess of bromine(I) fluorosulfate, $BrSO_3F$, where a crystalline intermediate of the approximate composition $Au(SO_3F)_3·2BrSO_3F$ was reported. A formulation of this intermediate as $[Br_2SO_3F]^+[Au(SO_3F)_4]^-$ seems reasonable in view of the aforementioned SO_3F^- ion acceptor ability of $Au(SO_3F)_3$.

The purpose of this study is to characterize the intermediate more fully, to attempt the SO_3F^- abstraction from $I(SO_3F)_3$ and $Br(SO_3F)_3$, and to extend the investigation to tetrakis(fluorosulfato)aurate(III) complexes with polybromine cations.

Experimental Section

(A) Chemicals. Bromine (BDH, reagent grade) was stored over KBr and P_2O_5 and distilled in vacuo before use. Gold powder (100 mesh of 99.995% purity) was obtained from the Ventron Corp. Resublimed iodine (analytical reagent) was purchased from Fisher Scientific.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[3] and bromine(I) fluorosulfate, $BrSO_3F$.[4]

(B) Instrumentation. Raman spectra were obtained with either a Cary 81 or a Spex Ramalog 5 spectrophotometer equipped with a helium–neon laser (Spectra Physics Model 125) at λ 632.8 nm or an argon ion laser (Spectra Physics Model 164) at λ 514.5 nm respectively. A cell, suitable to record Raman spectra with the Spex Ramalog at 80 K, has been described by us.[6]

Infrared spectra were recorded on either a Perkin-Elmer 457 or 225 grating spectrophotometer. The latter was equipped with a low-temperature cell, also described earlier by us[7] together with suitable sampling techniques. Spectra at room temperature were obtained on thin films between silver chloride or bromide windows (Harshaw Chemicals).

All reactions were performed in Pyrex reaction vials of about 40-mL capacity, fitted with Kontes Teflon stem valves. Volatile materials were handled by using vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. "Dri Lab" Model No. HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train" Model No. HE-93-B circulating unit.

Electrical conductance measurements were carried out with a Wayne–Kerr universal bridge, Type B221. The measuring temperature of 25.00 ± 0.01 °C was maintained in an oil bath equipped with a Sargent Thermonitor Model ST temperature control unit. The conductivity cell was similar in design to the one described by Barr et al.[8]

(C) Synthetic Reactions. (i) Preparation of $Br_3[Au(SO_3F)_4]$. About 5 g of $BrSO_3F$ was distilled in vacuo into a Pyrex reactor containing 293 mg (1.488 mmol) of gold powder. A vigorous, exothermic reaction occurred as soon as the reactor was warmed to room temperature. To ensure complete reaction, we heated the mixture to 60 °C for 6 h. Removal of all volatiles at room temperature yielded 1239 mg (1.488 mmol) of a dark brown solid which was analyzed as $Br_3[Au(SO_3F)_4]$.

(ii) Preparation of $Br_5[Au(SO_3F)_4]$. In a typical reaction, 175 mg (0.888 mmol) of gold powder was converted into $Br_3[Au(SO_3F)_4]$ as described above. After removal of all volatiles, approximately 5

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