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Synthesis and Characterization of 1,4-Diazabicyclo[2.2.2]octane and Piperidine Adducts of Divalent Tin Halides

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The synthesis of two new series of diligand–tin(II) halide adducts involving piperidine and 1,4-diazabicyclo[2.2.2]octane is described. The new compounds were characterized by elemental analysis, IR and Mössbauer spectroscopy and their X-ray powder diffraction patterns are presented. The complexation isomer shifts suggest that the order of adduct stability is iodide > bromide > chloride and shifts in the N–H infrared stretching frequencies are in accord with this order.

Introduction

The Lewis acid character of tin(II) halides has been recognized for some time [1]. Recently we have been interested in amine adducts of divalent tin halides and factors which determine the stability of such adducts [2]. The present report describes the synthesis and characterization of bis(piperidine) and bis(1,4-diazabicyclo[2.2.2]octane) adducts of tin(II) chloride, bromide and iodide. The Mössbauer and infrared spectral parameters of the adducts were investigated to determine whether they reflect relative adduct stabilities.

Experimental

1. Equipment and Materials

All reactions were carried out under flowing dry nitrogen (prepurified, having less than 1 ppm oxygen) in a Labconco glove box equipped with a recirculating system containing activated 5A molecular sieves and a hot brass (500 °C) deoxygenation unit. Tin(II) chloride and bromide were prepared in a special apparatus described earlier [3]. Tin(II) iodide was prepared from tin and aqueous HI. Typically 20 g (168 mmol) of tin shot (Fisher) was added to 200 ml of aqueous HI in a 500 ml Erlenmeyer flask and the solution boiled until the volume was reduced to 100 ml. The hot solution was filtered, cooled and the crude yellow-orange product collected by filtration. After washing with three portions of distilled water and drying, the tin(II) iodide was placed in a 4 X 20 cm tube which was attached to the vacuum line and evacuated. Under dynamic vacuum, the product was heated to 140 °C causing any tin(IV) iodides to sublime away. The melting point of the purified SnI_2, obtained in a sealed capillary on a heated block, was 322.5 °C (Lit. [4] 320 °C). *Anal.* Calcd. for SnI_2: Sn, 31.9%. Found: Sn, 31.6%. The Mössbauer spectrum of the product consisted of a single peak at 3.90 ± 0.05 mm sec^{-1} (Lit. [5] 3.98 mm/sec). Reagent grade piperidine (pip) (Baker) was refluxed over sodium for 24 hr then distilled under nitrogen onto KOH pellets and stored under vacuum. Commercial 1,4-diazabicyclo[2.2.2]octane (dab) (Baker) was sublimed and stored under nitrogen. Reagent grade anhydrous HCl and HBr (Matheson) were used as obtained. Anhydrous ethyl ether (Malinckrodt) and 1,2-dimethoxyethane (J. T. Baker) were treated with copper(I) chloride, distilled under nitrogen from sodium onto $LiAlH_4$, refluxed and stored under vacuum.

X-ray powder diffraction patterns were obtained by the Debye–Scherrer Method using powdered samples in 0.5 mm glass capillaries in a 114.6 mm diameter camera on a Norelco water-coolded X-ray generator (CuK_α, Ni filtered). Infrared spectra were obtained in KBr pellets using a Beckman Model 4250 spectrophotometer equipped with speed suppression. The Mössbauer spectra were obtained using an Austin Science Associates spectrometer with a Tracor Northern 1024 channel multichannel analyzer and an ASA laser velocity calibrator. The source was $Ba^{119m}SnO_3$ and all isomer shifts are reported relative to SnO_2. X-ray powder diffraction, infrared and Mössbauer spectral data for the adducts are listed in Table Ia, b, IIa, b and III, respectively.

The yields cited are based on the tin(II) halide starting material.

2. Synthesis of Diazabicyclo[2.2.2]octane Adducts

(a) Bis(diazabicyclo[2.2.2]octane)dichlorotin(II), $(dab)_2SnCl_2$

Typically, 0.97 g (5.12 mmol) $SnCl_2$ was placed in a 125 ml Erlenmeyer flask and a solution of 3.0 g (25

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TABLE Ia. X-ray Powder Diffraction Pattern d Spacings for Diazabicyclo[2.2.2]octane Adducts, L_2SnX_2 (X = Cl, Br, I), Å(int).[a,b]

$(dab)_2SnCl_2$		$(dab)_2SnBr_2$	$(dab)_2SnI_2$	
10.11(vs)	2.21(w)	5.82(vvs)	6.08(vs)	1.59(m)
6.80(m)	2.17(w)	3.92(vvs)	5.31(w)	1.56(w)
6.03(m)	2.09(w)	3.56(m)	4.01(vvs)	1.54(m)
5.65(s)	2.04(w)	3.33(vs)	3.52(vs)	1.47(m)
5.13(vvs)	2.00(w)	2.90(m)	3.28(w)	1.43(m)
4.83(w)	1.19(dif)	2.89(s)	3.50(vs)	1.41(m)
4.54(s)	1.84(w)	2.86(s)	2.98(vs)	1.36(m)
4.02(w)	1.80(s)	2.87(w)	2.78(m)	1.34(dif)
3.89(s)	1.77(w)	2.41(s)	2.65(s)	1.30(w)
3.67(m)	1.73(w)	2.81(w)	2.49(w)	1.24(w)
3.55(s)	1.68(m)	2.08(w)	2.44(s)	1.23(w)
3.32(m)	1.60(s)	2.02(s)	2.32(s)	1.20(w)
3.20(w)		1.95(m)	2.12(vs)	
2.95(vvs)		1.93(m)	2.04(m)	
2.81(dif)		1.81(m)	2.01(m)	
2.68(s)		1.77(m)	1.91(m)	
2.63(m)		1.69(s)	1.77(m)	
2.56(m)		1.60(m)	1.75(s)	
2.49(m)		1.57(m)	1.71(m)	
2.43(s)			1.68(m)	
2.26(m)			1.62(s)	

[a]Intensities visually determined. [b]L = dab = 1,4-Diazabicyclo[2.2.2]octane.

TABLE Ib. X-ray Powder Diffraction Pattern d Spacings for Piperidine Adducts, L_2SnX_2 (X = Cl, Br, I), Å (int)[a].

$(pip)_2SnCl_2$	$(pip)_2SnBr_2$	$(pip)_2SnI_2$
11.79(s)	11.91(s)	9.26(m)
8.59(w)	9.19(vs)	6.28(s)
7.34(w)	5.18(m)	5.95(w)
5.95(w)	4.91(s)	5.51(dif)
4.87(vs)	4.26(m)	5.03(m)
4.41(w)	3.96(w)	4.65(vs)
3.66(dif)	3.82(s)	4.45(s)
3.43(w)	3.63(s)	4.24(w)
3.31(m)	3.42(s)	4.03(vs)
3.25(s)	3.24(w)	3.89(vvs)
3.07(m)	3.17(w)	3.63(s)
2.94(m)	3.01(s)	3.53(s)
2.84(m)	2.89(s)	3.29(m)
2.70(m)	2.84(w)	3.18(vs)
2.56(vs)	2.75(m)	2.97(s)
2.44(w)	2.59(m)	2.91(w)
2.32(w)	2.50(dif)	2.87(w)
	2.44(w)	2.79(w)
	2.38(m)	2.75(w)

[a]Intensities visually determined.

TABLE IIa. Infrared Absorption Bands for Diazabicyclo[2.2.2]octane and Adducts of the Type L_2SnX_2, (X = Cl, Br, I)[a].

dab[b]	$(dab)_2SnCl_2$	$(dab)_2SnBr_2$	$(dab)_2SnI_2$
2950(s)	2950(s)	3040(w)	3010(w)
2930(s)	2920(s)	3030(w)	2970(s)
2870(s)	2910(s)	2985(s)	2880(w)
2360(w)	2750(s)	2960(w)	2820(w)
2320(w)	2610(s)	2900(w)	2620(w)
2280(w)	2580(s)	2870(w)	2440(m)
2250(w)	2550(s)	2640(w)	2320(s)
2110(w)	2530(s)	2450(m)	2050(m)
2070(w)	2480(s)	2320(s)	1510(w)
2040(w)	2325(m)	2290(s)	1490(w)
1865(w)	1460(m)	2260(m)	1470(s)
1790(w)	1435(m)	1520(w)	1460(s)
1685(m)	1375(m)	1510(w)	1400(w)
1465(m)	1325(m)	1480(w)	1365(m)
1320(s)	1180(m)	1410(w)	1340(w)
1300(m)	1050(s)	1365(m)	1330(w)
1060(s)	835(s)	1345(m)	1310(w)
1055(s)	800(m)	1320(w)	1180(w)
990(s)	780(s)	1300(w)	1055(s)
900(w)		1185(w)	1005(s)
890(s)		1060(s)	900(m)
830(s)		1010(s)	850(m)
770(s)		900(w)	835(m)
750(s)		860(m)	800(s)
		800(s)	780(s)
		780(s)	620(s)
		620(s)	

[a]Intensities visually determined. [b]1,4-Diazabicyclo[2.2.2]-octane.

mmol) dab ion 50 ml $(C_2H_5)_2O$ added. The flask was capped and stirred magnetically overnight after which the product, a tan solid, was isolated by filtration followed by washing three times with ether and drying on the frit. The product, $(dab)_2SnCl_2$, (yield 76%) melted in a complex fashion beginning at 240 °C and culminating with a red liquid at 296 °C. *Anal.* Calcd. for $C_{12}H_{24}N_4Cl_2Sn$: Sn, 28.7%, Cl, 17.1%. Found: Sn, 28.3%; Cl, 17.6%.

(b) Bis(diazabicyclo[2.2.2]octane)dibromotin(II), $(dab)_2SnBr_2$

The $(dab)_2SnBr_2$ adduct was prepared by the same route as described for the tin(II) chloride adduct. The tan solid product (77% yield) melted at 295 °C with apparent changes beginning near 240 °C. *Anal.* Calcd. for $C_{12}H_{24}N_4Br_2Sn$: Sn, 23.6%; Br, 31.8%. Found: Sn, 23.1%; Br, 31.3%.

(c) Bis(diazabicyclo[2.2.2]octane)diiodotin(II), $(dab)_2SnI_2$

The $(dab)_2SnI_2$ adduct was prepared by the same general method as the previous adducts except that 1,2-dimethoxyethane was employed as the solvent. The orange SnI_2 was gradually converted to a nearly-white solid adduct (yield 84%) which melted in the range 210–220 °C. *Anal.* Calcd. for $C_{12}H_{24}N_4I_2Sn$:

TABLE IIb. Infrared Absorption Bands for Piperidine and Adducts of the Type L_2SnX_2, (X = Cl, Br, I)[a].

pip	$(pip)_2SnCl_2$	$(pip)_2SnBr_2$	$(pip)_2SnI_2$
3325(w)	3195(w)	3175(w)	3150(w)
3365(w)	2950(s)	2950(s)	2980(s)
2950(s)	2840(s)	2840(s)	2950(s)
2860(s)	2805(s)	2800(s)	2830(s)
2800(s)	2760(s)	2760(s)	2800(s)
2790(s)	2740(s)	2740(s)	2760(m)
2740(s)	2630(w)	2530(w)	2725(s)
2670(w)	2530(m)	2510(m)	2620(w)
2630(w)	2430(w)	2410(m)	2500(m)
1470(m)	2150(w)	2140(w)	2495(m)
1450(s)	1895(w)	1825(w)	2120(w)
1440(m)	1595(m)	1590(m)	1850(w)
1330(m)	1470(m)	1470(m)	1580(s)
1320(m)	1460(m)	1460(m)	1460(s)
1260(w)	1440(m)	1435(m)	1455(m)
1165(w)	1397(w)	1395(w)	1430(s)
1115(m)	1390(w)	1390(w)	1420(m)
1045(m)	1320(w)	1315(w)	1395(m)
1035(m)	1280(w)	1280(w)	1310(w)
860(s)	1165(m)	1165(m)	1280(w)
850(m)	1090(m)	1080(m)	1160(m)
745(s)	1080(m)	1030(m)	1080(m)
735(s)	1033(m)	950(m)	1030(s)
730(s)	950(m)	930(m)	950(m)
	940(m)	860(m)	925(m)
	860(m)		860(m)

[a] Intensities visually determined.

Sn, 19.9%; I, 42.5%; C, 22.4%; H, 4.0%; N, 9.4%. Found: Sn, 20.1%; I, 42.6%; C, 24.1%; H, 4.4%; N, 8.6%.

3. *Synthesis of Dipiperidinedihalotin(II) Adducts*

(a) Dipiperidinedichlorotin(II), $(pip)_2SnCl_2$

In a typical reaction 0.97 g (5.12 mmol) of $SnCl_2$ was added with stirring to a solution of 2.5 ml (25.6 mmol) of piperidine in 50 ml $(C_2H_5)_2O$. The reaction vessel was capped and allowed to stir overnight then the cap was removed allowing the solution to concentrate while stirring. After about half the ether had evaporated, the remaining solution was transferred to a large Petri dish where the remaining solvent was allowed to evaporate while the solid residue was agitated with a spatula. The dry solid product (92%) melted over the range 263–300 °C. *Anal.* Calcd. for $C_{10}H_{22}N_2Cl_2Sn$: Sn, 33.0%; Cl, 19.7%. Found: Sn, 32.6%; Cl, 19.6%.

(b) Dipiperidinedibromotin(II), $(pip)_2SnBr_2$

Using the same procedure, the adduct $(pip)_2SnBr_2$ was prepared (75% yield). *Anal.* Calcd. for $C_{10}H_{22}N_2Br_2Sn$: Sn, 26.4%; Br, 35.6%. Found: Sn, 26.3%; Br, 36.2%. The product exhibited complex changes beginning near 60 °C with melting at 110 °C.

(c) Dipiperidinediiodotin(II), $(pip)_2SnI_2$

The $(pip)_2SnI_2$ adduct was synthesized by the procedure described for the previous adducts except with 1,2-dimethoxyethane as the solvent. The white solid product exhibited changes beginning near 154 °C but did not melt until 210 °C. *Anal.* Calcd. for $C_{10}H_{22}N_2I_2Sn$: Sn, 21.9%; I, 46.8%; C, 22.1%; H, 4.1%; N, 5.2%. Found: Sn, 21.3%; I, 46.3%; C, 21.3%; H, 4.4%; N, 4.9%.

Results and Discussion

The title compounds were prepared by direct combination of freshly prepared tin(II) halides with excess base under dry, oxygen-free nitrogen. The solid products were found to be extremely air and water sensitive and syntheses could only be reproduced when those agents were effectively excluded. Their relatively low solubilities, especially of the dab adducts, dictated their study in the solid state by Mössbauer and infrared spectroscopy.

The ligands were chosen because they are elctronically and sterically comparable as donors. Piperidine was chosen in order to facilitate studies of the adduct stabilities by infrared spectroscopy (N–H stretching band). Both dab and pip present relatively small steric requirements making it unlikely that there will be significant steric control of adduct stabilities. The

TABLE III. Mössbauer Parameters of Diazabicyclo[2.2.2]octane and Piperidine Adducts, L_2SnX_2.

L	X	I.S.[a] (mm/sec)	Q.S.[b] (mm/sec)	FWHH[c] (mm/sec)
dab[d]	Cl	2.82	1.75	1.33
	Br	2.73	2.11	1.26
	I	2.76	2.11	1.17
pip[e]	Cl	2.79	2.14	1.18
	Br	2.76	2.11	1.19
	I	2.85	2.08	1.20

[a] Source $Ba^{119m}SnO_3$ at 25 °C. Samples at 103 K. Precision of isomer shifts (I.S.) was ±0.02 mm/sec. [b] Quadrupole splitting. [c] Full width at half height. [d] 1,4-diazabicyclo[2.2.2]octane. [e] Piperidine.

basicity of dab is significantly smaller (towards the proton at least) than might otherwise be expected because of lone pair interactions between the nitrogens [6] and we would expect that also to be reflected in the adducts under investigation here.

Base adducts of divalent tin halides have been prepared and studied by several investigators [1]. The relative stabilities of trimethylamine (TMA) adducts of tin(II) halides, determined according to dissociation pressure measurements [2], decreased in the order $(TMA)_2SnI_2 > (TMA)_2SnBr_2 > (TMA)_2SnCl_2 > (TMA)_2SnF_2$. Calorimetric measurements of the reaction of tin(II) halides dissolved in donor solvents with triethylamine showed that heats of reaction decreased as $SnI_2 > SnBr_2 > SnCl_2$ [7]. We are unaware of any other direct measurements of the stabilities of tin(II) halide adducts.

The limited data presently available precludes generalization of the observed stability trend and does not support the development of a better understanding of the factors which control the stabilities of such adducts. Fortunately, there is an indication that complexation Mössbauer isomer shifts and NMR shifts can be used to assess relative adduct stabilities [2]. Such a relationship (Mössbauer isomer shifts) was first suggested by Donaldson, *et al.* [8], and first demonstrated in this laboratory for $((CH_3)_3N)_nSnX_2$ (n = 1, 2; X = F, Cl, Br, I) adducts [2]. The decrease in isomer shift associated with complex formation was found to vary linearly with the free energy change.

The 1:1 and 1:2 adducts exhibited different linear correlation plots. Table IV lists complexation isomer shifts for the adducts prepared in this study. Since the isomer shifts of the free tin(II) halides occur at larger velocities than those of their adducts [9, 10], the complexation shifts are negative. Interestingly, however, the complexation shifts of the *weaker adducts* are *more negative*. We believe that the isomer shift decreases upon adduct formation primarily because of the change in the coordination number of tin. In solid SnX_2 compounds the tin has a large coordination number of bridging halogens [11] while in the 1:2 adducts the coordination number is probably smaller as a result of the steric requirements of the donors. Since the ^{119}Sn isomer shift is believed to reflect primarily the 5s electron density at the tin nucleus [12], it is understandable from charge flow considerations that the isomer shift in a series of isostructural L_2SnX_2 adducts increases as the adduct stability increases (Table III).

TABLE IV. Complexation Isomer Shifts of Diazabicyclo[2.2.2]octane and Piperidine Adducts, L_2SnX_2.

L	X	ΔIS[a] (mm/sec)
dab	Cl	−1.23 ± 0.02
	Br	−1.22 ± 0.02
	I	−1.14 ± 0.02
pip	Cl	−1.26 ± 0.02
	Br	−1.19 ± 0.02
	I	−1.07 ± 0.02

[a] $\Delta IS = IS(L_2SnX_2) - IS(SnX_2)$.

The complexation isomer shifts (Table IV) of the piperidine adducts exhibit the same order suggesting the same relative adduct stabilities as the trimethylamine adducts. The order of complexation shifts for the dab ligand adducts is not so clear cut with the ΔIS values of chloro and bromo adducts identical within experimental error. The iodo adduct exhibits a more positive ΔIS indicative of a more stable adduct in agreement with the other series of adducts.

Comparing the ΔIS values for adducts of a given tin(II) halide with trimethylamine and with the bases in study, the implied order of donor strength towards SnI_2, for example, is

$$\text{pip} > \text{dap} > (CH_3)_3N$$

Towards $SnCl_2$ and $SnBr_2$ the implied order is

$$\text{pip} \approx \text{dap} > (CH_3)_3N$$

If these are the actual orders of adduct stabilities, we note that the basicities of dap and $(CH_3)_3N$ are in the same order as their proton affinities in the gas phase [6] but the reverse of their pKa values.

The infrared spectra of the complexes provide another potential source of information on their stabilities. The use of IR parameters for assessing adduct stabilities has not been extensively developed but it has been observed, for example, that the B–H stretching frequencies in donor·BH_3 adducts decrease as the strength of the donor–acceptor link increases [13]. The variation was attributed to decreasing s character in the B–H bond as the borane moiety approaches tetrahedral geometry in the very stable adducts.

In this investigation we have determined the complexation shifts for the pip N–H stretching band. This band is probably relatively free from mixing with other bands and therefore its change upon complexation should reflect changes in the bond force constant to a reasonable degree of approximation. Table V lists the complexation shifts in νN–H for the $(pip)_2SnX_2$ adducts. The largest decrease in frequency occurred for the tin(II) iodide adducts which we believe to be the most stable. This result seems to be consistent with expected changes in the N–H bond force constant resulting from charge flow in the donor–acceptor interaction. It assumes however that no significant change occurs in the geometry around nitrogen upon adduct formation and that no significant hydrogen bonding interactions involving the N–H bonds occur in the solid adducts. Neither of

TABLE V. The Complexation Shifts in νN–H of the Piperidine Adducts, $(pip)_2SnX_2$.

Adduct	$\Delta\nu$N–H (cm^{-1})^a
$(pip)_2SnCl_2$	-150^b
$(pip)_2SnBr_2$	-170
$(pip)_2SnI_2$	-195

^{a}The average value [14] of ν axial (3325 cm^{-1}) and ν equatorial (3365 cm^{-1}) was used in $\Delta\nu$ calculation:

$\Delta\nu$N–H = νN–H(adduct) – νN–H(piperidine)

Only one N–H stretching frequency was observed in the spectra of the adducts. ^{b}Estimated maximum uncertainty = 5 cm^{-1}.

these assumptions can be convincingly proved without structure determinations of all the adducts.

The observation of single N–H stretching frequencies for $(pip)_2SnX_2$ adducts suggests that the two piperidines occupy equivalent or nearly equivalent sites in the coordination sphere of the tin. Although numerous L_2SnX_2 adducts are known, there is disagreement concerning the disposition of the ligands in such adducts. To our knowledge, the only structurally characterized example [15, 16] is $SnCl_2 \cdot 2H_2O$ in which one H_2O is directly coordinated to tin and the second is merely hydrogen bonded in the lattice outside the coordination sphere of tin. The mono-adduct character of the structure presumably derives from the presence of a single vacant (p) orbital in the valence shell of divalent tin [1]. On the other hand, experiments in this laboratory demonstrated a clear preference for the formation of diadducts with ligands where there should be little tendency for anything other than direct coordinate bonding. For example, treatment of SnI_2 with excess $(CH_3)_3N$ produces $[(CH_3)_3N]_2SnI_2$ in a well-defined stoichiometry [17]. Thermogravimetry measurements of $[(CH_3)_3N]_2SnX_2$ compounds showed no distinction between the loss of the first and second ligand [2]. Thermodynamic parameters also suggest that the binding of the two trimethylamines is not greatly different as would be expected if one were coordinated directly to tin and one were merely held in the solid lattice.

We conclude that the tin in L_2SnX_2 (L = amine) is at least four coordinate and, when L is piperidine, the ligands occupy equivalent or nearly equivalent coordination sites. Our inability to effect crystallization of any of the reported adducts in suitable form has precluded confirmation of this conclusion by X-ray crystallography but we hope to find more suitable examples in future work.

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