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Synthesis and ^{119}Sn Mössbauer Spectroscopic Studies of Inorganic Tin(IV) Halide and Mixed Halide/Pseudohalide Complexes with N-Donor Ligands

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A series of tin(IV) halide and tin(IV) halide isothiocyanate adducts of nitrogen-donor ligands, of general formulae, $X_nSn(NCS)_{4-n}\cdot L_2$, (n = 2–4), have been synthesized and studied by ^{119}Sn Mössbauer spectroscopy. The complexes all show single Mössbauer resonances and their isomer shift values are found to be a linear function of the average Mulliken electronegativities of the halide/isothiocyanate ligands around the tin atom.

Introduction

The coordination chemistry of tin(IV) isothiocyanate, $Sn(NCS)_4$, [1, 2], and mixed halide isothiocyanates, $X_nSn(NCS)_{4-n}$, (n = 1–3), has received little attention. There are very few examples of complexes of $Sn(NCS)_4$, [3, 4], and there have been no reports, to our knowledge, of adducts of mixed tin(IV) halide isothiocyanates. Interest in compounds of this type has recently arisen in connection with the observation that certain organotin(IV), [5], and inorganic tin(IV), [6], halide and pseudohalide complexes with nitrogen-donor ligands, exhibit antitumour activity.

In this paper, we report the synthesis and ^{119}Sn Mössbauer spectra of nine novel mixed adducts of the types, $X_3Sn(NCS)\cdot L_2$, {X = Cl, Br, I; L_2 = 2,2′-bipyridyl, (bipy), or 1,10-phenanthroline, (phen)}, and $X_2Sn(NCS)_2\cdot$bipy, (X = Cl, Br, I), along with fifteen tin(IV) halide complexes, $SnX_4\cdot L_2$, {X = Cl, Br, I; L_2 = bipy; phen; 3,4,7,8-tetramethyl-1,10-phenanthroline (TMphen); 4,7-diphenyl-1,10-phenanthroline (DPphen); 2 pyridine (2py)}, six of which are new.

Experimental

Syntheses

$SnX_4\cdot L_2$, (X = Cl, Br, I; L_2 = bipy, phen, TMphen, DPphen, 2py)

The tin(IV) halide (1 mol) in chloroform was added to a stirred solution of the organic ligand (1 mol; except in the case of pyridine-2 mol), in the same solvent, and the resulting solid product was filtered off, washed with chloroform, and dried in air.

$X_3Sn(NCS)\cdot L_2$, (X = Cl, Br, I; L_2 = bipy, phen)

A solution of potassium thiocyanate (2 mol) in methanol was added to a stirred solution of tin(IV) chloride or bromide (1 mol) in the same solvent, and the potassium halide precipitate was removed by filtration. The clear filtrate was then added to a methanol solution of the bidentate ligand (1 mol), and the crude solid product, which formed gradually, was filtered, recrystallized from acetone, and dried in air. The analogous iodo complexes were prepared by a similar procedure, except that ammonium thiocyanate was used (instead of the potassium salt), and, in these reactions, no NH_4I was deposited, due to its appreciable solubility in methanol.

$X_2Sn(NCS)_2\cdot$bipy, (X = Cl, Br, I)

Potassium thiocyanate (4 mol) in methanol was added to a stirred methanolic solution of tin(IV) chloride or bromide (1 mol), and the precipitate of potassium halide was removed by filtration. The clear filtrate was added to a solution of 2,2′-bipyridyl (1 mol) in methanol, and the solid product which gradually formed was collected, washed with a small volume of methanol, and dried in air. The iodo compound was synthesized in a similar manner, except that NH_4SCN was used instead of KSCN. Attempts to prepare analytically pure samples of the corresponding 1,10-phenanthroline adducts, $X_2Sn(NCS)_2\cdot$phen, were unsuccessful.

Mössbauer Spectra

^{119}Sn Mössbauer spectra were recorded at 80 K, using a constant acceleration microprocessor spectrometer described previously [7]. The experimental error in the measured values of isomer shift (δ) and full width at half-maximum (Γ) parameters is ±0.05 mm s^{-1}. Isomer shifts are relative to $CaSnO_3$.

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TABLE I. Analytical and Physical Data for Tin(IV) Halide and Pseudohalide Complexes with Nitrogen-Donor Ligands.

Complex	Colour	M.p. (°C)	Analyses: Found (Calc.) (%)				
			C	H	N	Hal.	S
(1) $SnCl_4$·bipy	White	>300 (>400)[a]	29.2 (28.8)	2.1 (1.9)	6.7 (6.7)	32.9 (34.0)	
(2) $SnBr_4$·bipy	White	>300 (>400)[a]	20.2 (20.2)	1.4 (1.4)	4.8 (4.7)	52.7 (53.8)	
(3) SnI_4·bipy	Orange	>300 (>400)[a]	15.5 (15.3)	1.1 (1.0)	3.6 (3.6)	64.6 (64.9)	
(4) $Cl_3Sn(NCS)$·bipy[b]	Pale yellow	251–4	30.4 (30.1)	1.9 (1.8)	9.9 (9.6)	22.5 (24.2)	8.3 (7.3)
(5) $Br_3Sn(NCS)$·bipy[b]	White	260 dec.	23.6 (23.1)	1.4 (1.4)	7.5 (7.3)	41.2 (41.9)	5.9 (5.6)
(6) $I_3Sn(NCS)$·bipy[b]	Orange	>300	18.3 (18.5)	1.1 (1.1)	5.8 (5.9)	53.2 (53.3)	4.3 (4.5)
(7) $Cl_2Sn(NCS)_2$·bipy[b]	White	221–6	31.9 (31.2)	1.9 (1.7)	11.9 (12.1)	15.9 (15.3)	13.2 (13.9)
(8) $Br_2Sn(NCS)_2$·bipy[b]	Pale pink	230–3	26.8 (26.2)	1.7 (1.5)	9.4 (10.2)	29.6 (29.0)	9.6 (11.6)
(9) $I_2Sn(NCS)_2$·bipy[b]	Orange	223–33	22.8 (22.3)	1.4 (1.3)	8.2 (8.7)	39.8 (39.4)	8.7 (9.9)
(10) $SnCl_4$·phen	White	>300	32.5 (32.7)	1.8 (1.8)	6.4 (6.4)	31.9 (32.2)	
(11) $SnBr_4$·phen	Pale yellow	>300	23.8 (23.3)	1.4 (1.3)	4.7 (4.5)	51.6 (51.7)	
(12) SnI_4·phen	Orange	>300	17.7 (17.9)	1.0 (1.0)	3.5 (3.5)	62.5 (62.9)	
(13) $Cl_3Sn(NCS)$·phen[b]	Yellow	278–80	34.6 (33.7)	1.8 (1.7)	9.3 (9.1)	20.3 (23.0)	7.1 (6.9)
(14) $Br_3Sn(NCS)$·phen[b]	Cream	>300	26.6 (26.2)	1.4 (1.4)	7.1 (7.0)	39.9 (40.2)	5.0 (5.4)
(15) $I_3Sn(NCS)$·phen[b]	Red	222 dec.	21.8 (21.2)	1.2 (1.1)	5.9 (5.7)	51.3 (51.6)	4.1 (4.3)
(16) $SnCl_4$·TMphen[b]	White	>300	37.9 (38.7)	3.2 (3.3)	5.3 (5.6)	30.1 (28.5)	
(17) $SnBr_4$·TMphen[b]	White	>300	29.4 (28.5)	2.5 (2.4)	4.3 (4.2)	47.8 (47.4)	
(18) SnI_4·TMphen[b]	Red	>300	22.2 (22.3)	1.8 (1.9)	3.1 (3.2)	58.0 (58.8)	
(19) $SnCl_4$·DPphen[b]	White	>300	47.2 (48.6)	2.5 (2.7)	4.3 (4.7)	24.9 (23.9)	
(20) $SnBr_4$·DPphen[b]	White	>300	37.6 (37.4)	2.1 (2.1)	3.6 (3.6)	41.1 (41.5)	
(21) SnI_4·DPphen[b]	Orange	>300	30.1 (30.1)	1.8 (1.7)	2.8 (2.9)	53.0 (52.9)	
(22) $SnCl_4$·2py	White	>300 (>300)[c] (208 dec.)[d]	28.1 (28.7)	2.4 (2.4)	6.5 (6.7)	33.5 (33.9)	
(23) $SnBr_4$·2py	White	288 dec. (290 dec.)[c] (186 dec.)[d]	19.8 (20.1)	1.7 (1.7)	4.5 (4.7)	53.4 (53.6)	

(Continued on facing page)

TABLE I. (*Continued*)

(*24*) $SnI_4{\cdot}2py$	Brown	227–38 (270 dec.)[c]	15.2 (15.3)	1.4 (1.3)	3.5 (3.6)	64.7 (64.7)

[a] Ref. 8. [b] New compound. [c] Ref. 9. [d] Ref. 10.

Results and Discussion

Analytical and physical data for the tin(IV) complexes are given in Table I.

From the products isolated, it is apparent that the degree of substitution of halogen in the tin(IV) tetrahalides by isothiocyanate groups, in methanol, is dependent upon the stoichiometry of the reactants. On mixing the stannic halide with KSCN (or NH_4SCN) in a 1:2 molar ratio, the predominant tin species in solution is presumably $X_3Sn(NCS)$, since the product obtained on complexation with either bipy or phen in methanol, followed by recrystallization from acetone, is the corresponding trihalogenotin(IV) isothiocyanate derivative (compounds *4–6*, *13–15*). However, when the stannic halide is mixed with the thiocyanate in a 1:4 molar ratio, the major tin species in solution is $X_2Sn(NCS)_2$, and reaction with bipy (in methanol), yields the pure dihalogenotin(IV) diisothiocyanate adduct (compounds *7–9*). No greater degree of replacement of halide by NCS to form $XSn(NCS)_3$ or $Sn(NCS)_4$, is evident in the reactions of stannic halide with larger excesses of thiocyanate, although this is not unexpected, since, in order to obtain the compound $Sn(NCS)_4$, prolonged refluxing times are reported [1, 2] to be necessary.

^{119m}Sn Mössbauer spectroscopic data for the tin(IV) adducts are given in Table II. The Mössbauer spectra of all of the compounds consist of single absorption maxima, having a full width at half-maximum (Γ) in the range 0.89–1.43 mm s^{-1}.

The isomer shifts (δ) of the tin(IV) halide complexes (Table II) are lower than those of the parent tetrahalides (Table III), as would be expected for increased coordination at tin [19], and the values are in good agreement with previously published data. An interesting trend is observed in the Mössbauer spectra of the complexes, where a decrease in the average Mulliken electronegativity (χ_M) of the substituents, X, in$SnX_4{\cdot}L_2$, results in an increase in δ. Additionally, an excellent linear relationship between the δ values and χ_M is obtained for the series of compounds, $X_nSn(NCS)_{4-n}{\cdot}bipy$, (X = Cl, Br, I; n = 2–4), (Fig. 1). Similar linear plots of isomer shift against average substituent electronegativity have been reported for stannic halides [20–23], hexahalogenostannate complexes, SnX_6^{2-}, [12, 17, 24, 25], and stannic oxyhalides [26]. It is of interest to note that the gradients of the two lines in Fig. 1 are identical, but the plots are separated by *ca.* 0.4 mm s^{-1}. This effect is ascribed to complexation of the SnX_4 compound with bipy, resulting in a constant drop in the isomer shift.

TABLE II. ^{119m}Sn Mössbauer Data[a] for the Complexes.

	Complex	δ (mm s^{-1})	Γ (mm s^{-1})
(*1*)	$SnCl_4{\cdot}bipy$	0.44	1.14
		0.47[b]	0.96[b]
		0.42[c]	1.31[c]
(*2*)	$SnBr_4{\cdot}bipy$	0.67	1.11
		0.73[b]	0.88[b]
		0.66[c]	1.17[c]
		0.71[d]	
		0.71[e]	
(*3*)	$SnI_4{\cdot}bipy$	1.03	1.22
		0.95[c]	1.42[c]
		1.00[f]	
(*4*)	$Cl_3Sn(NCS){\cdot}bipy$	0.33	1.07
(*5*)	$Br_3Sn(NCS){\cdot}bipy$	0.55	0.98
(*6*)	$I_3Sn(NCS){\cdot}bipy$	0.84	1.08
(*7*)	$Cl_2Sn(NCS)_2{\cdot}bipy$	0.25	1.18
(*8*)	$Br_2Sn(NCS)_2{\cdot}bipy$	0.39	1.26
(*9*)	$I_2Sn(NCS)_2{\cdot}bipy$	0.58	1.43
(*10*)	$SnCl_4{\cdot}phen$	0.41	1.15
(*11*)	$SnBr_4{\cdot}phen$	0.69	1.09
(*12*)	$SnI_4{\cdot}phen$	1.06	1.07
(*13*)	$Cl_3Sn(NCS){\cdot}phen$	0.32	1.26
(*14*)	$Br_3Sn(NCS){\cdot}phen$	0.57	1.01
(*15*)	$I_3Sn(NCS){\cdot}phen$	0.85	1.30
(*16*)	$SnCl_4{\cdot}TMphen$	0.44	0.89
(*17*)	$SnBr_4{\cdot}TMphen$	0.67	0.96
(*18*)	$SnI_4{\cdot}TMphen$	1.04	1.02
(*19*)	$SnCl_4{\cdot}DPphen$	0.43	0.93
(*20*)	$SnBr_4{\cdot}DPphen$	0.66	1.03
(*21*)	$SnI_4{\cdot}DPphen$	1.04	1.01
(*22*)	$SnCl_4{\cdot}2py$	0.45	1.12
		0.51[b]	0.91[b]
		0.49[d]	
		0.51[g]	0.95[g]
(*23*)	$SnBr_4{\cdot}2py$	0.67	1.20
		0.74[b]	0.87[b]
		0.73[e]	
		0.74[g]	0.92[g]
(*24*)	$SnI_4{\cdot}2py$	1.09	1.17
		1.00[f]	

[a] ΔE_Q = 0 for all complexes. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13. [e] Ref. 14. [f] Ref. 15. [g] Ref. 16.

TABLE III. Mössbauer Data and Mulliken Electronegativities, χ_M, of X, for tin(IV) halides, SnX_4.

Compound	δ (mm s^{-1})	χ_M[a]
$SnCl_4$	0.78[b]	8.29
$SnBr_4$	1.05[b]	7.59
SnI_4	1.47[b]	6.75
$Sn(NCS)_4$	0.56[c]	8.75[d]

[a] Values from ref. 17. [b] Ref. 18. [c] Ref. 2. [d] Value obtained from plot of δ *vs.* χ_M for SnX_4 (Fig. 1).

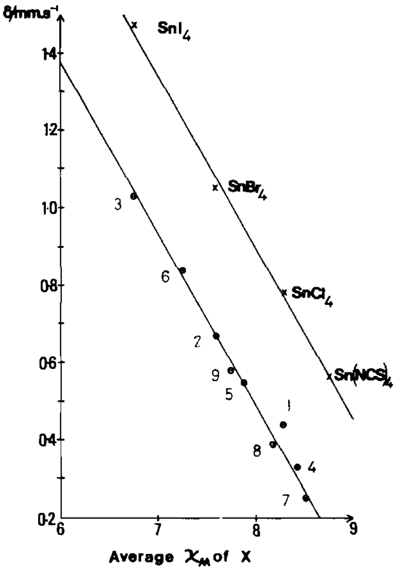

Fig. 1. Relationship between Mössbauer isomer shift and average Mulliken electronegativity of substituent X, in SnX_4 and SnX_4·bipy.

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