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THE SYNTHESIS AND TIN-119m MÖSSBAUER SPECTRA OF SOME DIORGANOTIN DIHALIDE AND DIPSEUDOHALIDE COMPLEXES WITH NITROGEN- AND OXYGEN-DONOR LIGANDS

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Summary

The synthesis and ^{119m}Sn Mössbauer spectra of 114 complexes of the type R_2SnX_2, L_2 (R = Me, Et, n-Pr, n-Bu, n-Oct, Ph, Bz; X = F, Cl, Br, I, NCS; L_2 = 2 monodentate or 1 bidentate O- or N-donor ligand(s)), 74 of which are new, are reported. The majority of the complexes are isostructural, having an octahedral *trans*-R_2SnX_4 geometry about tin, whilst five of the diphenyltin complexes (R = Ph; X = Cl; L_2 = AMP, Nphen; X = NCS; L_2 = bipy, phen, TMphen) adopt a *cis*-R_2SnX_4 octahedral structure.

A convenient method for the synthesis of a number of novel 1 : 1 diorganotin difluoride complexes using hot acetonitrile is reported and a structure for the unusual adduct, $Ph_2SnF_2 \cdot 0.5$ phen, is proposed.

Introduction

In the course of an investigation into the antitumour activity of organotin compounds, we have found [1,2] that many of the titled complexes exhibit reproducible in vivo activity towards the P388 lymphocytic leukaemia in mice. The ^{119m}Sn Mössbauer spectra of both the active and inactive complexes (a total of 114 compounds) have been recorded, so that structure/activity relationships may be investigated.

Diorganotin dihalide complexes are well known and some have had their structures determined by X-ray analysis. Table 1 lists these compounds and indicates their structures.

From the Table, it can be seen that the complexes adopt the *trans*-R_2SnX_4 octahedral geometry about tin (I) and it may be concluded that this is the preferred structure. However, a few complexes do have the *cis*-R_2SnX_4 octahedral structure (II) as will be described shortly.

Discrete monomeric diorganotin dihalide complexes with monodentate ligands may have *cis*- or *trans*-halogens, whereas those with bidentate ligands can

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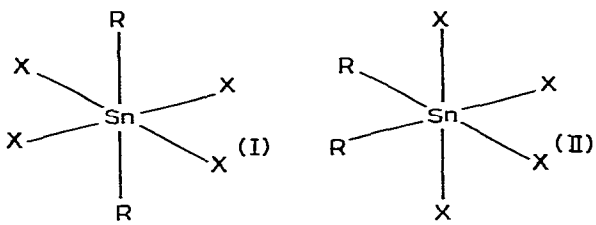
TABLE 1

X-RAY STRUCTURES OF DIORGANOTIN DIHALIDE COMPLEXES *

Complex	Structure	Configuration of halogens	Ref.
$Me_2SnCl_2 \cdot 2$ DMF	*trans*-R_2SnX_4	*cis*	3
$Me_2SnCl_2 \cdot 2$ DMSO	"	*cis*	3, 4
$Me_2SnCl_2 \cdot 2$ HMPT	"	*trans*	3
$Me_2SnCl_2 \cdot$ NiSalen	"	*cis*	5
$Me_2SnCl_2 \cdot 2$ py	"	*trans*	6
$Me_2SnCl_2 \cdot 2$ pyO	"	*trans*	7
$Me_2SnCl_2 \cdot$ salenH_2	"	*trans*	8
$Me_2SnBr_2 \cdot 2$ DMSO	"	*trans*	3, 9
$Me_2SnBr_2 \cdot 2$ HMPT	"	*trans*	3
$Me_2SnBr_2 \cdot 2$ py	"	*trans*	6
$Et_2SnCl_2 \cdot$ bipy	"	*cis*	10
$Ph_2SnCl_2 \cdot 2$ DMSO	"	*cis*	11
$Ph_2SnCl_2 \cdot$ bipy	"	*cis*	12
$Bz_2SnCl_2 \cdot$ bipy	"	*cis*	13

only have *cis*-halogens. From the results of his studies with platinum complexes, Rosenberg [14] was able to demonstrate that the presence of *cis*-halogens was



necessary for potential antitumour activity. For this reason, the majority of the complexes reported in this study contain bidentate donor ligands.

Although examples of diorganotin dihalide and dipseudohalide complexes with organic ligands, R_2SnX_2, L_2 (X = Cl, Br, I, NCS) are well known, the only report of a dialkyltin difluoride complex of this type is by May and Curran [15], who prepared $Bu_2SnF_2 \cdot$ phen by the reaction of Bu_2SnF_2 with 1,10-phenanthroline in DMSO. We have found that the 1 : 1 adducts of dialkyltin difluorides with 1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline may be conveniently synthesized using hot acetonitrile as a solvent. However, when the experiments were repeated using 2,2'-bipyridyl as the ligand, only starting materials were recovered, in agreement with the earlier work of Alleston and Davies [16].

Experimental

Preparation of complexes

Dimethyl-, diethyl-, di-n-propyl- and diphenyl-tin dichlorides were generous gifts from Mr. M. Ohata, Chugoku Marine Paints, Shiga-Ken, Japan, Dr. E.J. Bulten, Institute for Organic Chemistry TNO, Utrecht, The Netherlands, and

* A recent X-ray crystal structure determination of $Ph_2Sn(NCS)_2$, bipy has revealed a distorted octahedral *cis*-R_2SnX_4 geometry with *trans*-isothiocyanato groups [50].

Dr. D.A. Armitage, Queen Elizabeth College, London. Di-n-butyltin dichloride was obtained commercially from BDH Ltd. The other diorganotin dihalides and dipseudohalides, R_2SnX_2, were obtained from the dichlorides by heating in acetone with the appropriate sodium or potassium salt, MX. The organic ligands {bipy; DMSO; phen; py; 2-aminomethyl-pyridine (AMP); 2-mercaptopyridine (merpy); 2-(2-pyridyl)benzimidazole (PBI); 5-chloro-1,10-phenanthroline (Cphen); 5,6-dimethyl-1,10-phenanthroline (DMphen); 4,7-diphenyl-1,10-phenanthroline (DPphen); 5-nitro-1,10-phenanthroline (Nphen); 5-phenyl-1,10-phenanthroline (Pphen); 3,4,7,8-tetramethyl-1,10-phenanthroline (TMphen); pyrido{2,3-b}pyrazine (pypy)} were obtained commercially and were used without further purification.

Preparation of diorganotin difluoride complexes

The series of 1 : 1 adducts of dialkyltin difluorides with 1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline were prepared by the reaction of equimolar amounts of the starting materials in refluxing acetonitrile. The phenanthroline solution was added to a stirred suspension of the appropriate R_2SnF_2 compound in hot acetonitrile, whereupon the mixture immediately turned clear. The resulting solution was then cooled, and the complex separated out as white crystals. The 2 : 1 adduct of diphenyltin difluoride with phenanthroline was prepared similarly, although, in this case, filtration of the hot solution was necessary prior to cooling.

Preparation of diorganotin dihalide complexes

These compounds were prepared by mixing, typically, hot methanolic or dry ethereal solutions of the appropriate diorganotin dihalide and the ligand in a 1 : 1 or 1 : 2 molar ratio. The products, which formed immediately (or on cooling the solution to room temperature or below) as crystalline precipitates, were collected by filtration and dried in air. Pure samples of $R_2SnI_2 \cdot L_2$ (R = Me, n-Bu; L_2 = PBI, DPphen, TMphen; R = n-Pr, Et; L_2 = PBI; R = Ph; L_2 = PBI, DPphen) could not be obtained.

The 1 : 1 adduct of dimethyltin dichloride with *N,N'*-ethylene-bis(salicylideneiminato)nickel(II) (NiSalen) was prepared by the method of Pellerito et al. [17].

The analytical and melting point data for the complexes are shown in Table 2, together with literature values, where known.

Mössbauer spectra

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A 15 mCi $Ba^{119m}SnO_3$ source was used at room temperature and samples were packed in perspex discs and cooled to 80 K, using a liquid nitrogen cryostat.

The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters is ±0.05 mm s^{-1}.

(Continued on p. 230)

TABLE 2

MELTING POINT AND ANALYTICAL DATA FOR DIORGANOTIN DIHALIDE AND DIPSEUDOHALIDE COMPLEXES, $R_2SnX_2 \cdot L_2$

Complex		Microanalytical data. Found (calcd.) (%)				M.p. (°C)
		C	H	N	X	
$Me_2SnX_2 \cdot L_2$						
X = Cl,	L = DMSO	—	—	—	—	112—113 (113) [18]
	L = merpy	32.64 (32.58)	3.73 (3.62)	6.28 (6.33)	16.41 [a] (16.06)	141
	L = py	—	—	—	—	163 (163) [19]
	L_2 = AMP	29.31 (29.27)	4.50 (4.27)	8.53 (8.54)	21.15 (21.65)	190—192
	L_2 = bipy	—	—	—	—	233—235 (232—233 [20])
	L_2 = NiSalen	39.79 (39.69)	3.71 (3.67)	5.17 (5.14)	13.03 (13.02)	280 dec. (277 dec [17])
	L_2 = PBI	40.67 (40.48)	3.62 (3.61)	9.99 (10.12)	16.99 (17.11)	238—239
	L_2 = phen	—	—	—	—	284 (284 [21])
	L_2 = DPphen	55.53 (56.39)	4.39 (3.99)	4.82 (5.07)	12.22 (12.86)	232—235 (250—254 dec [22])
	L_2 = Tmphen	47.55 (47.37)	4.96 (4.82)	6.23 (6.14)	15.53 (15.57)	277—280 dec (267—270 dec [22])
	L_2 = pypy	30.70 (30.77)	3.15 (3.13)	12.04 (11.97)	20.37 (20.23)	120—121
X = Br,	L_2 = bipy	—	—	—	—	224 (224) [23]
	L_2 = PBI	34.25 (33.33)	3.26 (2.98)	8.43 (8.33)	32.72 (31.75)	221
	L_2 = phen	33.70 (34.36)	2.84 (2.86)	5.76 (5.73)	32.87 (32.72)	255—257 (232—235 [24])
	L_2 = DPphen	49.22 (48.67)	3.57 (3.43)	4.52 (4.37)	25.68 (24.96)	251—255
	L_2 = TMphen	40.32 (39.63)	4.20 (4.04)	5.18 (5.14)	30.10 (29.36)	271—273 dec
X = I,	L_2 = bipy	25.93 (25.76)	2.63 (2.50)	4.89 (5.81)	45.75 (45.44)	208—209 (214 [23])
	L_2 = phen	—	—	—	—	237—240 (235—245) [24]
X = NCS, L	L_2 = bipy	—	—	—	—	222—224 (219—220.5 [25])
	L_2 = phen	43.38 (43.15)	3.12 (3.15)	12.21 (12.58)	14.59 [b] (14.38)	250—251
$Et_2SnX_2 \cdot L_2$						
X = F,	L_2 = phen	48.27 (48.60)	4.55 (4.55)	7.06 (7.08)	—	164—167
	L_2 = TMphen	52.20 (53.22)	5.96 (5.76)	6.13 (6.20)	—	254—267
X = Cl,	L = DMSO	23.79 (23.76)	5.37 (5.45)	17.76 (17.57)	15.84 [b] (15.84)	57—59 (64 [26])
	L = merpy	35.81 (35.74)	4.41 (4.26)	6.43 (5.96)	14.80 [c] (15.11)	77—79
	L = py	40.93 (41.38)	4.90 (4.93)	6.82 (6.92)	17.93 (17.49)	119—121
	L_2 = AMP	34.19 (33.71)	5.03 (5.06)	8.37 (7.87)	20.70 (19.94)	157—159 dec

TABLE 2 (continued)

Complex		Microanalytical data. Found (calcd.) (%)				M.p. (°C)
		C	H	N	X	
	L_2 = bipy	—	—	—	—	177—179 (177—179) [24]
	L_2 = PBI	43.42 (43.34)	4.41 (4.29)	9.51 (9.48)	15.97 (16.03)	229—231
	L_2 = phen	—	—	—	—	235—236 (235—236 [16])
	L_2 = Cphen	41.34 (41.51)	3.67 (3.68)	6.09 (6.05)	22.83 (23.03)	211—212
	L_2 = DMphen	46.44 (47.37)	4.82 (4.82)	6.03 (4.14)	15.72 (15.57)	247—249
	L_2 = DPphen	57.47 (57.93)	4.54 (4.48)	4.73 (4.83)	12.21 (12.24)	231—232
	L_2 = Nphen	40.40 (40.49)	3.68 (3.59)	8.88 (8.88)	14.83 (15.01)	202—203
	L_2 = Pphen	53.24 (52.39)	4.49 (4.37)	5.43 (5.56)	13.86 (14.09)	246—249
	L_2 = TMphen	49.66 (49.59)	5.35 (5.37)	5.58 (5.78)	14.72 (14.67)	280 dec
X = Br,	L_2 = bipy	34.29 (34.08)	3.77 (3.65)	5.60 (5.68)	32.48 (32.45)	204—206 (201—202 [24])
	L_2 = PBI	36.55 (36.09)	3.58 (3.57)	8.01 (7.89)	30.30 (30.08)	224—225
	L_2 = phen	37.06 (37.14)	3.55 (3.48)	5.57 (5.42)	31.15 (30.95)	236—238 (225—230 dec [24])
	L_2 = DPphen	50.57 (50.22)	4.04 (3.89)	4.25 (4.19)	23.81 (23.92)	259—265 dec.
	L_2 = TMphen	42.84 (41.88)	4.81 (4.54)	4.99 (4.89)	28.60 (27.92)	>300
X = I,	L_2 = bipy	—	—	—	—	177—179 (177—179 [24])
	L_2 = phen	31.27 (31.42)	3.01 (2.95)	4.73 (4.58)	41.43 (41.57)	206—207 (202—203 [24])
	L_2 = DPphen	44.15 (44.04)	3.52 (3.41)	3.33 (3.67)	33.40 (23.29)	246—248
	L_2 = TMphen	36.07 (35.98)	3.89 (3.90)	4.06 (4.20)	38.30 (38.08)	dec. >260
X = NCS,	L_2 = bipy	—	—	—	—	221—223 (220—222.[27])
	L_2 = phen	45.87 (45.67)	3.78 (3.81)	11.68 (11.84)	13.18 [b] (13.53)	210—212
$Pr_2SnX_2 \cdot L_2$						
X = F	L_2 = phen	49.97 (51.06)	5.42 (5.20)	6.39 (6.61)	—	159—164
	L_2 = TMphen	54.39 (55.11)	6.37 (6.26)	5.81 (5.84)	—	234—237
X = Cl,	L = py	42.93 (44.24)	6.00 (5.53)	6.04 (6.45)	16.64 (16.36)	105—107
	L_2 = bipy	44.36 (44.44)	5.18 (5.09)	6.45 (6.48)	16.53 (16.44)	206—207 (204—205 [20])
	L_2 = PBI	46.05 (45.86)	4.95 (4.88)	9.08 (8.92)	14.89 (15.07)	189—190
	L_2 = phen	47.46 (47.37)	4.82 (4.82)	6.05 (6.14)	15.72 (15.57)	127—128
	L_2 = DPphen	58.02 (59.21)	4.94 (4.93)	4.53 (4.61)	11.30 (11.68)	228—229
	L_2 = TMphen	51.52 (51.56)	5.93 (5.86)	5.44 (5.47)	13.60 (13.87)	dec. >290

TABLE 2 (continued)

Complex		Microanalytical data. Found (calcd.) (%)				M.p. (°C)
		C	H	N	X	
X = Br	L_2 = bipy	36.71	4.29	5.29	30.72	205—206
		(35.85)	(4.22)	(5.37)	(30.71)	
	L_2 = PBI	38.92	4.26	7.52	29.73	228—232
		(38.57)	(4.11)	(7.50)	(28.57)	
	L_2 = phen	39.12	4.08	5.07	29.59	248—249
		(39.63)	(4.04)	(5.14)	(29.36)	
	L_2 = DPphen	51.54	4.51	3.95	23.11	226—227
		(51.65)	(4.30)	(4.02)	(22.96)	
	L_2 = TMphen	44.44	5.19	7.78	26.34	>300
		(43.92)	(4.99)	(4.65)	(26.62)	
	L_2 = bipy	31.52	3.64	4.45	41.55	188—190
		(31.22)	(3.58)	(4.55)	(41.30)	
	L_2 = PBI	33.10	3.81	6.30	38.44	146—150
		(33.03)	(3.52)	(6.42)	(38.84)	
	L_2 = phen	33.87	3.55	4.29	39.81	234—236
		(33.80)	(3.44)	(4.38)	(39.75)	
	L_2 = DPphen	45.36	3.98	3.61	32.19	209—211
		(45.51)	(3.79)	(3.54)	(32.11)	
	L_2 = TMphen	38.01	4.46	4.15	36.43	265—267 dec.
		(37.99)	(4.32)	(4.03)	(36.55)	
X = NCS,	L_2 = bipy	45.04	4.61	11.39	13.12 [b]	155—157
		(45.28)	(4.61)	(11.74)	(13.42)	
	L_2 = phen	47.51	4.60	11.11	12.30 [c]	225—227 dec.
		(47.90)	(4.39)	(11.18)	(12.77)	
$Bu_2SnX_2 \cdot L_2$						
X = F,	L_2 = phen	52.79	5.91	6.03	—	140—141
		(53.21)	(5.76)	(6.20)		(140—144 [15])
	L_2 = TMphen	56.44	6.70	5.58	—	>160
		(56.80)	(6.70)	(5.52)		
X = Cl,	L_2 = AMP	39.78	6.24	7.66	17.87	103—106
		(40.78)	(6.31)	(6.80)	(17.23)	
	L_2 = bipy	—	—	—	—	190—181
						(179—179.5 [16])
	L_2 = PBI	48.02	5.51	8.26	14.21	196—197
		(48.10)	(5.41)	(8.42)	(14.23)	
	L_2 = phen	—	—	—	—	199—200
						(200 [16])
	L_2 = DPphen	60.00	5.54	4.29	10.75	178—179
		(60.38)	(5.35)	(4.40)	(11.16)	
	L_2 = TMphen	53.29	6.47	5.19	12.93	dec. >245
		(53.33)	(6.30)	(5.19)	(13.15)	
X = Br,	L_2 = bipy	—	—	—	—	175—177
						(176—177 [16])
	L_2 = PBI	40.96	4.59	7.17	27.05	192—193
		(40.82)	(4.59)	(7.14)	(27.21)	
	L_2 = phen	41.49	4.67	4.78	27.60	203—205
		(41.88)	(4.54)	(4.89)	(27.92)	(199—200 [16])
	L_2 = DPphen	52.47	4.83	3.83	21.64	186—187
		(52.97)	(4.69)	(3.86)	(22.07)	
	L_2 = TMphen	46.06	5.55	4.31	25.78	256—257 dec.
		(45.74)	(5.41)	(4.45)	(25.43)	
X = I,	L_2 = bipy	34.51	4.22	4.44	37.30	160—161
		(33.59)	(4.04)	(4.35)	(39.50)	(163 [16])
	L_2 = phen	36.21	3.97	4.28	37.95	230—232
		(35.98)	(3.90)	(4.20)	(38.08)	(234—236 [16])
X = NCS, L	L_2 = bipy	47.57	5.14	11.21	12.21 [b]	151—152
		(47.52)	(5.15)	(11.09)	(12.67)	(152—153 [16])

TABLE 2 (continued)

Complex		Microanalysis data. Found (calcd.) (%)				M.p. (°C)
		C	H	N	X	
	L_2 = phen	49.84	5.18	10.73	11.47 [b]	211—212
		(49.91)	(4.91)	(10.59)	(12.10)	(208—210 [28])
$Ph_2SnX_2 \cdot L_2$						
X = F	L_2 = 0.5 phen	53.61	3.04	4.46	—	235—248
		(53.86)	(3.49)	(3.49)		
X = Cl,	L = DMSO	—	—	—	—	133—136
						(132—135 [29])
	L = py	52.19	4.08	5.58	14.17	141—143
		(52.59)	(3.98)	(5.58)	(14.14)	(150—151 [30])
	L_2 = AMP	39.78	6.24	7.66	17.87	103—106
		(40.78)	(6.31)	(6.80)	(17.23)	
	L_2 = bipy	—	—	—	—	248—250
						(245—248 [20])
	L_2 = PBI	52.38	4.07	7.37	12.62	222—223
		(52.43)	(3.53)	(7.79)	(13.17)	
	L_2 = phen	54.58	3.45	5.35	13.28	284—286
		(54.96)	(3.44)	(5.34)	(13.55)	(235 [16])
	L_2 = Cphen	51.07	3.11	4.93	19.10	258—260
		(51.57)	(3.04)	(5.01)	(19.07)	
	L_2 = DMphen	55.84	4.09	4.96	12.67	dec. >290
		(56.52)	(3.99)	(5.07)	(12.86)	
	L_2 = DPphen	63.29	3.91	4.15	10.19	242—243
		(63.91)	(3.81)	(4.14)	(10.50)	
	L_2 = Nphen	50.18	3.02	7.29	12.48	216—219
		(50.62)	(2.99)	(7.38)	(12.48)	
	L_2 = Pphen	59.01	3.72	4.61	11.83	269—270
		(60.00)	(3.67)	(4.67)	(11.83)	
	L_2 = TMphen	57.45	4.64	4.79	11.81	267—268 dec.
		(57.93)	(4.48)	(4.83)	(12.24)	
X = Br,	L_2 = bipy	45.60	3.25	4.78	27.70	236—240
		(44.82)	(3.06)	(4.75)	(27.16)	(245—248 [31])
	L_2 = PBI	45.79	3.42	6.46	24.49	227—228
		(45.86)	(3.03)	(6.69)	(25.48)	
	L_2 = phen	47.17	3.06	4.22	26.74	296—298
		(46.98)	(2.94)	(4.57)	(26.10)	
	L_2 = DPphen	56.06	3.38	3.59	20.81	203—205
		(56.47)	(3.40)	(3.66)	(20.92)	
	L_2 = TMphen	50.35	4.05	4.05	24.11	265—267 dec.
		(50.22)	(3.89)	(4.19)	(23.92)	
X = I,	L_2 = bipy	38.69	2.82	3.96	36.23	199—200
		(38.65)	(2.64)	(4.10)	(37.19)	(200 [30])
	L_2 = phen	40.88	2.49	3.88	35.34	280—281
		(40.74)	(2.55)	(3.96)	(35.93)	
	L_2 = DPphen	50.43	3.06	3.14	29.28	234—236
		(50.29)	(3.03)	(3.26)	(29.57)	
X = NCS,	L_2 = bipy	52.70	3.37	10.14	11.06 [b]	198—201
		(52.84)	(3.30)	(10.27)	(11.74)	(195—197 [28])
	L_2 = phen	54.58	4.41	9.52	10.76 [b]	250—255
		(54.83)	(3.16)	(9.84)	(11.24)	(>210 [28])
	L_2 = TMphen	56.83	4.12	8.73	9.39 [b]	241—244
		(57.06)	(4.16)	(8.96)	(10.24)	
$Bz_2SnCl_2 \cdot phen$		56.11	4.03	5.24	13.24	218—220 dec.
		(56.52)	(3.99)	(5.07)	(12.86)	
$Oct_2SnCl_2 \cdot L_2$						
	L_2 = bipy	—	—	—	—	130—132
						(133—135 [16])

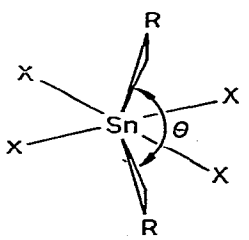
TABLE 2 (continued)

Complex	Microanalysis data. Found (calcd.) (%)				M.p. (°C)
	C	H	N	X	
L_2 = PBI	54.90 (55.35)	7.32 (6.43)	6.72 (6.92)	11.74 (11.70)	134—144
L_2 = phen	—	—	—	—	101 (101) [16]
L_2 = DPphen	63.67 (64.52)	6.66 (6.18)	3.80 (3.76)	9.36 (9.54)	104—105
L_2 = TMphen	58.71 (59.26)	7.86 (7.10)	4.18 (4.32)	10.82 (10.96)	202

[a] S 14.60 (14.48) %. [b] Sulphur. [c] S 14.48 (13.62) %.

Discussion

The quadrupole splitting parameter (ΔE_Q) has, with the application of the results of point charge calculations [47], proved useful in distinguishing between *cis*- and *trans*-R_2SnX_4 configurations in complexes with octahedral geometries. Thus, a compound with a *trans*-R_2SnX_4 configuration (I) would be expected to give rise to ΔE_Q values of ca. 4 mm s^{-1}, whilst a value of ca. 2 mm s^{-1} would be expected for a compound with a *cis*-R_2SnX_4 configuration (II). Sham and Bancroft [48] also using point charge calculations, have shown that the quadrupole splittings for *trans*-R_2SnX_4 compounds decrease smoothly away from 4 mm s^{-1} for a regular octahedral geometry (III, $\theta = 180°$) as the structure becomes more distorted, i.e. θ becomes less than 180°.



(III)

A study of the Mössbauer data for the complexes, presented in Table 3, indicates that the majority adopt a *trans*-R_2SnX_4 configuration (I) and a number of these, particularly the diphenyltin dihalide adducts, are of the distorted octahedral type (III). Five diphenyltin compounds, $Ph_2SnX_2 \cdot L_2$ (X = Cl, L_2 = AMP, Nphen; X = NCS, L_2 = bipy, phen, TMphen) adopt the *cis*-R_2SnX_4 structure (II). The reasons for this interesting change of geometry are not clear, but Parish and Johnson [46] have suggested that, since all *cis*-$R_2SnX_4 \cdot L_2$ complexes involve at least one chelating ligand and the majority are diphenyltin adducts, steric effects may be responsible for the *cis*-configuration.

Changing substituents on the ligand has very little effect on the Mössbauer parameters, i.e. change of the ligand substituents does not alter the electronic

(Continued on p. 233)

TABLE 3

^{119m}Sn MÖSSBAUER DATA FOR THE COMPLEXES AT 80 K

Complex		δ [a] (mm s^{-1})	ΔE_Q (mm s^{-1})	Structure	Ref.
$Me_2SnX_2 \cdot L_2$					
X = Cl,	L = DMSO	1.38	4.18	I	
		(1.40)	(4.16)		32
		(1.43)	(4.18)		33
		(1.52)	(4.42)		34
		(1.39)	(4.10)		43
	L = merpy	1.53	4.08	I	
	L = py	1.33	4.03	I	
		(1.27)	(3.83)		35
		(1.41)	(4.00)		36
	L_2 = AMP	1.37	3.90	I	
	L_2 = bipy	1.43	4.12	I	
		(1.45)	(4.02)		35
		(1.55)	(4.09)		37
		(1.39)	(4.08)		38
	L_2 = NiSalen	1.46	4.18	I	
		(1.50)	(4.06)		17
	L_2 = PBI	1.42	4.26	I	
	L_2 = phen	1.36	4.23	I	
		(1.48)	(4.18)		34
		(1.32)	(4.03)		37
	L_2 = DPphen	1.44	4.11	I	
		(1.49)	(4.07)		22
	L_2 = TMphen	1.28	3.93	I	
		(1.38)	(3.82)		22
	L_2 = pypy	1.46	3.68	III	
X = Br,	L_2 = bipy	1.48	4.18	I	
		(1.73)	(4.38)		34
	L_2 = PBI	1.56	4.33	I	
	L_2 = phen	1.52	4.16	I	
	L_2 = DPphen	1.39	3.90	I	
	L_2 = TMphen	1.43	4.13	I	
X = I,	L_2 = bipy	1.53	4.23	I	
		(1.73)	(4.38)		34
	L_2 = phen	1.44	4.11	I	
X = NCS,	L_2 = bipy	1.31	4.13	I	
		(1.28)	(4.09)		15
	L_2 = phen	1.28	4.18	I	
$Et_2SnX_2 \cdot L_2$					
X = F,	L_2 = phen	1.32	4.16	I	
	L_2 = TMphen	1.33	4.13	I	
X = Cl,	L = DMSO	1.52	4.21	I	
	L = merpy	1.71	4.08	I	
	L = py	1.56	4.18	I	
	L_2 = AMP	1.54	3.78	III	
	L_2 = bipy	1.53	4.03	I	
	L_2 = PBI	1.60	4.31	I	
	L_2 = phen	1.47	4.11	I	
	L_2 = Cphen	1.52	4.11	I	
	L_2 = DMphen	1.52	4.06	I	
	L_2 = DPphen	1.50	3.95	I	
	L_2 = Nphen	1.52	4.11	I	
	L_2 = Pphen	1.56	4.08	I	
	L_2 = TMphen	1.47	4.06	I	
X = Br	L_2 = bipy	1.61	3.93	I	
	L_2 = PBI	1.71	4.23	I	
	L_2 = phen	1.60	4.06	I	

TABLE 3

Complex		δ [a] (mm s^{-1})	ΔE_Q (mm s^{-1})	Structure	Ref.
	L_2 = DPphen	1.51	3.93	I	
	L_2 = TMphen	1.58	3.98	I	
X = I,	L_2 = bipy	1.69	4.03	I	
	L_2 = phen	1.71	4.18	I	
	L_2 = DPphen	1.67	3.80	III	
	L_2 = TMphen	1.69	3.93	I	
X = NCS,	L_2 = bipy	1.42	4.26	I	
	L_2 = phen	1.47	4.21	I	
$Pr_2SnX_2 \cdot L_2$					
X = F,	L_2 = phen	1.29	4.36	I	
	L_2 = TMphen	1.32	3.95	I	
X = Cl,	L = py	1.57	4.16	I	
	L_2 = bipy	1.48	4.03	I	
	L_2 = PBI	1.56	4.33	I	
	L_2 = phen	1.55	4.11	I	
	L_2 = DPphen	1.53	4.08	I	
	L_2 = TMphen	1.46	4.13	I	
X = Br,	L_2 = bipy	1.65	4.11	I	
	L_2 = PBI	1.67	4.26	I	
	L_2 = phen	1.57	4.06	I	
	L_2 = DPphen	1.58	3.98	I	
	L_2 = TMphen	1.57	4.06	I	
X = I,	L_2 = bipy	1.67	4.03	I	
	L_2 = PBI	1.71	4.21	I	
	L_2 = phen	1.70	4.01	I	
	L_2 = DPphen	1.61	3.93	I	
	L_2 = TMphen	1.62	4.21	I	
X = NCS, L	L_2 = bipy	1.50	4.31	I	
	L_2 = phen	1.44	4.26	I	
$Bu_2SnX_2 \cdot L_2$					
X = F,	L_2 = phen	1.32	4.06	I	
		(1.30)	(4.03)		15
	L_2 = TMphen	1.28	4.03	I	
X = Cl,	L_2 = AMP	1.38	3.22	III	
	L_2 = bipy	1.57	4.11	I	
		(1.56)	(3.83)		28
		(1.25)	(3.95)		39
		(1.64)	(4.10)		40
	L_2 = PBI	1.64	4.28	I	
	L_2 = phen	1.57	4.26	I	
		(1.63)	(3.94)		41
		(1.59)	(4.07)		42
	L_2 = Dphen	1.52	4.06	I	
	L_2 = TMphen	1.44	4.01	I	
X = Br,	L_2 = bipy	1.61	4.08	I	
		(1.62)	(3.95)		41
	L_2 = PBI	1.64	4.18	I	
	L_2 = phen	1.64	4.13	I	
		(1.63)	(3.94)		41
	L_2 = DPphen	1.60	4.01	I	
	L_2 = TMphen	1.61	4.08	I	
X = I,	L_2 = bipy	1.71	4.03	I	
		(1.70)	(3.82)		41
	L_2 = phen	1.67	4.06	I	
		(1.69)	(3.75)		41
X = NCS,	L_2 = bipy	1.51	4.18	I	
		(1.43)	(4.04)		28
	L_2 = phen	1.39	4.31	I	
		(1.42)	(4.18)		28

TABLE 3 (continued)

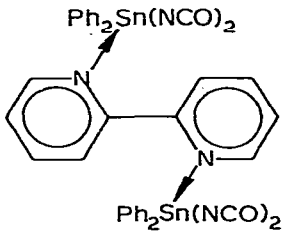
Complex		δ [a] (mm s^{-1})	ΔE_Q (mm s^{-1})	Structure	Ref.
$Ph_2SnX_2 \cdot L_2$					
X = F,	L_2 = 0.5 phen	0.68	1.98	V	
		1.22	3.04		
X = Cl,	L = DMSO	1.27	3.95	I	
		(1.30)	(3.86)		29,33
		(1.37)	(3.69)		34
		(1.23)	(3.54)		43
	L = py	1.23	3.57	III	
		(1.32)	(3.39)		30
	L_2 = AMP	0.93	2.26	II	
	L_2 = bipy	1.25	3.52	III	
		(1.22)	(3.93)		28
		(1.26)	(3.51)		30,43
		(1.35)	(3.90)		44
	L_2 = PBI	1.27	3.75	III	
	L_2 = phen	1.20	3.52	III	
		(1.21)	(3.37)		28
		(1.28)	(3.70)		44
	L_2 = Cphen	1.18	3.47	III	
	L_2 = DMphen	1.22	3.35	III	
	L_2 = DPphen	1.24	3.50	III	
	L_2 = Nphen	0.87	2.31	II	
	L_2 = Pphen	1.23	3.57	III	
	L_2 = TMphen	1.20	3.63	III	
X = Br,	L_2 = bipy	1.33	3.60	III	
		(1.33)	(3.52)		30
	L_2 = PBI	1.28	3.93	I	
	L_2 = phen	1.29	3.55	III	
	L_2 = DPphen	1.31	3.73	III	
	L_2 = TMphen	1.25	3.72	III	
X = I,	L_2 = bipy	—	—		
		(1.41)	(3.35)	III	30
	L_2 = phen	1.33	3.42	III	
	L_2 = DPphen	1.41	3.52	III	
X = NCS,	L_2 = bipy	0.80	2.26	II	
		(0.82)	(2.13)		28
	L_2 = phen	0.80	2.46	II	
		(0.81)	(2.34)		28
		(0.82)	(2.36)		45, 46
	L_2 = TMphen	0.70	2.46	II	
$Bz_2SnCl_2 \cdot phen$		1.51	3.52	III	
$Oct_2SnCl_2 \cdot L_2$					
	L_2 = bipy	1.52	4.11	I	
		(1.59)	(4.00)		32
	L_2 = PBI	1.64	4.23	I	
	L_2 = phen	1.57	4.16	I	
		(1.56)	(4.11)		32
	L_2 = DPphen	1.57	3.80	III	
	L_2 = TMphen	1.44	4.11	I	

[a] Relative to $CaSnO_3$.

situation at the tin atom to a large degree. (See, for example, $R_2SnCl_2 \cdot L_2$ where R = Et, Ph and L_2 = phen and substituted phen). This is in agreement with the work of Honnick et al. [22], who observed a similar lack of effect for a series of

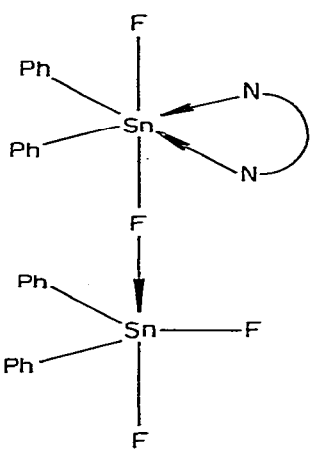
dimethyltin dichloride complexes with 1,10-phenanthroline and substituted phenanthroline ligands.

The observation of two quadrupole split doublets in the Mössbauer spectrum of $Ph_2SnF_2 \cdot 0.5$ phen is most interesting. Mufti and Poller [49] have reported the preparation of $Ph_2Sn(NCO)_2 \cdot 0.5$ bipy and have proposed it to have the structure IV, which contains a bridging bipyridyl group. Phenanthroline, however, is a



(IV)

rigid ligand and so cannot behave in a similar manner. The Mössbauer parameters obtained for $Ph_2SnF_2 \cdot 0.5$ phen are consistent with the presence of a *cis*-R_2SnX_4 octahedral group ($\delta = 0.68$; $\Delta E_Q = 1.98$ mm s^{-1}) and a *cis*-R_2SnX_3 trigonal bipyramidal group ($\delta = 1.22$; $\Delta E_Q = 3.04$ mm s^{-1}). Based on this data, we suggest that this complex has the structure V, which contains a bridging fluorine between the 6-coordinate and 5-coordinate tin atoms.



(V)

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