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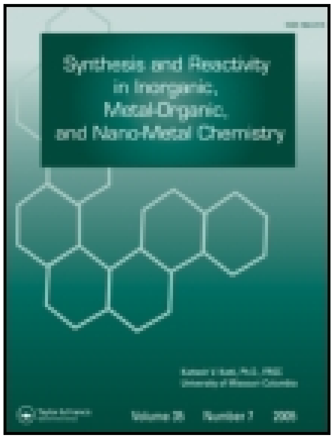

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SYNTHESIS OF NEW TIN(IV) COMPOUNDS OF SUBSTITUTED DIPHENYLSULFIDE DERIVATIVES AND THEIR COMPLEXES WITH SOME NEUTRAL LIGANDS

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SYNTHESIS OF NEW TIN(IV) COMPOUNDS OF SUBSTITUTED DIPHENYLSULFIDE DERIVATIVES AND THEIR COMPLEXES WITH SOME NEUTRAL LIGANDS

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ABSTRACT

Some new tin(IV) compounds of the general formula $Sn(SC_6H_4R)_4$, where $R = o\text{-}NH_2$, p-Me, p-Bu-t have been obtained from the direct reaction of $(RC_6H_5S)_2$ and tin metal in the molar ratio 2:1 in refluxing toluene. Similarly, a mixture of tin $(RC_6H_5S)_2$ and iodine in 1.0:1.5:0.5 or 1.0:1.0:1.0 molar ratios in refluxing toluene leads to the formation of $Sn(SC_6H_4R)_3I$ or $Sn(SC_6H_4R)_2I_2$, respectively. Complexes of the new tin compounds with triphenylphosphine, 4-picoline, 1,10-phenanthroline and 2,2′-bipyridine have been synthesized by the direct reaction between the tin compound and the

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neutral ligand. The tin compounds and their adducts have been characterized physio-chemically and spectroscopically.

INTRODUCTION

Compounds of both main group and transition metals with sulfur donor ligands are a subject of current interest. Substituted disulfide derivatives of main group metals have received much less attention than those of the corresponding transition metals. The chemistry of $Sn(SR)_4$, $R_xSn(SR')_{4-x}$, tin(II) thiolate and of the corresponding lead compounds have been reviewed[1–4]. For indium, $In(SC_6H_5)_3$ has been prepared either by metathesis of $InCl_3$ and $Na(SC_6H_5)$[5] or, more simply, by a direct thermal reaction between indium or tin metal with $(C_6H_5E)_2$ (E = S, Se) in refluxing toluene to give the neutral compounds $In(EC_6H_5)_3$ or $Sn(EC_6H_5)_4$, respectively[6]. The synthesis of dihalobis(2-pyridinethiolato)tin(IV) by an oxidative-addition reaction of di-2-pyridyldisulfide to tin(II) halides represents an example of preparing other similar dihalodithiolatotin(IV) compounds[7]. In our recent article, we have describe the direct reaction between bismuth metal with $(o\text{-}H_2NC_6H_4S)_2$ and $(p\text{-}MeC_6H_4S)_2$ in refluxing toluene to give the corresponding bismuth compounds $Bi(SC_6H_4NH_2\text{-}o)_3$ and $Bi(SC_6H_4Me\text{-}p)_3$, respectively[8].

In the present work, the oxidative addition of the -S-S- linkage of $(RC_6H_4S)_2$, R = o-NH_2, p-Me, p-Bu-t to tin metal alone and to tin metal in the presence of iodine in different molar ratios are discussed. Also reported is the synthesis of complexes of the new tin(IV) compounds with some neutral donor ligands, *i.e.*, triphenylphosphine (PPh_3), 4-picoline (4-pic), 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy), as a part of our continued interest in investigating this type of interaction between tin metal and various donor ligands[9–12].

EXPERIMENTAL

Measurements

IR spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer over the range 200–4000 cm^{-1} using CsI pellets. Analyses of the compounds were carried out with a type 1106 (Carlo Erba) CHN analyser. UV-Vis. spectra were recorded on a UV 1160 Shimadzu UV-Vis. recording spectrophotometer. Conductivity measurements were obtained in 10^{-3} M, solutions of the compounds in DMF at room temperature (25 °C), using a model 4070 Jenway conductivity meter.

Starting Materials

Tin metal, toluene and substituted thiols were commercial products (Fluka) and used as supplied. The disulfides, $(RC_6H_4S)_2$, R = *o*-NH_2, *p*-Me, *p*-Bu-*t*, were synthesized by standard methods[13].

Preparation of Tin(IV) Compounds

$Sn(SC_6H_4R)_4$. A mixture of finely cut tin metal (0.12 g, 1.0 mmol) and the disulfide $(RC_6H_4S)_2$ (2.0 mmol) in toluene (30 mL) was refluxed for 4 h. The reaction mixture was filtered through Celite and the resultant yellow solution was reduced to *ca.* 10 mL by evaporation under reduced pressure. The solid thus obtained, after cooling in an ice-bath, was collected by filtration, washed with petroleum ether (60–80 °C) and dried *in vacuo*.

$Sn(SC_6H_4R)_3I$. Finely cut tin metal (0.12 g, 1.0 mmol) was refluxed with the disulfide $(RC_6H_4S)_2$ (1.5 mmol) and iodine (0.064 g, 0.50 mmol) in toluene (30 mL) for 4 h. The reaction mixture was filtered through Celite and the resultant yellow or brown solution was reduced to *ca.* 10 mL by evaporation under reduced pressure. The solid thus obtained, after cooling in an ice-bath, was collected by filtration, washed with petroleum ether (60–80 °C) and dried *in vacuo*.

$Sn(SC_6H_4R)_2I_2$. These compounds were prepared in a manner similar to the $Sn(SC_6H_4R)_3I$ compounds, except that equimolar quantities of both tin, disulfide and iodine (1.0 mmol) were used.

Preparation of $Sn(SC_6H_4R)_4 \cdot 2L$ or L′ Complexes

$Sn(SC_6H_4NH_2\text{-}o)_4 \cdot 2PPh_3$. The tin compound $Sn(SC_6H_4NH_2\text{-}o)_4$ (0.54 g, 1.0 mmol) was added to a solution of the ligand PPh_3 (0.52 g, 2.0 mmol) in *n*-pentane (20 mL) at room temperature. The reaction mixture was stirred for 4 h, during which time a precipitate formed. It was collected by filtration, washed with *n*-pentane and dried *in vacuo*.

$Sn(SC_6H_4NH_2$-*o*$)_4 \cdot 2$(4-pic). The tin compound $Sn(SC_6H_4NH_2$-*o*$)_4$ (0.54 g, 1.0 mmol) and 4-picoline (0.186 g, 2.0 mmol) was mixed in methanol (15 mL) to yield a green oil, which became a solid on stirring for *ca.* 4 h. The solid was then collected by filtration, washed 3 times with 5 mL of methanol and dried *in vacuo*.

$Sn(SC_6H_4NH_2$-*o*$)_4 \cdot$ phen. The tin compound $Sn(SC_6H_4NH_2$-*o*$)_4$ (0.54 g, 1.0 mmol) was stirred with 1,10-phenanthroline (0.18 g, 1.0 mmol) in methanol (10 mL) for *ca.* 4 h, during which time a red-orange oil formed, which became a solid upon stirring for further 2 h. The solid was filtered off, washed 3 times with 5 mL of methanol and dried *in vacuo*.

$Sn(SC_6H_4NH_2$-*o*$)_4 \cdot$ bip. The tin compound $Sn(SC_6H_4NH_2{}'$-*o*$)_4$ (0.54 g, 1.0 mmol) was stirred with 2,2′-bipyridine (0.16 g, 1.0 mmol) in benzene (20 mL) for *ca.* 2 h, during which time a yellow oily layer was separated from the colourless solution, and the colourless layer was decanted. The oil was triturated with diethyl ether (30 mL) until it solidified and the resultant yellow solid was filtered, washed with ether and dried *in vacuo*.

The analogous complexes with R = *p*-Me and *p*-Bu-*t* were prepared similarly.

RESULTS AND DISCUSSION

The method described in this work clearly represents a simple and efficient one-pot synthesis of a number of $Sn(SC_6H_4R)_4$ compounds, where R is *o*-NH_2, *p*-Me or *p*-Bu-*t*, by a direct oxidative addition reaction of the disulfides to tin metal. These reactions are noticeably simpler than those used in the past for the preparation of $M(SPh)_n$ compounds of main group elements, involving metathesis reactions of MCl_n with Na(SPh), Li(SPh) or Mg(SPh})$_2$[5,14]. Also, the thermal reactions are clearly different from those involving the electrochemical oxidation of metal anodes in non-aqueous media, since the latter method is known to give benzenthiolates of zinc, tin and thallium[15,16].

The most likely primary reaction is that shown in eq (1), giving a 1+ or 2+ oxidation state species. In the case of bismuth, indium and tin, this would be followed by the reaction of eq (2).

$$2M + (RS)_2 \longrightarrow 2M(SR) \qquad (1)$$

$$2M(SR) + (n-1)(RS)_2 \longrightarrow 2M(SR)_n \qquad (2)$$

$$(M = Bi \text{ or } In, n = 3 \text{ and } M = Sn,\ n = 4)$$

The oxidative insertion process of eq (2) is clearly analogous to the known reactions involving the conversions[7,8]:

$$In^0 \longrightarrow In^{3+} \quad \text{or} \quad Sn^{2+} \longrightarrow Sn^{4+}$$

The analytical data of the tin compounds $Sn(SC_6H_4R)_4$ (R = *o*-NH_2, *p*-Me, *p*-Bu-*t*) and their adducts with the neutral ligands 2L and L′ are given in Table I. These data are in good agreement with the proposed formulas. All of the compounds are air-stable at room temperature and insoluble in the common organic solvents. They are, however, soluble in dimethylformamide (DMF) and other donor solvents.

The most important diagnostic features of the IR spectra are listed in Table II. The IR bands of the free disulfide species are included here for comparison. At a quick glance at Table II, one can see that a drastic decrease in the $\nu(NH_2)$ frequency of the free disulfide $(o\text{-}NH_2C_6H_4S)_2$ from 3395 to *ca.* 3260 cm^{-1} upon forming $Sn(SC_6H_4NH_2\text{-}o)_xI_{4\text{-}x}$, x = 4,3,2, *i.e.*, compounds **(1)**, **(4)** and **(7)**, respectively. This may well be attributed to intramolecular coordination between the NH_2 group and Sn, in which two NH_2 groups are bonded to metal through the nitrogen atoms[17], in addition to four sulfur atoms forming an octahedral geometry around the tin atom. It seems likely that this coordination is only temporary in these compounds because when reacted with the neutral ligands 2L or L′, the former coordination with NH_2 is displaced by the stronger intermolecular coordination with P or N atoms of the neutral ligands (*vide infra*). The frequency of the (C-S) band observed at 1000–1040 cm^{-1} for the free disulfides is only slightly increased upon forming the corresponding tin compounds (Table II), which indicates that the tin compounds $Sn(SC_6H_4NH_2\text{-}o)_xI_{4\text{-}x}$ had formed. Further support for this is provided by the appearance of new bands at about 323–342 cm^{-1} and 400–440 cm^{-1} which are tentatively attributed to (Sn-S) and (Sn-N), respectively. Furthermore, the IR spectra of the complexes $Sn(SC_6H_4R)\cdot 2L$ or L′, *i.e.*, complexes (**10**)–(**21**) (Table I and II) show a clear strong band at *ca.* 3385 cm^{-1}, which is assigned to uncoordinated (NH_2) while the (C-S) band which is observed at 1018–1060 cm^{-1} indicates that the S atom is still bonded to Sn and no drastic change was observed on going from the tin compound to its complex. Similarly, the IR band at 323–336 cm^{-1} in the complexes (**10**)–(**21**) is assigned to (Sn-S) while the (Sn-N) absorptions are dependent on the free ligand used. The (Sn-N) band at 264–300 cm^{-1} is due to phen and bipy ligands [complexes (**16**)–(**21**)] and this is in a good agreement with the reported values for InX_3.1.5phen (X = Cl, Br)[18,19] which fall in the range 220–290 cm^{-1}. With the ligand 4-pic, the (Sn-N) band was observed at 429–446 cm^{-1} [complexes (**11**), (**13**) and (**15**)] and the (Sn-P) band for complexes (**10**), (**12**) and (**14**) was observed at 488–514 cm^{-1}

Table I. Physical Properties and Analyses of $Sn(SC_6H_4R)_xI_{4\text{-}X}$ (x = 4, 3,2) Compounds and $Sn(SC_6H_4R)_4 \cdot 2L$ or L′ Complexes[a]

Seq.	Compound	Color	M.p. (°C)	Empirical Formula	Formula Weight	Yield (%)	Analysis: Found (Calcd.)%			Cond.[b] Λ_M
							C	H	N	
(1)	$Sn(SC_6H_4NH_2\text{-}o)_4$	yellow	106–108	$C_{24}H_{24}N_4S_4Sn$	614.6	97	47.02 (46.85)	4.10 (3.90)	8.88 (9.11)	32
(2)	$Sn(SC_6H_4Me\text{-}p)_4$	yellow	86–88	$C_{28}H_{28}S_4Sn$	610.7	83	55.12 (55.02)	4.71 (4.58)		15
(3)	$Sn(SC_6H_4Bu^t\text{-}p)_4$	yellow	100–102	$C_{40}H_{52}S_4Sn$	778.7	96	61.14 (61.14)	6.62 (6.67)		23
(4)	$Sn(SC_6H_4NH_2\text{-}o)_3I$	golden yellow	185–187	$C_{18}H_{18}N_3S_3ISn$	617.7	98	35.11 (34.97)	3.09 (2.91)	6.55 (6.80)	63
(5)	$Sn(SC_6H_4Me\text{-}p)_3I$	yellow	300[c]	$C_{21}H_{21}S_3ISn$	614.7	73	40.87 (41.00)	3.51 (3.42)		59
(6)	$Sn(SC_6H_4Bu^t\text{-}p)_3I$	yellow	>300	$C_{30}H_{39}S_3ISn$	740.7	60	48.54 (48.60)	5.19 (5.26)		67
(7)	$Sn(SC_6H_4NH_2\text{-}o)_2I_2$	brown	193–196	$C_{12}H_{12}N_2S_2I_2Sn$	620.7	82	22.89 (23.20)	2.08 (1.93)	4.29 (4.51)	90
(8)	$Sn(SC_6H_4Me\text{-}p)_2I_2$	orange	124–126	$C_{14}H_{14}S_2I_2Sn$	618.7	69	27.10 (27.15)	2.28 (2.26)		101
(9)	$Sn(SC_6H_4Bu^t\text{-}p)_2I_2$	orange	>360	$C_{20}H_{26}S_2I_2Sn$	702.7	65	34.20 (34.15)	3.65 (3.70)		112
(10)	$Sn(SC_6H_4NH_2\text{-}o)_4 \cdot 2PPh_3$	yellow	66–68	$C_{60}H_{54}N_4S_4P_2Sn$	1138.7	86	63.13 (63.23)	4.80 (4.74)	4.87 (4.92)	16
(11)	$Sn(SC_6H_4NH_2\text{-}o)_4 \cdot 2(4\text{-}Pic)$	yellow	94–95	$C_{36}H_{38}N_6S_4Sn$	800.7	65	52.95 (5395)	4.54 (4.75)	10.39 (10.49)	20
(12)	$Sn(SC_6H_4Me\text{-}p)_4 \cdot 2PPh_3$	pale yellow	76–78	$C_{64}H_{58}P_2S_4Sn$	1134.7	96	66.81 (67.68)	5.09 (5.11)		17
(13)	$Sn(SC_6H_4Me\text{-}p)_4 \cdot 2(4\text{-}Pic)$	yellow	90–92	$C_{40}H_{42}N_2S_4Sn$	796.7	80	60.17 (60.02)	5.19 (5.27)	3.62 (3.51)	18
(14)	$Sn(SC_6H_4Bu^t\text{-}p)_4 \cdot 2PPh_3$	pale yellow	60–62	$C_{76}H_{82}P_2S_4Sn$	1302.7	92	70.08 (70.00)	6.38 (6.29)		10
(15)	$Sn(SC_6H_4Bu^t\text{-}p)_4 \cdot 2(4\text{-}Pic)$	pale yellow	90–92	$C_{52}H_{66}N_2S_4Sn$	964.7	82	64.65 (64.68)	6.82 (6.29)	2.92 (2.90)	24

(16) $Sn(SC_6H_4NH_2\text{-}o)_4 \cdot phen$	orange red	100–102	$C_{36}H_{32}N_6S_4Sn$	794.7	89	53.99 (54.36)	4.10 (4.03)	10.51 (10.57)	22
(17) $Sn(SC_6H_4NH_2\text{-}o)_4 \cdot bipy$	pale yellow	113–114	$C_{34}H_{32}N_6S_4Sn$	770.7	78	53.54 (52.94)	4.22 (4.15)	10.66 (10.90)	25
(18) $Sn(SC_6H_4Me\text{-}p)_4 \cdot phen$	lemon	152–154	$C_{40}H_{36}N_2S_4Sn$	790.7	90	60.39 (60.71)	4.69 (4.55)		16
(19) $Sn(SC_6H_4Me\text{-}p)_4 \cdot bipy$	orange	98–100	$C_{38}H_{36}N_2S_4Sn$	766.7	98	60.04 (59.48)	4.82 (4.70)	3.62 (3.65)	14
(20) $Sn(SC_6H_4Bu^t\text{-}p)_4 \cdot phen$	lemon	198–200	$C_{52}H_{60}N_2S_4Sn$	958.7	93	64.99 (65.09)	6.29 (6.26)	2.85 (2.92)	10
(21) $Sn(SC_6H_4Bu^t\text{-}p)_4 \cdot bipy$	lemon	112–115	$C_{50}H_{60}N_2S_4Sn$	934.7	75	64.09 (64.19)	6.39 (6.42)	2.98 (3.00)	19

[a] For R, L and L′, see Fig. 1.

[b] Conductivity measured in DMF ($ohm^{-1} mol^{-1} cm^2$).

[c] Compound melts with decomposition.

Table II. IR Absorptions and Electronic Spectral Data for the Disulfides, Tin(IV) Compounds, and Their Complexes

Compound[a]	Selected IR Bands (cm^{-1})[b]					U.V./Vis. Bands
Seq.	ν(NH_2)	ν(C-S)	ν(Sn-S)	ν(Sn-N)	ν(Sn-P)	λ_{max} (nm) (ε_{max} ($dm^3\,mol^{-1}\,cm^{-1}$))
(o-$NH_2C_6H_4S)_2$[c]	3395 s	1040 s				284 (12100), 348 (23400)
(p-$MeC_6H_4S)_2$[c]		1015 s				250 (6500), 294 (23930)
(p-$Bu^tC_6H_4S)_2$[c]		1000 s				247 (5610), 298 (24920)
(**1**)	3264 w	1058 s	323 m	441 s		280 (24700), 308 (16800), 383 (13780)
(**2**)		1027 s	342 s			268 (25480), 310 (18720)
(**3**)		1112 s	333 s			265 (21420), 348 (9130)
(**4**)	3260 m	1060 s	329 w	[d]		254 (13710), 344 (2085)
(**5**)		1032 s	329 w			270 (25400), 325 (21280)
(**6**)		1115 s	336 w			244 (7810), 298 (23780)
(**7**)	3216 w	1069 s	340 w	399 w		281 (21900), 378 (22980)
(**8**)		1033 m	336 w			283 (24930), 339 (24860)
(**9**)		1020 s	340 m			252 (8230), 378 (16720)
(**10**)	3388 s	1055 s	323 m		514 w	290 (22810), 381 (25730)
(**11**)	3378 s	1060 s	325 m	446 b		283 (24940), 346 (15680), 371 (18250)
(**12**)		1028 m	308 w		492 s	281 (22370), 387 (19870)
(**13**)		1033 s	315 w	443 m		268 (23180), 344 (11270)
(**14**)		1020 s	335 m		488 b	270 (14820), 318 (24910), 365 (20900)
(**15**)		1018 s	336 w	429 m		267 (14500), 299 (21730), 356 (12310)
(**16**)	3387 s	1050 s	326 m	264 w		289 (24940), 381 (16780)

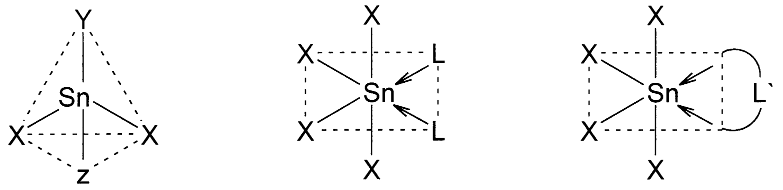
(**17**)	3390 s	1054 s	326 m	463 w	285 (23890), 361 (17520), 381 (21730)
(**18**)		1027 m	329 w	288 w	283 (25400), 376 (16970)
(**19**)		1032 s	335 m	265 sh	270 (24910), 313 (16840), 361 (10190)
(**20**)		1018 s	326 w	275 w	273 (24170), 303 (12340), 346 (7630)
(**21**)		1018 s	333 w	300 w	263 (21300), 371 (13860)

[a] For the compounds (1)–(21), see Fig. 1 and Table I.

[b] For IR data: s, strong; m, medium; w, weak; b, broad; sh, shoulder bands.

[c] Data for disulfides included here for comparisons.

[d] Band not observed.



X = Y = Z = SC_6H_4-R	X = SC_6H_4R; R = *o*-NH_2	X = SC_6H_4R; R = *o*-NH_2
(**1**) R = *o*-NH_2	(**10**) L = PPh_3	(**16**) L′ = phen
(**2**) R = *p*-Me	(**11**) L = 4-pic	(**17**) L′ = bipy
(**3**) R = *p*-Bu-*t*	R = *p*-Me	R = *p*-Me
Y = I, X = Z = SC_6H_4R	(**12**) L = PPh_3	(**18**) L′ = phen
(**4**) R = *o*-NH_2	(**13**) L = 4-pic	(**19**) L′bipy
(**5**) R = *p*-Me	R = *p*-Bu-*t*	R = *p*-Bu-*t*
(**6**) R = *p*-Bu-*t*	(**14**) L = PPh_3	(**20**) L′ = phen
Y = Z = I, X = SC_6H_4R	(**15**) L = 4-pic	(**21**) L′ = bipy
(**7**) R = *o*-NH_2		
(**8**) R = *p*-Me		
(**9**) R = *p*-Bu-*t*		

Figure 1. The suggested structures for the tin(IV) compounds and their complexes with neutral ligands. For the expected structures of compounds (**1**), (**4**) and (**7**), see text.

(Table II); similar observations were reported by Roundhill[20]. It is concluded that the tin complexes $Sn(SC_6H_4\text{-}R)_4 \cdot 2L$ or L′ obtained in this study might well have octahedral structures (Fig. 1), probably with some distortion. A similar study of complexes such as $Sn(SC_6H_5)_4 \cdot$ bipy by X-ray single crystal diffraction showed it to have a distorted octahedral SnS_4N_2 unit[5].

The UV/Vis. spectra of the tin compounds and their complexes are similar to one another but different from those of the free disulfides (Table II). The broad bands observed in the range 247–348 nm are due to $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the free disulfides, while a new additional band was observed for almost all tin compounds and their complexes in the range 356–387 nm. This band may be attributed to the charge transfer from filled ligand orbitals to the vacant metal orbitals.

The molar conductivities of 10^{-3} M solutions of the tin compounds and their complexes (Table I) indicate that they are non-electrolytes in DMF[21], except for the compounds (**4**)–(**6**) which are 1:1 electrolytes and compounds (**7**)–(**9**) which are 1:2 electrolytes. This could be due to displacement of iodide ion/ions in the compounds by DMF[22,23].

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