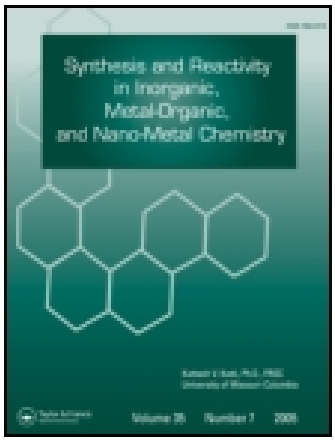

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Highly Versatile Synthesis of Some Organotin(IV) Complexes of 2-Hydroxyacetophenone Semicarbazone and Thiosemicarbazone

M. S. Singh [a] & P. K. Singh [a]
[a] Department of Chemistry , D.D.U. Gorakhpur University , Gorakhpur, 273 009 (U.P.), India
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Highly Versatile Synthesis of Some Organotin(IV) Complexes of 2-Hydroxyacetophenone Semicarbazone and Thiosemicarbazone

M. S. Singh* and P. K. Singh

Department of Chemistry, D.D.U. Gorakhpur University,
Gorakhpur, India

ABSTRACT

Some di- and triorganotin(IV) complexes of 2-hydroxyacetophenone semicarbazone (H_2MeSSC) and thiosemicarbazone (H_2MeSTSC) have been synthesized by the reactions of corresponding di- and triorganotin(IV) chlorides with the anionic form of the ligands in desired molar ratios. All the compounds have been characterized by elemental analyses and spectral (IR, ^{1}H, ^{13}C and ^{119}Sn NMR) studies.

Key Words: Organotin(IV) complexes; 2-Hydroxyacetophenone semicarbazone; Thiosemicarbazone; Spectral studies; Dianion.

*Correspondence: M. S. Singh, Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur 273 009 (U.P.), India; E-mail: singhms1960@rediffmail.com.

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INTRODUCTION

The chemistry of organotin compounds recently has developed not only as reagents[1] but also as intermediates in organic synthesis.[2,5] Semicarbazones and thiosemicarbazones are versatile ligands in both neutral and anionic forms.[6,7] Chelates of organotin(IV) moieties with N, O and S donor ligands[8–13] have received much attention during the last few years. Certain penta-coordinated and hexa-coordinated organotin(IV) complexes,[14] a number of oximates[15,16] and complexes of isatin 3- and 2-thiosemicarbazones[17] have been reported in the literature having interesting stereochemistry.[18,19] An overview of the development of antitumour organotin derivatives has been presented and discussed for selected classes of compounds.[20] Organotin compounds having the general formulae R_nSnX_{4-n} are almost biologically active.[21–25] The nature of the alkyl group is of prime importance in determining their toxicity towards particular living species.[26] A recent review deals with metal complexes of semicarbazones and thiosemicarbazones.[27] Thus, in view of the synthetic and biological importance of organotin(IV) compounds and in continuation of our recent report on organotin(IV),[28–38] we report herein the synthesis and characterization of some new organotin(IV) derivatives of 2-hydroxyacetophenone semicarbazone and thiosemicarbazone (Figure 1).

EXPERIMENTAL

All reactions were carried out under argon atmosphere and analytical grade chemicals were used. Solvents were purified and dried according to standard procedures.[39,40] All melting points are uncorrected. The progress of reactions was monitored by TLC on silica gel. Elemental analyses were performed by the Central Drug Research Institute, Lucknow. Tin in the complexes was determined by a gravimetric method.[41] IR spectra were recorded on a Perkin–Elmer model 377 spectrometer in the range 4000–200 cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded at 270.13 and 67.93

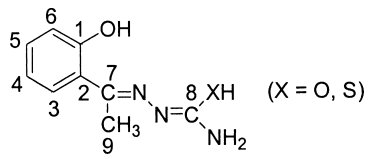

Figure 1. Structure of the ligands.

MHz, respectively, on a Bruker AM 270 instrument. The ^{119}Sn NMR spectra were recorded at 186.50 MHz on a Bruker WM 500 instrument. Chemical shifts are quoted in ppm downfield from TMS for ^{1}H and relative to tetramethyltin for ^{119}Sn and referenced to residual protons of $CDCl_3$ ($\delta = 7.24$) for ^{1}H NMR. The ligands were synthesized by the condensation of 2-hydroxyacetophenone and semicarbazide/thiosemicarbazide in 1:1 molar ratio.[26]

Reaction of Triphenyltin Chloride with the Sodium Salt of 2-Hydroxyacetophenone Semicarbazone in 1:1 Molar Ratio

Sodium hydride (0.048 g, 2.00 mmols) and 20 mL of dry isopropanol were placed in a 100 mL three-necked, round-bottomed flask equipped with an efficient magnetic stirrer, an addition funnel, a condenser and two-way balloon system. The mixture was stirred for about half an hour till a clear solution of sodium isopropoxide was obtained. 2-Hydroxyacetophenone semicarbazone (0.420 g, 2.00 mmols) in 25 mL of dry benzene was then added slowly, and the mixture was refluxed. After 30 minutes a pinkish colour was obtained which changed to light yellow after 2 h. The contents were allowed to attain room temperature. A solution of triphenyltin(IV) chloride (0.789 g, 2.00 mmols) in benzene (20 mL) was added dropwise. After complete addition, the contents were refluxed further for 2 h to ensure the completion of the reaction, during which no specific change was observed. The mixture was then filtered to remove the NaCl formed during the reaction. Removal of the solvent from the filtrate under reduced pressure on a rotary evaporator gave the desired compound as yellow solid, which was recrystallized from a benzene–petroleum ether (2:1; 40–60°) mixture.

All other organotin(IV) derivatives of H_2MeSSC and H_2MeSTSC were synthesized analogously as described above in the desired molar ratios (Tables 1 and 2).

RESULTS AND DISCUSSION

Triorganotin(IV) and diorganotin(IV) derivatives of 2-hydroxyacetophenone semicarbazone and thiosemicarbazone have been synthesized by the reaction of corresponding tri- or diorganotin(IV) chlorides with the sodium salt of the ligand (prepared in situ) in the desired molar ratios in Eqs. 1 and 2.

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Table 1. Synthetic and analytical data of compounds (**1**)–(**8**).

	Reactants g (mmol)						Analysis: % found (calcd.)				
Compound	L	NaH	R_xSn Cl_{4-x}	Molar ratio	Yield (%)	M.p. (°C)	C	H	N	Sn	Cl
(**1**) $C_{21}H_{37}N_3O_2Sn$	0.39	0.048	0.651	1:1:1	80	176	59.55	4.41	7.62	21.62	–
(482)	(2.0)	(2.0)	(2.0)				(59.78)	(4.61)	(7.75)	(21.95)	
(**2**) $C_{27}H_{25}N_3O_2Sn$	0.39	0.048	0.771	1:1:1	81	178	52.13	7.41	8.50	24.89	–
(542)	(2.0)	(2.0)	(2.0)				(52.28)	(7.68)	(8.71)	(24.69)	
(**3**) $C_{11}H_{16}ClN_3O_2Sn$	0.39	0.048	0.439	1:1:1	83	181	35.23	4.13	11.28	31.87	9.62
(376.50)	(2.0)	(2.0)	(2.0)				(35.06)	(4.25)	(11.15)	(31.61)	(9.43)
(**4**) $C_{21}H_{20}ClN_3O_2Sn$	0.39	0.048	0.688	1:1:1	76	176	50.23	4.18	8.23	23.49	6.97
(500.50)	(2.0)	(2.0)	(2.0)				(50.35)	(4.00)	(8.39)	(23.78)	(7.09)
(**5**) $C_{17}H_{28}ClN_3O_2Sn$	0.39	0.048	0.608	1:1:1	78	183	44.18	5.91	9.03	25.99	7.97
(460.50)	(2.0)	(2.0)	(2.0)				(44.30)	(6.08)	(9.12)	(25.84)	(7.71)
(**6**) $C_{11}H_{15}N_3O_2Sn$	0.39	0.096	0.439	1:2:1	82	182	38.57	4.27	12.22	35.17	–
(340)	(2.0)	(4.0)	(2.0)				(38.82)	(4.41)	(12.35)	(35.00)	
(**7**) $C_{21}H_{19}N_3O_2Sn$	0.39	0.096	0.688	1:2:1	85	179	54.16	3.97	9.19	25.84	–
(464)	(2.0)	(4.0)	(2.0)				(54.31)	(4.09)	(9.05)	(25.65)	
(**8**) $C_{17}H_{27}N_3O_2Sn$	0.39	0.096	0.608	1:2:1	78	182	48.03	6.17	9.76	27.97	–
(424)	(2.0)	(4.0)	(2.0)				(48.11)	(6.37)	(9.90)	(28.07)	

Table 2. Synthetic and analytical data of compounds (**9**)–(**16**).

Compound	Reactants g (mmol)			Molar ratio	Yield (%)	M.p. (°C)	Analysis: % found (calcd.)					
	L	NaH	R_xSnCl_{4-x}				C	H	N	S	Sn	Cl
(**9**) $C_{21}H_{37}N_3OSSn$ (498)	0.42 (2.0)	0.048 (2.0)	0.651 (2.0)	1:1:1	76	160	58.17 (58.06)	4.32 (4.48)	7.63 (7.53)	5.63 (5.73)	21.47 (21.33)	–
(**10**) $C_{27}H_{25}N_3OSSn$ (558)	0.42 (2.0)	0.048 (2.0)	0.771 (2.0)	1:1:1	81	163	50.53 (50.60)	7.26 (7.43)	8.31 (8.43)	6.50 (6.42)	23.66 (23.89)	–
(**11**) $C_{11}H_{16}ClN_3OSSn$ (392.50)	0.42 (2.0)	0.048 (2.0)	0.439 (2.0)	1:1:1	69	150	33.41 (33.63)	4.01 (4.08)	10.52 (10.70)	8.07 (8.15)	30.59 (30.32)	9.13 (9.04)
(**12**) $C_{21}H_{20}ClN_3OSSn$ (516.50)	0.42 (2.0)	0.048 (2.0)	0.688 (2.0)	1:1:1	76	164	48.49 (48.79)	3.59 (3.87)	8.27 (8.13)	6.23 (6.19)	23.17 (23.04)	6.63 (6.87)
(**13**) $C_{17}H_{28}ClN_3OSSn$ (476.50)	0.42 (2.0)	0.048 (2.0)	0.608 (2.0)	1:1:1	78	158	42.58 (42.81)	5.59 (5.88)	8.62 (8.81)	6.43 (6.71)	24.78 (24.97)	7.59 (7.45)
(**14**) $C_{11}H_{15}N_3OSSn$ (356)	0.42 (2.0)	0.096 (4.0)	0.439 (2.0)	1:2:1	76	100	37.22 (37.08)	4.37 (4.21)	11.52 (11.80)	8.73 (8.99)	33.67 (33.43)	–
(**15**) $C_{21}H_{19}N_3OSSn$ (480)	0.42 (2.0)	0.096 (4.0)	0.688 (2.0)	1:2:1	85	154	52.17 (52.50)	3.63 (3.96)	8.58 (8.75)	6.43 (6.67)	24.93 (24.79)	–
(**16**) $C_{17}H_{27}N_3OSSn$ (440)	0.42 (2.0)	0.096 (4.0)	0.608 (2.0)	1:2:1	78	148	46.21 (46.36)	6.03 (6.14)	9.23 (9.55)	7.39 (7.27)	27.22 (27.05)	–

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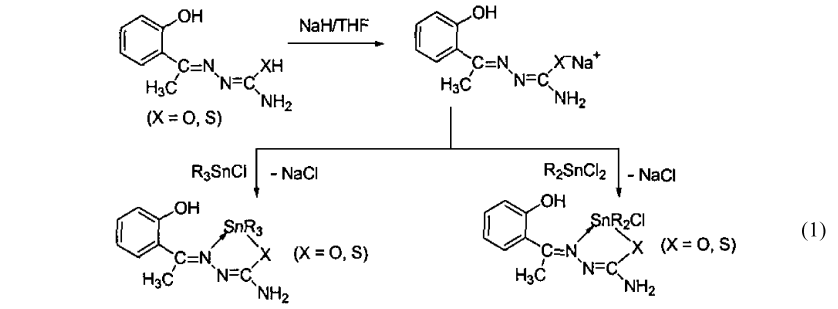
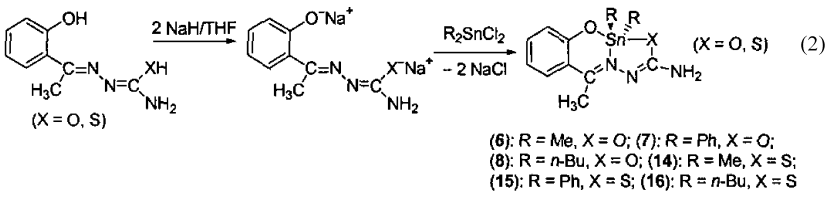


(1)



(2)

Eqs. 1 and 2 show the initial formation of the monoanion and dianion which attack the corresponding tri- and diorganotin(IV) chlorides leading to the formation of the desired compounds. The weight of the recovered salt is consistent with the various stoichiometric ratios of the reactions. All of these compounds are soluble in common organic and coordinating solvents e.g. C_6H_6, CH_2Cl_2 $CHCl_3$, THF, DMF and DMSO etc.

Infrared Spectra

The IR spectra of the complexes have been compared with the ligand and from the shifts in frequency and/or from the intensity lowering, the coordination sites have been ascertained. The IR spectrum of the ligand shows bands in the region 3496, 3442–3244, 1615 and 1024 cm^{-1} assignable to ν(N–OH), ν(NH_2), ν(C=N) and ν(C=S), respectively. The strong bands observed at 3442, 3276 and 3244 cm^{-1} in all the complexes rule out coordination of the NH_2 group to the metal. The presence of OH vibrations in all the complexes derived from the monoanion by Eq. 1 shows that the phenolic OH group is non-ionized and uncoordinated, whereas in complexes derived from the dianion by Eq. 2, the OH bands are absent indicating deprotonation and metallation of both the phenolic and enolic

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OH groups. This view is corroborated by the appearance of new bands in the region 585–568 cm^{-1}, ascribable to the (Sn–O) vibration.[28–31,41] Bands due ν(C=O) and ν(C=S) modes in the ligands are observed at 1686 and 1024 cm^{-1}, respectively. These disappear in the spectra of the complexes suggesting thereby enolization[14] of the ligands and their chelation through enolic oxygen or thiolic sulfur. Further, some new bands observed in the far-IR region of the metal complexes at $\sim$575, 415 and 360 $cm^{-1}$are assigned to ν(Sn–O),[28,29] ν(Sn–N)[30,31] and ν(Sn–S)[10,11] modes, respectively (Tables 3 and 4).

One strong band in both ligands at 1600 ± 10 cm^{-1} due to ν(C=N) is split into two sharp bands at 1620 ± 10 cm^{-1} and 1585 cm^{-1} on complex formation. The band at 1620 ± 10 cm^{-1} in the metal complexes indicates the cordination of the azomethine nitrogen to the tin atom, whereas the other one is due to an uncoordinated azomethine group.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the complexes exhibit the usual features. The signal due to phenolic OH of the ligands that appears around 11.45 ppm is found at almost the same position in all the compounds derived from the monoanion (Eq. 1) and is absent in the spectra of complexes derived from the dianion (Eq. 2) showing deprotonation of both phenolic and enolic OH groups. The presence of a sharp singlet in the range 5.48–5.88 ppm in all the compounds shows that the NH_2 group is intact, non-ionized and uncoordinated. The resonance due to the phenyl moiety at 7.86–6.52 ppm remains almost unchanged in all the complexes. The methyl protons attached to tin appear as a sharp singlet in the region 0.92–0.78 ppm. The resonances due to butyl tin protons are observed in the region 0.40–1.70 ppm (Tables 3 and 4). The spectral features and integrations are consistent with the various stoichiometries and bonding sites as inferred from the infrared spectra.

^{13}C NMR Spectra

^{13}C NMR spectra of the compounds were recorded in $CDCl_3$. The number of observed carbon signals is in agreement with that expected in the appropriate regions for the proposed structures. Aromatic carbons display signals in the range 145.83–116.23 ppm. The amido, thioamido and azomethine carbons appear at 198.40, 178.54 and 156.82 ppm, respectively, in the ligand. On coordination, the resonances of the carbon atoms attached to the C=N, OH and SH groups shift downfield, suggesting coordination of

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Table 3. Spectral data of compounds (**1**)–(**8**).

	IR (cm^{-1})				NMR ($CDCl_3$, δ ppm)	
Compd. no.	ν(C=N)	ν(OH)/NH_2	ν(Sn–O)	ν(Sn–N)	^{1}H	^{119}Sn
(**1**)	1630 s 1588 s	3495–3122 m	585 m	415 m	11 11.38 (s, 1H, OH); 6.56–7.86 (m, 4H, Ph); 5.82 (s, 2H, (s, NH_2); 1.58 (s, 3H, CH_3); 0.48–1.45 (m, 27H, n-Bu).	– 224.2
(**2**)	1628 s 1582 s	3480–3116 m	582 m	420 m	11.36 (s, 1H, OH); 6.56–7.78 (m, 19H, Ph); 5.88 (s, 2H, NH_2); 1.52 (s, 3H, CH_3).	– 243.6
(**3**)	1632 s 1586 s	3494–3126 m	576 m	418 m	11.48 (s, 1H, OH); 6.66–7.75 (m, 4H, Ph); 5.66 (s, 2H, NH_2); 1.62 (s, 3H, CH_3); 0.84 (s, 6H, Sn–CH_3).	– 187.6
(**4**)	1624 s 1590 s	3485–3120 m	568 m	426 m	11.40 (s, 1H, OH); 6.68–7.82 (m, 14H, Ph.); 1.64 (s, 3H, CH_3); 5.58 (s, 2H, NH_2).	– 251.2
(**5**)	1632 s 1588 s	3490–3118 m	570 m	422 m	11.44 (s, 1H, OH); 6.58–7.72 (m, 4H, Ph.); 1.74 (s, 3H, CH_3);5.52 (s, 2H, NH_2); 0.42–1.58 (m, 18H, n-Bu).	– 231.7
(**6**)	1626 s 1586 s	3316 s 3126 s	578 m	430 m	6.56–7.48 (m, 4H, Ph); 5.56 (s, 2H, NH_2); 1.65 (s, 3H, CH_3); 0.78 (s, 6H, Sn–CH_3).	– 182.8
(**7**)	1618 s 1576 s	3320 s 3132 s	580 m	428 m	6.62–7.64 (m, 14H, Ph); 1.54 (s, 3H, CH_3); 5.48 (s, 2H, NH_2).	– 253.9
(**8**)	1624 s 1590 s	3312 s 3124 s	574 m	416 m	6.58–7.72 (m, 4H, Ph.); 1.74 (s, 3H, CH_3); 5.52 (s, 2H, NH_2); 0.58–1.70 (m, 18H, n-Bu).	– 234.6

Table 4. Spectral data of compounds (**9**)–(**16**).

Compd. no.	IR (cm^{-1})					NMR ($CDCl_3$, δ ppm)	
	ν(C=N)	ν(OH)/NH_2	ν(Sn–S)	ν(Sn–N)	ν(Sn–Cl)	^1H	^{119}Sn
(**9**)	1632 s 1588 s	3466–3130 m	358 m	416 m	–	11.48 (s, 1H, OH); 6.76–7.66 (m, 4H, Ph); 5.82(s, 2H, NH_2); 1.58 (s, 3H, CH_3); 0.40–1.45 (m, 27H, n-Bu).	−227.6
(**10**)	1626 s 1592 s	3470–3124 m	362 m	418 m	–	11.36 (s, 1H, OH); 6.66–7.78 (m, 19H, Ph); 5.88 (s, 2H, NH_2); 1.52 (s, 3H, CH_3).	−248.4
(**11**)	1630 s 1586 s	3474–3116 m	366 m	418 m	324 s	11.40 (s, 1H, OH); 6.56–7.65 (m, 4H, Ph); 5.66 (s, 2H, NH_2); 1.62 (s, 3H, CH_3); 0.94 (s, 6H, Sn–CH_3).	−183.2
(**12**)	1628 s 1586 s	3475–3124 m	355 m	414 m	318 s	11.44 (s, 1H, OH); 6.78–7.86 (m, 14H, Ph.); 1.64 (s, 3H, CH_3); 5.58 (s, 2H, NH_2).	−244.6
(**13**)	1624 s 1584 s	3470–3114 m	360 m	412 m	320 s	11.52 (s, 1H, OH); 6.68–7.62 (m, 4H, Ph.); 1.74 (s, 3H, CH_3); 5.52 (s, 2H, NH_2); 0.44–1.58 (m, 18H, n-Bu).	−235.6
(**14**)	1630 s 1588 s	3314 s 3138 m	364 m	420 m	–	6.64–7.58 (m, 4H, Ph); 5.62 (s, 2H, NH_2); 1.65 (s, 3H, CH_3); 0.88 (s, 6H, Sn–CH_3).	−185.8
(**15**)	1626 s 1586 s	3324 s 3122 m	362 m	422 m	–	6.52–7.74 (m, 14H, Ph); 1.54 (s, 3H, CH_3); 5.48 (s, 2H, NH_2).	−253.5
(**16**)	1632 s 1584 s	3320 s 3118 s	358 m	416 m	–	6.68–7.82 (m, 4H, Ph.); 1.64 (s, 3H, CH_3); 5.42 (s, 2H, NH_2); 0.52–1.62 (m, 18H, n-Bu).	−232.4

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Table 5. ^{13}C NMR spectral data of compounds (**1**)–(**16**).

Compd. no.	Chemical shifts δ (ppm)											
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	Sn–Bu	Sn–Me	Sn–Ph
(**1**)	158.62	122.24	116.84	123.53	119.47	116.42	148.34	178.54	28.24	26.77, 26.58, 26.10, 13.46	–	–
(**2**)	158.54	122.53	116.67	123.23	119.33	116.21	148.52	178.48	28.43	–	–	117.74–144.56
(**3**)	158.74	122.46	116.72	123.47	119.52	116.37	148.42	178.52	28.36	–	9.56	–
(**4**)	158.68	122.34	116.78	123.28	119.42	116.48	148.57	178.62	28.28	–	–	116.54–145.46
(**5**)	157.82	122.64	116.93	123.59	119.56	116.57	148.62	178.76	28.38	26.57, 26.48, 26.40, 13.66	–	–
(**6**)	158.42	122.54	116.35	123.72	119.63	116.58	148.67	178.87	27.84	–	10.23	–
(**7**)	158.48	122.34	116.54	123.63	119.57	116.62	148.54	178.74	28.63	–	–	116.94–145.76
(**8**)	158.76	122.53	116.67	123.46	119.23	116.58	148.62	178.67	28.86	26.72, 26.53, 26.24, 13.26	–	–
(**9**)	158.69	122.27	116.85	123.58	119.42	116.48	148.39	166.56	28.29	26.63, 26.46, 26.56, 13.76	–	–
(**10**)	158.46	122.57	116.48	123.93	119.68	116.85	148.67	166.32	28.97	–	–	117.58–143.86
(**11**)	157.92	122.84	116.67	123.86	119.58	116.58	148.78	166.87	28.67	–	9.76	–
(**12**)	157.82	122.38	116.57	123.87	119.38	116.45	148.27	166.63	28.57	–	–	116.23–145.83
(**13**)	158.43	122.67	116.82	123.58	119.39	116.56	148.47	166.76	28.63	26.35, 26.64, 26.85, 13.67	–	–
(**14**)	158.58	122.57	116.64	123.92	119.68	116.32	148.65	166.32	28.56	–	10.46	–
(**15**)	158.41	122.37	116.62	123.74	119.89	116.36	148.74	166.28	28.47	–	–	118.56–144.97
(**16**)	158.27	122.56	116.76	123.82	119.54	116.65	148.67	166.52	28.58	26.48, 26.37, 26.56, 13.78	–	–

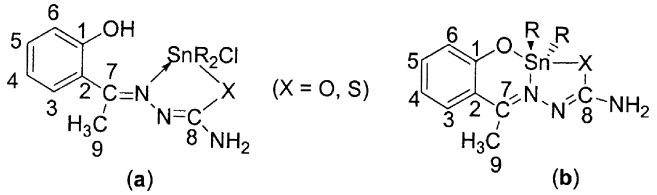

Figure 2. Organotin(IV) complexes derived from (a) monoanion, (b) dianion.

C=N, OH and SH groups to the metal atom. Compounds (**1**), (**3**), (**6**), (**9**) and (**14**) show $^{1}J(^{119}Sn-^{13}C)$ values of 562, 598.6, 613.4, 567 and 622.2 Hz, respectively, and these are characteristic of 5-coordinate tin. Methyl carbons appear in the region 10.46–9.56 ppm. Butyl carbons display peaks in the region 13.26–26.77 ppm (Table 5).

^{119}Sn NMR Spectra

^{119}Sn NMR spectra of all compounds have been recorded and exhibit a sharp ^{119}Sn resonance in the region −253.9 to −182.8 ppm which is compatible with a penta-coordinate geometry.[42,43]

CONCLUSION

Thus, on the basis of the above studies and reports already available in the literature, the potentially bifunctional tridentate ligands 2-hydroxyacetophenone semicarbazone and thiosemicarbazone are only (X,N)-bidentate, five-coordinated in a trigonal bipyramidal arrangement with N and Cl occupying the axial positions in complexes (Figure 2a) derived from the monoanion (Eq. 1). The ligands behave as (O,N,O) or (O,N,S)-tridentates in the *Z*-configuration of a *cis*-trigonal bipyramidal coordination polyhedron with the phenolic hydroxyl oxygen in one axial position and semicarbazonate oxygen or thiosemicarbazonate sulfur in the other (Figure 2b) in all complexes derived from the dianion (Eq. 2).

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