

4-Aroylhydrazino-4-thioxo-3-thiabutyrates and their Complexes with Tin(IV)

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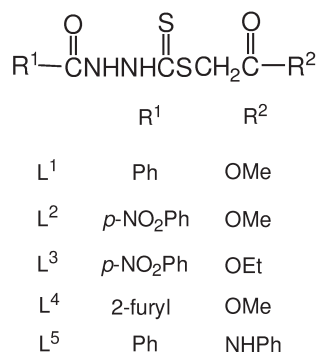
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Five new 4-arylhydrazino-4-thioxo-3-thiabutyrates ligands, synthesized by the reaction of 4-arylhydrazinodithiocarbamate and chloroacetic ester, and their complexes with tin(IV) have been prepared and characterized by elemental analyses, IR, ¹H NMR spectra and molar conductance. It is shown that the O, N, and S atoms of the ligand coordinate to tin to form a chelating dimer and these ligands are tridentate and coordinate to tin(IV) in the enol form in the mole ratio 1 : 1. The central tin atom appears to be six-coordinated.

A considerable amount of work has been reported on the synthesis of tin(IV) coordination compound with ligands containing nitrogen, oxygen, and sulfur [1, 2]. The dithiocarbamates are an interesting class of thioligands and their complexes have been found to be active against viruses, bacteria, fungi, and in cancer [3, 4]. Furthermore, their stereochemistry is also quite interesting.

In this paper five new ligands, esters of 4-benzoylhydrazino- (H₂L¹), 4-(*p*-nitrobenzoylhydrazino)- (H₂L²), (H₂L³), 4-(2-furylhydrazino)-4-thioxo-3-thiabutyrates acid (H₂L⁴), as well as *N*-phenyl-4-benzoylhydrazino-4-thioxo-3-thiabutyrates (H₂L⁵) are reported.



They react with dichlorodibutyltin in the presence of sodium methylate to produce five new complexes in which the central tin(IV) is six-coordinated.

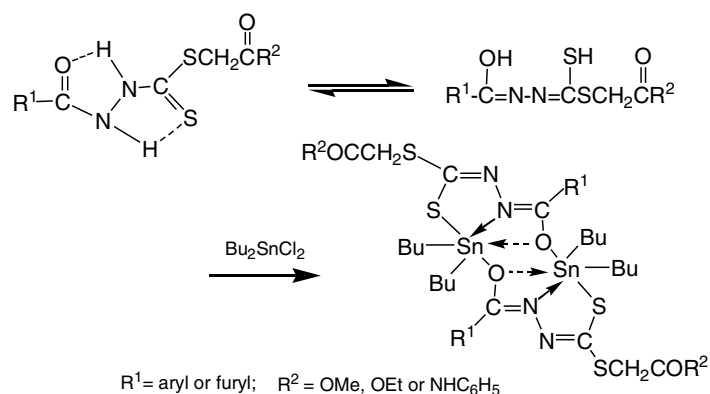
All complexes obtained are thermostable and photostable under dry conditions and are soluble in common organic solvents such as C₆H₆, CH₂Cl₂, CHCl₃, CH₃COOC₂H₅, CH₃COCH₃, THF, MeOH, *etc.*, but insoluble in water and petroleum ether. Their elemental analyses and some physical properties of the ligands and their complexes are listed in Table 1. The value of the molar conductivity, 24.6–38.0 S cm² mol⁻¹, shows that they are nonelectrolytes [5].

The important IR absorptions of these ligands and their complexes are listed in Table 2. The characteristic absorption bands of the ligands at *ca.* 1700 cm⁻¹, 1300 cm⁻¹, and 3200 cm⁻¹ due to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{S})$, and $\nu(\text{N}-\text{H})$, respectively, have disappeared compared with those of their complexes. The IR spectra of the complexes show new bands at 1480 cm⁻¹, 630 cm⁻¹, 320 cm⁻¹, and 510 cm⁻¹, assignable to $\nu(\text{C}=\text{N})$ (formed by enolization), $\nu(\text{C}-\text{S})$, $\nu(\text{S}-\text{Sn})$, and $\nu(\text{O}-\text{Sn})$, respectively [6, 7].

¹H NMR spectra of the ligands and their complexes are given in Table 3. It is shown that the signals of two protons of the hydrazine in the complexes disappeared when compared with those of the ligands.

Summarizing the above data and results reported in the literature [8–10], we consider these polyfunctional ligands to undergo enolization and thioenolization before coordination. Thus, the O, N, and S atoms of the ligand coordinate to tin to form a chelating dimer as shown in Scheme 1.

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Scheme 1. Proposed structure for the complexes.

Table 1. Elemental Analyses and Physical Properties of the Ligands and their Complexes

Compound	Formula	M_r	$w_i(\text{found})/\%$ $w_i(\text{calc.})/\%$			Yield ^a %	M.p. °C	Λ S cm ² mol ⁻¹	Colour	
			C	H	N					
<i>I</i>	H ₂ L ¹	C ₁₁ H ₁₂ N ₂ O ₃ S ₂	284.4	46.37 46.46	4.33 4.25	9.51 9.85	80	157—158	—	White
<i>II</i>	H ₂ L ²	C ₁₁ H ₁₁ N ₃ O ₅ S ₂	329.4	40.10 40.11	3.37 3.37	12.72 12.76	88	138—140	—	White
<i>III</i>	H ₂ L ³	C ₁₂ H ₁₃ N ₃ O ₅ S ₂	343.4	42.03 41.97	3.82 3.82	12.23 12.24	87	133—134	—	Yellow
<i>IV</i>	H ₂ L ⁴	C ₉ H ₁₀ N ₂ O ₄ S ₂	274.3	39.44 39.40	3.70 3.67	10.21 10.21	88	102—104	—	White
<i>V</i>	H ₂ L ⁵	C ₁₆ H ₁₅ N ₃ O ₂ S ₂	345.4	55.29 55.63	4.50 4.38	12.31 12.17	88	138—140	—	White
<i>VI</i>	Bu ₂ SnL ¹	C ₁₉ H ₂₈ N ₂ O ₃ S ₂ Sn	515.3	44.23 44.55	5.39 5.51	5.46 5.47	77	151—153	38.0	White
<i>VII</i>	Bu ₂ SnL ²	C ₁₉ H ₂₇ N ₃ O ₅ S ₂ Sn	560.3	40.63 40.73	4.86 4.86	7.51 7.50	54	111—113	28.7	Red
<i>VIII</i>	Bu ₂ SnL ³	C ₂₀ H ₂₉ N ₃ O ₅ S ₂ Sn	574.3	41.63 41.83	5.20 5.09	7.19 7.32	66	250 (dec)	27.4	Orange
<i>IX</i>	Bu ₂ SnL ⁴	C ₁₇ H ₂₆ N ₂ O ₄ S ₂ Sn	505.2	40.54 40.41	5.30 5.19	5.52 5.55	63	209—210	24.6	White
<i>X</i>	Bu ₂ SnL ⁵	C ₂₄ H ₃₁ N ₃ O ₂ S ₂ Sn	576.3	50.05 50.01	5.43 5.42	7.30 7.29	79	154—156	29.1	White

a) Isolated yield.

Table 2. Characteristic IR Data of the Ligands and their Complexes ($\tilde{\nu}_i/\text{cm}^{-1}$)

Compound	$\nu(\text{N—H})$	$\nu(\text{C=O})$	$\nu(\text{C=S})$	$\nu(\text{C—O—C})$	$\nu(\text{C=N})$	$\nu(\text{N—N})$	$\nu(\text{C—S})$	$\nu(\text{S—Sn})$	$\nu(\text{O—Sn})$
<i>I</i>	3126 s	1734 s	1311 s	1156 m 1037 m	—	996 m	—	—	—
<i>II</i>	3128 vs	1738 s	1304 s	1159 s 1017 s	—	977 m	—	—	—
<i>III</i>	3254 s	1728 s	1301 s	1161 s 1015 s	—	972 m	—	—	—
<i>IV</i>	3122 s	1743 s	1302 s	1160 w 1016 m	—	947 w	—	—	—
<i>V</i>	3188 m	1736 vs	1641 s	—	—	—	—	—	—
<i>VI</i>	—	—	—	—	1480 vs	972 s	651 m	359 s	511 w
<i>VII</i>	—	—	—	—	1483 s	981 s	654 m	361 m	529 m
<i>VIII</i>	—	—	—	—	1446 s	1008 s	657 m	360 w	534 w
<i>IX</i>	—	—	—	—	1477 s	966 s	642 m	365 w	509 m
<i>X</i>	—	—	—	—	1511 s	968 s	637 w	348 m	522 m

vs = very strong, s = strong, m = medium, w = weak.

Table 3. ^1H NMR Data for the Ligands and their Complexes (δ_i)

Compound	Ar	NH	SCH ₂	OCH ₂	OCH ₃	CH ₂ + CH ₃
<i>I</i>	7.42—7.96 (m, 5H)	8.76 (s, 1H) 10.40 (s, 1H)	4.11 (s, 2H)		3.61 (s, 3H)	
<i>II</i>	8.01—8.45 (m, 4H)	11.0 (br s, 2H)	4.09 (s, 2H)		3.72 (s, 3H)	
<i>III</i>	8.01—8.44 (m, 4H)	10.5 (br s, 2H)	4.04 (s, 2H)	4.36 (q, 2H)		1.36 (t, 3H)
<i>IV</i>	4.5—4.8 (m, 3H)	9.98 (br s, 2H)	4.19 (s, 2H)		3.77 (s, 3H)	
<i>V</i>	7.02—7.87 (m, 10H)	10.29 (s, 1H) 11.00 (s, 1H) 11.25 (s, 1H)	4.41 (s, 2H)			
<i>VI</i>	7.35—8.35 (m, 5H)		4.14 (s, 2H)		3.81 (s, 3H)	0.84—1.87 (m, 18H)
<i>VII</i>	7.48—7.89 (m, 4H)		4.17 (s, 2H)		3.87 (s, 3H)	0.94—1.90 (m, 18H)
<i>VIII</i>	8.0—8.3 (m, 4H)		4.16 (s, 2H)	4.17 (q, 2H)		0.96—1.80 (m, 21H)
<i>IX</i>	6.72—7.65 (m, 3H)		4.17 (s, 2H)		3.78 (s, 3H)	2.59—3.50 (m, 18H)
<i>X</i>	7.38—8.26 (m, 10H)	10.41 (s, 1H)	4.15 (s, 2H)		3.61 (s, 3H)	0.94—1.70 (m, 18H)

s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

EXPERIMENTAL

All materials and solvents employed were of anal. grade. Dichlorobutyltin, ethyl chloroacetate, and all 4-arylhaziridinodithiocarbamates were prepared according to the literature [11—13].

Melting points were determined on a Thomas Hoover capillary melting point apparatus. Elemental analyses were determined on an Erba 1106 elemental analyzer. The IR spectra were recorded with a Nicolet-100X spectrometer using KBr discs in the range 200—4000 cm^{-1} . The ^1H NMR spectra were obtained on a Varian FT-80A spectrometer using CDCl_3 as a solvent and TMS as an internal standard. Conductivity measurements were performed using a DDS-II A conductometer made in the Shanghai Second Apparatus Factory, using DMF as solvent at room temperature.

Ligands L¹—L⁵

4-Arylhaziridinodithiocarbamate (10 mmol) in 20 cm^3 of ethanol was added to a solution of ethyl chloroacetate (1.5 g; 12 mmol) in ethanol (5 cm^3) containing several drops of glacial acetic acid, and kept at room temperature for 2 h. The formed precipitate was filtered off after cooling, washed with cold methanol, recrystallized with methanol and dried *in vacuo*.

Complexes

A solution of dichlorodibutyltin (1.22 g; 4 mmol)

in absolute methanol (25 cm^3) was added dropwise with stirring at 0 °C to a solution of sodium methylate (0.22 g; 4 mmol) in 10 cm^3 of methanol and stirred for about 1 h. Then the mixture was added to a solution of the ligand (4 mmol) in methanol (25 cm^3), refluxed for about 1 h until the reaction was complete (TLC) and filtered after cooling. The mother liquid was concentrated under reduced pressure and the residue obtained was recrystallized in benzene—petroleum ether (30—60 °C).

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