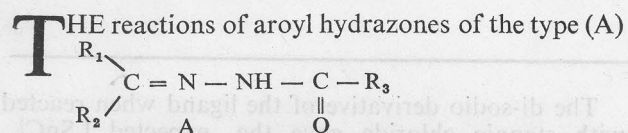


## New Organoxytitanium(IV) & Organotin(IV) Derivatives of N-Salicylidene-N'-Salicylhydrazide†

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Received 21 December 1978; revised and accepted 21 February 1979

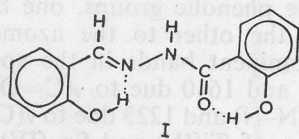
N-Salicylidene-N'-salicylhydrazide (LH<sub>2</sub>) forms stable Ti (IV) compounds LTiCl<sub>2</sub>, LTi(OPr)<sub>2</sub> and L<sub>2</sub>Ti. Compounds of the type (Sal)<sub>2</sub>TiL are obtained when LTi(OPr)<sub>2</sub> further reacts with salicylaldehyde, or other chelating ligands. LTiCl<sub>2</sub> forms 1:1 addition compounds with nitrogen bases. Coordinated tin compounds LSnCl<sub>2</sub>, R<sub>2</sub>SnL and (R<sub>3</sub>Sn)<sub>2</sub>L where R = methyl, butyl, octyl and phenyl have also been prepared. Evidence for coordination has been obtained from infrared, PMR and electronic spectra. Molecular weight determination of those compounds which are soluble in benzene indicate their monomeric nature.



where R<sub>1</sub> = H, CH<sub>3</sub>; and R<sub>2</sub> = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>; and R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>

with transition metal ions, especially Ni(II), Co(II) and Cu(II) were reported by Iskander *et al*<sup>1</sup> to give compounds of the type M(HL)<sub>2</sub>X<sub>2</sub>. N-Salicylidene-N'-salicylhydrazide, a Schiff base derived from salicylaldehyde, a salicylic ester and hydrazine, was first reported by Curtius<sup>2</sup> as early as 1910. Compounds of this and other similar Schiff bases with some transition metals have been reported by Syamal *et al*.<sup>3</sup> and Narang *et al*.<sup>4</sup> Metal aroylhydrazones are known to possess biological activity and they are potent inhibitors for many enzymes<sup>5</sup>. Our interest in the chelated titanium and organotin compounds led us to investigate these Schiff base derivatives.

The ligand (LH<sub>2</sub>) was prepared according to the method detailed by Dexter<sup>6</sup>; m. p. 281°; yield 90%.



**Preparation of LTiCl<sub>2</sub>**—Titanium tetrachloride (1.90 g; 0.01 mol) was diluted with benzene (50 ml) and mixed with LH<sub>2</sub> (2.56 g; 0.01 mol). Vigorous reaction took place with the evolution of HCl. The mixture was refluxed for 2 hr the product separated by filtration, washed with hexane and dried at reduced pressure at 60°. The chocolate coloured solid weighed 3.7 g (yield almost quantitative).

†NCL Communication No. 2383.

**Preparation of adducts of LTiCl<sub>2</sub> with nitrogen bases**—The addition compounds of LTiCl<sub>2</sub> were prepared by stirring it with an excess of bases like pyridine, quinoline and pyridine N-oxide in benzene. The 1:1 addition compounds formed were soluble in benzene and were purified by precipitation from benzene with hexane, washing and drying under reduced pressure. The compounds prepared are listed in Table 1.

**Preparation of LTi(OPr)<sub>2</sub> and L<sub>2</sub>Ti**—Freshly distilled isopropyl titanate (2.84 g; 0.01 mol) and the ligand (2.56 g; 0.01 mol) were mixed in benzene (100 ml) and refluxed using a partial take off condenser to remove azeotropically the liberated isopropanol which was estimated using gas chromatography. The product was isolated from benzene by concentration followed by crystallization. The dark orange crystals obtained were washed with hexane and dried in vacuum. Yield 3.15 g (75% of theory).

The fully substituted titanium compound, L<sub>2</sub>Ti, was similarly obtained using two mol of the ligand and one mol of isopropyl titanate. The yield was 80% of theory.

**Preparation of bis-8-hydroxyquinolinoTiL**—8-Hydroxyquinoline (0.29 g; 0.002 mol) was mixed with LTi(OPr)<sub>2</sub> (0.42 g; 0.001 mol) and refluxed in benzene (50 ml) with continuous removal of the liberated isopropanol. Upon processing as above the red solid obtained weighed 0.47 g (80%). Other chelated titanium compounds similarly prepared are listed in Table 1.

**L<sub>2</sub>SnCl<sub>2</sub>**—This was prepared from stannic chloride and sodio/derivative of the ligand. Sodium methoxide, prepared from sodium (0.46 g; 0.02 mol) was mixed with the ligand (2.56 g; 0.01 mol) and refluxed with stannic chloride (2.61 g; 0.01 mol) in benzene (50 ml) for 2 hr. The contents were then centrifuged to remove the insolubles and the clear benzene extract concentrated to crystallization. The crystals on washing with hexane and drying yielded 3.77 g(85%) of the yellow solid.

TABLE 1 — CHARACTERIZATION DATA OF Ti(IV) AND Sn(IV) DERIVATIVES OF N-SALICYLIDENE-N'-SALICYLHYDRAZIDE(LH<sub>2</sub>)

Sl. No.	Reactants		Molar ratio A:B	Product	Found (%) (calc)			
	A	B			(°C)	Ti or Sn	C	H
1.	TiCl <sub>4</sub>	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> TiCl <sub>2</sub>	300d	12.74(12.85)	45.17(45.07)	2.77(2.68)
2.	Ti(OPr) <sub>4</sub>	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>3</sub> H <sub>7</sub> O <sub>2</sub> )	200d	11.54(11.41)	57.00(57.16)	5.60(5.72)
3.	do	LH <sub>2</sub>	1:2	[C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> ] <sub>2</sub> Ti	200d	8.86(8.62)	60.25(60.43)	3.34(3.60)
4.	LTi(OPr) <sub>2</sub>	Acetylacetone	1:2	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	200d	9.81(9.58)	57.40(57.62)	4.60(4.80)
5.	do	Benzoyl acetone	1:2	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	145	7.97(7.68)	65.20(65.40)	4.17(4.49)
6.	do	Salicylaldehyde	1:2	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>2</sub>	155	9.01(8.81)	61.53(61.77)	3.42(3.68)
7.	do	8-Hydroxy quinoline	1:2	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub>	160	8.32(8.12)	64.61(65.09)	3.90(3.73)
8.	do	Acetoacetanilide	1:2	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>10</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>2</sub>	200d	7.60(7.32)	61.07(62.40)	5.02(4.59)
9.	do	Dehydroacetic acid	1:2	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Ti(C <sub>8</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	135	7.35(7.53)	56.25(56.58)	3.57(3.77)
10.	LTiCl <sub>3</sub>	Pyridine	1:4	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> TiCl <sub>3</sub> (C <sub>5</sub> H <sub>5</sub> N)	200d	10.45(10.67)	50.12(50.46)	3.02(3.32)
11.	do	Quinoline	1:4	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> TiCl <sub>3</sub> (C <sub>8</sub> H <sub>7</sub> N)	200d	9.89(9.55)	55.23(55.00)	3.12(3.39)
12.	do	Pyridine N-oxide	1:4	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> TiCl <sub>3</sub> (C <sub>5</sub> H <sub>5</sub> NO)	200d	10.53(10.24)	48.36(48.74)	3.07(3.21)
13.	SnCl <sub>4</sub>	LH <sub>2</sub> *	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> SnCl <sub>2</sub>	280d	26.54(26.76)	37.74(37.87)	2.13(2.25)
14.	(CH <sub>3</sub> ) <sub>2</sub> SnO	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> SN(CH <sub>3</sub> ) <sub>2</sub>	155	29.21(29.47)	47.32(47.76)	3.62(3.98)
15.	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnO	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Sn(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	55	24.20(24.40)	54.02(54.25)	5.52(5.75)
16.	(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> SnO	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> Sn(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub>	Viscous liquid	19.58(19.83)	59.07(60.13)	7.93(7.35)
17.	[(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn] <sub>2</sub> O	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> [Sn(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> ] <sub>2</sub>	do	27.46(27.29)	55.32(54.73)	8.10(7.68)
18.	[(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn] <sub>2</sub> O	LH <sub>2</sub>	1:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> [Sn(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> ] <sub>2</sub>	do	20.89(20.37)	64.36(63.63)	10.10(9.58)
19.	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SnOH	LH <sub>2</sub>	2:1	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> [Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	235	24.29(24.90)	62.57(62.94)	4.91(4.20)

\*Disodium salt was used.

(CH<sub>3</sub>)<sub>2</sub>SnL— Freshly prepared and dried dimethyltin oxide (1.64 g; 0.01 mol) was mixed with the ligand (2.56 g; 0.01 mol) in benzene (100 ml) and refluxed with a partial take off condenser to remove azeotropically the water formed. The benzene solution upon concentration to crystallization gave yellow crystals of the product; yield 3 g (75%).

Other organotin chelates similarly prepared are listed in Table 1.

### Results and Discussion

The ligand N-salicylidene-N'-salicylhydrazide (LH<sub>2</sub>), is a dibasic tetradentate hydrazine derivative having two hydroxyl, one carbonyl and one azomethine groups.

It forms stable, well-defined coordination compounds with organotitanium (IV) and tin (IV). With titanium tetrachloride it gives a dichloride, LTiCl<sub>2</sub>, by the elimination of HCl; attempts to prepare a trichloride were not successful. The dichloride further gave 1:1 addition compounds with pyridine, quinoline and pyridine N-oxide. When reacted with isopropyl titanate in the molar ratios 1:1 and 1:2, two products, LTi(OPr)<sub>2</sub> and L<sub>2</sub>Ti respectively, were obtained. The di-isopropoxide, LTi(OPr)<sub>2</sub>, when further reacted with strong bidentate ligands such as acetylacetone, benzoylacetone, salicylaldehyde, 8-hydroxyquinoline, acetoacetanilide and dehydroacetic acid gave the expected dialkoxy substituted products which were soluble in benzene. However, the di-compound L<sub>2</sub>Ti, did not react with any chelating ligand.

The new titanium compounds are orange to red stable solids with high melting or decomposing points. Most of them are only slightly soluble in cold benzene, but more so in hot benzene, the dichloride LTiCl<sub>2</sub> is insoluble in this solvent. Ethanol dissolves these with partial decomposition.

The di-sodio derivative of the ligand when reacted with stannic chloride gave the expected LSnCl<sub>2</sub>. Organotin oxides and hydroxides however, readily reacted with the ligand itself and produced chelated organotin compounds; these reactions proceeded smoothly when the water formed was continuously removed azeotropically. Methyl-, butyl-, octyl- and phenyl- tin compounds were thus obtained in good yields. The new tin compounds are yellow solids, moderately soluble in benzene, insoluble in hexane, and soluble with partial decomposition in alcohols. All these titanium and tin chelated compounds which are sufficiently soluble in boiling benzene are found to be monomeric by ebulliometry.

*Infrared spectra*— The infrared spectrum ( $\nu_{\max}$  in cm<sup>-1</sup> throughout the paper) of LH<sub>2</sub> both in nujol and hexachlorobutadiene showed bands characteristic of  $\nu$ NH (3180) and  $\nu$ OH (2650, 2560). The spectrum taken after deuteration of the ligand exhibited  $\nu$ OH at two different positions which could be attributed to the difference in strength of hydrogen bonding of the phenolic groups, one bonded to the carbonyl and the other to the azomethine group. The other prominent bands in the spectrum were 1655 sh, 1625 and 1610 due to  $\nu$ (C=O and C...N), 1030 due to  $\nu$ (N-N) and 1223 due to  $\nu$ (C-O) phenolic. In the chelates of Ti(IV) and Sn(IV) the  $\nu$ OH was absent.

The infrared spectra of the new compounds in nujol did not show the expected N-H band; but this band was seen in the spectra of the tin compounds when taken in CCl<sub>4</sub> solution. The  $\nu$ C=O is damped by 10-15 cm<sup>-1</sup> in the complexes as compared to that of the free ligand and this shift suggests coordination of the carbonyl group to the metal. The  $\nu$ C=O bands of LTiCl<sub>2</sub> and LSnCl<sub>2</sub> were observed at 1610 and 1620 respectively, and this small shift in  $\nu$ (C=O) might be due to the slight difference in the

strength of M-O-C bonds in the two compounds, as expected. There was no change in the  $\nu$ C-N of the ligand and in its chelates indicating non-coordinated azomethine group. Similarly there was no shift in  $\nu$  N-N again indicating non-coordination of the C...N group with the metal. This phenomenon points out the possibility of the ligand acting as a dibasic tridentate moiety. Further, model studies showed the non-availability of the non-bonding electrons of azomethine nitrogen atom for coordination. The  $\nu$ C-O (phenolic) appearing at 1223 in the ligand shifted to 1240 in the metal dichlorides. In the di-isopropoxide, the band due to the group Ti-O-C was seen as broad peaks around 1020 and 1140.

In *bis*-acetylacetonodichlorotin, Okawara *et al*<sup>7</sup> reported  $\nu$ Sn-O between 461 and 404 and  $\nu$ Sn-O (coordinated) below 400. In the spectrum of  $\text{LSnCl}_2$ , a broad and strong band at 477 may be assigned to  $\nu$ Sn-O (phenolic) and the band at 368 to the coordinated  $\nu$ (Sn-O). Two more bands at 341  $\nu_{as}$  (Sn-Cl) and 312  $\nu_s$  (Sn-Cl) were also observed in the spectrum of  $\text{LSnCl}_2$ . The appearance of more than one  $\nu$ Sn-Cl suggests a trigonal bipyramidal structure for  $\text{LSnCl}_2$  with two chlorine atoms in the *cis*-position. Exact geometry can, however, be assigned only after X-ray diffraction studies of the compound.

The IR spectra of dimethyl-, dibutyl- and dioctyltin chelates with the ligand showed evidence for the coordination of the carbonyl group of the ligand to the metal, thereby making the central tin atom penta-coordinated. In the triphenyltin compound, the ligand also acted as a bridge for the two triphenyltin groups; the spectra of the compound in *nujol* as well as in  $\text{CCl}_4$  showed evidence for the coordination of the C=O and the C...N to two different tin atoms.

In the mixed chelate of titanium containing the ligand and salicylaldehyde,  $\text{LTi}(\text{Sal})_2$  the spectrum showed the presence of two different types of carbonyl bands; one at 1670 and the other at 1630. This might suggest that only one salicylaldehyde is coordinated through its carbonyl group thereby making the titanium atom hexa-coordinated. In the mixed complex containing 8-hydroxyquinoline, the non-coordinated oxine C...N vibrations were also seen. The mixed chelates of titanium containing the ligand and acetylacetone, benzoyl acetone, acetoacetanilide and dehydroacetic acid, exhibited a similar behaviour.

In the spectra of pyridine and quinoline adducts of  $\text{LTiCl}_2$  the expected bands for coordinated C...N group should appear around 1610; but these vibrations could not be identified from those of  $\text{LTiCl}_2$  due to the complexity of the spectra in this region since ligand also exhibited bands in this region. However in the pyridine N-oxide adduct, the  $\nu$ N-O at 1265 in the ligand was shifted to 1220. The  $\nu$ N-O at 840 in the ligand was split into two bands at 830 and 845. These changes in the behaviour of N-O absorption bands indicate the coordination to a metal<sup>8</sup>.

**Electronic spectra**—The ultraviolet spectrum of the ligand in acetonitrile showed bands at 219 ( $\epsilon$  21800), 246 ( $\epsilon$  12000), 296 ( $\epsilon$  16400) and 333 nm ( $\epsilon$  18790). The spectra of chelated tin dichloride and organotin chelates show distinct bands around 226, 259, 325, 337 and 402-409 nm with varying intensities. The ligand absorption bands are split into several bands in these complexes which can be attributed to the effect of chelation. The appearance of a new band in the region 402-409 nm in the spectra of tin complexes may be due to the ligand-metal charge transfer transition<sup>4</sup>.

**PMR spectra** — The PMR spectrum (chemical shift in  $\delta$ , ppm) of the ligand was studied in DMSO due to solubility reasons. The aromatic protons appeared as multiplets between 6.6 and 7.9 and azomethine proton at 8.53. The two phenolic hydroxyl protons together with the N-H proton gave a broad signal at 11.3 which disappeared on deuteration. The spectra of the organotin complexes (in  $\text{CCl}_4$ ) gave distinct signals for different groups as follows: The methyl proton of the dimethyltin chelate appeared as a singlet at 0.83; the aromatic protons resonated in the range 6.43 to 7.70. Azomethine proton gave a signal at 8.43. The N-H proton resonated at 11.16. In all the organotin complexes the resonance range of the aromatic and azomethine protons was the same, 6.53 - 8.00 and 8.36 - 8.43, respectively. Only the N-H proton suffered a small shielding : 11.16 for methyl-, 11.13 for butyl- and 11.00 for the octyl- tin compounds. The spectrum of the dioctyltin compound was studied both in  $\text{CCl}_4$  and DMSO. The absorption due to the aromatic protons (6.53 - 8.00) was not affected in these two solvents but the azomethine and N-H protons underwent some deshielding in DMSO probably due to solvent effect. The deshielding effect on the N-H proton due to change in solvent was more than that on azomethine proton (N-H proton at 11.00 and 12.60 and azomethine proton at 8.36 and 8.70 in  $\text{CCl}_4$  and DMSO respectively). All these indicate that the carbonyl group is involved in coordination with tin atom.

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