

Chelated Titanium(IV) & Organotin(IV) Derivatives of Schiff Bases Derived from Isonicotinic Acid Hydrazide & Salicylaldehyde, Acetylacetone, Trifluoro- acetylacetone or Thenoylacetone†

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Schiff bases derived from isonicotinic acid hydrazide and salicylaldehyde (SAINH), acetylacetone (AcAcINH), 1, 1, 1-trifluoroacetylacetone (TFAINH) or thenoylacetone (THAINH) form chelated titanium(IV) and organotin(IV) compounds by proton replacement of the ligands. The new compounds have been characterized and probable structures assigned to them.

Derivatives of isonicotinic acid (isoniacin) and its hydrazide (isoniazid) are well known for their high specific antitubercular activity, but their metal complexes have not attracted much attention. The coordination chemistry of isoniazid has been reported by Cymerman-Craig¹. Some complexes of transition metals with schiff bases derived from this hydrazide have been mentioned in the literature²⁻⁴. The present note deals with the synthesis and characterisation of the title compounds.

The reactions were carried out under dry nitrogen using carefully purified and dried solvents. Acetylacetoneisoniacin hydrazone was obtained from isoniazid (13.71 g; 0.1 mol) and acetylacetone (10.00 g; 0.1 mol) by refluxing them in methanol (50 ml) for 1 hr. The crystals obtained on cooling the mixture were recrystallized from benzene, washed with hexane and dried *in vacuo* at 60°; yield, 95% (21 g); m.p. 137°. Other hydrazones were similarly obtained. Titanium(IV) diisopropoxide of acetylacetone-isoniacin hydrazone was prepared by reacting isopropyl titanate with the ligand in 1:1 molar ratio.

$Ti(Sal)_2(AcAcINH-2H)$ —Acetylacetone-isoniacin hydrazone titanium diisopropoxide (3.82 g; 0.01 mol) was dissolved in benzene (50 ml), mixed with salicylaldehyde (2.44 g; 0.02 mol) and refluxed for 2 hr using a partial take off condenser. The isopropanol liberated was removed azeotropically along with benzene and estimated by gas chromatographic techniques. The benzene solution in the flask upon concentration gave crystals which were washed with

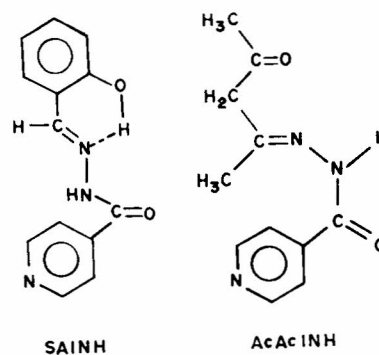
hexane and dried *in vacuo* at 60°; yield, 90% (4.5 g). Other chelated titanium derivatives (Table 1) were prepared similarly.

$(CH_3)_2Sn(AcAcINH-2H)$ —This compound was prepared in benzene by reacting dimethyltin oxide (1.64 g; 0.01 mol) with the ligand (2.19 g; 0.01 mol) by refluxing the mixture for 2 hr when the water formed was azeotropically removed. The benzene solution upon concentration gave crystals of the product, yield, 80% (2.92 g). Other organotin compounds were prepared by similar methods.

Chlorotitanium derivatives were obtained when $TiCl_4$ and the ligand were reacted in 1:1 molar proportion; the tin dichlorides were prepared using the disodium salt of the ligand and stannic chloride. Sodium chloride, separated during the reaction, was filtered off and the dichloride isolated from the benzene solution.

Salicylaldehyde-isoniacin hydrazone (SalINH, I) is a monobasic, tridentate ligand; it also acts as a dibasic, tridentate ligand by enolisation in presence of a metal ion. With isopropyl titanate, the ligand forms the coordinated compound $(L)Ti(OPr)_2$ where $L = SalINH-2H$; this diisopropoxide reacts with bidentate ligands such as acetylacetone, benzoylacetone, salicylaldehyde and 8-hydroxyquinoline to give the expected alkoxy substitution products. Organotin oxides/hydroxides condense with the ligand producing new organotin compounds and water. Methyl-, butyl-, octyl- and phenyl-tin compounds were thus prepared. The new titanium and tin chelated compounds are orange to red stable substances soluble and monomeric in benzene and insoluble in hexane.

Depending upon the reaction conditions, the β -diketone-isoniacin hydrazones act as monobasic bidentate or dibasic tridentate ligands after enolisation of both the C=O groups. Thus, with $TiCl_4$ they give



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LTiCl₃.HCl; the amide part of the ligands gets enolised and the liberated HCl gets fixed by the pyridine residue. The hydrochlorides are dark-brown solids, insoluble in common solvents.

Table 1—Titanium(IV) and Tin(IV) Compounds of Schiff Bases Derived from Isoniacin Hydrazide and Salicylaldehyde, Acetylacetone, Trifluoroacetylacetone or Thenoylacetone

Compound*	Colour, m.p. (C)
(a) Salicylaldehyde-isoniacin hydrazone (SalINH)	
(SalINH-2H)TiCl ₂	Dark-brown, >200(d)
(SalINH-2H)Ti(OPr) ₂	Brown, >250(d)
(SalINH-2H)Ti(Sal) ₂	Brown, >250(d)
(SalINH-2H)Ti(Ba) ₂	Brown, >200(d)
(SalINH-2H)Ti(8-Hq) ₂	Brown, >250(d)
(SalINH-2H)SnCl ₂	Yellow, >250(d)
(SalINH-2H)Sn(Me) ₂	Yellow, 184
(SalINH-2H)Sn(Bu) ₂	Yellow, low melting
(SalINH-2H)Sn(Oct) ₂	yellow, low melting
(SalINH-2H)[SnPh ₃] ₂	Yellow, 164
(b) Acetylacetone-isoniacin hydrazone (AcAcINH)	
(AcAcINH-H)TiCl ₃ .HCl	Dark-brown, >200(d)
(AcAcINH-2H)Ti(OPr) ₂	Brown, >200(d)
(AcAcINH-2H)Ti(Sal) ₂	Brown, >200(d)
(AcAcINH-2H)Ti(AcAc) ₂	Brown, 134
(AcAcINH-2H)SnCl ₂	Yellow, 150
(AcAcINH-2H)Sn(Me) ₂	Yellow, 132
(AcAcINH-2H)Sn(Bu) ₂	Yellow, low melting
(AcAcINH-2H)Sn(Oct) ₂	Yellow, low melting
(AcAcINH-2H)[SnPh ₃] ₂	Yellow, 118
(c) Trifluoroacetylacetone-isoniacin hydrazone (TFAINH)	
(TFAINH-H)TiCl ₃ .HCl	Brown, >250d
(TFAINH-2H)Ti(OPr) ₂	Brown, >250d
(TFAINH-2H)Ti(Sal) ₂	Brown, >250d
(TFAINH-2H)Ti(Ba) ₂	Brown, >250d
(TFAINH-2H)Ti(8-Hq) ₂	Brown, 145
(TFAINH-2H)Sn(Me) ₂	Yellow, 110
(TFAINH-2H)Sn(Bu) ₂	Yellow liquid
(TFAINH-2H)Sn(Oct) ₂	Yellow liquid
(TFAINH-2H)[SnPh ₃] ₂	Yellow, 145
(d) Thenoylacetone-isoniacin hydrazone (THAINH)	
(THAINH-2H)TiCl ₂	Dark, >240d
(THAINH-2H)Ti(OPr) ₂	Orange, >250d
(THAINH-2H)Ti(Sal) ₂	Red, >200d
(THAINH-2H)Ti(8-Hq) ₂	Red, 160
(THAINH-2H)Sn(Me) ₂	Orange, 140
(THAINH-2H)Sn(Bu) ₂	Orange, low melting
(THAINH-2H)Sn(Oct) ₂	Orange, low melting
(THAINH-2H)[SnPh ₃] ₂	Orange, 230

* Satisfactory elemental analyses were obtained

OPr = isopropyl, Sal-H = salicylaldehyde.

Ba-H = benzoylacetone, 8-Hq-H = 8-hydroxyquinoline.

AcAc-H = acetylacetone, Me = methyl.

Bu = *n*-butyl, Oct = *n*-octyl.

Ph = phenyl

The IR spectra of hydrazones derived from salicylaldehyde, acetylacetone, etc. and isoniazid [ν_{\max} in cm⁻¹] show a broad band due to $\nu_{\text{N-H}}$ in the range 3350-3180. The β -diketone hydrazones exist in keto form and do not show any OH band. Salicylaldehydeisoniacin hydrazone shows a broad OH stretching band (of salicylaldehyde) strongly hydrogen bonded with azomethine nitrogen⁶. The amide (C=O) bands for derivatives of salicylaldehyde, acetylacetone, trifluoroacetylacetone and thenoylacetone are observed at 1680, 1630, 1660 and 1665, but are often mixed with the CO of the diketone. The $\nu_{\text{C}=\text{N}}$ mode is seen along with $\nu_{\text{C}=\text{C}}$ in the range 1620-1600 as a strong band. The phenolic C-O of salicylaldehyde and enolic C-O of β -diketone appear between 1330 and 1290 and $\nu_{\text{N-N}}$ at 900-800.

The chelated titanium trichloride hydrochlorides of β -diketones show a broad band in the region 3500-2900 due to hydrogen bonded NH⁺. The $\nu_{\text{C}=\text{O}}$ is observed at 1710 and the amide C=O is absent indicating the enolisation of the isoniazid residue. The compound formation is also indicated by the splitting of N-N and its shifting to higher frequency side and by the appearance of $\nu_{\text{Ti-N}}$ at 560, $\nu_{\text{Ti-O}}$ at 460 and $\nu_{\text{Ti-Cl}}$ at 360 (refs 8, 9).

Chelated titanium diisopropoxides of these ligands do not show $\nu_{\text{N-H}}$. The $\nu_{\text{Ti-O-C}}$ mode is seen at 1015, $\nu_{\text{Ti-O}}^{10}$ (propoxy) at 590 and 570, $\nu_{\text{Ti-N}}$ at 510 and $\nu_{\text{Ti-O}}$ (amide and enolic) at 485 and 450 as medium intensity bands. These observations fit well with a penta-coordinated structure with *cis* isopropoxy groups for these compounds.

Bis(salicylaldehydato)titanium isoniazid derivatives obtained from the diisopropoxide of the ligand and salicylaldehyde, do not show $\nu_{\text{O-H}}$ or $\nu_{\text{N-H}}$. They show $\nu_{\text{C}=\text{O}}$ at 1660 and 1630, corresponding to non-coordinated and coordinated carbonyl groups respectively of salicylaldehyde, giving a hexa-coordinated titanium atom. The IR spectra of dialkyl tin compounds resemble those of the titanium counterparts. The $\nu_{\text{Sn-C}}$ appears at 560 and 520¹¹, $\nu_{\text{Sn-O}}$ at 450¹² and $\nu_{\text{Sn-N}}$ at 360¹³; these observations point to a penta-coordinated tin atom with trigonal-bipyramidal geometry with alkyl groups *cis* to each other. The dichlorotin derivatives show ν_{as} and ν_{s} Sn-Cl at 310 and 290 respectively. The ligand acts as a bridge between two tin atoms in the case of triphenyltin derivatives.

In the PMR spectrum, the methyl protons of acetylacetone-isoniacin hydrazone resonate [in CDCl₃, chemical shift in δ ppm] at 2.03 and the corresponding signals for trifluoroacetylacetone-isoniacin hydrazone and thenoylacetone-isoniacin hydrazone are observed at 2.06 and 2.20 respectively. This downward shift is due to the presence of electron

withdrawing trifluoromethyl and thiophene groups in place of methyl group. These ligands show four signals due to methylene protons with a coupling constant of 16 Hz. Unlike in acetylacetone (keto form), the methylene protons of these ligands are attached to different groups; hence, they become magnetically nonequivalent and show splitting due to geminal coupling. The amino proton absorbs around 5.00 and aromatic protons resonate as multiplets between 7.00 and 9.60. Absence of enolic and methine protons strongly suggests the existence of the keto form in the ligand even in solution. The spectra of organotin chelates show downfield shift for the methyl protons indicating coordination of azomethine nitrogen to tin atom, and absence of signals due to CH₂ and NH protons and appearance of =CH protons suggest the dibasic tridentate nature of the ligands.

The UV spectra of isoniazin hydrazones with aliphatic β -diketones (in acetonitrile) show only one absorption band around 265 nm. In the case of thenoyl acetone-isoniazid hydrazone, two bands (at 265 and 350 nm) are observed. The corresponding organotin derivatives show a band at 390 nm in addition to the one at 260 nm. Thenoyl isoniazid hydrazone tin

complex gives the corresponding band at 465 nm. The band in the long wave length region may be attributed to the ligand-metal charge transfer transition¹⁴.

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