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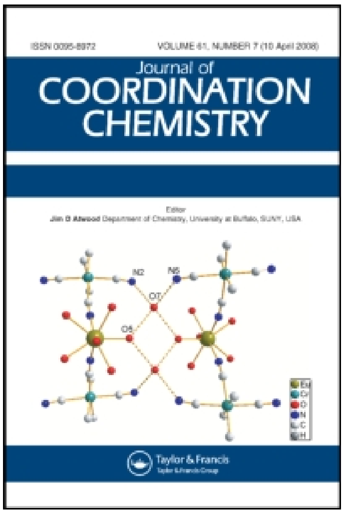

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# Coordination complexes of titanium, zirconium and tin having metal-carbon bonds with dibasic NSO donor Schiff base ligand. Syntheses and characterization

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The reaction of 3-formylsalicylic acid with morpholine *N*-thiohydrazide produces 3-carboxy-2-hydroxybenzaldehyde morpholine *N*-thiohydrazone ($H_2$chbmth) which remains in equilibrium in solution with its corresponding thiol form $H_3$chbmthol having an NSO donor set of atoms. The reactions of the thiohydrazone ligand with different organometallic compounds *viz.* $R_2MCl_2$ ($R = \pi\text{-}C_5H_5$ & $M = Ti/Zr$; $R = Me/Ph$ & $M = Sn$; $R = OMe$ & $M = Sn$), $(\pi\text{-}C_5H_5)_2Ti(OMe)Cl_2$ and RMCl3 ($R = Me/Ph$ & $M = Sn$; $R = \pi\text{-}C_5H_5$ & $M = Ti$) leading to the syntheses of many new organometallic derivatives have been studied. In all of the complexes the dianion of the $H_3$chbmthol ligand functions as a dibasic tridentate NSO donor. The reactions of [($\pi$-$C_5H_5$)Ti(Hchbmthol)Cl] and [MeSn(Hchbmthol)Cl], isolated in this study, with $Me_3SiE$ (where, E stands for $NMe_2$ and C≡CPh) and MeSH have also been studied and many new organoderivatives of these two metal ions isolated. All the compounds under study have been characterized by elemental analyses, magnetic susceptibilities, molar conductance values, molecular weights and spectroscopic (UV-Vis, IR, $^1$H NMR) data. Based upon these data the geometry of the compounds has also been proposed.

*Keywords*: Schiff base; Organoderivatives; NSO donor; Thiohydrazone; Electronic spectra

## 1. Introduction

It is demonstrated earlier [1] that hydrazone ligands have enzyme inhibiting properties. The tuberculostic properties of hydrazides and their derivatives have also been extensively studied [2] and the condensation products of hydrazides with different carbonyl compounds (aldehydes/ketones) are known to be less toxic than the parent hydrazides; this is probably due to the blocking of the free amino group. Because of this and as a part of our systematic studies of hydrazide and hydrazone ligands [3–7], we have very recently synthesized 3-carboxy-2-hydroxybenzaldehyde morpholine *N*-thiohydrazone ($H_2$chbmth) by condensation of 3-formylsalicylic acid with

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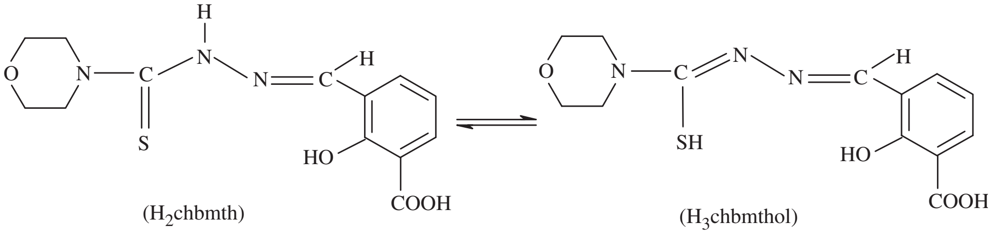

Figure 1. Tautomerism between the thioketo ($H_2$chbmth) and thiol ($H_3$chbmthol) form of the ligand.

morpholine *N*-thiohydrazide and studied its reactions with first and second row transition metal salts under varied reaction conditions [8], isolating many new metal complexes of the ligand $H_3$chbmthol which is the thiol form of the hydrazone $H_2$chbmth (figure 1) [9]. In most of the cases $H_3$chbmthol functions as a dibasic tridentate NSO donor ligand, the COOH group remaining free. Complex formation through the tautomeric enethiol form of the ligand under discussion after deprotonation is commonly observed in the same type ligands and metal salts. The driving force of such reactions is possibly the stable complex formation [9]. In continuation of this work we further studied the reactions of $H_2$chbmth with $(\pi\text{-}C_5H_5)_2TiCl_2$, $(\pi\text{-}C_5H_5)_2ZrCl_2$, $Me_2SnCl_2$, $Ph_2SnCl_2$, $(\pi\text{-}C_5H_5)_2Ti(OMe)Cl_2$, $(OMe)_2TiCl_2$, $(\pi\text{-}C_5H_5)TiCl_3$, $MeSnCl_3$ and $PhSnCl_3$ and isolated new organoderivatives of Ti(IV), Zr(IV) and Sn(IV). This article records the results of this investigation and also describes the reactions of $[(\pi\text{-}C_5H_5)Ti(Hchbmthol)Cl]$ and [MeSn(Hchbmthol)Cl], isolated in this study, with MeSH, $Me_3SiNMe_2$ and $Me_3SiC{\equiv}C\text{–}Ph$.

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## 2. Experimental

### 2.1. *Materials and instruments*

The chemicals used were of AR grade. All solvents were purified and dried according to the standard procedures before use [10]. Manipulations were carried out under an atmosphere of nitrogen. The elemental analyses of the complexes were carried out on Elementar Vario EL III, Carlo Erba 1108 elemental analyzers at the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India. Infrared spectra were recorded in KBr on Perkin-Elmer 1330 and L120-000A spectrophotometers. The electronic spectra were recorded on a Hitachi 200-20 and Simadzu UV-2401PC spectrophotometers. Conductance measurements were made with a conductivity bridge (Elico Pvt. Ltd., Model CM 80). Molecular weights were determined cryoscopically and Rast's method [11]. Di($\pi$-cyclopentadienyl)-titanium(IV)dichloride, $(\pi\text{-}C_5H_5)_2TiCl_2$ and di($\pi$-cyclopentadienyl)zirconium(IV) dichloride, $(\pi\text{-}C_5H_5)_2ZrCl_2$ were purchased from Alfa Inorganics. The compounds $(\pi\text{-}C_5H_5)_2Ti(OMe)Cl_2$, $(OMe)_2TiCl_2$ and $(\pi\text{-}C_5H_5)TiCl_3$ were prepared by literature methods [12–14]. The tin compounds $Me_2SnCl_2$, $Ph_2SnCl_2$, $MeSnCl_3$ and $PhSnCl_3$ were prepared by the methods of Luijten and van der Kerk [15], while $Me_3SiC{\equiv}CPh$ was prepared as described [16, 17].

### 2.2. *Preparation of the ligand*

The Schiff-base ligand was prepared by a previously published method [8]. Yield 70%.

### 2.3. *Preparation of the complexes*

**2.3.1. Organotitanium(IV), organozirconium(IV) and organotin(IV) complexes.** To the thiohydrazone ligand $H_2$chbmth (0.773 g, 2.5 mmol) in methanol-nitromethane mixture (40 mL, 50 : 50, v/v) was added $(\pi\text{-}C_5H_5)_2TiCl_2$ (0.622 g, 2.5 mmol) or $(\pi\text{-}C_5H_5)_2ZrCl_2$ (0.73 g, 2.5 mmol) in dry toluene (40 mL) in the presence of a stoichiometric amount of $Et_3N$, stirred for 8 h at ~50°C and the solvent removed under reduced pressure. *n*-Hexane (20 mL) was then added to this crude product and cooled to −10°C affording reddish-brown $[(\pi\text{-}C_5H_5)$Ti(Hchbmthol)Cl] (**1**) and brown $[(\pi\text{-}C_5H_5)$Zr(Hchbmthol)Cl] (**2**) respectively. These were filtered off, washed with *n*-hexane and dried *in vacuo*, yield 75% for **1** and 70% for **2**. Similarly, the reaction of $H_2$chbmth (0.773 g, 2.5 mmol) with $(\pi\text{-}C_5H_5)TiCl_3$ (0.55 g, 2.5 mmol) or $Me_2SnCl_2$ (0.55 g, 2.5 mmol) or $MeSnCl_3$ (0.60 g, 2.5 mmol) or $Ph_2SnCl_2$ (0.86 g, 2.5 mmol) or $PhSnCl_3$ (0.755 g, 2.5 mmol) or $(OMe)_2TiCl_2$ (0.45 g, 2.5 mmol) yielded reddish-brown $[(\pi\text{-}C_5H_5)$Ti(Hchbmthol)Cl] (**1**) reddish-brown [MeSn(Hchbmthol)Cl] (**3**), reddish-brown [PhSn(Hchbmthol)Cl] (**4**) and yellowish-brown [MeOTi(Hchbmthol)Cl] (**5**), respectively. The compounds **1**, **3** and **4** could be isolated from two different reactions. Yields of the compounds vary between 65–75%.

Analogous reaction of $H_2$chbmth (0.773 g, 2.5 mmol) in dry chloroform–ethanol mixture (40 mL, 50 : 50, v/v) with hot $(\pi\text{-}C_5H_5)Ti(MeO)Cl_2$ (0.374 g, 2.5 mmol) in dry chloroform (70 mL) afforded $[(\pi\text{-}C_5H_5)$Ti(Hchbmthol)(MeO)] (**6**). Yields of the compounds vary between 65–75%.

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#### 2.3.2. Reactions of $[(\pi\text{-}C_5H_5)$Ti(Hchbmthol)Cl] (1) and[MeSn(Hchbmthol)Cl] (3)

**2.3.2.1.** ***Reaction with MeSH*** One equivalent of [MeSn(Hchbmthol)Cl] (**3**) (0.476 g, 1 mmol) was added to one equivalent of MeSH (0.048, 1 mmol) in THF–toluene (50 : 50, v/v) (50 mL) and stirred at room temperature in the presence of a stoichiometric amount of $Et_3N$ (0.1 g, 1 mmol) for four days. Solid $Et_3N \cdot HCl$ that separated was removed by filtration and the volume of the filtrate was reduced under vacuum. The solution was cooled to −10°C yielding the solid compound [MeSn(Hchbmthol)SMe] (**7**), which was washed with *n*-hexane and dried *in vacuo*. Yield 70%.

**2.3.2.2.** ***Reaction with*** $Me_3Si(NMe_2)$ The complex [MeSn(Hchbmthol)Cl] (**3**) (0.476 g, 1 mmol) was treated with an equimolar quantity of $Me_3Si(NMe_2)$ (0.117 g, 1 mmol) in the same solvent system (60 mL) and a brown compound [MeSn(Hchbmthol)$NMe_2$] (**8**) was isolated. Yield 75%.

**2.3.2.3.** ***Reaction with*** $Me_3SiC{\equiv}CPh$ Similarly, **3** (0.476 g, 0.001 mol) when treated with $Me_3SiC{\equiv}CPh$ (0.174 g, 0.001 mol) (1 : 1 equivalent) in THF, yielded a brown compound [MeSn(Hchbmthol)(C≡CPh)] (**9**). Yield 60%.

Similarly, the reactions of $[(\pi\text{-}C_5H_5)$Ti(Hchbmthol)Cl] (**1**) with MeSH, $Me_3Si(NMe_2)$ and $Me_3SiC{\equiv}CPh$ under the same reaction conditions yielded red $[(\pi\text{-}C_5H_5)$

Ti(Hchbmthol)SMe] (**10**), light-brown [($\pi$-$C_5H_5$)Ti(Hchbmthol)($NMe_2$)] (**11**) and light-brown [($\pi$-$C_5H_5$)Ti(Hchbmthol)(C≡CPh)] (**12**), respectively. Yields of the compounds vary between 70–75%.

## 3. Results and discussion

### 3.1. *Syntheses*

The reaction of 3-formylsalicylic acid with morpholine *N*-thiohydrazide in 1 : 1 molar ratio in dehydrated ethanol afforded 3-carboxy-2-hydroxybenzaldehyde morpholine *N*-thiohydrazone (abbreviated to $H_2$chbmth) (figure 1), the formation of which is supported by the analytical and spectral data (see latter discussion).

The thiohydrazone $H_2$chbmth has a proton adjacent to the thione group. It is known that the thione group is relatively unstable in the monomeric form and tends to the more stable C–S bond by enethiolization if there is at least one proton adjacent to the thione group [18]. Therefore, the thione form $H_2$chbmth and the thiol form $H_3$chbmthol may remain in equilibrium in solution (figure 1). It was observed by us earlier [8] that the reactions of $H_2$chbmth with different metal salts under varied reaction conditions yielded complexes of the corresponding thiol form of the ligand where it functions as dibasic tridentate fashion bonding through O, N and S atoms with different metal ions. Neutral and bidentate behaviour was also encountered in certain cases with bonding through thione S and azomethine N [8]. However, in the present study the ligand uniformly acts as dibasic tridentate, bonding through thiol S (after deprotonation), azomethine N and phenolic O (after deprotonation) and the carboxylic acid group was always found to be free without participation in complex formation (schemes 1 and 2). Despite our best efforts we could not grow crystals suitable for structural analyses.

All the isolated complexes are stable at laboratory conditions and have been characterized by elemental analyses, molecular weights, molar conductances, magnetic moments and spectroscopic (UV-Vis, IR and $^1$H NMR) data. Some characterization data are collected in table 1.

The reactivity of the Sn–Cl bond in [MeSn(Hchbmthol)Cl] (**3**) with different substrates was studied leading to the syntheses of many new organotin(IV) derivatives. Thus **3** on reaction with MeSH in THF–toluene ($Et_3N$) gave [MeSn(Hchbmthol)SMe] (**7**). Similarly, it reacted smoothly with $Me_3Si(NMe_2)$ and $Me_3SiC{\equiv}CPh$ in a mixed solvent system and afforded amino- and phenyl-ethynyl complexes of organotin(IV) (scheme 2) *via* desilylation of the reagents, which is the driving force of the above reactions. Since the by-product $Me_3SiCl$ is a low boiling liquid and miscible with common organic solvents, it is easily removed by low-pressure distillation. Hence, the new organotin(IV) compounds of the type [MeSn(Hchbmthol)L] were obtained in very pure form and good yield (where, L = $NMe_2$ (**8**); C≡CPh (**9**)). Similarly, reactions of the Ti–Cl bond in the complex [($\pi$-$C_5H_5$)Ti(Hchbmthol)Cl] (**1**) were studied and new organotitanium(IV) derivatives, [($\pi$-$C_5H_5$)Ti(Hchbmthol)L/] isolated in pure form and good yield (scheme 2) (where, $L'$ = SMe (**10**); $NMe_2$ (**11**); C≡CPh (**12**)). Treatment of [($\pi$-$C_5H_5$)Ti(Hchbmthol)($NMe_2$)] (**11**) with $SnPh_3H$ in THF gave a solution from which a

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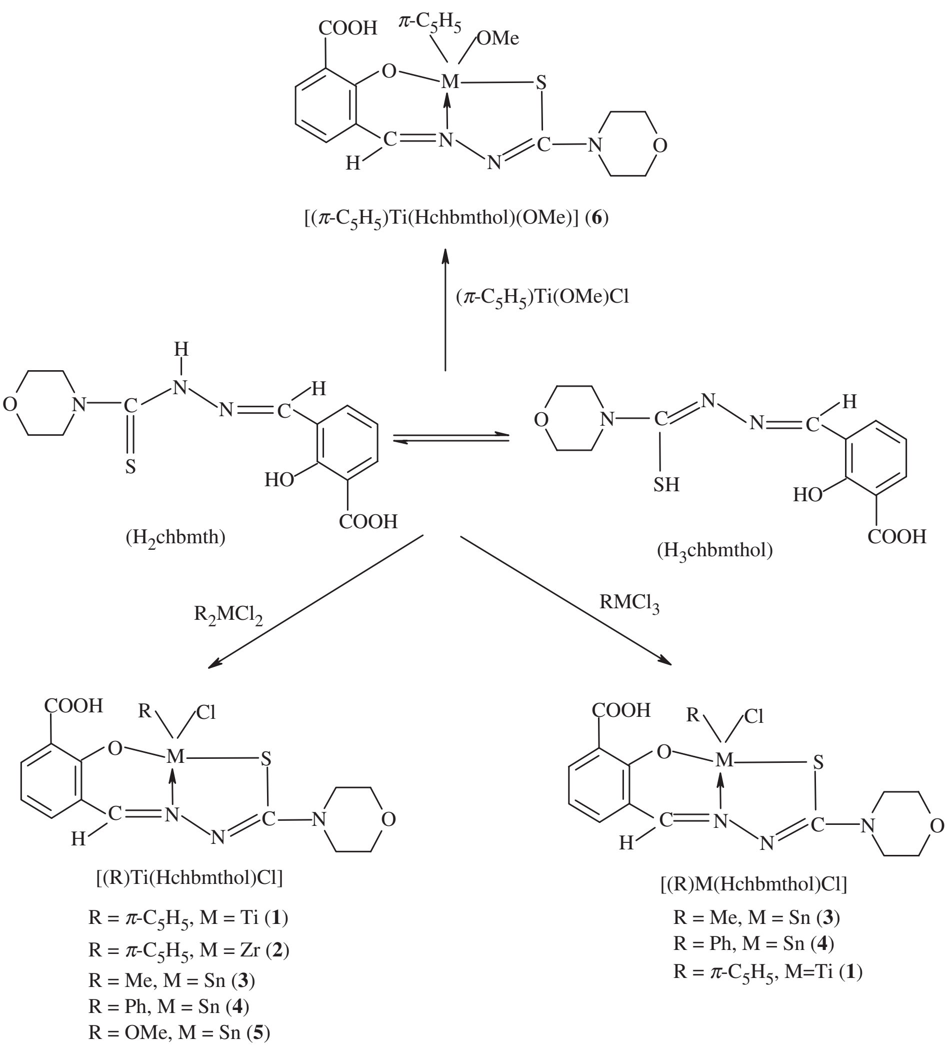


N.B. The compounds (**1**), (**3**) and (**4**) were isolated
from different reactions/starting materials

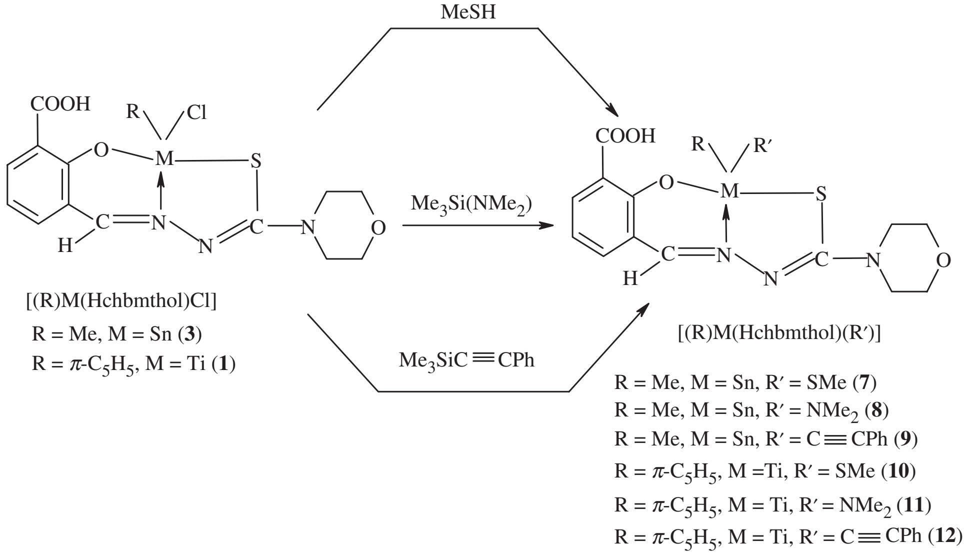
Scheme 1. Reactions of the ligand with the organotin, organotitanium and organozirconium compounds.

brown solid compound $[(\pi\text{-}C_5H_5)Ti(Hchbmthol)(SnPh_3)]$ (**13**) could be isolated (equation (1)):

$$[(\pi - C_5H_5)Ti(Hchbmthol)(NMe_2)] + SnPh_3H \overset{THF}{\rightarrow} [(\pi - C_5H_5) Ti(Hchbmthol)(SnPh_3)] + HNMe_2 \tag{1}$$

The complex **13** is unstable in air and decomposes on heating at 250–254°C.

The elemental analyses of the isolated complexes agree well with their formulations (table 1). The molecular weights are also in good agreement with the theoretical values.



Scheme 2. Reactions of [(π-$C_5H_5$)Ti(Hchbmthol)Cl] (**1**) and [(Me)Sn(Hchbmthol)Cl] (**3**) with MeSH, $Me_3SiNMe_2$ and $Me_3SiC{\equiv}CPh$.

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The complexes are soluble in coordinating solvents like DMSO, DMF, and Py and also in other solvents like chloroform and methanol. All the complexes are insoluble in *n*-hexane and ether.

### 3.2. *Molar conductances*

The molar conductance values of the complexes in DMSO solutions show very low values, in the range 9.9 to 21.88 $cm^2 ohm^{-1} mol^{-1}$ (table 1), indicating their non-electrolytic [19] nature. The molar conductance values of 1 : 1 electrolytes range from ~23 to 42 $cm^2 ohm^{-1} mol^{-1}$. The conductance data published [20] for complexes $[MCl_2(en)_2]Cl$ (M = Ru, Co) also fall in this range. Our observed values are always less than this range and support the nonelectrolytic nature.

### 3.3. *Electronic spectra*

The ligand $H_2$chbmth shows two very intense bands around 260 and 370 nm in solution of DMSO, due to the intra-ligand charge transfer transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. These bands are very slightly red-shifted along with other bands in the complexes. The titanium and zirconium complexes showed another band around 440–445 nm assignable to charge-transfer [21, 22] in accordance with the $(n-1)d^0ns^0$ electronic configuration of Ti(IV) and Zr(IV). The data available for **1**, **2**, **6**, **10** to **12** suggest the coordination number five for these complexes [23–25]. The complexes are all diamagnetic.

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Table 1. Some characterization data of the complexes.

| | | | | | Analyses | | Found | (Calcd) | % | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Mol. wt. Found (Calcd) | M.p.[a] (°C) | Colour | Yield (%) | C | H | N | Cl | M | $\Lambda_M$[b] ($\Omega^{-1}\,cm^2\,mol^{-1}$) |
| $H_3$chbmthol ($H_3$L) | 317 | 185–187 | Yellow | 70 | 50.52 | 4.93 | 13.63 | – | – | – |
| $C_{13}H_{15}O_4N_3S$ | (309.24) | | | | (50.48) | (4.89) | (13.58) | | | |
| [($\pi$-$C_5H_5$)Ti(HL)Cl] (**1**) | 462 | 201–205 | Reddish-brown | 75 | 47.49 | 3.93 | 9.16 | 7.75 | 10.57 | 10.2 |
| $C_{20}H_{18}O_4N_3SClTi$ | (455.75) | | | | (47.44) | (3.98) | (9.22) | (7.78) | (10.50) | |
| [($\pi$-$C_5H_5$)Zr(HL)Cl] (**2**) | 510 | 250–255 | Brown | 70 | 43.29 | 3.60 | 8.37 | 7.17 | 18.23 | 9.9 |
| $C_{20}H_{18}O_4N_3SClZr$ | (499.10) | | | | (43.32) | (3.63) | (8.42) | (7.10) | (18.28) | |
| [MeSn(HL)Cl] (**3**) | 483 | 248–250 | Orange-red | 70 | 35.32 | 3.42 | 8.86 | 7.49 | 24.94 | 21.88 |
| $C_{14}H_{16}O_4N_3SClSn$ | (476.52) | | | | (35.29) | (3.38) | (8.82) | (7.44) | (24.91) | |
| [PhSn(HL)Cl] (**4**) | 550 | 240–244 | Reddish-purple | 70 | 42.41 | 3.43 | 7.84 | 6.63 | 22.11 | 18.80 |
| $C_{19}H_{18}O_4N_3SClSn$ | (538.59) | | | | (42.37) | (3.37) | (7.80) | (6.58) | (22.04) | |
| [OMeTi(HL)Cl] (**5**) | 403 | 232–236 | Yellow | 75 | 39.76 | 3.53 | 9.88 | – | 11.28 | 14.76 |
| $C_{14}H_{15}O_5N_3SClSn$ | (420.67) | | | | (39.97) | (3.59) | (9.98) | | (11.38) | |
| [($\pi$-$C_5H_5$)Ti(HL)Ome] (**6**) | 443 | 210–213 | Brown | 65 | 50.61 | 4.65 | 9.27 | – | 10.57 | 16.87 |
| $C_{19}H_{21}O_5N_3STi$ | (451.33) | | | | (50.56) | (4.69) | (9.31) | | (10.61) | |
| [MeSn(HL)(SMe)] (**7**) | 493 | 260–264 | Reddish-brown | 70 | 36.89 | 3.85 | 8.55 | – | 24.27 | 13.09 |
| $C_{15}H_{19}O_4N_3S_2Sn$ | (488.16) | | | | (36.96) | (3.92) | (8.61) | | (24.32) | |
| [MeSn(HL)($NMe_2$)] (**8**) | 499 | 230–232 | Brown | 70 | 39.55 | 4.51 | 11.48 | – | 24.51 | 14.18 |
| $C_{16}H_{22}O_4N_4SSn$ | (485.15) | | | | (39.61) | (4.57) | (11.55) | | (24.47) | |
| [MeSn(HL)(C=CPh)] (**9**) | 556 | 200–203 | Brown | 70 | 48.80 | 3.96 | 7.71 | – | 21.94 | 14.18 |
| $C_{22}H_{21}O_4N_3SSn$ | (542.20) | | | | (48.73) | (3.90) | (7.75) | | (21.89) | |
| [($\pi$-$C_5H_5$)Ti(HL)(SMe)] (**10**) | 481 | 240–244 | Red | 70 | 48.76 | 4.50 | 8.91 | – | 10.20 | 16.97 |
| $C_{19}H_{21}O_4N_3S_2Ti$ | (467.39) | | | | (48.83) | (4.53) | (8.99) | | (10.24) | |
| [($\pi$-$C_5H_5$)Ti(HL)($NMe_2$)] (**11**) | 480 | 220–225 | Light-brown | 65 | 51.67 | 5.17 | 12.12 | – | 10.26 | 15.83 |
| $C_{20}H_{24}O_4N_4STi$ | (464.38) | | | | (51.73) | (5.21) | (12.06) | | (10.31) | |
| [($\pi$-$C_5H_5$)Ti(HL)(C≡CPh)] (**12**) | 534 | 190–194 | Light-brown | 70 | 59.95 | 4.53 | 8.13 | – | 9.23 | 14.07 |
| $C_{26}H_{23}O_4N_3STi$ | (521.43) | | | | (59.89) | (4.45) | (8.06) | | (9.18) | |

[a]Decomposition temperature; [b]$10^{-3}$ M solution in DMSO at room temperature.

### 3.4. *Infrared and $^1H$ NMR spectra*

The infrared spectra of the ligand and the metal complexes have been measured in KBr pellets. The thiohydrazone, $H_2$chbmth shows no band in the region ca 2570 cm$^{-1}$ assignable to $\nu$(SH) [26], instead a band at 770 cm$^{-1}$ assignable to $\nu$(C=S) is observed suggesting that in the solid state the ligand remains in the thioketo form (figure 1). However, in solution, both the thioketo ($H_2$chbmth) and thiolo ($H_3$chbmthol) tautomeric forms may remain in equilibrium [27, 28] (figure 1).

The uncomplexed ligand shows bands assignable to $\nu$(NH) in the region 3200–2900 cm$^{-1}$. But the $\nu$(OH) band at 3500 cm$^{-1}$ is not observed and this may be due to strong hydrogen bonding, which probably shifts $\nu$(OH) to lower frequency. The bands due to $\nu$(OH/NH) disappeared in all the complexes indicating conversion of thione to thiolo form and coordination of phenolic oxygen atom after deprotonation. The disappearance of $\nu$(NH) and concomitant appearance of a new band at 1600 cm$^{-1}$ due to azine chromophore >C=N–N=C< support the conversion of $H_2$chbmth to $H_3$chbmthol and formation of complexes by bonding through ONS donor sites (see latter discussion). However, presence of free –COOH group makes the interpretation difficult. The C=N stretching vibration of the free ligand occurs [29, 30] at 1630 cm$^{-1}$ but on complexation this band, in all the cases, is shifted to lower frequency suggesting that the ligand is coordinated to the metal *via* the azomethine nitrogen atom [31]. This lowering of C=N bond order as a result of M–N bond formation [32] is evident from the appearance of new $\nu$(M–N) bands in the far infrared region.

The free ligand possesses potential thioamide groups and therefore displays characteristic thioamide bands I to IV in the region 1560–770 cm$^{-1}$. The thioamide bands of the free ligand are located at 1560, 1440, 1305 and 770 cm$^{-1}$ and these are affected appreciably in metal complexes [33–35]. The thioamide band IV, mainly due to $\nu$(C=S) disappeared in the metal complexes indicating coordination of sulphur after deprotonation from thiol, $H_3$chbmthol (see above discussion) [36–38], which gets further support by the appearance of new M–S bands in the far infrared region.

It is evident that in the present complexes both the phenolic OH and thioamide band IV disappeared, instead a new band due to $\nu$(C–S) around 720–700 cm$^{-1}$ is observed suggesting coordination of metal ion through thiolo-sulphur and phenolic oxygen *via* deprotonation. Moreover, a new $\nu$(C=N) stretching mode is also lowered by about 25 cm$^{-1}$. It may, therefore, be inferred that in the present complexes **1** to **12** the ligand is dibasic tridentate, bonding through O, N and S atoms. All the complexes show broad medium bands in the region 3600–2990 cm$^{-1}$, which are assignable to free carboxyl group [39, 40].

The bands at 1210–1200 [$\nu$(CO)], 1250–1240 [$\nu$(CN)], 1105 and 920–895 cm$^{-1}$ (out of plane and in plane deformation) of the morpholine ring are not affected appreciably in the metal complexes, indicating that the morpholine ring oxygen and nitrogen are not involved in coordination [36, 37].

The organotitanium(IV) and organozirconium(IV) complexes **1**, **2**, **6**, **10**, **11** and **12** show additional bands in the regions 590–610 and 520–530 cm$^{-1}$ assignable to $\nu$(Ti–O), $\nu$(Zr–O), $\nu$(Ti–N) and $\nu$(Zr–N) respectively. The $\nu$(Ti–Cl) and $\nu$(Zr–Cl) are observed in the range 340–350 cm$^{-1}$ in **1** and **2**. In the organotin(IV) complexes **3**–**5** and **7**–**9** new bands around 540, 430 and 340 cm$^{-1}$ may be attributed to $\nu$(Sn–O), $\nu$(Sn–N) and $\nu$(Sn–Cl), respectively [42, 43]. The $\nu$(M–S) (M = Ti, Zr or Sn) in all the

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complexes appeared in the range 355–370 cm$^{-1}$ [42, 43]. The infrared data are summarized in table 2.

The $^1$H NMR data (in DMSO-d$_6$) showed the absence of $\delta$(CHO) at 9.25 ppm in the ligand H$_2$chbmth which was found in 3-formylsalicylic acid. The azomethine proton signal $\delta$(CH=N) could be detected at $\delta$ 8.56 ppm, which appeared at $\delta$ 8.25 ppm in the complexes. The signals for $\delta$(OH) and $\delta$(NH) disappeared after the addition of $D_2O$. The broad signal at $\delta$ 6.5 ppm to $\delta$ 7.9 ppm may be assigned to the phenyl resonance region. The resonance peak for the COOH protons could be detected around $\delta$ 11.90 ppm (broad signal) [44]. A very negligible change is observed in the COOH proton in the complexes as indicated in table 3. The integral ratio of the three protons on the morpholine ring, phenyl group, carboxyl group, and also the proton(s) on carbon and nitrogen is quite consistent with the formulations of the complexes. As expected, there is no remarkable change in the chemical shifts of morpholine ring proton signals, which appeared at $\delta$ 3.68–3.91 ppm. However, the NH proton ($\delta$ 10.10 ppm) signals completely disappeared in all the complexes suggesting dibasic tridentate NSO donor nature of the ligand (see IR discussion above). In addition, signals for $\pi$-C$_5$H$_5$, CH$_3$S, NMe$_2$, MeSn appeared at $\delta$ 6.5 (slightly broadened singlet), 3.44 (s), 3.52 (slightly broadened singlet) and 0.91 (s) ppm respectively, supporting the formulations of the complexes [43] (schemes 1 and 2).

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Table 2. Some important infrared bands of the ligand and some of the complexes with their tentative assignments.

| | Frequencies (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|
| Complex | C=S/C–S | C=N | M–N + M–O | M–S | M–Cl |
| H$_2$chbmth | 770 | 1630 | – | – | – |
| [($\pi$-C$_5$H$_5$)Ti(Hchbmthol)Cl] (**1**) | 702 | 1603 | 603, 592, 520 | 358 | 342 |
| [($\pi$-C$_5$H$_5$)Zr(Hchbmthol)Cl] (**2**) | 710 | 1606 | 610, 600, 527 | 366 | 348 |
| [MeSn(Hchbmthol)Cl] (**3**) | 716 | 1601 | 538, 425 | 370 | 337 |
| [PhSn(Hchbmthol)Cl] (**4**) | 720 | 1610 | 532, 429 | 369 | 335 |
| [MeSn(Hchbmthol)(SMe)] (**7**) | 715 | 1608 | 540, 430 | 365 | – |
| [($\pi$-C$_5$H$_5$)Ti(Hchbmthol)(NMe$_2$)] (**11**) | 705 | 1605 | 610, 595, 523 | 355 | – |
| [($\pi$-C$_5$H$_5$)Ti(Hchbmthol)(C≡CPh)] (**12**) | 700 | 1605 | 609, 590, 525 | 362 | – |

Table 3. $^1$H NMR spectral data[a] of the ligand and some of the complexes ($\delta$ values in ppm).

| Compound | –COOH | –OH | –NH | –C$_6$H$_3$ | –CH=N | Morpholine ring protons |
|---|---|---|---|---|---|---|
| H$_3$chbmthol | 11.90 (s) | 10.40 (s) | 10.10 (s) | 6.88–7.8 (m) | 8.56 (s) | 3.68–3.91 (m) |
| [($\pi$-C$_5$H$_5$)Ti(Hchbmthol)Cl] (**1**) | 11.83 (s) | – | – | 6.65–7.7 (m) | 8.21 (s) | 3.31–3.5 (m) |
| [($\pi$-C$_5$H$_5$)Zr(Hchbmthol)Cl] (**2**) | 11.85 (s) | – | – | 6.60–7.7 (m) | 8.29 (s) | 3.30–3.5 (m) |
| [MeSn(Hchbmthol)Cl] (**3**) | 11.80 (s) | – | – | 6.48–7.65 (m) | 8.25 (s) | 3.12–3.7 (m) |
| [PhSn(Hchbmthol)Cl] (**4**) | 11.82 (s) | – | – | 6.43–7.69 (m) | 8.27 (s) | 3.2–3.68 (m) |
| [MeSn(Hchbmthol)(Sme)] (**7**) | 11.81 (s) | – | – | 6.52–7.68 (m) | 8.23 (s) | 3.15–3.75 (m) |
| [($\pi$-C$_5$H$_5$)Ti(Hchbmthol)(NMe$_2$)] (**11**) | 11.82 (s) | – | – | 6.68–7.72 (m) | 8.20 (s) | 3.3–3.56 (m) |
| [($\pi$-C$_5$H$_5$)Ti(Hchbmthol)(C≡CPh)] (**12**) | 11.80 (s) | | | 6.65–7.76 (m) | 8.26 (s) | 3.17–3.62 (m) |

[a] In DMSO-d$_6$.

## 4. Conclusion

The present study describes the syntheses and characterization of some new organotitanium, organozirconium and organotin complexes with dibasic tridentate NSO donor Schiff-base ligand. New routes have been suggested for the synthesis of metal-carbon bonded compounds. The studies of the different solid-state properties of such compounds might focus their use as valuable materials. As envisaged from other reports, some of the complexes might show important biological activities, which are yet to be investigated.

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