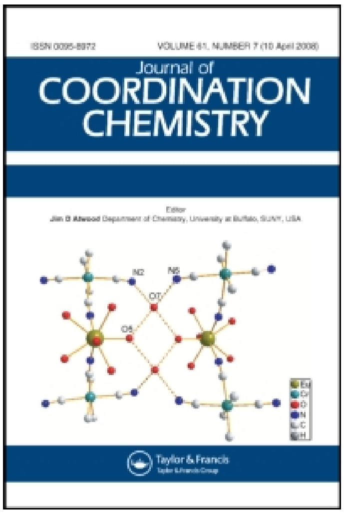

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Synthesis, characterization and coordination behavior of 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine

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Synthesis, characterization and coordination behavior of 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine

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The reaction of 3-formylsalicylic acid with 2-aminoethanethiol produces 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (H_2chptz) which remains in equilibrium in solution with its corresponding Schiff base, 3-carboxysalicylidenethioethanolimine (H_3mcsalim) having an NSO-donor set of atoms. The reactions of the thiazolidine ligand with different metal salts leading to the synthesis of many new metal complexes and organometallic derivatives have been studied. For all the complexes the dianion of the Schiff base, H_3mcsalim acts as a tridentate NSO donor ligand. The reactions of [(Hmcsalim)Ti(π-C_5H_5)Cl] and [(Hmcsalim)Sn(Me)Cl], isolated in this study, with Me_3SiE (where, E stands for SMe, NMe_2 and C≡CPh) have also been studied. The elemental analyses, magnetic susceptibilities, molar conductance values, EPR-study, CV, molecular weights and spectroscopic (UV-Vis, IR, ^{1}H NMR) data characterize all the compounds under study. Based upon these data the geometry of the compounds has also been proposed.

Keywords: Schiff base; Thiazolidine; Organogroup(IV) compounds; Organometallics; Transition metals

1. Introduction

Extensive studies have been made by us [1–3] and others [5–8] on the metal complexes of ligands derived from 3-formylsalicylic acid. Of late, we have been interested in the metal complexes of NS and NSO donor ligands, importance of which is well documented in the literature [9, 10]. Recently, we synthesized a new benzothiazoline, 2-(1-carboxyl-2-hydroxyphenyl)benzothiazoline, by reaction of 3-formylsalicylic acid and 2-aminobenzenethiol and studied its reactions with different metal salts [1, 2]. In continuation of that study, we recently synthesized a new thiazolidine, 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (abbreviated as H_2chptz), by the condensation of 3-formylsalicylic acid with 2-aminoethanethiol and studied its reactions with

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$Ni(OAc)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot 2H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cd(OAc)_2 \cdot 2H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, $VOSO_4$, $VOCl_3$, Na_2PdCl_4, $(\pi\text{-}C_5H_5)_2TiCl_2$, $(\pi\text{-}C_5H_5)_2ZrCl_2$, Me_2SnCl_2, Ph_2SnCl_2 and $MeSnCl_3$ under varied reaction conditions. This article records the results of this investigation and also includes the reactions of $[(\pi\text{-}C_5H_5)Ti(Hmcsalim)Cl]$ and [MeSn(Hmcsalim)Cl], isolated in this study, with Me_3SiE (where E stands for SMe, NMe_2 and C≡C–Ph) affording new organotitanium(IV) and organotin(IV) compounds. The thiazolidine (H_2chptz) and the corresponding Schiff base (H_3mcsalim) remain in equilibrium in solution and it is the Schiff base that ultimately forms the metal complexes as a dibasic tridentate NSO donor.

2. Experimental

2.1. *Materials and instruments*

The chemicals used were AR grade. The solvents and chemicals were purified and dried before use by standard procedures. Elemental analyses were carried out at the Regional Sophisticated Instrumentation Centre, the Central Drug Research Institute, Lucknow. The electronic spectra (ethanol, DMSO or nujol) were recorded on a Hitachi 200-20 and Shimadzu UV-2401PC spectrophotometers and infrared spectra (KBr or Nujol or hexachlorobutadiene; more than one medium was used for some compounds) on a Perkin-Elmer 1330 and L120-000A FTIR spectrophotometers. The molar conductances were measured using an Elico conductivity bridge. Magnetic susceptibilities were determined by the Guoy method. Molecular weights were determined by Rast's method and osmometrically. Di(π-cyclopentadienyl)-titanium(IV)dichloride, $(\pi\text{-}C_5H_5)_2Ti^{IV}Cl_2$ and di(π-cyclopentadienyl)zirconium(IV) dichloride, $(\pi\text{-}C_5H_5)_2Zr^{IV}Cl_2$ were purchased from Alfa Inorganics. Dimethyldichlorostannane(IV), $Me_2Sn^{IV}Cl_2$, diphenyldichlorostannane(IV), $Ph_2Sn^{IV}Cl_2$ and methyltrichlorostannane(IV), $MeSn^{IV}Cl_3$ were prepared by the method of Luijten and vander Kirk [11]. The compound $Me_3SiC{\equiv}CPh$ was prepared as described in the literature [12].

2.2. *Preparation of the ligand*

The ligand 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (H_2chptz) was prepared by the following method: a solution of 2-aminoethanethiol hydrochloride (1.13 g, 10 mmol) in freshly distilled methanol (30 mL) was added to a stirred solution of CH_3COONa (0.82 g, 10 mmol) in the same solvent (20 mL) and filtered. The filtrate was added to a cold solution of 3-formylsalicylic acid (1.66 g, 10 mmol) in freshly distilled methanol (35 mL) dropwise with constant stirring. The mixture was allowed to stir for 1 h followed by reflux for 1 h. The resulting yellow solution, on concentration and cooling, yielded yellow powdery compound. It was filtered off, washed with cold methanol and dried *in vacuo*. Yield 1.35 g (60%).

2.3. *Preparation of complexes*

$[Ni_2(Hmcsalim)_2]$ (1). A solution of H_2chptz (4.5 g, 20 mmol) in dry methanol (40 mL) was added to a solution of $Ni^{II}(OAc)_2 \cdot 4H_2O$ (2.49 g, 10 mmol) in the same solvent (50 mL) and the mixture was stirred at 40°C for 10 h. The resulting brown solution yielded a reddish brown powdery compound **1** which was filtered off, washed with methanol and dried *in vacuo*. Yield 4.06 g (72%). The compound is soluble in DMF, DMSO and Py.

NH_4[(Hmcsalim)Ni(OAc)] (2). The ligand H_2chptz (2.25 g, 10 mmol) was dissolved in ethanol (30 mL), to which a solution of $Ni^{II}(OAc)_2 \cdot 4H_2O$ (2.48 g, 10 mmol) in the same solvent (30 mL) was added with stirring and the mixture was heated under reflux for 2 h to yield a brown solution. On adding NH_4OH solution (15%) to this brown solution (pH ~ 8) with stirring a microcrystalline reddish compound separated. It was collected by filtration and washed with ethanol and dried *in vacuo*. Yield 1.97 g (55%). The compound is soluble in boiling water, hot methanol and also in DMF, DMASO and Py and insoluble in non-polar organic solvents.

[(Hmcsalim)Ni(Py)] (3). Brown compound **1** (5.63 g, 10 mmol) was dissolved in freshly distilled pyridine (25 mL) and the solution was heated (2 h) on a water bath at gentle reflux. The dark brown solution, thus obtained, was kept in the refrigerator for 2 days, when brown powder was obtained. It was filtered off, washed with cold ethanol and dried *in vacuo*. Yield 2.45 g (68%). The compound is soluble in DMF, DMSO and appreciably so in methanol. It is insoluble in non-polar organic solvents.

$(NH_4)_2$[Ni(Hmcsalim)$_2$] (4). Similarly the reaction of H_2chptz (2.25 g, 10 mmol) with $Ni^{II}Cl_2 \cdot 6H_2O$ (2.37 g, 10 mmol) in ethanol afforded a light brown solution, which on treatment with NH_4OH solution (15%) yielded this microcrystalline gray complex which was collected by filtration, washed with ethanol and dried *in vacuo*. Yield 3.79 g (70%). The compound is soluble in water, DMF, DMSO and Py.

[Cu_2(Hmcsalim)$_2$] (5). A solution of $Cu^{II}(OAc)_2 \cdot H_2O$ (1.99 g, 10 mmol) in methanol (50 mL) and sodium acetate (1.64 g, 20 mmol) was added with stirring to a solution of H_2chptz (4.5 g, 20 mmol) in dry methanol (40 mL) and the resulting mixture was gently refluxed for 8 h. The precipitated green solid was filtered off, washed with methanol and dried *in vacuo*. Yield 3.55 g (62%). It is soluble in DMF, DMSO and Py. Similar reaction with $Cu^{II}(NO_3)_2 \cdot 3H_2O$ and $Cu^{II}Cl_2 \cdot 2H_2O$ yielded the same complex.

[(Hmcsalim)Cu(NH_3)] (6). The ligand H_2chptz (2.25 g, 10 mmol) was dissolved in methanol (30 mL), to which a solution of $Cu^{II}(NO_3)_2 \cdot 3H_2O$ (2.41 g, 10 mmol) in the same solvent (30 mL) was added with stirring and the mixture was heated under reflux for 2 h to yield a green solution. On adding NH_4OH solution (15%) to this green solution (pH ~ 8) with stirring a light green powdery compound separated,was collected by filtration, washed with methanol and dried *in vacuo*. Yield 1.67 g (55%). It is soluble in DMF, DMSO, Py, methanol and nitromethane.

[(Hmcsalim)Co(H_2O)] (7). A solution of $Co^{II}(NO_3)_2 \cdot 6H_2O$ (2.91 g, 10 mmol) in methanol (30 mL) was added with stirring to a solution of H_2chptz (2.25 g, 10 mmol) in dry methanol (25 mL) under N_2. The resulting mixture was heated under gentle reflux for 2 h. The brown solution afforded greenish brown microcrystalline compound on concentration and cooling. It was filtered, washed with methanol and dried *in vacuo*. Yield 1.80 g (60%). The compound is soluble DMF, DMSO, Py, methanol and nitromethane.

$NH_4[Co(Hmcsalim)_2]H_2O$ (8). A solution of $Co^{II}(OAc)_2 \cdot 4H_2O$ (2.49 g, 10 mmol) in methanol (30 mL) was added with stirring to a solution of H_2chptz (4.5 g, 20 mmol) in same solvent (25 mL). To this mixture NH_4NO_3 (1.0 g) was added and the pH was raised to ~9 by adding NH_4OH. Air was then drawn through the solution for about 8 h. The brown solution thus obtained, afforded brown solid compound on concentration and cooling. Yield 3.79 g (70%). The compound is soluble in water, methanol, DMF, DMSO and Py.

$[Co(Hmcsalim)(NO_3)(H_2O)_2]$ (9). To an equimolar (10 mmol) refluxing mixture of 3-formylsalicylic acid (1.66 g, 10 mmol) and 2-aminoethanethiol (0.77 g, 10 mmol) was added a methanolic solution (20 mL) of $Co^{II}(NO_3)_2 \cdot 6H_2O$ (2.91 g, 10 mmol) (pH ~ 4). The mixture was further heated under reflux for 4 h, when a dark brown powdery compound separated, was filtered, washed with cold methanol and dried *in vacuo*. Yield 1.90 g (50%). The compound is soluble in DMF, DMSO, Py and appreciably so in hot methanol.

$[Co(H_2mcsalim)(H_2O)_2](NO_3)$ (10). The filtrate from (**9**), described above, was concentrated at reduced pressure to afford this light brown microcrystalline compound. It was filtered and washed with pet-ether (40–60°C) and dried *in vacuo*. Yield 1.71 g (45%). The compound is soluble in methanol, hot water, DMF, DMSO and Py.

$[Cd(Hmcsalim)H_2O]$ (11). A solution of $Cd^{II}(NO_3)_2 \cdot 4H_2O$ (3.08 g, 10 mmol) in methanol (30 mL) was added with stirring to a solution of H_2chptz (2.25 g, 10 mmol) in dry methanol (25 mL). The yellow solution formed was heated under reflux for 2 h and filtered. The filtrate, on concentration and cooling, yielded the powdery yellow compound. Yield 2.12 g (60%). The compound is soluble in methanol, DMF, DMSO and Py.

$[Zn(Hmcsalim)H_2O]$ (12). Similarly the reaction between $Zn^{II}(NO_3)_2 \cdot 6H_2O$ (2.97 g, 10 mmol) and the ligand H_2chptz (2.25 g, 10 mmol) in ethanol (50 mL) yielded this light yellow powdery compound. Yield 1.84 g (60%). The compound is soluble in methanol, DMF, DMSO and Py.

$[(Hmcsalim)VO]_2$ (13). The reaction of H_2chptz (2.25 g, 10 mmol) with $V^{IV}OSO_4$ (1.63 g, 10 mmol) in methanol (60 mL) under reflux gave this brown microcrystalline compound. The compound was filtered off, washed with methanol and dried *in vacuo*. Yield 3.94 g (68%). The compound is soluble in DMF, DMSO and Py.

$[(Hmcsalim)VO(H_2O)]$ (14). The light brown filtrate, obtained from compound **13** described above, gave this greenish yellow solid on concentration and cooling. Yield 0.92 g (30%). The compound is soluble in hot methanol, DMF, DMSO and Py.

$[(Hmcsalim)VO(Cl)]$ (15). Similar to compound **13**, the reaction of H_2chptz (2.25 g, 10 mmol) and V^VOCl_3 (1.73 g, 10 mmol) yielded this reddish brown powdery compound.

It was washed with methanol and dried *in vacuo*. Yield 1.85 g (60%). The compound is soluble in DMF, DMSO and Py.

$[Pd(Hmcsalim)]_2$ (16). A solution of H_2chptz (4.5 g, 20 mmol) in dry methanol (40 mL) was added to a solution of $Na_2Pd^{II}Cl_4$ (2.94 g, 10 mmol) in the same solvent (60 mL) and the mixture was stirred at 40°C for 10 h yielding a yellow solid microcrystalline compound. Yield 4.28 g (65%). The compound is soluble in DMF, DMSO and Py.

$[(\pi\text{-}C_5H_5)M(Hmcsalim)Cl]$ {M = Ti (17) and Zr (18)}. To a solution of thiazolidine ligand H_2chptz (5.62 g, 25 mmol) in methanol–nitromethane mixture (50 : 50 V/V) (50 mL) was added $(\pi\text{-}C_5H_5)_2TiCl_2$ (6.22 g, 25 mmol) or $(\pi\text{-}C_5H_5)_2ZrCl_2$ (7.3 g, 25 mmol) in a chloroform–methanol mixture (50 : 50 V/V) (40 mL) with stirring. The mixture was heated under reflux at neutral pH for 6 h and filtered when hot. A brown (for Ti) or yellow brown (for Zr) filtrate was obtained from which the solvent was removed under reduced pressure. *n*-Hexane (20 mL) was then added to this crude product and the mixture was cooled to about −5°C to obtain orange red **17** or yellow brown **18** solids. The microcrystalline compounds were collected by filtration, washed with ethanol and *n*-hexane and dried *in vacuo*. Yield 6.5 g (70%) for **17** and 6.2 g (60%) for **18**. The compounds are soluble in methanol, nitromethane, chloroform, DMF and DMSO.

$[(\pi\text{-}C_5H_5)Ti(Hmcsalim)(SMe)]$ (19). One equivalent of **17** (0.37 g, 1 mmol) was added to one equivalent of MeSH (0.048 g, 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 (0.101 g, 1 mmol) for 4 d. Solid $Et_3N \cdot HCl$ which had separated was removed by filtration and then the volume of the solution was reduced to half under vacuum. Standing at about −10°C gave a brown solid **19** which was filtered, washed with *n*-hexane and dried *in vacuo*. Yield 0.27 g (70%). The compound is soluble in methanol, nitromethane, chloroform, DMF and DMSO.

$[(\pi\text{-}C_5H_5)Ti(Hmcsalim)(NMe_2)]$ (20). Complex **17** (0.37 g, 1 mmol) was treated with an equimolar quantity of Me_3SiNMe_2 (0.117 g, 1 mmol) as described above in the same solvent system (60 mL) and powdery yellow brown **20** was isolated. Yield 0.25 g (65%). The solubility of the compound was found to be similar to that of compound **19**.

$[(\pi\text{-}C_5H_5)Ti(Hmcsalim)(C{\equiv}CPh)]$ (21). Similar to compound **20**, compound **17** (0.37 g, 1 mmol), when treated with $Me_3SiC{\equiv}CPh$ (0.174 g, 1mmol) in THF, yielded the light brown microcrystalline compound **21**. Yield 0.28 g (65%). The solubility is similar to that found for compound **19**.

$[R_2M(Hmcsalim)]$ {M = Sn, R = Me (22) and Me = Sn, R = Ph (23)}. To the solution of the thiazolidine ligand H_2chptz (5.6 g, 25 mmol) in methanol–nitromethane mixture (50 : 50, V/V) (40 mL) was added Me_2SnCl_2 (5.49 g, 25 mmol) or Ph_2SnCl_2 (8.59 g, 25 mmol) in dry toluene (40 mL) with stirring. The reaction mixture was stirred for 18 h at 50–55°C and the solvent removed under reduced pressure. *n*-Hexane (25 mL) was then added to this crude product and cooled to about −20°C to get red brown microcrystalline compounds **22** and **23**. These were filtered, washed with *n*-hexane and dried *in vacuo*. Yield 6.5 g (70%) for **22** and 9.9 g (80%) for **23**. Both are soluble in methanol, nitromethane, chloroform, DMF and DMSO.

[MeSn(Hmcsalim)(Cl)] (24). Similarly the reaction of H_2chptz (11.25 g, 50 mmol) with $MeSnCl_3$ (12.00 g, 50 mmol) in methanol–nitromethane mixture (100 mL) afforded yellow brown powdery compound **24**. Yield 14.7 g (70%). The solubility of the compound is similar to that observed for **17**.

[MeSn(Hmcsalim)(SMe)] (25); [MeSn(Hmcsalim)(NMe$_2$)] (26) and [MeSn(Hmcsalim)(C≡CPh)] (27). As observed with compound **17**, described above, the compound [MeSn(Hmcsalim)(Cl)] (**24**) (3.92 g, 10 mmol) smoothly reacts with MeSH (0.48 g, 10 mmol), Me_3SiNMe_2 (1.17 g, 10 mmol) and $Me_3SiC{\equiv}CPh$ (1.74 g, 10 mmol) affording the light yellow **25**, yellow brown **26** and light brown **27** compounds, respectively. All the compounds are powdery in nature. Yield 2.19 g (70%) for **25**, 2.80 g (70%) for **26** and 2.75 g (75%) for **27**. The solubility of the compounds are similar to that observed for **19**.

The characterization details are available in table 1.

3. Results and discussion

3.1. *Syntheses*

Condensation of 2-aminobenzenethiol and 2-aminoethanethiol with an aldehyde normally yields benzothazoline and thiazolidine, respectively [13]. Some oxidized products can also be isolated in both the cases. The reactions of α-diketone and 2-aminoethanethiol gives the bis(thiazolidine) (A) as the main product, along with a small amount of the tautomeric Schiff base (B), which may remain in equilibrium in solution (scheme 1) [13–15]. However, the presence of nickel(II) ion gives formation of nickel(II) complex of the corresponding Schiff base (B) in good yield.

In the present investigation, we observed that the reaction of 3-formylsalicylic acid with 2-aminoethanethiol under dry nitrogen atmosphere and mild reaction conditions afforded yellow 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (H_2chptz) (I) in excellent yield. As proposed by earlier workers [14, 15], we may presume that this thiazolidine, in solution, remains in equilibrium with small amounts of the corresponding Schiff base, 3-carboxysalicylidenethioethanolimine (H_3mcsalim) (II) (figure 1).

In the solid state the thiazolidine structure has been suggested from infrared spectral data. The reaction of the thiazolidine, H_2chptz with a stoichiometric amount of the metal salts under varied reaction conditions afforded new complexes **1**–**18**, **21**–**24** of nickel(II), copper(II), cobalt(II), cadmium(II), zinc(II), oxovanadium(IV & V), palladium(II), organotin(IV), organotitanium(IV) and organozirconium(IV). For all the complexes (table 1) the dianion of the Schiff base $(\text{Hmcsalim})^{2-}$ functions as a tridentate NSO donor ligand. The isolated metal complexes **1** to **27** are stable at room temperature and have been characterized by elemental analyses, molecular weights, molar conductance values, magnetic moments, EPR, CV and spectroscopic (UV-Vis, IR and ^{1}H NMR) data. Some of the characterization data are shown in table 1 and some of the preparative reactions of H_2chptz (solution) with different

Table 1. Some characterization data of the complexes.

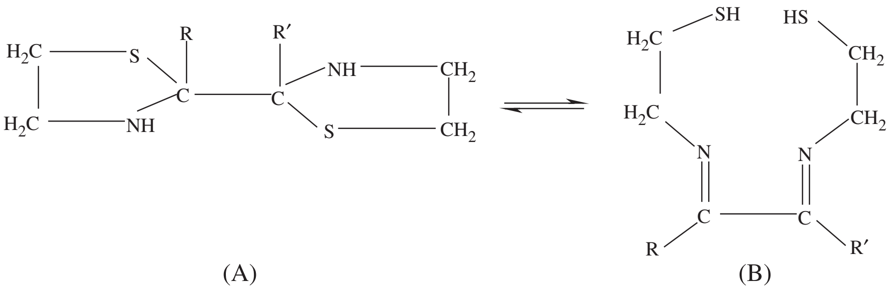
Compound	Mol. Wt. Found (Calcd)	Yield (%)	Analyses		Found	(Calcd)	%	$\mu_{\mathrm{eff}}^{\mathrm{a}}$ (B.M.)	$\Lambda_{\mathrm{M}}^{\mathrm{b}}$ ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$)
			C	H	N	Cl	M		
H_2chptz	229.42	60	53.15	4.82	6.07	–	–	–	–
$C_{10}H_{11}O_3NS$	(225)		(53.33)	(4.89)	(6.22)				
[Ni_2(Hmcsalim)$_2$] (**1**)	572	72	42.70	3.08	5.01	–	20.71	Dia$^{\mathrm{c}}$	12.8
$C_{20}H_{18}O_6N_2S_2Ni_2$	(563.56)		(42.58)	(3.21)	(4.97)		(20.83)		
NH_4[(Hmcsalim)Ni(OAc)] (**2**)	349	55	40.44	4.98	7.68	–	16.59	Dia	52.88
$C_{12}H_{16}O_5N_2SNi$	(358.83)		(40.13)	(4.49)	(7.80)		(16.36)		
[(Hmcsalim)Ni(Py)] (**3**)	372	68	50.11	4.00	7.88	–	16.38	Dia	11.08
$C_{15}H_{14}O_3N_2SNi$	(360.82)		(49.88)	(3.91)	(7.76)		(16.27)		
$(NH_4)_2$[Ni(Hmcsalim)$_2$] (**4**)	–	70	44.65	4.68	10.72	–	10.92	3.38	79.82
$C_{20}H_{26}O_6N_4S_2Ni$			(44.37)	(4.84)	(10.35)		(10.85)		
[Cu_2(Hmcsalim)$_2$] (**5**)	588	62	41.77	3.30	4.98	–	22.30	0.80	15.22
$C_{20}H_{18}O_6N_2S_2Cu_2$	(573.22)		(41.86)	(3.16)	(4.88)		(22.17)		
[(Hmcsalim)Cu(NH_3)] (**6**)	328	55	39.70	3.82	9.00	–	20.58	1.92	16.80
$C_{10}H_{12}O_3N_2SCu$	(303.63)		(39.52)	(3.98)	(9.22)		(20.92)		
[(Hmcsalim)Co(H_2O)] (**7**)	291	60	40.11	3.46	4.76	–	19.88	2.49	14.52
$C_{10}H_{11}O_4NSCo$	(300.02)		(39.99)	(3.69)	(4.66)		(19.64)		
NH_4[Co(Hmcsalim)$_2$]H_2O (**8**)	–	70	44.62	4.58	7.99	–	10.66	Dia	58.0
$C_{20}H_{24}O_7N_3S_2Co$			(44.35)	(4.47)	(7.76)		(10.89)		
[Co(Hmcsalim)(NO_3)(H_2O)$_2$] (**9**)	391	50	31.80	3.42	7.39	–	15.90	Dia	11.88
$C_{10}H_{13}O_8N_2SCo$	(380.04)		(31.57)	(3.44)	(7.36)		(15.50)		
[Co(H_2mcsalim)(H_2O)$_2$](NO_3) (**10**)	–	45	31.69	3.99	7.68	–	15.70	4.20	–
$C_{10}H_{14}O_8N_2SCo$			(31.49)	(3.70)	(7.34)		(15.46)		
[(Hmcsalim)Cd(H_2O)] (**11**)	368	60	34.02	3.38	3.88	–	31.70	Dia	11.98
$C_{10}H_{11}O_4NSCd$	(353.49)		(33.95)	(3.13)	(3.96)		(31.80)		
[(Hmcsalim)Zn(H_2O)] (**12**)	298	60	39.28	3.88	4.77	–	21.58	Dia	12.87
$C_{10}H_{11}O_4NSZn$	(306.46)		(39.15)	(3.61)	(4.56)		(21.33)		
[(Hmcsalim)VO]$_2$ (**13**)	592	68	41.87	3.50	4.62	–	17.66	1.30	12.00
$C_{20}H_{18}O_8N_2S_2V_2$	(580.04)		(41.37)	(3.12)	(4.82)		(17.56)		
[(Hmcsalim)VO(H_2O)] (**14**)	320	30	39.98	3.44	4.88	–	16.92	1.78	11.08
$C_{10}H_{11}O_5NSV$	(308.03)		(38.95)	(3.59)	(4.54)		(16.54)		
[(Hmcsalim)VO(Cl)] (**15**)	–	60	36.42	2.89	4.60	10.79	15.42	Dia	18.04
$C_{10}H_9O_4NSVCl$			(36.86)	(2.78)	(4.30)	(10.90)	(15.65)		
[Pd(Hmcsalim)]$_2$ (**16**)	670	65	36.58	2.69	4.08	–	32.48	Dia	12.33

(*Continued*)

Table 1. Continued.

Compound	Mol. Wt. Found (Calcd)	Yield (%)	Analyses		Found	(Calcd)	%	μ_{eff}^{a} (B.M.)	Λ_{M}^{b} (Ω^{-1} cm^{2} mol^{-1})
			C	H	N	C1	M		
$C_{20}H_{18}O_6N_2S_2Pd_2$	(658.94)		(36.42)	(2.75)	(4.25)		(32.29)		
[(π-C_5H_5)Ti(Hmcsalim)Cl] (**17**)	380	70	48.59	3.61	3.92	9.76	12.70	Dia	10.98
$C_{15}H_{14}O_3NSClTi$	(371.51)		(48.45)	(3.78)	(3.77)	(9.55)	(12.89)		
[(π-C_5H_5)Zr(Hmcsalim)Cl] (**18**)	430	60	43.50	3.62	3.29	8.79	22.01	Dia	11.00
$C_{15}H_{14}O_3NSClZr$	(414.83)		(43.39)	(3.40)	(3.37)	(8.56)	(21.99)		
[(π-C_5H_5)Ti(Hmcsalim)(SMe)] (**19**)	372	70	50.38	4.90	3.86	9.01	12.38	Dia	12.89
$C_{16}H_{17}O_3NS_2Ti$	(383.03)		(50.12)	(4.47)	(3.65)	(9.27)	(12.50)		
[(π-C_5H_5)Ti(Hmcsalim)(NMe_2)] (**20**)	–	65	53.90	5.50	7.59	–	12.99	Dia	13.42
$C_{17}H_{20}O_3N_2STi$			(53.67)	(5.30)	(7.36)		(12.60)		
[(π-C_5H_5)Ti(Hmcsalim)(C≡CPh)] (**21**)	–	65	63.57	4.82	3.02	–	10.72	Dia	13.90
$C_{23}H_{19}O_3NSTi$			(63.15)	(4.38)	(3.20)		(10.96)		
[Me_2Sn(Hmcsalim)] (**22**)	388	70	38.51	4.19	3.61	–	32.01	Dia	12.00
$C_{12}H_{15}O_3NSSn$	(371.82)		(38.72)	(4.06)	(3.76)		(31.92)		
[Ph_2Sn(Hmcsalim)] (**23**)	510	80	53.64	3.51	2.61	–	23.88	Dia	12.99
$C_{22}H_{19}O_3NSSn$	(495.85)		(53.24)	(3.86)	(2.82)		(23.93)		
[MeSn(Hmcsalim)(Cl)] (**24**)	412	75	33.51	3.27	3.66	9.12	30.31	Dia	11.48
$C_{11}H_{12}O_3NSClSn$	(392.29)		(33.65)	(3.08)	(3.57)	(9.05)	(30.25)		
[MeSn(Hmcsalim)(SMe)] (**25**)	–	70	35.99	3.50	3.10	–	29.80	Dia	12.00
$C_{12}H_{15}O_3NS_2Sn$			(35.66)	(3.74)	(3.46)		(29.39)		
[MeSn(Hmcsalim)(NMe_2)] (**26**)	428	70	38.42	4.69	7.00	–	29.79	Dia	17.08
$C_{13}H_{18}O_3N_2SSn$	(400.84)		(38.92)	(4.42)	(6.98)		(29.61)		
[MeSn(Hmcsalim)(C≡CPh)] (**27**)	–	75	50.01	3.68	3.22	–	26.04	Dia	16.88
$C_{19}H_{17}O_3NSSn$			(49.89)	(3.74)	(3.05)		(25.92)		

[a] Solid state at room temperature, [b] 10^{-3} M solution in DMSO at room temperature, [c] Diamagnetic.



Scheme 1. Equilibrium between the bis(thiazolidine) (A) and its corresponding Schiff base (B).

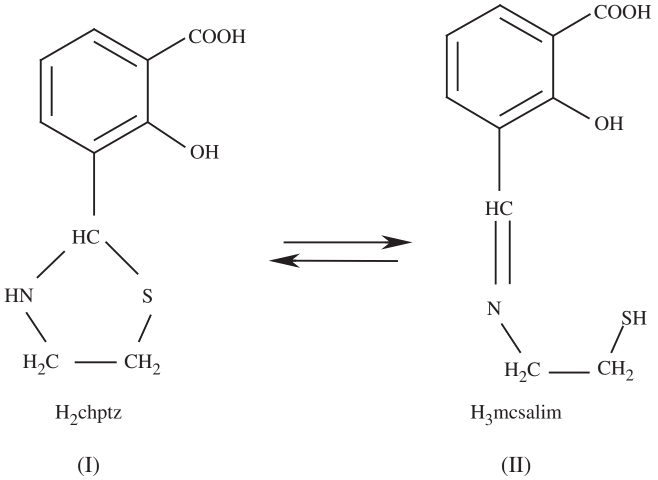


Figure 1. Equilibrium between the thiazolidine (I) and its corresponding Schiff base (II).

metal salts are shown in figures 2–5. The formations of the mononuclear complexes are shown in figures 2–4 and the dinuclear complexes are shown in figure 5. *Initu* reactions of metal salts with a stoichiometric amount of the ligand may also be used to synthesize complexes of the Schiff base H_3mcsalim. Unfortunately no single crystals could be grown in spite of our best efforts.

3.2. *IR and ^{1}H NMR Spectra*

The IR spectrum of the ligand H_2chptz shows important vibrations at 1705(s), 3100(br) and 3350(br) cm^{-1} assignable to ν(COOH), ν(OH) and ν(NH), respectively. The complete elimination of ν(CHO) at 1660 cm^{-1} (observed in 3-formylsalicylic acid) and also the absence of bands around 2500 cm^{-1} and 1600 cm^{-1} assignable to ν(SH) and ν(C=N) respectively, gives further support for the thiazolidine structure [2] (see I in figure 1).

The ^{1}H NMR data (in DMSO-d_6) showed the absence of δ(CHO) at 9.65 ppm in the thiazolidine H_2chptz that was found in 3-formylsalicylic acid. No azomethine proton signal δ(CH=N) could be detected around δ 8.5 ppm. The broad δ(OH) signal

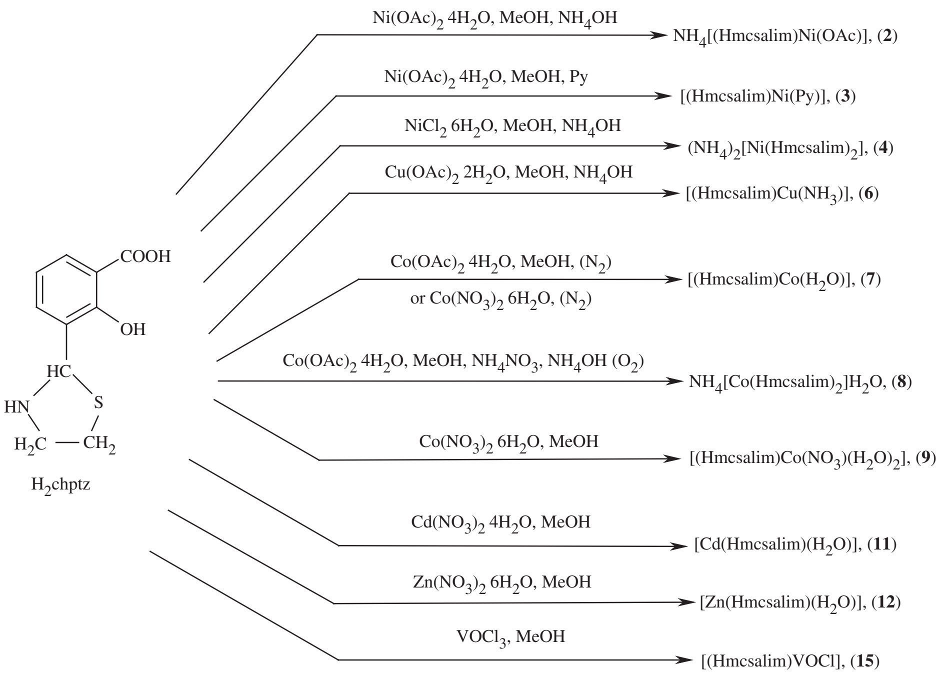


Figure 2. Reactions of H_2chptz with metal salts leading to mononuclear complexes.

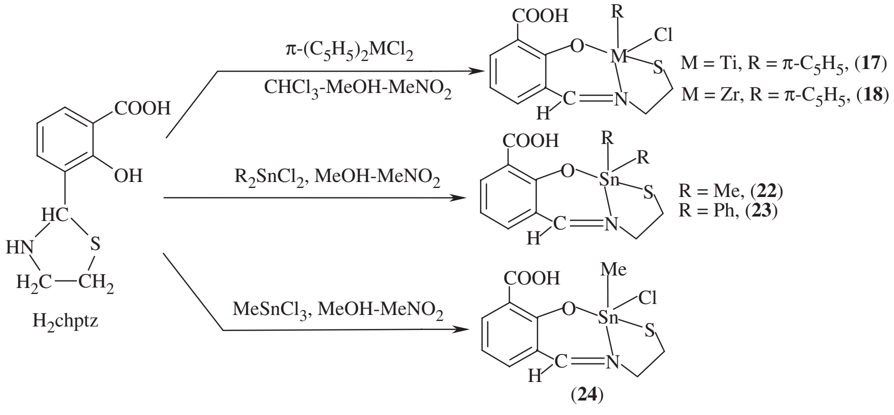
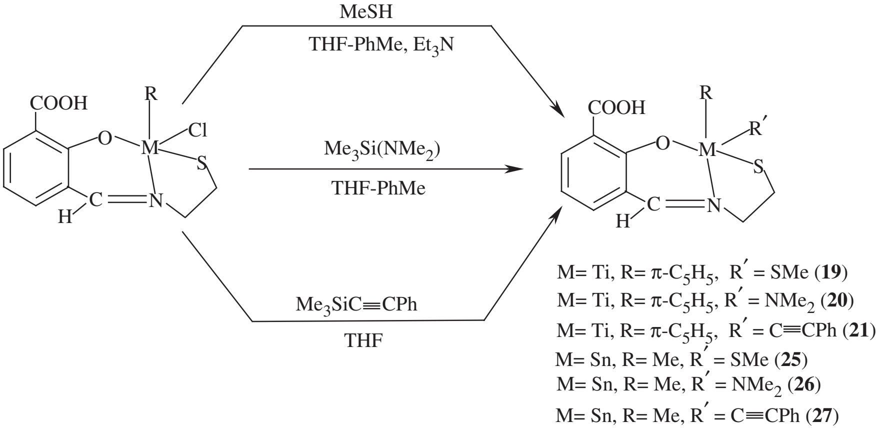


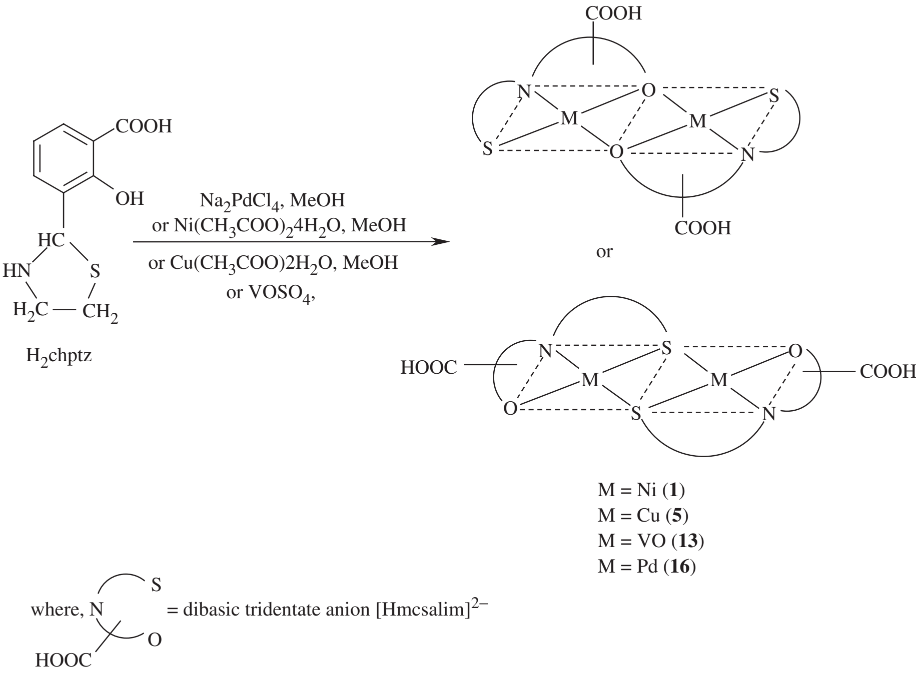
Figure 3. Some reactions of H_2chptz leading to the synthesis of organo derivatives of Ti(IV), Zr(IV) and Sn(IV).

at 8.8 ppm vanishes after the addition of D_2O. The multiplets in the region δ 6.6 ppm to δ 8.1 ppm may be assigned to the phenyl resonances. It was not possible to assign definitely a resonance peak to the hydrogen atom of the CHN linkage of the thiazolidine form, which may possibly be obscured by δ(NH) (see figure 1). The resonance peak for the COOH proton could be detected around δ 12.8 ppm (broad signal) [2, 3, 16]. The ^{1}H NMR spectrum (in DMSO-d_6) of [Zn(Hmcsalim)H_2O] **(12)** exhibits a sharp singlet at δ 8.5 ppm which corresponds to δ(CH=N) and indicates



M= Ti, R= π-C_5H_5, R′ = SMe (**19**)
M= Ti, R= π-C_5H_5, R′ = NMe_2 (**20**)
M= Ti, R= π-C_5H_5, R′ = $C{\equiv}CPh$ (**21**)
M= Sn, R= Me, R′ = SMe (**25**)
M= Sn, R= Me, R′ = NMe_2 (**26**)
M= Sn, R= Me, R′ = $C{\equiv}CPh$ (**27**)

Figure 4. Reactions of [RM(Hmcsalim)Cl] leading to the formation of organometallic complexes.



M = Ni (**1**)
M = Cu (**5**)
M = VO (**13**)
M = Pd (**16**)

where, N S O HOOC = dibasic tridentate anion $[Hmcsalim]^{2-}$

Figure 5. Reactions of H_2chptz leading to binuclear complexes of Pd, Ni, Cu and V.

the rearrangement of thiazolidine, H_2chptz to the Schiff base H_3mcsalim which ultimately forms complexes with the metal ion as a dibasic tridentate NSO donor. Integration of all peak positions supports this interpretation.

In the infrared spectra of the complexes the bands due to N–H and O–H vibrations are absent, suggesting bond formation of the ligand to the metal through oxygen, nitrogen and sulphur. In addition, a new band around 1600–1640 cm^{-1} is observed, assignable to the $\nu(C{=}N)$ vibration. This also supports the fact that the thiazolidine

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

	Frequencies ($\mathrm{cm^{-1}}$)					
Complex	OH	COOH	C=N	N–H	M–N + M–O	M–S
$\mathrm{H_2chptz}$	3100	1705	–	3350	–	–
[(Hmcsalim)Ni(Py)] (**3**)	–	1715	1627	–	552, 530, 516	345–325
$[\mathrm{Cu_2(Hmcsalim)_2}]$ (**5**)	–	1721	1615	–	560, 550, 510	338–320
$[\mathrm{(Hmcsalim)Co(H_2O)}]$ (**7**)	–	1710	1635	–	545, 525, 505	355–330
$[\mathrm{(Hmcsalim)Cd(H_2O)}]$ (**11**)	–	1725	1632	–	540, 510	340–325
$[\mathrm{(Hmcsalim)Zn(H_2O)}]$ (**12**)	–	1718	1640	–	530, 510	350–330
$[\mathrm{(Hmcsalim)VO}]_2$ (**13**)	–	1720	1630	–	555, 540, 520	360–335
$[\mathrm{Pd(Hmcsalim)}]_2$ (**16**)	–	1724	1628	–	530, 520, 500	330–320
$[(\pi\text{-}\mathrm{C_5H_5})\mathrm{Ti(Hmcsalim)Cl}]$ (**17**)	–	1723	1636	–	560, 535	350–325
$[(\pi\text{-}\mathrm{C_5H_5})\mathrm{Zr(Hmcsalim)Cl}]$ (**18**)	–	1720	1635	–	550, 530, 515	345–325
[MeSn(Hmcsalim)(SMe)] (**25**)	–	1720	1630	–	550, 540, 520	350–335

ring in the presence of metal ions, rearranges to its Schiff base form and finally acts as a dibasic tridentate NSO donor ligand in the complexes (table 1). The ν(C–S) mode of the ligand around 770–730 $\mathrm{cm^{-1}}$ is shifted to 730–700 $\mathrm{cm^{-1}}$ in the metal complexes indicating an M–S linkage. This is further substantiated by the appearance of new bands in the region 360–320 $\mathrm{cm^{-1}}$ in the metal complexes, which is assignable to ν(M–S) (M = metal ions) [17, 18]. The appearance of bands in the region 560–500 $\mathrm{cm^{-1}}$ in the complexes is additional support of N and O linkage to the metal atom [2, 19]. Some important infrared bands of the ligand and some of the complexes with their tentative assignments are shown in table 2.

The COOH groups in all the complexes remained free as evidenced by the appearance of infrared bands in the region 1710–1725 $\mathrm{cm^{-1}}$. The very slight blue-shifting from the free ligand value may be due to the combined effect of the rearrangement of the ligand structure, stereospecific interaction with the coordinated metal ion and the presence of coordinated water in some cases. The presence of coordinated acetate group in complex **2** is confirmed by the appearance of bands at 1650 and 1360 $\mathrm{cm^{-1}}$ [19]. Furthermore, the presence of broad bands around 3540–3330 $\mathrm{cm^{-1}}$ in some of the complexes due to ν(OH) indicates presence of water molecules. Complexes **7**, **9**, **11**, **12** and **14** show broad bands in the region 3340–3330 $\mathrm{cm^{-1}}$ along with the appearance of bands at 985–940 $\mathrm{cm^{-1}}$ (wagging modes of water) indicating coordinated water molecules [19].

The coordination of $\mathrm{NH_3}$ in complex **6** is indicated by the presence of bands at 3400–3000, 1600, 1280 and 880 $\mathrm{cm^{-1}}$ assignable to $\nu(\mathrm{NH_3})$, $\delta_d(\mathrm{NH_3})$, $\delta_s(\mathrm{NH_3})$ and $\rho_r(\mathrm{NH_3})$, respectively [19, 20].

The presence of $\mathrm{NH_4^+}$ in complexes **2** and **4** is inferred from the infrared bands in the region 3080 and 1440 $\mathrm{cm^{-1}}$ [19, 21]. However, presence of free COOH groups poses some difficulties in proper interpretation of the bands. The presence of coordinated pyridine in complex **3** may tentatively be inferred by the appearance of ν(CH) (aromatic) at $\sim$3000 $\mathrm{cm^{-1}}$ and ν(C–C) (aromatic) and ν(CN) (ring) at 1440–1590 $\mathrm{cm^{-1}}$ [22]. The infrared bands at about 1460 and 1250 $\mathrm{cm^{-1}}$ in complex **9** are assignable to ν_1 (NO stretching) and ν_4 ($\mathrm{NO_2}$ asymmetric stretching) vibrations, respectively, demonstrating thereby the presence of bonded (unidentate) $\mathrm{NO_3^-}$ groups [23]. Complex **10** shows bands at 1385 and 1370 $\mathrm{cm^{-1}}$, demonstrating thereby the presence of free $\mathrm{NO_3^-}$ in the complex.

The oxovanadium(IV) complexes [(Hmcsalim)VO]$_2$ (**13**) and [(Hmcsalim)VO(H_2O)] (**14**) exhibit ν(V=O) stretching frequencies at 900 cm^{-1} and 970 cm^{-1}, respectively. These assignments were made by comparison with the infrared spectra of the corresponding copper(II) chelates. The low value of the V=O stretching frequency in **13** may be attributed to the bridging nature of the VO unit in the complex [24]. However, the value suggests that the V=O$\cdots$V=O interaction is not strong. The ν(V=O) value of 970 cm^{-1} found for complex **14** supports monomeric V=O in the chelate. This value of 970 cm^{-1} for ν(V=O) is slightly lower than the value observed (996 cm^{-1}) for ν(V=O) in VO(acac)$_2$ perhaps due to the strong ligand fields of the ligand Hmcsalim^{2-}. The V=O stretching frequency in the oxovanadium(V) complex **15**, observed at 950 cm^{-1}, is slightly lower than that observed for analogous oxovanadium(IV) complex **14**. The difference in oxidation states of the metal in these two types of complexes prevents any meaningful interpretation.

The ^{1}H NMR spectrum of the organotin(IV) complex [Me_2Sn(Hmcsalim)] (**22**) displays the Sn–CH_3 protons as one sharp singlet at δ 0.89 ppm. The observed ^2J (^{119}Sn–CH_3), ^2J (^{117}Sn–CH_3) and ^3J (^{119}Sn–N=CH)$^+$ (74.5, 72.1 and 38.8, respectively) are within the ranges reported for other trigonal bipyramidal $(CH_3)_2$Sn(IV) chelate complexes with two *cis* methyl groups [10]. Multiplets observed in the range δ 6.4–7.8 ppm may be assigned to phenyl protons, while the sharp singlet at δ 8.4 ppm signifies the presence of –N=CH protons. The protons of the free –COOH group appear at about δ 11.8 ppm as a slightly broad peak. The integrations are quite satisfactory. On the basis of the above discussion we may tentatively propose the following structures (figure 6) for complex **22**.

Chemical shifts of CH_3S protons in the complexes [(π-C_5H_5)Ti(Hmcsalim)SMe] (**19**) and [MeSn(Hmcsalim)SMe] (**25**) are observed at δ 3.45 (s) ppm and δ 3.56 ppm; while the $(CH_3)_2$N protons in the complexes [(π-C_5H_5)Ti(Hmcsalim)NMe$_2$] (**20**) and [MeSn(Hmcsalim)NMe$_2$] (**26**) appear at about δ 3.6 ppm as a slightly broadened singlet at room temperature.

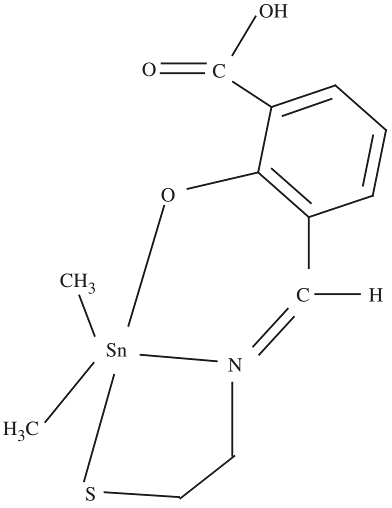


Figure 6. Proposed structure of [Me_2Sn(Hmcsalim)] (**22**).

3.3. *Magnetic moments, CV and ESR Data*

The complexes [Ni(Hmcsalim)]$_2$ (**1**), NH$_4$[(Hmcsalim)Ni(OAc)] (**2**), [(Hmcsalim)Ni(Py)] (**3**), NH$_4$[Co(Hmcsalim)$_2$]H$_2$O (**8**), [Co(Hmcsalim)(NO$_3$)(H$_2$O)$_2$] (**9**), [Cd(Hmcsalim) H$_2$O] (**11**), [Zn(Hmcsalim)H$_2$O] (**12**), [(Hmcsalim)VOCl] (**15**), [Pd(Hmcsalim)]$_2$ (**16**) and the organotitanium(IV) compounds **17**–**21** and organotin(IV) compounds **22**–**27** are all diamagnetic (table 1), while nickel(II), copper(II), cobalt(II), and oxovanadium(IV) compounds **4**–**7**, **10**, **13** and **14**, respectively, are paramagnetic.

The diamagnetic nature of the nickel(II) complexes **1**–**3** suggests square–planar geometry (see electronic spectral discussion). On the other hand the nickel(II) complex **4** is found to be paramagnetic ($\mu_{\text{eff}} = 3.38$ BM), which is in good agreement with an octahedral structure [25]. The magnetic moment of the copper(II) complex [Cu$_2$(Hmcsalim)$_2$] (**5**) at room temperature is found to be 0.80 BM, which is anomalously low and the moment decreases with decrease in temperature (table 3). This suggests that antiferromagnetic interactions are involved. However, the temperature dependence of the susceptibility could not be used to assign a definite structure to this copper(II) complex because of the large errors involved in measuring such low susceptibilities. Nevertheless, the oxygen-bridged, binuclear structure (figure 3) is tentatively suggested for compound **5**. The occurrence of ν(C–O) at 1550 cm^{-1} in the infrared spectrum suggests the presence of bridging phenolic oxygen [26–28].

Copper(II) complex **6**, however, shows a magnetic moment value of 1.92 BM, a value close to the spin-value of 1.73 BM, expected for S = 1/2 system. Based on this magnetic moment value, either a distorted octahedral or a square planar geometry may be proposed for complex **6** in the solid state [29].

The ESR data of complex **5** in polycrystalline and solution phase (DMF) at room temperature (300 K) exhibit four lines (^{63}Cu, I = 3/2) slightly anisotropic spectra at higher magnetic field. At liquid nitrogen temperature (77 K) the spectrum is axial with $g_{||}$ (2.280) and $g_{\perp}$ (2.091) with respect to DPPH marker. The trend $g_{||} > g_{\perp} > g_e$ (2.0048) suggests that the unpaired electron is localized in d$_{x^2-y^2}$ [30, 31].

The cyclic voltammogram of the copper(II) complex **5** exhibits one quasi-reversible redox couple at $E_{1/2} = 0.16$ V ($\Delta E_p = 150$ mV) and an irreversible peak at 0.8 V versus SCE. First response is reductive due to Cu$^{\text{II}}$ → Cu$^{\text{I}}$ and the second one is oxidative Cu$^{\text{II}}$ → Cu$^{\text{III}}$.

The magnetic moment values of cobalt(II) complexes are generally diagnostic of the coordination geometry around the metal ion. Low-spin, square–planar cobalt(II)

Table 3. Magnetic data for [Cu$_2$(Hmcsalim)$_2$] (**5**) at different temperatures.

Temperature (K)	μ (B.M.) per Cu atom
373	1.12
323	0.99
303	0.89
283	0.84
273	0.81
253	0.76
233	0.72
193	0.66
123	0.46
93	0.38

Table 4. Magnetic moments of [(Hmcsalim)VO]$_2$ (**13**) at different temperatures.[a,b]

	Temperature (K)					
Complex	78	120	150	190	228	296
[(Hmcsalim)VO]$_2$ (**13**)	0.51	0.97	1.18	1.25	1.28	1.30

[a] J value is found to be 240 cm^{-1}.
[b] g_{av} value = 1.98 (from ESR data).

complexes may be readily identified by the values for μ_{eff} in the range of 2.1–2.9 BM arising from one unpaired electron and an apparently large orbital contribution [32–35]. One should remember that mixed phosphine arsine ligand yields low-spin, five-coordinate complexes with moments near 2.2 BM [32, 33]. Tetrahedral and high-spin octahedral cobalt(II) complexes each possesses three unpaired electrons but may be distinguished by the magnitude of the deviation of effective magnetic moment value (μ_{eff} value) from the spin-only value. Magnetic moments of tetrahedral cobalt(II) complexes with an orbitally degenerate ground term are increased above the spin-only value *via* contribution from higher orbitally degenerate terms and occur in the range of 4.2–4.7 BM [32, 33]. Octahedral cobalt(II), however, maintains a large contribution due to the $^4T_{1g}$ ground term and exhibits effective magnetic moment in the range of 4.8–5.6 BM [32, 33]. Square planar complexes of cobalt(II) can be distinguished from tetrahedral complexes both spectroscopically and magnetically [36]. A number of ligands are known to give five-coordinate complexes of cobalt(II), all of which are high-spin with magnetic moments of 4.5–4.8 BM [37–39].

The observed magnetic moment value of [(Hmcsalim)Co(H$_2$O)] (**7**) is 2.49 BM, within the range of square–planar Co(II) complexes. Similar square–planar complexes of Co(II) with Schiff bases having magnetic moment values in the range 2.2–2.9 BM are also known [40, 41].

On the other hand the observed magnetic moment at room temperature is 4.20 BM for cobalt(II) complex **10** suggesting tetrahedral arrangement of the donor atoms [32]. The room temperature magnetic moments of the oxovanadium(IV) complexes **13** and **14** (table 1) are found to be 1.30 BM and 1.78 BM, respectively. The value of 1.30 BM is much lower than the spin-only value expected for a d^1 system. The magnetic moment of complex **13** decreased appreciably as the temperature was lowered (table 4), which is characteristic of antiferromagnetic exchange interactions [42]. On the other hand, the value of 1.78 BM for complex **14** is quite close to the spin-only value for one unpaired electron as expected for oxovanadium(IV) complexes. This approximately normal magnetic moment value indicates that there are no significant interactions between neighbouring vanadium ions.

The exchange integral J was calculated using Bleaney and Bowers' equations [43]. The g_{av} value 1.98 of this vanadyl complex **13** was obtained from ESR measurements, which were recorded at room temperature in polycrystalline complexes [44–46]. Two lines at 1600 and 3390 G were observed at room temperature and the 1600 G line may be assigned to the half field line arising out of the $\Delta M_s = 2$ transition. The J value of **13** is observed at 240 cm^{-1}; similar observations were made earlier with analogous oxo-bridged divanadyl complexes [47].

A dimeric oxygen-bridged structure, which provides an approximate symmetry for the 3d$_{xy}$ orbitals of vanadium(IV) to overlap with each other and form a strong σ metal–metal bond, has been suggested for the magnetic abnormality of oxovanadium(IV) complexes of 5-substituted N-(2-hydroxyphenyl)salicylidenimine by Zelentsov [48]. Ginsberg *et al.* have supported this proposed structure, from a study of the cryomagnetic data [49]. The copper(II) complex of the tridentate Schiff base acetylacetone(*o*-hydroxyanil) exhibits a subnormal magnetic moment and has been shown to have a dimeric oxygen-bridged structure from a single crystal *x*-ray study [50]. The present oxovanadium(IV) complex VO(ONS) (**13**) is similar to Zelentsov's complexes. It is reasonable, in the absence of structural data, to assume VO(ONS) complex to be binuclear (see figure 5). However, other structures cannot be ruled out. In the binuclear structure the $3d_{xy}$ orbitals of vanadium(IV) have the appropriate symmetry for overlap and this σ metal–metal interaction should be the principle path for spin–spin coupling. Such an interaction leads to a singlet spin state and a higher spin state with an energy separation equal to the exchange integral, J. The magnitude of J and the available internal energy both make a contribution to the population of the upper triplet state, giving rise to the magnetic moment of 1.30 BM at room temperature for complex **13**.

3.4. *UV-Vis spectra*

The thiazolidine ligand, H_2chptz showed two intense bands around 260 and 370 nm in DMSO solution due to the intra-ligand charge transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. These bands are very slightly red-shifted in the complexes. The titanium and zirconium complexes showed another band around 440–445 nm assignable to charge-transfer [2, 51] in accordance with the $(n-1)d^0ns^0$ electronic configuration of titanium(IV) and zirconium(IV). The data available for **17**–**21** complexes suggest coordination number of five for these complexes [2, 52, 53]. Tin(IV) complexes also had additional bands (broad) in the region 400–450 nm, which may be considered as charge transfer.

The nickel(II) and palladium(II) complexes $[Ni(Hmcsalim)]_2$ (**1**) and $[Pd(Hmcsalim)]_2$ (**16**) are possibly sulphur-bridged dinuclear species (figure 5) and the dinuclear nature has been supported by their molecular weight values. Molar conductance values of these complexes also indicate their non-electrolytic nature in DMSO solution (table 1). They are diamagnetic suggesting square–planar geometry. The nickel(II) complex **1** in the visible region shows two bands at 392 and 515 nm assignable (tentatively) to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions in a square–planar field [2, 54]. A band at 469 nm for the palladium(II) complex **16** is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ $(d_{xy} \rightarrow d_{x^2-y^2})$ transition in a square–planar geometry. The nickel(II) complexes $NH_4[(Hmcsalim)Ni(OAc)]$ (**2**) and $[(Hmcsalim)Ni(Py)]$ (**3**) are also diamagnetic which suggests square–planar geometry. Molecular weights suggest monomeric nature of these complexes. These two nickel(II) complexes **2** and **3** show bands in the visible region 600–570 nm and 480–430 nm which are assigned tentatively to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions in a square–planar field [2, 54] around nickel(II) ion. It is pertinent to mention here that these bands may be influenced by the tail of the charge transfer bands. On the other hand, the nickel(II) complex, $(NH_4)_2[Ni(Hmcsalim)]_2$ (**4**) is found to be paramagnetic (table 1), which is in good agreement with an octahedral structure [25, 54]. This geometry for complex **4** is also supported by the appearance of absorption bands in the electronic spectrum of the complex at about 840 and 620 nm assignable to the transitions $^3A_{2g} \rightarrow {}^1E_g$ (D) and

Table 5. Electronic spectra of [(Hmcsalim)Co(H_2O)] (**7**).

λ_{max} (cm^{-1}) (in MeOH)	ε	λ_{max} (cm^{-1}) (in Nujol mull)
10,000	40	10,200
18,070	1500	16,800, 18,100, 20,000
21,000	2400	20,800
24,200	4180	23,640
27,000	5100	26,500
30,000	7500	28,400
33,300	9100	37,700
38,400	12,100	43,500
43,860	22,000	46,000

$^3A_{2g} \rightarrow {}^3T_{1g}$ (F), respectively, in octahedral symmetry [25, 54]. The molar conductance values (table 1) of these complexes also support their formulations. Almost diamagnetic nature of the copper(II) complex [Cu(Hmcsalim)]$_2$ (**5**) (table 1) suggests a strong spin–spin interaction involving an oxygen-bridged, dimeric structure (figure 5). Furthermore, complex **5** displays electronic spectral bands in the regions ~670 and 455 nm which may be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions in a square–planar geometry [54, 55]. The copper(II) complex [Cu(Hmcsalim)(NH_3)] (**6**) displays two or three bands in the region 700–455 nm suggesting a square–planar geometry. The magnetic moment value (μ_{eff}) of 2.49 BM observed for [Co(Hmcsalim)(H_2O)] (**7**) suggests a square–planar geometry for the complex. The electronic spectra of the present cobalt(II) complex, [(Hmcsalim)Co(H_2O)] (**7**) have been measured in methanol and nujol mull and the band positions are shown in table 5. In general the solution and the solid state spectra are in agreement with each other. From these observations, we tentatively suggest that the geometry may be the same in both the states. Hence the possibility of solid state interactions resulting in tetragonal distortion of the metal ion is unlikely.

The spectra are characterized by the presence of a large number of bands in the visible and ultraviolet regions. As discussed above, bands at energies of approximately 20000–34000 cm^{-1} are assigned as either M → L; L → M or ligand transitions. The similarities in the visible spectra of the complex (**7**) with those of known square–planar complexes containing oxygen–nitrogen, oxygen–sulphur, nitrogen–sulphur and sulphur–sulphur donor atoms strongly suggest square planar geometry for complex **7** [41]. Low-spin, square–planar cobalt(II) complexes commonly show a weak band in the 8000–10000 cm^{-1} range [56, 57]; in the present cobalt(II) complex it is observed at 10000 cm^{-1}. Most of the remaining d–d transitions lie under the onset of charge-transfer absorptions above 18000 cm^{-1}. However, interpretations of the electronic spectral data of low-spin, square–planar cobalt(II) complexes are very difficult due to uncertainty of ground terms in the complexes with different types of ligands [58]. On the other hand, the μ_{eff} value for the cobalt(II) complex [Co(H_2mcsalim)(H_2O)$_2$]NO_3 (**10**) is found to be 4.20 BM, which is quite close to the range of tetrahedral cobalt(II) complexes. This is supported by the visible spectra in the range of 675–640 nm assignable to the $^4A_2 \rightarrow {}^4T_1$(P) transition in a pseudo-tetrahedral geometry [55]. The other cobalt complexes NH_4[Co(Hmcsalim)$_2$]H_2O (**8**) and [Co(Hmcsalim)(NO_3)(H_2O)$_2$] (**9**) are diamagnetic cobalt(III) species, showing bands in the region 600–580 and 465–425 nm assignable to $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions in an octahedral environment [55].

The electronic spectrum of [(Hmcsalim)VO(H_2O)} (**14**) in nujol mull exhibits two bands at about 714 nm and 526 nm. These bands are not well developed and are observed as shoulders. These two bands may be assigned to an unresolved band resulting from the $d_{xy} \rightarrow d_{xz}$, d_{yz} transition [59]. The second shoulder observed at 526 nm is attributed to $d_{xy} \rightarrow d_{x^2-y^2}$ [59]. The other transition $d_{xy} \rightarrow d_z^2$, is probably underneath intraligand and charge transfer bands. On the other hand, [(Hmcsalim)VO]$_2$ (**13**) exhibits a broad absorption band as a shoulder at 540 nm. Similar observations were made earlier [42] with VO(ONS)$\cdot$nH_2O complexes having subnormal magnetic moments.

4. Conclusion

A new ligand, 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (H_2chptz) has been synthesized and characterized. The thiazolidine H_2chptz in solution and in the presence of metal ion rearranges to its Schiff base form, 3-carboxysalicylidenethioethanolimine (H_3csalim) which ultimately forms metal complexes as a dibasic tridentate NSO donor ligand. The cobalt(II) complex, [(Hmcsalim)Co(H_2O)] (**7**), isolated in this study, is found to be low-spin ($\mu_{\text{eff}} = 2.49$ BM). Based on the magnetic moment value and also on the electronic spectral data, a square planar geometry has been tentatively proposed for this complex. The reactions of [(Hmcsalim)Ti(π-C_5H_5)Cl] and [(Hmcsalim)Sn(Me)Cl], isolated in this study, with Me_3SiE (where, E stands for SMe, NMe_2 and C≡CPh) have been studied and many new organotitanium(IV) and organotin(IV) compounds have been isolated. Desilylation is possibly the driving force of such reactions, and the by-product Me_3SiCl can be easily removed from the reaction mixture.

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