

Synthesis and spectroscopic studies of some new organometallic chelates derived from bidentate ligands

Kiran SINGH*, Parvesh PURI, DHARAMPAL

*Department of Chemistry, Kurukshetra University, Kurukshetra,
136119 Haryana-INDIA
e-mail: kiransinghkuk@yahoo.co.in*

Received 10.12.2009

A series of organosilicon(IV) and organotin(IV) complexes having the formulae $R_2MCl(L^1)$, $R_2MCl(L^2)$, $R_2MCl(L^3)$, $R_2MCl(L^4)$, $R_2M(L^1)_2$, $R_2M(L^2)_2$, $R_2M(L^3)_2$, and $R_2M(L^4)_2$, where $M = Si$ and Sn , and $R = CH_3$, were synthesized with Schiff bases 5-mercapto-4-(pyridine-2-carboxalideneamino)-s-triazole (HL^1), 4-(furfuralideneamino)-5mercapto-s-triazole (HL^2), 4-(2-chlorobenzylideneamino)-5-mercapto-s-triazole (HL^3), and 4-(4-fluorobenzylideneamino)-5-mercapto-s-triazole (HL^4). These complexes were characterized by elemental analysis, molar conductance, and spectroscopic studies, including UV, IR, 1H , ^{13}C , ^{29}Si , and ^{119}Sn NMR spectroscopy. On the basis of these studies, the resulting complexes are proposed to have trigonal bipyramidal and octahedral geometries.

Key Words: 4-Amino-5-mercapto-s-triazole, Schiff bases, silicon complexes, tin complexes, spectroscopy

Introduction

Metal complexes of organosilicon(IV) and organotin(IV) halides with nitrogen, oxygen, and sulfur donor ligands have received much more attention during the last few years.^{1,4} The study of these complexes has been a fascinating area of current research interest to inorganic chemists all over the world. Silicon and tin complexes have a variety of industrial^{5,6} and environmental^{7,8} applications. Nitrogen, oxygen, and sulfur donor ligands have been used to enhance the biological activity of organotin and organosilicon derivatives.⁹ The interest in the organosilicon(IV) compounds is generated due to their versatile applications in the pharmaceutical and chemical industries.^{10,11} The coordination chemistry of silicon and tin is extensive, with various geometries and

*Corresponding author

coordination numbers known for both inorganic and organometallic complexes.¹² Higher coordination numbers can be generated by inter/intramolecular interactions, especially in complexes where tin and silicon are bonded to electronegative atoms such as O, N, and S. Many organotin and organosilicon complexes show antifungal and antibacterial properties.^{13,14} Some organotin complexes show anticancer properties.¹⁵ Many organosilicon complexes were synthesized and their structures were explained by crystallography.¹⁶ In view of the diverse fields of applications of these complexes, we synthesized and characterized some novel organosilicon(IV) and organotin(IV) complexes with nitrogen and sulfur donor ligands.

Experimental

All of the chemicals and solvents were used under dry conditions. Adequate care was taken to keep the chemicals, glass apparatuses, and the organosilicon(IV) and organotin(IV) complexes free from moisture. To attain dry conditions, all of the apparatuses used during the experimental work were fitted with quick fit interchangeable standard ground joints. All of the reagents, namely 2-pyridinecarboxaldehyde (Himedia), furfuraldehyde (Himedia), 2-chlorobenzaldehyde (Himedia), 4-fluorobenzaldehyde (Himedia), dimethylsilicondichloride (Acros), and dimethyltin dichloride (Acros), were used as received.

Analytical methods and physical measurements

Silicon and tin were determined gravimetrically as silicon dioxide (SiO₂) and tin dioxide (SnO₂). Melting points were determined on a capillary melting point apparatus.

Conductance measurements

Molar conductance measurements of a 10⁻³M solution of metal complexes in dry dimethylformamide (DMF) were measured at room temperature (25 ± 1 °C) with a conductivity bridge, type 305 Systronic model.

Electronic spectra

The electronic spectra of the ligands and their metal complexes were recorded in dry methanol on a Hitachi U-2000 spectrophotometer in the range of 1100-200 nm.

IR spectra

The IR spectra of the ligands and metal complexes were recorded in Nujol mulls/KBr pellets using a BUCK scientific M5000 grating spectrophotometer in the range of 4000-250 cm⁻¹.

NMR measurements

Multinuclear magnetic resonance spectra (¹H, ¹³C, ²⁹Si, and ¹¹⁹Sn) were recorded on a BRUKER-400ACF spectrophotometer in dimethylsulfoxide (DMSO-d₆) using tetramethylsilane (TMS) as an internal standard.

Synthesis of ligands

4-Amino-5-mercapto-s-triazole (AMT) was synthesized by a reported method.¹⁷ Schiff bases were prepared by condensation of an equimolar ratio of triazole (AMT) and corresponding aldehydes, namely pyridine-2-carboxaldehyde, furfuraldehyde, 3-chlorobenzaldehyde, and 4-fluorobenzaldehyde (Figure 1). The contents were refluxed for 4-5 h in absolute ethanol. After refluxing, the reaction mixture was kept overnight at room temperature and the product was filtered, washed, and recrystallized from the same solvent. The analysis and physical properties of the ligands are reported in Table 1. The 4 ligands are: HL¹, 5-mercapto-4-(pyridine-2-carboxalideneamino)-s-triazole (MPCT); HL², 4-(furfuralideneamino)-5-mercapto-s-triazole (FMT); HL³, 4-(2-chlorobenzylideneamino)-5-mercapto-s-triazole (CBMT); and HL⁴, 4-(4-fluorobenzylideneamino)-5-mercapto-s-triazole (FBMT).

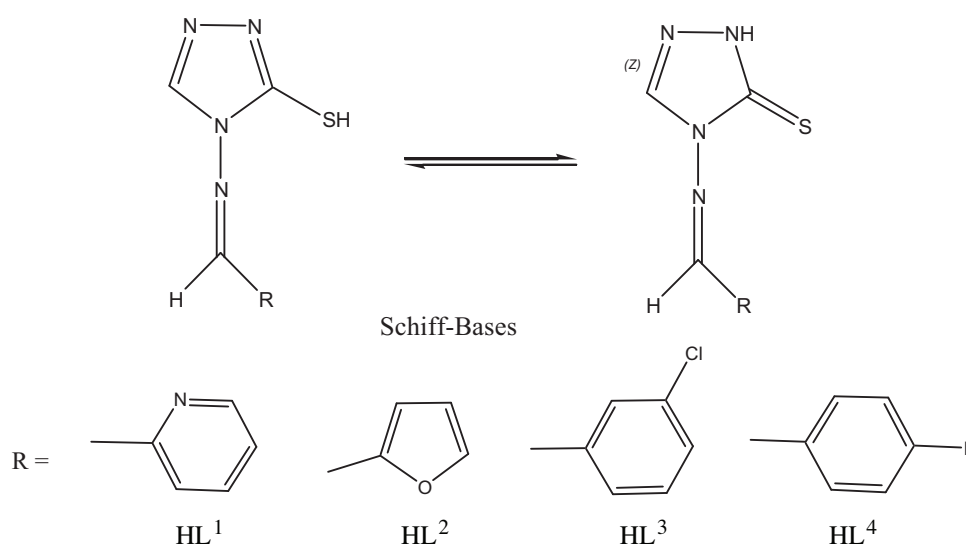


Figure 1. Structure of Schiff bases.

Synthesis of metal complexes

To a weighed amount of Me₂SiCl₂ and Me₂SnCl₂ in approximately 30 mL of dry methanol, was added the calculated amount of the sodium salt of the ligand in 1:1 and 1:2 molar ratios. The sodium salts of the ligands were prepared by dissolving the appropriate amount of the sodium metal and ligands in approximately 30 mL of dry methanol. The reaction mixture was refluxed for about 12 h and then allowed to cool at room temperature. The excess of solvent was removed under reduced pressure by vacuum pump, and the resulting solid was repeatedly washed with 5-10 mL of dry cyclohexane and again dried under a vacuum. The elemental analysis and physical properties of the complexes are reported in Table 1.

Results and discussion

All of the newly synthesized complexes were colored and soluble in DMSO, DMF, and MeOH. The molar conductivity values measured for 10⁻³M solutions in anhydrous DMF were in the range of 10-15 cm² mol⁻¹

Table 1. Physical characteristics and analytical data of ligands and their metal complexes.

Complex	Empirical formula	Color	M.Pt. (°C)	Found(Calc.) %				
				C	H	N	S	Si/Sn
HL ¹ (MPCT)	C ₈ H ₇ N ₅ S	Light yellow	170	46.49 (46.82)	3.35 (3.41)	34.11 (34.14)	16.05 (15.63)	-
Me ₂ SiCl(L ¹)	C ₁₀ H ₁₂ N ₅ SClSi	Light green	151	60.87 (60.91)	4.0 (4.04)	23.46 (23.56)	11.67 (11.49)	9.33 (9.42)
Me ₂ Si(L ¹) ₂	C ₁₈ H ₁₈ N ₁₀ S ₂ Si	Dirty green	167	46.32 (46.35)	3.88 (3.86)	29.89 (30.04)	19.91 (19.75)	6.2 (6.0)
Me ₂ SnCl(L ¹)	C ₁₀ H ₁₂ N ₅ ClSn	Light brown	187	31.0 (30.96)	3.01 (3.09)	17.98 (18.06)	48.01 (47.89)	30.20 (30.58)
Me ₂ Sn(L ¹) ₂	C ₁₈ H ₁₈ N ₁₀ S ₂ Sn	Brown	198	38.94 (38.81)	3.12 (3.23)	25.0 (25.15)	32.94 (32.81)	21.14 (21.29)
HL ² (FMT)	C ₇ H ₆ N ₄ OS	Creamish	184	43.10 (43.2)	3.0 (3.09)	28.7 (28.8)	25.2 (24.91)	-
Me ₂ SiCl(L ²)	C ₉ H ₁₁ N ₄ OSClSi	Light green	140	37.82 (37.76)	3.78 (3.84)	19.55 (19.58)	38.85 (38.82)	9.61 (9.79)
Me ₂ Si(L ²) ₂	C ₁₆ H ₁₆ N ₈ O ₂ S ₂ Si	Green	156	43.30 (43.24)	3.65 (3.60)	25.13 (25.22)	27.92 (27.94)	5.44 (6.3)
Me ₂ SnCl(L ²)	C ₉ H ₁₁ N ₄ OSClSn	Light yellow	211	28.86 (28.68)	3.04 (2.92)	14.77 (14.87)	53.33 (53.53)	30.12 (31.47)
Me ₂ Sn(L ²) ₂	C ₁₆ H ₁₆ N ₈ O ₂ S ₂ Sn	Brown	222	35.98 (35.92)	3.0 (2.99)	20.89 (20.95)	40.13 (40.14)	22.2 (22.17)
HL ³ (CBMT)	C ₉ H ₇ N ₄ SCl	Light yellow	192	45.31 (45.28)	2.91 (2.93)	13.50 (13.41)	38.28 (38.38)	-
Me ₂ SiCl(L ³)	C ₁₁ H ₁₂ N ₄ (Cl) ₂ SSi	Yellow	156	40.13 (40.0)	3.66 (3.63)	16.86 (16.96)	39.35 (39.41)	8.40 (8.48)
Me ₂ Si(L ³) ₂	C ₂₀ H ₁₈ N ₈ S ₂ (Cl) ₂ Si	Pale yellow	159	45.33 (45.11)	3.35 (3.38)	21.0 (21.05)	30.32 (30.46)	5.12 (5.26)
Me ₂ SnCl(L ³)	C ₁₁ H ₁₂ N ₄ (Cl) ₂ SSn	Light brown	206	31.56 (31.39)	2.89 (2.85)	13.26 (13.31)	52.2 (52.45)	28.33 (28.18)
Me ₂ Sn(L ³) ₂	C ₂₀ H ₁₈ N ₈ S ₂ (Cl) ₂ Sn	Yellow	212	38.66 (38.55)	2.95 (2.89)	17.68 (17.99)	40.71 (40.57)	19.14 (19.03)
HL ⁴ (FBMT)	C ₉ H ₇ N ₄ SF	Creamish	142	48.30 (48.60)	3.3 (3.1)	25.1 (25.2)	23.3 (23.1)	-
Me ₂ SiCl(L ⁴)	C ₁₁ H ₁₂ N ₄ ClFSSi	Light green	125	42.14 (42.03)	3.8 (3.82)	17.78 (17.83)	36.28 (36.82)	8.86 (8.91)
Me ₂ Si(L ⁴) ₂	C ₂₀ H ₁₈ N ₈ F ₂ S ₂ Si	Green	133	48.12 (48.0)	3.4 (3.6)	22.3 (22.4)	26.18 (26.00)	5.62 (5.60)
Me ₂ SnCl(L ⁴)	C ₁₁ H ₁₂ N ₄ ClFSSn	Light green	169	32.58 (32.63)	3.0 (2.96)	13.67 (13.84)	50.75 (50.57)	29.11 (29.29)
Me ₂ Sn(L ⁴) ₂	C ₂₀ H ₁₈ N ₈ F ₂ S ₂ Sn	Brown	181	40.62 (40.69)	3.0 (3.04)	18.88 (18.96)	37.5 (37.31)	20.10 (20.06)

solutions, showing that all of the 1:1 and 1:2 complexes were nonelectrolytic in nature. The range of the conductivity values indicated that the solutions of the complexes were not ionic and that all of the atoms were present in the coordination sphere. The analytical data were in good agreement with the proposed stoichiometry of the complexes. The physical characteristics and analytical data of the complexes are given in Table 1.

Electronic spectra

The electronic spectra of the ligand HL³ (CBMT) and its metal complexes with Si(IV) and Sn(IV) were recorded. The test solutions were prepared by dissolving the ligand and its metal complexes in dry methanol. The electronic spectra of the ligand HL³ (CBMT) exhibited maxima at 363 nm, which can be assigned to the $n \rightarrow \pi^*$ transition of the azomethine group, which undergoes a blue shift in the 1:1 and 1:2 metal complexes and appears at 332 nm {Me₂SiCl(L³)}, 324 nm {Me₂Si(L³)₂}, 348 nm {Me₂SnCl(L³)}, and 330 nm {Me₂Sn(L³)₂}. This blue shift is due to the polarization within the >C=N chromophore group caused by the metal-ligand interaction, which clearly indicates the coordination of the azomethine nitrogen atom to the metal atom.¹³ A further medium intensity band at around 245 nm due to the $\pi \rightarrow \pi^*$ transition in the ligand remained unchanged in the spectra of the metal complexes.

IR spectra

The IR spectra of the ligands showed a characteristic band due to $\nu(\text{N-H})$ at about 3250 cm⁻¹, and another band at about 1100 cm⁻¹ was assigned to $\nu(\text{C=S})$,¹⁸ indicating the thione form, while a weak band observed around 2400 cm⁻¹ due to $\nu(\text{S-H})$ vibrations suggests that the Schiff bases exhibit thiol-thione tautomerism (Figure 1).^{19,20} The deprotonation of the -N-H moiety of triazole was indicated by the absence of a band in the metal complexes at about 3250 cm⁻¹ and 1100 cm⁻¹, which appears to be due to $\nu(\text{N-H})$ and $\nu(\text{C=S})$, respectively, in the spectra of the ligands, indicating complexation through the sulfur atom. In the IR spectra of complexes, a new band appeared at about 748 cm⁻¹, which was assigned to $\nu(\text{C-S})$ and which further confirms the coordination of the ligand through the sulfur atom. The metal-sulfur bond formation was further supported by a band at about 440 cm⁻¹ and about 455 cm⁻¹ for $\nu(\text{Sn-S})$ and $\nu(\text{Si-S})$,^{21,22} respectively. A sharp and strong band in the region of 1616-1603 cm⁻¹ for $\nu(\text{N=CH})$ ²³ in the case of the ligands was shifted to a higher wavenumber and appeared in the region of 1612-1625 cm⁻¹ in the spectra of the metal complexes, indicating coordination through the azomethine nitrogen atom to the metal atom. Formation of a metal-nitrogen bond was further supported by the presence of a band at about 570 cm⁻¹ and about 535 cm⁻¹ for $\nu(\text{Si-N})$ ²⁴ and $\nu(\text{Sn-N})$,^{21,25} respectively, indicating the coordination of the ligand to the central metal atom through the azomethine nitrogen atom. A strong band in the region of 425-381 cm⁻¹ has been observed due to $\nu(\text{M-Cl})$.²⁶ The infrared spectral data of the ligands and their metal complexes are listed in Table 2.

¹H-NMR spectra

The ¹H-NMR spectra of the ligands and their metal complexes were recorded in DMSO-d₆ using tetramethylsilane (TMS) as the internal standard. The ¹H-NMR spectra of the ligands showed the -SH proton signal at δ 11.2-11.7 ppm.^{13,23,27} Disappearance of this signal due to the -SH proton in the metal complexes indicates the

Table 2. IR spectroscopic data (cm⁻¹) of the ligands and their metal complexes.

Compound	$\nu(\text{N-H})$	$\nu(-\text{C}=\text{N})$	$\nu(\text{C}=\text{S})^a/\nu(\text{C-S})^b$	$\nu(\text{M-S})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
HL ¹ (MPCT)	3292	1616	1093	-	-	-
Me ₂ SiCl(L ¹)	-	1621	747	451	567	422
Me ₂ Si(L ¹) ₂	-	1623	748	454	570	-
Me ₂ SnCl(L ¹)	-	1625	741	444	532	381
Me ₂ Sn(L ¹) ₂	-	1623	743	446	535	-
HL ² (FMT)	3250	1607	1116	-	-	-
Me ₂ SiCl(L ²)	-	1613	746	455	573	417
Me ₂ Si(L ²) ₂	-	1615	748	458	576	-
Me ₂ SnCl(L ²)	-	1617	743	447	533	390
Me ₂ Sn(L ²) ₂	-	1613	744	450	539	-
HL ³ (CBMT)	3255	1605	1093	-	-	-
Me ₂ SiCl(L ³)	-	1616	752	453	577	412
Me ₂ Si(L ³) ₂	-	1617	753	455	579	-
Me ₂ SnCl(L ³)	-	1615	758	441	530	396
Me ₂ Sn(L ³) ₂	-	1612	761	446	535	-
HL ⁴ (FBMT)	3275	1603	1106	-	-	-
Me ₂ SiCl(L ⁴)	-	1611	749	462	574	425
Me ₂ Si(L ⁴) ₂	-	1613	745	467	575	-
Me ₂ SnCl(L ⁴)	-	1613	740	445	537	387
Me ₂ Sn(L ⁴) ₂	-	1616	744	447	537	-

a = Ligands.

b = Complexes.

deprotonation of the thiol group, and this supported the coordination of the ligands through the sulfur atom to the metal atom. A signal at δ 8.5-9.7 ppm was observed in the spectra of free ligands, which shows the shielding in the ¹H-NMR spectra of metal complexes, which indicates bonding through the azomethine nitrogen atom to the central metal atom. Aromatic protons gave signals at δ 7.0-8.8 ppm. A strong singlet was observed at δ 4.0-4.3 ppm due to the triazole proton. The ¹H-NMR spectroscopic data of some of the ligands and their metal complexes are given in Table 3.

¹³C-NMR spectra

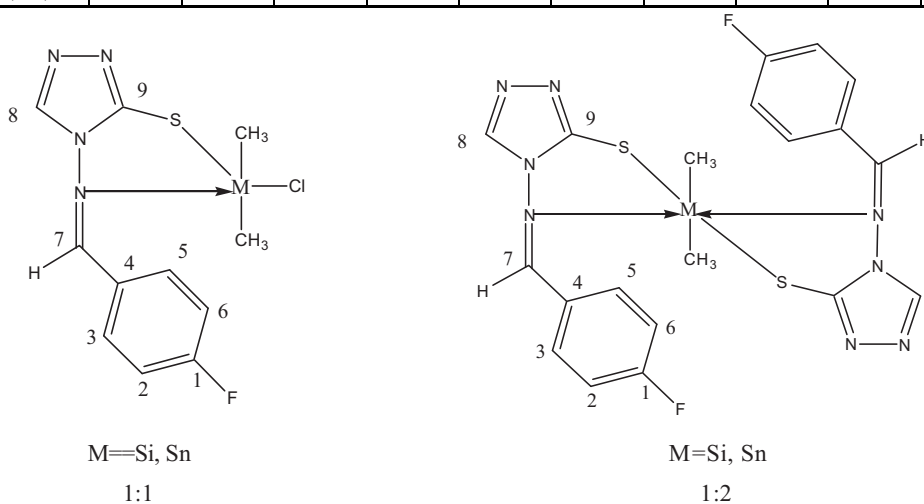
The ¹³C-NMR spectral data of ligand HL⁴ and its silicon(IV) and tin(IV) metal complexes were recorded and are given in Table 4. The ¹³C-NMR spectra also support the structures proposed for the Si and Sn complexes. The signal due to the carbon atom attached to the azomethine nitrogen atom in the ligand appeared at δ 158.2 ppm. However, in the spectra of the metal complexes, the signal appeared at the lower δ values. This considerable shift in the spectra of metal complexes indicates the coordination of nitrogen to the central metal

Table 3. $^1\text{H-NMR}$ chemical shifts of the ligands and their metal complexes.

Compound	Aromatic-H	Triazole-H	-CH=N	-SH
HL ² (FMT)	7.5-8.5(m)	4.2(s)	8.5(s)	11.7(s)
Me ₂ SiCl(L ²)	7.6-8.6(m)	4.1(s)	7.6(s)	-
Me ₂ Si(L ²) ₂	7.6-8.7(m)	4.0(s)	7.8(s)	-
Me ₂ SnCl(L ²)	7.7-8.8(m)	4.1(s)	7.6(s)	-
Me ₂ Sn(L ²) ₂	7.6-8.7(m)	4.1(s)	7.7(s)	-
HL ⁴ (FBMT)	7.0-8.2(m)	4.3(s)	9.7(s)	11.2(s)
Me ₂ SiCl(L ⁴)	7.1-8.3(m)	4.2(s)	9.0(s)	-
Me ₂ Si(L ⁴) ₂	7.2-8.3(m)	4.1(s)	9.1(s)	-
Me ₂ SnCl(L ⁴)	7.1-8.4(m)	4.2(s)	8.8(s)	-
Me ₂ Sn(L ⁴) ₂	7.1-8.4(m)	4.2(s)	8.5(s)	-

Table 4. $^{13}\text{C-NMR}$ chemical shifts of the ligands and their metal complexes.

Compound	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	M-CH ₃
HL ⁴ (FBMT)	162.8	115.7	128.5	123.6	130.3	115.3	158.2	148.9	149.7	-
Me ₂ SiCl(L ⁴)	162.6	115.6	128.1	123.1	129.1	115.2	153.3	148.8	147.7	18.1
Me ₂ Si(L ⁴) ₂	162.4	115.4	127.9	122.8	130.0	115.0	153.8	148.8	147.3	25.5
Me ₂ SnCl(L ⁴)	162.2	115.0	128.3	123.2	129.5	115.1	152.8	148.8	147.2	30.1
Me ₂ Sn(L ⁴) ₂	162.3	115.2	128.0	123.3	129.9	115.2	153.1	148.8	147.7	35.5



atom in complexes. Furthermore, the shifting of the ^{13}C -resonance, which is attached to the sulfur atom in the spectra of 1:1 and 1:2 metal complexes, compared to the free ligand indicates coordination through sulfur to the metal atom. The new signal due to the methyl group attached to the metal atom in the spectra of metal complexes was also recorded and is shown in Table 4.

²⁹Si- and ¹¹⁹Sn-NMR spectra

In order to confirm the geometry of the complexes, the ²⁹Si- and ¹¹⁹Sn-NMR spectra of the ligand HL⁴ complexes were recorded. The values of δ ²⁹Si and δ ¹¹⁹Sn²⁸ reflect the coordination number of the central metal atom (nucleus) in the corresponding compound. In general, ²⁹Si and ¹¹⁹Sn chemical shifts move to a lower frequency with an increasing coordination number of the nuclei. The spectrum shows in each case only a sharp singlet, indicating the formation of a single species. The ²⁹Si- and ¹¹⁹Sn-NMR spectra of the {Me₂SiCl(L⁴)}, {Me₂Si(L⁴)₂}, {Me₂SnCl(L⁴)}, and {Me₂Sn(L⁴)₂} complexes show sharp signals at δ -92.64 ppm, δ -117.23 ppm, δ -143.93 ppm, and δ -240.30 ppm, respectively.

Conclusion

On the basis of the above mentioned different spectral studies, the deprotonation of the thiol group and bonding through sulfur and azomethine nitrogen atoms to silicon and tin central atoms are suggested. Finally, the geometries around the silicon and tin atoms in the complexes have been suggested as trigonal bipyramidal and octahedral in 1:1 and 1:2 complexes, respectively, as shown in Figure 2.

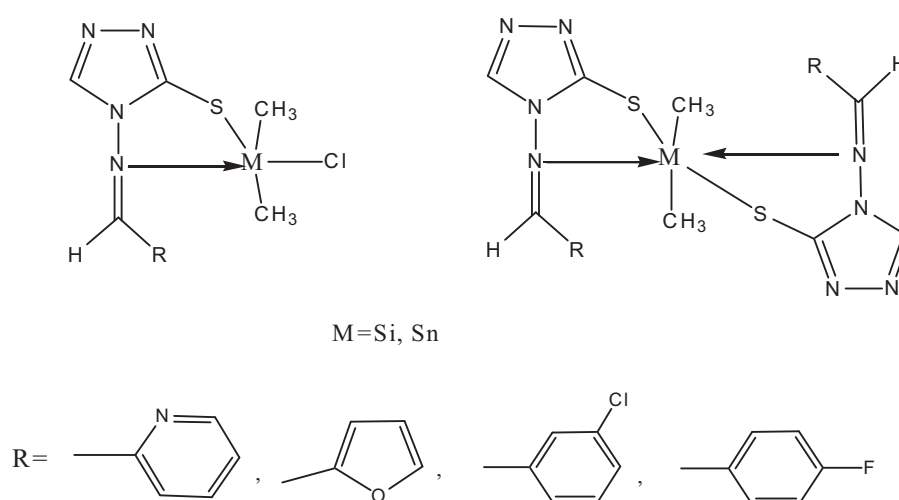


Figure 2. Proposed structures of the 1:1 and 1:2 complexes.

Acknowledgements

This investigation received financial assistance from UGC, New Delhi, via Major Research Project F. No. 34-317/2008(SR), which provided a Project fellowship to one of the authors (Parvesh Puri). The authors are also thankful to the Head, SAIF, Punjab University – Chandigarh, for providing metal NMR and elemental analysis.

References

1. Fernandes, R. M.; Lang, E. S.; Lopez, E. M. V.; de Sousa, G. F. *Polyhedron* **2002**, *21*, 1149-1153.
2. Jain, M.; Gaur, S.; Singh, V. P.; Singh, R. V. *Appl. Organomet. Chem.* **2004**, *18*, 73-82.
3. Singh, R. V.; Jain, M.; Deshmukh, C. N. *Main Group Met. Chem.* **2005**, *19*, 879-886.
4. Khan, M. I.; Baloch, M. K.; Malik, A.; Ashfaq, M. *J. Organomet. Chem.* **2004**, *689*, 238-245.
5. Mender, F. M.; Catlin, K. K. *Chem. Ed. Engl.* **1995**, *34*, 2147-2150.
6. Mehrotra, R. C.; Singh, A. *Organometallic Chemistry*, New Age International, New Delhi, 2000.
7. Pellerito, L.; Nagy, L. *Coord. Chem. Rev.* **2002**, *224*, 111-150.
8. Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, *4*, 443- 448.
9. Joshi, K. C.; Pathak, V. N.; Arya, P. *Agric. Biol. Chem.* **1977**, *41*, 543- 546.
10. McGowan, P. C. *Annu. Rep. Prog. Chem. Sect. A* **2005**, *101*, 631-648.
11. Allen, R. B.; Kochs, P.; Chandra, G. In *The Handbook of Environmental Chemistry*; Chandra, G., Ed.; Springer-Verlag, Berlin, 1997.
12. Smith, P. J. *Chemistry of Tin*. Blackie, London, 1998.
13. Singh, K.; Dharampal; Parkash, V. *Phosphorus, Sulfur Silicon Relat. Elem.* **2008**, *183*, 2784-2794.
14. Singh, K.; Dharampal; Dhiman, S. S. *Main Group Met. Chem.* **2009**, *8*, 47-59.
15. Gerasimchuk, N.; Maher, T.; Durham, P.; Domasevitch, K. V.; Wilking, J.; Mokhir, A. *Inorg. Chem.* **2007**, *46*, 7268-7284.
16. Metz, S.; Burschka, C.; Tacke, R. *Organometallics*, **2009**, *28*, 2311-2317.
17. Bala, S.; Gupta, R. P.; Sachdeva, M. L.; Singh, A.; Pujari, H. K. *Indian J. Chem.*, **1978**, *16*, 481-483.
18. Singh, G.; Singh, P. A.; Singh, K.; Singh, D. P.; Handa, R. N.; Dubey, S. N. *Proc. Nat. Acad. Sci. Ind.* **2002**, *72*, 87-95.
19. Avaji, P. G.; Patil, S. A.; Badami, P. S. *J. Coord. Chem.* **2008**, *61*, 1884-1896.
20. Sinha, B. K.; Singh, R.; Srivastva, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1797.
21. Belwal, S.; Singh, R. V. *Appl. Organomet. Chem.* **1998**, *12*, 39-46.
22. Singh, K.; Singh, R. V.; Tondon, J. P. *Polyhedron* **1988**, *7*, 151-154.
23. Singh, K.; Singh, D. P.; Barwa, M. S.; Tyagi, P.; Mirza, Y. *Enz. Inh. Med. Chem.*, **2006**, *21*, 557-562.
24. Nath, M.; Goyal, S. *Synth. React. Inorg. Met. Org. Chem.* **2000**, *30*, 1791-1804.
25. Nath, M.; Saini, P. K.; Eng, G.; Song, X. *J. Organomet. Chem.* **2008**, *693*, 2271- 2278.
26. Chaudhary, A.; Singh, R. V. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 615-626.
27. Singh, K.; Singh, D. P.; Barwa, M. S.; Tyagi, P.; Mirza, Y. *Enz. Inh. Med. Chem.*, **2006**, *21*, 749-755.
28. Pellei, M.; Lobbia, G. G.; Ricciutelli, M.; Santini, L. *J. Coord. Chem.* **2005**, *58*, 409-420.