

**COORDINATION CHEMISTRY OF ORGANOTIN(IV)
COMPLEXES WITH BIDENTATE AND TRIDENTATE
(NN/NNN) DONOR LIGANDS**

Imelda Sim Siew Ping

**Bachelor of Science with Honours
Faculty of Resource Science and Technology
(Resource Chemistry)
2007**

DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of qualification of this or any other university of institution of higher learning.

Imelda Sim Siew Ping

Program of Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my supervisor, Dr. Md. Abu Affan of Resource Chemistry Program, UNIMAS, for his constant guidance and continuous encouragement without which this work would not have been possible. I would also like to express my appreciation to Mr. Liew Yew Zion, M.Sc Student of Resource Chemistry Program, UNIMAS, for his occasional help to complete this project work. I sincerely thank all the Lab assistants and staffs of this chemistry program for their help and advice. Finally, I would like to express my gratitude to my parents and my brother who were constantly lending a shoulder to lean on and giving inspirational words of patience and faith during the whole plight of this project research work. Thanks to all my friends for the encouragements. Last but not least, to those who had directly or indirectly contributed in this project research work, I cannot thank you more. With greatest gratitude, I thank you all and may GOD bless all of you.

TABLE OF CONTENT

	Page
ABSTRACT	ix
LIST OF TABLES	vi
LIST OF FIGURES	vii
1.0 Introduction	1
1.1 Objectives	2
2.0 Literature Review	2
2.1 Characteristics of nitrogen	2
2.2 Characteristics of organotin(IV)	4
2.3 Monodentate nitrogen donor ligands (N)	5
2.4 Bidentate nitrogen donor ligands (NN)	5
2.5 Tridentate nitrogen donor ligands (NNN)	7
2.6 Tetradentate nitrogen donor ligands (NNNN)	10
2.7 Chelate effect	11
2.8 Organotin(IV) complexes with NN/NNN donor ligands	12
3.0 Research Methodology	17
3.1 Solvent distillation	17
3.2 Synthesis procedures of ligand (1) and its organotin(IV) complexes (3-7)	18
3.2.1 Synthesis of 2-acetylpyridine- <i>o</i> -phenylenediamine ligand [C ₁₃ H ₁₁ N ₃] containing NN donor atoms (1)	18
3.2.2 Synthesis of [Me ₂ SnCl ₂ (C ₁₃ H ₁₁ N ₃)] (3)	18
3.2.3 Synthesis of [Bu ₂ SnCl ₂ (C ₁₃ H ₁₃ N ₃)] (4)	19
3.2.4 Synthesis of [Ph ₂ SnCl ₂ (C ₁₃ H ₁₃ N ₃)] (5)	19
3.2.5 Synthesis of [MeSnCl ₃ (C ₁₃ H ₁₃ N ₃)] (6)	19
3.2.6 Synthesis of [BuSnCl ₃ (C ₁₃ H ₁₃ N ₃)] (7)	19
3.3 Synthesis procedures of ligand (2) and its organotin(IV) complexes (8-11)	20
3.3.1 Synthesis of 2-acetylpyridine- <i>o</i> -phenylenediamineacetophenone ligand [C ₂₁ H ₁₉ N ₃] containing NNN donor atoms (2)	20
3.3.2 Synthesis of [Me ₂ SnCl ₂ (C ₂₁ H ₁₉ N ₃)] (8)	20

3.3.3 Synthesis of [Bu ₂ SnCl ₂ (C ₂₁ H ₁₉ N ₃)] (9)	21
3.3.4 Synthesis of [Ph ₂ SnCl ₂ (C ₂₁ H ₁₉ N ₃)] (10)	21
3.3.5 Synthesis of [BuSnCl ₃ (C ₂₁ H ₁₉ N ₃)] (11)	21
4.0 Results And Discussion	22
4.1 Physical and analytical data	24
4.2 Spectroscopic studies of ligand (1) and its organotin(IV) complexes (3-7)	26
4.2.1 UV spectra analyses of ligand (1) and its organotin(IV) complexes (3-7)	26
4.2.2 IR spectra analyses of ligand (1) and its organotin(IV) complexes (3-7)	28
4.3 Spectroscopic studies of ligand (2) and its organotin(IV) complexes (8-11)	32
4.3.1 UV spectra analyses of ligand (2) and its organotin(IV) complexes (8-11)	32
4.3.2 IR spectra analyses of ligand (2) and its organotin(IV) complexes (8-11)	34
5.0 Conclusion	40
6.0 Suggestion for future research	40
7.0 References	41
8.0 Appendix	47

LIST OF TABLES

	Page
Table 1: Elemental analyses for the ligands (1-2) and their organotin(IV) complexes (3-11)	24
Table 2: Molar conductivities for organotin(IV) complexes (3-11)	25
Table 3: The λ_{\max} (nm) peaks of ligand (1) and its organotin(IV) complexes (3-7)	26
Table 4: Main IR data of ligand (1) and its organotin(IV) complexes (3-7) (cm ⁻¹) ^a	29
Table 5: The λ_{\max} (nm) peaks of ligand (2) and its organotin(IV) complexes (8-11)	32
Table 6: Main IR data of ligand (2) and its organotin(IV) complexes (8-11) (cm ⁻¹) ^a	35

LIST OF FIGURES

	Page
Figure 1: Some of the nitrogen donors with tertiary sp^3 -hybridized nitrogen atoms	2
Figure 2: Some of the nitrogen donors with tertiary sp^2 -hybridized nitrogen atoms	3
Figure 3: 2,2-bipyridine	5
Figure 4: 6,6'-bis(pirazolyl)-2,2'-bipyridine	6
Figure 5 : [7-(<i>D</i> -2-amino-2-phenylacetamido)-3-3-cephem-4-carboxylic acid]	6
Figure 6 : (a) 2,2'-bipyrimidine	7
(b) 2,3-bis(2-pyridyl)pyrazine	
Figure 7 : Pentamethyldiethylenetriamine	7
Figure 8 : (a) 2-amino-4,6-di-(pyridine-2-yl)-1,3,5-triazine	8
(b) 4,6-di-(pyridine-2-yl)-2-(3,5,5-trimethylhexanoylamino)-1,3,5-triazine	
Figure 9 : Structures of several tridentate [NNN] ligands	8
Figure 10 : 2,6-diacetylpyridine bis(4-phenylthiosemicarbazone)	9
Figure 11 : <i>N,N</i> -bis(2-pyridylmethyl)amine	9
Figure 12 : <i>N</i> -(2-pyridylmethyl)- <i>N,N'</i> -diethylethylenediamine	9
Figure 13: <i>N,N'</i> -(2-hydroxypropane-1,3-diyl)bis(pyridine-2-aldimine)	10
Figure 14: Pyridine-2-carbaldehyde azine	10
Figure 15: (a) Hexaamine Nickel(II) ion	11
(b) Triethylenediamine Nickel(II) ion	
Figure 16: Dimethyltin(IV) and mono- <i>N</i> -butyltin(IV) trichloride with several <i>N</i> -substituted pyridine-2-carbaldimine	12
Figure 17: R_2SnCl_2 -3,5-dimethyl-1-(2'-pyridyl)pyrazole	13
Figure 18: Structures of di- <i>n</i> -butyltin(IV) complexes with pyruvoylamino acid oximes	13
Figure 19: Structure of $Bu_2Sn(IV)$ -2-hydroxyimino-3-phenyl-propionic acid complex	14
Figure 20: Structures of a) ${}^nBu_2Sn(6\text{-thiopurine})_2$ and b) $Ph_3Sn(6\text{-thiopurine})$	14
Figure 21: Structures of stannacyclohexyl and stannacycloheptyl derivatives	15
Figure 22: Structures for organotin(IV) derivatives of 1-methylimidazole	15
Figure 23: Propose structure of 2-acetylpyridine- <i>o</i> -phenylenediamine ligand $[C_{13}H_{11}N_3]$ (1)	18
Figure 24: Propose structure of 2-acetylpyridine- <i>o</i> -phenylenediamineacetophenone ligand $[C_{21}H_{19}N_3]$ (2)	20

	Page
Figure 25: UV-Vis spectra of ligand (1) and its dimethyltin(IV) complex (3) (1×10^{-4} M) in benzene	27
Figure 26: IR spectrum of ligand (1) (As KBr disc)	30
Figure 27: IR spectrum for $[\text{Me}_2\text{SnCl}_2(\text{C}_{13}\text{H}_{11}\text{N}_3)]$ (3) (As KBr disc)	31
Figure 28: UV-Vis spectra of ligand (2) and its dimethyltin(IV) complex (8) (1×10^{-4} M) in benzene.	34
Figure 29: IR spectrum of ligand (2) (As KBr disc)	36
Figure 30: IR spectrum for $[\text{Me}_2\text{SnCl}_2(\text{C}_{21}\text{H}_{19}\text{N}_3)]$ (8) (As KBr disc)	37
Figure 31: Proposed structure of the diorganotin(IV) complexes (3-5) of the ligand (1)	38
Figure 32: Proposed structure of the mono-organotin(IV) complexes (6-7) of the ligand (1)	38
Figure 33: Proposed structure of the diorganotin(IV) complexes (8-10) of the ligand (2)	39
Figure 34: Proposed structure of the mono-organotin(IV) complex (11) of the ligand (2)	39
Figure 35: IR spectrum for $[\text{Bu}_2\text{SnCl}_2(\text{C}_{13}\text{H}_{13}\text{N}_3)]$ (4) (As KBr disc)	47
Figure 36: IR spectrum for $[\text{Ph}_2\text{SnCl}_2(\text{C}_{13}\text{H}_{13}\text{N}_3)]$ (5) (As KBr disc)	48
Figure 37: IR spectrum for $[\text{MeSnCl}_2(\text{C}_{13}\text{H}_{13}\text{N}_3)]$ (6) (As KBr disc)	49
Figure 38: IR spectrum for $[\text{BuSnCl}_2(\text{C}_{13}\text{H}_{13}\text{N}_3)]$ (7) (As KBr disc)	50
Figure 39: IR spectrum for $[\text{Bu}_2\text{SnCl}_2(\text{C}_{21}\text{H}_{19}\text{N}_3)]$ (9) (As KBr disc)	51
Figure 40: IR spectrum for $[\text{Ph}_2\text{SnCl}_2(\text{C}_{21}\text{H}_{19}\text{N}_3)]$ (10) (As KBr disc)	52

Coordination chemistry of organotin(IV) complexes with NN/NNN donor ligands

Imelda Sim Siew Ping

Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

ABSTRACT

Two ligands have been prepared by condensation reaction of 2-acetylpyridine with *o*-phenylenediamine and 2-acetylpyridine-*o*-phenylenediamine with acetophenone in 1:1 mole ratio. Organotin(IV) complexes have been synthesized where the ligands acted as bidentate N,N and tridentate N,N,N chelating agents, respectively. The characterization of the ligands (**1-2**) and their organotin(IV) complexes (**3-11**) has been made on the basis of elemental analyses, UV-visible and FTIR spectra studies. On the basis of analytical and spectral data, six-membered geometry and seven-membered geometry around organotin(IV) moiety have been proposed.

Key words: 2-acetylpyridine-*o*-phenylenediamine; 2-acetylpyridine-*o*-phenylenediamineacetophenone; organotin(IV) complexes; spectral studies

ABSTRAK

*Dua jenis ligan telah dihasilkan melalui tindakbalas kondensasi di antara 2-asetilpiridina dengan o-fenilindiamina dan 2-asetilpiridina-o-fenilindiamina dengan asetofenon dalam nisbah mol 1:1. Kompleks organotin(IV) telah disintesis melalui beberapa siri tindakbalas dimana 2-asetilpiridina-o-fenilindiamina dan 2-asetilpiridina-o-fenilindiaminaasetofenon masing-masing bertindak sebagai ligan N,N bidentat dan ligan N,N,N tridentat. Pencirian terhadap ligan (**1-2**) serta kompleks (**3-11**) telah dilakukan dengan menggunakan beberapa kaedah iaitu analisis elemen, kajian spectra UV-Vis dan FTIR. Berdasarkan kajian ke atas data analitikal dan spektra, struktur koordinasi 6-ahli dan 7-ahli telah dicadangkan.*

Kata kunci: 2-asetilpiridina-o-fenilindiamina; 2-asetilpiridina-o-fenilindiaminaasetofeno; kompleks organotin(IV); kajian spektra

1.0 INTRODUCTION

Organotin(IV) complexes are highly interested areas especially for their complex structures of different geometries and properties and also their biological activities (Mahmood *et al.*, 2004; Singh and Varshney, 2006). Organotin(IV) complexes with ligands containing O, N and S donor atoms. For example, complexes having nitrogen and sulphur ligands where the bonding patterns are supported by proton magnetic resonance indicates chelation of the ligand moiety to tin with sulphur atom. The chelate formation increased the fungi toxic action (Singh and Varshney, 2006). Besides that, according to Xanthopoulou *et al.*, (2003), organotin(IV) complexes have been demonstrated to exhibit relative high anti-tumor activity. For complexes $[\text{SnR}_2\text{X}_2(\text{LL})]$ where LL is an N,N-bidentate ligand, anti-tumor activity depends on the distance of Sn-N ($>2.39\text{\AA}$ and $<2.39\text{\AA}$) for the active and inactive compounds (Alvarez-Boo *et al.*, 2001; Szorcisk *et al.*, 2005), respectively which have suggested that dissociation of ligands is a significant step in their mechanism, while the coordinated ligand may favour transport of the active species to the site of action in the cells, where they are released by hydrolysis. The unique properties that have been exhibited and applied by organotin(IV) complexes makes these complexes particularly interesting and this in turn, attracts more attention for further studies. This present research project reported the preparation and characterization of several organotin(IV) complexes with the proposed NN/NNN- donor ligands.

1.1 OBJECTIVES

The objectives of this study are:

1. To synthesize bidentate and tridentate nitrogen (NN/NNN) donor ligands.
2. To synthesize organotin(IV) complexes with NN/NNN donor ligands.
3. To characterize NN/NNN- donor ligands and their organotin(IV) complexes using CHN analyses, UV-visible and FTIR spectra analyses.
4. To determine the molar conductivities of the synthesized organotin(IV) complexes

2.0 LITERATURE REVIEW

2.1 CHARACTERISTICS OF NITROGEN DONOR LIGANDS

The study of the coordination chemistry of nitrogen donor ligands has expanded to major areas of research since the past three decades. This is due to the significant contribution of nitrogen donor ligands to the development of modern coordination chemistry. Therefore, the range of nitrogen donors is more extensive than other donor atom.

Nitrogen donor ligands can be classified based on the hybridization of the nitrogen atom, which is known as sp^3 , sp^2 and sp . For example, some of the sp^3 -hybridized nitrogen donor atoms are given in **Figure 1**.

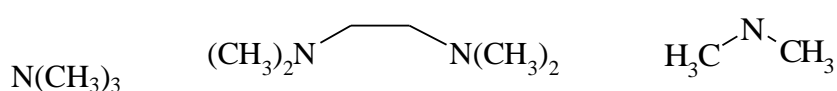


Figure 1: Some of the nitrogen donors with tertiary sp^3 -hybridized nitrogen atoms.

Complexes with nitrogen donor containing N-H bonds are normally not suitable for most of the organometallic reaction because an H atom on the coordination nitrogen is

sufficiently acidic to react nucleophilically. Furthermore, coordinated nitrogen atom containing non-bonding pairs of electron is more susceptible to attack electrophile which is lack of electrons. That is why **Figure 1** does not include the common nitrogen donors having N-H bonds. However, coordinated “nitrogen anions” showed an extensive and useful coordination chemistry, particularly when associated with sp^3 -hybridized carbon atoms, which is already shown in **Figure 1**.

Ligands containing sp^2 -hybridized nitrogen atoms, mostly have very extensive coordination chemistry when the atom is a part of an aromatic system in which, some of the examples are listed in **Figure 2**. A much more extensive and functional coordination chemistry is possible when the ligands for this type of donors are bidentate, tridentate or tetradentate. Nevertheless, the presence of stereogenic substituent is required for the use of such ligands in asymmetric catalysis.

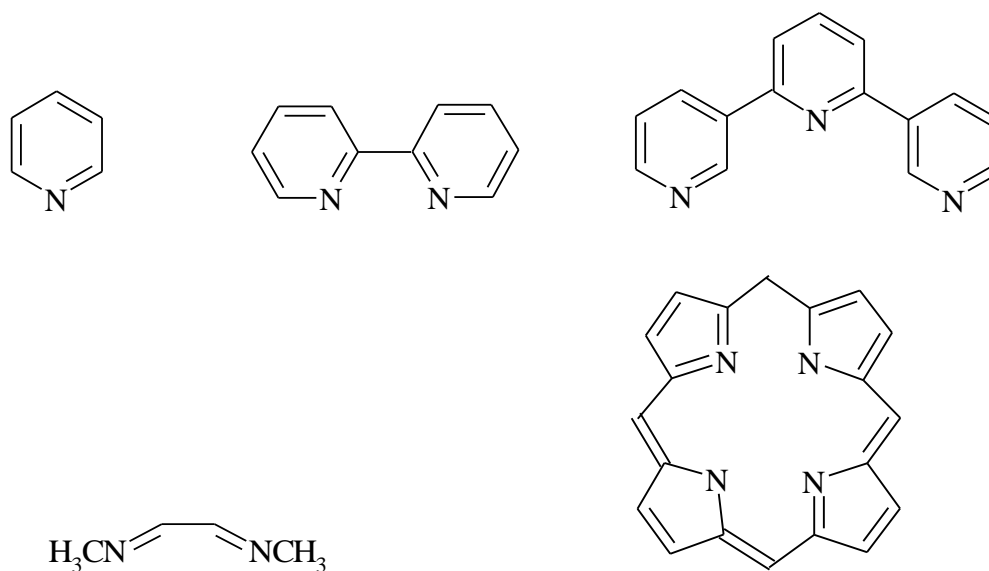


Figure 2: Some of the nitrogen donors with tertiary sp^2 -hybridized nitrogen atoms.

However, if there are C=N and C=C double bonds presented in these molecules, it will render them for further reactions such as nucleophilic attack. The only classes of organic

nitrogen donors with *sp*-hybridization are nitriles. Their major function is as labile ligand, which is weak and could be replaced easily by appropriate reagents. In addition, nitriles are quite liable towards nucleophilic attack once coordinated.

Nitrogen atoms could form strong bonds with the metal centers where the strength of the bonds depends on the covalence with a potentially significant contribution from the ionic character of the bond itself. In this project, bidentate NN- and tridentate NNN- nitrogen donor ligands have been synthesized for the synthesis of organotin(IV) compounds.

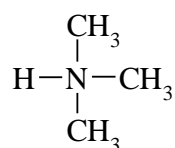
2.2 CHARACTERISTICS OF ORGANOTIN(IV) COMPLEXES

Organotin(IV) complexes are 5- and 6- coordinated according to Singh and Varshney, (2006). The atomic number for this element is 118.7 g/mol. This compound exerts high biological activities due to the presence of organic groups at the Sn atom in any member of an $R_nSnX_{(4-n)}$ whereby $n=1,2$ and 3 (Chiavarini *et al.*, 1996). The atom R stands for any alkyl or acyl groups while X atom stands for halogen atoms. It may also stand for oxygen or any other organic elements. Organotin(IV) are considered to be Lewis acids of different strengths, depending on the groups bound to the Sn(IV). Mono-organotin(IV) compounds, considered the least toxic among organotin(IV) derivatives as shown in the toxicity scale whereby $R_3Sn(IV)^+ > R_2Sn(IV)^{2+} > RSn(IV)^{3+} > Sn^{4+}$ have not achieved as much commercial application as diorgano- and triorganotin(IV) derivatives (Singh and Varshney, 2006). However, they are often used as hydrophobic agents for building materials and cellulosic matter and can be present in the aquatic system as the first step in the alkylation of inorganic Sn (Pellerito and Nagy, 2002).

2.3 MONODENTATE NITROGEN DONOR LIGANDS

Nitrogen donor ligands have great influence upon coordination chemistry environment. These donor ligands are classified into three groups that are sp^3 , sp^2 and sp . The classification is based upon the hybridization of nitrogen atom as has been stated in its properties.

In monodentate N- donor ligand, nitrogen atoms that are attached with hydrogen atoms are unsuitable for organometallic reaction due to the acidic presence of α -hydrogen in the environment. For example, sp^3 -hybridized nitrogen donor atoms such as trimethylamine.



Any sp -hybridized ligands that contains nitrogen atoms in an aromatic system has bigger potential in coordination chemistry. These kinds of ligands have more functions especially if they are polydentate aromatic ligands.

2.4 BIDENTATE NITROGEN DONOR LIGANDS

N,N-bidentate donor ligands are compounds that have two nitrogen atoms that are able to bond to any central metal cation. Below is one of the common examples of the N,N-bidentate donor ligand.

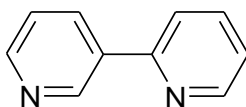


Figure 3: 2,2-bipyridine

Kowalczyk and Skarzewski, (2005) have synthesized 6,6'-bis(pyrazolyl)-2,2'-bipyridine which acts as chiral NN- bidentate donor ligand. The reaction is shown in **Figure 4**.

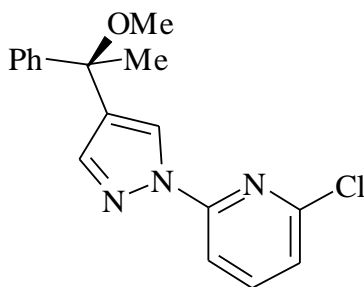


Figure 4: 6,6'-bis(pyrazolyl)-2,2'-bipyridine

Di Stefano *et al.*, (2004) synthesized a biologically active [7-(D-2-amino-2-phenylacetamido)-3-3-cephem-4-carboxylic acid] or cephalexin in **Figure 5** where he reported that within the potential donor atoms of cephalexin, amino and peptide nitrogens, carboxylate and β -lactam and peptide carbonyls could be involved in coordinating the metallic centre.

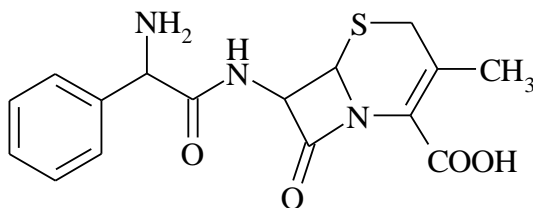


Figure 5: [7-(D-2-amino-2-phenylacetamido)-3-3-cephem-4-carboxylic acid]

Two N,N'-bidentate donor ligands have been reported by Shavaleev *et al.*, (2002). Both ligands act as bidentate nitrogen donor through the external diimine binding sites. The structures of these ligands are shown in **Figure 6**.

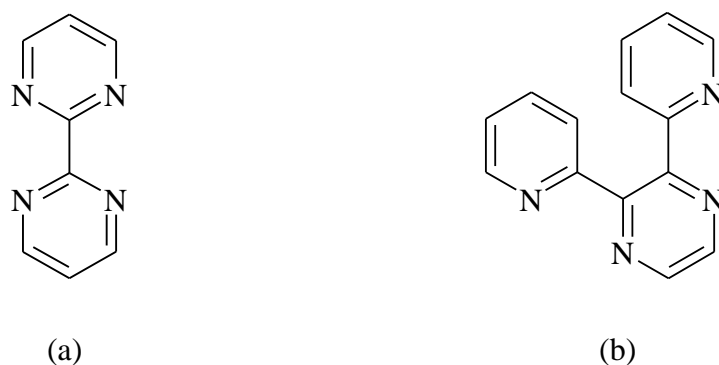


Figure 6: (a) 2,2'-bipyrimidine
(b) 2,3-bis(2-pyridyl)pyrazine

2.5 TRIDENTATE NITROGEN DONOR LIGANDS

Tridentate NNN- donor ligands are ligands that have each of their three atoms of nitrogen attached to the central metal cation. The most common tridentate donor ligand is pentamethyldiethylenetriamine that have been reported by Patel *et al.*, (2004). The molecular structure is shown in **Figure 7**.

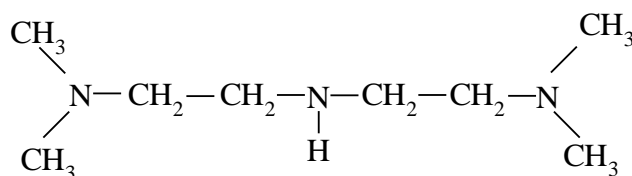


Figure 7: Pentamethyldiethylenetriamine

Miguirditchian *et al.*, (2005) reported two tridentate nitrogen donor ligands as depicted in **Figure 8** that were used in understanding the complexation process of these ligands. It was reported that there are strong ionic bonding of cations with the ligands.

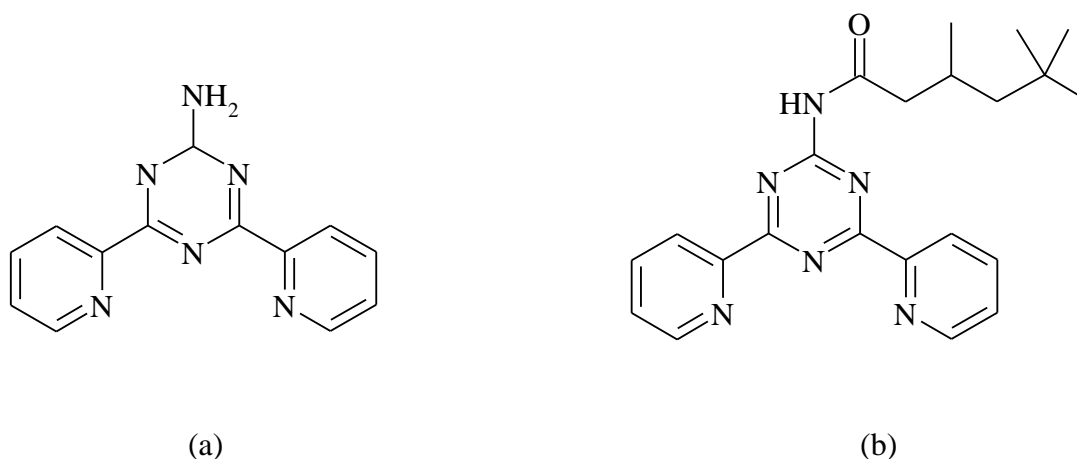


Figure 8: (a) 2-amino-4,6-di-(pyridine-2-yl)-1,3,5-triazine

(b) 4,6-di-(pyridine-2-yl)-2-(3,5,5-trimethylhexanoylamino)-1,3,5-triazine

A series of tridentate [NNN] donor ligands that are shown in **Figure 9** containing a central pyridine or amine unit and two peripherals amine or imine donors with either *N*-alkyl or *N*-aryl substituents was synthesized by Reilly *et al.*, (2004). It was reported that ligands derived from alkyl amines or pyridine groups which are the most active for atom transfer radical polymerization.

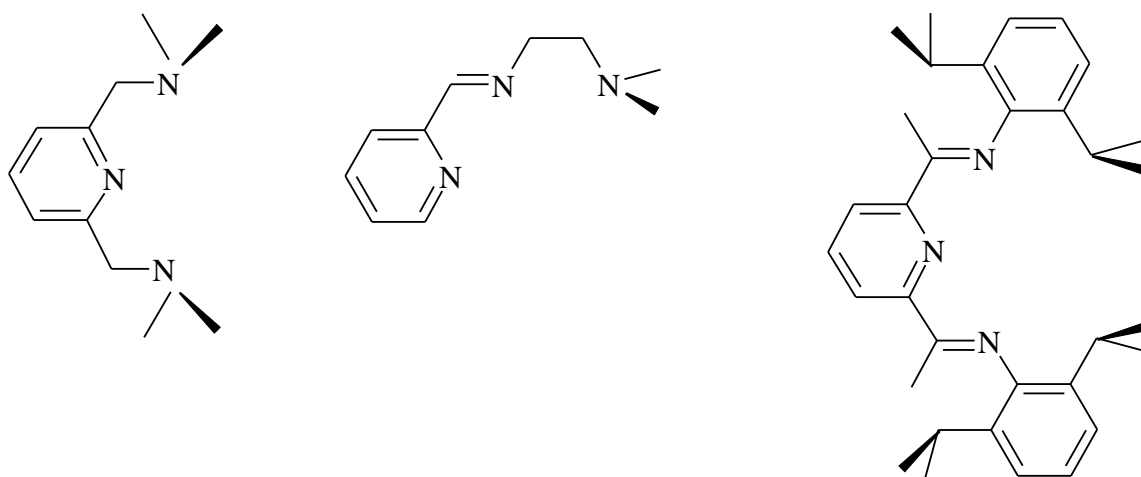


Figure 9: Structures of several tridentate [NNN] ligands

Sousa *et al.*, (2001) have synthesized a tridentate ligand, 2,6-diacetylpyridine *bis*(4-phenylthiosemicarbazone) as depicted in **Figure 10**. The structure determination revealed a neutral complex of Sn(IV) in a distorted pentagonal bipyramidal (PBP) geometry with the equatorial plane defined by the SNNNS- donor system of the ligand and with the two *n*-butyl groups in the axial positions.

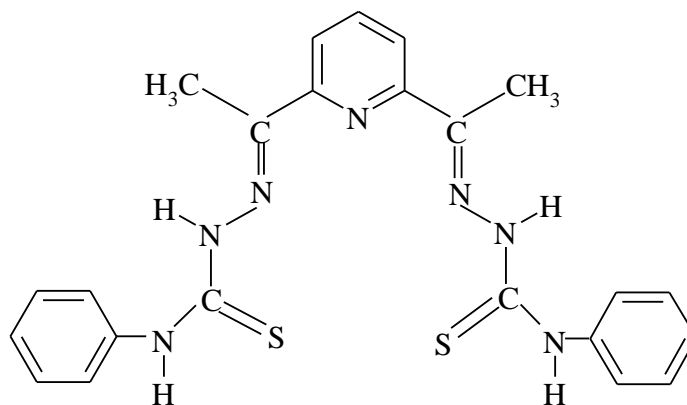


Figure 10: 2,6-diacetylpyridine *bis*(4-phenylthiosemicarbazone)

Recently, another two types of tridentate nitrogen donor ligands shown in **Figure 11-12** have been reported by Sarkar *et al.*, (2006).

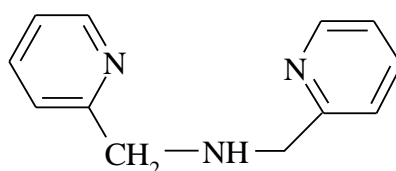


Figure 11: *N,N*-bis(2-pyridylmethyl)amine

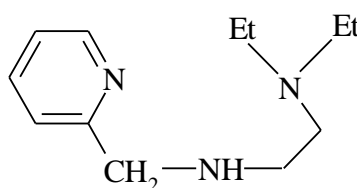


Figure 12: *N*-(2-pyridylmethyl)-*N,N'*-diethylethylenediamine

2.6 TETRADENTATE NITROGEN DONOR LIGANDS

Mukherjee *et al.*, (2004) have synthesized a tetradentate nitrogen donor ligand namely *N,N'*-(2-hydroxypropane-1,3-diyl)*bis*(pyridine-2-aldehyde). The structure is shown in the **Figure 13**. It was reported that the imine functionalities of the metal-bound Schiff base undergo oxidative conversion with hydrogen peroxide through the formation of an intermediate amido species.

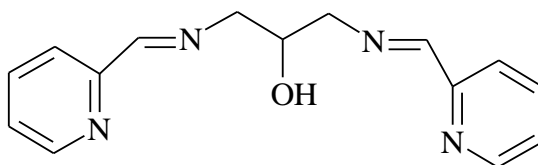


Figure 13: *N,N'*-(2-hydroxypropane-1,3-diyl)*bis*(pyridine-2-aldehyde)

Toupance *et al.*, (2002) reported a tetradentate donor ligand having a pyridyl backbone. The nitrogen atoms contain lone pair electrons that will attach to a central metal cation (**Figure 14**).

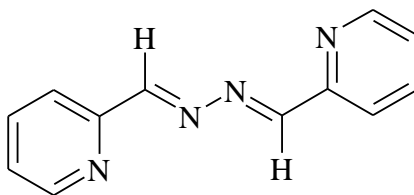


Figure 14: Pyridine-2-carbaldehyde azine

2.7 CHELATE EFFECT

Chelate means that any ligand that has the capability to bond with any central metal cation through more than one donor atom. Any complexes that contain chelate rings are far more stable than similar complexes containing no rings. Chelate effect is termed when multidentate ligands in general are form more stable complexes than the monodentate ligands.

The comparisons of the chelate effect are given below.

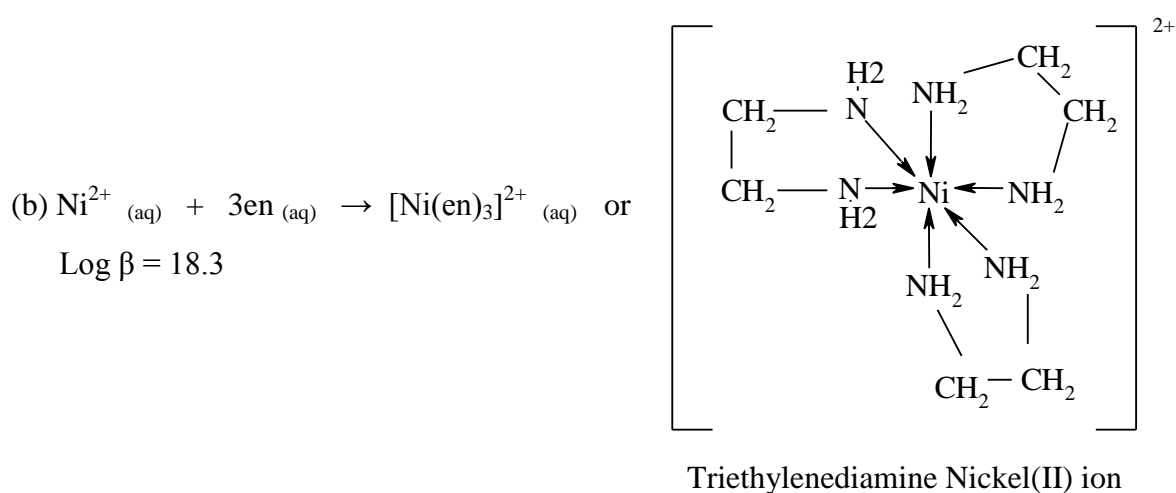
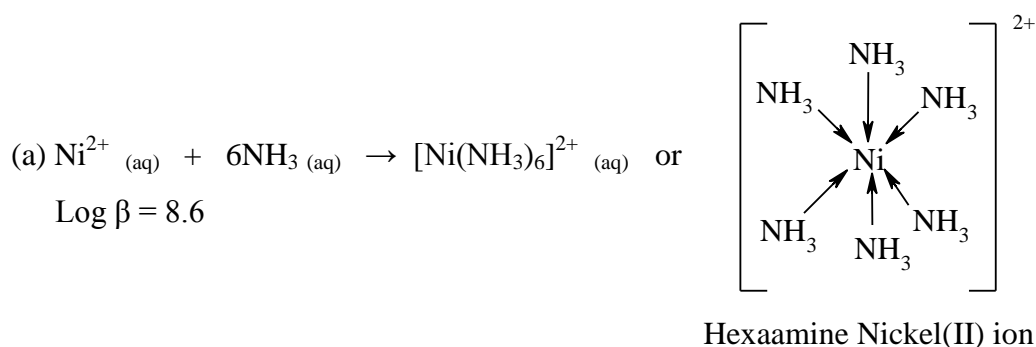


Figure 15: (a) Hexamine Nickel(II) ion

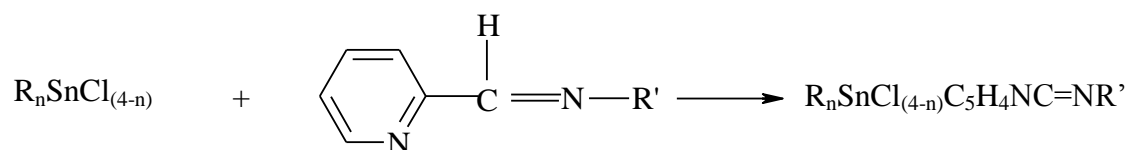
(b) Triethylenediamine Nickel(II) ion

The stability of the chelate complexes also depends on the size of the rings that are formed. 5-membered rings are more stable than 6-membered chelates when the atoms in the ring are joined by single bonds. On the other hand, when the rings are joined by double bonds, 6-membered rings are more stable than 5-membered rings.

2.8 ORGANOTIN(IV) COMPLEXES WITH NN/NNN DONOR LIGANDS

Three primary factors are involved in the structural-activity relationship for organotin(IV) derivatives which are the natures of the organic group (R), the nature of halide or pseudohalide (X), and the nature of donor ligand (Szorcsik *et al.*, 2005).

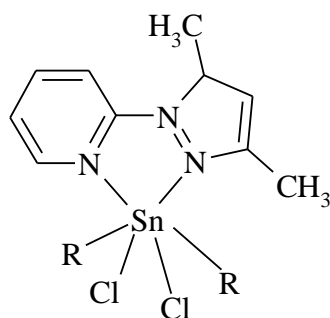
Tanaka and his co-workers (1979), have synthesized 1:1 molecular adducts of dimethyltin(IV) and mono-*N*-butyltin(IV) trichloride with several *N*'-substituted pyridine-2-carbaldimine. The reaction is shown in **Figure 16**.



where $n = 1$ and 2 , $\text{R} = n\text{-butyl}$, $\text{R}' = \text{Me}, 4\text{-MeC}_6\text{H}_4$

Figure 16: Dimethyltin(IV) and mono-*N*-butyltin(IV) trichloride with several *N*-substituted pyridine-2-carbaldimine

When the substituent R on the imine nitrogen atom is Me, Et or CH₂Ph, the adduct exist as a mixture of two isomers in acetonitrile on the basis of ¹HNMR chemical shifts of the ligand protons and their spin-spin coupling constants with the tin nuclei. Alvarez-Boo and his co-workers, (2003), have synthesized a complex compound containing organotin(IV) where it forms six-coordinated complex. The structure is shown as in **Figure 17**.



Where R=Me, n-Bu or ⁿBu, Ph, etc

Figure 17: R_2SnCl_2 -3,5-dimethyl-1-(2'-pyridyl)pyrazole

Szorcsik and his co-workers (2003), have also been synthesized 1:1 molecular adducts of pyruvoylamino acid oximes with Bu_2SnO that is shown in **Figure 18**.

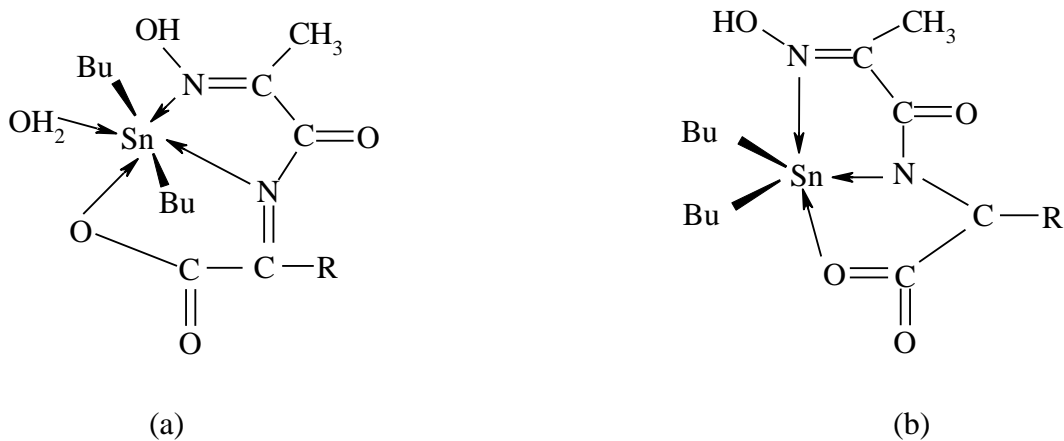


Figure 18: Structures of di-*n*-butyltin(IV) complexes with pyruvoylamino acid oximes

The organotin(IV) moieties react with the carboxylate [O] and peptide and oxime [N] atoms of the ligands are clearly seen by using FTIR and Raman spectra (Szorcsik *et al.*, 2003). In most cases, it was found out that the $-COO^-$ group monodentately coordinate to the central metal cation and most of the complexes probably have monomeric structures (Szorcsik *et al.*, 2003) (**Figure 19**).

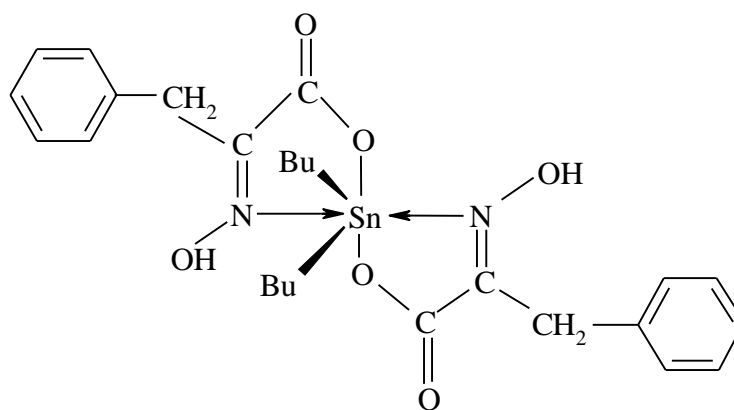


Figure 19: Structure of $\text{Bu}_2\text{Sn(IV)}$ -2-hydroxyimino-3-phenyl-propionic acid complex

Zhang and his co-workers (2004), have synthesized triphenyl(6-thiopuriny)tin(IV) complex and have investigated the molecular structure by using X-ray diffraction studies. The structures of the complexes are depicted in **Figure 20**.

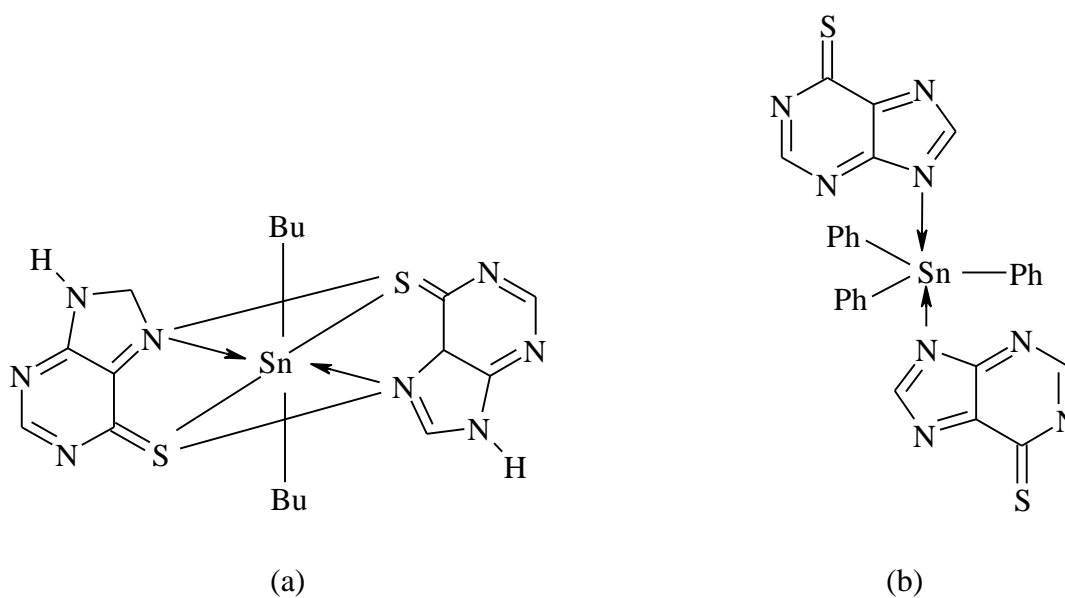


Figure 20: Structures of a) ${}^n\text{Bu}_2\text{Sn(6-thiopurine)}_2$ and b) $\text{Ph}_3\text{Sn(6-thiopurine)}$

Pellerito and Nagy, (2002) have synthesized stannacyclohexyl and stannacycloheptyl derivatives (**Figure 21**) and also determine their X-ray structure. It clearly demonstrated that

there are no basic restrictions for Sn(IV) to extend its coordination sphere (at least to attain pentacoordination) when it is an integral part of a cycloalkyl system.

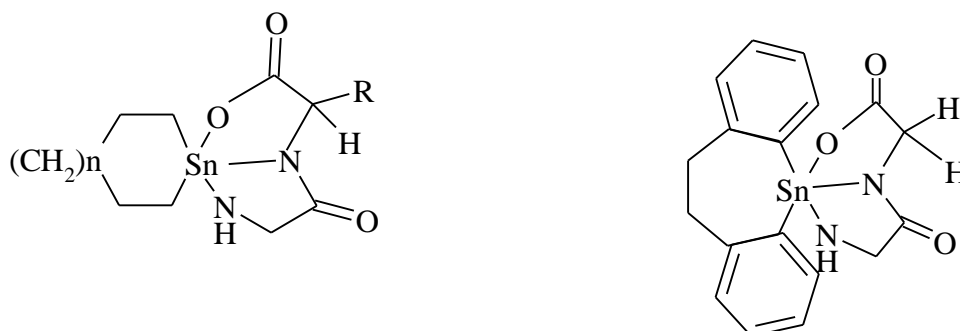
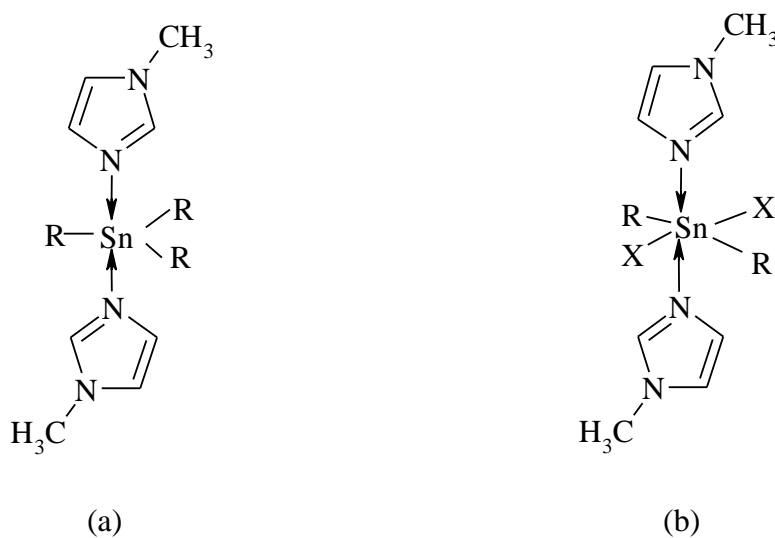


Figure 21: Structures of stannacyclohexyl and stannacycloheptyl derivatives

Organotin(IV) complexes containing monodentate or bidentate nitrogen donor ligands as 1-methylimidazole derivatives (**Figure 22**) have been reported by Pettinari *et al.*, (1998).



R=Me, Et, ⁿBu or Ph; n=1,2,3

R=Me, Et, ⁿBu or Ph; n=1,2,3 ;

X=halogens

Figure 22: Structures for organotin(IV) derivatives of 1-methylimidazole