



Faculty of Resource Science and Technology

**SYNTHESIS AND CHARACTERIZATION OF GALLIUM(III),  
ZINC(II), IRON(III), NICKEL(II), COPPER(II) AND  
COBALT(II) WITH CHALCONE'S DERIVATIVE**

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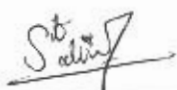
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Bachelor of Science with Honours  
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2005

## DECLARATION

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



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**Siti Salwa Ahmad Zur**

Program of Resource Chemistry

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Universiti Malaysia Sarawak

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## ABSTRACT

Synthesis and spectroscopic characterization of gallium(III), zinc(II), iron(III), nickel(II), copper(II) and cobalt(II) complexes with chalcone's derivative are reported in this thesis. Structural rearrangement was occurred in chalcone before coordinated with gallium(III), zinc(II), iron (III), nickel(II), copper(II) and cobalt(II) complexes. Reaction of chalcone with respective complexes of gallium(III), zinc(II), iron(III), nickel(II), copper(II) and cobalt(II) gave a new coordination mode of Ga-O, Zn-O, Fe-O, Ni-O, Cu-O and Co-O bonds. Chalcone acted as monodentate ligand in each complex. The ratio between metals: ligand is 1:1 ratio for all the metal complexes in this research.

Key words: Chalcone, structural rearrangement, gallium(III), zinc(II), iron(III), nickel(II), copper(II), cobalt(II) complexes

## **ABSTRAK**

*Sintesis dan pencirian spektroskopi bagi kompleks galium(III), zink(II), ferum(III), nikel(II), kuprum(II) dan kobalt(II) dengan kalkon telah dilaporkan dalam tesis ini. Penstrukturan semula telah berlaku di dalam kalkon sebelum berkoordinat dengan kompleks galium(III), zink(II), ferum(III), nikel(II), kuprum(II) dan kobalt(II). Tindak balas kalkon dengan kompleks galium(III), zink(II), ferum(III), nikel(II), kuprum(II) dan kobalt(II) masing-masing telah menghasilkan mod koordinatan yang baru iaitu ikatan Ga-O, Zn-O, Fe-O, Ni-O, Cu-O and Co-O. Kalkon bertindak sebagai ligan monodentat dalam setiap kompleks. Nisbah antara logam: ligan adalah 1: 1 bagi kesemua kompleks dalam kajian ini.*

*Kata kunci: Kalkon, penstrukturan semula, kompleks galium(III), zink(II), ferum(III), nikel(II), kuprum(II), kobalt(II)*

## CHAPTER ONE: INTRODUCTION

This research is proposed to investigate the complexation of gallium(III), zinc(II), iron(III), nickel(II), copper(II) and cobalt(II) complexes with chalcone's derivative. The general objective of this study is to investigate the complexation reactions from various metals located in the period four in periodic table. Therefore, from the result of this study, the coordination number as well as its geometrical structure can be determined. On top of this, the spectroscopic characteristic of each complex also be studied.

### 1.1 Chalcone

Chalcone is generally defined as a type of pigment formed by the chemical compound called benzylideneacetophenone (Horowitz *et al.*, 1975). Chalcone can be divided into three different groups namely regular chalcone, chalcone having  $\beta$ -oxygenation and retrochalcone (Harbone, 1994). Chalcones are frequently employed in the synthesis of flavones and isoflavones (Harbone, 1994). For example 2'-hydroxy-3',4'-methylenedioxy-4-methoxy-chalcone (Figure 1.1) and 2'-hydroxy-3'-methoxy-4'-benzyloxy-3,4-methylenedioxychalcone (Figure 1.2) as intermediates in the synthesis of new naturally occurring isoflavones (Parmar *et al.*, 1987,1988). Chalcone is usually used as the inhibitor on some specific enzyme, stabilization agent for heating process and makes use as a pigment in color photography field (Dhar, 1981). Recently, chalcone bearing non-natural substituents have been synthesized in order to develop drugs active against cancer, malaria, leishmaniasis, tuberculosis, and cardiovascular diseases (Eddarir *et al.*, 2003). On top of this, chalcones and its derivatives also play an important role in photochemistry. They were applied in photo-alignment layer of liquid crystal display since they possess high photo-reactivity can combine with polyimide to facilitate the photoreaction and generate stable alignment layers (Song *et al.*, 2002).

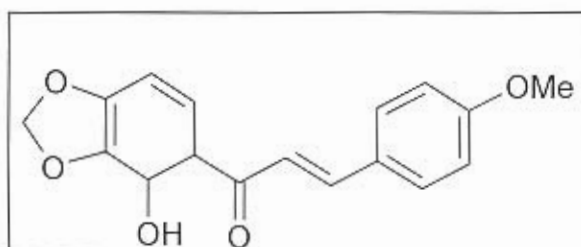


Figure 1.1: 2'-hydroxy-3', 4'-methylenedioxy-4-methoxy-chalcone  
(Parmar *et al.*, 1987, 1988)

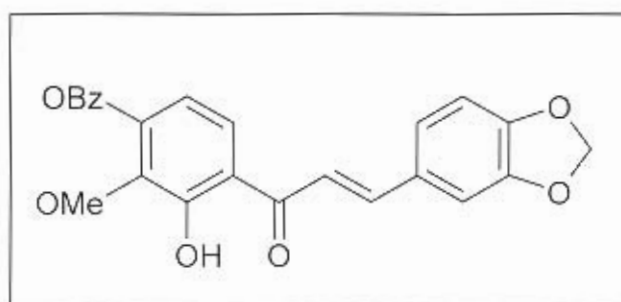


Figure 1.2: 2'-hydroxy-3'-methoxy-4'-benzyloxy-3,4-methylenedioxychalcone  
(Parmar *et al.*, 1987, 1988)

## 1.2 Gallium

Gallium is an element in Group IIIA and period four in periodic table. Its atomic number is 31 and the atomic weight is 69.72. The electronic configuration of gallium is  $[Ar]3d^{10}4s^24p^1$  and classified among rare and trace elements (Sheka, 1966).

Gallium is superficially oxidized in air and oxygen, and loses its luster becoming coated with a thin film of grayish-blue oxide (Sheka, 1966). The stable charge for Gallium is +3, but it is also found in unipositive +1 and bipositive +2 states such as gallium monobromide ( $GaBr$ ), gallium dibromide ( $GaBr_2$ ) and gallium tribromide ( $GaBr_3$ ) (Elschenbroich, 1992).  $Ga^+$  and  $Ga^{2+}$  are less stable than  $Ga^{3+}$ , and their salt have reducing properties (Sheka, 1966).

High purity gallium is used in semiconductors (Sheka, 1966). Gallium arsenide and phosphide are employed in crystal amplifiers, rectifiers and spacitors (Sheka, 1966). Due to

its wide of temperature range (melting point  $29.78^{\circ}\text{C}$ , boiling point  $1983^{\circ}\text{C}$ ), gallium is used for filling quartz thermometers for measuring temperatures between  $600$  and  $1500^{\circ}\text{C}$  (Sheka, 1966).

### 1.3 Zinc

Zinc is an element in group IIB and period four in periodic table. Its atomic number is 30 and its molecular weight is 63.8. The electronic configuration is  $[\text{Ar}]3d^{10}4s^2$ . It forms only one oxidation state, Zn(II) which is  $3d^{10}$  (Lister & Renshaw, 2000).

Its abundance in the earth's crust is about 76 ppm, slightly more abundant than copper (68 ppm) (Greenwood & Earnshaw, 1998). The major ores of zinc are ZnS and  $\text{ZnCO}_3$ . Less important ores are hemimorphite,  $\text{ZnSi}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$  and franklinite,  $(\text{Zn.Fe})\text{O.Fe}_2\text{O}_3$  (Greenwood & Earnshaw, 1998). Zinc is tarnish quickly in most air and combines with oxygen, sulfur, phosphorus and the halogens when heated (Greenwood & Earnshaw, 1998).

One of the most important manufactured zinc, ZnO is important in the industrial of rubber where it shortens the time of vulcanization. It is also use as a pigment in the paint production (Greenwood & Earnshaw, 1998). It is also improves the chemical durability of glass and so it is used in the production of special glasses, enamels and glazes (Greenwood & Earnshaw, 1998). In the chemical industries, it is the usual starting material for other zinc chemicals for example soaps (Greenwood & Earnshaw, 1998).

## 1.4 Iron

Iron is an element in group VIII and period four in periodic table. Its atomic number is 26 and its molecular weight is 55.9. The electronic configuration for Iron is  $[\text{Ar}] 3d^6 4s^2$ . Iron nuclei are stable, giving it a comparability high cosmic abundance and it is thought to be the main constituents of the earth's core (Greenwood & Earnshaw, 1998).

It is the second most abundant in the Earth's core and it is found as the ores haematite,  $\text{Fe}_2\text{O}_3$  and magnetite,  $\text{Fe}_3\text{O}_4$  which are obtained by quarrying or open cast mining (Lister & Renshaw, 2000). Iron pyrite ( $\text{FeS}_2$ ) is also common but it is not used as a source of iron because of the difficulty to eliminate the sulfur (Greenwood & Earnshaw, 1998). The distribution of iron has been influenced by weathering. Leaching from sulfide and silicate deposits occurs readily as  $\text{FeSO}_4$  and  $\text{Fe}(\text{HCO}_3)_2$  respectively (Greenwood & Earnshaw, 1998).

Because of their availability, production of iron ores can be confined to those of the highest grade in gigantic operations (Greenwood & Earnshaw, 1998). The most stable charges for iron are +2 and +3 and the highest oxidation state known is +6 in  $[\text{FeO}_4]^{2-}$  and even this is obviously easily reduced (Greenwood & Earnshaw, 1998). Iron is a reactive metal. It is pyrophoric if finely divided and dissolving readily in dilute acids to give  $\text{Fe}^{2+}$  salts (Greenwood & Earnshaw, 1998).

## 1.5 Nickel

Nickel is an element in VIII and period four in periodic table. Its atomic number is 28 and its molecular weight is 58.69. The electronic configuration for nickel is  $[\text{Ar}]3d^8 4s^2$ . It is the seventh most abundant transition metal and the twenty-second most abundant element in the earth's crust (Greenwood & Earnshaw, 1998).

Its important ores are of two types:

- a) Laterites, which are oxide and silicate ores such as garnierite  $(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$  and nickeliferous limonite  $(\text{Fe,Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$
- b) Sulfides such as pentlandite,  $(\text{NiFe})_9\text{S}_8$ , associated with copper, cobalt and precious metals so that the ores typically contain about 5% Ni (Greenwood & Earnshaw, 1998).

Nickels react on heating with B, Si, P, S and the halogens though slowly with the  $\text{F}_2$  than most metals do (Greenwood & Earnshaw, 1998). It is oxidized at red heat by steam, and will dissolve in dilute mineral acids (Greenwood & Earnshaw, 1998).

## 1.6 Copper

Copper is an element in Group IB and in period four in periodic table. Its atomic number is 29 and its molecular weight is 63.5. The electronic configuration is  $[\text{Ar}]3\text{d}^{10}4\text{s}^1$ . Copper forms only two stable oxidation state, copper(I) and copper(II) in its compound (Lister & Renshaw, 2000).

It is found mainly as the sulfides, oxides and carbonates, its major ores are copper pyrite (chalcopyrite),  $\text{CuFeS}_2$  (Greenwood & Earnshaw, 1998). Copper(III) is generally regarded as uncommon, being very easily reduced, but because of its possible involvement in biological electron transfer reactions, a number of  $\text{Cu}^{3+}$  peptides have been prepared (Greenwood & Earnshaw, 1998).

The best known simple salt is the sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  which is widely used in electroplating processes, as a fungicide to protect crops and as an algicide in water purification (Greenwood & Earnshaw, 1998). It is also the starting material in production of most other copper compounds (Greenwood & Earnshaw, 1998).



## 1.7 Cobalt

Cobalt is an element in Group VIII and in period four in periodic table. Its atomic number is 27 and its molecular weight is 58.9. The electronic configuration for cobalt is  $[\text{Ar}]3d^7 4s^2$ . Cobalt is appreciably less reactive than iron and it is stable to atmospheric oxygen unless heated, when it is oxidized first to  $\text{Co}_3\text{O}_4$ ; above  $900^\circ\text{C}$  the product is  $\text{CoO}$  (Greenwood & Earnshaw, 1998).

It dissolved rather slowly in dilute mineral acid giving salts of  $\text{Co}^{2+}$  (Greenwood & Earnshaw, 1998). The most stable oxidation states of cobalt are +2 and +3.  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  is a strong oxidizing agent in aqueous solution (Greenwood & Earnshaw, 1998).

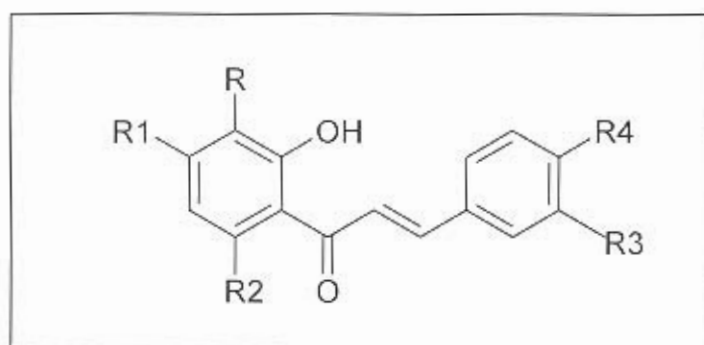
The largest use of cobalt is in the production of chemical for the ceramics and paints industries. The main used in paint industries is providing white colour by counterbalancing the yellow tint arising from iron impurities (Greenwood & Earnshaw, 1998). It is also used in the manufacture of magnetic alloys for example is "Alnico", steel containing aluminium, and nickel as well as cobalt. It is used for permanent magnets which are up to 25 times more powerful than ordinary steel magnets (Greenwood & Earnshaw, 1998).

## 1.8 Literature Review

### 1.8.1 Chalcone

There are several methodologies for the synthesis of chalcone. 2'-hydroxychalcones with a variety of substitution patterns (Figure 1.3) have been synthesized in excellent yields (75-90.5%) by the Claisen-Schmidt (Figure 1.4) condensation of hydroxyacetophenones with aldehydes in the presence of partially dehydrated barium hydroxide,  $\text{Ba}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  (Sathyanarayana & Krishnamurty, 1988). This method is similar with the methods that used in this project. Herdan and his coworkers (1990) described the synthesis of a small series of

chalcone compounds under acidic condition and the yield was 75–80%. Two pathways are obviously available for chalcone synthesis, which include: (1) the coupling between activated cinnamic acids and phenylboronic acids as shown in Figure 1.5; and (2) the coupling between activated benzoic acids and phenylvinylboronic acids (Figure 1.6) (Eddarir *et al.*, 2003). Based on these two pathways, the yield obtained (1) and (2) were 51% and 93%, respectively. Synthesized of 2'-hydroxy-4',5',6'-trimethoxychalcone (Figure 1.7) from 3,4,5-trimethoxyphenol and cinnamoyl chloride by using aluminium chloride being the catalyst (Ichino *et al.*, 1988b). Suresh and his coworkers (1986) used fused  $\text{ZnCl}_2$ ,  $\text{PoCl}_3$  and cinnamic acid to synthesize the chromanochalcone (Figure 1.8). The most frequently method used for preparing chalcones involves condensation of acetophenone and benzaldehydes in the base condition. A procedure taken from Rani (1986) involves the synthesis of eriodictyol 7-methyl ether. A solution of 2-hydroxy-4,6-dimethoxyacetophenone and 3,4-dibenzyloxybenzaldehyde in ethanol was treated with a solution of KOH and allowed to stand at room temperature for 48 hour. The reaction mixture was poured into ice and HCl but the yield was not mentioned in the research.



R, R2, R4 = H; R1 = H, OMe, Obz ; R3 = H, OH, Ome

Figure 1.3: 2'-hydroxychalcones with a variety of substitution patterns

(Sathyanarayana and Krishnamurty, 1988)

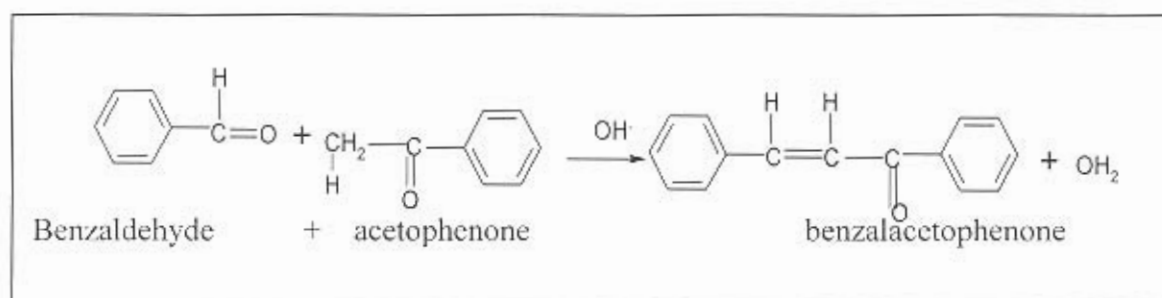


Figure 1.4: Claisen-Schmidt Reaction (Sathyanarayana and Krishnamurty, 1988)

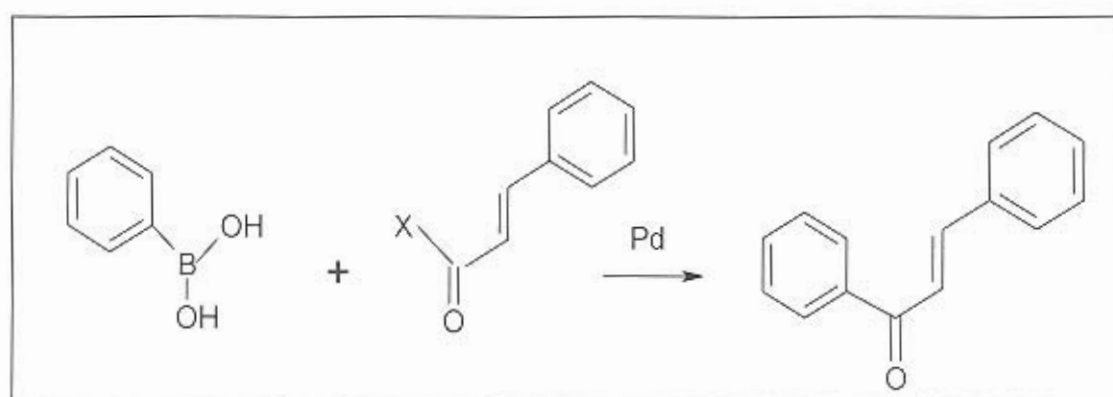


Figure 1.5: Pathway A (Eddarir *et al.*, 2003)

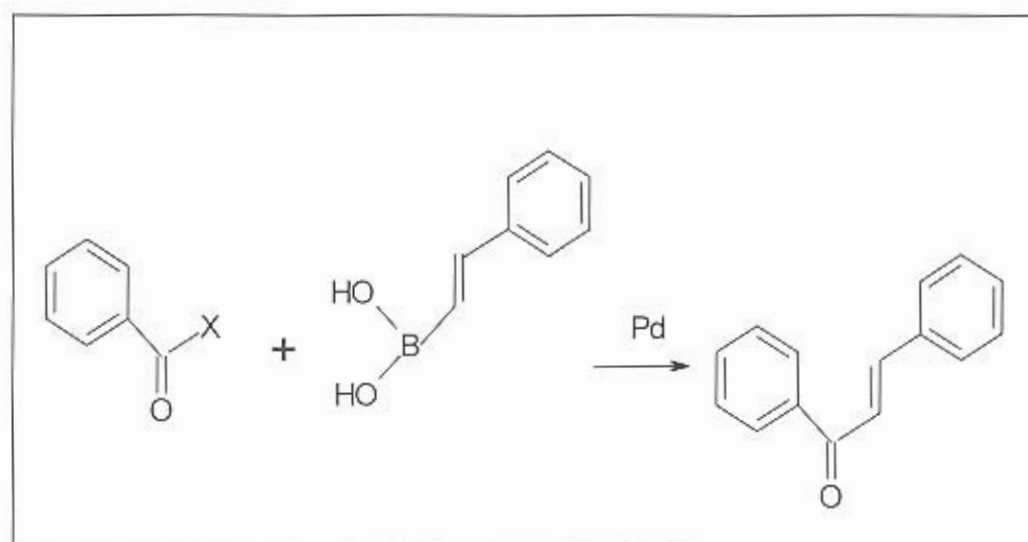


Figure 1.6: Pathway B (Eddarir *et al.*, 2003).

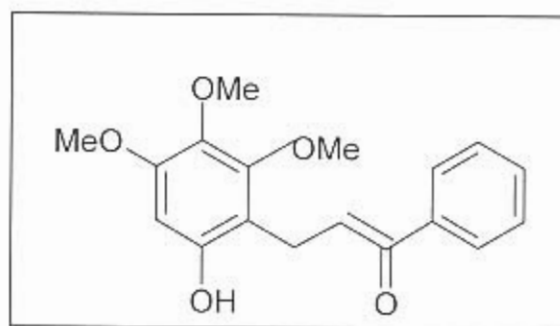


Figure 1.7: 2'-hydroxy-4' 5' 6'-trimethoxychalcone (Ichino *et al.*, 1988).

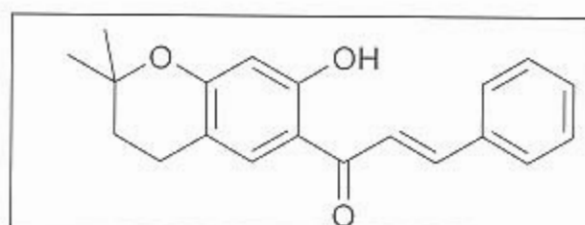


Figure 1.8: Chromanochalcone (Suresh *et al.*, 1986)

### 1.8.2 Gallium

Six dimethylgallium (indium) complexes of type  $\text{Me}_2\text{ML}$  [ $\text{M}=\text{Ga}$ ,  $\text{L}=1\text{-phenyl-3-N-}$ (phenylimino)-1-butanonato (1), 1-phenyl-3-N-(p-methoxyphenylimino)-1-butanonato (2), 1-phenyl-3-N-(o-chloro phenylimino)-1-butanonato (3);  $\text{M}=\text{In}$ ,  $\text{L}=1\text{-phenyl-3-N-}$ (phenylimino)-1-butanonato (4), 1-phenyl-3-N-(p-methoxyphenylimino)-1-butanonato (5), 1-phenyl-3-N-(o-chlorophenylimino)-1-butanonato] (6) have been synthesized by reaction of trimethylgallium (indium) with appropriate 1-phenyl-3-N-(arylimino)-1-butanones (Shen *et al.*, 2004). The complexes obtained have been characterized by elemental analysis  $^1\text{H-NMR}$ , IR and mass spectroscopy. Structure of (2) has been determined by X-ray single-crystal analysis, in which Ga atom is four coordinated and the gallium atom exhibits tetrahedral geometry (Shen *et al.*, 2004).

Manessi and his coworkers (2004) have studied the gallium(III) complexes of the peptide ligand N-(2-(imidazolyl)ethyl)pyridine-2-carboxamide (pypepH<sub>2</sub>) resembling a fragment of the metal-binding domain of bleomycins (BLMs), have been isolated. Reaction of pypepH<sub>2</sub> with (Et<sub>4</sub>)[GaCl<sub>4</sub>] and Ga(acac)<sub>3</sub>[acac<sup>-</sup> is the acetylacetonate (-1) ions] affords the mononuclear complex [Ga(pypenH<sub>2</sub>)]Cl.2H<sub>2</sub>O (1) and the tetranuclear complex [Ga<sub>4</sub>(acac)<sub>4</sub>(pypep)<sub>4</sub>].4.4H<sub>2</sub>O (2), respectively. Both complexes were characterized by single-crystal X-ray crystallography, IR spectroscopy and thermal decomposition data. The crystal system for (1) is triclinic and tetragonal for (2).

### 1.8.3 Zinc

Novel complexes of ZnX<sub>2</sub> [X=Br, CN, Cl] containing the alkaloid  $\alpha$ -isospartine as bidentate symmetrical ligand have been prepared and there are characterized by spectroscopic and X-ray methods (Jasiewicz *et al.*, 2005). The compounds that have been synthesized in this study were [ZnBr<sub>2</sub>(C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>)], [Zn(CN)<sub>2</sub>(C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>)] and [ZnCl<sub>2</sub>(C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>)] (Jasiewicz *et al.*, 2005). These compounds have been synthesized by a direct synthetic route mixing methanolic solution of ZnX<sub>2</sub> and the alkaloid (Jasiewicz *et al.*, 2005). The geometry around the zinc(II) ion is distorted from tetrahedral and the complexes utilize their twofold symmetry in the crystal structure (Jasiewicz *et al.*, 2005).

Alves de Sousa and his coworkers (2005) have studied a series of Zn(N<sub>2</sub>S<sub>2</sub>) complexes. They have been prepared and characterized IR, UV-Vis and X-ray methods. They have different nitrogen donors such as two amidates, two amines, two imines or one amidate and one imine. A bis-amidato dithiolate complex has been structurally characterized by single crystal X-ray diffraction analysis and exhibits a distorted tetrahedral structure. Oxidation of all these complexes with dioxirane or anhydrous H<sub>2</sub>O<sub>2</sub> results in the formation of unique product,

the disulfonate species. Zinc was found to be released during the course of the oxidation. The bis-imine/bis-sulfonate species is the only one to retain zinc. This complex was crystallized with two pyridine molecules. Its crystal structure reveals a distorted octahedral environment around the zinc cation.

#### 1.8.4 Iron

A series of mononuclear iron(III) complexes as functional and structural model compounds for intradiol cleaving catechol dioxygenases were synthesized (Pascaly *et al.*, 2001). The novel iron(III) catecholate complexes that have been synthesized are  $[\text{Fe}(\text{bpia})(\text{tcc})]\text{ClO}_4$ ,  $[\text{Fe}(\text{bppa})(\text{tcc})]\text{ClO}_4 \cdot (\text{CH}_3)_2\text{CO}$ ,  $[\text{Fe}(\text{bpqa})(\text{tcc})]\text{ClO}_4 \cdot (\text{CH}_3)_2\text{CH}_2\text{OH}$  (3) and  $[\text{Fe}(\text{me}_1\text{tpa})(\text{tcc})]\text{NO}_3$  (4) (Pascaly *et al.*, 2001).

For all model compounds the iron(III) cores are in a distorted octahedral environment derived from tripodal tetradentate  $\text{N}_4$ -donor ligands and a catechol (Pascaly *et al.*, 2001). The model complexes were characterized by spectroscopic, electronic methods and X-ray crystallography (Pascaly *et al.*, 2001).

Ogden and his coworkers (2001) have synthesized the Fe(III) complexes of 5,11,17,23-tetra-tert-butyl-24-hydroxy-26,27,28-tris(diethylcarbamoylmethoxy)calyx[4]arene tetrakis(diethylcarbamoylmethoxy)calyx[6]arene.

#### 1.8.5 Nickel

Bu and his coworkers (2001) have studied the formation of two unique  $\mu$ -phenoxo-bridged nickel(II) complexes with 1,5-diaza-cyclooctane (DACO) ligands functionalized by additional phenol donor pendants. The complexes have been prepared and characterized by IR, elemental analyses, conductivity, thermal analyses and UV-Vis techniques. The ligands

that have synthesized are 1-(2-hydroxybenzyl)-1,5-diazacyclooctane ( $HL^1$ ) and 1,5-bis(2-hydroxybenzyl)-1,5-diazacyclooctane ( $H_2L^2$ ) and the two complexes that have been synthesized are  $[NiL^1(N_3)]_2 \cdot 0.5H_2O$  and  $[Ni_3(L^2)_2(C_2H_5OH)_2Cl_2]$ . Since DACO has only two nitrogen donors, two or more of this ligands are required to complete the coordination geometry for a metal center such as nickel. In  $[NiL^1(N_3)]_2 \cdot 0.5H_2O$ , nickel(II) are in five coordinated distorted square pyramidal environments while in  $[Ni_3(L^2)_2(C_2H_5OH)_2Cl_2]$ , the two terminal nickel(II) are in nearly ideal square pyramidal coordination environments and the central nickel(II) takes an octahedral configuration by axial coordination. These results indicate that the coordination chemistry of the nickel(II) complexes with DACO ligands can be controlled by altering the pendant donors.

The sodium salt of the dihydrobis(1-methyl-5-thiotetrazolyl)borato anion  $[Btt^{Me}]^-$  has been synthesized by the reaction of  $NaBH_4$  with 1-methyl-5-thiotetrazole (Wang *et al.*, 2005). Treatment of  $Na[Btt^{Me}]$  with anhydrous  $CoCl_2$  and  $NiCl_2 \cdot 6H_2O$ , respectively gives the complexes  $Co(Btt^{Me})_2$  (1) and  $Ni(Btt^{Me})_2$  (2). The compounds have been characterized by IR,  $^1H$ -NMR, UV-Vis spectroscopy as well as X-ray crystallography (Wang *et al.*, 2005).

Compound (1) contains a central  $[CoSO_4]$  core and exhibits slightly distorted trigonal-bipyramidal coordination geometry while compound (2) features a central  $[NiS_4H_2]$  core in distorted octahedral geometry. These results indicate that the ligand can act in the bidentate or tridentate mode (Wang *et al.*, 2005).

#### 1.8.6 Copper

Three new thiodiaceto-Cu(II) chelates have been synthesized and studied by X-ray crystallography, thermal, spectral and magnetic methods (Alacon-Peyer *et al.*, 2005).

The three compounds that have been synthesized were poly-[(thiodiacetato)copper(II)] (1), aqua-bis(imidazole)(thiodiacetato)copper(II) (2) and (5-methyl-1,10-phenanthroline)(thiodiacetato)copper(II) (3) (Alacon-Peyer *et al.*, 2005).

Tudor and his coworkers (2005) have been synthesized A  $\mu$ -alkoxo- $\mu$ -1-acetato trinuclear copper(II) complex  $[\text{Cu}_3(\text{H}_2\text{tea})(\text{Htea})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$  by reacting copper(II) perchlorate, triethanolamine and sodium acetate. The unit cell contains two centrosymmetric, crystallographically independent trinuclear copper(II) complexes and two  $\text{ClO}_4^-$  ions. The crystallographically independent trinuclear copper(II) complexes differ mainly in some of their geometry parameters. The coordination environment of the central copper atom is square-planar, in one trinuclear entity and elongated octahedral in the other one (the coordination number of the central copper atom increases through the semicoordination of an oxygen atom arising from the aminoalcohol).

#### 1.8.7 Cobalt

Cobalt(II) and (III) complexes of pentadentate  $\text{N}_4\text{S}$  ligands based on methyl 2-aminocyclopent-1-ene-1-carbodithioate with appended pyrazolyl groups (3,5- $\text{Me}_2\text{C}_3\text{HN}_2\text{CH}_2$ ) $_2\text{NCH(R)CH}_2\text{NHC}_5\text{H}_6\text{C(=S)SCH}_3$  ( $\text{R}=\text{H}$ , Hmmed;  $\text{CH}_3$ , Hmmpcd) have been prepared and characterized by IR,  $^1\text{H-NMR}$  and electronic spectroscopy. Two of these compounds have also structurally been characterized by X-ray single crystal diffraction analyses (Bhattacharyya *et al.*, 2000).

Cobalt(II) in  $[\text{Co}(\text{mmpcd})]\text{ClO}_4$  shows a five coordinate, trigonal bipyramidal geometry while cobalt(III) in  $[\text{Co}(\text{mmpcd})\text{Cl}]\text{ClO}_4$  reveals a six coordinated distorted octahedral structure (Bhattacharyya *et al.*, 2000).