Investigation of Chemical Compounds Formed from a Solution Mixture Containing a Cobalt Salt, 1,10-phenanthroline and N,O-donor Ligand

(N,O-donor Ligand = Glycine or Sarcosine)

By

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The dedication of this thesis is split five ways :

To the Almighty God Lord Jesus Christ for His unconditional love and grace.

To my parents and caretakers for nursing me with knowledge and love.

To Dr. Neo Kian Eang for his inspiration, enthusiasm and supervision.

To my soulmate, Yeoh Yu Xuan, for motivating me with her love and faith.

To the strongest and toughest person I know, me.

ABSTRACT

Investigation of Chemical Compounds Formed from a Solution Mixture Containing a Cobalt Salt, 1,10-phenanthroline and N,O-donor Ligand

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The aim of this project was to identify the chemical compounds formed from a solution mixture containing cobalt(II) nitrate hexahydrate as the cobalt salt, 1,10-phenanthroline (phen) as the N-heterocyclic ligand, glycine (gly) or sarcosine (sar) as the N,O-donor ligands. The products formed were characterized by FTIR, UV-Visible spectroscopy, elemental analysis, ESI-MS, ^{1}H-NMR and ^{13}C{^{1}H}-NMR. The data obtained suggested the coordination of the ligands to the cobalt atom. The chemical formulae and the chemical structures of the complexes formed were proposed based on the elemental analytical data, spectroscopic and spectrometric data obtained. The complexes formed were determined to be $[Co(gly)_2(phen)](NO_3).H_2O$ and $[Co(phen)(sar)_2](NO_3).2H_2O$. Both the N,O-donor ligand and the 1,10-phenanthroline ligand coordinated to the central cobalt atom in a bidentate modes. The cobalt(III) centre adopts an octahedral geometry. The oxidation of cobalt(II) to cobalt(III) could have caused by the oxygen present in air.

ABSTRAK

Projek ini bertujuan untuk mengenalpasti sebatian kimia yang terbentuk daripada campuran larutan yang mengandungi kobalt(II) nitrat hexahidrat sebagai garam kobalt, 1,10-phenanthrolin (phen) sebagai ligan N-heterosiklik, glysin (gly) atau sarkosin (sar) sebagai ligan penderma-N,O. Produk yang terbentuk telah dicirikan dengan spektroskopi FTIR, spektroskopi UV-nampak, analisis unsur, ESI-MS, ^{1}H-NMR dan $^{13}C\{^{1}H\}$-NMR. Data yang diperolehi mencadangkan pengkoordinatan ligan ke atom kobalt. Formula kimia dan struktur kimia bagi kompleks yang terbentuk telah dicadangkan berdasarkan data analisis unsur, data spektroskopi and spektrum jisim. Kompleks terbentuk telah dikenalpasti sebagai $[Co(gly)_2(phen)](NO_3).H_2O$ dan $[Co(phen)(sar)_2](NO_3).2H_2O$. Pengkoordinatan ligan penderma unsur N, O dan 1,10-phenanthrolin ke unsur pusat kobalt adalah dalam bentuk bidentat. Pusat kobalt (III) mengambil geometri pengkoordinatan oktaheral. Pengoksidaan kobalt(II) kepada kobalt(III) kemungkinan disebabkan oleh kemunculan oksigen dalam udara.

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Moreover, I would also like to thank UTAR's laboratory officers and staff for their kind help in glassware and equipment renting, as well as their guidance on handling various instruments. As a result, I am able to handle the instruments in a proper manner.

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

(LOO SONG WEI)

APPROVAL SHEET

This project entitled **"Investigation of Chemical Compounds Formed from a Solution Mixture Containing a Cobalt Salt, 1,10-phenanthroline and N,O-donor Ligand (N,O-donor Ligand = Glycine or Sarcosine)"** was prepared by LOO SONG WEI and submitted as partial fulfilment of the requirements for the degree of Bachelor of Science (Hons) Chemistry at Universiti Tunku Abdul Rahman.

Approved by :

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(Dr. Neo Kian Eang) Date : ....

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FACULTY OF SCIENCE

UNIVERSITI TUNKU ABDUL RAHMAN

Date : ____________________

PERMISSION SHEET

It is hereby certified that **Loo Song Wei (13ADB03160)** has completed this final year project entitle "Investigation of Chemical Compounds Formed from a Solution Mixture Containing a Cobalt Salt, 1,10-phenanthroline and N,O-donor Ligand (N,O-donor Ligand = Glycine or Sarcosine)" under the supervision of Dr. Neo Kian Eang (Supervisor) from the Department of Chemical Science, Faculty of Science.

I hereby give permission to the University to upload softcopy of my final year project thesis in pdf format into the UTAR Institutional Repository, which may be made able to the UTAR community and public.

Yours truly,

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(LOO SONG WEI)

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LIST OF ABBREVIATIONS

bpy	2,2'-bipyridine
C	Carbon
Cu	Copper
Co	Cobalt
DMF	Dimethylformamide
DMSO-d_6	Dimethyl sulfoxide-d_6
dipico	2,6-dipicolinic acid
dpq	Dipyrido[3,2-d:2',3'-f]quinoxaline
dppz	Dipyrido[3,2-a:2',3'-c]phenazine
en	Ethylenediamine
gly	Glycine
H	Hydrogen
IR	infrared
L-ala	L-alanine
L-arg	L-arginine
L-ile	L-isoleucine
L-leu	L-leucine
L-phe	L-phenylalanine
L-ser	L-serine
L-Thr	L-Threonine
N	Nitrogen
NaOH	Sodium hydroxide

NH_3	Ammonia
NO_3^-	Nitrate ion
O	Oxygen
phen	1,10-phenanthroline
sar	Sarcosine
Zn	Zinc
λ_{max}	Wavelength at which the absorbance is greatest
π	Pi

CHAPTER 1

INTRODUCTION

1.1 Chemistry of cobalt

Cobalt is a chemical element with an atomic symbol Co and atomic number 27. The name of cobalt is derived from the German word kobold, which means goblin (Pappas, 2015). Such name was given by medieval miners who believed that goblins substituted the precious metals in their ores with a substance that released toxic vapours when smelted. Swedish scientist Georg Brandt was attributed for the discovery and isolation of cobalt from the Riddarhyttan mines that his family owned in Sweden circa 1735. He further identified some of cobalt's valuable properties, including its magnetism (Boland and Kropschot, 2011).

Cobalt is a lustrous, silvery-blue metal that is widely used to produce an intense blue colour in paints and glass and it is still used as an important pigment today. Cobalt salts were applied on ancient Chinese pottery to give vivid blue colours (Pappas, 2015). Researchers also reported that cobalt blue glass beads were found in ancient Egyptian pharaoh tombs, including King Tutankhamen's tomb where large amount of glass beads were found in the burial chambers (Varberg, 2014). Apart from that, the properties of cobalt is being studied extensively, typically in the United States as cobalt was vastly used in the manufacture of super-alloys, which have high resistance to corrosion, thus being able to retain their strength at extreme temperatures. Therefore, most of the gas turbine engines and other vital components used in aircraft depend on the high stability of cobalt-based super-alloys towards high temperatures. Besides, cobalt also exhibits stunning magnetic properties that retains at elevated temperatures as high as 1121˚C. It serves as a main component in magnets used in electric motors and computer disc drives, thus allowing the devices to function more efficiently over a wide range of temperatures (Boland and Kropschot, 2011).

Cobalt plays a crucial role in human health. It is an essential trace element that forms the backbone of vitamin B12, which aids in blood formation and helps to ensure proper brain function. Cobalt-60 is a manmade isotope that is commonly used in cancer treatments (Pappas, 2015). According to the American Brain Tumor Association, gamma radiation generated by cobalt-60 is used to destroy tumours, particularly brain tumours as cobalt-60 therapy is so precise, allowing doctors to administer higher doses of radiation to the targeted tumour with minimal damage to neighbouring healthy tissues and organs (ABTA, 2014). Furthermore, cobalt-60 is also used to sterilize medical equipments and to kill bacteria and other harmful pathogens in food in a process known as cold pasteurization (Boland and Kropschot, 2011).

1.2 1,10-phenanthroline (phen) as N-heterocyclic ligand

Among the main applications of transition metal complexes containing organic ligands are their medical testing as antitumour and antibacterial agents, thus seeking towards the discovery of a safer and more effective therapeutic regimen for cancer treatment and bacterial infections treatment (Prashanthi *et al.*, 2012). The selection of suitable central metal ions and organic ligands is critical in the construction of complexes. The use of N-heterocylic ligands has concentrated much interest as a new perspective to drug discovery and development (Mohamed, Mahmoud and El-Dessouky, 2014).

N-heterocylic ligands, typically 1,10-phenanthroline, is commonly used as chelating nitrogen donor ligands as it is one of the most efficient chelators for transition metal ions with which it gives stable complexes in solution. The presence of heteroaromatic groups in 1,10-phenanthroline provides this ligand with additional properties, such as the photophysical properties exhibited by the poly nitrogen donors consisting of heteroaromatic groups. As a result, 1,10-phenanthroline has been studied and used extensively as chemosensors for metal ions in a specific solution. The coordination of 1,10-phenanthroline with metal ions may influence the properties of the photosenstive group, resulting in an optical response (Mohamed, Mahmoud and El-Dessouky, 2014). It was also reported that ternary copper(II) complexes of 1,10-phenanthroline showed a higher antiproliferative activity as compared to cisplatin, thus possessing the potential for development into anticancer drugs (Ng *et al.*, 2013). Besides, it was also reported that zinc complexes of 1,10-phenanthroline exhibit anticancer properties (Chin *et al.*, 2012).

1,10-phenanthroline (phen) is a classic bidentate ligand for transition metal ions that contributes greatly towards the development of coordination chemistry. It has a planar, rigid, hydrophobic, electron-poor heteroaromatic system with two nitrogen atoms that act cooperatively in cation binding. The phen ligand acts as a weak base when dissolved in aqueous solution whose basicity is lower than aliphatic diamines, for instance, ethylenediamine (en). Apart from that, phen exhibits observable coordination ability for transition metal cations, in which it can easily forms octahedral complexes with first-row transition metal cations. Another distinct property of phen ligand includes its π-electron deficiency that makes phen ligand an excellent π-acceptor ligand which can stabilize metal ions in lower oxidation states. In addition, such metal complexes can be easily characterized by strong absorption bands in the ultraviolet spectrum due to the presence of π-antibonding orbitals of the ligand (Bencini and Lippolis, 2010).

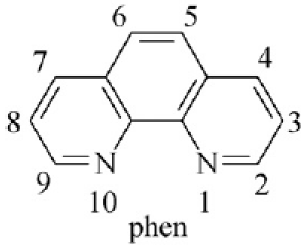


Figure 1.1: Structure of 1,10-phenanthroline (This figure was taken from Bencini and Lippolis, 2010)

1.3 The role of amino acids as N,O-donor ligands

Chelated amino acid complexes have become a research area of increasing interest for a long time due to their substantial potential in the field of catalysis and medicine (Rajalakshmi *et al.*, 2008). It was reported that amino acidato complexes of transition elements in various oxidation states may display certain properties that are very useful in different fields such as the production of sol-gel-derived coatings, asymmetric synthesis, bioorganometallic and solid-state chemistry, and anticancer therapy (Pampaloni *et al.*, 2015).

Amino acids are essential biological compounds containing carboxylic acid and amine functional groups, differing only in the structures of their side chains, known as the R-group. Among the twenty amino acids that are commonly found in proteins, glycine is the smallest amino acid with a hydrogen substituent as its side chain. On the contrary, sarcosine, an N-methyl derivative of glycine, is a metabolite of glycine (Bhattacharyya and Saha, 1978). Both glycine and sarcosine have a neutral donor nitrogen atom at one end, while an acidic replaceable hydrogen atom at the other end. Therefore, these two amino acids have a sufficient length to stretch the two adjacent coordinating sites, resulting in the formation of a chelate compound (Alam *et al.*, 2010). In addition, glycine and sarcosine do not show optical properties due to the absence of a chiral centre (Na'aliya and Aliyu, 2010).

A detailed investigation of complex formation between glycine and various metal ions such as cobalt(II), copper(II), nickel(II), manganese(II), zinc(II), cadmium(II) and lead (II) were carried out by using spectroscopic methods (Al-Jeboori and Al-Shimiesawi, 2013). It was also reported that copper(II) and cobalt(II) complexes of glycine are potent antifungal agent (Indira Devi and Smitha, 2013). Apart from that, the ternary copper(II)-1,10-phenanthroline complexes of N,O-donor ligands, such as glycine and sarcosine also showed cytoselective anticancer properties (Seng *et al.*, 2012).

1.4 Techniques used for complexes characterization

There are numerous types of instruments used to characterize the complexes formed from a solution mixture. The techniques that are commonly used are Fourier transform infrared (FTIR) spectroscopy, UV-Visible spectrophotometry, CHN elemental analysis, mass spectrometry and X-ray crystallography (Chin *et al.*, 2012; Ng *et al.*, 2013; Rao, Patra and Chetana, 2008).

FTIR is a simple and effective analytical technique that is used to identify the functional groups for both organic and inorganic sample. The functional groups present in a sample can be determined by the sample's characteristic absorption of infrared radiation. By analyzing the infrared spectrum, abundant structural information of a molecule can be obtained (ChemWiki, n.d.).

On the other hand, UV-Visible spectrophotometry is used to study the electronic transition involved in the chemical compound formed. In contrast, CHN elemental analyzer is used to analyze the elemental composition of a sample, thus being able to aid in the determination of the chemical formula and purity of the sample. Mass spectrometry plays an important role in characterizing a complex formed by measuring the sample's mass-to-charge ratio, hence correlating the unknown sample with known compound through their characteristic fragmentation pattern. As for X-ray crystallography, it is used to identify the three-dimensional molecular structure of a compound from its crystal (Smyth and Martin, 2000).

1.5 Implications

Recent studies showed that metal complexes of phen and N,O-donor ligands exhibited antimicrobial and antifungal activities. Apart from that, such complexes also showed antiproliferative properties, this could be further developed into anticancer agents. For the past decades, the synthesis and characterization of platinum, copper, nickel and zinc complexes of N-heterocyclic ligand and N,O-donor ligand have been carried out extensively. However, the studies on cobalt complexes of N-heterocyclic ligand and N,O-donor ligand are less exploited. Therefore, this project aimed to investigate the chemical compounds formed from a solution mixture containing N-heterocyclic ligand, N,O-donor ligand and a cobalt salt. This work could serve as a platform for future research work to systematically prepare new complexes for the study of their chemical reactivity and biological properties.

1.6 Objective

This project aimed to investigate the chemical compounds formed from a solution mixture containing a cobalt(II) salt, 1,10-phenanthroline and a N,O-donor ligand, namely glycine and sarcosine. The identities of the compounds formed were characterized using spectroscopic and spectrometric techniques. The possible structures for the complexes formed are $[Co(phen)_2(N,O)](NO_3)_2$, $[Co(phen)(N,O)_2](NO_3)$, $[Co(phen)_3](NO_3)_3$ and $[Co(N,O)_3]$ where N,O is glycine or sarcosine.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the discussion will be focused on reviewing the published work on the synthesis and characterization of various metal complexes of N-heterocyclic ligand and N,O-donor ligand. Apart from that, this chapter provides an overview on the biomedical properties of the metal complexes that were previously prepared.

2.2 Synthesis of metal complexes of 1,10-phenanthroline and N,O-donor ligands

Chin and co-workers (2012) had synthesized and characterized zinc complexes of 1,10-phenanthroline with 2,6-dipicolinic acid and L-threonine as the ligand precursors. Aqueous solutions of zinc salt, NaOH and dipicolinic acid or L-threonine were prepared by dissolving the compounds in a water-methanol mixture. A methanolic solution of phen was then added to the solution mixture. The resulting solution was then heated until the volume was about half the initial volume. The solution was left aside to stand overnight and the product was collected by suction filtration. Cold deionized water was used to wash the product. Pure products were obtained as white crystals. The complexes formed were characterized with several techniques such as CHN analysis, FTIR spectroscopy, UV-Vis spectrophotometry, photoluminescence spectrophotometry, conductivity measurement and electrospray ionization mass spectrometry (ESI-MS).

Rao, Patra and Chetana (2008) had reported the synthesis and characterization of ternary (L-leucine/isoleucine) copper(II) complexes of heterocyclic bases. A copper (II) salt was added to the aqueous solution of L-leucine or L-isoleucine treated with NaOH. The mixture was stirred at room temperature. A heterocyclic base, namely bpy, phen and dpq, was dissolved in methanol and added to the solution. The resulting reaction mixture was stirred at room temperature. The solution was cooled and the filtrate was left to evaporate in room temperature to obtain crystalline product. Cold aqueous methanol was used to wash the solid and the solid was dried over P_4O_{10}. The products formed were characterized using FT-IR spectroscopy, UV-Vis spectrophotometry, elemental analysis and X-ray crystallography.

2.3 Characterization of metal complexes of 1,10-phenanthroline and N,O-donor ligands

Ng *et al.* (2013) had reported the synthesis and characterization of two ternary copper(II)-polypyridyl enantiomers. The biomedical properties of the two compounds were also investigated. The complexes formed were characterized using FTIR spectroscopy, UV-Vis spectrophotometry, ESI-MS, elemental analysis, photoluminescence spectroscopy, conductivity measurements and circular dichroism spectropolarimetry. Both the complexes showed significant peaks at 3400 cm^{-1}, 1600 cm^{-1}, 1380 cm^{-1}, 850 cm^{-1} and 720 cm^{-1} in their infrared spectrum due to $\nu(OH)$, $\nu(COO)_{asym}$, $\nu(COO)_{sym}$ and σ_{oop} $\nu(C\text{-}H)_{aromatic}$, respectively.

The visible spectra of the complexes formed were measured in 5 x 10^{-3} M of 1:1 v/v water-methanol solution of the complexes, while the UV spectra of the complexes formed were obtained in 3 x 10^{-5} M of 1:1 v/v water-methanol solution of the complexes formed. Two absorption bands were observed at the range of 224-225 nm and 272 nm as a result of coordinated phen. The free phen ligand gave two absorption bands at 227 nm (band A) and 264 nm (band B), in which band B corresponded to a π to π^* transition to the lowest energy excited state $^1\pi$ to π^*. Band A of the phen shifted slightly to a shorter wavelength by 2-3 nm, while band B was greatly red-shifted by 9 nm upon coordination of free phen to Cu(II) in the complexes formed. Such red shift in band B revealed that the coordination of the phen ligand caused the energy gap between the π to π^* transition to be lowered, thus resulting in the absorption of light at longer wavelength.

Patra and coworkers (2009) had synthesized and characterized copper(II) complexes of heterocyclic bases and L-arginine. The complexes formed were characterized by obtaining their infrared, electronic and fluorescence spectra. Elemental analysis, molar conductivity measurements and cyclic voltammeric measurements were also performed. Based on their infrared spectra, most of the complexes formed gave peaks at approximate 3350 cm^{-1}, 3180 cm^{-1}, 1650 cm^{-1}, 1450 cm^{-1} and 750 cm^{-1} due to $\nu(OH)$, $\nu(NH_2)$, $\nu(COO)_{asym}$, $\nu(COO)_{sym}$ and σ_{oop} $\nu(C\text{-}H)_{aromatic}$, respectively.. As for their electronic spectra, most of the complexes formed showed bands at 230 nm, 270 nm and 600 nm. The complexes formed displayed a metal-centered d-d transition band in the range of 590-690 nm in 1:1 v/v aqueous DMF. The complexes of dpq and dppz exhibited strong band at around 350 nm, possibly due to the π to π^* transition of the phenazine or quinoxaline moieties of the ligands, in which such band was not observed in the complexes of bpy and phen.

Li and coworkers (2011) had reported on the synthesis, crystal structures and biomedical properties of copper complexes with 1,10-phenanthroline and amino acid. The products formed were characterized using FTIR spectroscopy, elemental analysis and X-ray crystallography. It was found that most of the complexes showed several significant peaks in their IR spectra, particularly at around 3400 cm^{-1}, 3200 cm^{-1}, 3050 cm^{-1}, 1600 cm^{-1}, 1520 cm^{-1}, 1430 cm^{-1}, 1380 cm^{-1} and 720 cm^{-1}. The peak for the asymmetric stretching vibration of the complexes were observed at around 1600 cm^{-1}, while symmetric stretching vibration peak were found to be around 1380 cm^{-1}. The difference between the asymmetric stretching vibration and symmetric stretching vibration peaks of the carboxylate group are greater than 200 cm^{-1}, thus indicating that the carboxylate groups of the complexes are coordinated to the central copper atom in a monodentate mode. Moreover, the bands appeared at 1520 cm^{-1} and 1430 cm^{-1} can be attributed to the ring stretching frequencies of phen.

2.4 Structural features of metal complexes containing 1,10-phenanthroline and N,O-donor ligands

Patra and coworkers (2009) had synthesized and characterized copper(II) complexes of heterocyclic base and L-arginine. [Cu(phen)(L-arg)Cl]Cl formed was structurally characterized by performing a single-crystal X-ray diffraction study. The complex was found to crystallize in a non-centrosymmetric P1 space group of the triclinic crystal system, consisting of four independent molecules in the crystallographic asymmetric unit. Based on its crystal structure, it revealed the mono-cationic nature of the complex made up of chelating

N,O-donor L-arginine, and N,N-donor 1,10-phenanthroline, in a square pyramidal geometry with a weakly bound chloride ligand.

Rao, Patra and Chetana (2008) had synthesized ternary (L-leucine/isoleucine) copper(II) complexes of heterocyclic bases. The structures of bpy and dpq complexes of L-isoleucine were characterized by performing the single-crystal X-ray diffraction analysis. The crystal structures of [Cu(L-leu)(phen)(H_2O)](NO_3) and [Cu(L-ile)(phen)(H_2O)](NO_3) were determined to exist in a distorted square-pyramidal geometry, where the central copper(II) ion coordinated with one of the carboxylate oxygen atom of L-leu/ile and the amino nitrogen atom, together with two nitrogen atoms of 1,10-phenanthroline in the equatorial position, while the oxygen atom of water was located at the elongated axial position.

Li *et al.* (2011) had reported the synthesis of copper complexes with 1,10-phenanthroline and amino acids. The amino acids used were L-serine, glycine, L-alanine and L-phenylalanine. The crystal structure of [Cu(phen)(L-Ser)(H_2O)Cl] was determined by using X-ray crystallography. The complex was found to crystallize in P1 space group, where the unit cell consists of two asymmetric units. It was also found that the copper(II) ion was coordinated in a distorted octahedron structure through the amino nitrogen and carboxylate oxygen of L-Ser and two nitrogen atoms of phen in the basal plane, while the chloro atom and water molecule were located in the apical position.

Chin *et al.* (2012) had synthesized zinc complexes of 1,10-phenanthroline with 2,6-dipicolinic acid and L-threonine. Both [Zn(phen)(dipico)(H_2O)].H_2O and [Zn(phen)(L-thr)(H_2O)Cl].2H_2O had similar octahedral structures. The flat, rigid bidentate phen chelates to the central Zn(II) atom. The tridentate dipicolinato ligand in [Zn(phen)(dipico)(H_2O)].H_2O was determined to be flat and rigid. However such complex was highly distorted due to the constraint caused by ligand rigidity, ligand denticity, ligand planarity and the limited span width of the terminal oxygen ligating atoms of dipico. As a result, phen and the dipicolinato ligand were found to be unable to chelate on the same plane to Zn(II). In contrast, Zn(phen)(L-thr)(H_2O)Cl].2H_2O was found to be less distorted where the ligating atoms of phen and L-thr are about in the same plane. The chelating atoms of L-thr and phen occupied the equatorial position, while the oxygen atom and chloride ion coordinated to the axial position. The aqua and chlorido ligands at the axial position had longer bond lengths, thus indicating that they were both weakly bonded.

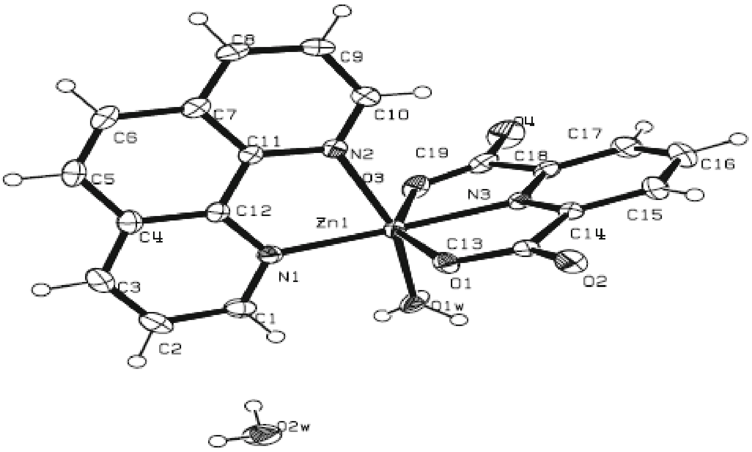


Figure 2.1: Crystal structure of [Zn(phen)(dipico)(H_2O)].H_2O with 40 % thermal ellipsoids. (This figure was taken from Chin *et al.*, 2012)

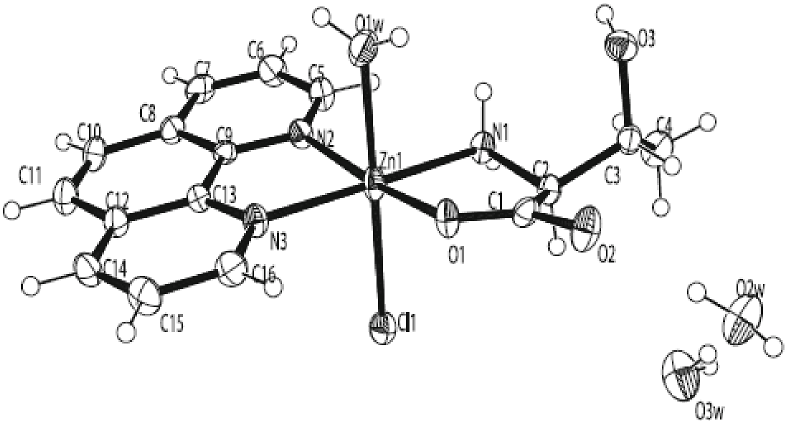


Figure 2.2: Crystal structure of $[Zn(phen)(L\text{-}thr)(H_2O)Cl].2H_2O$ with 40 % thermal ellipsoids. (This figure was taken from Chin *et al.*, 2012)

2.5 Biomedical properties of metal complexes of 1,10-phenanthroline containing N,O-donor ligands

Zn(II) complexes prepared by Chin *et al.* (2012) were found to have better anticancer activity as compared to cisplatin against nasopharyngeal cancer cell lines. They were able to induce cell death by apoptosis. The use of different ligands can affect the spectral properties of the coordinated phen ligand, nucleobase sequence-selective binding and the binding affinity for certain DNA sequences.

Copper(II) complexes of heterocyclic base and L-arginine also exhibited significant oxidative photoinduced DNA cleavage activity under ultraviolet light of 365 nm and red light of 647 nm (Patra *et al*, 2009). Most of the complexes were found to exhibit efficient DNA photocleavage activity. Due to the presence of L-arginine and dpq or dppz as two photosensitizers in the molecules of [Cu(L-arg)(dpq)Cl]Cl and [Cu(L-arg)(dppz)Cl]Cl, both of them showed notable double-strand breaks of DNA, particularly in red light of 647.1 nm. Ternary (L-leucine/isoleucine) copper(II) complexes of phen and dpq synthesized by Rao, Patra and Chetana (2008) were determined to be excellent binders to calf thymus DNA. However, [Cu(bpy)(AA)(H_2O)]X where AA is L-leucine or L-isoleucine and X is ClO_4^- or NO_3^-, failed to show any noticeable binding to the DNA, thus showing poor DNA cleavage activity. As for [Cu(phen)(AA)(H_2O)]X and [Cu(dpq)(AA)(H_2O)]X complexes, they showed efficient oxidative cleavage of supercoiled DNA under the influence of the reducing agent 3-mercaptoproprionic acid (MPA) that involves hydroxyl radical ($^{\bullet}OH$) species.

Ng and coworkers (2013) had reported the study of the biomedical properties of two ternary copper(II)-polypyridyl enantiomers. As compared to cisplatin, the complexes formed were found to be more antiproliferative against several cancer cell lines. In addition, they were more selective towards nasopharyngeal cancer cells over non-tumorigenic cells of similar organ type. Modification of DNA binding selectivity depends on the type of ligand used, chirality and ligand modification.

Li and coworkers (2011) had reported on the synthesis, crystal structure and biomedical properties of copper complexes with 1,10-phenanthroline and amino acid. The following four complexes, which were [Cu(phen)(L-Ser)(H_2O)Cl], [Cu(phen)(Gly)(H_2O)]Cl.3H_2O, [Cu(phen)(L-Ala)(H_2O)]Cl.H_2O and [Cu(phen)(L-Phe)(H_2O)]Cl·2.5H_2O were found to be able to promote the growth of *E. coli* when their concentrations were low. However, the complexes exhibited antibacterial activities at their higher concentration. It was reported that the membrane-phen molecule has the advantages due to its lipophilicity and structure of aromatic macro ring that are able to transport copper through cellular membranes, hence causing the accumulation of copper in cells that can lead to the inhibition of cell growth.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

All chemicals and reagents were purchased from several commercial sources. They were used as received without additional purification. The chemicals and reagents used in this project were Cobalt(II) Nitrate Hexahydrate (Acros Organics), 1,10-phenanthroline Monohydrate (R&M), Glycine (R&M), Sarcosine (Acros Organics), Ammonia (R&M), Methanol (GENE), Ethanol (GENE) and Deionized Water.

3.2 Apparatus

Beaker, Hot plate with Magnetic Stirrer, Magnetic Stir Bar, Measuring Cylinder, Micropipette, Spatula, Digital Analytical Balance, Sample Vial, Perkin-Elmer RXI-IR spectrophotometer, Shimadzu UV-1700 UV-visible spectrophotometer, Elementar vario MICRO cube CHNS elemental analyzer, Thermo Finnigan LCQ benchtop quadrupole ion trap mass spectrometer, JEOL JNM-ECX 400 (400MHz) FT-NMR spectrometer.

3.3 Methodology

3.3.1 Preparation of cobalt complex with 1,10-phenanthroline and glycine

A methanolic solution (10 mL) of $Co(NO_3)_2.6H_2O$ (0.2961 g, 1 mmol) was added to an aqueous solution (10 mL) of glycine (0.2281 g, 3 mmol) with constant stirring. The pH of the solution was basified to pH 10 using a 10 M ammonia solution. The solution was heated on a hot plate at 55˚C. The solution was then added into the methanolic solution (10 mL) of 1,10-phenanthroline monohydrate (0.1997 g, 1 mmol). The resulting solution was then basified to pH 7 with drop wise addition of 10 M ammonia solution. The solution was stirred and heated at 55˚C until the volume was half of its initial volume. Once the solution was cooled to room temperature, the solution was allowed to stand at room temperature. Red crystals (0.3677 g, 79 %) were obtained upon slow solvent evaporation. The crystals obtained were then re-crystallized using 2:1 methanol:water as the solvent system. The percentage yield of the product was calculated based on the proposed structure. The reaction scheme for the preparation of cobalt complex with 1,10-phenanthroline and glycine is illustrated in Figure 3.1.

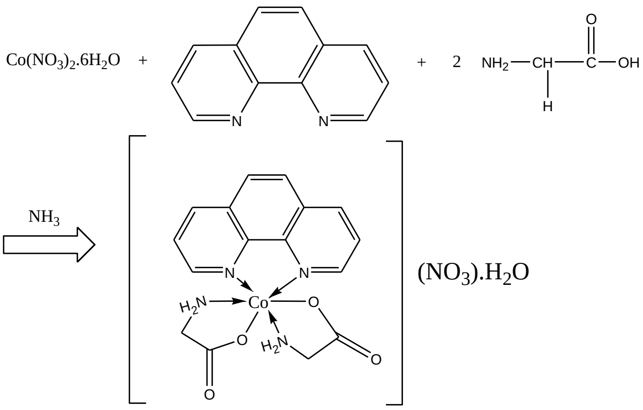


Figure 3.1: Reaction scheme for the preparation of cobalt complex with 1,10-phenanthroline and glycine

3.3.2 Preparation of cobalt complex with 1,10-phenanthroline and sarcosine

$Co(NO_3)_2.6H_2O$ (0.2996 g, 1 mmol) was weighed into a beaker and dissolved with methanol (10 mL). The sarcosine solution was prepared by dissolving sarcosine (0.2704 g, 3 mmol) in deionized water (10 mL). Upon addition of sarcosine solution to the methanolic solution of $Co(NO_3)_2.6H_2O$, the pH of the solution was basified to pH 11 using a 10 M ammonia solution. The solution was then added into the methanolic solution (10 mL) of phen monohydrate (0.1999 g, 1 mmol). The resulting solution was then basified to pH 8 with drop wise addition of a 10 M ammonia solution. The solution was stirred and heated at 55°C until the volume was half of its initial volume. Once the solution was cooled to room temperature, the solvent was allowed to evaporate at room temperature. Red crystals (0.2100 g, 41 %) were obtained upon slow solvent evaporation. The crystals obtained were then re-crystallized using 2:1 methanol:water as the solvent system. The percentage yield of the product was calculated based on the proposed structure. The reaction scheme for the preparation of cobalt complex with 1,10-phenanthroline and sarcosine is shown in Figure 3.2.

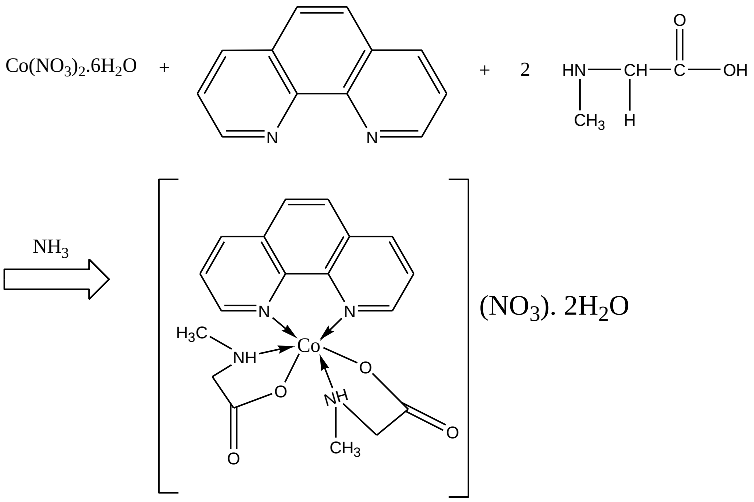


Figure 3.2: Reaction scheme for the preparation of cobalt complex with 1,10-phenanthroline and sarcosine

3.4 Characterization of metal complexes

3.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 3.3: A Perkin Elmer RXI-IR spectrophotometer

The infrared spectra of cobalt complexes formed were obtained by using a Perkin Elmer RXI-IR spectrophotometer (Figure 3.3) in the range of 4000 - 400 cm^{-1}. All the apparatus used were cleaned with absolute ethanol before proceeding with sample preparations. Approximately 1 mg of sample was mixed with 10 mg of dried IR-grade KBr powder in the ratio of 1:10. The mixture was ground clockwise in the mortar until no crystalline material was observed to prevent scattering effect. After that, small amount of sample was placed in the die set and subjected to compression with a manual hydraulic press at approximately 4000 Psi. The pressure of the hydraulic press was released slowly after a few seconds. The die set was then removed from the hydraulic press, followed by disassembling the die set. Then, the thin pellet formed was removed carefully and placed onto the sample holder as to be analyzed by using FT-IR. The infrared spectra obtained were able to provide basic information about the functional groups present in the compounds, thus enabling further determination of the structure of the unknown compounds.

3.4.2 UV-Vis spectroscopy

Figure 3.4: A Shimadzu UV-1700 UV-Visible spectrophotometer

A Shimadzu UV-1700 UV-Visible spectrophotometer (Figure 3.4) was used to obtain the electronic spectra of the cobalt complexes formed. The spectra region was measured in the range of 200 - 900 nm. Before measuring the samples, auto zero was performed as to minimize instrumental error. For both complexes, the solvent used was a methanol-water mixture in the ratio of 2:1. Freshly prepared solvent was used to dissolve the sample. Besides, the molar absorptivities of the complexes formed were also obtained. The calculations involved in the preparation of UV-Vis sample solutions were shown in **Appendix A**. The electronic spectra were able to provide information about the electronic transition that took place within the molecular orbital of the metal, or the ligands that were present in the metal complexes.

3.4.3 CHN elemental analysis

Figure 3.5: A Elementar vario MICRO cube CHNS elemental analyzer (This figure was taken from Elementar, 2016)

An Elementar vario MICRO cube CHNS elemental analyzer (Figure 3.5) was used to perform the analysis on the composition of carbon, hydrogen and nitrogen present in the sample. Both the cobalt complexes formed were subjected to CHN elemental analysis at the National University of Singapore (NUS). Only about 2 mg of sample was needed for such analysis. The samples were subjected to rapid combustion at an elevated temperature, which was around 1800˚C. The combusted products were then eluted in a packed chromatographic column and were sent to the thermal conductivity detector. The percentages of carbon, hydrogen and nitrogen present in the samples were determined.

3.4.4 Mass spectrometry

Figure 3.6: A Thermo Finnigan LCQ benchtop quadrupole ion trap mass spectrometer (This figure was taken from NUS, 2015)

Thermo Finnigan LCQ benchtop quadrupole ion trap mass spectrometer (Figure 3.6) was used to obtain the electrospray ionization mass spectra of the complexes formed. Both the cobalt complexes formed were analyzed at the National University of Singapore (NUS). An approximate of 30 mg sample was dissolved in solvent. The solvent used for mass spectrometry analysis was a water-methanol mixture in the ratio of 1:1. The dissolved samples were then filtered prior to sample introduction into the instrument as to remove any undissolved samples that might block the sample introduction line. The data obtained from mass spectrometry analysis were able to provide crucial information about the relative molecular mass of the cobalt complexes formed through the formation of distinct fragmentation patterns and molecular ion peak.

3.4.5 Nuclear Magnetic Resonance (NMR) spectroscopy

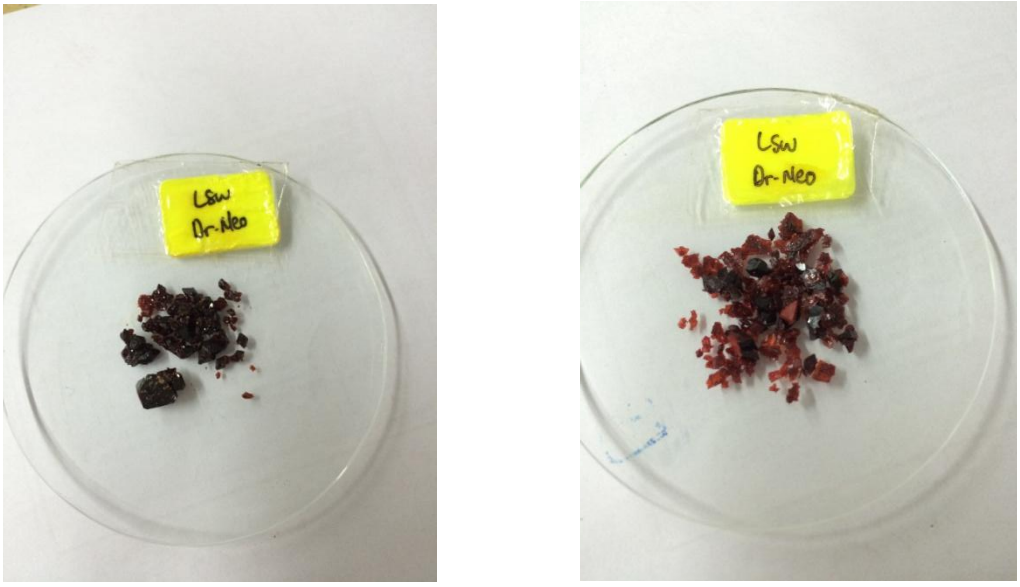
Figure 3.7: A JEOL JNM-ECX 400 (400MHz) FT-NMR spectrometer (This figure was taken from Jeol Resonance, 2016)

A JEOL JNM-ECX 400 (400MHz) FT-NMR spectrometer (Figure 3.7) was used to obtain the ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra of the cobalt complexes formed. In order to obtain the ^{1}H-NMR spectra for the complexes formed, approximately 10 mg of samples were dissolved in DMSO-d_6. As for the sample preparation for ^{13}C{^{1}H}-NMR analyses, about 30 mg of samples were dissolved in DMSO-d_6. The dissolved samples were then filtered into a NMR tube through a Pasteur pipette equipped with glass wool plug. The purpose of performing filtration was to remove any suspended particles or undissolved samples that might affect the resolution of the NMR spectra obtained. The NMR tube was then topped up with DMSO-d_6 to a depth of approximately 4 cm. The NMR spectra obtained were able to provide detailed information about the chemical environment and structure of the complexes formed. The chemical shifts were referred to tetramethylsilane (TMS) for both ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Physical appearance of cobalt complexes



(a) (b)

Figure 4.1 (a): $[Co(gly)_2(phen)](NO_3).H_2O$, Complex **1**

(b): $[Co(phen)(sar)_2](NO_3).2H_2O$, Complex **2**

Figure 4.1 (a) showed the physical appearance of cobalt complex of 1,10-phenanthroline and glycine, while Figure 4.1 (b) showed the physical appearance of cobalt complex of 1,10-phenanthroline and sarcosine. Both the complexes formed were in dark red colour and were obtained in crystalline form. Besides, both the complexes formed were found to be soluble in water, methanol, ethanol and methanol:water in the ratio of 2:1, but insoluble in acetone, ethyl acetate and tetrahydrofuran.

4.2 Characterization of the cobalt complexes

The complexes formed were characterized using various analytical techniques, namely infrared spectroscopy, UV-Vis spectrophotometry, elemental analysis, mass spectrometry, ^{1}H-NMR spectroscopy and ^{13}C{^{1}H}-NMR spectroscopy. The results were presented and discussed in the following sections.

4.2.1 FT-IR spectroscopy

The IR spectra of cobalt complexes **1** and **2** were obtained and compared with the reported data of Alam *et al.* (2010) and Agwara *et al.* (2010). The bonding of the ligands with the central cobalt atom were revealed mainly by two significant IR peaks like ν(COO^-) and ν(NH_2). For both complexes **1** and **2**, the ν(NH_2) and ν(COO^-) peaks that corresponded to the N,O-donor ligands, namely glycinato (gly) and sarcosinato (sar) were observed. The presence of ν(O-H) in both complexes were found to be a strong and broad peak in the range of 3211-3397 cm^{-1}, which were due to the presence of water of hydration in the complexes formed. The ν(NH_2) peak found in the infrared spectra of complex **1** might be overlapped by the strong ν(O-H) peak of the water of hydration. The asymmetric vibration of ν(COO^-) was found in the range of 1643-1659 cm^{-1}, while the symmetric vibration of ν(COO^-) was found within the range of 1351-1376 cm^{-1}. The differences between the asymmetric and symmetric vibrations of ν(COO^-) were determined to be more than 200 cm^{-1}. According to Garcia-Raso and coworkers (2003), such differences indicated that the carboxyl group of glycine and sarcosine had bonded to the central cobalt ion in a monodentate mode.

Based on the reported data by Boghaei and Gharagozlou (2007), free phen exhibited strong characteristic bands at 732 cm^{-1} and 850 cm^{-1} which was attributed to the distinct aromatic out-of-plane ring stretching of phen. Upon coordination to the central cobalt atom, the original characteristic σ_{oop} $\nu(C\text{-}H)_{aromatic}$ peaks were shifted to lower frequencies, which were observed at 716-720 cm^{-1} and 847-853 cm^{-1}, respectively. Such shifts to lower frequencies had indicated that phen had coordinated to the central cobalt atom, resulting in the formation of cobalt complexes of 1,10-phenanthroline and amino acids, namely glycine and sarcosine (Boghaei and Gharagozlou, 2007). The assignments of the peaks in the IR spectra of complexes **1** and **2** were tabulated and presented in Table 4.1. The data obtained were consistent with the data reported by Alam *et al.* (2010) and Agwara *et al.* (2010). The infrared spectra for both complexes **1** and **2** are shown in Figures 4.2 and 4.3, respectively.

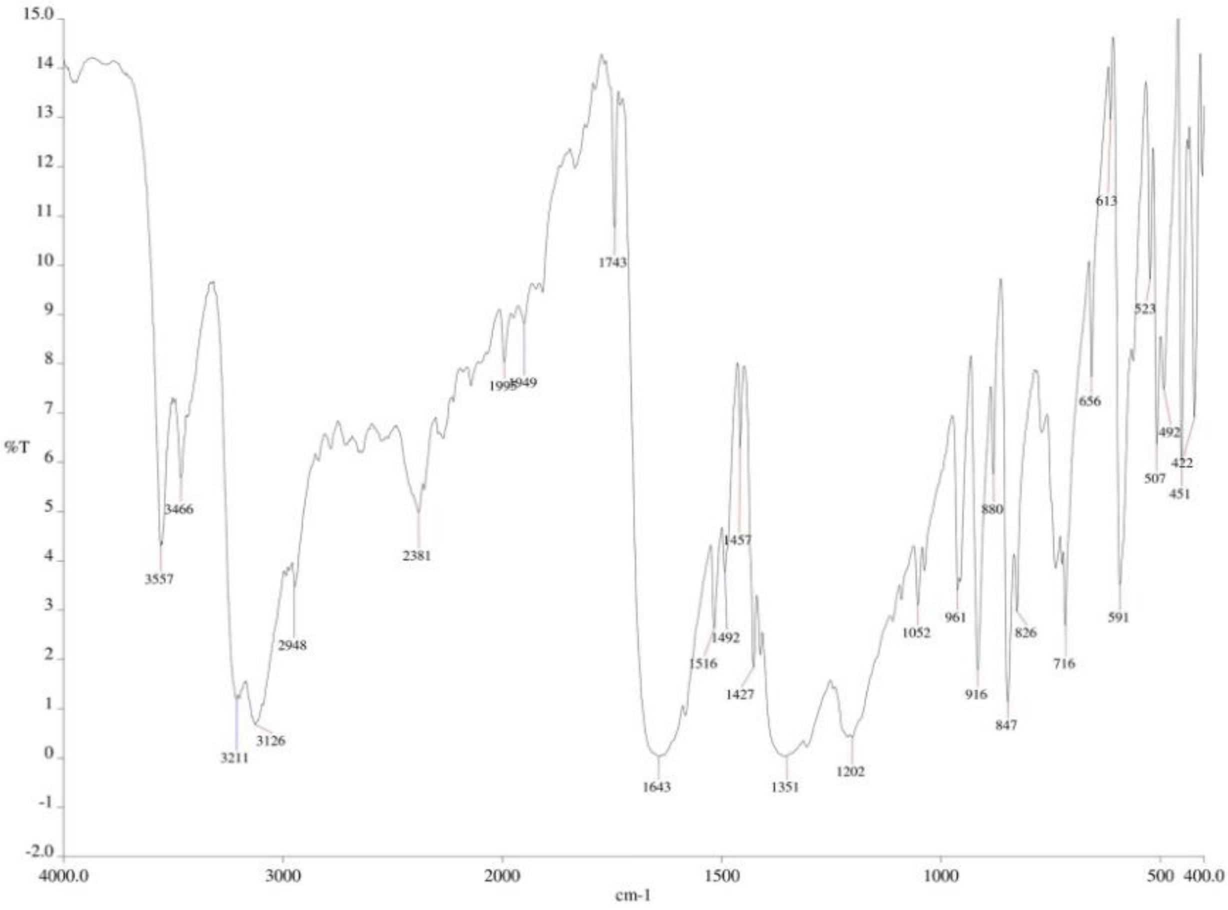


Figure 4.2: FT-IR spectrum of $[Co(gly)_2(phen)](NO_3).H_2O$, **1**

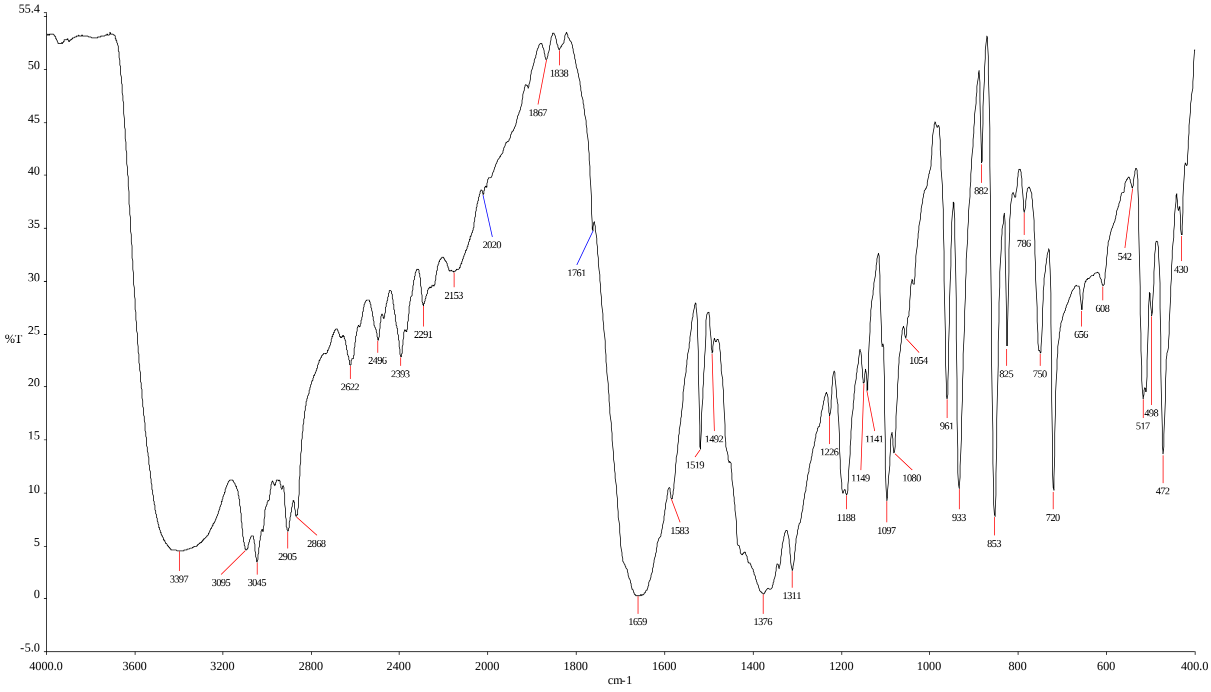


Figure 4.3: FT-IR spectrum of $[Co(phen)(sar)_2](NO_3).2H_2O$, **2**

Table 4.1: Assignment of peaks for the IR spectra of complexes **1** and **2** in cm^{-1}

Complex	ν(OH)	$\nu(NH_2)$	$\nu(COO^-)_{asym}$	$\nu(COO^-)_{sym}$	Δν	ν(C=C)	σ_{oop} $\nu(C\text{-}H)_{aromatic}$	ν(Co-N)
fac-$[Co(gly)_3]$ [1]	-	3229 (s)	1684 (m)	1394 (m)	298	-	-	609 (m)
$[Co(bpy)(phen)_2](NO_3)_2.2H_2O$ [2]	Not reported	-	-	-	-	1446 (m)	726 (s)	446 (m)
$[Co(gly)_2(phen)](NO_3).H_2O$, **1**	3211 (b,s)	3126 (s)	1643 (s)	1351 (s)	292	1516 (m)	847 (s), 716 (s)	451 (m)
$[Co(phen)(sar)_2](NO_3).2H_2O$, **2**	3397 (b,s)	3095 (s)	1659 (s)	1376 (s)	283	1519 (m)	853 (s), 720 (s)	472 (m)

Note : w = weak, m = medium, s = strong, n = narrow, b = broad, asym = asymmetric, sym = symmetric, $\Delta\nu = \nu(COO^-)_{asym} - \nu(COO^-)_{sym}$, σ = bend

1. Alam, M. M., Rahman, S. M. M., Rahman, M. M. and Islam, S. M. S., 2010. Simultaneous preparation of facial and meridional isomer of cobalt-amino acid complexes and their characterization. *Journal of Scientific Research*, 2(1), pp. 91-98.

2. Agwara, M. O., Ndifon, P. T., Ndosiri, N. B., Paboudan, A. G., Yufanyi, D. M. and Mohamadou, A., 2010. Synthesis, characterisation and antimicrobial activities of cobalt(II), copper(II) and zinc(II) mixed-ligand complexes containing 1,10-phenanthroline and 2,2'-bipyridine. *Bulletin of the Chemical Society of Ethiopia*, 24(3), pp. 383-389.

4.2.2 UV-Vis spectroscopic analysis

The peaks appeared in the UV-Vis spectra of complexes **1** and **2** were assigned based on the reported data of Alam *et al.* (2010) and Chin *et al.* (2012). The results are shown in Table 4.2 and Table 4.3. At the visible region (Table 4.2), complex **1** showed the absorption band at 484 nm while complex **2** showed the absorption band at 493 nm. According to Alam and coworkers (2010), such visible band at λ_{max} ~ 520 nm was attributed to the d-d electronic transition of the cobalt ion. The UV-Vis spectra in the visible region of complexes **1** and **2** are shown as Figures 4.4 and 4.5, respectively.

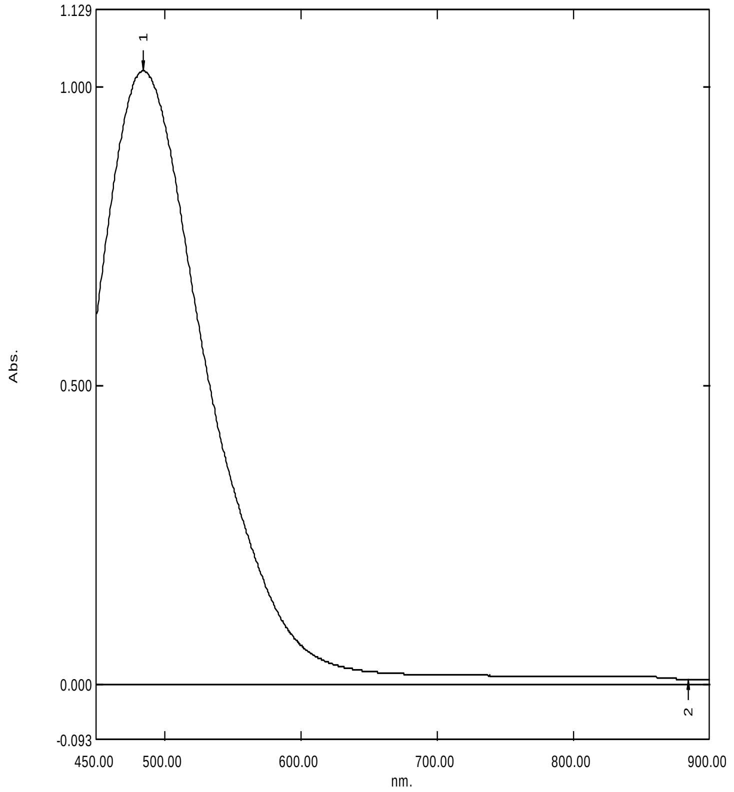


Figure 4.4: UV-Vis spectrum (visible region) for complex **1**

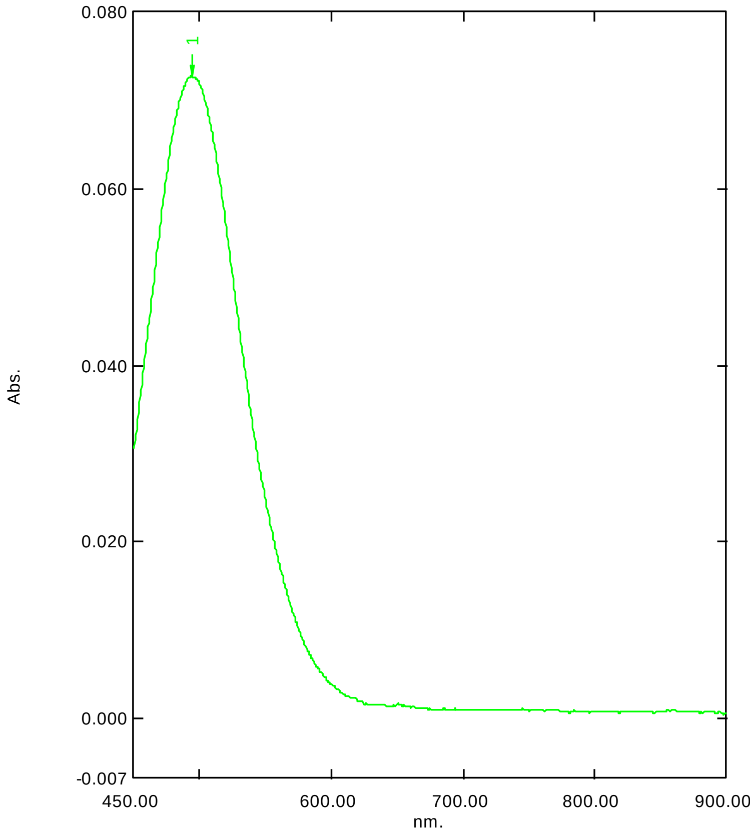


Figure 4.5: UV-Vis spectrum (visible region) for complex **2**

Table 4.2: UV-Vis data (visible region) for complexes **1** and **2**

Complex	**Peak (λ_{max}) nm**	**Assignment of transition band**
$[Co(gly)_3]$ [1]	520	d-d transition
$[Co(gly)_2(phen)](NO_3).H_2O$, **1**	484	d-d transition
$[Co(phen)(sar)_2](NO_3).2H_2O$, **2**	493	d-d transition

1. Alam, M. M., Rahman, S. M. M., Rahman, M. M. and Islam, S. M. S., 2010. Simultaneous preparation of facial and meridional isomer of cobalt-amino acid complexes and their charactreization. *Journal of Scientific Research*, 2(1), pp. 91-98.

At the UV region, the UV-Vis data were assigned as per reference to the data obtained by Chin *et al.* (2012) in Table 4.3. The UV spectrum of free phen showed two absorption bands at 229 nm and 264 nm, which were termed as band A and band B, respectively. Such spectrum recorded was consistent with the data reported by Chin *et al.* (2012). These bands were assigned to the π-π^* transition to the lowest energy singlet excited state $^1\pi$-π^* of the phen ligand. Upon coordination to the cobalt center, band A of phen was shifted (4-6 nm) to a shorter absorption wavelength (λ_{max}), while band B of phen experienced a bathochromic shift by 11 nm (λ_{max}). According to Chin and coworkers (2012), such changes were caused by the coordination of phen ligand to the central metal atom which resulted in the reducing of ΔE of the π-π^* transition, thus causing light to absorb at longer λ_{max}. Therefore, it was confirmed that the phen ligand in both complexes **1** and **2** were coordinated to their respective central metal atom. The data obtained were consistent with the data reported by Chin *et al.* (2012). It was observed that there were several peaks in the range of 300-370 nm in the UV-Vis spectra of complexes **1** and **2**. However, these peaks were proven to belong to phen as it was also shown in the UV-Vis spectrum of phen, which were not significant enough to be taken into account. The UV-Vis spectra in the visible region for 1,10-phenanthroline, complexes **1** and **2** were shown as Figures 4.6, 4.7 and 4.8, respectively.

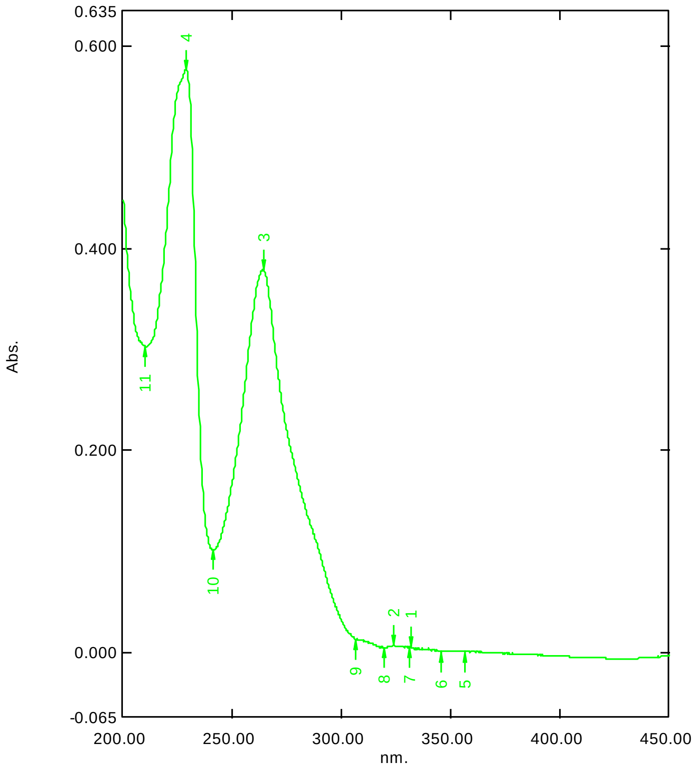


Figure 4.6: UV-Vis spectrum (UV region) for 1,10-phenanthroline

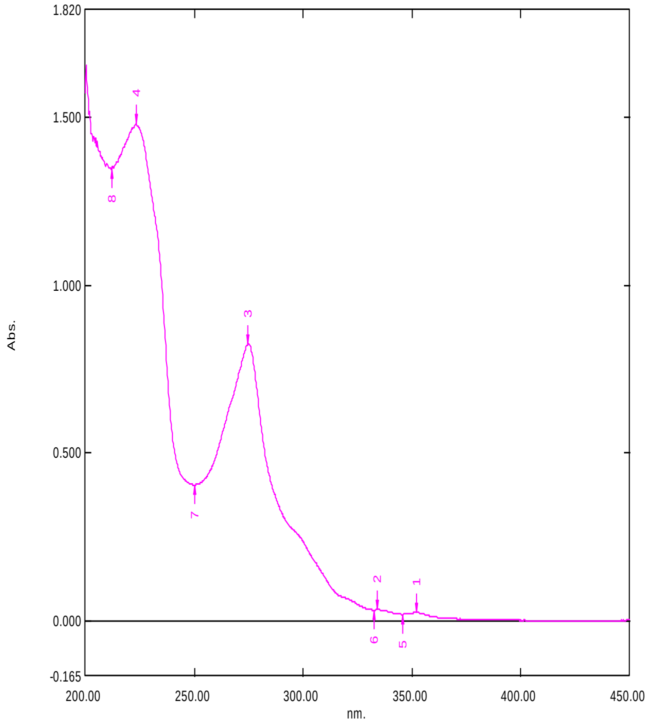


Figure 4.7: UV-Vis spectrum (UV region) for complex **1**

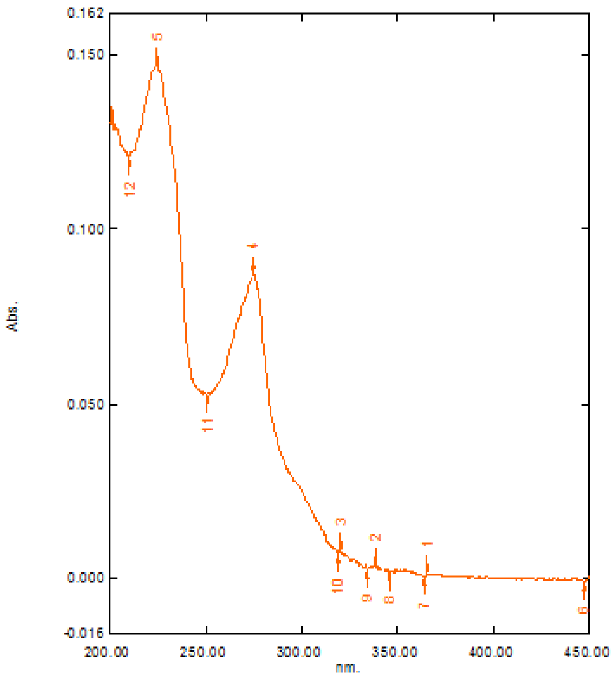


Figure 4.8: UV-Vis spectrum (UV region) for complex **2**

Table 4.3: UV-Vis data (UV region) for complex **1** and **2**

Complex	**Band A (λ_{max}) nm**	**Band B (λ_{max}) nm**	**Assignment of transition band**
1,10-phenanthroline [1]	229	264	π-π^* transition
1,10-phenanthroline (current study)	229	264	π-π^* transition
[Co(gly)$_2$(phen)](NO$_3$).H$_2$O, **1**	223	275	π-π^* transition
[Co(phen)(sar)$_2$](NO$_3$).2H$_2$O, **2**	225	275	π-π^* transition

1. Chin, L.-F., Kong, S.-M., Seng, H.-L., Tiong, Y.-L., Neo, K.-E., Maah, M. J., Khoo, A. S.-B., Ahmad, M., Hor, T.-S- A., Lee, H.-B., San, S.-L., Chye, S.-M. and Ng, C.-H., 2012. [Zn(phen)(O,N,O)(H$_2$O)] and [Zn(phen)(O,N)(H$_2$O)] with O,N,O is 2,6-dipicolinate and N,O is L-threoninate: synthesis, characterization, and biomedical properties. *Journal of Biological Inorganic Chemistry*, 17(7), pp. 1093-1105.

The molar absorptivities of both complexes formed were obtained. Both complexes **1** and **2** showed two absorption peaks in the ultraviolet region of their respective UV-Visible spectra. Based on the UV-Visible spectra of complexes **1** and **2**, it was observed that both complexes absorbed light much more strongly in 223-225 nm (band A) than they did in 275 nm (band B). As a result, the molar absorptivities of complexes **1** and **2** at 223-225 nm were determined to have larger values as compared to their molar absorptivities at 275 nm. The absorbance values obtained from the measurements for complexes **1** and **2** were tabulated in Tables 4.4 and 4.5, respectively. The calibration graphs for complex **1** at 223 nm and 275 nm were plotted and illustrated in Figures 4.9 and 4.10, respectively, while the calibration graphs for complex **2** at 225 nm and 275 nm were plotted and shown in Figures 4.11 and 4.12, respectively. The molar absorptivities of complexes **1** and **2** at given wavelengths were determined using Beer-Lambert law and shown in Tables 4.6 and 4.7, respectively.

Table 4.4: Absorbance values for complex **1**

Concentration (x 10^{-5} M)	Absorbance at 223 nm	Absorbance at 275 nm
1	0.115	0.054
2	0.434	0.214
3	0.796	0.441
4	1.217	0.676
5	1.482	0.824

Table 4.5: Absorbance values for complex **2**

Concentration (x 10^{-5} M)	Absorbance at 225 nm	Absorbance at 275 nm
1	0.609	0.365
2	1.332	0.792
3	1.785	1.057
4	2.474	1.464
5	3.014	1.734

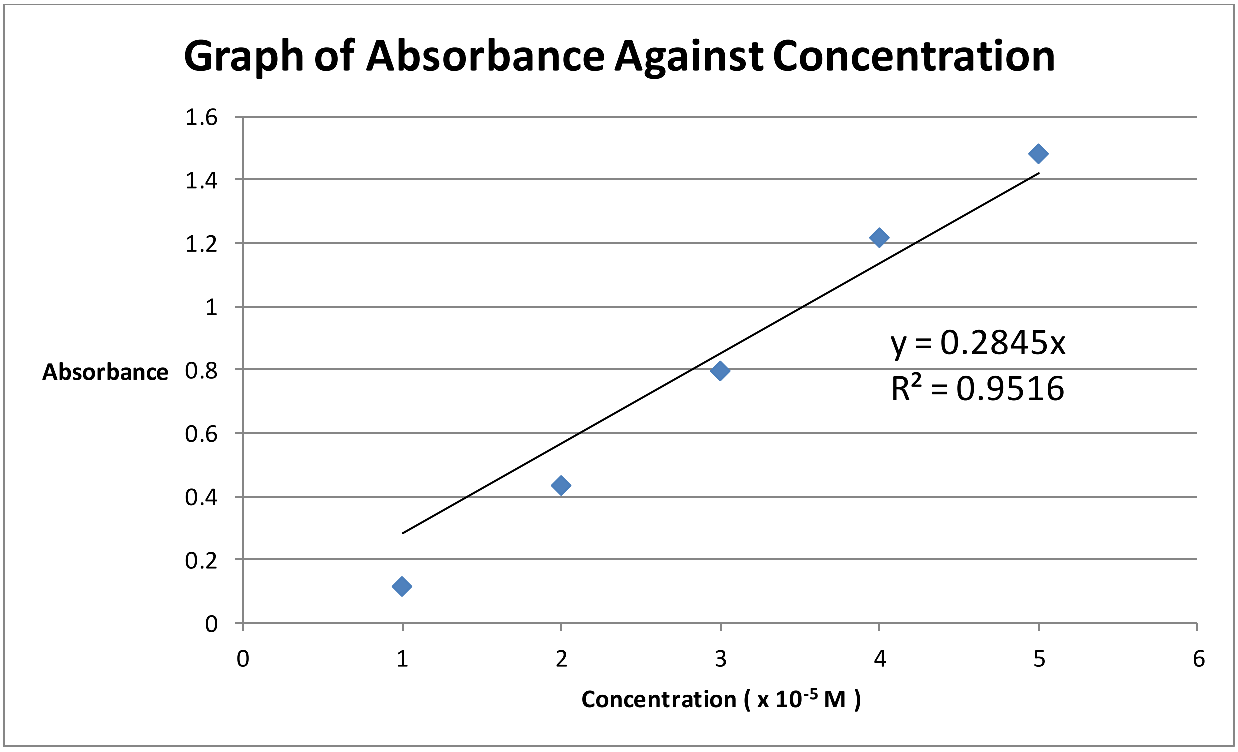


Figure 4.9: Calibration graph for complex **1** at 223 nm

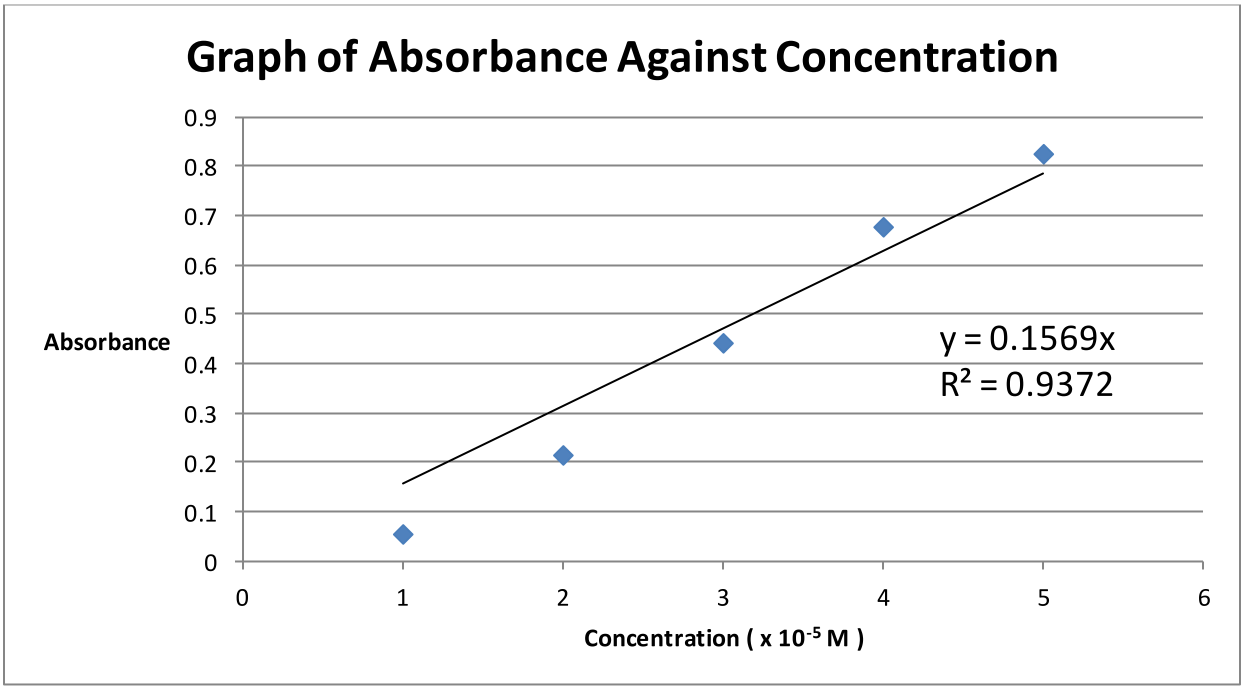


Figure 4.10: Calibration graph for complex **1** at 275 nm

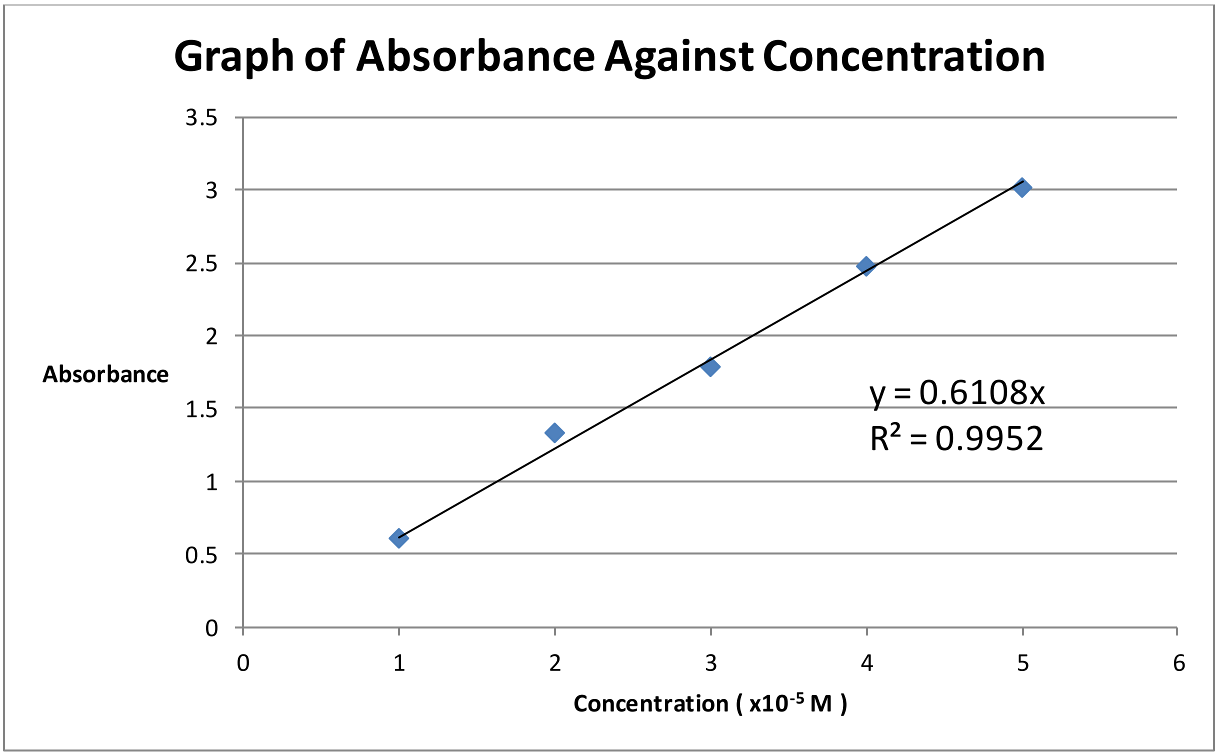


Figure 4.11: Calibration graph for complex **2** at 225 nm

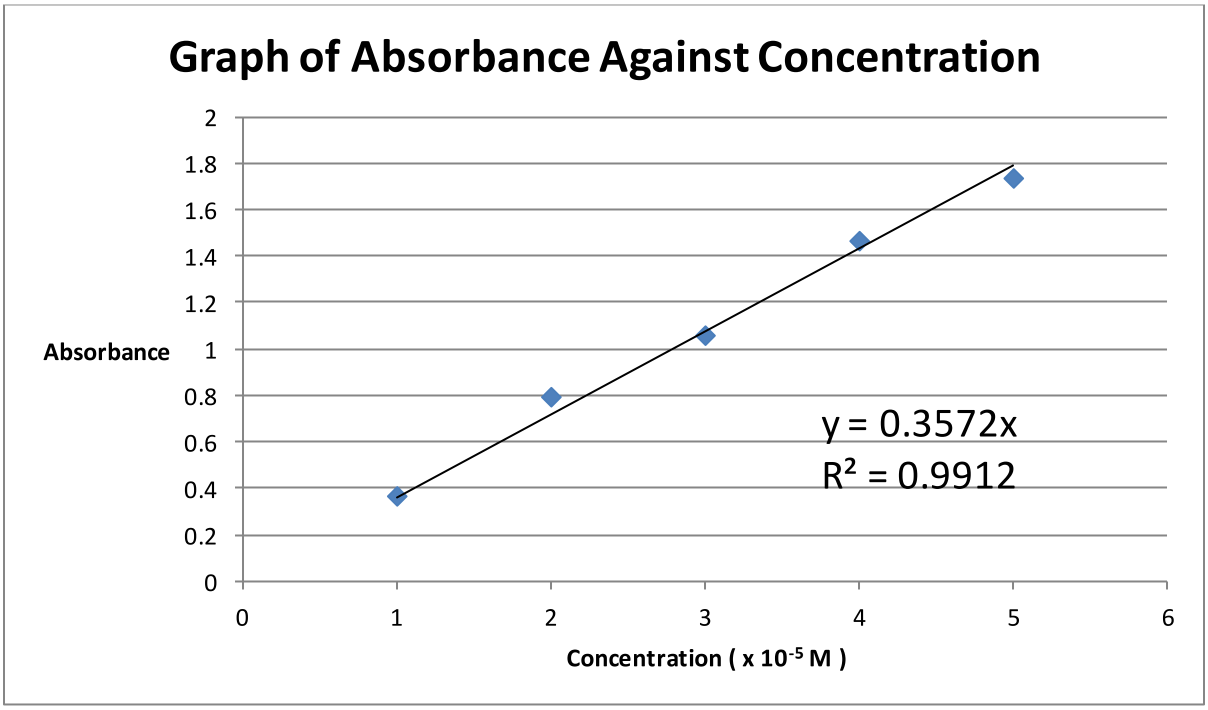


Figure 4.12: Calibration graph for complex **2** at 275 nm

Table 4.6: Molar absorptivities of complex **1**

Complex	Molar absorptivity at 223 nm (M^{-1} cm^{-1})	Molar absorptivity at 275 nm (M^{-1} cm^{-1})
[Co(gly)$_2$(phen)](NO$_3$).H$_2$O, **1**	28450	15690

Table 4.7 : Molar absorptivities of complex **2**

Complex	Molar absorptivity at 225 nm (M^{-1} cm^{-1})	Molar absorptivity at 275 nm (M^{-1} cm^{-1})
[Co(phen)(sar)$_2$](NO$_3$).2H$_2$O, **2**	61080	35720

4.2.3 CHN elemental analysis

Elemental analyses were performed on both complexes **1** and **2** to determine the percentage of carbon, hydrogen and nitrogen in the complexes formed. The carbon, hydrogen and nitrogen content in both complexes had deviations within ±3 %. Complexes **1** and **2** formed can be thus considered pure since the acceptable deviation for a compound to be termed pure was within ±3 %.

The chemical formula for complexes **1** and **2** were proposed according to their percentage of carbon, hydrogen and nitrogen. The analysis and the proposed chemical formula for the complexes **1** and **2** were shown in Table 4.8. Calculations for the percentage yields were based on the proposed chemical formulae. The percentage yields of the complexes formed were also shown in Table 4.8.

Table 4.8 : Proposed chemical formulae for complexes **1** and **2**

Complex	**CHN Analysis Found (Calculated)**			**Chemical Formula**	**Molecular Weight (g/mol)**	**% yield**
	C	H	N			
[Co(gly)$_2$(phen)](NO$_3$).H$_2$O, **1**	41.47 (41.13)	3.31 (3.88)	15.19 (14.99)	$[Co(C_2H_4NO_2)_2(C_{12}H_8N_2)](NO_3).H_2O$	467.27	79
[Co(phen)(sar)$_2$](NO$_3$).2H$_2$O, **2**	42.32 (42.12)	4.10 (4.71)	13.75 (13.64)	$[Co(C_{12}H_8N_2)(C_3H_6NO_2)_2](NO_3).2H_2O$	513.33	41

4.2.4 Mass spectrometry

Complexes **1** and **2** were further studied by ESI-MS in a positive ion mode. The ESI mass spectra of water-methanol solutions of complexes **1** and **2** had showed molecular ion peaks at *m/z* 386.9 and *m/z* 414.9, which were assigned to $[Co(gly)_2(phen)]^+$ (Calculated m/z value for $CoC_{16}H_{16}N_4O_4$ = 387.3) and $[Co(phen)(sar)_2]^+$ (Calculated m/z value for $CoC_{18}H_{20}N_4O_4$ = 415.3), respectively. Based on the isotopic patterns of the molecular ion peaks, it was further proven that the species formed from both complexes possessed a +1 charge, which were consistent with the assigned molecular ion peaks to $[Co(gly)_2(phen)]^+$ and and $[Co(phen)(sar)_2]^+$. The mass spectra for complexes **1** and **2** were shown in Figure 4.13 and Figure 4.14, respectively.

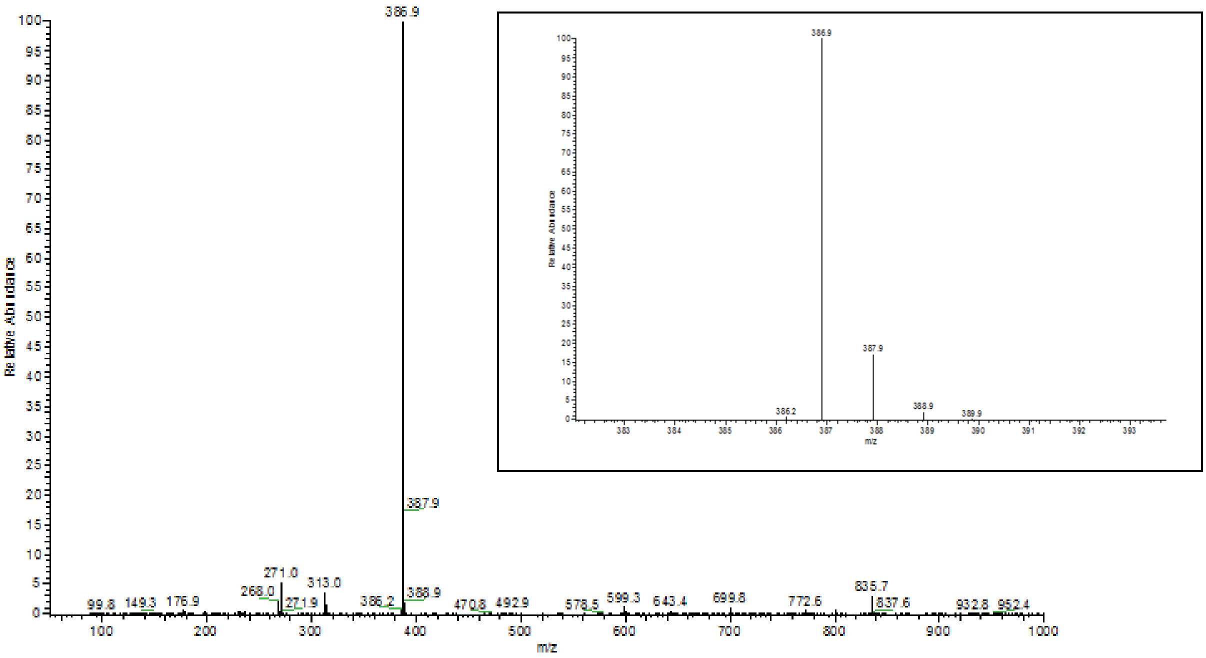


Figure 4.13: ESI mass spectrum for complex **1** (The insert showed the isotopic pattern of the molecular ion peak)

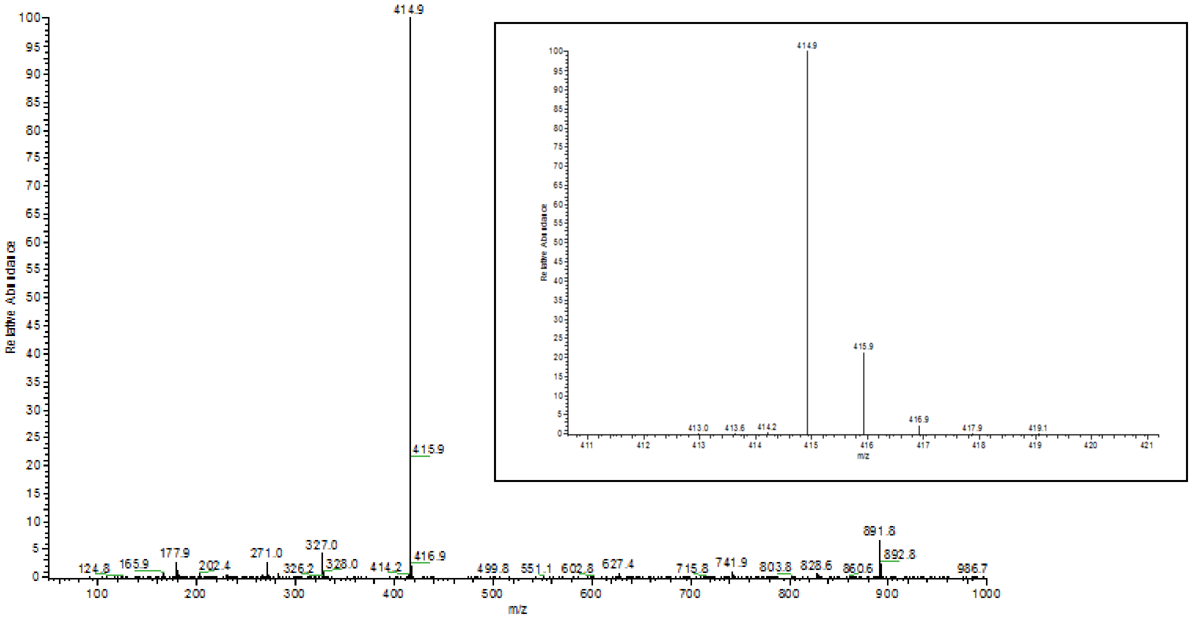


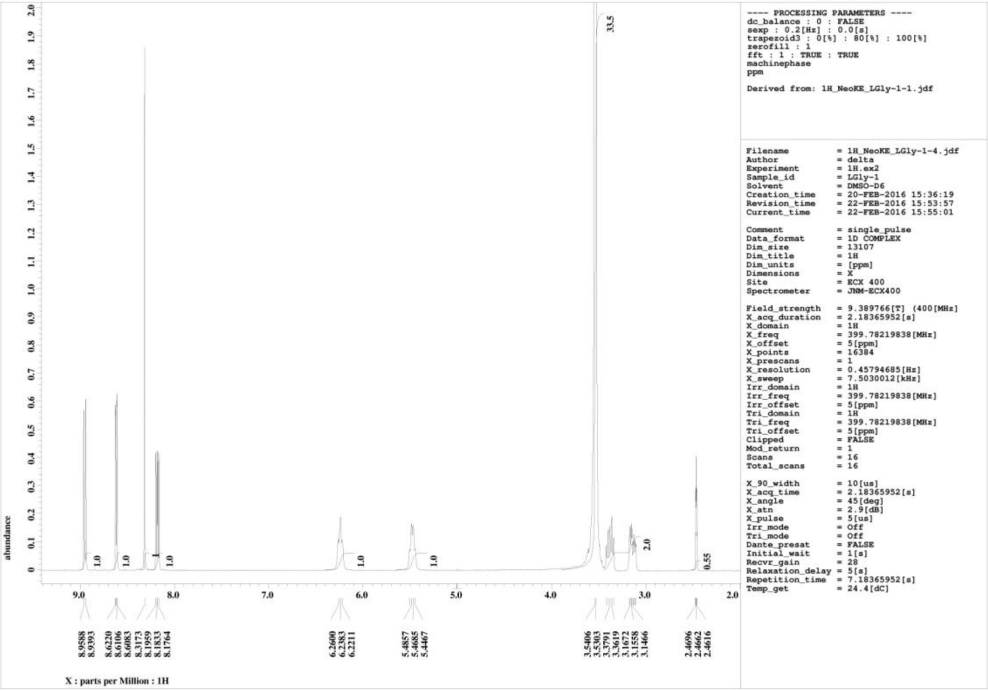
Figure 4.14: ESI mass spectrum for complex **2** (The insert showed the isotopic pattern of the molecular ion peak)

4.2.5 Nuclear Magnetic Resonance (NMR) spectroscopy

Based on the ^{1}H-NMR spectra of both complexes **1** and **2** recorded in DMSO-d_6, the phen moiety protons had shifted downfield upon coordination to the cobalt atom and the peaks appeared within the range of 8.10-9.08 ppm. Such phenomenon could be explained due to the magnetic anisotropy generated by the aromatic fused ring systems of phen which caused the phen moiety protons to be deshielded. The peaks in the range of 3.3-3.5 ppm were assigned to the amine hydrogens of glycinato and sarcosinato ligands. The broadened appearance of the peaks in this region was masked by the intense solvent peak and the hydrogen bonding effects caused by the solvent used, which was DMSO-d_6. For complex **2**, the peak corresponded to the N-methyl hydrogen of sarcosinato ligand was overlapped by the peaks assigned to the amine hydrogens of glycinato and sarcosinato ligands. The peaks in the region of 2.4-2.5 ppm were assigned to the alpha-hydrogens of the glycinato and sarcosinato ligands. However, the peaks corresponded to the carboxylate hydrogen of both glycinato and sarcosinato ligands did not appear since both N,O-donor ligands were deprotonated upon coordination to the cobalt atom.

While in the ^{13}C{^{1}H}-NMR spectra of complexes **1** and **2**, the aromatic carbons of phen had also shifted downfield upon coordination of phen to the cobalt atom and they appeared as six sharp peaks in the range of 126-154 ppm. This could be explained as 1,10-phenanthroline is a symmetrical compound, therefore it has six chemically equivalent carbons and it should show six peaks in the ^{13}C{^{1}H}-NMR spectrum of the complexes formed, which were in agreement with the ^{13}C{^{1}H}-NMR spectrum obtained for both complexes **1** and **2**. The carboxylate carbon of glycinato and sarcosinato ligands appeared in the downfield region of 179-183 ppm due to the deshielding effect caused by the more electronegative carboxylate oxygen atoms. The peaks appeared in the upfield region of 46-57 ppm were assigned to the α-carbon of the glycinato and sarcosinato ligands as both the α-carbons were shielded by the hydrogen atoms surrounding the aliphatic α-carbons. For complex **2**, the peak corresponded to the N-methyl carbon of sarcosinato ligand was shown at the upfield region of 39.5-39.8 ppm. According to Boghaei and Gharagozlou (2007), the observed downfield shift of the phen moiety protons and carbons in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra of complexes **1** and **2** were due to the coordination of phen to the cobalt atom via its aromatic fused ring nitrogen atoms.

Complexes **1** and **2** formed were found to be Co(III) complexes, presumably adopted the d^6 low-spin octahedral configuration. As a result, the six d-electrons of Co(III) occupied the three lower energy t_{2g} level and had no unpaired electrons, thus both complexes **1** and **2** were determined to be diamagnetic. According to Murthy and coworkers (1997), such explanation could be further supported by the appearance of sharp peaks in the NMR spectra of both complexes formed. In the case for paramagnetic compounds, they had unpaired electrons which in turn, had their own magnetic field. Such paramagnetism could induced the hyperfine shifts of NMR peaks and the shortening of nuclear relaxation time. When the nuclear relaxation time for paramagnetic compounds was too fast, the NMR peaks appeared to be broad and resolution might become poor. The ^{1}H-NMR spectra of complexes **1** and **2** are shown in Figure 4.15 and 4.16, respectively, while the ^{13}C{^{1}H}-NMR spectra of complexes **1** and **2** are shown in Figures 4.17 and 4.18, respectively.



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fft : 1 : TRUE : TRUE
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Dimensions          = X
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X_sweep             = 7.5030012[kHz]
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Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
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X_atn               = 2.9[dB]
X_pulse             = 5[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 28
Relaxation_delay    = 5[s]
Repetition_time     = 7.18365952[s]
Temp_get            = 24.4[dC]
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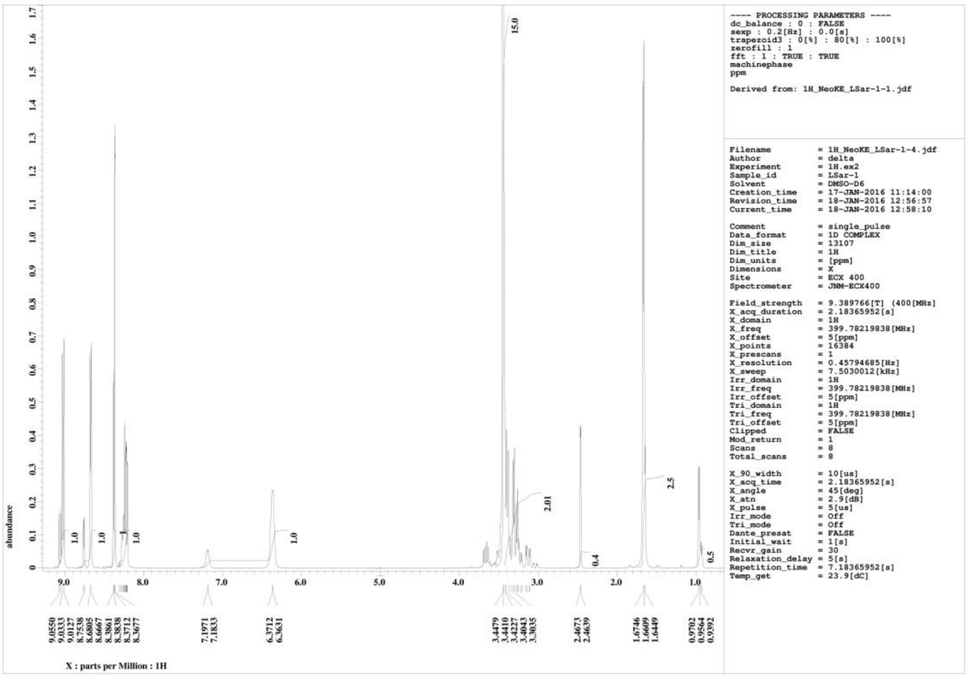
Figure 4.15: ^{1}H-NMR spectrum for complex **1**



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zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

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Solvent             = DMSO-D6
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Dim_units           = [ppm]
Dimensions          = X
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Spectrometer        = JNM-ECX400

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X_acq_duration      = 2.18365952[s]
X_domain            = 1H
X_freq              = 399.78219838[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_resolution        = 0.45794685[Hz]
X_sweep             = 7.5030012[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Tri_domain          = 1H
Tri_freq            = 399.78219838[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 8
Total_scans         = 8

X_90_width          = 10[us]
X_acq_time          = 2.18365952[s]
X_angle             = 45[deg]
X_atn               = 2.9[dB]
X_pulse             = 5[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 30
Relaxation_delay    = 5[s]
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Temp_get            = 23.9[dC]
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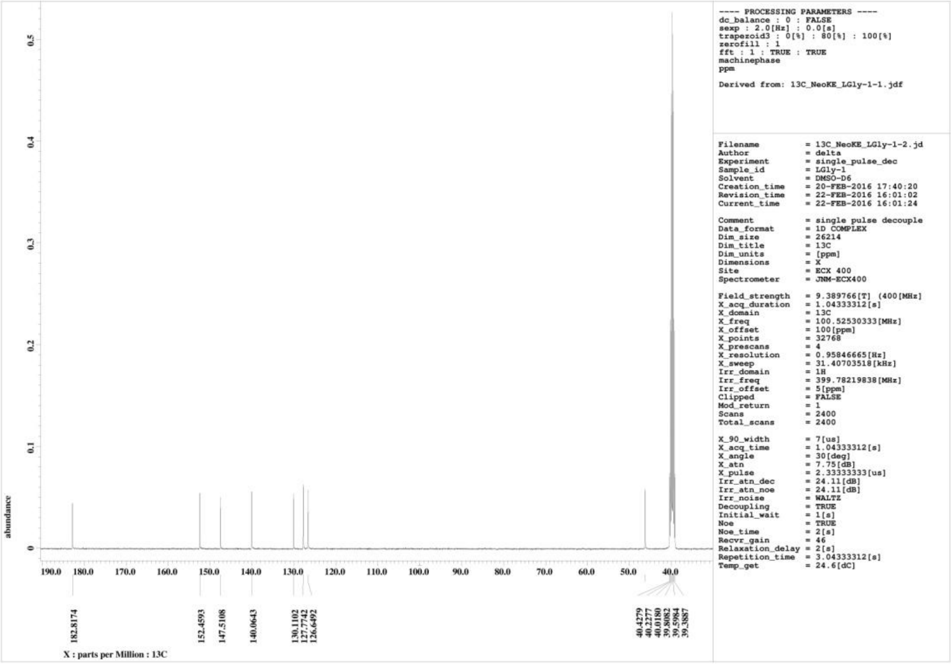
Figure 4.16: ^{1}H-NMR spectrum for complex **2**



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sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C_NeoKE_LGly-1-1.jdf
```

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Experiment        = single_pulse_dec
Sample_id         = LGly-1
Solvent           = DMSO-D6
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Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400

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X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2400
Total_scans       = 2400

X_90_width        = 7[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 7.75[dB]
X_pulse           = 2.33333333[us]
Irr_atn_dec       = 24.11[dB]
Irr_atn_noe       = 24.11[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 46
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.6[dC]
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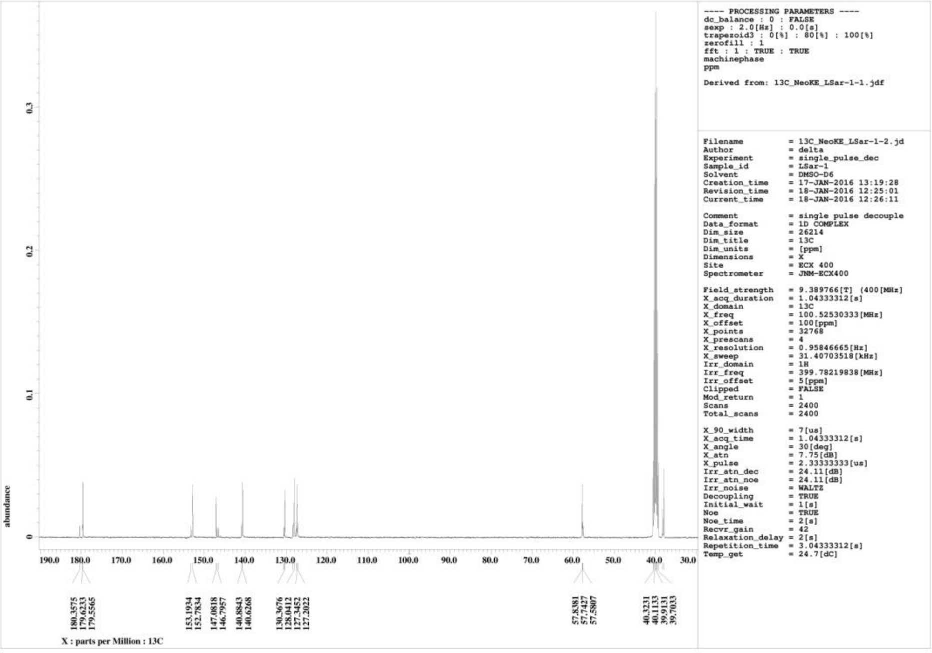
Figure 4.17: $^{13}C\{^{1}H\}$-NMR spectrum for complex **1**



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Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
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X_90_width        = 7[us]
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X_pulse           = 2.33333333[us]
Irr_atn_dec       = 24.11[dB]
Irr_atn_noe       = 24.11[dB]
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Noe               = TRUE
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Recvr_gain        = 42
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.7[dC]
```

Figure 4.18: $^{13}C\{^{1}H\}$-NMR spectrum for complex **2**

4.3 Proposed chemical structures for complexes 1 and 2

The data obtained from IR spectra, UV-Vis spectra, CHN elemental analysis, mass spectra, ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra were gathered to give the proposed chemical structures for complexes **1** and **2** as shown in Figures 4.19 and 4.20, respectively. The proposed chemical structures for complexes **1** and **2** were in good agreement with the overall data obtained.

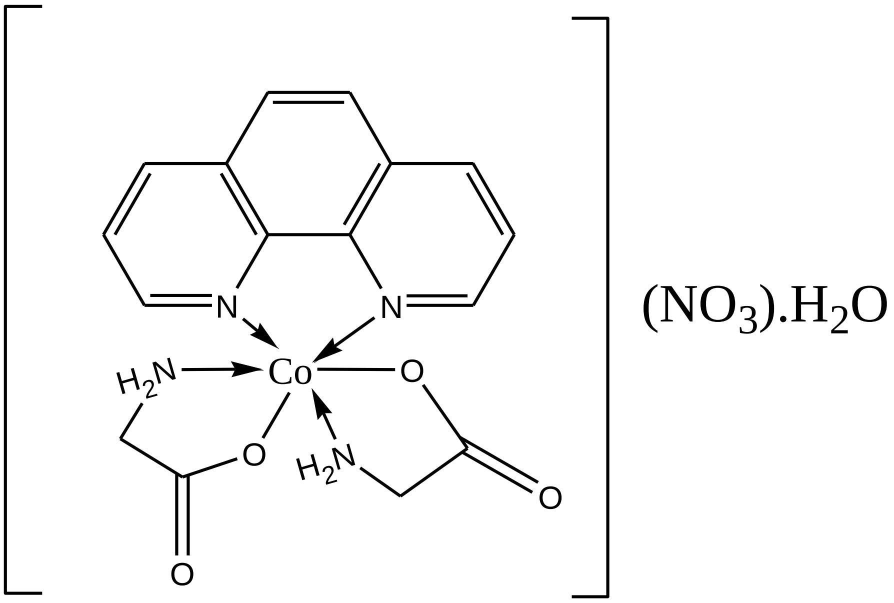

Figure 4.19: Proposed structure of $[Co(gly)_2(phen)](NO_3).H_2O$, **1**

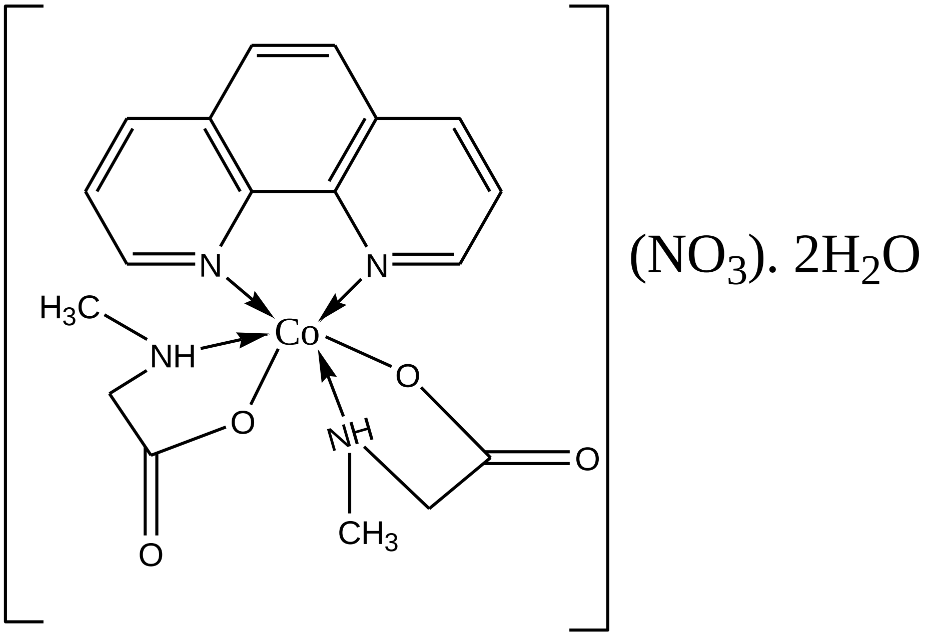

Figure 4.20: Proposed structure of $[Co(phen)(sar)_2](NO_3).2H_2O$, **2**

Based on Figure 4.19, it was proposed that one phen ligand and two glycinato ligands were coordinated to the central cobalt atom in complex **1**. While based on Figure 4.20, it was suggested that one phen ligand and two sarcosinato ligands were bonded to the central cobalt atom in complex **2**. In both complexes **1** and **2**, the phen ligands were coordinated to the central cobalt atom through its nitrogen atoms in a bidentate mode. The central cobalt atom for both complexes were proposed to adopt an octahedral geometry. Further confirmations on the structures of complexes **1** and **2** will be the subject for future research. The percentage yields for complexes **1** and **2** were determined to be 79% and 41%, respectively. Calculations for the percentage yields were based on the proposed structures of complexes **1** and **2** as shown in the previous Figures 4.15 and 4.16.

4.4 General discussion

Complexes **1** and **2** formed were determined to be eighteen-electron complexes according to the 18-electron rule. These complexes formed had achieved stable eighteen-electron configuration, therefore they were predicted to be less reactive towards oxidation and reduction. Complexes **1** and **2** were presumably Co(III) complexes which adopted the d^6 low-spin octahedral configuration, therefore the Co(III) atom contributed six d-electrons. On the other hand, four electrons were contributed by each phen ligand, while eight electrons were contributed by two glycinato ligands of complex **1**, or by two sarcosinato ligands of complex **2**. As a result, both the complexes formed were deduced to have eighteen valence electrons.

One of the starting materials used in the synthesis of complexes **1** and **2** were cobalt(II) nitrate hexahydrate. However, complexes **1** and **2** were found to be cobalt(III) complexes, which were formed without the addition of any oxidizing agent. The reaction mechanism for the oxidation of Co(II) to Co(III) still remained unknown, presumably due to the air oxidation of Co(II) compound as reported by Eaton and O'Reilly (1987). In this project, N,O-donor ligands were added first instead of phen monohydrate. The coordination of the phen ligand seemed to suggest that phen had stronger binding affinity as compared to N,O-donor ligands due to the presence of delocalized electrons in its extended planar aromatic rings system that led to stronger chelate effect with greater stability (Rao, Patra and Chetana, 2008). Therefore, phen ligand might saturate the coordination sites of the cobalt atom, making the N,O-donor ligands to be relatively hard to displace phen ligand and bind to the cobalt atom. Hence, N,O-donor ligands were introduced first to the methanolic solution of cobalt instead of phen monohydrate.

Besides, 3 mmol of N,O-donor ligands, namely glycine and sarcosine were added, instead of 2 mmol as per suggested by the reaction stoichiometry. The purpose of such addition was to saturate the coordination sites of the central cobalt atom, before introducing 1 mmol of phen monohydrate. Since glycine and sarcosine were both bidentate ligands, thus they had stronger binding affinities to the central cobalt atom through chelate effect as compared to water molecules that might bind as aqua ligands. As a result, water molecules could be prevented from binding to the central cobalt atom. Ammonia solution was added dropwise to both glycine and sarcosine solution. Such addition was performed as to raise the pH of the aqueous solution of glycine and sarcosine, thus deprotonating the ligands and making the ligands available for binding through their oxygen atom. Apart from that, the percentage yield for complex **2** was found to be lower than the percentage yield calculated for complex **1**.

This could be due to the steric effect caused by the additional methyl group found on the sarcosinato ligand, thus affecting the stability and packing of the molecules of complex **2**. Therefore, complex **2** had a lower percentage yield.

CHAPTER 5

CONCLUSION

5.1 Conclusion

In this project, the chemical compounds formed from a solution mixture containing a cobalt(II) salt, 1,10-phenanthroline and N,O-donor ligand, namely glycine and sarcosine were investigated. The identities of complexes **1** and **2** formed were studied by using FT-IR spectroscopy, UV-Visible spectroscopic analysis, CHN elemental analysis, mass spectrometry, ^{1}H-NMR and $^{13}C\{^{1}H\}$-NMR spectroscopy. Based on the IR spectra, it revealed the functional groups that were expected to be observed for the products obtained. UV-Visible spectra showed significant bands that were assigned to the π-π^* transition of the coordinated phen ligand and the d-d transition of the central cobalt atom. The chemical formulae, molecular masses and the chemical structures for the complexes **1** and **2** formed were proposed based on the data obtained from elemental analysis, spectroscopic and spectrometric analyses. By gathering the data obtained from the aforementioned analysis, the chemical formula of complex **1** was proposed to be $[Co(gly)_2(phen)](NO_3).H_2O$ with molecular mass of 467.27 g/mol, while the chemical formula of complex **2** was proposed to be $[Co(phen)(sar)_2](NO_3).2H_2O$ with a molecular mass of 513.33 g/mol. The proposed chemical structures of the complexes are shown in Figures 5.1 and 5.2.

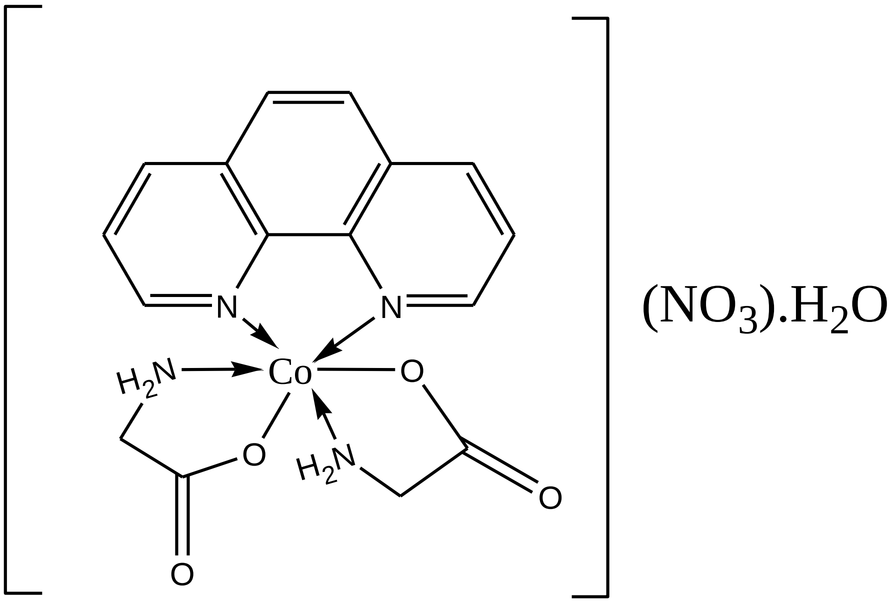

Figure 5.1: Proposed structure of $[Co(gly)_2(phen)](NO_3).H_2O$, **1**

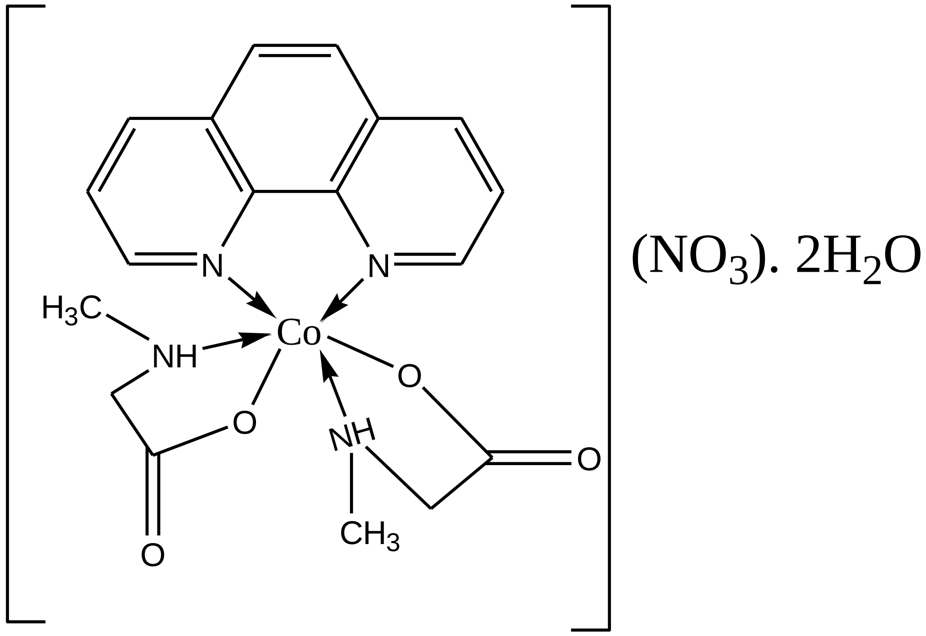

Figure 5.2: Proposed structure of $[Co(phen)(sar)_2](NO_3).2H_2O$, **2**

5.2 Suggestion for future research

It is crucial to conduct future research as to gather more information on the structures of the products obtained. Fluorescence spectroscopy can be used to study the fluorescence nature and the quenching effect of the products obtained. A molar conductivity study will be helpful in investigating the electrolyte nature and stability of the products obtained in solutions. Single crystal X-ray crystallography analysis can be beneficial to further study the length of chemical bonds and molecular structures of the products obtained in solid state. Magnetic measurements can be carried out for both complexes to confirm the magnetic properties of the complexes. Besides, the biological properties of the products formed can also be exploited.

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APPENDICES

Appendix A

Preparation of 5×10^{-3} M sample solution for UV/Visible analysis in the visible region :

For complex **1**, 0.0234 g of sample was measured and dissolved in 10 mL of freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

For complex **2**, 0.0257 g of sample was measured and dissolved in 10 mL of freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

Preparation of 5×10^{-6} M sample solution for UV/Visible analysis in the UV region and molar absorptivity study :

0.01 mL of sample was measured from previously prepared 5×10^{-3} M of sample and diluted to 10 mL with freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

Preparation of 4×10^{-6} M sample solution for molar absorptivity study :

8 mL of sample was measured from previously prepared 5×10^{-6} M sample and diluted to 10 mL with freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

Preparation of 3×10^{-6} M sample solution for molar absorptivity study :

7.5 mL of sample was measured from previously prepared 4 x 10^{-6} M sample and diluted to 10 mL with freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

Preparation of 2×10^{-6} M sample solution for molar absorptivity study :

6.67 mL of sample was measured from previously prepared 3 x 10^{-6} M sample and diluted to 10 mL with freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

Preparation of 1×10^{-6} M sample solution for molar absorptivity study :

5 mL of sample was measured from previously prepared 2 x 10^{-6} M sample and diluted to 10 mL with freshly prepared solvent. The solvent used is a methanol:water mixture in the ratio of 2:1.

Appendix B

Calculation of CHN elemental analysis for complex [Co(gly)$_2$(phen)](NO$_3$).H$_2$O, 1

Element	No. of atoms	Molar mass (g /mol)	Sum (g/mol)	Calculated (%)	Found (%)	Difference (%)
C	16	12.0107	192.17	41.13	41.47	0.34
H	18	1.0079	18.14	3.88	3.31	0.57
N	5	14.0067	70.03	14.99	15.19	0.20
O	8	15.9994	128.00	27.39	-	-
Co	1	58.9332	58.93	12.61	-	-
Grand Total			467.27	100.00		

Calculation of CHN elemental analysis for complex [Co(phen)(sar)$_2$](NO$_3$).2H$_2$O, 2

Element	No. of atoms	Molar mass (g /mol)	Sum (g/mol)	Calculated (%)	Found (%)	Difference (%)
C	18	12.0107	216.19	42.12	42.32	0.20
H	24	1.0079	24.19	4.71	4.10	0.61
N	5	14.0067	70.03	13.64	13.75	0.11
O	9	15.9994	143.99	28.05	-	-
Co	1	58.9332	58.93	11.48	-	-
Grand Total			513.33	100.00		

Appendix C

Calculation of percentage yield for complex 1

Relative molecular mass of complex **1** = 467.27 g/mol

Expected number of mole of complex **1** formed = 1 mmol

Theoretical yield of complex **1** = 0.4673 g

Actual yield of complex **1** = 0.3677 g

Percentage yield of complex **1** = $\frac{\text{Actual yield of complex } \mathbf{1}}{\text{Theoretical yield of complex } \mathbf{1}}$ x 100 %

= $\frac{0.3677\ \text{g}}{0.4673\ \text{g}}$ x 100 %

= 79 %

Calculation of percentage yield for complex 2

Relative molecular mass of complex **2** = 513.33 g/mol

Expected number of mole of complex **2** formed = 1 mmol

Theoretical yield of complex **2** = 0.5133 g

Actual yield of complex **2** = 0.2100 g

Percentage yield of complex **2** = $\frac{\text{Actual yield of complex } \mathbf{1}}{\text{Theoretical yield of complex } \mathbf{1}}$ x 100 %

= $\frac{0.2100\ \text{g}}{0.5133\ \text{g}}$ x 100 %

= 41 %