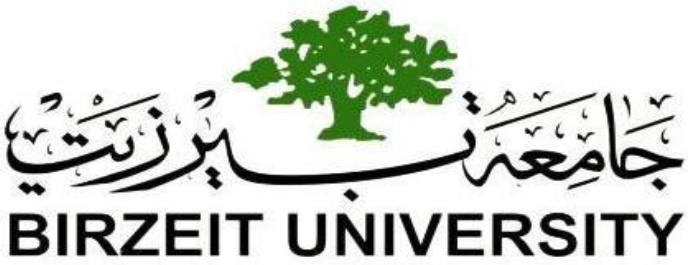

Faculty of Graduate Studies

Non-steroidal Zn(II) and Co(II) Sulindac Drugs and Bioactive Nitrogen-Donor Ligands: Synthesis, Characterization, Anti-bacterial Effect, Anti-malarial Effect and The Use as Phosphate Hydrolyzing Enzymes.

العقاقير غير الاستيرويدية من الزنك والكوبالت سولنيداك والقواعد النيتروجينية النشطة بيولوجيا: التحضير، التشخيص، التأثير ضد البكتيريا، التأثير ضد الملاريا و الإستعمال كإنزيمات تكسير الفوسفات.

This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Masters in Applied Chemistry. Faculty of Graduate Studies.

Birzeit University, Ramallah, Palestine

Asia M. Shalash

Under Supervision of

Dr. Hijazi Abu Ali

May, 2015

Non-steroidal Zn(II) and Co(II) Sulindac Drugs and Bioactive Nitrogen-Donor Ligands: Synthesis, Characterization, Anti-bacterial Effect, Anti-malarial Effect and The Use as Phosphate Hydrolyzing Enzymes.

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ACKNOWLEDGEMENTS

Thanks to Allah. Who granted me the power to finish this work. I would also like to express my deep appreciation to my supervisor Dr. Hijazi Abu Ali for his support and guidance. I would also like to thank Dr. Mazen Hamed and Prof. Abdul Latif Abu Hijleh for spending their precious time to read and discuss my work.

Thanks to my professors and lab technicians in the Department of Chemistry, and also to Drug Division in central Public Health Laboratory, especially to Suha Al-Akhras and Eng. Manal Hanani for their encouragement & support.

I would also like to thank my research group, Hadeel Faris and Mohannad Darweesh for their support & help. Thank to all my friends with special thank to Sadieh Abu-Sirriah, Ahlam Alrimawi and Shireen Zedany.

Encouragement, contribution and support of my family; my lovely father and mother, brothers (Ahmad, Omar and Bilal) and sister (Aysha) are highly appreciated and acknowledged.

Thanks to my husband Eng. Abudallah Ryahi who has always been my pillar, my joy and my guiding light.

Finally, thanks to everyone who helped me &supported me during my study…

May, 2015

Asia Shalash

TABLE OF CONTENTS

List of figures

List of tables

List of schemes

ABBREVATIONS

Sul	Sulindac
K(sul)	Potassium sulindac
2-ampy	2-Amino pyridine
2-ammepy	2-Aminomethyl pyridine
1,10-phen	1,10-Phenanthroline
2,9-dimephen	2,9-Dimethyl-1,10-phenanthroline
DMSO	Dimethyl sulfoxide
MeOH	Methanol
ACE	Acetone
ACN	Acetonitrile
DCM	Dichloromethane
DMF	Dimethylformamide
EtOH	Ethanol
CQ	Chloroquine
h	Hour
M.p.	Melting point
^{1}H-NMR	Proton Nuclear Magnetic Resonance
^{13}C-NMR	Carbon-13 Nuclear Magnetic Resonance
UV-Vis	Ultraviolet-Visible
IR	Infra Red
s	Singlet
d	Doublet
t	Triplet
IZD	Inhibition Zone Diameter
RT	Room Temperature
BNPP	Bis(4-nitrophenyl) phosphate

ABSTRACT

The complexes [$Zn(sul)_2.2H_2O$] **1**, [$Zn(sul)_2$(2-ampy)] **2,** [Zn(sul) (2-ammepy)] **3**, [$Zn(sul)_2$(1,10-phen)] **4**, [$Zn(sul)_2$(2,9-dimephen)] **5**, [$Co(sul)_2.4H_2O$] **6,** [$Co(sul)_2(2\text{-ampy})_2$] **7,** [$Co(sul)_2$(1,10-phen).$2H_2O$] **8**, and [$Co(sul)_2$(2,9-dimephen)] **9** were prepared. These compounds were characterized by IR-spectroscopy, UV- Visible spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, single crystal X-ray diffraction and other physical techniques. Sin

gle crystal structures of complexes **4**, **5**, **6** and **9** were determined.

In-vitro biological activity of the complexes and their parent ligands were scanned to view the effect of complexation on their activity. In addition, anti-bacterial activities for the prepared complexes against Gram-positive (*Staphylococcus epidermidis, Staphylococcus aureus*) and Gram-negative (*Bordetella, Escherichia coli*) bacteria and Yeast species(*Saccharomyces and Candida*) were performed using agar well-diffusion method. Complexes **5** and **9** showed reasonable activity against yeast. All compounds showed more anti-bacterial activity against G^+ bacteria than G^-. Adding to that, Zn(II)compounds were tested for their anti-malarial activity using two methods: semi-quantitative micro assay and a previously self-developed quantitative *in-vitro* method. This method was used to study the efficiency of these complexes in inhibiting the formation of the Malaria pigment. Results showed that the efficiency of complex **5** in preventing the formation of β-Hematin was 67.6 %. The efficiency of CQ as a standard drug was reported to give 93%. Also, the phosphatase activity of Zn(II) and Co(II) complexes were studied and showed the effect of zinc or cobalt complexation on the phosphatase activity. In general, results showed that phosphate diester hydrolysis decreased in the following order complex [$Zn(sul)_2$(1,10-phen)] **4** > [$Zn(sul)_2$(2,9-dimephen)] **5** > [$Co(sul)_2$(1,10-phen).$2H_2O$] **8** > [$Co(sul)_2$(2,9-dimephen)] **9**.

ملخص

المركبات المعقدة التالية قد تم تحضيرها:

[Zn $(sul)_2.2H_2O$] **1**, [$Zn(sul)_2$(2-ampy)] **2,** [Zn(sul) (2-ammepy)] **3**, [$Zn(sul)_2$(1,10-phen)] **4**, [$Zn(sul)_2$(2,9-dimephen)] **5**, [$Co(sul)_2.4H_2O$] **6,** [$Co(sul)_2(2\text{-ampy})_2$] **7,** [$Co(sul)_2$(1,10-phen).$_2H_2O$] **8**, and [$Co(sul)_2$(2,9-dimephen)] **9**.

هذه المركبات المعقدة تم تشخيصها من خلال مطياف الأشعة تحت الحمراء (IR)وجهاز الرنين المغناطيسي (^{1}H-NMR,^{13}C-NMR) وجهاز مطياف الأشعة فوق البنفسجية والمرئية (UV-Vis) وجهاز دراسة العينات احادية البلورة باستخدام الأشعة السينية (X-ray). وتحديد البنية البلورية للمركبات المعقدة (**9، 4،5 ،6**).

في المختبر الفعالية الحيوية لهذه المركبات تمت دراستها لمشاهدة تأثير الارتباط على الفعالية لهذه القواعد. بالإضافة الفعالية ضد البكتيريا لهذه المركبات المعقدة التي تم تحضيرها ضد البكتيريا ايجابية غرام، Staphylococcus (epiderimids) Staphylococcus aureus وبكتيريا سلبية غرام (*Bordetella, Escherichia coli*) وضد جزيئات الخميرة (*Saccharomyces and Candida*) باستخدام طريقة الانتشار المفتوحة في الاجار. المركبات المعقدة **5** و**9** أظهرت فعالية جيدة ضد الخميرة وجميع المركبات اظهرت فعالية ضد البكتيريا ايجابية غرام اكثر من سلبية غرام.إضافة إلى ذلك، مركبات الزنك ثنائية الشحنة تم اختبارها ضد فعالية الملاريا باستخدام طريقتين:فحص ميكرو شبه الكمية وطريقة الكمية المتقدمة ذاتيا في المختبر. واستخدمت هذه الطريقة لدراسة فعالية المركبات المعقدة في تثبيط تشكيل صباغ الملاريا. وأظهرت النتائج أن فعالية المركب المعقد **5** في منع تشكيل β-الهيماتين كانت 67.6٪. و أنفعالية الكلوروكوينون كدواء مقياس قد سجلت 93٪. وأيضا تم دراسة نشاط انزيم الفوسفاتيز من مركبات الزنك ثنائي الشحنة ومن الكوبالت ثنائي الشحنة وتوضيح تأثير الارتباط مع الزنك أو الكوبالت على نشاط انزيم الفوسفاتيز, نتائج تحلل مجموعة الفوسفات داي ايستر بشكل عام مرتبة ترتيبا تنازليا **9** < **8** < **6** < **5** < **4**.

1. Introduction

1.1. General principles

The chemical elements which are essential to life can be divided into four categories. Firstly, the bulk elements containing hydrogen, nitrogen, carbon, oxygen, sulfur and phosphorus. These elements appears in cellular components such as amino acid, polysaccharides, lipids membranes.[1] Secondly, macrominerals such as sodium and potassium ion, the biological functions of these ions as charge carrier and osmotic balance, calcium ion act as structure, trigger, and charge carriers in biological systems, magnesium ion used in isomerase, hydolase, and have structural role[2], sulfate and phosphate ions. Thirdly, the trace elements are essential in specific functions associated with the life processes such as iron and copper used as dioxygen transport in metalloproteins and zinc present in metalloenzymes and also present in most RNA and DNA polymerases.[3] Finally, ultra trace elements comprise of (a) nonmetals (F, I, Se, Si, As and B) (b) metals: (Mn, Mo, Co, Cr, V, Ni, Cd, Sn Pb and Li) these metals play important role in controlling the life cycle and some of these metals used in medicine such as vanadium.[1]

The Periodic Table below shows abundant bulk elements and essential trace elements to be essential for biosphere and biological system.

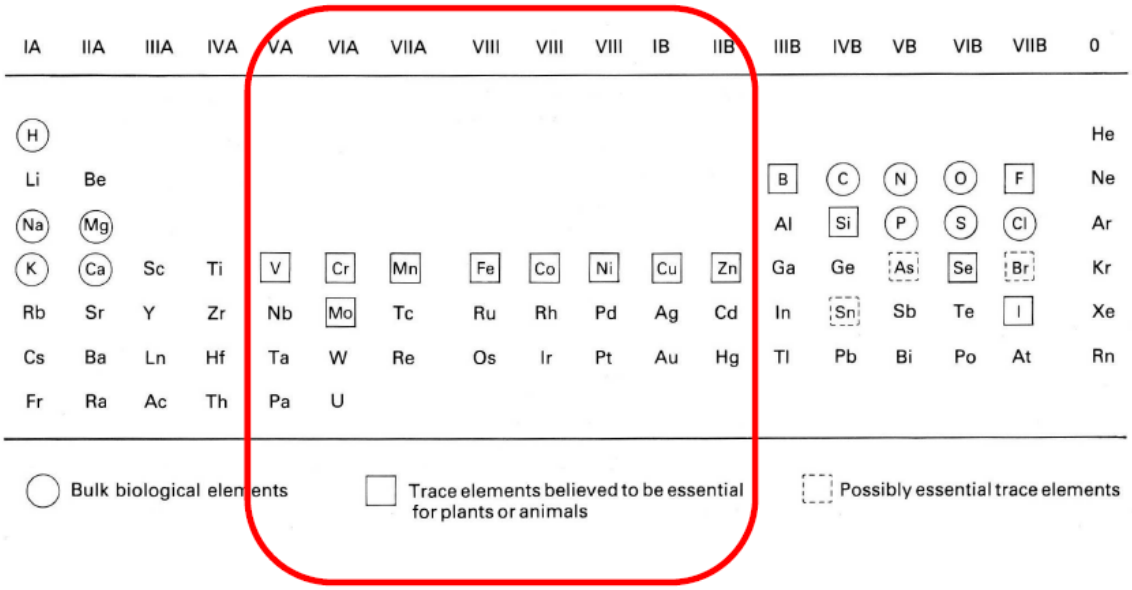


Figure 1.1: Bulk biological elements (circle), trace elements believed to be essential for biosphere (square), possibly essential trace elements (square with dashed lines) and the red square containing the most transition metals.[4]

Table (1.1) shows that there is no any life without transition metals, but only small amounts are required for essential functions: oxygen transport and storage, electron transport, protection of organisms, metabolization, in some enzymes .....etc .

Table 1.1: Average elemental composition of a human body (adult, 70 kg)[5]

Element	**symbol**	**Mass (g)**	**Years of discovery as an essential element**
Oxygen	O	45500	
Carbon	C	12600	
Hydrogen	H	7000	
Nitrogen	N	2100	
Calcium	Ca	1050	
Phosphorus	P	700	
Sulfur	S	175	
Potassium	K	140	
Chlorine	Cl	105	
Sodium	Na	105	
Magnesium	Mg	35	
Iron	Fe	4.2	17th century
Zinc	Zn	2.3	1896
Silicon	Si	1.4	1972
Rubidium	Rb	1.1	
Fluorine	F	0.8	1931
Zirconium	Zr	0.3	
Bromine	Br	0.2	
Strontium	Sr	0.14	
Copper	Cu	0.11	1925
Aluminum	Al	0.1	
Lead	Pb	0.08	
Antimony	Sb	0.07	
Cadmium	Cd	0.03	1977
Tin	Sn	0.03	1970
Iodine	I	0.03	1820
Manganese	Mn	0.02	1931
Vanadium	V	0.02	1971
Selenium	Se	0.02	1957
Barium	Ba	0.02	
Arsenic	As	0.01	
Boron	B	0.01	
Nickel	Ni	0.01	1971
Chromium	Cr	0.005	1959
Cobalt	Co	0.003	1935
Molybdenum	Mo	<0.005	1953
Lithium	Li	0.002	

1.2. Zinc

1.2.1. Zinc as an element

Zinc has the electron configuration [Ar] $4s^2\ 3d^{10}$, atomic weight 65.39 and atomic number 30. Zinc is group 12 first row transition metal. Zn is the 24th most abundant element in the earth's crust and has 5 stable isotopes. The largest exploitable deposits are found in Canada, United States, and Australia. Metallurgy of zinc involves roasting, extraction using electricity and final froth floatation of the ore.

Zinc occurs in solution mainly as Zn^{+2} ion. It exists in a wide range of enzymes. Its role in enzymes appears as a Lewis acid in catalytic reactions, and it plays a role in enzymes structure determination. Zinc(II), being a d^{10} ion has no *d-d* transitions which means no absorption in the visible range and the LFSE is zero for any geometry. Zinc prefers regular octahedral or tetrahedral geometries. However, in biological systems Zn(II) is usually found in distorted environments necessary for its structural or catalytic role.[6]

In hard soft acid base concept (HSAB) zinc is a borderline acidic metal[4] and binds sulfur or nitrogen donor ligands in human body such as cysteine and histidine, and can bind oxygen ligands such as aspartate.[7]

1.2.2. Importance of zinc in biology

Zinc is essential to all forms of life. Congenital disorders and a large number of diseases have been attributed to zinc deficiency.[8] In adult human body there is two to three g of zinc as compared to four to six g of iron and only 250 mg of copper. Biochemists were slow to appreciate the importance and presence of zinc because it is non-magnetic and colorless complexes. Generally not easily noticed as copper and iron.[9] However, today there are effective methods for measuring zinc at a level as low as 10^{-14} g.

Zinc is a fundamental mineral of importance to health and biological applications.[10] Zinc deficiency is associated with many diseases and it affects about two billion people in the developing world.[11] In children it causes diarrhea, growth retardation, infection susceptibility and delaying sexual maturation, contributing to the death of about 800,000 children worldwide per year. Consumption of excess zinc can cause copper deficiency, ataxia, and lethargy.

Zinc enzymes which have a Zn^{+2} ion in the reactive center are widespread in biochemistry, for example alcohol dehydrogenase in humans. Figure 1.2 shows different examples of dinuclear and mono zinc enzymes. Zinc ions are found to form chelates with ligands containing oxygen and nitrogen donors. They do not promote the formation of free radicals.[12]

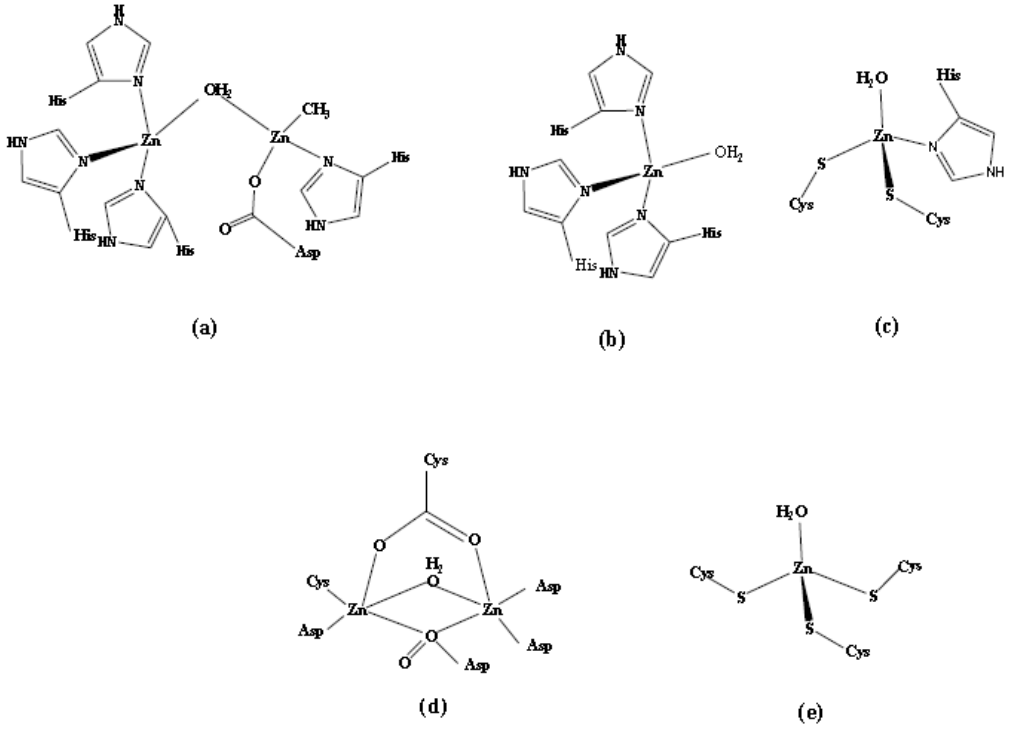


Figure 1.2: Active sites of mono and dinuclear zinc enzymes: (a) metallo-β-lactamase, (b) human carbonic anhydrase, (c) alcohol dehydrogenase, (d) leucine amino peptidase, and (e) 5-aminolaevulinate.[13] The ligands are part of long chain protein (His = histidine, Asp = aspartate, Cys = cysteine, Glu = glutamate, Lys = lysine).

Zinc is known as a component of zinc finger proteins which participates in the reliable transfer of genetic information and to regulate activity in over three hundred metalloenzymes.[14] Metallothionein (MTs), an unusual and unconventional protein, one third of its plus amino acids are cysteines and eight are lysine's. It contains neither aromatic amino acids nor histidine. Metallothionein proteins participate in the regulation, transport, and uptake of zinc in biological systems. The zinc binding sites are often cysteine rich and usually bind four or three zinc ions. By releasing and binding zinc, metallothionenis (MTs) regulate its level within the body. Zinc is required in plants for leaf formation, in the anaerobic respiration (alcoholic fermentation) and the synthesis of indole acetic acid (auxin). It is also present as activator of specific enzymes, such as alcohol dehydrogenase and carbonic anhydrase. Carbonic anhydrase is significant in the transfer carbon dioxide in vertebrate blood.[15]

In addition to physiological functions, zinc and its compounds have important roles in the clinical medicine. Anti-viral and anti-bacterial activity and the wound-healing effect of zinc-containing ointments have been known for some centuries.[16-20] Zinc may act as an anti-sickling agent and it may be applied as a therapeutic agent and play a role in the prevention of pain crises in sickle-cell disease. Zn has been successfully applied in the treatment of a crodermatitis enteropthica, infertility, Wilson's disease, gastrointestinal disorders, and other diseases.[21-22]

In addition to traditional zinc compounds like zinc oxide and zinc sulfate, its complexes with organic ligands are also often used in the cosmetics and clinical medicine. Zinc(II) acetate complex with erythromycin is applied for acne therapy.[23] The complex of Zn(II) with pyrithione is used in shampoos as an anti-dandruff agent.[24]

Among much nutritional and pharmacological roles zinc metal ion was found in 1980 to stimulate rat adipocytes lipogenesis similar to the action of insulin.[25] Based on these important results, $ZnCl_2$ was administered to diabetic mice and rats and was found to normalize their high blood glucose levels when a high dose was given or a long-term administration of the compound was continued. Since this discovery, many zinc complexes with picolinic acid, amino acids, maltol, and their derivatives have been prepared and have higher insulinomimetic activity than free zinc(II), as estimated by in *vitro* and *vivo* exeperiments.[26]

1.2.3. Stereochemistry of zinc compounds

In addition to the significance of the biological activities of zinc structural chemistry of its compounds with different donor ligands is a fast rising area of research. As a d^{10} metal ion Zn^{+2} is especially suitable for the construction of networks and coordination polymers. The d^{10} configuration is a spherical, so it is associated with elastic coordination environment so that geometries of Zn compounds can differ from octahedral through square pyramidal and trigonal bipyramidal to tetrahedral and severe distortion of the ideal polyhedron readily appear. In addition, due to the public responsibility of Zn compounds the formation of coordination bonds is reversible which enables ligands and metal ions to rearrange through the process of polymerization to give highly ordered network structures.

1.2.4. Reactivity of Zn

Zinc has temperate reactivity and powerful action. The surface of the pure zinc pollute speedily, lastly forming a conservative passivating layer of the basic zinc carbonate, $Zn_5(OH)_6CO_3$, by reaction with atmospheric carbon dioxide.[27] this layer assistance prevent further reaction with water and air.

Extremely pure Zn reacts only slowly at room temperature with acid. Strong acids, such as sulfuric acid or hydrochloric, can eliminate the passivating layer and following reaction with water releases hydrogen gas.[28] Zn burns in atmospheric oxygen producing a bright bluish-green flame, giving off fumes of ZnO. Zn reacts easily with alkalis and other non metals.[29]

Zn predominantly shows divalent cation oxidation state. Complex with oxidation state II is formed by loss of two electrons from s sub shell; leaving Zn ion presenting the electronic configuration as [Ar]$3d^{10}$. Zn^{+2} can accept four electrons to form four covalent bonds and obey octet rule. The stereochemistry is therefore tetrahedral and the bonds perhaps qualified as being formative from sp^3 hybrid orbital on the Zn ion.[30] In aqueous solution predominantly an octahedral compound, $[Zn(H_2O)_6]^{+2}$ is formed. The volatilization of Zn in aggregation with $ZnCl_2$ at temperature over 285 $^{\circ}$C shows the forming of Zn_2Cl_2, a zinc complex with a monovalent cation oxidation state.

1.2.5. Zn in medicine

Metals can play an important role in the mechanism of action of organic drugs, Table 1.2.

Table 1.2: Some metals used in medicine.[31]

Medicinal usage	**Metal**	**Medicinal usage**	**Metal**
Superoxide Dismutase mimics	Mn	MRI	Gd
Alzheimer, Inflammatory agent	Zn	Scintigraphy in diagnosis	Tc
Diabetes (Insulin mimics)	V		
Alzheimer, MRI contrast agent	Fe		
Alzheimer	Al		
Anti-cancer agent	Pt		
Anti-cancer agent	Ru		

Zn possess as antioxidant properties, which protect early aging of the skin and muscles of the body. It is included in vitamin supplements.[32] Zn also speeds up the recovery process next an injury.

The efficiency of zinc complexes when used to decrease the duration or severity of cold symptoms is controversial. Preparations including zinc gluconate, zinc acetate, and zinc oxide. Zinc gluconate is one compound applied for the delivery of zinc as dietary supplement. Zinc acetate and zinc gluconate glycine are applied in throat lozenges or tablets to reduce the duration and the severity of cold symptoms.[33]

Zinc lactate is used in toothpaste to prevent halitosis.[34] Zn ions are efficient anti-microbial agents even at minimal concentrations.

Gastroenteritis is hardly attenuated by ingestion of Zn and this impact could be due to direct anti-microbial action of the zinc ions in the gastrointestinal tract or the absorption of zinc and re-release from immune cells or both.[35]

1.2.6. Zinc as anti-bacterial agent

The most efficient biological activity of metal carboxylate is when metal carboxylate compounds coordinate with N-donor biological active ligands. Zelank (2002) studied compounds of zinc with $RCOO^-$ (R = XCH_2(X = Br, Cl), CH_3-, $CH_3CH_2CH_2$-, H-,and $(CH_3)_2CH_2$-) and coordination of these compounds with nicotinamide and caffeine. These complexes exhibit the gram-positive bacteria staphylococcus aureus.[36]

The zinc complexes of formate, acetate, propionate, butyrate, isobutyrate, and other aliphatic carboxylate ligands were studied and their interactions with N-donor ligands like phenazone, papaverine, nicotinamide, caffeine, and theophylline. The anti-microbial effect of these complexes were also studied.[37-43]

Many complexes of benzoic acid and its analogues like salicylic acid and its derivatives were studied with biologically active ligands like thiourea, nicotinamide, caffeine, the bromine, theophylline, and urea.[44-49] In general these complexes show a stronger antimicrobial activity than the organic ligands alone do.[50]

Zinc complexes of 2,2-bipyridine and 1,10-phenanthroline showed anti-microbial effect.[51]

The carboxylate complexes of these ligands with 2-nitrobenzoate, 1,2-phenyllinediacetate, salicylate, 4-hydroxybenzoate, and 3,5-di-tert-butylsalicylate were studied.[52-56]

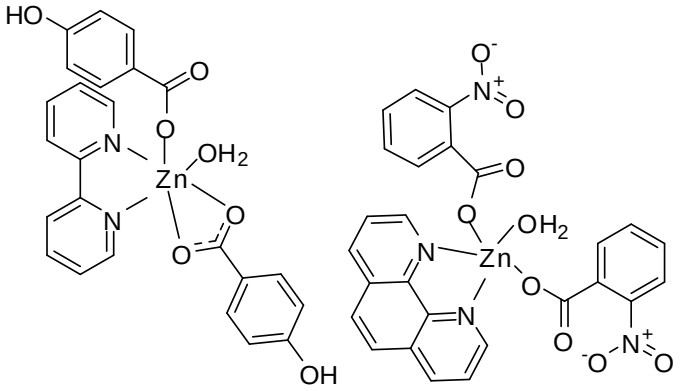


Figure 1.3: Example for coordination environments of [Zn(*trans*-4-hydroxybenzoate)$_2$(H_2O)(2,2-bipy) and [Zn(2-nitrobenzoate)$_2$(1,10-phen)(H_2O)].[51]

1.3. Cobalt

1.3.1. Cobalt as an element

Cobalt is a metallic element with electron configuration [Ar]$4s^2 3d^7$, atomic weight 58.93, atomic number 27, and the symbol of cobalt is Co. Its common oxidation state is +2 or +3.

1.3.2. Biological importance of cobalt

Cobalt like other transition metals is an essential trace element for higher organisms. Cobalt has significant role in proteins; there are at least eight cobalt-dependent proteins. Moreover, cobalt is needed in the active center of coenzymes, called cobalamins especially cyanocobalamins (Vitamin B_{12}) which regulates indirectly the synthesis of DNA. Cobalamins alone are pharmaceutical agents and are treated in pathologies arising from a lack of vitamin B_{12}.

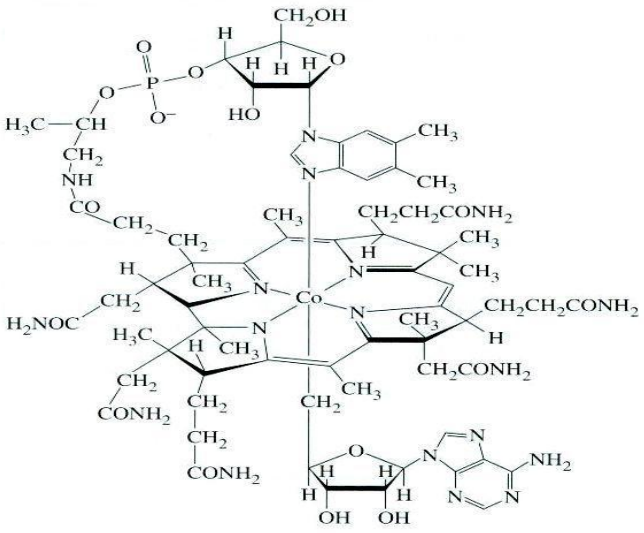


Figure 1.4: Structure of vitamin B_{12}[57]

The cobalt compounds are of very limited medicinal usage compared to other metals such as zinc and copper compounds. The first reported study about the biological activity of cobalt compounds was in 1952, there has been interest in cobalt(III) compounds of bidentate mustards, which seem to act as hypoxia-selective agents.[58] Several compounds showed considerable activity against bacteria strains. Moreover, against leukemia and lymphoma cell lines.[59] Furthermore, cobalt complexes possess *in-vivo* insulin-like properties,[60] anti-fungal and anti-oxidant activity.[61]

1.3.3. Cobalt complexes with anti-microbial activity

Several Co(III) complexes with anti-microbial activities have been reported. For instance, a Co(III) complex of the known anti-ulcer drug famotidine turned out to have greater anti-microbial activity against *M. lysodeikticus and E. coli* than the metal free drug.[62]

The pyrazine-2,3-dicarboxylate compounds of alkyl diamines and 1,10-phenanthroline have recently shown activity against fungi *C. Albicans* and against bacterial strains Gram(-) and Gram(+). Co(II) compounds of hinikitiol, 4-isopropyltropolone, seem to be reactive, in comparison to Cu(II) compounds.[63]

Cobalt(II) complexes showed anti-microbial and anti-fungal activities. The complex of imidazole-2-carbaldehyde semicarbazone turned out to be reactive against *C. tropicalis* and the yeasts *S. cerevisiae*. Activity was most noticeable against such phytopathogenic fungi as *Sclerotinia or Alternaria*.[64]

Moreover, some Co(II)-2-methylthionicotinate compounds of different N-heterocyclic ligands displayed significant activity against fungi and bacterial strains. Complexation between cobalt and nicotinate derivatives increased their biological activity. Also development of several Co(II) compounds with Schiff bases and their anti-fungal and anti-microbial properties have been performed.[65]

Polyether ion sphere anti-biotics of Monensin produced by *Streptomyces* are biologically active complexes. Co(II) complex was found ineffective against Gram negative bacteria, most likely because of its large molecular weight and hydrophobicity, but cobalt(II) complex of the sodium salt of Monensin (Figure 1.5), was found reactive against the Gram positive bacteria.[66]

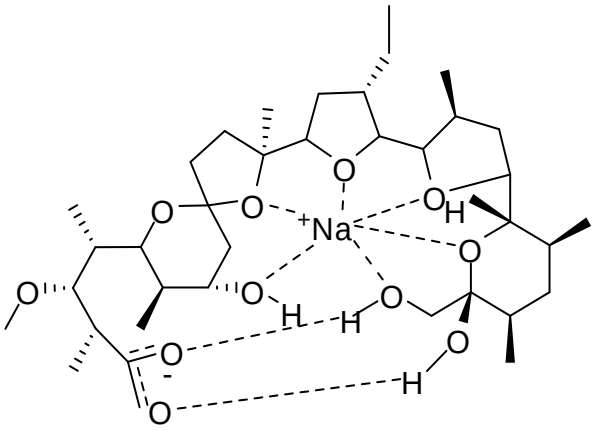


Figure 1.5: The structure of sodium monensin.[66]

1.3.4. Cobalt complexes with anti-tumor activity

Co(III) compounds have been widely studied as anti-cancer agents.[67] In 1956 the first structures of Co(III) compound were described. These compounds are known to target specific enzymes. Their potential activity in murine leukemia cells was firstly observed for a compound consisting of an acetyl ligand. The cobalt-alkyne analogue of the NSAID (Nonsteroidal anti-inflammatory drugs) group of compounds is highly active against breast cancer cell lines (Figure 1.6). The complexes showed high intracellular levels of cobalt and were more lipophilic than their free ligands. It has been suggested that the COX inhibition is responsible for the powerful activity. [68]

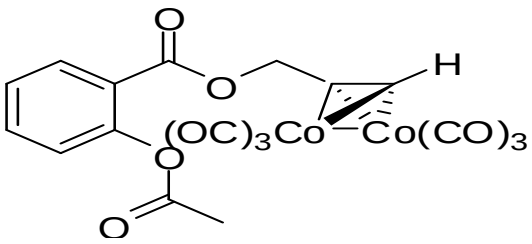


Figure 1.6: Cobalt-alkyne analogue of the non-steroidal anti-inflammatory drug aspirin.[68]

Other researchers studied the complexation of a Co(III) chaperone to a matrix metalloproteinase inhibitor marimastat, aiming to inhibit over-expressed matrix metalloproteinases in tumor patients (Figure 1.7). The cobalt(III) carrier is utilize as a carrier for the activation and the drug by a bio reductive pathway to the cobalt(II) compound which releases the inhibitor ligand intracellularly. Unfortunately, it was found that the free inhibitor and the prodrug both potentiate metastasis.[69]

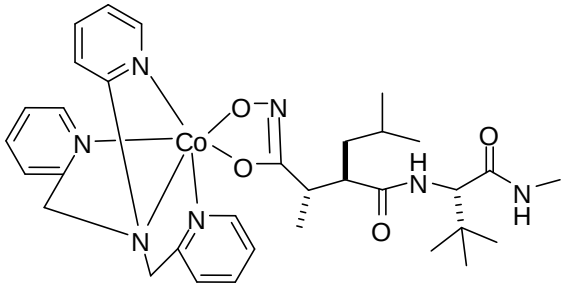
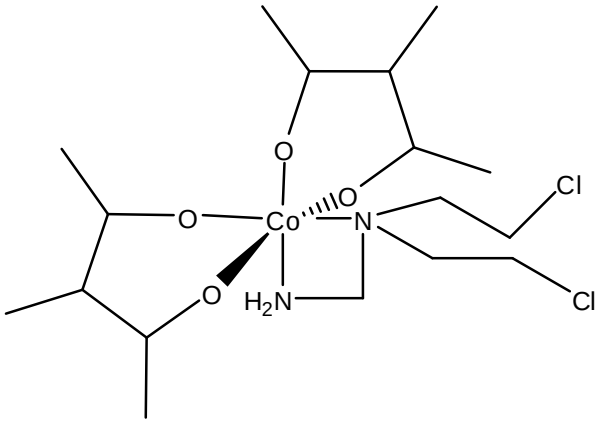


Figure 1.7: Cobalt-marimastat chaperone complex with matrix metalloproteinase inhibitory activity.[69]

Figure 1.8 describes the Co(III) compounds as hypoxia selective anti-tumor agents. The notion of this design is based on the truth that the tumor cells improve resistance to chemotherapeutic agents under anaerobic conditions. However, they can be reduced under hypoxic conditions to Cobalt(II) species followed by loss of neutral ligand.



$$[Co^{III}L_3]^{+3} \rightleftharpoons [Co^{II}L_3]^{+2} \xrightarrow{H_2O} [Co^{II}(H_2O)_6]^{+2} + 3L$$

$$O_2^{\cdot -} \rightarrow O_2$$

Figure 1.8: Cobalt(III) compound consisting of a nitrogen mustard ligand.[69]

The cobalt(II) salen complex is another example of anti-tumor active agent (Figure 1.9) In anti-proliferation studies the relationship between the structure and activity has been found.[70]

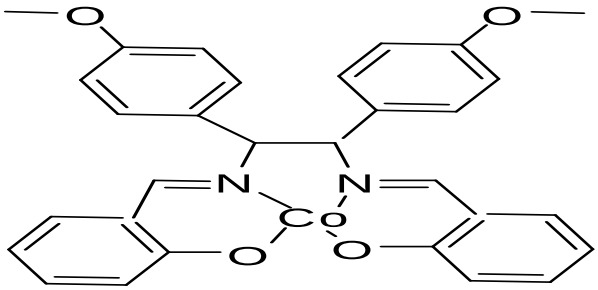


Figure 1.9: Structure of a cobalt(II) salen complex.[70]

Co(II) complexes of 2-substituted benzimidazoles have also shown to possess anti-tumor activity against the HCT-15 and HeLa cancer cell lines.[71]

1.3.5. Cobalt coordination chemistry

The most important cobalt minerals are smaltite ($CoAs_2$) and cobaltite (CoAsS). Cobalt has many oxidation states but the most stable are cobalt(II) and cobalt(III) complexes. There are some binary cobalt compounds known (oxides Co_3O_4, halides CoF_2 or sulfides CoS) as well as cobalt salts ($Co_2(SO_4)_3*18H_2O$).

1.3.5.1. Cobalt(II) complexes

There are many forms of cobalt(II) complexes. The Co^{2+} ion has a d^7 configuration. The most frequent are with tetrahedral geometry. Tetrahedral complexes are mostly either in the form of $[CoX_4]^{-2}$ or CoX_2L_2.

Square planar complexes are obtained with bidentate mono anions or neutral bidentate ligands. Moreover, the tetradentate ligands (salen or porphyrins) also form square planar complexes. Octahedral complexes are formed with halides, pseudo halides and O-donors. There are many known dinuclear carboxylate complexes that are stabilized with nitrogen ligands. Five coordinate complexes are tbP or sp with phosphine adducts. Bridged metal-metal bonded structures are growing in numbers.[72]

1.3.5.2. Cobalt(III) complexes

Cobalt(III) complexes of d^6 configuration are also numerous. Almost all are octahedral but a few are tetrahedral or square planar. Generally, these complexes are prepared in a few steps, starting with oxidation of the Co(II) ion by O_2 or H_2O_2 often with a catalyst. Such complexes can act as photosensitizers in DNA.[72]

1.4. Coordination of metal carboxylates

Metal(II) carboxylate compounds with nitrogen or oxygen-donor ligands have been important from biological and chemical aspects for last decades. The interaction between heterocyclic compounds and metal ions is very important in biological systems that appears in some drugs and vitamins.[73]

Carboxylates are susceptible of binding with a metal ion in four different patterns such as ionic, bidentate, monodentate, or bridging mode leading to polymer structures and both mono and polynuclear structures. These bonding patterns were determined by crystallographic methods or infrared spectroscopy (IR).

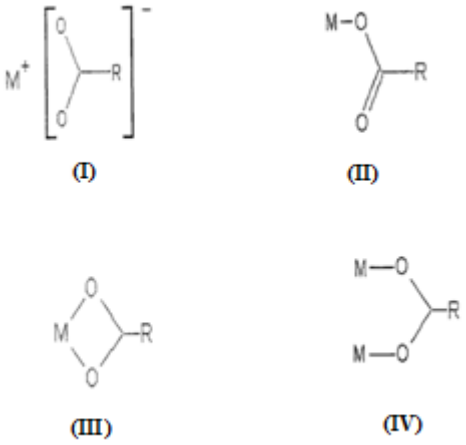
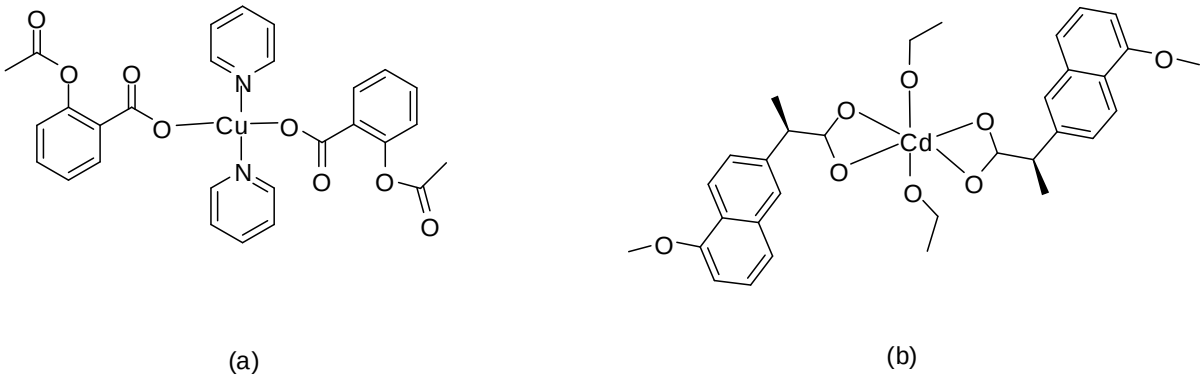


Figure 1.10: Metal carboxylate modes according to metal-ligand interaction. (I) ionic or uncoordinated form, (II) unidentate coordination, (III) bidentate chelating coordination, (IV) bidentate bridging coordination.[74]

The bonding mode of carboxylate with metal determination by infrared spectroscopy (IR) through ν_{as} (COO^-) (asymmetric vibration frequency of the carboxylate), and $\Delta = \nu_{as}$ (COO^-) – ν_s (COO^-) (The difference between the carboxylate stretches).

In General, the suggested mode of interaction for divalent metal carboxylates in the following order[75]:

Δ(Chelating) < Δ(bridging) < Δ(ionic) < Δ(monodentate)



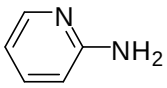
(a) (b)

Figure 1.11: The bonding mode of carboxylates with metals (a) monodentate, $[Cu(Asp)_2(py)_2]$ (b) bidentate chelate, $[Cd(nap)_2(EtOH)_2]$.[76]

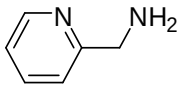
Zinc carboxylate compounds play important role in material chemistry, catalysis and biological systems. Polynuclear zinc carboxylate compounds are effective catalyst for epoxidecopolymerization reactions. The substituents on zinc caroxylate have influence on reactivity of these compounds.[77]

In previous studies cobalt(II) compounds explain anti-fungal and anti-microbial activities. The compound of the imidazole-2-carbaldehyde semicarbazone turned out to be active against yeasts C.tropicalis and S. cerevisiae. Activity was most noticeable against such phytopathogenic fungi as Alternaria or Sclerotinia.[78]

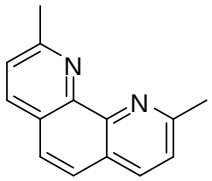
In the present work different bioactive nitrogen base compounds were chosen: **(a)** 2-aminopyridine (2-ampy); **(b)** 2-aminomehtylpyridine, (2-ammepy); **(c)** 2,9-dimethyl-1,10-phenanthroline, (2,9-dimephen) and **(d)** 1,10-phenanthroline, (1,10-phen) (Figure 1.12).



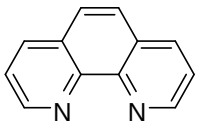
(a) 2-aminopyridine



(b) 2-aminomethylpyridine



(c) 2,9-dimethyl-1,10-phenanthrolin



(d) 1,10-phenanthrolin

Figure 1.12: Structures of nitrogen ligands.[79]

Sulindac,{(1Z)-5-fluoro-2-methyl-1-[4-(methylsulfinyl)benzylidene]-1H-indene-3-yl}acetic acid, in the form of potassium salt has a wide spectrum of activity as non-steroidal anti-inflammatory drug (NSAIDs). NSAIDs usually used as anti-pyretic agents, analgesic, and anti-inflammatory. The exact mechanism of NSAIDs is unknown, but thought through inhibition the cyclo-oxygenase (COX)-mediated production of prostaglandins.

The chemical classes of NSAIDs comprise phenylalkanoic acids, anthranilic acids, salicylate derivatives, oxicams, furanones and sulfonamides.[80] Sulindac belong to phenylalkanoic acids, are a potent NSAIDs for the treatment of inflammatory conditions, such as treating pain, fever and inflammation.

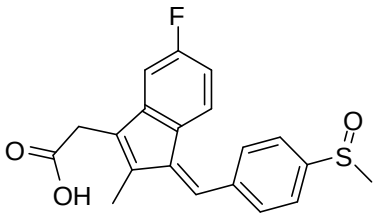


Figure 1.13: Sulindac structure.[81]

The transition metal coordination with NSAIDs caused many enhanced anti-inflammatory activity,[82-83] some compounds of NSAIDs coordinate with transition metals as have been synthesized and tested for their biological and pharmacological activity, the most transition metal that have been reported is Cu(II)-NSAIDs complexes.[84] Their characterization and crystal structure are available in literature,[85-90] such as $[Cu(diclofenac)_2(H_2O)]_2$ (Figure 1.14), $[Pd(diclofenac)_2].2H_2O$, [Cu(ibuprofen)$_2$2,9-dimephen], $[Fe(diclofenac)_2(H_2O)]$, $[Co(diclofenac)_2(H_2O)].2H_2O$, and $[Ni(diclofenac)_2(H_2O)].2H_2O$. Compounds of ibuprofen and diclofenac enhanced anti-inflammatory activity and act as anti-oxidant complexes, a property that is absent from ibuprofen and diclofenac.

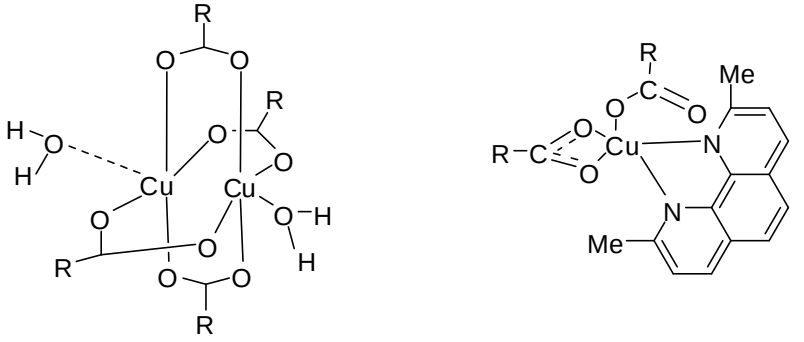


Figure 1.14: Structure of $[Cu(diclo)_2(H_2O)]_2$ on the left, and on the right the structure of [Cu(ibup)$_2$2,9-dimephen].[91]

1.5. Malaria disease

Malaria caused by a protozoan belongs to the genus plasmodium; it is borne parasitic disease through female anopheles mosquito, which is widely distributed in many tropical and subtropical regions of the world. The one of the major globally public health concerns is malaria. About 40% of the world's population is currently at risk of this disease killing millions of poor people in developing countries primarily African children. Four plasmodium species can infect humans, P. falciparum is the most severe form of the disease, causing 90% of the deaths while Plasmodium vivax is less widely spread, P. ovale is limited to tropical regions and P. malaria is the least common.[92]

Carrying malaria through female anopheles mosquito causes in feeding parasites on a human and inject the parasites in the human body in the form of sporozoites in the bloodstream. The sporozoites invade liver cells and within the hepatocyte, the intracellular parasites grow and divide resulting in the production of another form called merozoites, which exit in the liver cells and re-enter the bloodstream infecting red blood cells. This stage of blood infection known as the intra erythrocytic stage, merozoites undergo atrophic period that leads to the enlargement of the parasites and the formation of what is known as the ring stage.[93-94] During this stage, active metabolism including ingestion of the host cytoplasm and hemoglobin digestion by the parasite takes place. Hemoglobin digestion occurs within an acidic lysosome-like organelle with a pH of about (5.0-5.4) called the food vacuole.[95-96]

The parasite leads to digestion of hemoglobin, so continual liberation of Iron protoporphyrin IX- venomous free heme, Ferriprotoporphyrin IX formation. This can lead to damage of parasitized erythrocyte's membrane due to oxidative stress. However, malaria parasite develops an instantaneous detoxification mechanism of this Ferric form of heme, through its biomineralization into insoluble, inert, crystalline, black-brown pigment named hemozoin.[97] This stops the accumulation of toxic free heme, making this process crucial for the parasite's survival.

The dimers of hematin molecules that are bonding together through hydrogen bonding to produce the huge structure called hemozoin. The hematin contains in the center ferric iron, these iron links with oxygen from carboxylate group.[98-100]

Chloroquine is considered the most successful and widely used drug for malaria treatment. Nevertheless, in the early sixties resistance to chloroquine has emerged,[101-102] and considered a major universal challenging problem so a new effective anti-malarial drug has become urgently needed.

1.6. BNPP hydrolysis

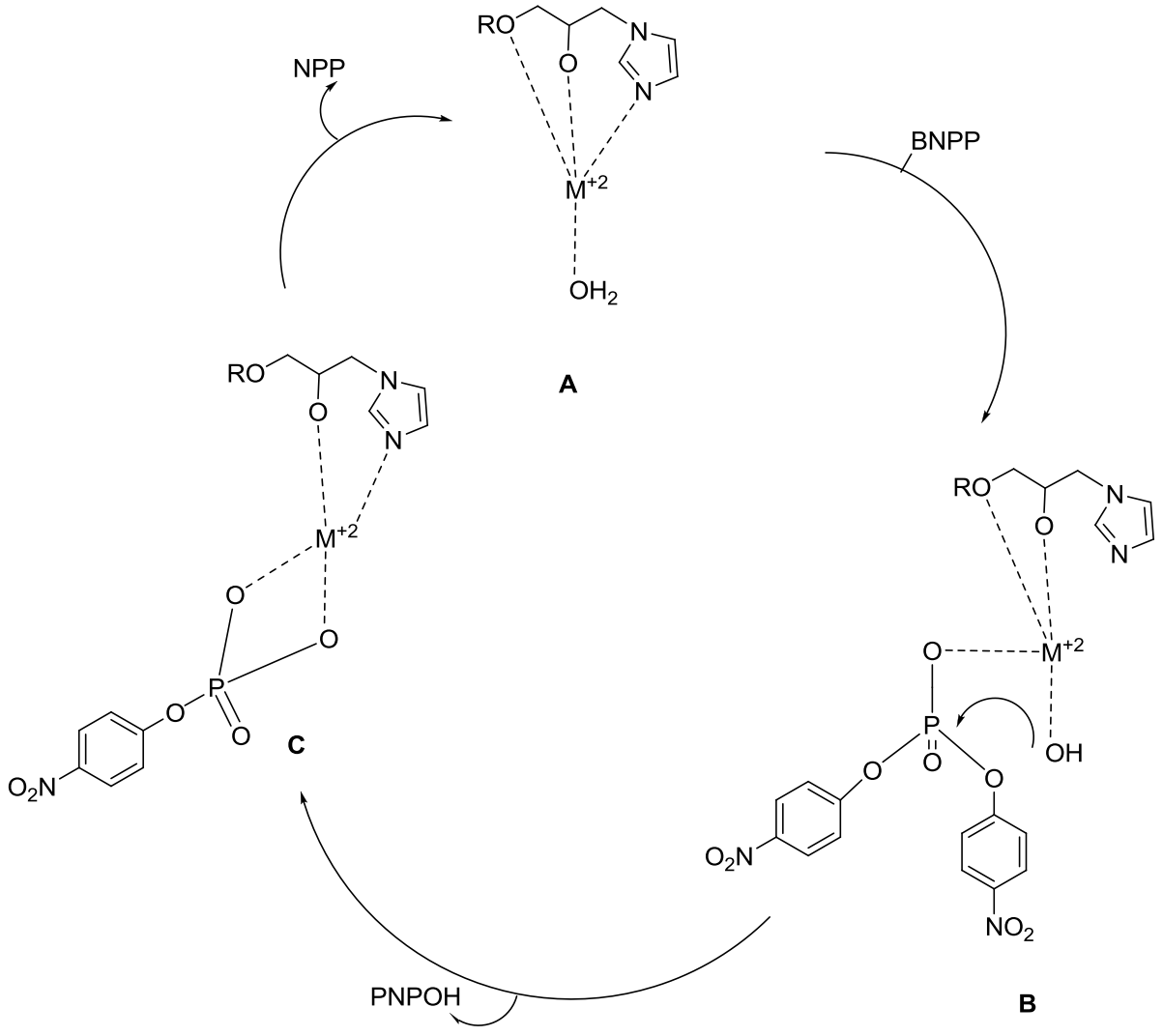
Metal can have many catalytic activity applications such as the hydrolysis of phosphate esters, and also in the detoxification of man-made phosphorous(V) toxin of some chemical weapons and pesticides. Actually the hydrolysis of these phosphate esters is very important in chemistry, biochemistry, also the mechanism of phosphodiester bond hydrolysis, both non-enzymatic and enzymatic, have been highly important for physical organic chemist.[103]

Different studies showed that the rate constant is first order and spontaneous reaction for the hydrolysis of a phosphodiesters bond under physiological conditions has been approximated to be $1*10^{-11}$ s^{-1} and $1*10^{-10}$ for double strand and single strand DNA respectively.[104]

These rates can be improved by pH and concentration of metal ions, controlling the temperature at 37 °C on a physiologically relevant time scale. BNPP; "bis(p-nitrophenyl)phosphate" is an example of these phosphate esters, this compound is distinctive because it has a very reactive leaving group (p-nitrophenol), and $k \approx 1.1*10^{-11}$ s^{-1} means easily hydrolyzed (by P-O bond cleavage) under mild conditions.[105]

In the last decades, the catalytic mechanisms were studied with different inorganic and organic catalysts for the hydrolysis of phospho-esters. Many studies explained that metal ions with variety of ligands could work as catalyst for the BNPP hydrolysis. There are different examples for these catalysts which are the modified crowned Schiff base complexes, i.e. the manganese(III) complexes that used to hydrolyze BNPP.[104,106]

Scheme **1** shows the suggested probable mechanism. In the first step, the metal complex **A** is formed, M^{+2} coordinates as octahedral geometry up to six donor ligands. Secondly, the ternary complex **B** is formed, which is the key step of hydrolysis. Thirdly, the transphosphorylation intermediate **C** is formed by apseudo-intramolecular nucleophilic attack of the activated hydroxyl ligand on the phosphoryl atom of the BNPP which results in the release of p-nitrophenol and the formation of a phosphorylated intermediate **C**. Finally, the intermediate **C** was cleaved, to release the NPP and the catalytic species regenerated by the attack of hydroxide ion from the coordinated ester group bound with the free or metal ion, thus defining the catalytic cycle.[104]



Scheme 1.1. Suggested mechanism for BNPP hydrolysis**.**[104]

1.7 Aim of the Project.

The main objectives of this research are to synthesize and characterize novel Co(II) and Zn(II) complexes that have new structural features and may possess effective biological activity i.e. anti-microbial, anti-malarial and hydrolysis. The compounds contain heterocyclic nitrogen based ligands with sulindac as carboxylate ligand. These compounds will be characterized using UV-visible spectroscopy, NMR, IR spectroscopy and X-ray structural analysis when possible.

In-vitro study of the anti-microbial activity, anti-malaria activity and the BNPP hydrolysis of the novel compounds will be performed.

2. Experimental

2.1 Reagents, biological species and chemicals

All chemicals and reagents used for the synthesis of the desired complexes were purchased from different commercial sources i.e. Sigma Aldrich and Fluka, and used without further purification. Biological species: *Escherichia coli, Staphylococcus Aureus, Staphylococcus epidermidis, Bordetella* and Yeast species*: Saccharomyces and candida* were kindly obtained from the Drugs Department at Central Public Health Laboratory.

2.2 Instrumentation

Melting points were determined by B-545 melt apparatus in capillary tube. Characterization by IR spectroscopy as KBr pellets in range 450-4000 cm^{-1} region by using Perkin Elmer FT-IR spectrometer (2004). UV-Vis spectra in DMSO in the 200–800 nm region was performed on a Hewlett Packard 8453 photo diode-array spectrometer. NMR spectra in DMSO at 75 MHZ for $^{13}C\{^{1}H\}$ measurements and at 400 MHz for ^{1}H measurements on a varian unity spectrometer operating. Me_4Si used as internal standard, the chemical shifts down field were given in ppm and coupling constants are given in Hz. The magnetic susceptibility measurements were determined by used Gouy method, mercury cobalt-thiocyanate complex, ($HgCo(NSC)_4$) as standard. Calculation of the effective magnetic moment was obtained by using the following**:** $\mu_{eff} = 2.83*(X_mT)^{1/2}$ (Molar susceptibility, X_m, and T is the temperature with K).

2.3 Synthesis and characterization of Zinc(II) compounds

All zinc(II) compounds were prepared at room temperature.

2.3.1 Zinc sulindac complex, $[Zn(sul)_2]$ (1)

Potassium hydroxide (0.84 g, 15 mmol), and sulindac (5.35 g, 15 mmol) in 75 ml of MeOH were mixed and dissolved. Then the solution was added with stirring to $ZnCl_2$ (1.02 g, 7.5 mmol) in 15 ml of MeOH, a yellow ppt formed and the reaction mixture was stirred for additional 12 h. The ppt was then filtered, washed with cold water and air dried to give 4.81 g of solid product.

M.p. 240 ˚C; Yield 75%; IR (KBr, cm^{-1}): 3444, 3056, 3018, 2983, 2938, 2915, 1644, 1601, 1587, 1538, 1464, 1421, 1396, 1367, 1334, 1320, 1299, 1268, 1233, 1203, 1165, 1137, 1088, 1054, 1012, 985, 968, 946, 917, 892, 853, 823, 813, 704, 670, 656, 602, 569, 545, 532, 507, 481, 444; ^{1}H-NMR (DMSO, δ): 2.11 (s, 6H, $2CH_3$), 2.80 (s, 6H, $2CH_3$), 3.38 (s, 4H, $2CH_2$), 6.63 (t, 2H, 2CH, $^{3}J_{H-H}$ = 10.0 Hz), 6.98 (d, 2H, 2CH, $^{3}J_{H-H}$ = 12.0 Hz), 7.10 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8 Hz), 7.27 (s, 2H, 2CH), 7.69 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz), 7.75 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz); ^{13}C{^{1}H}-NMR (DMSO, δ): 10.69 ($2CH_3$), 33.73 ($2CH_2$), 43.53 ($2CH_3$), 106.73 (2CH), 110.35 (2CH), 123.33 (CH), 124.32 (4CH), 128.81 (4CH), 129.99 (2CH), 130.38 (2C), 131.24 (2CH), 135.68 (2CH), 139.22 (2C), 141.24 (2C), 146.39 (2C), 161.71 (2C), 175.03 (2C=O); UV-Vis (DMSO, λ (nm), (ϵ/$Lmol^{-1}cm^{-1}$): 213 (3000), 284 (400), 328 (288).

2.3.2 Zinc sulindac 2-amino pyridine complex, $[Zn(Sul)_2$ 2-ampy] (2)

Potassium hydroxide (0.47 g, 8.4 mmol) and sulindac (3.0 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, then the solution was added to $ZnCl_2$ (0.57 g, 4.2 mmol) in 10 ml of MeOH, then 2-ampy (0.79 g, 8.4 mmol) was dissolved in 15 ml MeOH was added, a yellow ppt formed and the reaction mixture was stirred for additional 24 h, then the ppt was filtered, washed with cold water and then air dried to give 4.01 g of solid product.

M.p. 205 ˚C; Yield 83%; IR (cm^{-1}, KBr): 3412, 3262, 3065, 2913, 1602, 1588, 1486, 1463, 1438, 1391, 1360, 1292, 1262, 1194, 1164, 1138, 1089, 1032, 1014, 957, 915, 857, 852, 761, 716, 702, 655, 594, 566, 541, 447, 411; ^{1}H-NMR (DMSO, δ): 2.17 (s, 6H, $2CH_3$), 2.77 (s, 6H, $2CH_3$), 3.47 (s, 4H, $2CH_2$), 4.74 (s, 2H, NH_2), 6.55 (t, 2H, 2CH, $^{3}J_{H-H}$ = 10.0Hz), 6.99 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8.0 Hz), 7.17 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8 Hz), 7.27 (s, 2H, 2CH), 7.42 (t, 1H, CH_{py}), 7.55 (d, 1H, $2CH_{py}$, $^{3}J_{H-H}$ = 8 Hz), 7.72 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz), 7.79 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz), 7.97 (t, 1H, CH_{py}), 8.68 (d, 1H, CH_{py}); ^{13}C{^{1}H}-NMR (δ, DMSO): 10.66 ($2CH_3$), 33.95 ($2CH_2$), 43.53 ($2CH_3$), 106.80 (2CH), 110.39 (2CH), 110.55 (CH_{py}),123.12 (CH_{py}), 123.31 (2CH), 124.33 (4CH), 128.75(4CH), 129.94 (2CH), 130.36 (2C), 135.74 (2CH), 136.55 (2CH), 139.21 (2C), 139.73 (CH_{py}), 141.23 (2C), 146.40 (2C), 148.33(CH_{py}), 157.98 (2C), 161.67 (C-NH_2), 175.05 (2C=O); UV-Vis (DMSO, λ (nm), (ϵ/$Lmol^{-1}cm^{-1}$): 210 (3216), 289 (472), 327 (334).

2.3.3 Zinc sulindac 2-amino methyl pyridine complex, [Zn(Sul)$_2$ 2-ammepy] (3)

Potassium hydroxide (0.47 g, 8.4 mmol) and sulindac (3.0 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, then the solution was added to $ZnCl_2$ (0.57 g, 4.2 mmol) in 10 ml of MeOH, then 2-ammepy (0.866 ml, 8.4 mmol) dissolved in 10 ml MeOH was added, a yellow ppt formed and the reaction mixture was stirred for additional 24 h. The solution was left to evaporate in air then extracted with dichloromethane and washed with water, the organic layer was dried using magnesium sulfate as drying agent. After filtration petroleum ether was added to give 3.01 g of a yellow solid product.

M.p. 146 ˚C; Yield 75%; IR (cm^{-1}, KBr): 3438, 3354, 3208 ,3013, 2911, 2850, 1646, 1597, 1573, 1541, 1494, 1466, 1445, 1414, 1372, 1335, 1267, 1199, 1161, 1133, 1084, 1030, 1009, 960, 918, 894, 850, 826, 805, 765, 737, 716, 655, 624, 590, 559, 534, 440; ^{1}H-NMR (DMSO, δ): 2.12 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 3.53 (s, 2H, CH_2), 4.63 (s, 2H, CH_{2me}), 5.29 (s, H, NH), 6.43 (d, 1H, CH_{py}, $^3J_{H-H}$ = 8.0 Hz), 6.49 (t, 1H, CH_{py}), 6.51 (t, 1H, CH, $^3J_{H-H}$ = 10.0 Hz), 6.99 (d, 1H, CH, $^3J_{H-H}$ = 8.0 Hz), 7.08 (d, 1H, CH, $^3J_{H-H}$ = 8 Hz), 7.26 (s, 1H, CH), 7.41 (t, 1H, $CH_{py,}$ $^3J_{H-H}$ = 7.0 Hz), 7.6 (d, 1H, $2CH_{py}$, $^3J_{H-H}$ = 8 Hz), 7.70 (d, 2H, 2CH, $^3J_{H-H}$ = 8 Hz), 7.76 (d, 1H, $CH_{py,}$ $^3J_{H-H}$ = 8.0 Hz); ^{13}C{^{1}H}-NMR (DMSO, δ): 10.68 (CH_3), 33.88 (CH_2), 43.52 (CH_3), 106.70 (CH), 110.23 (CH), 110.57 (CH_{py}),123.24 (CH_{py}), 123.37 (CH), 124.33 (2CH), 128.79 (2CH), 129.97 (CH), 130.38 (C), 135.61 (CH), 136.68 (CH), 138.10 (C), 139.23 (CH_{py}), 141.24 (C), 146.33 (C), 148.23 (CH_{py}), 160.01 (C-CH_2), 161.72 (C), 174.92 (C=O); UV-Vis (DMSO, λ (nm), (ϵ/$Lmol^{-1}cm^{-1}$)): 211 (2500), 261 (470), 286 (350), 328 (300).

2.3.4 Zinc sulindac 1,10-phenanthroline,[Zn (sul)$_2$(1,10 phen)] (4)

Potassium hydroxide (0.47 g, 8.4 mmol) and sulindac (3.0 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, then the solution was added to $ZnCl_2$ (0.57 g, 4.2 mmol) in 10 ml of MeOH, then 1,10-phenanthroline (0.756 g, 4.2 mmol) dissolved in 15 ml MeOH was added, an orange ppt formed and the reaction mixture was stirred for additional 24 h. The solution was evaporate in air then extracted with dichloromethane and water (using magnesium sulfate as drying agent), after that the dichloromethane was evaporated and crashed with petroleum ether; filtration gave 3.28 g of yellow solid product. Recrystallization from 1:1 acetone: acetonitrile gave crystals suitable for X-ray determination.

M.p. 165 ˚C; Yield 76%; IR (cm^{-1}, KBr): 3419, 3056 , 2911, 2852, 1723, 1716, 1602, 1520, 1428, 1398, 1379, 1269, 1199, 1166, 1140, 1093, 1032, 1011, 957, 894, 850, 817, 772, 726, 657, 620, 594, 536, 442, 423; ^{1}H-NMR (DMSO, δ): 2.16 (s, 6H, $2CH_3$), 2.80 (s, 6H, $2CH_3$), 3.58 (s, 4H, $2CH_2$), 6.42 (t, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 10.0 Hz), 6.75 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 10.0Hz), 7.04 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 8 Hz), 7.26 (s, 2H, 2CH), 7.61 (d, 4H, 4CH, $^{3}J_{H\text{-}H}$ = 8Hz), 7.68 (d, 4H, 4CH, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.80 (t, 1H, $2CH_{phen}$, $^{3}J_{H\text{-}H}$ = 10.0 Hz), 7.96 (s, 1H, $2CH_{phen}$), 8.47 (d, H, $2CH_{phen}$, $^{3}J_{H\text{-}H}$ = 16.0 Hz), 9.16 (d, H, $2CH_{phen}$, $^{3}J_{H\text{-}H}$ = 4.0 Hz); ^{13}C{^{1}H}-NMR (DMSO, δ): 10.51 ($2CH_3$), 32.56 ($4CH_2$), 43.85 ($4CH_3$), 106.03 (4CH), 110.23 4CH), 123.77 ($2CH_{phen}$), 125.32 (2CH), 126.80 (2CH), 127.22 ($2CH_{phen}$), 128.73 (2CH), 129.49 ($2C_{phen}$), 130.252 (2CH), 134.96 (2CH), 134.15 (CH), 137.06 ($2CH_{phen}$), 139.09 (2C), 140.05 (2C), 145.07(2C), 147.43 ($2C_{phen}$), 150.17 ($2CH_{phen}$), 161.59 (2C), 178.11 (2C=O); UV-Vis (DMSO, λ (nm), (ϵ/$Lmol^{-1}cm^{-1}$)): 206 (1838), 226 (863), 272 (651), 328 (303).

2.3.5 Zinc sulindac 2,9-dimethyl-1,10-phenanthroline,[$Zn(sul)_2$(2, 9-dimephen)] (5)

Potassium hydroxide (0.47 g, 8.4 mmol) and sulindac (3.0 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, the solution was added to $ZnCl_2$ (0.57 g, 4.2 mmol) in 10 ml of MeOH, then 2,9-dimethyl-1,10-phenanthroline (0.875 g, 4.2 mmol) dissolved in 10 ml MeOH was added, an orange ppt was formed and the reaction mixture was stirred for additional 24 h, the orange ppt was then filtered, washed with cold water and air dried to give 4.55 g of solid product. Recrystallization from 1:1 mixture of chloroform: acetonitrile gave crystals suitable for X-ray determination.

M.p. 170 ˚C (decomposed); Yield 95%; IR (cm^{-1}, KBr): 3418, 3061 , 2908, 1599, 1503, 1468, 1381, 1365, 1297, 1271, 1186, 1172, 1156, 1083, 1037, 1008, 957, 920, 892, 857, 817, 782, 737, 728, 665, 629, 589, 552, 540, 494, 435; ^{1}H-NMR (DMSO, δ): 2.14 (s, 6H, $2CH_3$), 2.79 (s, 6H, $2CH_3$), 3.09 (s, 6H, $2CH_{3phen}$), 3.48 (s, 4H, $2CH_2$), 6.40 (t, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 10.0 Hz), 6.78 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.01 (d, 21H, 2CH, $^{3}J_{H\text{-}H}$ = 8 Hz), 7.07 (s, 2H, 2CH), 7.54 (d, 4H, 4CH, $^{3}J_{H\text{-}H}$ = 12.0 Hz), 7.63 (d, 4H, 4CH, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.60 (d, 1H, $2CH_{phen}$, $^{3}J_{H\text{-}H}$ = 10.0 Hz), 7.82 (s, 1H, $2CH_{phen}$), 8.32 (d, H, $2CH_{phen}$, $^{3}J_{H\text{-}H}$ = 16.0 Hz); ^{13}C{^{1}H}-NMR (DMSO, δ): 10.49 ($2CH_3$), 24.76 (CH_{3phen}), 33.30 ($2CH_2$), 43.85 ($2CH_3$), 106.16 (2CH), 110.1 (2CH), 123.68 ($2CH_{phen}$), 125.72 (2CH), 126.36 (2CH), 127.04 ($2CH_{phen}$), 129.73 (2CH), 130.22 (2CH), 134.96 (2CH), 136.47 (2CH), 136.47 ($2C_{phen}$), 139.16 (2C), 140.29 (2C), 142.2 ($2C_{phen}$), 144.9 (2C), 147.73 ($2C_{phen}$), 161.85 (2C), 177.18 (2C=O); UV-Vis (DMSO, λ (nm), (ϵ/$Lmol^{-1}cm^{-1}$)): 207 (2000), 227 (642), 274 (424), 330 182).

2.4 Synthesis and characterization of cobalt(II) complexes

All cobalt(II) complexes were prepared at room temperature.

2.4.1 Cobalt sulindac, $[Co(sul)_2(H_2O)_4]$ (6)

Sulindac (3.0 g, 8.4 mmol) and potassium hydroxide (0.47 g, 4.2 mmol) in 75 ml of MeOH were mixed until dissolved, then the solution was added with stirring to $CoCl_2.7H_2O$ (1.0 g, 4.2 mmol) in 15 ml of MeOH, a yellow ppt was formed and the reaction mixture was stirred for additional 24 h. The yellow ppt was then filtered, washed with cold water and air dried to give 3.81 g of solid product. Single crystals suitable for X-ray determination were obtained by recrystallization from MeOH.

M.p. 201°C; Yield 85%; IR (cm^{-1}, KBr): 3376, 3050, 2911, 2850, 1600, 1563, 1485, 1465, 1416, 1369, 1326,1268, 1217, 1203, 1171, 1133, 1086, 1024, 1008, 967, 918, 891, 891, 868, 805, 776, 717, 672, 659, 572, 473;UV-Vis (DMSO, λ (nm)(ϵ/$Lmol^{-1}cm^{-1}$)): 211 (3283), 258 (872), 264 (850), 252 (828), 282 (771), 328 (514); μ_{eff} = 2.26 BM .

2.4.2 Cobalt sulindac 2-amino pyridine complex, $[Co\ (Sul)_2$ 2-Ampy] (7)

Potassium hydroxide (0.47 g, 8.4 mmol) and sulindac (3.0 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, then the solution was added to $CoCl_2.7H_2O$ (1.0 g, 4.2 mmol) in 10 ml of MeOH, then 2-Ampy (0.79 g, 8.4 mmol) dissolved in 15 ml MeOH was added, an orange ppt was formed and the reaction mixture was stirred for additional 24 h. The solution was evaporated in air then product was extracted with dichloromethane and water (using magnesium sulfate as drying agent).The dichloromethane was evaporated and the solid product was washed with petroleum ether. The product was filtered to give 2.5 g of solid product.

M.p. 180 °C (Decomposed); yield 56%; IR (cm^{-1}, KBr): 3374, 3268, 3015, 2914, 2860, 1599, 1515, 1494, 1464, 1424, 1380, 1267, 1195, 1164, 1137, 1086, 1031, 1010, 955, 915, 891, 846, 811, 727, 651, 593, 533, 474, 449; UV-Vis (DMSO, λ (nm); (ϵ/$Lmol^{-1}cm^{-1}$)): 207 (1828), 286 (450), 329 (348), 655 (12.7); μ_{eff} = 2.41 BM.

2.4.3 Cobalt sulindac 1,10-phenanthroline,[Co (sul)$_2$(1,10 phen)] (8)

Sulindac (3.0 g, 8.4 mmol) and potassium hydroxide (0.47 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, then the solution was added to $ZnCl_2$ (0.57 g, 4.2 mmol) in 10 ml of MeOH, then 1,10-phenanthroline (0.756 g, 4.2 mmol) dissolved in 10 ml MeOH was added, an orange ppt formed and the reaction mixture was stirred for additional 24 h. The solution was evaporated in air then the product was extracted with dichloromethane and water (using magnesium sulfate as drying agent).The dichloromethane was evaporated and the solid product was washed with petroleum ether. The product was filtered to give 1.0 g of solid product.

M.p.140 $^{\circ}$C; Yield 22%; IR (cm^{-1}, KBr): 3415, 3059, 2911, 2852, 1600, 1515, 1464, 1424, 1380, 1267, 1195, 1164, 1137, 1086, 1010, 956, 915, 891, 846, 811, 727, 651, 593, 533, 474, 441; UV-Vis (DMSO, λ (nm) (ϵ/$Lmol^{-1}cm^{-1}$)): 208 (2152), 226 (700), 271 (535), 328 (224), 431 (16.3), 488 (13.2); μ_{eff} = 2.4BM.

2.4.4 Cobalt sulindac 2,9-dimethyl-1,10-phenanthroline, [Co(sul)$_2$(2,9-1,10-phen)] (9)

Potassium hydroxide (0.47 g, 8.4 mmol) and sulindac (3.0 g, 8.4 mmol) in 40 ml of MeOH were mixed and dissolved, then the solution was added to $ZnCl_2$ (0.57 g, 4.2 mmol) in 10 ml of MeOH, then 2, 9- dimethyl-1,10-phenanthroline (0.875 g, 4.2 mmol) dissolved in 15 ml MeOH was added, an orange ppt was formed and the reaction mixture was stirred for additional 24 h. The green ppt was filtered, washed with cold water and air dried to give 1.54 g of solid product. Single crystals suitable for X-ray determination were obtained by recrystallization from 1:1 mixture of chloroform: acetonitrile.

M.p. 150 $^{\circ}$C (decompose); Yield 34%; IR (cm^{-1}, KBr): 3040, 2912, 2845, 1599, 1566, 1465, 1441, 1359, 1194, 1157, 1135, 1086, 1031, 954, 916, 891, 855, 812, 761, 728, 644, 533, 474; UV-Vis (DMSO, λ (nm) (ϵ/$Lmol^{-1}cm^{-1}$)): 207 (2263), 229 (933), 274 (621), 328 (261), 432 (13.3); μ_{eff} = 2.4 BM.

2.5 X-ray crystallography

Single crystals suitable for X-ray structure were obtained for complexes **(4)**, **(5)**, **(6)** and **(9)**.Single crystal was attached to a glass fiber by epoxy glue, and transported to an X-ray diffractometer system (Bruker SMART APEX CCD), controlled by (SMART-NT V5.6, Bruker AXS GMBH, Karlsruhe, Germany) Pentium-based PC running the SMART software package. A three-circle goniometer was mounted the crystal with χ fixed at +54.76°. The (Mo Kα radiation λ = 0.71073 A) diffracted graphite-monochromated was detected on a phosphor screen the crystal operating at -43 °C and held at a distance of 6.0 cm from the crystal. A detector array of 512 X 512 pixels, with a pixel size of about 120 μm, was worked to collect data. Calibration centroid of detector and detector-to-crystal distance by used a least-squares analysis of the unit cell parameters from a carefully centered YLID reference crystal.

The crystal of the compound centered within the X-ray beam, after that a series of 30 data frames measured at 0.3° for calculation a preliminary unit cell and to assess the overall crystal quality through increases of ω were collected with three variant φ and θ values. To collect the intensity data, put the detector at a θ value of -28° and the intensity images were measured at 0.3° intervals of ω for duration of 20 sec.

Directly after collection, the raw data frames were transported to another PC computer to integrate by the (SAINT-NT V5.0, BRUKER AXS GMBH, Karlsruhe, Germany) SAINT program package. The background frame information was updated according to the equation B’ = (7B+C)/8, where B is the background pixel value before updating, B’ is the update pixel value, and C is the pixel value in the current frame. The integration was also corrected for distortion induced by the detector. The structure was refined and solved by the (SHELXTL-NT V6.1, BRUKER AXS GMBH, Karlsruhe, Germany) SHELXTL software package. More details about crystal data collections and refinements are summarized in Tables 2.1 & 2.2.

Table 2.1: Structure refinement and crystal data for compounds **(4)** and (**5**).

	Complex **(4)**	Complex **(5)**
Empirical formula	C52 H40 F2 N2 O6.50 S2 Zn	C54 H44 F2 N2 O10.50 S2 Zn
Formula weight	964.35	1056.40
Wavelength	0.71073 Å	0.71073 Å
Temperature	295(1) K	173(1) K
Space group	P2(1)/c	P-1
Crystal system	Monoclinic	Triclinic
Unit cell dimensions	a = 21.330(3) Å α = 90°.	a = 12.390(1) Å α = 109.177(2)°.
	b = 10.609(2) Å β = 104.673°.	b = 13.191(1) Å β = 96.538(2)°.
	c = 20.666(3) Å γ = 90°.	c = 17.252(2) Å γ = 101.702(2)°.
Volume	4523.6(1) $Å^3$	2557.6(4) $Å^3$
Z	4	2
Absorption coefficient	0.699 mm^{-1}	0.630 mm^{-1}
Density (calculated)	1.416 Mg/ m^3	1.372 Mg/m^3
Crystal size	0.40 x 0.40 x 0.08 mm^3	0.32 x 0.20 x 0.10 mm^3
F(000)	1992	1092
Reflections collected	48956	28360
Theta range for data collection	2.03 to 27.00°.	1.71 to 27.00°.
Index ranges	-27<=h<=27, -13<=k<=13, -26<=l<=26	-15<=h<=15, -16<=k<=16, -22<=l<=22
Completeness to theta = 26.99°	99.9 %	98.7 %
Independent reflections	9886 [R(int) = 0.0950]	11005 [R(int) = 0.0419]
Max. and min. transmission	0.9462 and 0.7675	0.9121 and 0.6514
Absorption correction	Semi-empirical from equivalents	multi-scan
Data / restraints / parameters	9886 / 0 / 599	11005 / 0 / 691
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Largest diff. peak and hole	0.951 and -0.890 e.$Å^{-3}$	1.241 and -0.786 e.$Å^{-3}$
Goodness-of-fit on F^2	1.171	1.210
R indices (all data)	R1 = 0.1644, wR2 = 0.2750	R1 = 0.1266, wR2 = 0.2525
Final R indices [a] [I>2sigma(I)]	R1 = 0.1219, wR2 = 0.2523	R1 = 0.1091, wR2 = 0.2422

a: $R1 = \Sigma||F_o|-|F_c|| / \Sigma F_o$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table 2.2: Structure refinement of crystal data for compounds **(6)** and **(9)**.

	Complex **(6)**	Complex **(9)**
Empirical formula	C40 H34 Co F2 O12 S2	C53 H38 Co F2 N2 O5 S2
Formula weight	867.72	943.90
Wavelength	0.71073 Å	0.71073 Å
Temperature	295(1) K	295(1) K
Space group	P-1	P2(1)/c
Crystal system	Triclinic	Monoclinic
Unit cell dimensions	a = 5.012(3) Å α = 81.85(1)°.	a = 20.930 (3) Å α= 90°.
	b = 12.640(8) Å β = 82.230(9)°.	b = 14.836(2) Å β= 101.705°.
	c = 16.22(1) Å γ = 86.40(1)°.	c =15.807(2) Å γ = 90°.
Volume	1006.9(11) $Å^3$	4806.3(11) $Å^3$
Z	1	4
Absorption coefficient	0.601 mm^{-1}	0.500 mm^{-1}
Density (calculated)	1.431Mg/ m^3	1.304 Mg/m^3
Crystal size	0.50 x 0.16 x 0.06 mm^3	0.53 x 0.46 x 0.05 mm^3
F(000)	447	1948
Reflections collected	10787	52864
Theta range for data collection	2.56 to 27.00°.	1.69 to 27.00°.
Index ranges	-6<=h<=6, -16<=k<=16, -20<=l<=20	-26<=h<=26, -18<=k<=18, -20<=l<=19
Completeness to theta = 26.99°	98.5 %	99.7 %
Independent reflections	4334[R(int) = 0.0625]	10468 [R(int) = 0.0766]
Absorption correction	None	None
Data / restraints / parameters	4334 / 0 / 273	10468 / 0 / 603
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Largest diff. peak and hole	1.331 and -0.664 e.$Å^{-3}$	2.147 and -0.686 e.$Å^{-3}$
Goodness-of-fit on F^2	1.210	1.576
R indices (all data)	R1 = 0.1355, wR2 = 0.2727	R1 = 0.2349, wR2 = 0.4718
Final R indices [a] [I>2sigma(I)]	R1 = 0.1158, wR2 = 0.2599	R1 = 0.1941, wR2 = 0.4496

a: $R1 = \Sigma||F_o|-|F_c|| / \Sigma F_o$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2 \}^{½}$

2.6 Anti-bacterial activity

Agar diffusion method[107]was used for screening the antibacterial activity of the synthesized zinc complexes. Different types of gram-negative bacteria (*Bordetella, Escherichia coli*) and gram-positive (*Staphylococcus epidermidis*, *Staphylococcus aureus*) and Yeast species (*Saccharomyces and Candida*) were used in this study.

In sterile saline single bacterial colonies was dissolved until the suspended cells reached the turbidity of McFarland 0.5 Standard. The bacterial inocula were spread on the surface of the Muller Hinton nutrient agar by means of a sterile cotton swab. Sterile glassy borer were used to make a 6 mm in diameter wells in the agar plate. Samples were dissolved in DMSO in concentration equal to (8 mg/ml), (4 mg/ml) and (2 mg/ml), then 50 µL of the test samples were introduced in the respective wells. DMSO was used as negative control while gentamycin used as positive control. Immediately the plate was incubated at 37 °C for 24 h. The anti-bacterial activity was determined by measuring the diameter inhibition zone of complete growth in millimeter (mm). The averages of two trials determined the results and are stated as average ± standard deviation.

2.7 Anti-malarial activity

2.7.1 Semi-quantitative method

Semi-Quantitative method [108] was used for *in vitro* testing the anti-malarial activity of the synthesized zinc complexes according to Deharo et.al.[109] In a non-sterile flat bottom normal 96-well plate put a mixture containing freshly 50 µL of (0.5 mg/ml) hemin chloride dissolved in (DMSO), 100µL of (0.5 M) sodium acetate buffer (pH 4.4), and 50 µL of variant concentrations of the compounds dissolved in pure water at 37 ºC was incubated for 18-24 h, then the plate was centrifuged at 4000 rpm for 10 min. The supernatant was removed and the pH of mixture was measured. The final pH of the reaction was between (5.0-5.2). Free hemin chloride was removed by washing the wells with 200 µL DMSO per well. The plate was centrifuged again and the supernatant was removed. The residual β –hematin was dissolved in 200 µL of 0.1 M NaOH to form an FP that spectrophotometrically can be measured. The absorbance was measured at 405 nm using ELISA reader Note. Chloroquine dissolved in ultra-pure water was used as positive control and ultra-pure water as negative control.

2.7.2 Quantitative test

Quantitative tests were performed according to Akkawi and Blauer method.[110] Freshly prepared stock solution of hemin chloride was incubated the dissolved salt in (DMSO) at 30°C for 30 min, stock solution of the complex was prepared using DMSO, and also sodium acetate buffer (0.5 M) (pH 4.4) was prepared. The final concentration of the complex and hemin in the mixture were 0.4 and 0.2 mM, respectively. The whole reaction mixture at 37 °C for 18-24 h without stirring. The final pH was 4.9 to 5.2, and the total volume of the whole mixture was 32 ml. After that, the mixture was centrifuged for 10 min using a serological (Jouan B4). The supernatant was discarded and was washed the precipitate by DMSO. The precipitates transferred quantitatively to a Millipore Swinnex 13 Whatman filter paper No. 50, then lyophilized to a constant weight in (Labconco Freezone) freeze-drying machine. The DMSO was passed slowly through the filter until the filtrate remained feebly colored and washed again with ultra-pure water. The remaining sample was then lyophilized to a constant weight.

2.8 BNPP hydrolysis

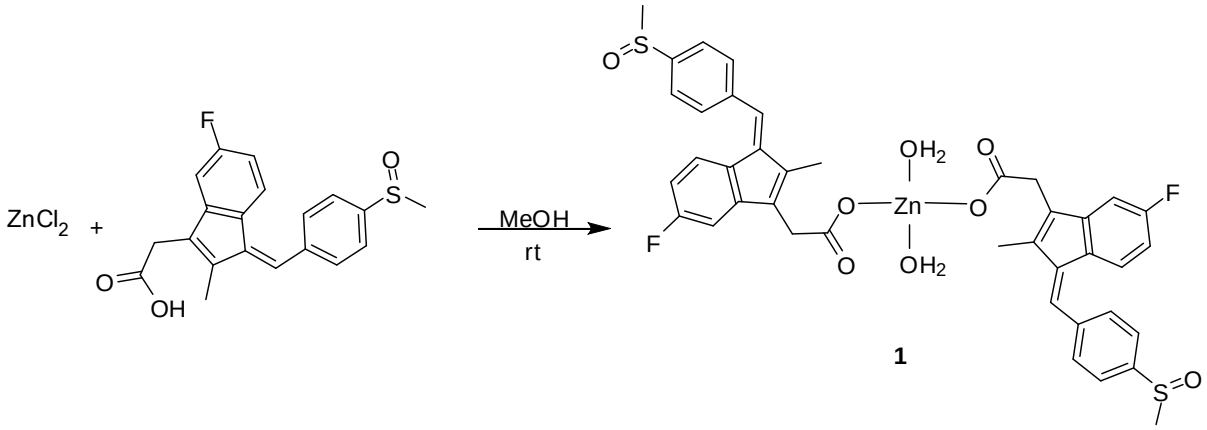
HEPES "4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid") buffers were prepared at pH 7.4 with concentration of 50 µM by dissolving the desired amount in minimum amount of deionized water then controlling the pH to 7.4 and the volume was adjusted to 100 ml. BNPP was dissolved in the prepared buffer to obtain a certain concentration of $1.0x10^{-4}$ M solution.

After that, $2.0x10^{-4}$ M solutions of each complex was prepared using methanol as solvent (the best solvent for BNPP analysis), then the two solutions were mixed in a quartz cell at 37 ºC, kinetic data were used to measure the rate of release of p-nitophenol using UV-Vis spectrophotometer at λ = 400 nm and an extinction coefficient of 13400 $Lmol^{-1}cm^{-1}$. A 1.0 ml of BNPP solution was added to 1.0 ml of the desired complex in a quartz cell at constant temperature of 37 ºC, and the UV-Vis spectra of the sample were directly measured. The kinetic data of the interested compounds were collected. The concentration effect of BNPP solution on the hydrolysis process was measured by preparing 10^{-4}, 10^{-5} and 10^{-6} M solutions and the rate of hydrolysis was calculated.

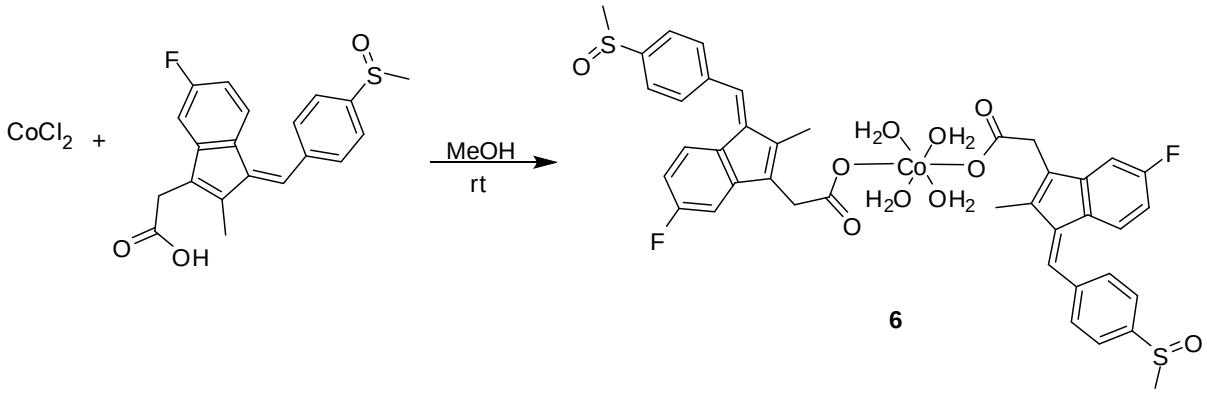
3. Results and discussion

3.1 Synthesis of Co(II) and Zn(II) complexes

Zinc sulindac and cobalt sulindac were prepared at ambient condition by simple reaction of 1 equivalent of $ZnCl_2$ or $CoCl_2$ with 2 equivalents of potassium sulindac in methanol to give $[Zn(sul)_2(H_2O)_2]$ **(1)** and $[Co(sul)_2(H_2O)_4]$ **(6)**, Scheme 3.1and Scheme 3.2, respectively. The complexes were obtained as solid products in different yields; their physical properties were determined and listed in Table 3.1.

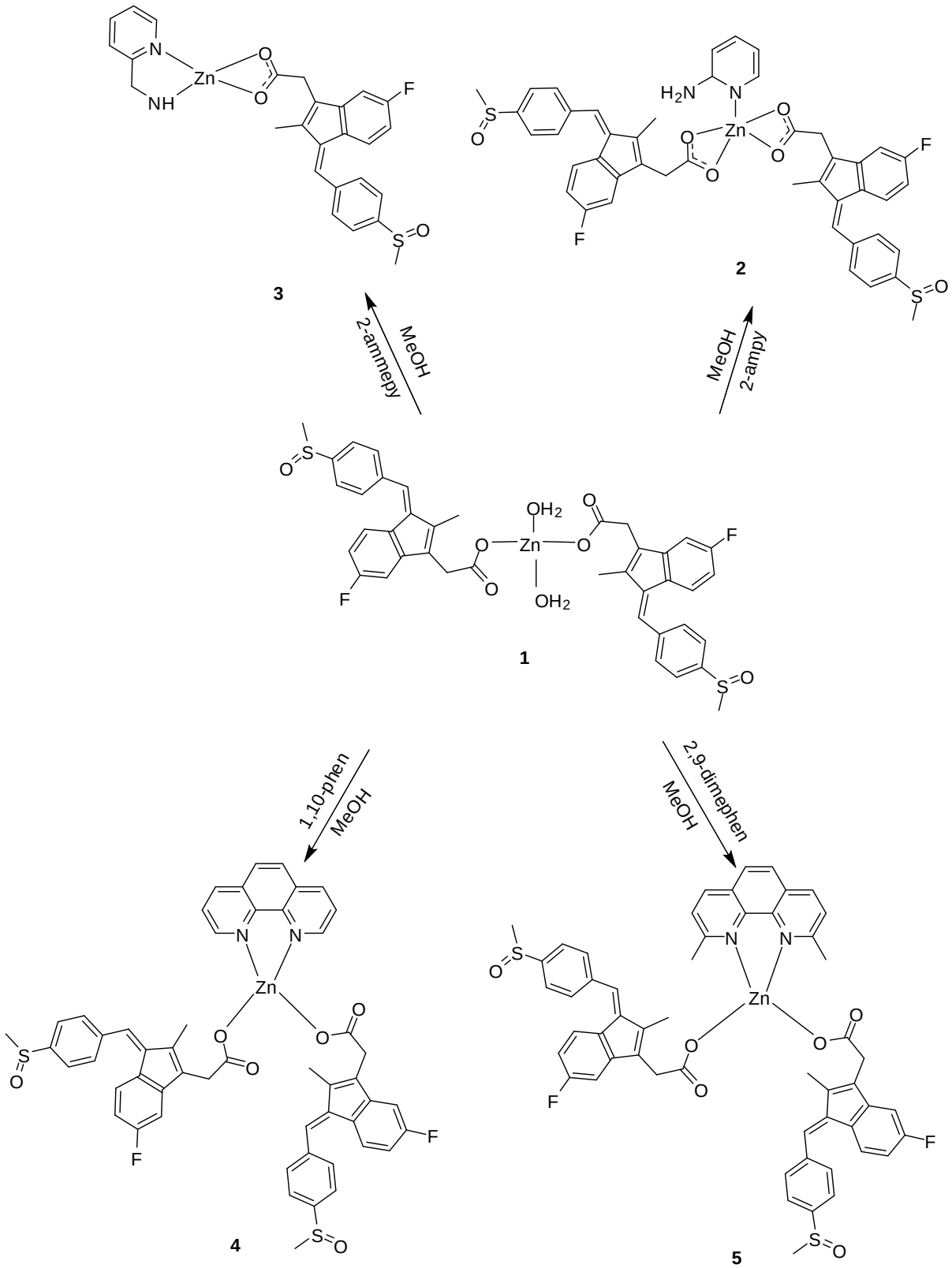


Scheme 3.1 Synthesis of complex (**1**) $[Zn(sul)_2.2H_2O]$, proposed structure

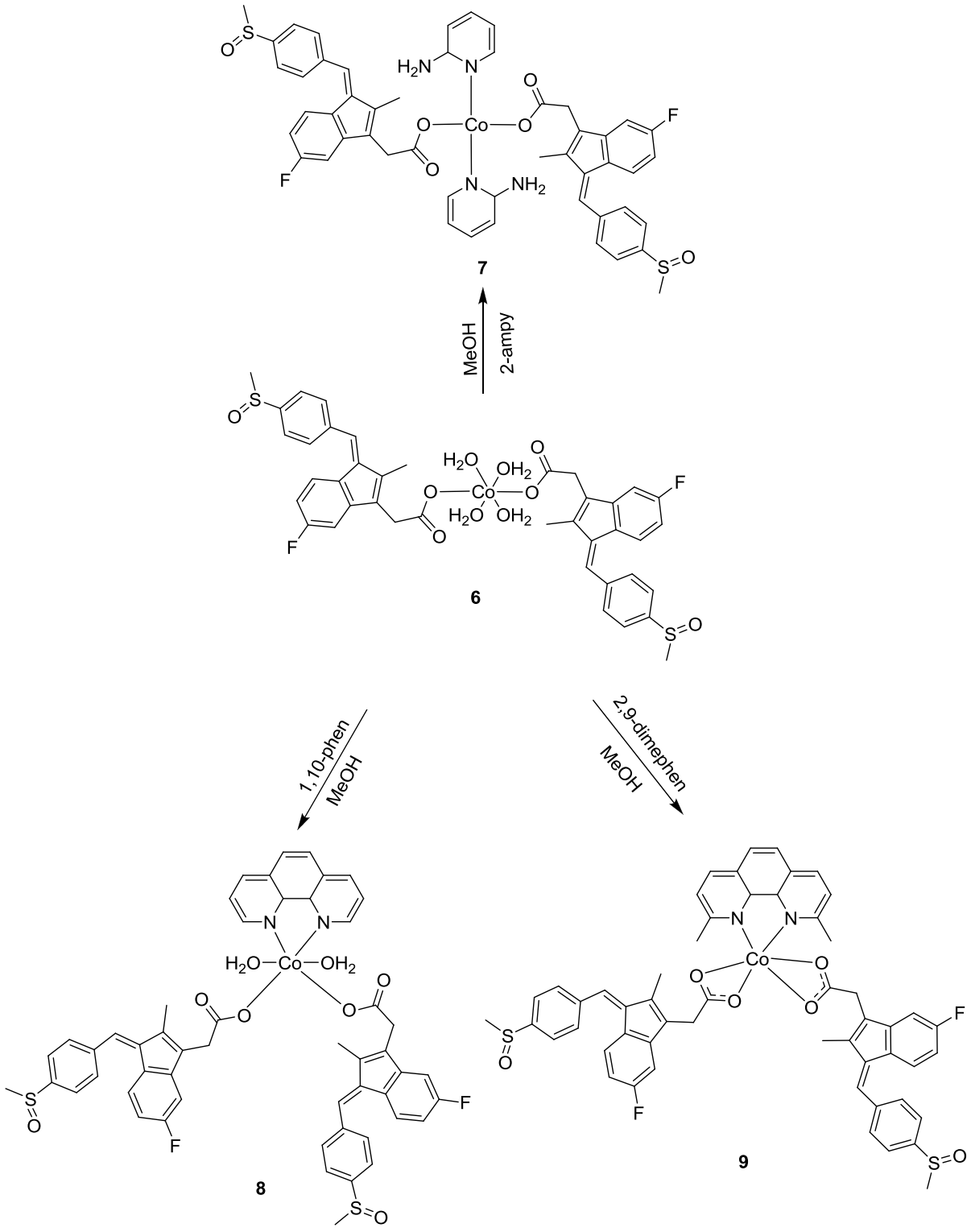


Scheme 3.2. Synthesis of complex (**6**), $[Co(sul)_2.4H_2O]$

Mixed zinc or cobalt sulindac complexes with different nitrogen donor ligands were synthesized and their proposed structures are shown in Scheme 3.3 and Scheme 3.4.



Scheme 3.3. Synthesis of zinc(II) complexes, proposed structures.



Scheme 3.4. Synthesis of cobalt(II) complexes, proposed structures.

Table 3.1: Physical properties and yield of Zinc(II) sulindac and Cobalt(II) sulindac compounds.

Compounds	%Yield	m.p (°C)	Solubility
$[Zn(sul)_2.2H_2O]$ (**1**)	75	240	Hot (MeOH, CHL, DCM), DMF, DMSO
[Zn(sul) (2-ampy)] (**2**)	83	205	ACE, Hot (MeOH, EtOH), DMF, DMSO
$[Zn(sul)_2$(2-ammepy)] (**3**)	75	146	MeOH, CHL, DCM, ACE, EtOH, DMF, DMSO
$[Zn(sul)_2$(1,10-phen)] (**4**)	76	165	MeOH, CHL, DCM, ACE, DMF, DMSO
$[Zn(sul)_2$(2,9-dimephen)] (**5**)	95	170[d]	CHL, DCM, Hot (ACE, MeOH), DMF, DMSO
$[Co(sul)_2.4H_2O]$ (**6**)	85	201	MeOH, DMF, DMSO
$[Co(sul)_2$ $(2\text{-ampy})_2]$ (**7**)	56	180[d]	MeOH, DMF, DMSO
$[Co(sul)_2$(1,10-phen)] (**8**)	22	140	MeOH, CHL, DCM, DMF, DMSO
$[Co(sul)_2$(2,9-dimephen)] (**9**)	34	150[d]	MeOH, CHL, DCM, DMF, DMSO

d: decomposition

3.2. Magnetic properties of cobalt(II) complexes

The magnetic moment measurements of compounds **6-9** are given in Table 3.2. The value of magnetic moments for all complexes indicate that each compound has paramagnetic properties with one unpaired electron, which indicates that in each complex Co(II) adopted a low spin, d^7 octhedral geometry.

Table 3.2: Magnetic properties of cobalt(II) compounds.

Compounds	Magnetic moment (μ_{eff} BM)	unpaired electron (n)
$[Co(sul)_2.4H_2O]$ (**6**)	2.26±0.05	1
$[Co(sul)_2$ $(2\text{-ampy})_2]$ (**7**)	2.41±0.15	1
$[Co(sul)_2$(1,10-phen)] (**8**)	2.40±0.12	1
$[Co(sul)_2$(2,9-dimephen)] (**9**)	2.40±0.09	1

3.3. NMR spectroscopy

The ^{1}H-NMR and ^{13}C{^{1}H} NMR spectral data of complex **1** and sulindac are shown in Table 3.2. In general most ^{1}H-NMR resonances of complex **1** showed slight upfield shift compared to sulindac which might be metal coordination effect. In addition, the O-H resonance in the spectra of complex **1** was absent confirming the coordination with the metal center as shown in Figure 3.1. On the other hand, the C=O resonance in complex **1** was shifted downfield from 171. 5 to 175.0 ppm in the ^{13}C NMR indicating a deshielding effect due to electron density donation from the carboxylate sulindac group to the Zn(II) center.

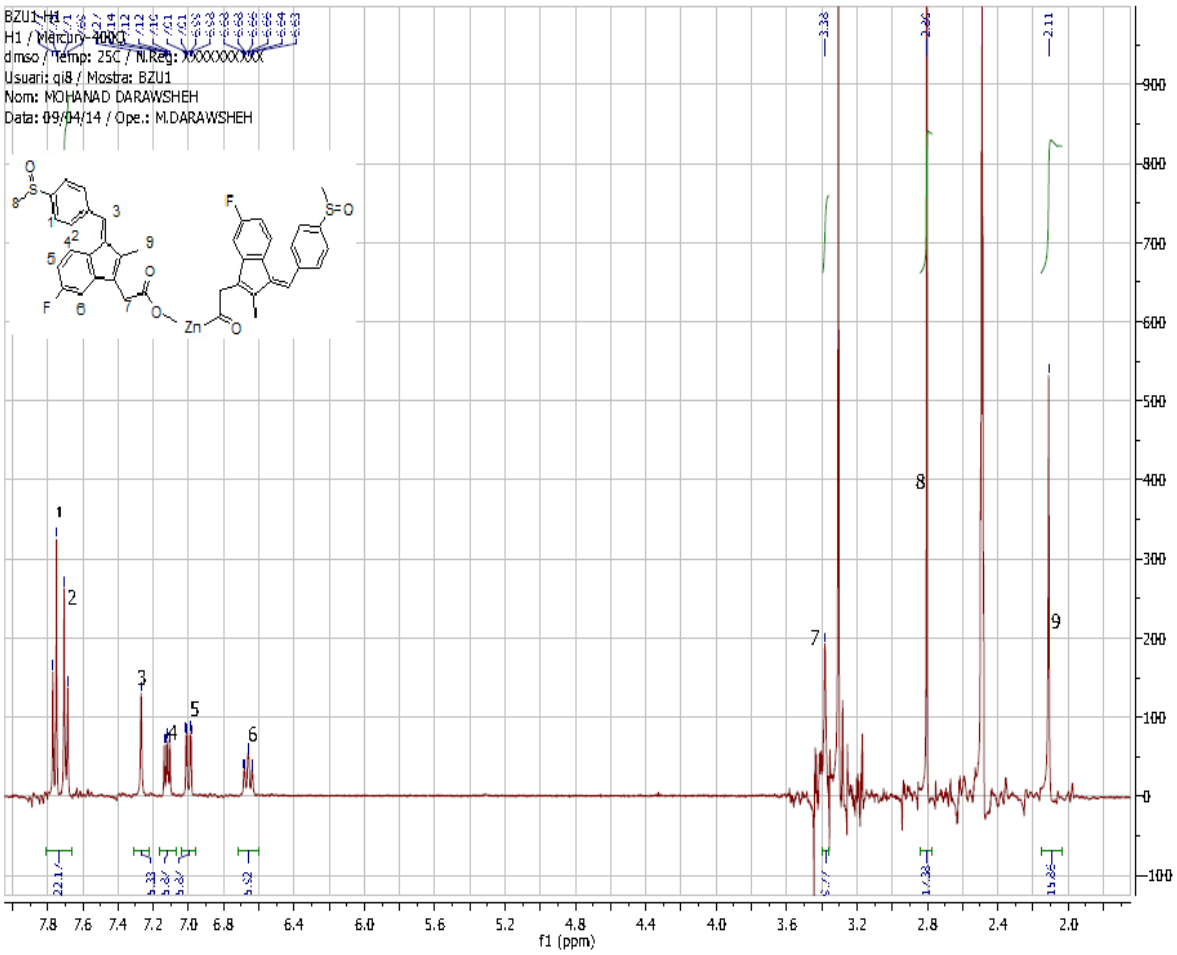


Figure 3.1: ^{1}H-NMR spectra for complex **1**

Table 3.3: ^{1}H-NMR and ^{13}C-{^{1}H}NMR spectral data of complex **1** and **sulindac**.

^{1}H-NMR		^{13}C-{^{1}H}NMR	
Complex **1**	^{1}H(sul)[111]	Complex **1**	^{13}C(sul)[112]
2.17 (s, 6H, 2CH_3)	2.21	10.69 (2CH_3)	10.2
2.77 (s, 6H, 2CH_3)	2.64	33.73 (2CH_2)	31.2
3.47 (s, 4H, 2CH_2)	2.9	43.53 (2CH_3)	44
6.63 (t, 2H, 2CH, $^{3}J_{H-H}$ = 10.0 Hz)	6.74	106.73 (2CH)	106
6.98 (d, 2H, 2CH, $^{3}J_{H-H}$ = 12.0 Hz)	6.96	110.35 (2CH)	110.5
7.10 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8 Hz),	7.12	123.33 (CH)	123.0
7.27 (s, 2H, 2CH)	7.43	124.32 (4CH)	125.2
7.69 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz)	7.58	128.81 (4CH)	137.5
7.75 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz)	7.72	129.99 (2CH)	129.2
- (OH)	12.1	130.38 (2C)	129.7
		131.24 (2CH)	137.6
		135.68 (2CH)	132.5
		139.22 (2C)	135.7
		141.24 (2C)	141.0
		146.39 (2C)	146.8
		161.71 (2C)	162.0
		175.03 (2C=O)	171.5

^{1}H-NMR and ^{13}C{^{1}H}NMR spectral data of nitrogen based ligands and complexes **2-5** are listed in Tables 3.4 to Table 3.7.

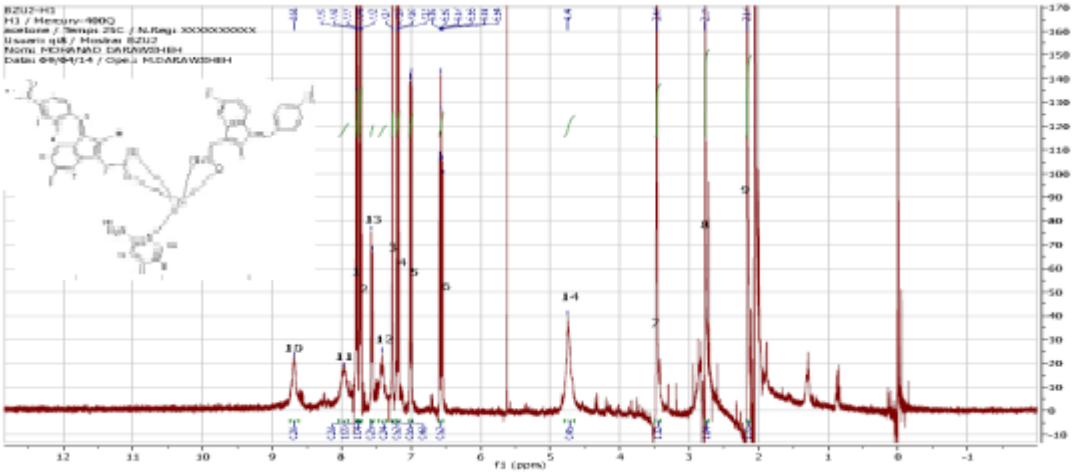


Figure 3.2: ^{1}H-NMR spectra of complex **2**

Table 3.4: ^{1}H-NMR and ^{13}C- NMR spectral data of complex **2** and **2-ampy**.

^{1}H-NMR		^{13}C-{^{1}H}NMR	
Complex **2**	^{1}H(2-ampy)[113]	Complex **2**	^{13}C(2-ampy)[114]
2.11 (s, 6H, $2CH_3$)		10.66 ($2CH_3$)	
2.80 (s, 6H, $2CH_3$)		33.95 ($2CH_2$)	
3.38 (s, 4H, $2CH_2$)		43.53 ($2CH_3$)	
4.74 (s, 2H, NH_2)	4.45	106.8 (2CH)	
6.55 (t, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 10.0 Hz)		110.39 (2CH)	
6.99 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 8.0 Hz)		110.55 (CH_{py})	108.5
7.17 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 8 Hz),		123.12 (CH_{py})	117.9
7.27 (s, 2H, 2CH)		123.31 (CH)	
7.42 (t, 1H, CH_{py})	6.62	124.33(4CH)	
7.55 (d, 1H, $2CH_{py}$, $^{3}J_{H\text{-}H}$ = 8 Hz)	7.55	128.75 (4CH)	
7.72(d, 4H, 4CH, $^{3}J_{H\text{-}H}$ = 8 Hz)		129.94 (2CH)	
7.79 (d, 4H, 4CH, $^{3}J_{H\text{-}H}$ = 8 Hz)		130.36 (2C)	
7.97 (t, 1H, CH_{py})	6.7	135.74 (2CH)	
8.68 (d, 1H, CH_{py})	8.07	136.55 (2CH)	
		139.21 (2C)	
		139.73 (CH_{py})	138.3
		141.23 (2C)	
		146.40 (2C)	
		148.33(CH_{py})	148.1
		157.98 (2C)	
		161.67 (C-NH_2)	160.4
		175.05 (2C=O)	

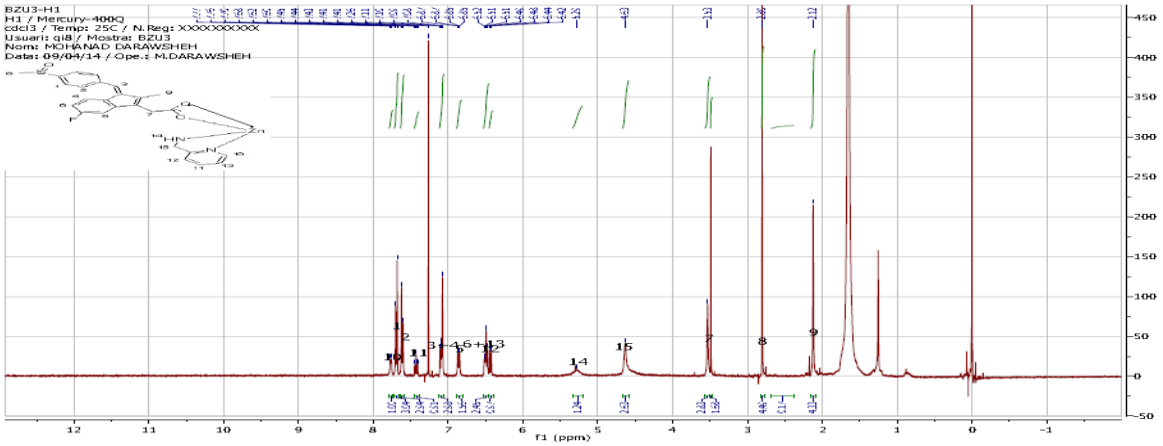


Figure 3.3: ^{1}H-NMR spectra of complex **3**

Table 3.5:^{1}H-NMR and ^{13}C-{^{1}H}NMR spectral data of complex **3** and **2-ammepy**.

^{1}H-NMR		^{13}C-{^{1}H}NMR	
Complex **3**	^{1}H(2-ammepy)[115]	Complex **3**	^{13}C(2-ammepy)[116]
2.12 (s, 3H, CH_3)		10.49 (CH_3)	
2.80 (s, 3H, CH_3)		33.88 (CH_2)	
3.53 (s, 2H, CH_2)		43.52 (CH_3)	
4.63 (s, 2H, CH_{2me})	4.57	106.7 (CH)	
5.29 (s, H, NH)	1.84	110.23(CH)	
6.43 (d, 1H, CH_{py}, $^{3}J_{H-H}$ = 8.0 Hz)	7.31	110.57 (CH_{py})	120.9
6.49 (t, 1H, CH_{py})		123.24 (CH_{py})	124.1
6.51(t, H, CH, $^{3}J_{H-H}$ = 10.0 Hz)		123.37 (CH)	
6.99 (d, H, CH, $^{3}J_{H-H}$ = 8.0 Hz)		124.33(2CH)	
7.08 (d, H, CH, $^{3}J_{H-H}$ = 8.0 Hz)		128.79 (2CH)	
7.26 (s, H, CH)		129.97 (CH)	
7.41 (t, 1H, $CH_{py,}$ $^{3}J_{H-H}$ = 7.0 Hz)	7.73	130.38 (C)	
7.6 (d, 1H, $2CH_{py}$, $^{3}J_{H-H}$ = 8 Hz)	7.35	135.61 (CH)	
7.70(d, 2H, 2CH, $^{3}J_{H-H}$ = 8 Hz)		136.68 (CH)	
7.76 (d, 1H, $CH_{py,}$ $^{3}J_{H-H}$ = 8.0 Hz)	8.46	138.10 (C)	
		139.23 (CH_{py})	139.6
		141.24 (C)	
		146.33 (C)	
		148.23 (CH_{py})	148.6
		160.01 (C-CH_2)	156.1
		174.92 (C=O)	

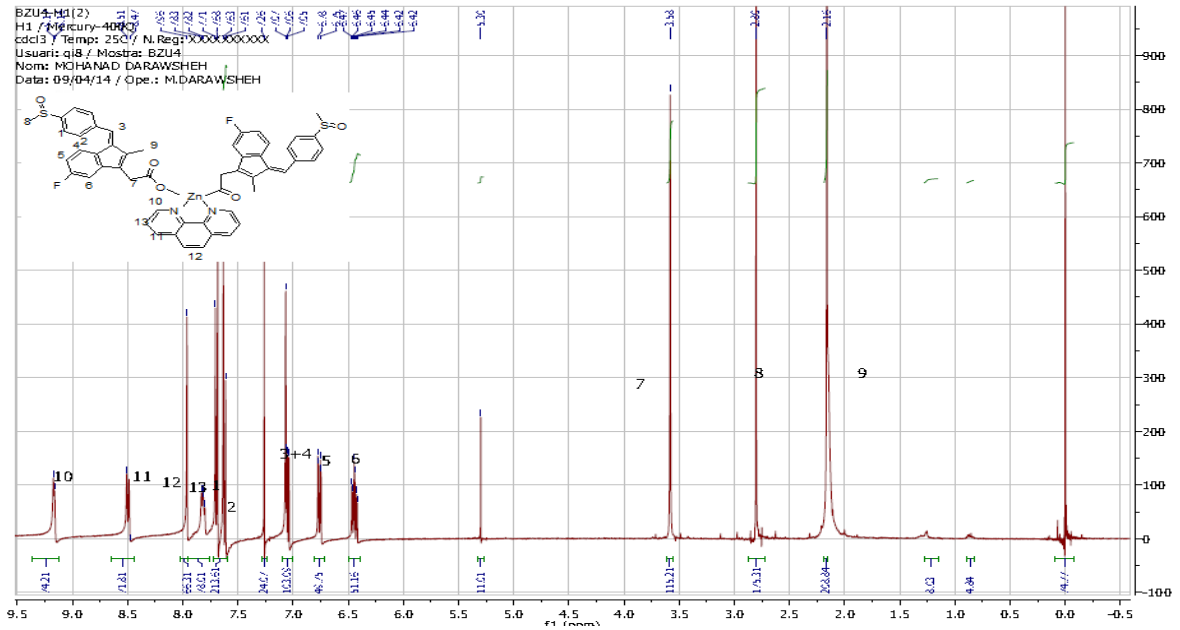


Figure 3.4: ^{1}H-NMR spectra of complex **4**

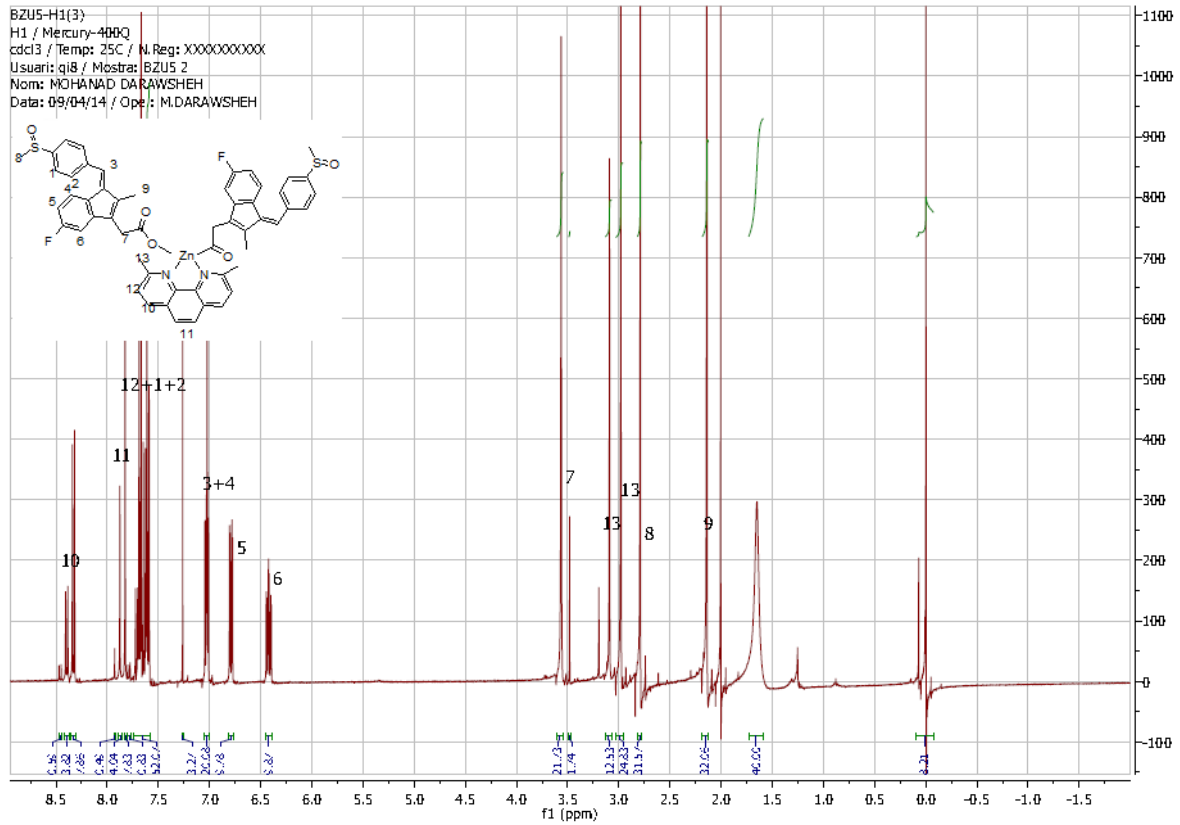


Figure 3.5: ^{1}H-NMR spectra of complex **5**

Table 3.6: ^{1}H-NMR and ^{13}C-{^{1}H}NMR spectral data of complex **4** and **1,10-phen**.

^{1}H-NMR		^{13}C-{^{1}H}NMR	
Complex **4**	^{1}H(1,10-phen)[117]	Complex **4**	^{13}C(1,10-phen)[118]
2.16 (s, 6H, $2CH_3$)		10. 51 ($2CH_3$)	
2.80 (s, 6H, $2CH_3$)		32.56 ($2CH_2$)	
3.58 (s, 4H, $2CH_2$)		43.85 ($2CH_3$)	
6.42(t, 2H, 2CH, $^{3}J_{H-H}$ = 10.0 Hz)			
6.75 (d, 2H, 2CH, $^{3}J_{H-H}$ = 10.0 Hz)		106.03 (2CH)	
7.04 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8 Hz),		110.23(2CH)	
7.26 (s, 2H, 2CH)		123.77 ($2CH_{phen}$)	123.4
7.61(d, 4H, 4CH, $^{3}J_{H-H}$ = 8 Hz)		125.32 (2CH)	
7.68 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8.0 Hz)		126.80 (2CH)	
7.80 (t, 1H, $2CH_{phen}$, $^{3}J_{H-H}$ = 10.0 Hz)	7.58	127.22 ($2CH_{phen}$)	126.80
7.96 (s, 1H, $2CH_{phen}$)	8.20	128.73 (2CH)	
8.47 (d, H, $2CH_{phen}$, $^{3}J_{H-H}$ = 16.0 Hz)	8.22	129.49 ($2C_{phen}$)	129.1
9.16 (d, H, $2CH_{phen}$, $^{3}J_{H-H}$ = 4.0 Hz)	9.18	130.252 (2CH)	
		134.15 (2CH)	
		134.96 (2CH)	
		137.06 ($2CH_{phen}$)	136.3
		139.09 (2C)	
		140.05 (2C)	
		145.07(2C)	
		147.43 ($2C_{phen}$)	146.5
		150.17 ($2CH_{phen}$)	150.6
		161.59 (2C)	
		178.11 (2C=O)	

Table 3.7: ^{1}H-NMR and ^{13}C-{^{1}H}NMR spectral data of complex **5** and **2,9-dimephen**.

^{1}H-NMR		^{13}C-{^{1}H}NMR	
Complex **5**	^{1}H(2,9-dimephen)[119]	Complex **5**	^{13}C(2,9- dimephen)[120]
2.14 (s, 6H, $2CH_3$)		10. 49 ($2CH_3$)	
2.79 (s, 6H, $2CH_3$)		24.76 (CH_{3phen})	25.79
3.09 (s, 6H, $2CH_{3phen}$)	2.92	33.30 ($2CH_2$)	
3.48 (s, 4H, $2CH_2$)		43.85 ($2CH_3$)	
6.40(t, 2H, 2CH, $^{3}J_{H-H}$ = 10.0 Hz)		106.16 (2CH)	
6.78 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8.0 Hz)		110.1(2CH)	
7.01 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8.0 Hz)		123.68 ($2CH_{phen}$)	123.44
7.07 (s, 2H, 2CH)		126.36 (2CH)	
7.54(d, 4H, 4CH, $^{3}J_{H-H}$ = 12 Hz)		127.04 ($2CH_{phen}$)	125.04
7.63 (d, 4H, 4CH, $^{3}J_{H-H}$ = 8.0 Hz)		129.73 (2CH)	126.78
7.60 (d, 1H, $2CH_{phen,}$ $^{3}J_{H-H}$ = 10.0 Hz)	7.46	130.22 (2CH)	
7.82 (s, 1H, $2CH_{phen}$)	7.69	134.96(2CH)	
8.32 (d, H, $2CH_{phen,}$ $^{3}J_{H-H}$ = 16.0 Hz)	8.1	136.47 (2CH)	
		136.47 ($2C_{phen}$)	136.23
		139.16 (2C)	
		140.29 (2C)	
		142.2 ($2C_{phen}$)	145.25
		144.9 (2C)	
		147.73 ($2C_{phen}$)	159.23
		161.85 (2C)	
		177.18 (2C=O)	

Slight chemical shifts in the ^{1}H and $^{13}C\{^{1}H\}$NMR spectra were observed. The coordination number and the stoichiometric ratio of the complexes and therefore their structures may be proposed depending on relative intensity, (integration) of the ^{1}H-NMR signals of the sulindac group and the nitrogen based ligands. In complex **3** the ratio between sulindac and nitrogen based ligand was 1:1, respectively; however, it was 2:1 in complexes **2**, **4** and **5**.

The ^{1}H-NMR and $^{13}C\{^{1}H\}$NMR spectra of cobalt(II) compounds were hampered by the paramagnetism Co(II).

3.4. Electronic absorption spectroscopy

Generally, three types of electronic transitions have been observed for coordination compounds: (1) Metal to ligand, (MLCT) or ligand to metal, (LMCT) charge-transfer absorption bands. (2) *d-d* transition bands. (3) (LC) ligand transition bands.[121,122]

The electronic transition data of all compounds are listed in Table 3.8. Zn(II) metal ion has d^{10} configuration, so no *d-d* electronic transition can be observed, but MLCT bands were observed around (206-213 nm) with ϵ value around 3000 $Lmol^{-1}cm^{-1}$. On the other hand, Co(II) metal ion with low spin d^{7} electronic configuration showed two low intensity bands with small ϵ value (12-13 $Lmol^{-1}cm^{-1}$) in the visible region. The source of these two bands is due to the *d-d* transition between $^{2}E \longrightarrow {}^{2}T_{1g}$ and $^{2}E \longrightarrow {}^{2}T_{2g}$. LMCT was observed at (206-213 nm) with ϵ value more than 1000 $Lmol^{-1}cm^{-1}$. All other bands are similar to nitrogen based ligand $\Pi \longrightarrow \Pi^{*}$ transitions with small blue or red shifts for zinc or cobalt coordination complexes.

Table 3.8: UV-visible spectral data for compounds (**1-9**).

Compounds	λ_{max} (nm)	ϵ(Lmol^{-1}cm^{-1})
[Zn(sul)$_2$.2H$_2$O] (**1**)	213	3000
	284	400
	328	288
[Zn(sul) (2-ampy)] (**2**)	210	3216
	289	472
	327	334
[Zn(sul)$_2$(2-ammepy)] (**3**)	211	2500
	261	470
	286	350
	328	300
[Zn(sul)$_2$(1,10-phen)] (**4**)	206	1838
	226	863
	272	651
	328	303
[Zn(sul)$_2$(2,9-dimephen)] (**5**)	207	2000
	227	642
	274	424
	330	182
[Co(sul)$_2$.4H$_2$O] (**6**)	211	3283
	258	872
	264	850
	252	828
	282	771
	328	514
[Co(sul)$_2$ (2-ampy)$_2$] (**7**)	207	1828
	286	450
	329	348
	655	12.7
[Co(sul)$_2$(1,10-phen)] (**8**)	208	2152
	226	700
	271	535
	328	224
	431	16.3
	488	13.2
[Co(sul)$_2$(2,9-dimephen)] (**9**)	207	2263
	229	933
	274	621
	328	261
	432	13.3

3.5. X-ray crystallography

The crystal structures of compounds **4, 5, 6** and **9** were determined, suitable crystals were prepared by recrystallization from 1:1 mixture of ACE: ACN, 1:1 mixture of CHL: ACN, MeOH and 1:1 mixture of CHL:ACN, respectively. Crystal data collections are listed in Table 2.1. and 2.2. Crystallographic information files (CIF) are given in the Appendices.

3.5.1. X-ray crystal structure of [Zn(sul)$_2$(1,10-phen)] (4)

Figure 3.6 shows the crystal structure of complex **4**. Acoording to this figure the Zn(II) ion bounded to two monodentate sulindac ligands. The bond distances of O-Zn 1.994(4) Å and 1.962(4) Å are similar to the reported value (1.84-2.33 Å).[123] The N-Zn 2.084(5) Å and 2.110(5) Å bond distances of are in the range of other reported Zn(II)1,10-phenanthroline complexes.[124-126] Selected angles and distances are listed in Table 3.9.

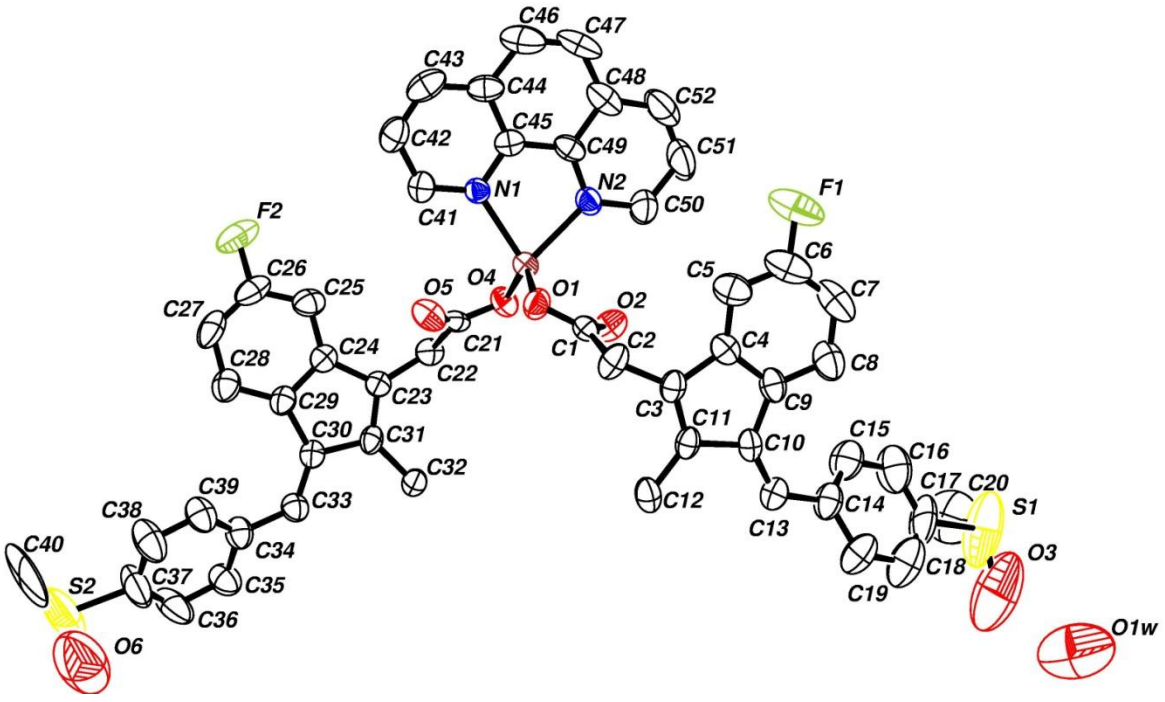


Figure 3.6: Molecular structure of compound **4** showing the labeling atom scheme.

Table 3.9: Selected bond angles and bond distances (Å) of **4.**

Bond distance (Å)		Bond angle (Å)	
C(1)-O(1)	1.271(7)	O(2)-C(1)-O(1)	122.6(6)
C(1)-O(2)	1.223(7)	O(2)-C(1)-C(2)	121.1(6)
C(1)-C(2)	1.514(9)	O(1)-C(1)-C(2)	116.3(6)
C(50)-N(2)	1.335(9)	N(1)-C(45)-C(44)	121.7(6)
C(49)-N(2)	1.349(8)	N(1)-C(45)-C(49)	117.7(5)
C(45)-N(1)	1.344(7)	N(2)-C(50)-C(51)	121.6(8)
C(41)-N(1)	1.317(7)	N(2)-C(50)-H(50)	119.2
C(21)-O(5)	1.233(8)	C(1)-O(1)-Zn(1)	100.3(4)
C(21)-O(4)	1.269(7)	C(21)-O(4)-Zn(1)	100.3(4)
N(1)-Zn(1)	2.084(5)	O(4)-Zn(1)-O(1)	125.91(19)
N(2)-Zn(1)	7.46	O(4)-Zn(1)-N(1)	112.33(19)
O(1)-Zn(1)	1.994(4)	O(1)-Zn(1)-N(1)	106.75(18)
O(4)-Zn(1)	1.962(4)	O(4)-Zn(1)-N(2)	114.5(2)
		O(1)-Zn(1)-N(2)	108.34(19)
		N(1)-Zn(1)-N(2)	79.08(19)
		O(1)-Zn(1)-N(1)	106.75(18)
		O(4)-Zn(1)-N(2)	114.5(2)

Complex **4** adopted slightly distorted tetrahedral geometry around the central Zn(II) center. O(4)-Zn(1)-O(1) = 125.91(19)˚, O(4)-Zn(1)-N(1) = 112.33(19)˚, O(1)-Zn(1)-N(2) = 108.34(19)˚, O(1)-Zn(1)-N(1) = 106.75(18)˚ and O(4)-Zn(1)-N(2) = 114.5(2)˚.

3.5.2. X-ray crystal structure of [Zn (sul)$_2$(2, 9-dime phen)] (5)

Figure 3.7 shows the crystal structure of complex **5**. According to this figure Zn(II) is bounded to two monodentate sulindac ligands. The bond distances of O-Zn 1.960(4) Å and 1.928(3) Å are similar to reported values (1.84-2.33 Å).[123] The coordination distances of N-Zn 2.055(5) Å and 2.054(5) Å are also similar reported values Zn(II)2,9-dimethyl-1,10-phenanthroline complexes.[124-126] Selected angles and distances are listed in Table 3.10.

Table 3.10: Selected bond angles and distances (Å) of **5**.

Bond distance (Å)		Bond angle (Å)	
C(15)-O(1)	1.231(6)	O(1)-C(15)-O(2)	124.9(5)
C(15)-O(2)	1.264(6)	O(1)-C(15)-C(16)	121.1(6)
C(15)-C(16)	1.523(7)	O(2)-C(15)-C(16)	119.1(5)
C(1)-N(1)	1.331(10)	C(1)-N(1)-C(12)	121.3(6)
C(12)-N(1)	1.398(9)	C(11)-N(2)-C(10)	120.3(6)
C(11)-N(2)	1.330(10)	N(2)-C(11)-H(12)	119.2
C(10)-N(2)	1.361(10)	C(15)-O(2)-Zn(1)	120.1(3)
C(35)-O(4)	1.254(9)	C(35)-O(4)-Zn(1)	107.5(5)
C(35)-O(5)	1.201(9)	O(2)-Zn(1)-O(4)	113.27(18)
N(1)-Zn(1)	2.054(5)	O(4)-Zn(1)-N(1)	126.66(19)
N(2)-Zn(1)	2.055(5)	O(4)-Zn(1)-N(2)	98.0(2)
O(2)-Zn(1)	1.928(3)	O(2)-Zn(1)-N(2)	125.61(18)
O(4)-Zn(1)	1.960(4)	N(1)-Zn(1)-N(2)	79.08(19)
		O(2)-Zn(1)-N(1)	108.64(18)

Complex **5** shows a slight deviation from regular tetrahedral angles; O(2)-Zn(1)-O(4) = 113.27(18)˚, O(4)-Zn(1)-N(2) = 98.0(2)˚, O(2)-Zn(1)-N(1) = 108.64(18)˚, O(2)-Zn(1)-N(2) = 125.61(18)˚ and O(4)-Zn(1)-N(1) = 126.66 (19)˚.

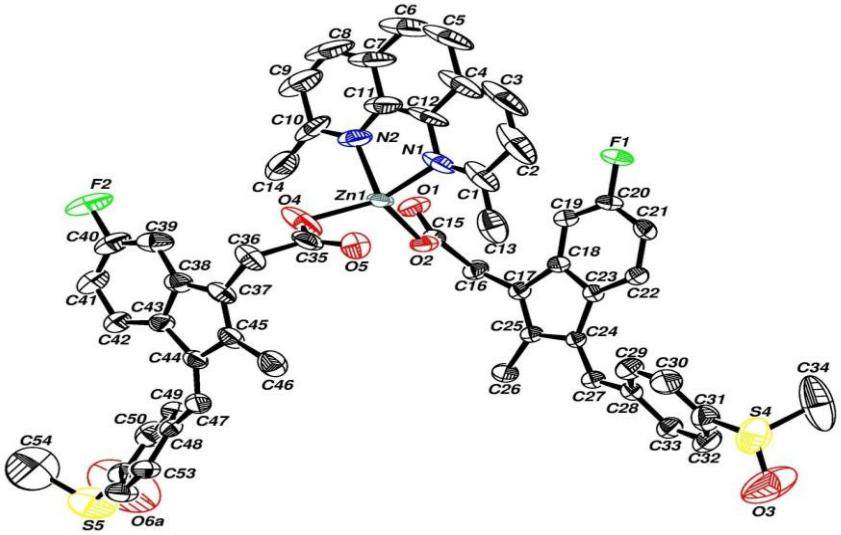


Figure 3.7: Molecular structure of compound **5** showing the labeling atom scheme.

3.5.3. X-ray crystal structure of $[Co(sul)_2(H_2O)_4]$ (6)

Figure 3.8 shows the crystal structure of compound **6**. According to this figure Co(II) is bounded to two monodentate sulindac ligands. The bond Co-O distances is 2.089(4) Å for sulindac oxygen coordinate and 2.100(5) Å, 2.141(4) Å for water oxygen coordination, these values are similar to the reported values.[127] Selected angles and distances are listed in Table 3.11.

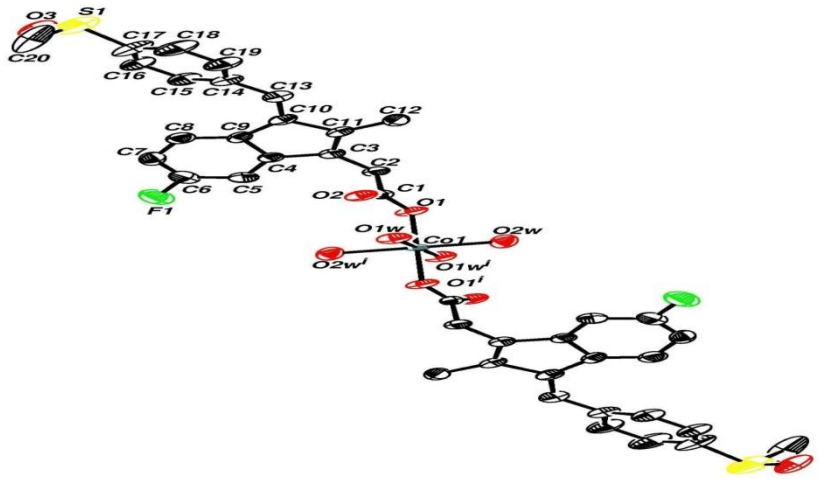


Figure 3.8. Molecular structure of compound **6** showing the labeling atom scheme.

Table 3.11: Selected bond angles and bond distances (Å) of **6**.

Bond distance (Å)		Bond angle (Å)	
C(1)-O(1)	1.276(7)	O(2)-C(1)-O(1)	124.9(5)
C(1)-O(2)	1.229(7)	O(2)-C(1)-C(2)	120.0(5)
C(1)-C(2)	1.530(8)	O(1)-C(1)-C(2)	115.1(5)
Co(1)-O(1)	2.089(4)	C(1)-O(1)-Co(1)	126.2(4)
Co(1)-O(1)#1	2.089(4)	O(1W) -Co(1)-O(1W)#1	180.000(2)
Co(1)-O(2W)#1	2.100(5)	O(2W) -Co(1)-O(2W)#1	180.000(1)
Co(1)-O(2W)	2.100(5)	O(1) -Co(1)-O(1)#1	180.000(2)
Co(1)-O(1W)	2.141(4)	O(1)#1-Co(1)-O(2W)#1	87.9(2)
Co(1)-O(1W)#1	2.141(4)	O(1)-Co(1)-O(2W)	87.9(2)
		O(1)-Co(1)-O(1W)	92.09(17)
		O(1)#1-Co(1)-O(1W)	87.91(17)
		O(2W)#1-Co(1)-O(1W)	89.4(2)

From the bonding angles in complex **6**; O(1)#1-Co(1)-O(2W)#1 = 87.9(2)°, O(1)-Co(1)-O(2W) = 87.9(2)°, O(1)-Co(1)-O(1W) = 92.09(17)°, O(1)#1-Co(1)-O(1W) = 87.91(17)° and O(2W)#1-Co(1)-O(1W) = 89.4(2)° a slight distortion from regular octahedral geometry was observed due to the expected *Jahn-Teller* effect which is also confirmed by the appearance of a shoulder in the *d-d* visible transition of this and other cobalt complexes.

3.5.4. X-ray crystal structure of [Co(sul)$_2$(2, 9-dimephen] (9)

According to Figure 3.9, Co(II) was bounded to one monodentate and one bidentate sulindac ligands. The Co-O bond distances of 2.117(8)Å, 2.128(6) Å, 2.220(10) Å and 2.220(10) Å are similar to reported values.[127] Co-N bond distances of 2.090(7) Å and 2.100(7) Å are similar to reported values.[126] Selected angles and distances are listed in Table 3.12.

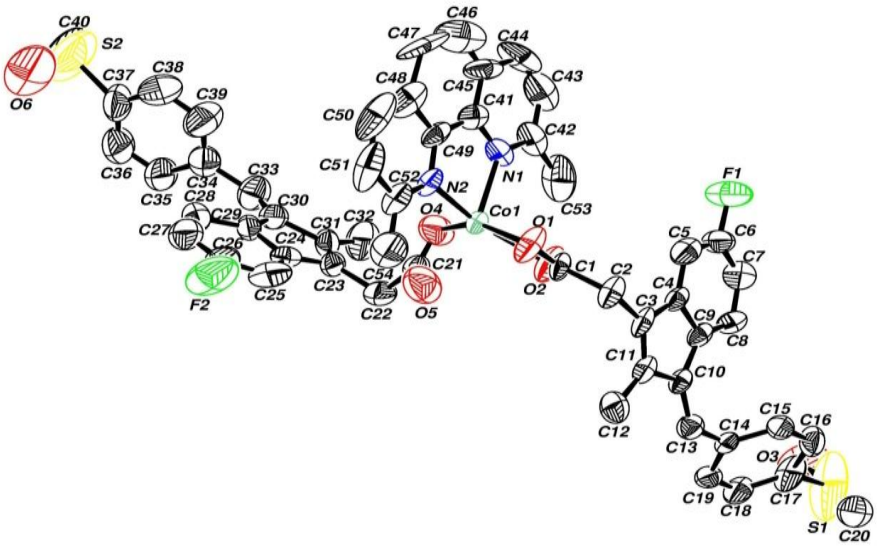


Figure 3.9: Molecular structure of compound **9** showing the labeling atom scheme.

From bonding angles in complex **9**, a slight deviation from octahedral geometry was observed, N(1)-Co(1)-O(1) = 108.2(3)˚, N(2)-Co(1)-O(4) = 112.3(3)˚, N(2)-Co(1)-O(5) = 102.5(4)˚, N(2)-Co(1)-N(1) = 79.8(3) and N(1)-Co(1)-O(2) = 104.3 (19)˚.

Table 3.12: Selected bond angles and bond distances (Å) of **9.**

Bond distance (Å)		Bond angle (Å)	
C(1)-O(1)	1.231(9)	O(2)-C(1)-O(1)	118.6(7)
C(1)-O(2)	1.214(10)	O(2)-C(1)-C(2)	122.4(7)
C(1)-C(2)	1.509(10)	O(1)-C(1)-C(2)	118.8(7)
C(21)-O(4)	1.190(12)	O(4)-C(21)-O(5)	119.7(11)
C(21)-O(5)	1.257(14)	O(5)-C(21)-C(22)	118.2(11)
C(21)-C(22)	1.473(15)	O(4)-C(21)-C(22)	121.9(11)
Co(1)-O(1)	2.133(7)	C(1)-O(2)-Co(1)	91.5(5)
Co(1)-O(4)	2.117(8)	C(21)-O(4)-CO(1)	94.2(7)
Co(1)-O(2)	2.128(6)	C(21)-O(5)-Co(1)	87.6(7)
Co(1)-O(5)	2.220(10)	N(2)-Co(1)-N(1)	79.8(3)
Co(1)-N(1)	2.100(7)	N(1) -Co(1)-O(1)	108.2(3)
Co(1)-N(2)	2.090(7)	N(2) -Co(1)-O(4)	112.3(3)
		N(1) -Co(1)-O(2)	104.3(3)
		N(2) -Co(1)-O(5)	102.5(4)
		O(4) -Co(1)-O(1)	155.4(3)
		O(2)-Co(1)-O(5)	91.9(4)
		O(2)-Co(1)-O(1)	59.1(3)
		C(1)-O(1)-Co(1)	90.7(5)

3.6. IR spectroscopy

IR spectroscopy is considered one of the most important tools in the determination of the nature of carboxylate coordination. The carboxylate ion may be coordinate to the metal in three different modes monodentate, bidentate and bridging complexes. The frequency of the symmetric (υ_s) and asymmetric (υ_{as}) of carbonyl stretching vibrations (COO^-) and the variation between asymmetric and symmetric $\Delta\upsilon(COO^-)$ are considered the major characteristic of the IR spectra in metal carboxylate complexes. The types of coordination mode of the carboxylate ligand determine the frequency of these bands. The main behavior is: Δ(chelating) < Δ(bridging) < Δ(monodentate).[128]

KBr pellets of zinc and cobalt compounds were prepared and measured in the (400-4000 cm^{-1}) range. The IR frequencies for potassium sulindac salt and **1** are given in Table 3.13. The stretching vibrations for potassium sulindac $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ have been observed at 1576 cm^{-1} and 1398 cm^{-1}, respectively and ($\Delta\upsilon$ COO^-) = 178 cm^{-1}.

In complex **1**; $\upsilon_{as}(COO^-)$ is at 1601 cm^{-1} and $\upsilon_s(COO^-)$ at 1397 cm^{-1}, $\Delta\upsilon$ COO^- = 204 cm^{-1} which is close to that of potassium sulindac supporting a monodentate coordination mode. The O-H vibration frequency at 3444 cm^{-1} indicates the presence of water molecules in the structure. In complex **6**; $\upsilon_{as}(COO^-)$ is at 1600 cm^{-1} and $\upsilon_s(COO^-)$ at 1416 cm^{-1}, $\Delta\upsilon$ COO^- = 184 cm^{-1} which is also close to that of potassium sulindac supporting a monodentate coordination mode. The O-H vibration frequency at 3376 cm^{-1} indicates the presence of water molecules in the coordination geometry, [Co $(sul)_2.4H_2O$] as also supported by single crystal determination.

Table 3.13: Comparison between some of principle peaks in IR for K(sul) and complex **1** and **6** (cm^{-1})

Assignments	K(sul)	Complex **1**	Complex **6**
υ $(C-H)_{ar}$	3066	3056	3050
υ $(C-H)_{aliph}$	2970, 2880	2983, 2939, 2916	2911, 2850
$\upsilon_{as}(COO^-)$	1576	1601	1600
$\upsilon_s(COO^-)$	1398	1397	1416
υ (ring)+δ (C-H)	1476, 1367	1367, 1464	1465, 1369
$\Delta\upsilon$ (COO^-)	178	204	184

Table 3.14: Summary of principle peaks in IR for complexes **2, 3, 4** and **5** (cm^{-1})

Assignments	Complex **2**	Complex **3**	Complex **4**	Complex **5**
υ_{as}(N-H)	3354	3262 (2 ammine)	-	-
υ_s(N-H)	3208	-	-	-
$\upsilon(C-H)_{ar}$	3065	3013	3056	3061
$\upsilon(C-H)_{aliph}$	2913	2911, 2850	2911, 2852	2909
υ(ring)	1602	1646	1716	-
$\upsilon_{as}(COO^-)$	1602	1597	1602	1599
υ(ring) + δ(C-H)	1463, 1360	1465, 1372	1428, 1379	1468, 1365
υ_s (COO^-)	1391	1414	1398	1381
υ(ring)	1262, 1086	1266, 1084	1269, 1093	1269, 1093
γ (C-H)	857	850	850	857
$\delta(COO^-)$	761, 716	765, 716	772	782, 728
υ(ring)	702	737	725	737
$\Delta(COO^-)$	211	183	204	218

As shown in Table 3.14 complexes **2**, **4** and **5** have $\upsilon_{as}(COO^-)$ at 1602, 1602, and 1599 cm^{-1}, respectively and $\upsilon_s(COO^-)$ appear at 1391, 1398 and 1381 cm^{-1}, respectively. So $\Delta\upsilon$ (COO^-) are 211, 204 and 218 cm^{-1}, respectively that is larger than $\Delta\upsilon(COO^-)_{ionic}$ = 178 cm^{-1}, which indicate monodentate coordination mode as also confirmed by X-ray structure determination of complexes **4** and **5**.

Moreover, it was observed that complex **2** has one absorption frequency at 3262 cm^{-1} which has been assigned to 2˚-NH_2 group, due to complexation through the nitrogen atoms of amine group. However**,** for complex **3** the absorption at 1597 cm^{-1} and 1414 cm^{-1} were observed and assigned to $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$, respectively. The $\Delta\upsilon(COO^-)$ are 183 cm^{-1}, which is close to $\Delta\upsilon(COO^-)_{ionic}$ = 178 cm^{-1}, this supports bidentate or bridging coordination mode of carboxylate group, also observed two absorption frequencies at $\upsilon_{as}(NH_2)$ = 3354, $\upsilon_s(NH_2)$ = 3208 cm^{-1} and $\Delta\upsilon$ (NH_2) = 146 cm^{-1} have been assigned to 1˚-NH_2 group, due to complexation through the nitrogen atoms of pyridine.

Table 3.15: Summary of principle peaks in IR for complexes **7, 8 and 9** (cm^{-1})

Assignments	Complex **7**	Complex **8**	Complex **9**
υ_{as}(N-H)	3374	-	-
υ_s(N-H)	3268	-	-
$\upsilon(C-H)_{ar}$	3015	3059	3040
$\upsilon(C-H)_{aliph}$	2914, 2860	2911, 2852	2912, 2845
υ(ring)	1599	1600	1599
$\upsilon_{as}(COO^-)$	1599	1600	1599
υ(ring) + δ(C-H)	1464, 1424	1464, 1424	1465, 1359
υ_s (COO^-)	1380	1380	1441
υ(ring)	1267, 1086	1267, 1086	1194, 1086
γ(C-H)	891	846	855
$\delta(COO^-)$	727	727	761, 728
$\Delta(COO^-)$	219	220	158

As shown in Table 3.15 complexes **7** and **8** have $\upsilon_{as}(COO^-)$ at 1599, and 1600 cm^{-1}, but $\upsilon_s(COO^-)$ appear at 1390 and 1380 cm^{-1}, so $\Delta\upsilon$ (COO^-) are 219 and 220 cm^{-1}, respectively that is larger than $\Delta\upsilon(COO^-)_{ionic}$ = 178 cm^{-1}, this supports monodentate coordination mode of carboxylate groups, also in complex **8** an absorption frequency at 3415 cm^{-1} was observed may indicates a water molecules in coordination geometry.

However, in complex **9** $\upsilon_{as}(COO^-)$ was observed at 1599 cm^{-1}, and $\upsilon_s(COO^-)$ was at 1441 cm^{-1}, so $\Delta\upsilon$ (COO^-) = 158 cm^{-1}, this supports bidentate coordination mode of carboxylate groups, this result was confirmed by X-ray structure determination of complex **9**.

Moreover, in complex **7** two absorption frequencies at $\upsilon_{as}(NH_2)$ = 3374, $\upsilon_s(NH_2)$ = 3268 cm^{-1} and $\Delta\upsilon$ (NH_2) = 106 cm^{-1} were observed. These frequencies are assigned to 1˚-NH_2 group, due to complexation through pyridine nitrogen atom.

3.7 *In-vitro* biological activity

3.7.1 Anti-bacterial activity

The anti-bacterial activities of the synthesized zinc complexes were screened as shown in Section 2.6. Different types of gram-negative bacteria (*Bordetella, Escherichia coli*) and gram-positive (*Staphylococcus epidermidis, Staphylococcus aureus*) and yeast species (*Saccharomyces and Candida*) were used in this study. The average of three trials are stated as average ± standard deviation and listed in Table 3.16.

Potassium sulindac, $CoCl_2$ and $ZnCl_2$ showed different behavior of anti-bacterial activity. $ZnCl_2$ and potassium sulindac did not show any anti-bacterial activity against all tested micro-organisms. DMSO was used as negative control to resist any tested microorganisms, but gentamicin sulfate was used as positive control for G^- and G^+ bacteria whereas nystatin was used as positive control for yeast.

As shown in Table 3.16 complexes **1**, **2**, and **3** showed low or zero activity against G- or G+ bacteria. Complexes **4**, **5** and **6** showed high activity against G- or G+ bacteria except against E.coli. Complexes **8** and **9** showed low activity against G- bacteria and high activity against G+ bacteria. Complex **7** showed high activity against S. epi and low or zero activity against other bacteria. However, in yeast all complexes didn't show any activity expect complexes **5** and **9** showed high activity.

Table 3.16: Anti-bacterial and yeast results of complexes **1-9**

Compounds	*Bordetella*	*E. coli*	*S. epi*	*S. aureus*	*Candida*	*Sacc.*
	G-	G-	G+	G+	Yeast	Yeast
(1)	13.5±0.5	12.2±0.4	10.9±1.1	-	-	-
(2)	-	-	12.9±1.3	-	-	-
(3)	13.4±0.6	9.9±0.8	14.5±0.5	13.0±0.5	-	-
(4)	35.0±0.7	16.9±1.1	27.5±0.6	19.9±1.5	-	-
(5)	30.5±0.9	11.2±2.5	27.2±1.5	22.9±0.9	36.8±0.9	38.8±1.9
(6)	15.3±0.5	10.1±0.4	21.0±0.4	19.2±0.7	-	-
(7)	12.6±1.3	-	22.5±0.9	10.7±1.2	-	-
(8)	11.9±2	8.5±1.5	26.7±0.6	20.5±0.9	-	-
(9)	16.2±1.9	12.0±2.2	38.7±1.2	25.0±1.5	42.0±0.8	41.12±0.5
$ZnCl_2$	-	-	-	-	-	-
$CoCl_2$	21.9±1.7	12.4±2.1	30.0±0.5	10.9±0.8	20.0±0.7	22.3±0.9
sulindac	-	-	-	-	-	-
Genta.	29.7±1.1	36.6±1.3	28.1±1.0	32.7±0.6	-	-
Nes.	-	-	-	-	35.5±0.2	40.5±0.4

IZD: Inhibition zone diameter (IZD) in mm.

The activity of complexes and nitrogen donor ligands against all Gram-positive and Gram-negative bacteria was determined to show the effect of complexation on anti-bacteria activity. The same procedure was used in different dilutions of compounds and their parent ligands. All anti-bacterial data are listed in Tables 3.17-3.19.

Table 3.17: Comparison of anti-bacterial activity of complex **2** with **2-ampy**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+
IZD of **2** (mm)				
8	-	-	12.9±1.3	-
4	-	-	12.3±0.7	-
2	-	-	11.0±1.6	-
IZD of **2-ampy**				
8	-	-	-	-
4	-	-	-	-
2	-	-	-	-

As shown in Table 3.17 the complexation of zinc-sulindac with 2-ampy increased the anti-bacterial activity for S. epi.

As shown in Table 3.18 the complexation of zinc-sulindac with 2-ammepy increased the anti-bacterial activity against all microorganisms.

Table 3.18: Comparison of anti-bacterial activity of complex **3** with **2-ammepy**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+
IZD of **3** (mm)				
8	13.4±0.6	9.9±0.8	14.5±0.5	13.0±0.5
4	10.6±0.5	-	11.2±0.7	12.9±0.4
2	-	-	7.5±1.6	11.2±0.9
IZD of **2-ammepy**				
8	-	-	-	-
4	-	-	-	-
2	-	-	-	-

Table 3.19: Comparison of anti-bacterial activity of complex **4** with **1,10-phen**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+
IZD of **4** (mm)				
8	35.0±0.7	16.9±1.1	27.5±0.6	19.9±1.5
4	23.4±0.5	13.0±1.7	21.7±0.7	17.3±0.5
2	12.6±1.2	11.0±0.7	16.9±1.6	14.4±0.7
IZD of **1,10-phen**				
8	33.0±0.7	33.3±1.1	36±0.6	38.5±1.5
4	21.6±0.5	31.5±1.7	33.6±0.7	35.4±0.5
2	11.0±1.2	29.0±0.7	24±1.6	28.6±0.7

It is clear from the results in Table 3.19 that the complexation of zinc-sulindac with 1,10-phen in complexes **4** decreased the anti-bacterial activity against most tested bacteria.

Table 3.20: Comparison anti-bacterial activity of complex **5** with **2,9-dimephen**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+	*Sacc* Yeast
IZD of **5** (mm)					
8	30.5±0.9	13.0±2.5	27.2±1.5	22.9±0.9	38.8±1.9
4	23.4±0.5	11.2±1.7	21.7±0.7	17.3±0.5	36.6±0.8
2	12.6±1.2	11.0±0.7	16.9±1.6	14.4±0.7	29.9±0.5
IZD of **2, 9-dimephen**					
8	14.6±0.9	-	36.9±1.5	38.5±0.9	43.9±1.9
4	9.2±0.5	-	35.5±0.7	35.4±0.5	42.3±0.8
2	8.3±1.2	-	33.0±1.6	31.3±0.7	38.4±0.5

The data in Table 3.20 indicate that complexation of zinc-sulindac with 2,9-dimephen in complex **5** decreased the anti-bacterial activity against gram positive bacteria and increased the anti-bacterial activity against gram negative bacteria. The yeast results showed almost similar behavior.

Table 3.21: Comparison of anti-bacterial activity of complex **7** with **2-ampy**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+
IZD of **7** (mm)				
8	12.6±1.3	-	22.5±0.9	10.7±1.2
4	10.5±0.7	-	18.8±0.7	-
2	-	-	13.7±1.6	-
IZD of **2-ampy**				
8	-	-	-	-
4	-	-	-	-
2	-	-	-	-

As shown in Table 3.21 the complexation of cobalt-sulindac with 2-ampy increased the anti-bacterial activity against all microorganism except E. coli which did not show any activity.

Table 3.22: Comparison of anti-bacterial activity of complex **8** with **1,10-phen**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+
IZD of **8** (mm)				
8	11.9±2	8.5±1.5	26.7±0.6	20.5±0.9
4	10.3±0.5	-	24.6±1.5	18.7±0.5
2	-	-	22.6±1.6	10.9±0.7
IZD of **1,10-phen**				
8	33.0±0.7	33.3±1.1	36±0.6	38.5±1.5
4	21.6±0.5	31.5±1.7	33.6±0.7	35.4±0.5
2	11.0±1.2	29.0±0.7	24±1.6	28.6±0.7

The results in Table 3.22 indicate that the complexation process of cobalt-sulindac with 1,10-phen in complex **8** decreased the anti-bacterial activity considerably for both gram negative and gram positive bacteria.

Table 3.23: Comparison of anti-bacterial activity of complex **9** with **2,9-dimephen**

Concentration (mg/ml)	*Bordetella* G-	*E. coli* G-	*S. epi* G+	*S. aureus* G+	*Sacc* Yeast
IZD of **9** (mm)					
8	16.2±1.9	12.0±2.2	38.7±1.2	25.0±1.5	41.12±0.5
4	13.7±0.5	-	34.6±0.7	24.3±0.5	40.6±0.8
2	11.4±1.2	-	30.4±1.6	21.9±0.7	35.9±0.5
IZD of **2, 9-dimephen**					
8	14.6±0.9	-	36.9±1.5	38.5±0.9	43.9±1.9
4	9.2±0.5	-	35.5±0.7	35.4±0.5	42.3±0.8
2	8.3±1.2	-	33.0±1.6	31.3±0.7	38.4±0.5

It is clear from Table 3.23 that complexation of cobalt-sulindac with 2,9-dimephen in complexes **9** mostly showed similar behavior against S. epi and yeast, but decreased the activity against S. aureus and increased the anti-bacterial activity against gram negative bacteria.

3.7.2 Anti-malarial activity

3.7.2.1 Semi-quantitative method

Anti-malarial results by the semi-quantitative method for zinc(II) complexes are shown in Figure 3.10 and Figure 3.11. Complex **5** has an absorbance value of 0.086 at a concentration of 1 mg/ml and it is the only complex which showed comparable activity with chloroquine as positive control, but complexes **1**, **2**, **3** and **4** did not show any important inhibitory effect on *in-vitro* beta-hematin formation. The absorption is inversely proportional with the efficiency of the drug, higher efficiency indicates low absorption and vice versa. Repetition with lower concentrations of **5** for farther investigation of the activity for this complex was done. The results of variant dilutions of complex **5** were done as shown in Figure 3.11.

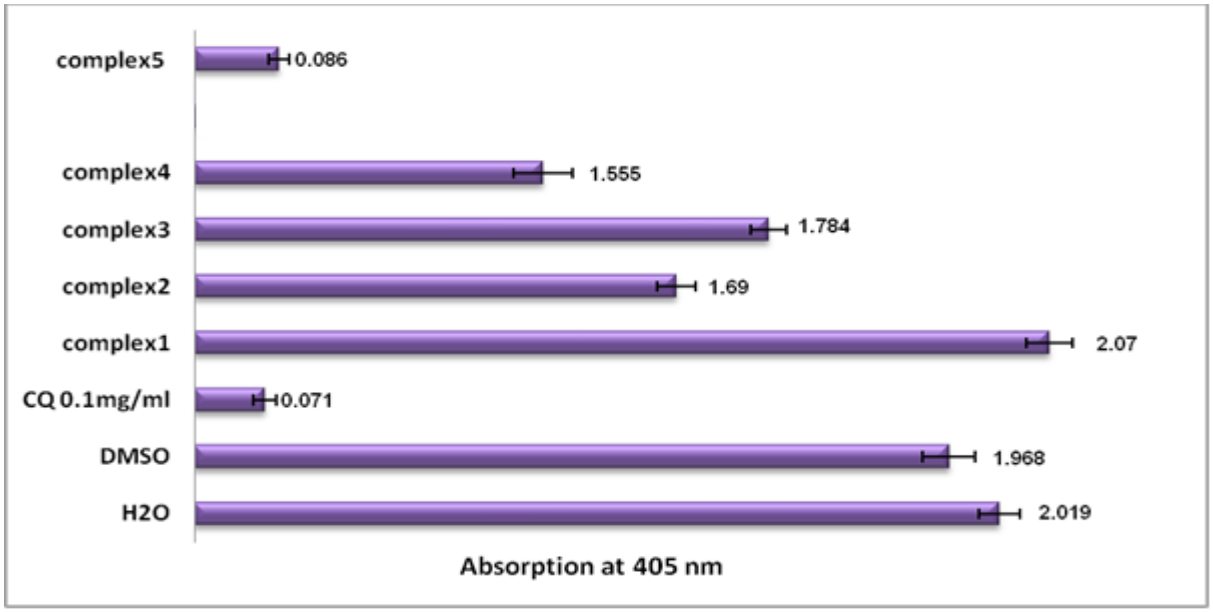


Figure 3. 10: Column diagram representing Semi-Quantitative test results of potential anti-malarial drugs, (complex **1**): [Zn(sul)$_2$1,10-phen], (complex **2**): [Zn(sul)$_2$], (complex **3**): [Zn(sul)$_2$2-ampy], (complex **4**): [Zn(sul)$_2$2-ammepy], and (complex **5**): [Zn(sul)$_2$2,9-dimephen], all at concentration 1mg/ml –dissolved in DMSO, compared to Chloroquine (CQ as positive control, while water and DMSO were used as negative controls, absorption is inversely proportional to drugs efficiency, the lower the absorption is, the drug is considered to be more efficient

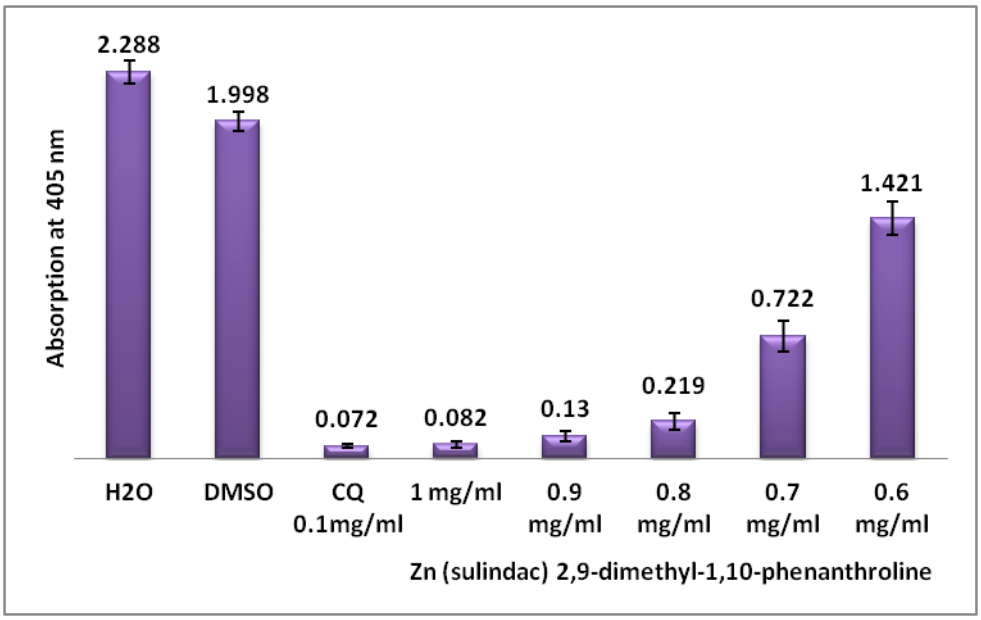


Figure 3.11: Results of Semi-Quantitative test of potential anti-malarial drug by used representing column diagram (complex **5**): [Zn(sul)$_2$2,9-dimephen] dissolved in DMSO, Chloroquine (CQ) were used as positive controls, while water and DMSO were used as negative controls, In this figure the absorption values of dissolved β-Hematin (alkaline hematin) at 405 nm using ELISA reader were shown.

3.7.2.2. Quantitative test

According to the quantitative method mentioned in Section 2.7.2, screening of the anti-malarial activity of **5** compared to CQ and DMSO in terms of β-Hematin formation was preformed and the results were shown in Figure 3.12 and Figure 3.13.

As shown in Figure 3.12, determination of the percentage yield of β-Hematin formation was determined. For [Zn(sul)$_2$2,9-dimephen] with 0.4 mM the percentage yield of β-hematin formation was 32.4% and that of CQ as positive control was 7.0% in the same concentration, both compared with DMSO as negative control with a yield of 86.2%. In Figure 3.13 the efficiency of **5** was 67.6% compared to CQ **(**93.0%) and DMSO (13.8%).

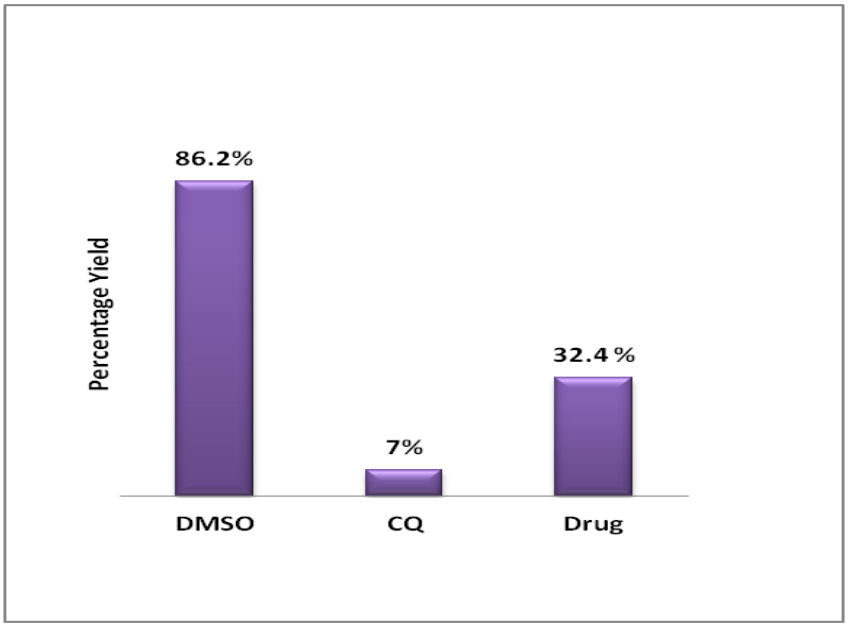


Figure 3. 12: Column diagram representing the percentage yields of the complex: [Zn (sulindac)$_2$-2,9-dimephen] as potential anti-malarial drug, compared to Chloroquine and DMSO at 0.4 mM. Yields are inversely proportional to drugs efficiency, the lower the yield is, the drug is considered to be more efficient.

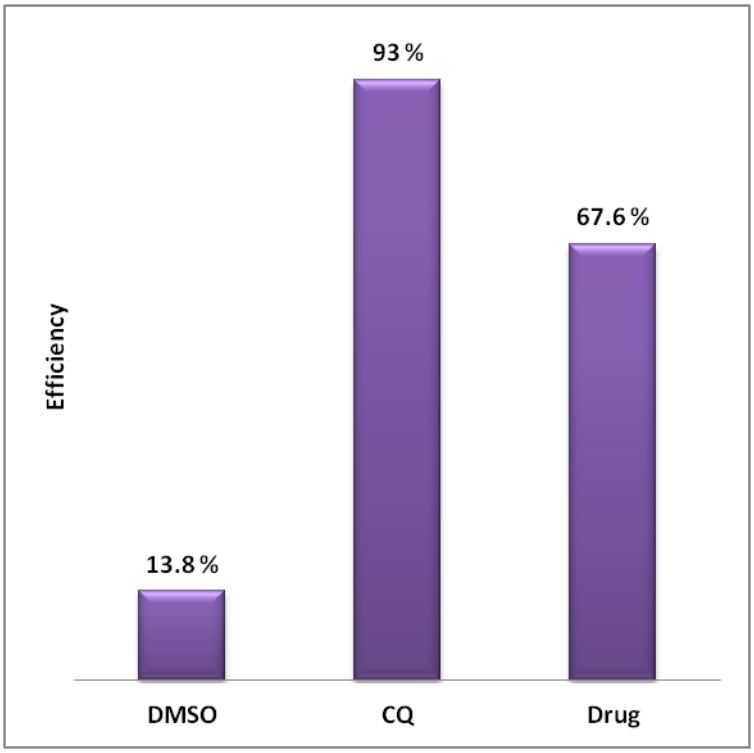


Figure 3.13: Column diagram representing the efficiencies of potential anti-malarial drug, complex: [Zn (sulindac)$_2$-2,9- dimephen] compared to Chloroquine, all at a concentration of 0.4 mM.

The interactions between Zn(sulindac)$_2$-2,9-dimephenand ferri-heme may enhance the *in-vitro* inhibition activity of β-hematin. Their interaction involve hydrogen bonding interaction between oxygen atoms from sulindac and propanoic acid of the ferri-heme and the coordination bond between the N-donor groups of the heme and zinc(II). On other hand, other forces may increase the stability of these interactions due to π-π stacking forces of the phenanthroline ring over the porphyrin.[129]

3.8. BNPP Hydrolysis

BNPP is always used as a DNA model. The ability of the metal complexes for phosphate hydrolysis was studied. The suggested or proposed mechanism for the hydrolysis process was shown in Scheme 1.1. Determination of the initial rate hydrolysis was determined by measuring the absorption of 4-nitrophenolate ion at 400 nm and plot the absorbance versus time (Figure 3.14). All prepared complexes were used as catalyst to hydrolysis the phosphate diester group, but complexes **4**, **5**, **8**, and **9** were showed the best trend in BNPP hydrolysis. Moreover, Michaelies-Menten equation was used for measuring the initial rate against different concentrations of BNPP.

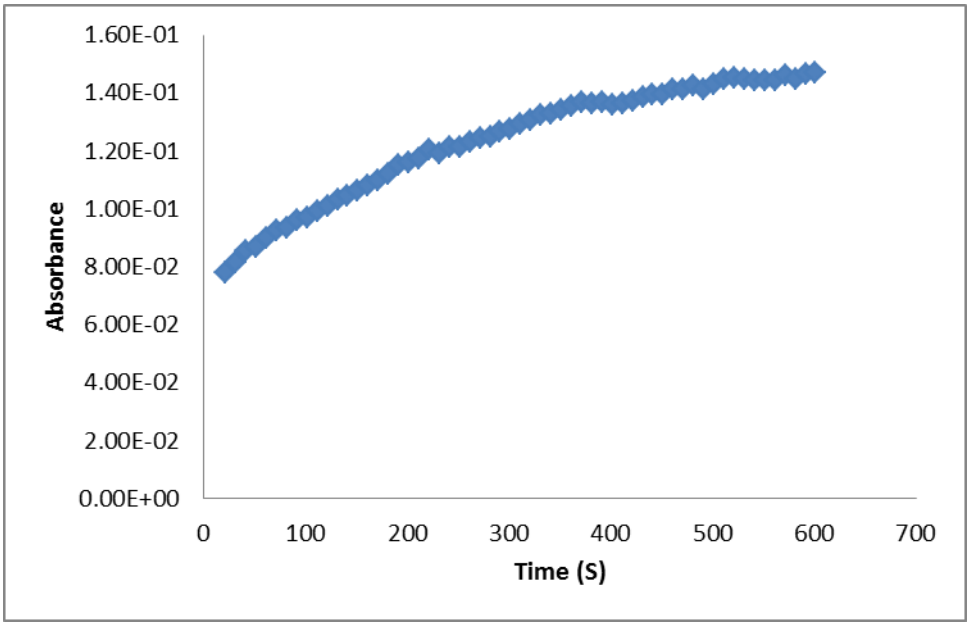


Figure 3.14. BNPP hydrolysis by complex **4** in MeOH/Hebs buffer solution at pH = 7.4, 37 °C and [complex] $2*10^{-4}$ M.

The linear equation Y = 49.09x + 83333 results from a plot of y = 1/initial rate vs x = 1/[BNPP] and the kinetic parameters for these complexes were tabulated in Table 3.24. The results showed that BNPP hydrolysis were decreased in the following order: complex **4** > **5** > **8** > **9**, the results also showed that these complexes, especially **4** can act as good phosphate hydrolysis.

Table 3.24. Kinetic parameters of the BNPP hydrolysis by complexes **4**, **5**, **8**, and **9** at different [BNPP].

Concentration (M)	*Initial rate,* V_0 mol $L^{-1}S^{-1}$	*Max.Rate,*V_{max} mol $L^{-1}S^{-1}$	*Michaelis constant,* K_m mol L^{-1}	*Catalytic rate constant,* K_{cat} [a] s^{-1}	*2-order rate constant*[b]*,*$K_{[PNPP]}$ mol $L^{-1}S^{-1}$
Complex **4** ($2*10^{-4}$ M)					
$1*10^{-4}$	$5*10^{-7}$	$5.9*10^{-5}$	$2.9*10^{-3}$	$2.9*10^{-1}$	10^2
$1*10^{-5}$	$2*10^{-7}$				
$1*10^{-6}$	$2*10^{-8}$				
Complex **5** ($2*10^{-4}$ M)					
$1*10^{-4}$	$3*10^{-8}$	$7.3*10^{-6}$	$1.6*10^{-3}$	$3.7*10^{-2}$	$2.3*10^1$
$1*10^{-5}$	$2*10^{-8}$				
$1*10^{-6}$	$4*10^{-9}$				
Complex **8** ($2*10^{-4}$ M)					
$1*10^{-4}$	$5*10^{-8}$	$4.7*10^{-6}$	$4.4*10^{-4}$	$2.4*10^{-2}$	$5.3*10^1$
$1*10^{-5}$	$4*10^{-8}$				
$1*10^{-6}$	$9*10^{-9}$				
Complex **9** ($2*10^{-4}$ M)					
$1*10^{-4}$	$7*10^{-9}$	$1.7*10^{-6}$	$6.1*10^{-4}$	$8.5*10^{-3}$	$1.4*10^1$
$1*10^{-5}$	$5*10^{-9}$				
$1*10^{-6}$	$2*10^{-9}$				

a: $K_{cat} = V_{max}/[complex]$, b: $K_{BNPP} = K_{cat}/K_m$.

4. Conclusion

In the present work, we have demonstrated the synthesis of nine new metal(II) complexes with the general formula $[M(sul)_n L_n]$ (M = Zn or Co, sul = sulindac, L = ligands such as; 2-ampy, 2-ammepy, 1,10-phen and 2,9-dimephen). The complexes were characterized by IR-spectroscopy, UV-spectroscopy, single crystal X-ray diffraction and other physical properties.

Single crystal X-ray diffraction was used to determine the geometry of metal ion in complexes **4, 5, 6** and **9**. Complexes **4** and **5** adopted distorted tetrahedral arrangements, but complexes **6** and **9** adopted a distorted octahedral geometry of the M(II) ion. Central Metal atom binds two monodentate sulindac groups and one 1,10-phen ligand for complex **4** and with two sulindac groups and one 2,9-dimephen in complex **5**, in complex **6** the cobalt binds two monodentate sulindac groups and in complex **9** cobalt binds to two bidentate sulindac groups and one 2,9-dimephen. On other hand, the structures of the remaining complexes were proposed depending on ^{1}H NMR, ^{13}CNMR, IR and UV-Vis results.

The anti-bacterial activity of all compounds was screened to determine the complexation effect on the activity of these ligands. In general, metal(II) carboxylates have shown the highest efficiency on the Gram-positive and low efficiency on the Gram-negative bacteria. Moreover, complexes **5** and **9** have demonstrated the highest efficiency against yeast.

The anti-malarial activity of zinc compounds were manipulated to determine the effect of zinc complexes on the activity as anti-malarial drugs, In general, the results showed that $[Zn(sul)_2$-2,9-dimephen] has the highest efficiency as potential anti-malarial drug.

The BNPP hydrolysis of Zn(II) and Co(II) compounds were studied to determine the effect of zinc or cobalt complexes on the phosphatase hydrolysis, In general, the BNPP rate of hydrolysis was decreased in the following order: **4** > **5** > **8** > **9**.

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APPENDICES

APPENDIX A

Crystal structure data of [Zn(sul)$_2$(1,10-phen)] (4)

Table A 1: Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^2 x10^3) for **4**.U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3711(3)	-534(6)	2468(3)	40(1)
C(2)	3806(4)	-1840(7)	2213(4)	56(2)
C(3)	3339(3)	-2799(6)	2348(3)	42(2)
C(4)	2658(3)	-2824(6)	1977(3)	44(2)
C(11)	3449(3)	-3729(6)	2814(3)	41(1)
C(5)	2331(4)	-2092(8)	1453(4)	64(2)
C(6)	1691(5)	-2369(11)	1178(4)	81(3)
C(7)	1379(4)	-3347(11)	1393(4)	83(3)
C(8)	1704(4)	-4076(9)	1930(4)	68(2)
C(9)	2346(3)	-3799(7)	2239(3)	47(2)
C(10)	2830(3)	-4373(6)	2799(3)	42(2)
C(12)	4072(3)	-4041(7)	3302(4)	52(2)
C(13)	2781(3)	-5249(6)	3250(3)	49(2)
C(14)	2205(4)	-5787(7)	3406(4)	56(2)
C(15)	1667(4)	-5071(9)	3374(4)	74(2)
C(16)	1139(5)	-5557(12)	3566(5)	94(3)
C(17)	1167(6)	-6784(13)	3805(6)	101(4)
C(18)	1703(6)	-7499(11)	3849(6)	105(4)
C(19)	2217(5)	-7021(8)	3655(5)	80(3)
C(20)	399(7)	-6251(17)	4644(8)	162(6)
C(21)	4455(3)	2446(5)	3855(3)	39(1)
C(22)	4708(3)	2795(6)	4591(3)	42(2)
C(23)	5426(3)	2778(6)	4852(3)	35(1)
C(24)	5855(3)	3743(6)	4696(3)	39(1)
C(25)	5697(4)	4841(7)	4324(3)	53(2)
C(26)	6194(5)	5666(7)	4327(4)	60(2)
C(27)	6823(4)	5465(8)	4661(4)	66(2)
C(28)	6985(4)	4358(7)	5024(3)	55(2)
C(29)	6500(3)	3479(6)	5042(3)	42(2)
C(30)	6486(3)	2319(6)	5426(3)	37(1)

C(31)	5792(3)	1965(6)	5294(3)	40(1)
C(32)	5562(3)	885(7)	5637(4)	56(2)
C(33)	6948(3)	1650(7)	5850(3)	45(2)
C(34)	7661(3)	1777(7)	6045(3)	51(2)
C(35)	7981(4)	1494(8)	6705(4)	60(2)
C(36)	8642(4)	1583(11)	6924(4)	88(3)
C(37)	8988(4)	1933(11)	6472(5)	93(3)
C(38)	8687(4)	2173(10)	5813(4)	81(3)
C(39)	8032(3)	2090(8)	5604(4)	58(2)
C(40)	10050(5)	3010(20)	6279(9)	286(17)
C(41)	4389(3)	3980(6)	2154(3)	43(2)
C(42)	4430(4)	4933(7)	1705(4)	57(2)
C(43)	3899(4)	5241(7)	1220(4)	63(2)
C(44)	3321(4)	4611(7)	1174(3)	52(2)
C(45)	3312(3)	3669(6)	1651(3)	39(1)
C(46)	2739(5)	4852(10)	680(4)	80(3)
C(47)	2188(5)	4247(10)	670(4)	79(3)
C(48)	2156(4)	3307(8)	1156(4)	64(2)
C(49)	2726(3)	3003(6)	1644(3)	43(2)
C(50)	2216(4)	1489(8)	2126(4)	64(2)
C(51)	1620(4)	1753(10)	1659(6)	87(3)
C(52)	1596(4)	2631(10)	1195(5)	81(3)
F(2)	6039(3)	6777(4)	3999(3)	91(2)
F(1)	1351(3)	-1643(7)	663(3)	118(2)
N(1)	3845(2)	3370(4)	2131(2)	36(1)
N(2)	2756(2)	2123(5)	2123(3)	43(1)
O(1)	4073(2)	330(4)	2336(2)	48(1)
O(2)	3301(2)	-335(4)	2776(2)	53(1)
O(3)	685(8)	-8558(16)	4446(10)	272(9)
O(4)	3851(2)	2246(4)	3653(2)	49(1)
O(5)	4827(2)	2401(5)	3487(2)	52(1)
O(6)	9999(5)	888(13)	6701(8)	222(7)
O(1W)	110(40)	-10310(60)	4930(40)	239(16)
S(1)	469(3)	-7375(6)	4045(3)	193(3)
S(2)	9851(2)	2282(6)	6778(3)	174(2)
Zn(1)	3711(1)	1824(1)	2703(1)	37(1)

Table A2: Bond lengths [Å] and angles [°] for complex

C(1)-O(2)	1.223(7)
C(1)-O(1)	1.271(7)
C(1)-C(2)	1.514(9)
C(2)-C(3)	1.499(9)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(11)	1.357(9)
C(3)-C(4)	1.460(9)
C(4)-C(5)	1.371(10)
C(4)-C(9)	1.410(9)
C(11)-C(10)	1.478(8)
C(11)-C(12)	1.490(9)
C(5)-C(6)	1.371(12)
C(5)-H(5)	0.9300
C(6)-F(1)	1.363(10)
C(6)-C(7)	1.367(14)
C(7)-C(8)	1.386(12)
C(7)-H(7)	0.9300
C(8)-C(9)	1.387(9)
C(8)-H(8)	0.9300
C(9)-C(10)	1.474(9)
C(10)-C(13)	1.340(9)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.463(9)
C(13)-H(13)	0.9300
C(14)-C(15)	1.364(11)
C(14)-C(19)	1.404(11)
C(15)-C(16)	1.385(11)
C(15)-H(15)	0.9300
C(16)-C(17)	1.389(16)
C(16)-H(16)	0.9300
C(17)-C(18)	1.355(16)
C(17)-S(1)	1.797(9)
C(18)-C(19)	1.358(13)

C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-S(1)	1.753(17)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-O(5)	1.233(8)
C(21)-O(4)	1.269(7)
C(21)-C(22)	1.524(8)
C(22)-C(23)	1.490(8)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(31)	1.352(8)
C(23)-C(24)	1.462(8)
C(24)-C(25)	1.389(9)
C(24)-C(29)	1.410(9)
C(25)-C(26)	1.373(10)
C(25)-H(25)	0.9300
C(26)-F(2)	1.358(8)
C(26)-C(27)	1.362(11)
C(27)-C(28)	1.389(11)
C(27)-H(27)	0.9300
C(28)-C(29)	1.400(9)
C(28)-H(28)	0.9300
C(29)-C(30)	1.468(9)
C(30)-C(33)	1.344(9)
C(30)-C(31)	1.483(8)
C(31)-C(32)	1.494(9)
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(33)-C(34)	1.477(9)
C(33)-H(33)	0.9300
C(34)-C(39)	1.390(10)
C(34)-C(35)	1.395(10)
C(35)-C(36)	1.369(11)
C(35)-H(35)	0.9300
C(36)-C(37)	1.382(13)

C(36)-H(36)	0.9300
C(37)-C(38)	1.373(13)
C(37)-S(2)	1.826(9)
C(38)-C(39)	1.358(10)
C(38)-H(38)	0.9300
C(39)-H(39)	0.9300
C(40)-S(2)	1.437(14)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(41)-N(1)	1.317(7)
C(41)-C(42)	1.391(10)
C(41)-H(41)	0.9300
C(42)-C(43)	1.348(11)
C(42)-H(42)	0.9300
C(43)-C(44)	1.384(11)
C(43)-H(43)	0.9300
C(44)-C(45)	1.409(9)
C(44)-C(46)	1.415(11)
C(45)-N(1)	1.344(7)
C(45)-C(49)	1.432(9)
C(46)-C(47)	1.336(13)
C(46)-H(46)	0.9300
C(47)-C(48)	1.429(12)
C(47)-H(47)	0.9300
C(48)-C(49)	1.407(9)
C(48)-C(52)	1.413(12)
C(49)-N(2)	1.349(8)
C(50)-N(2)	1.335(9)
C(50)-C(51)	1.416(11)
C(50)-H(50)	0.9300
C(51)-C(52)	1.329(13)
C(51)-H(51)	0.9300
C(52)-H(52)	0.9300
N(1)-Zn(1)	2.084(5)
N(2)-Zn(1)	2.110(5)
O(1)-Zn(1)	1.994(4)
O(2)-Zn(1)	2.470(5)

O(3)-S(1)	1.509(19)
O(3)-O(1W)	2.56(7)
O(4)-Zn(1)	1.962(4)
O(6)-S(2)	1.530(12)
O(1W)-O(1W)#1	0.90(6)

O(2)-C(1)-O(1)	122.6(6)
O(2)-C(1)-C(2)	121.1(6)
O(1)-C(1)-C(2)	116.3(6)
C(3)-C(2)-C(1)	113.6(6)
C(3)-C(2)-H(2A)	108.8
C(1)-C(2)-H(2A)	108.8
C(3)-C(2)-H(2B)	108.8
C(1)-C(2)-H(2B)	108.8
H(2A)-C(2)-H(2B)	107.7
C(11)-C(3)-C(4)	109.2(6)
C(11)-C(3)-C(2)	128.5(6)
C(4)-C(3)-C(2)	122.3(6)
C(5)-C(4)-C(9)	121.5(7)
C(5)-C(4)-C(3)	130.1(7)
C(9)-C(4)-C(3)	108.4(6)
C(3)-C(11)-C(10)	109.2(6)
C(3)-C(11)-C(12)	127.3(6)
C(10)-C(11)-C(12)	123.4(6)
C(4)-C(5)-C(6)	117.5(8)
C(4)-C(5)-H(5)	121.3
C(6)-C(5)-H(5)	121.3
F(1)-C(6)-C(7)	118.4(9)
F(1)-C(6)-C(5)	118.7(10)
C(7)-C(6)-C(5)	122.9(8)
C(6)-C(7)-C(8)	119.9(8)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(7)-C(8)-C(9)	119.0(8)
C(7)-C(8)-H(8)	120.5
C(9)-C(8)-H(8)	120.5
C(8)-C(9)-C(4)	119.1(7)
C(8)-C(9)-C(10)	133.4(7)

C(4)-C(9)-C(10)	107.4(5)
C(13)-C(10)-C(9)	132.0(6)
C(13)-C(10)-C(11)	122.2(6)
C(9)-C(10)-C(11)	105.7(6)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-C(14)	130.1(7)
C(10)-C(13)-H(13)	115.0
C(14)-C(13)-H(13)	115.0
C(15)-C(14)-C(19)	118.4(7)
C(15)-C(14)-C(13)	121.0(7)
C(19)-C(14)-C(13)	120.4(8)
C(14)-C(15)-C(16)	120.9(9)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	119.1(10)
C(15)-C(16)-H(16)	120.4
C(17)-C(16)-H(16)	120.4
C(18)-C(17)-C(16)	120.5(9)
C(18)-C(17)-S(1)	122.0(10)
C(16)-C(17)-S(1)	117.5(11)
C(17)-C(18)-C(19)	120.1(11)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(18)-C(19)-C(14)	121.0(10)
C(18)-C(19)-H(19)	119.5
C(14)-C(19)-H(19)	119.5
S(1)-C(20)-H(20A)	109.5
S(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
S(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(5)-C(21)-O(4)	123.4(6)

O(5)-C(21)-C(22)	120.4(6)
O(4)-C(21)-C(22)	116.2(6)
C(23)-C(22)-C(21)	115.4(5)
C(23)-C(22)-H(22A)	108.4
C(21)-C(22)-H(22A)	108.4
C(23)-C(22)-H(22B)	108.4
C(21)-C(22)-H(22B)	108.4
H(22A)-C(22)-H(22B)	107.5
C(31)-C(23)-C(24)	108.0(5)
C(31)-C(23)-C(22)	128.1(6)
C(24)-C(23)-C(22)	123.7(5)
C(25)-C(24)-C(29)	121.1(6)
C(25)-C(24)-C(23)	129.2(6)
C(29)-C(24)-C(23)	109.5(5)
C(26)-C(25)-C(24)	116.9(7)
C(26)-C(25)-H(25)	121.5
C(24)-C(25)-H(25)	121.5
F(2)-C(26)-C(27)	118.3(7)
F(2)-C(26)-C(25)	117.4(8)
C(27)-C(26)-C(25)	124.2(7)
C(26)-C(27)-C(28)	119.0(7)
C(26)-C(27)-H(27)	120.5
C(28)-C(27)-H(27)	120.5
C(27)-C(28)-C(29)	119.5(7)
C(27)-C(28)-H(28)	120.2
C(29)-C(28)-H(28)	120.2
C(28)-C(29)-C(24)	119.2(6)
C(28)-C(29)-C(30)	133.6(6)
C(24)-C(29)-C(30)	106.8(5)
C(33)-C(30)-C(29)	133.0(6)
C(33)-C(30)-C(31)	121.2(6)
C(29)-C(30)-C(31)	105.7(5)
C(23)-C(31)-C(30)	109.9(5)
C(23)-C(31)-C(32)	127.4(6)
C(30)-C(31)-C(32)	122.7(6)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5

C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(30)-C(33)-C(34)	131.6(6)
C(30)-C(33)-H(33)	114.2
C(34)-C(33)-H(33)	114.2
C(39)-C(34)-C(35)	118.3(7)
C(39)-C(34)-C(33)	124.1(6)
C(35)-C(34)-C(33)	117.5(6)
C(36)-C(35)-C(34)	121.1(7)
C(36)-C(35)-H(35)	119.5
C(34)-C(35)-H(35)	119.5
C(35)-C(36)-C(37)	118.5(8)
C(35)-C(36)-H(36)	120.8
C(37)-C(36)-H(36)	120.8
C(38)-C(37)-C(36)	121.6(8)
C(38)-C(37)-S(2)	118.9(8)
C(36)-C(37)-S(2)	119.0(8)
C(39)-C(38)-C(37)	119.3(8)
C(39)-C(38)-H(38)	120.4
C(37)-C(38)-H(38)	120.4
C(38)-C(39)-C(34)	121.1(7)
C(38)-C(39)-H(39)	119.4
C(34)-C(39)-H(39)	119.4
S(2)-C(40)-H(40A)	109.5
S(2)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
S(2)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
N(1)-C(41)-C(42)	122.5(6)
N(1)-C(41)-H(41)	118.8
C(42)-C(41)-H(41)	118.8
C(43)-C(42)-C(41)	119.2(7)
C(43)-C(42)-H(42)	120.4
C(41)-C(42)-H(42)	120.4
C(42)-C(43)-C(44)	120.1(7)
C(42)-C(43)-H(43)	120.0

C(44)-C(43)-H(43)	120.0
C(43)-C(44)-C(45)	117.6(7)
C(43)-C(44)-C(46)	124.4(8)
C(45)-C(44)-C(46)	118.0(7)
N(1)-C(45)-C(44)	121.7(6)
N(1)-C(45)-C(49)	117.7(5)
C(44)-C(45)-C(49)	120.6(6)
C(47)-C(46)-C(44)	122.1(8)
C(47)-C(46)-H(46)	118.9
C(44)-C(46)-H(46)	118.9
C(46)-C(47)-C(48)	121.5(7)
C(46)-C(47)-H(47)	119.3
C(48)-C(47)-H(47)	119.3
C(49)-C(48)-C(52)	115.6(8)
C(49)-C(48)-C(47)	118.6(8)
C(52)-C(48)-C(47)	125.8(8)
N(2)-C(49)-C(48)	123.8(7)
N(2)-C(49)-C(45)	117.1(5)
C(48)-C(49)-C(45)	119.1(7)
N(2)-C(50)-C(51)	121.6(8)
N(2)-C(50)-H(50)	119.2
C(51)-C(50)-H(50)	119.2
C(52)-C(51)-C(50)	119.6(8)
C(52)-C(51)-H(51)	120.2
C(50)-C(51)-H(51)	120.2
C(51)-C(52)-C(48)	121.2(8)
C(51)-C(52)-H(52)	119.4
C(48)-C(52)-H(52)	119.4
C(41)-N(1)-C(45)	118.9(5)
C(41)-N(1)-Zn(1)	127.7(4)
C(45)-N(1)-Zn(1)	113.1(4)
C(50)-N(2)-C(49)	118.1(6)
C(50)-N(2)-Zn(1)	129.1(5)
C(49)-N(2)-Zn(1)	112.3(4)
C(1)-O(1)-Zn(1)	100.3(4)
C(1)-O(2)-Zn(1)	79.5(4)
S(1)-O(3)-O(1W)	134.9(16)
C(21)-O(4)-Zn(1)	104.6(4)

O(1W)#1-O(1W)-O(3)	87(9)
O(3)-S(1)-C(20)	104.3(9)
O(3)-S(1)-C(17)	106.4(8)
C(20)-S(1)-C(17)	100.5(6)
C(40)-S(2)-O(6)	109.8(13)
C(40)-S(2)-C(37)	108.4(6)
O(6)-S(2)-C(37)	89.1(7)
O(4)-Zn(1)-O(1)	125.91(19)
O(4)-Zn(1)-N(1)	112.33(19)
O(1)-Zn(1)-N(1)	106.75(18)
O(4)-Zn(1)-N(2)	114.5(2)
O(1)-Zn(1)-N(2)	108.34(19)
N(1)-Zn(1)-N(2)	79.08(19)
O(4)-Zn(1)-O(2)	96.74(18)
O(1)-Zn(1)-O(2)	57.55(16)
N(1)-Zn(1)-O(2)	150.03(17)
N(2)-Zn(1)-O(2)	82.43(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y-2,-z+1

Table A3: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **4**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	38(3)	42(4)	34(3)	2(3)	-1(3)	-2(3)
C(2)	62(4)	45(4)	71(5)	0(4)	34(4)	-10(3)
C(3)	43(3)	35(3)	51(4)	-12(3)	18(3)	-5(3)
C(4)	43(4)	50(4)	38(3)	-10(3)	9(3)	3(3)
C(11)	41(3)	35(3)	50(4)	-11(3)	20(3)	-7(3)
C(5)	65(5)	75(6)	51(4)	4(4)	14(4)	13(4)
C(6)	81(7)	106(8)	49(5)	3(5)	4(5)	33(6)
C(7)	45(5)	132(9)	64(5)	-10(6)	0(4)	7(5)
C(8)	51(4)	93(6)	62(5)	-5(5)	15(4)	-12(4)
C(9)	40(3)	58(4)	43(4)	-13(3)	12(3)	-7(3)
C(10)	33(3)	46(4)	49(4)	-10(3)	13(3)	-7(3)
C(12)	35(3)	55(4)	65(5)	-13(4)	13(3)	-5(3)
C(13)	53(4)	44(4)	53(4)	-5(3)	17(3)	-8(3)
C(14)	62(5)	60(5)	53(4)	-7(4)	26(4)	-17(4)
C(15)	75(6)	81(6)	76(6)	3(5)	38(5)	-15(5)
C(16)	72(6)	124(10)	95(7)	-12(7)	41(5)	-23(6)
C(17)	90(8)	118(9)	106(8)	-5(7)	45(6)	-65(7)
C(18)	121(10)	88(8)	126(10)	-7(7)	66(8)	-37(7)
C(19)	98(7)	62(6)	93(7)	6(5)	48(6)	-17(5)
C(20)	138(12)	225(18)	156(13)	42(13)	96(11)	4(12)
C(21)	47(4)	27(3)	36(3)	-1(3)	-4(3)	8(3)
C(22)	50(4)	41(4)	35(3)	-6(3)	9(3)	1(3)
C(23)	43(3)	41(3)	21(3)	-4(2)	7(2)	-4(3)
C(24)	51(4)	39(3)	27(3)	-8(3)	10(3)	-5(3)
C(25)	67(5)	51(4)	37(4)	1(3)	7(3)	1(4)
C(26)	100(6)	42(4)	41(4)	4(3)	21(4)	-10(4)
C(27)	86(6)	68(5)	50(4)	-1(4)	29(4)	-36(5)
C(28)	59(4)	64(5)	45(4)	-1(4)	18(3)	-14(4)
C(29)	48(4)	47(4)	35(3)	-2(3)	14(3)	-9(3)
C(30)	41(3)	44(3)	28(3)	-5(3)	13(3)	-6(3)
C(31)	44(3)	40(3)	34(3)	-7(3)	9(3)	-13(3)
C(32)	51(4)	54(4)	55(4)	15(3)	-1(3)	-16(3)
C(33)	44(4)	53(4)	36(3)	-1(3)	8(3)	-3(3)
C(34)	47(4)	59(4)	46(4)	-7(3)	11(3)	-7(3)

C(35)	51(4)	78(6)	52(4)	4(4)	14(3)	6(4)
C(36)	55(5)	138(9)	59(5)	14(6)	-7(4)	13(5)
C(37)	36(4)	145(10)	92(7)	7(7)	5(4)	-9(5)
C(38)	46(4)	138(9)	62(5)	-7(5)	17(4)	-2(5)
C(39)	51(4)	81(6)	40(4)	-10(4)	8(3)	-4(4)
C(40)	21(5)	600(40)	228(18)	240(20)	17(7)	-31(11)
C(41)	41(3)	44(4)	47(4)	-7(3)	18(3)	-2(3)
C(42)	55(4)	51(4)	73(5)	-2(4)	31(4)	-6(4)
C(43)	92(6)	50(4)	61(5)	9(4)	48(5)	6(4)
C(44)	65(5)	52(4)	40(4)	7(3)	19(3)	17(4)
C(45)	46(4)	36(3)	38(3)	-2(3)	16(3)	8(3)
C(46)	89(7)	97(7)	51(5)	24(5)	14(5)	29(6)
C(47)	68(6)	107(8)	49(5)	11(5)	-11(4)	36(5)
C(48)	49(4)	79(6)	55(4)	-10(4)	-5(3)	15(4)
C(49)	41(3)	47(4)	37(3)	-6(3)	4(3)	14(3)
C(50)	47(4)	61(5)	83(6)	4(4)	16(4)	-8(4)
C(51)	38(4)	91(7)	124(8)	-2(6)	3(5)	-10(4)
C(52)	47(5)	92(7)	89(7)	-8(6)	-14(4)	12(5)
F(2)	141(5)	54(3)	79(3)	20(3)	31(3)	-12(3)
F(1)	105(4)	164(6)	69(3)	24(4)	-9(3)	44(4)
N(1)	33(3)	33(3)	39(3)	-1(2)	7(2)	2(2)
N(2)	33(3)	42(3)	51(3)	-2(2)	6(2)	2(2)
O(1)	47(3)	36(2)	61(3)	-3(2)	14(2)	-6(2)
O(2)	68(3)	42(3)	57(3)	-1(2)	30(3)	4(2)
O(3)	269(17)	237(16)	360(20)	12(15)	175(16)	-130(14)
O(4)	43(3)	56(3)	42(2)	-6(2)	1(2)	-3(2)
O(5)	51(3)	69(3)	34(2)	-11(2)	8(2)	10(2)
O(6)	133(9)	166(11)	340(19)	-65(12)	12(10)	27(8)
O(1W)	260(50)	230(60)	270(40)	70(40)	150(30)	80(30)
S(1)	177(4)	214(5)	240(6)	-46(5)	147(4)	-120(4)
S(2)	49(2)	245(6)	216(5)	39(4)	10(2)	16(2)
Zn(1)	34(1)	39(1)	37(1)	1(1)	5(1)	1(1)

Table 4: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **4**.

	x	y	z	U(eq)
H(2A)	3760	-1796	1734	67
H(2B)	4244	-2118	2421	67
H(5)	2536	-1434	1291	77
H(7)	949	-3523	1180	99
H(8)	1495	-4740	2082	82
H(12A)	4418	-3579	3192	77
H(12B)	4155	-4929	3285	77
H(12C)	4046	-3817	3745	77
H(13)	3173	-5564	3503	59
H(15)	1654	-4245	3220	89
H(16)	771	-5067	3536	112
H(18)	1718	-8318	4012	127
H(19)	2583	-7519	3686	96
H(20A)	124	-6573	4909	244
H(20B)	214	-5491	4423	244
H(20C)	820	-6072	4929	244
H(22A)	4553	3633	4657	51
H(22B)	4523	2215	4855	51
H(25)	5274	5009	4083	64
H(27)	7139	6059	4647	79
H(28)	7413	4203	5254	67
H(32A)	5098	845	5501	84
H(32B)	5700	1003	6113	84
H(32C)	5741	114	5518	84
H(33)	6791	987	6058	54
H(35)	7742	1240	7001	72
H(36)	8852	1413	7368	106
H(38)	8929	2390	5514	97
H(39)	7827	2244	5157	69
H(40A)	10202	2455	5985	429
H(40B)	10392	3574	6493	429
H(40C)	9688	3489	6026	429

H(41)	4759	3764	2482	51
H(42)	4819	5355	1738	69
H(43)	3921	5876	917	75
H(46)	2742	5450	351	95
H(47)	1816	4443	339	95
H(50)	2232	859	2442	77
H(51)	1248	1314	1677	105
H(52)	1203	2804	890	98

APPENDIX B

Crystal structure data of [Zn(sul)$_2$(2,9-dime-phen)] (5)

Table B1: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **5**.

	x	y	z	U(eq)
C(1)	7539(6)	2802(5)	2410(6)	67(2)
C(2)	8388(7)	2219(8)	2251(8)	105(4)
C(3)	8300(10)	1478(8)	1454(10)	118(5)
C(4)	7437(11)	1296(7)	818(8)	105(4)
C(5)	7272(16)	489(10)	-22(10)	146(8)
C(6)	6455(18)	372(9)	-584(9)	166(10)
C(7)	5536(11)	923(6)	-445(6)	101(4)
C(8)	4592(14)	788(7)	-1015(5)	127(6)
C(9)	3840(11)	1364(7)	-798(5)	105(4)
C(10)	3969(8)	2142(6)	28(4)	74(3)
C(11)	5641(9)	1694(5)	374(5)	74(3)
C(12)	6598(8)	1860(5)	991(6)	75(3)
C(13)	7594(6)	3616(6)	3265(5)	71(2)
C(14)	3184(7)	2818(7)	297(5)	79(2)
C(15)	3763(4)	2568(4)	2599(3)	33(1)
C(16)	3350(4)	2464(5)	3375(3)	40(1)
C(17)	4262(4)	2777(4)	4121(3)	36(1)

C(18)	5238(4)	2291(4)	4082(3)	35(1)
C(19)	5465(5)	1451(4)	3437(3)	42(1)
C(20)	6423(5)	1129(4)	3604(3)	45(1)
C(21)	7145(5)	1574(5)	4359(4)	49(1)
C(22)	6917(5)	2417(5)	5002(3)	43(1)
C(23)	5973(5)	2788(4)	4865(3)	37(1)
C(24)	5457(4)	3601(4)	5413(3)	35(1)
C(25)	4367(4)	3501(4)	4904(3)	36(1)
C(26)	3552(5)	4146(5)	5243(3)	44(1)
C(27)	5815(5)	4326(4)	6202(3)	37(1)
C(28)	6917(5)	4631(4)	6761(3)	37(1)
C(29)	7939(5)	4767(5)	6490(4)	46(1)
C(30)	8936(5)	5069(5)	7039(4)	54(2)
C(31)	8944(5)	5260(5)	7878(4)	54(2)
C(32)	7944(5)	5157(5)	8164(4)	53(2)
C(33)	6940(5)	4856(5)	7607(3)	44(1)
C(34)	10317(8)	4345(9)	8567(9)	137(5)
C(35)	6264(7)	5462(5)	2027(4)	58(2)
C(36)	6488(5)	6583(5)	1915(5)	54(2)
C(37)	5555(5)	7125(4)	2157(4)	44(1)
C(38)	4523(5)	6951(4)	1569(3)	41(1)
C(39)	4166(5)	6308(5)	722(4)	52(2)
C(40)	3175(6)	6371(5)	323(3)	55(2)
C(41)	2519(5)	7012(5)	706(4)	52(2)
C(42)	2855(5)	7630(5)	1562(3)	42(1)

C(43)	3837(4)	7574(4)	1999(3)	36(1)
C(44)	4429(4)	8130(4)	2884(3)	37(1)
C(45)	5518(5)	7822(4)	2919(3)	41(1)
C(46)	6369(5)	8212(5)	3706(4)	53(2)
C(47)	4121(5)	8766(4)	3557(3)	44(1)
C(48)	3023(5)	9031(4)	3633(3)	38(1)
C(49)	2025(5)	8211(5)	3285(3)	44(1)
C(50)	1009(6)	8449(5)	3372(4)	56(2)
C(51)	1002(5)	9532(6)	3805(4)	54(2)
C(52)	1976(6)	10348(5)	4182(4)	55(2)
C(53)	2985(5)	10093(4)	4097(3)	44(1)
C(54)	-753(11)	9750(15)	2873(9)	173(7)
F(1)	6670(3)	312(3)	2973(2)	60(1)
F(2)	2833(3)	5757(4)	-511(2)	77(1)
N(1)	6689(4)	2626(4)	1795(4)	52(1)
N(2)	4894(5)	2276(4)	596(3)	58(2)
O(1)	3206(3)	1960(3)	1903(2)	50(1)
O(2)	4676(3)	3289(3)	2730(2)	40(1)
O(3)	10051(6)	6287(9)	9444(4)	143(3)
O(4)	5391(4)	4743(4)	1587(4)	76(2)
O(5)	6909(7)	5301(5)	2521(3)	99(2)
O(6A)	-1094(12)	8782(19)	3781(18)	207(11)
O(6B)	-103(11)	11146(11)	4365(10)	121(5)
O(1WA)	831(8)	745(9)	1159(7)	66(3)
O(1WB)	1044(14)	1250(20)	1707(19)	191(11)

O(2WA)	8838(14)	6644(18)	3457(17)	128(8)
O(2WB)	9040(20)	6534(18)	3910(20)	173(15)
O(3W)	309(8)	1439(11)	-109(10)	226(6)
O(4WA)	9879(19)	6510(20)	4980(15)	177(9)
O(4WB)	9750(19)	5515(18)	5127(12)	163(8)
O(5W)	607(13)	12582(15)	3619(14)	155(7)
S(4)	10267(2)	5681(2)	8601(2)	83(1)
S(5)	-331(2)	9852(2)	3904(2)	98(1)
Zn(1)	5390(1)	3379(1)	1810(1)	35(1)

Table A3: Bond lengths [Å] and angles [°] for complex **5**.

C(1)-N(1)	1.331(10)
C(1)-C(2)	1.424(9)
C(1)-C(13)	1.497(11)
C(2)-C(3)	1.377(16)
C(2)-H(2)	0.9500
C(3)-C(4)	1.364(17)
C(3)-H(3)	0.9500
C(4)-C(12)	1.401(11)
C(4)-C(5)	1.451(18)
C(5)-C(6)	1.27(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.47(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.380(18)
C(7)-C(11)	1.417(10)
C(8)-C(9)	1.328(17)
C(8)-H(8)	0.9500
C(9)-C(10)	1.426(10)
C(9)-H(9)	0.9500
C(10)-N(2)	1.361(10)
C(10)-C(14)	1.462(12)
C(11)-N(2)	1.330(10)
C(11)-C(12)	1.429(12)

C(12)-N(1)	1.398(9)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-O(1)	1.231(6)
C(15)-O(2)	1.264(6)
C(15)-C(16)	1.523(7)
C(16)-C(17)	1.495(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(25)	1.347(7)
C(17)-C(18)	1.477(7)
C(18)-C(19)	1.390(7)
C(18)-C(23)	1.408(7)
C(19)-C(20)	1.370(8)
C(19)-H(19)	0.9500
C(20)-C(21)	1.364(8)
C(20)-F(1)	1.371(6)
C(21)-C(22)	1.391(7)
C(21)-H(21)	0.9500
C(22)-C(23)	1.381(7)
C(22)-H(22)	0.9500

C(23)-C(24)	1.484(6)
C(24)-C(27)	1.342(7)
C(24)-C(25)	1.482(7)
C(25)-C(26)	1.497(7)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-C(28)	1.475(7)
C(27)-H(27)	0.9500
C(28)-C(33)	1.388(7)
C(28)-C(29)	1.396(8)
C(29)-C(30)	1.367(9)
C(29)-H(29)	0.9500
C(30)-C(31)	1.383(9)
C(30)-H(30)	0.9500
C(31)-C(32)	1.383(9)
C(31)-S(4)	1.806(6)
C(32)-C(33)	1.380(8)
C(32)-H(32)	0.9500
C(33)-H(33)	0.9500
C(34)-S(4)	1.758(9)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-O(5)	1.201(9)

C(35)-O(4)	1.254(9)
C(35)-C(36)	1.527(8)
C(36)-C(37)	1.506(8)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-C(45)	1.346(8)
C(37)-C(38)	1.465(8)
C(38)-C(39)	1.392(8)
C(38)-C(43)	1.406(7)
C(39)-C(40)	1.370(9)
C(39)-H(39)	0.9500
C(40)-C(41)	1.358(9)
C(40)-F(2)	1.363(6)
C(41)-C(42)	1.396(7)
C(41)-H(41)	0.9500
C(42)-C(43)	1.385(7)
C(42)-H(42)	0.9500
C(43)-C(44)	1.482(7)
C(44)-C(47)	1.337(7)
C(44)-C(45)	1.486(7)
C(45)-C(46)	1.489(8)
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-C(48)	1.481(8)

C(47)-H(47)	0.9500
C(48)-C(53)	1.380(7)
C(48)-C(49)	1.386(8)
C(49)-C(50)	1.369(9)
C(49)-H(49)	0.9500
C(50)-C(51)	1.381(9)
C(50)-H(50)	0.9500
C(51)-C(52)	1.368(9)
C(51)-S(5)	1.799(6)
C(52)-C(53)	1.369(9)
C(52)-H(52)	0.9500
C(53)-H(53)	0.9500
C(54)-S(5)	1.747(14)
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
N(1)-Zn(1)	2.054(5)
N(2)-Zn(1)	2.055(5)
O(1)-O(1WB)	2.595(17)
O(1)-O(1WA)	2.959(11)
O(2)-Zn(1)	1.928(3)
O(3)-S(4)	1.496(7)
O(4)-Zn(1)	1.960(4)
O(5)-O(2WA)	2.64(2)
O(6A)-S(5)	1.47(2)

O(6B)-S(5)	1.577(13)
O(6B)-O(5W)	2.68(3)
O(1WA)-O(1WB)	0.93(3)
O(1WA)-O(3W)	2.696(19)
O(2WA)-O(2WB)	0.85(4)
O(2WB)-O(4WA)	2.03(4)
O(4WA)-O(4WB)	1.40(3)
O(4WB)-O(4WB)#1	1.56(5)

N(1)-C(1)-C(2)	119.9(8)
N(1)-C(1)-C(13)	119.6(5)
C(2)-C(1)-C(13)	120.5(9)
C(3)-C(2)-C(1)	118.4(10)
C(3)-C(2)-H(2)	120.8
C(1)-C(2)-H(2)	120.8
C(4)-C(3)-C(2)	122.2(8)
C(4)-C(3)-H(3)	118.9
C(2)-C(3)-H(3)	118.9
C(3)-C(4)-C(12)	118.5(10)
C(3)-C(4)-C(5)	124.7(11)
C(12)-C(4)-C(5)	116.6(13)
C(6)-C(5)-C(4)	121.1(12)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(7)	125.0(11)

C(5)-C(6)-H(6)	117.5
C(7)-C(6)-H(6)	117.5
C(8)-C(7)-C(11)	116.2(10)
C(8)-C(7)-C(6)	128.0(10)
C(11)-C(7)-C(6)	115.8(13)
C(9)-C(8)-C(7)	121.0(8)
C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5
C(8)-C(9)-C(10)	121.7(11)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-H(9)	119.1
N(2)-C(10)-C(9)	117.6(9)
N(2)-C(10)-C(14)	118.2(6)
C(9)-C(10)-C(14)	124.1(9)
N(2)-C(11)-C(7)	123.2(10)
N(2)-C(11)-C(12)	118.3(6)
C(7)-C(11)-C(12)	118.5(9)
N(1)-C(12)-C(4)	119.6(10)
N(1)-C(12)-C(11)	117.7(6)
C(4)-C(12)-C(11)	122.7(9)
C(1)-C(13)-H(13A)	109.5
C(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5

H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(1)-C(15)-O(2)	124.9(5)
O(1)-C(15)-C(16)	119.1(5)
O(2)-C(15)-C(16)	115.9(4)
C(17)-C(16)-C(15)	114.5(4)
C(17)-C(16)-H(16A)	108.6
C(15)-C(16)-H(16A)	108.6
C(17)-C(16)-H(16B)	108.6
C(15)-C(16)-H(16B)	108.6
H(16A)-C(16)-H(16B)	107.6
C(25)-C(17)-C(18)	108.9(4)
C(25)-C(17)-C(16)	129.1(5)
C(18)-C(17)-C(16)	122.0(4)
C(19)-C(18)-C(23)	120.8(5)
C(19)-C(18)-C(17)	130.4(5)
C(23)-C(18)-C(17)	108.7(4)
C(20)-C(19)-C(18)	117.0(5)
C(20)-C(19)-H(19)	121.5
C(18)-C(19)-H(19)	121.5

C(21)-C(20)-C(19)	124.0(5)
C(21)-C(20)-F(1)	118.1(5)
C(19)-C(20)-F(1)	118.0(5)
C(20)-C(21)-C(22)	118.9(5)
C(20)-C(21)-H(21)	120.6
C(22)-C(21)-H(21)	120.6
C(23)-C(22)-C(21)	119.7(5)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(22)-C(23)-C(18)	119.6(4)
C(22)-C(23)-C(24)	133.3(5)
C(18)-C(23)-C(24)	106.8(4)
C(27)-C(24)-C(25)	122.2(4)
C(27)-C(24)-C(23)	132.0(5)
C(25)-C(24)-C(23)	105.8(4)
C(17)-C(25)-C(24)	109.6(4)
C(17)-C(25)-C(26)	127.6(5)
C(24)-C(25)-C(26)	122.8(4)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-C(28)	129.4(5)

C(24)-C(27)-H(27)	115.3
C(28)-C(27)-H(27)	115.3
C(33)-C(28)-C(29)	118.3(5)
C(33)-C(28)-C(27)	118.1(5)
C(29)-C(28)-C(27)	123.4(5)
C(30)-C(29)-C(28)	120.9(5)
C(30)-C(29)-H(29)	119.6
C(28)-C(29)-H(29)	119.6
C(29)-C(30)-C(31)	120.1(6)
C(29)-C(30)-H(30)	120.0
C(31)-C(30)-H(30)	120.0
C(32)-C(31)-C(30)	120.1(6)
C(32)-C(31)-S(4)	120.2(5)
C(30)-C(31)-S(4)	119.7(5)
C(33)-C(32)-C(31)	119.6(5)
C(33)-C(32)-H(32)	120.2
C(31)-C(32)-H(32)	120.2
C(32)-C(33)-C(28)	121.0(5)
C(32)-C(33)-H(33)	119.5
C(28)-C(33)-H(33)	119.5
S(4)-C(34)-H(34A)	109.5
S(4)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
S(4)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5

H(34B)-C(34)-H(34C)	109.5
O(5)-C(35)-O(4)	122.8(7)
O(5)-C(35)-C(36)	120.2(7)
O(4)-C(35)-C(36)	117.0(6)
C(37)-C(36)-C(35)	109.5(5)
C(37)-C(36)-H(36A)	109.8
C(35)-C(36)-H(36A)	109.8
C(37)-C(36)-H(36B)	109.8
C(35)-C(36)-H(36B)	109.8
H(36A)-C(36)-H(36B)	108.2
C(45)-C(37)-C(38)	109.4(5)
C(45)-C(37)-C(36)	127.1(6)
C(38)-C(37)-C(36)	123.5(5)
C(39)-C(38)-C(43)	120.1(5)
C(39)-C(38)-C(37)	131.2(5)
C(43)-C(38)-C(37)	108.7(5)
C(40)-C(39)-C(38)	117.6(6)
C(40)-C(39)-H(39)	121.2
C(38)-C(39)-H(39)	121.2
C(41)-C(40)-F(2)	118.3(6)
C(41)-C(40)-C(39)	123.9(5)
F(2)-C(40)-C(39)	117.7(6)
C(40)-C(41)-C(42)	118.6(6)
C(40)-C(41)-H(41)	120.7
C(42)-C(41)-H(41)	120.7

C(43)-C(42)-C(41)	119.8(5)
C(43)-C(42)-H(42)	120.1
C(41)-C(42)-H(42)	120.1
C(42)-C(43)-C(38)	119.7(5)
C(42)-C(43)-C(44)	133.1(5)
C(38)-C(43)-C(44)	107.0(5)
C(47)-C(44)-C(43)	131.3(5)
C(47)-C(44)-C(45)	123.1(5)
C(43)-C(44)-C(45)	105.6(4)
C(37)-C(45)-C(44)	109.2(5)
C(37)-C(45)-C(46)	128.0(5)
C(44)-C(45)-C(46)	122.8(5)
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(44)-C(47)-C(48)	128.7(5)
C(44)-C(47)-H(47)	115.6
C(48)-C(47)-H(47)	115.6
C(53)-C(48)-C(49)	118.9(5)
C(53)-C(48)-C(47)	120.0(5)
C(49)-C(48)-C(47)	121.0(5)
C(50)-C(49)-C(48)	121.1(5)

C(50)-C(49)-H(49)	119.4
C(48)-C(49)-H(49)	119.4
C(49)-C(50)-C(51)	118.3(6)
C(49)-C(50)-H(50)	120.9
C(51)-C(50)-H(50)	120.9
C(52)-C(51)-C(50)	121.7(6)
C(52)-C(51)-S(5)	119.8(5)
C(50)-C(51)-S(5)	118.4(5)
C(51)-C(52)-C(53)	119.1(6)
C(51)-C(52)-H(52)	120.4
C(53)-C(52)-H(52)	120.4
C(52)-C(53)-C(48)	120.7(6)
C(52)-C(53)-H(53)	119.6
C(48)-C(53)-H(53)	119.6
S(5)-C(54)-H(54A)	109.5
S(5)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
S(5)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(1)-N(1)-C(12)	121.3(6)
C(1)-N(1)-Zn(1)	129.2(4)
C(12)-N(1)-Zn(1)	109.5(5)
C(11)-N(2)-C(10)	120.3(6)
C(11)-N(2)-Zn(1)	111.7(5)

C(10)-N(2)-Zn(1)	128.0(5)
C(15)-O(1)-O(1WB)	119.8(8)
C(15)-O(1)-O(1WA)	137.4(4)
O(1WB)-O(1)-O(1WA)	17.8(7)
C(15)-O(2)-Zn(1)	120.1(3)
C(35)-O(4)-Zn(1)	107.5(5)
C(35)-O(5)-O(2WA)	128.2(7)
S(5)-O(6B)-O(5W)	121.8(9)
O(1WB)-O(1WA)-O(3W)	120(2)
O(1WB)-O(1WA)-O(1)	58.4(15)
O(3W)-O(1WA)-O(1)	104.4(5)
O(1WA)-O(1WB)-O(1)	104(2)
O(2WB)-O(2WA)-O(5)	115(3)
O(2WA)-O(2WB)-O(4WA)	166(3)
O(4WB)-O(4WA)-O(2WB)	120.1(16)
O(4WA)-O(4WB)-O(4WB)#1	137(3)
O(3)-S(4)-C(34)	107.0(7)
O(3)-S(4)-C(31)	106.3(4)
C(34)-S(4)-C(31)	96.6(4)
O(6A)-S(5)-O(6B)	143.5(10)
O(6A)-S(5)-C(54)	93.4(13)
O(6B)-S(5)-C(54)	99.8(9)
O(6A)-S(5)-C(51)	103.7(7)
O(6B)-S(5)-C(51)	107.9(5)
C(54)-S(5)-C(51)	97.9(4)

O(2)-Zn(1)-O(4)	113.27(18)
O(2)-Zn(1)-N(1)	108.64(18)
O(4)-Zn(1)-N(1)	126.66(19)
O(2)-Zn(1)-N(2)	125.61(18)
O(4)-Zn(1)-N(2)	98.0(2)
N(1)-Zn(1)-N(2)	82.6(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table 3B: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **5**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	60(4)	48(4)	126(7)	51(4)	51(5)	33(3)
C(2)	82(6)	88(6)	210(12)	100(8)	81(7)	58(5)
C(3)	137(9)	80(6)	226(14)	98(8)	142(10)	87(7)
C(4)	159(10)	52(4)	168(10)	65(6)	128(9)	69(6)
C(5)	280(20)	66(6)	194(15)	84(10)	209(16)	111(10)
C(6)	370(30)	45(5)	144(12)	51(7)	206(16)	81(11)
C(7)	206(11)	30(3)	76(6)	12(4)	103(7)	19(5)
C(8)	283(17)	35(4)	40(4)	0(4)	67(8)	-7(7)
C(9)	191(11)	56(5)	37(4)	10(4)	22(5)	-23(6)
C(10)	127(7)	52(4)	23(3)	15(3)	8(4)	-22(4)
C(11)	146(8)	29(3)	52(4)	11(3)	58(5)	15(4)
C(12)	130(7)	25(3)	106(6)	32(3)	97(6)	40(4)
C(13)	50(4)	65(4)	104(6)	43(4)	-1(4)	18(3)
C(14)	99(6)	83(5)	45(4)	27(4)	-5(4)	4(5)
C(15)	43(3)	35(3)	29(2)	11(2)	13(2)	25(2)
C(16)	46(3)	50(3)	34(3)	21(2)	20(2)	20(2)
C(17)	46(3)	43(3)	29(2)	17(2)	14(2)	24(2)
C(18)	49(3)	37(3)	29(2)	15(2)	17(2)	23(2)
C(19)	60(3)	43(3)	28(2)	12(2)	14(2)	26(3)
C(20)	71(4)	40(3)	34(3)	10(2)	23(3)	33(3)
C(21)	68(4)	57(3)	46(3)	27(3)	22(3)	46(3)

C(22)	59(3)	51(3)	30(3)	16(2)	11(2)	34(3)
C(23)	55(3)	40(3)	29(2)	16(2)	14(2)	28(2)
C(24)	51(3)	42(3)	26(2)	18(2)	17(2)	30(2)
C(25)	50(3)	41(3)	26(2)	15(2)	16(2)	25(2)
C(26)	52(3)	54(3)	39(3)	20(3)	21(2)	33(3)
C(27)	50(3)	40(3)	29(2)	14(2)	13(2)	23(2)
C(28)	50(3)	38(3)	33(3)	16(2)	13(2)	24(2)
C(29)	54(3)	51(3)	39(3)	20(3)	15(3)	17(3)
C(30)	54(4)	61(4)	58(4)	26(3)	22(3)	20(3)
C(31)	52(4)	58(4)	57(4)	26(3)	5(3)	19(3)
C(32)	64(4)	67(4)	36(3)	23(3)	14(3)	25(3)
C(33)	51(3)	53(3)	36(3)	20(2)	14(2)	23(3)
C(34)	63(5)	111(8)	248(15)	116(9)	-40(7)	-2(5)
C(35)	88(5)	46(4)	64(4)	25(3)	48(4)	45(4)
C(36)	54(4)	39(3)	79(4)	28(3)	22(3)	20(3)
C(37)	48(3)	23(2)	58(3)	11(2)	11(3)	9(2)
C(38)	49(3)	27(2)	41(3)	10(2)	11(2)	4(2)
C(39)	58(4)	36(3)	53(3)	6(3)	26(3)	-1(3)
C(40)	60(4)	58(4)	29(3)	6(3)	5(3)	-10(3)
C(41)	46(3)	68(4)	35(3)	19(3)	4(2)	3(3)
C(42)	45(3)	46(3)	32(3)	13(2)	4(2)	9(2)
C(43)	42(3)	29(2)	32(2)	8(2)	7(2)	6(2)
C(44)	45(3)	26(2)	37(3)	7(2)	0(2)	12(2)
C(45)	44(3)	26(2)	48(3)	9(2)	-2(2)	10(2)
C(46)	49(3)	43(3)	60(4)	15(3)	-9(3)	11(3)

C(47)	58(3)	33(3)	34(3)	7(2)	-4(2)	12(2)
C(48)	56(3)	34(3)	23(2)	9(2)	2(2)	13(2)
C(49)	61(4)	37(3)	37(3)	12(2)	12(3)	16(3)
C(50)	57(4)	58(4)	51(3)	24(3)	13(3)	1(3)
C(51)	59(4)	67(4)	47(3)	23(3)	25(3)	27(3)
C(52)	74(4)	46(3)	48(3)	11(3)	24(3)	23(3)
C(53)	57(3)	37(3)	36(3)	8(2)	14(2)	14(2)
C(54)	121(10)	285(19)	182(14)	102(13)	56(9)	155(12)
F(1)	89(3)	56(2)	48(2)	11(2)	29(2)	50(2)
F(2)	76(3)	89(3)	30(2)	-5(2)	12(2)	-11(2)
N(1)	60(3)	31(2)	80(4)	24(2)	42(3)	26(2)
N(2)	104(4)	30(2)	38(3)	9(2)	37(3)	7(3)
O(1)	55(2)	60(3)	29(2)	9(2)	8(2)	15(2)
O(2)	55(2)	36(2)	29(2)	7(2)	17(2)	16(2)
O(3)	101(5)	245(10)	65(4)	29(5)	-9(4)	63(6)
O(4)	76(3)	36(2)	140(5)	40(3)	61(3)	27(2)
O(5)	185(7)	69(3)	63(3)	32(3)	26(4)	62(4)
O(6A)	58(9)	200(20)	370(30)	90(20)	70(14)	42(11)
O(6B)	108(10)	101(9)	158(13)	11(9)	62(9)	73(8)
O(1WA)	31(5)	57(6)	77(7)	-18(5)	0(5)	14(4)
O(1WB)	55(9)	200(20)	290(30)	110(20)	-23(15)	-28(12)
O(2WA)	53(7)	105(13)	240(30)	92(14)	25(11)	-6(7)
O(2WB)	210(30)	87(11)	310(40)	111(18)	200(30)	65(14)
O(3W)	104(7)	219(12)	378(19)	165(13)	19(9)	11(7)
O(4WA)	169(18)	147(17)	170(20)	15(15)	-41(15)	56(15)

O(4WB)	169(19)	150(20)	123(15)	34(16)	-22(12)	1(16)
O(5W)	90(10)	145(14)	230(20)	76(14)	2(11)	41(10)
S(4)	62(1)	109(2)	84(2)	50(1)	-3(1)	18(1)
S(5)	67(1)	118(2)	122(2)	37(2)	51(1)	42(1)
Zn(1)	52(1)	25(1)	32(1)	7(1)	20(1)	14(1)

Table 4B: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for complex **5**.

	x	y	z	U(eq)
H(2)	9000	2339	2684	125
H(3)	8859	1081	1344	142
H(5)	7786	41	-153	175
H(6)	6434	-108	-1137	199
H(8)	4479	275	-1572	153
H(9)	3200	1255	-1205	126
H(13A)	8051	4346	3325	106
H(13B)	7934	3365	3687	106
H(13C)	6833	3668	3344	106
H(14A)	2951	2726	799	119
H(14B)	2523	2581	-151	119
H(14C)	3553	3601	423	119
H(16A)	2827	2941	3523	48
H(16B)	2922	1687	3238	48
H(19)	4979	1115	2904	50
H(21)	7792	1312	4445	59
H(22)	7409	2737	5533	52
H(26A)	3921	4942	5452	65
H(26B)	3299	3939	5701	65

H(26C)	2904	3978	4798	65
H(27)	5281	4698	6435	44
H(29)	7941	4648	5916	55
H(30)	9624	5148	6845	65
H(32)	7948	5292	8741	63
H(33)	6255	4803	7807	53
H(34A)	10984	4398	8958	206
H(34B)	10353	3888	7999	206
H(34C)	9640	4004	8726	206
H(36A)	7216	7067	2270	65
H(36B)	6529	6474	1324	65
H(39)	4595	5842	431	63
H(41)	1846	7040	398	62
H(42)	2412	8086	1843	50
H(46A)	7038	7947	3584	80
H(46B)	6053	7920	4108	80
H(46C)	6578	9025	3943	80
H(47)	4683	9092	4053	53
H(49)	2045	7473	2981	53
H(50)	327	7882	3141	67
H(52)	1954	11081	4499	66
H(53)	3665	10653	4360	53
H(54A)	-705	9032	2487	260
H(54B)	-261	10351	2766	260
H(54C)	-1530	9809	2788	260

APPENDIX C

Crystal structure data of $[Co(sul)_2(H_2O)_4]$ (6)

Table 1C: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **6.**

	x	y	z	U(eq)
C(1)	3583(12)	5722(5)	8248(4)	31(1)
C(2)	1753(12)	6421(6)	7689(4)	36(2)
C(3)	2966(12)	6717(5)	6794(4)	32(1)
C(4)	4977(12)	7518(5)	6544(4)	34(1)
C(5)	6234(14)	8071(6)	7049(4)	42(2)
C(6)	8236(15)	8745(6)	6654(5)	49(2)
C(7)	9006(15)	8884(6)	5815(5)	51(2)
C(8)	7693(14)	8328(6)	5304(5)	45(2)
C(9)	5644(13)	7669(5)	5664(4)	36(1)
C(10)	3983(13)	6931(5)	5338(4)	36(1)
C(11)	2410(13)	6333(5)	6098(4)	37(2)
C(12)	452(15)	5506(6)	6046(4)	45(2)
C(13)	3700(15)	6765(6)	4542(4)	43(2)
C(14)	4799(15)	7346(6)	3726(4)	46(2)
C(15)	5016(16)	8459(6)	3583(5)	52(2)
C(16)	6057(18)	8967(7)	2801(5)	61(2)
C(17)	6840(20)	8365(9)	2152(5)	82(3)
C(18)	6470(20)	7266(8)	2267(5)	82(3)
C(19)	5460(20)	6765(7)	3044(5)	63(2)
C(20)	11220(50)	8670(20)	1035(19)	123(14)
C(20A)	9010(70)	7910(30)	540(20)	135(11)
Co(1)	5000	5000	10000	22(1)
F(1)	9538(10)	9287(4)	7141(3)	74(2)
O(1)	2762(9)	5633(4)	9033(3)	44(1)
O(2)	5623(9)	5267(4)	7930(3)	41(1)
O(3)	7820(30)	10286(8)	1173(8)	77(4)
O(3A)	10030(40)	9231(13)	1384(9)	89(5)
O(1W)	7619(9)	4079(4)	9189(3)	45(1)
O(2W)	2316(9)	3751(4)	10293(3)	49(1)
O(3W)	3250(40)	1622(9)	10870(8)	232(8)
S(1)	7871(10)	8985(4)	1097(2)	130(2)

Table 2C: Bond lengths [Å] and angles [°] for complex **6**.

C(1)-O(2)	1.229(7)
C(1)-O(1)	1.276(7)
C(1)-C(2)	1.530(8)
C(2)-C(3)	1.501(8)
C(3)-C(11)	1.358(9)
C(3)-C(4)	1.451(9)
C(4)-C(5)	1.383(9)
C(4)-C(9)	1.409(9)
C(5)-C(6)	1.387(11)
C(6)-C(7)	1.352(11)
C(6)-F(1)	1.368(8)
C(7)-C(8)	1.409(11)
C(8)-C(9)	1.377(9)
C(9)-C(10)	1.484(10)
C(10)-C(13)	1.364(9)
C(10)-C(11)	1.504(9)
C(11)-C(12)	1.496(10)
C(13)-C(14)	1.475(10)
C(14)-C(15)	1.402(10)
C(14)-C(19)	1.404(10)
C(15)-C(16)	1.387(11)
C(16)-C(17)	1.385(13)
C(17)-C(18)	1.396(14)
C(17)-S(1)	1.801(9)
C(18)-C(19)	1.374(12)
C(20)-S(1)	1.70(2)
C(20A)-S(1)	1.77(3)
Co(1)-O(1)	2.089(4)
Co(1)-O(1)#1	2.089(4)
Co(1)-O(2W)#1	2.100(5)
Co(1)-O(2W)	2.100(5)
Co(1)-O(1W)	2.141(4)
Co(1)-O(1W)#1	2.141(4)
O(3)-S(1)	1.664(12)
O(3A)-S(1)	1.305(14)
O(3W)-H(2W2)	1.9813

O(2)-C(1)-O(1)	124.9(5)
O(2)-C(1)-C(2)	120.0(5)
O(1)-C(1)-C(2)	115.1(5)
C(3)-C(2)-C(1)	115.2(5)
C(11)-C(3)-C(4)	108.8(6)
C(11)-C(3)-C(2)	128.3(6)
C(4)-C(3)-C(2)	122.9(6)
C(5)-C(4)-C(9)	121.1(6)
C(5)-C(4)-C(3)	128.5(6)
C(9)-C(4)-C(3)	110.5(6)
C(4)-C(5)-C(6)	117.1(7)
C(7)-C(6)-F(1)	118.1(7)
C(7)-C(6)-C(5)	123.8(7)
F(1)-C(6)-C(5)	118.2(7)
C(6)-C(7)-C(8)	118.8(7)
C(9)-C(8)-C(7)	119.6(7)
C(8)-C(9)-C(4)	119.6(6)
C(8)-C(9)-C(10)	134.0(6)
C(4)-C(9)-C(10)	106.1(5)
C(13)-C(10)-C(9)	132.2(6)
C(13)-C(10)-C(11)	122.1(7)
C(9)-C(10)-C(11)	105.7(5)
C(3)-C(11)-C(12)	128.0(6)
C(3)-C(11)-C(10)	108.8(6)
C(12)-C(11)-C(10)	123.1(6)
C(10)-C(13)-C(14)	130.2(7)
C(15)-C(14)-C(19)	118.6(7)
C(15)-C(14)-C(13)	123.1(7)
C(19)-C(14)-C(13)	118.1(7)
C(16)-C(15)-C(14)	120.8(8)
C(17)-C(16)-C(15)	119.3(8)
C(16)-C(17)-C(18)	120.7(8)
C(16)-C(17)-S(1)	121.6(8)
C(18)-C(17)-S(1)	117.0(8)
C(19)-C(18)-C(17)	119.7(8)
C(18)-C(19)-C(14)	120.7(8)
O(1)-Co(1)-O(1)#1	180.000(2)

O(1)-Co(1)-O(2W)#1	92.1(2)
O(1)#1-Co(1)-O(2W)#1	87.9(2)
O(1)-Co(1)-O(2W)	87.9(2)
O(1)#1-Co(1)-O(2W)	92.1(2)
O(2W)#1-Co(1)-O(2W)	180.000(1)
O(1)-Co(1)-O(1W)	92.09(17)
O(1)#1-Co(1)-O(1W)	87.91(17)
O(2W)#1-Co(1)-O(1W)	89.4(2)
O(2W)-Co(1)-O(1W)	90.6(2)
O(1)-Co(1)-O(1W)#1	87.91(17)
O(1)#1-Co(1)-O(1W)#1	92.09(17)
O(2W)#1-Co(1)-O(1W)#1	90.6(2)
O(2W)-Co(1)-O(1W)#1	89.4(2)
O(1W)-Co(1)-O(1W)#1	180.000(2)
C(1)-O(1)-Co(1)	126.2(4)
O(3A)-S(1)-O(3)	68.9(10)
O(3A)-S(1)-C(20)	39.2(13)
O(3)-S(1)-C(20)	101.0(13)
O(3A)-S(1)-C(20A)	103.5(14)
O(3)-S(1)-C(20A)	149.5(12)
C(20)-S(1)-C(20A)	64.5(15)
O(3A)-S(1)-C(17)	85.8(7)
O(3)-S(1)-C(17)	104.3(6)
C(20)-S(1)-C(17)	99.3(9)
C(20A)-S(1)-C(17)	104.5(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table 3C: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **6**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	30(3)	37(3)	25(3)	2(3)	-6(2)	-2(3)
C(2)	34(3)	46(4)	26(3)	2(3)	-5(2)	6(3)
C(3)	38(3)	32(3)	27(3)	-1(3)	-5(2)	5(3)
C(4)	37(3)	31(3)	31(3)	4(3)	-9(3)	5(3)
C(5)	46(4)	43(4)	38(4)	-4(3)	-12(3)	7(3)
C(6)	51(4)	33(4)	66(5)	-6(4)	-23(4)	1(3)
C(7)	51(4)	35(4)	63(5)	15(4)	-14(4)	-4(3)
C(8)	45(4)	49(4)	38(4)	5(3)	-8(3)	4(3)
C(9)	38(3)	32(3)	33(3)	6(3)	-2(3)	4(3)
C(10)	43(4)	36(4)	25(3)	-1(3)	2(3)	10(3)
C(11)	47(4)	33(4)	26(3)	5(3)	-3(3)	6(3)
C(12)	51(4)	44(4)	38(4)	-2(3)	-3(3)	-8(3)
C(13)	56(4)	38(4)	33(4)	-4(3)	-4(3)	6(3)
C(14)	61(4)	45(4)	27(3)	2(3)	-5(3)	11(3)
C(15)	70(5)	42(4)	40(4)	3(3)	-7(4)	10(4)
C(16)	85(6)	47(5)	44(5)	15(4)	-8(4)	9(4)
C(17)	118(9)	81(7)	32(5)	16(4)	11(5)	13(6)
C(18)	130(9)	76(7)	32(4)	-9(4)	12(5)	16(6)
C(19)	106(7)	47(5)	32(4)	-7(3)	1(4)	7(4)
C(20)	94(17)	89(17)	130(20)	46(15)	80(16)	62(14)
Co(1)	15(1)	40(1)	11(1)	-7(1)	-2(1)	9(1)
F(1)	74(3)	68(3)	87(4)	-16(3)	-26(3)	-15(3)
O(1)	39(2)	67(3)	19(2)	4(2)	-2(2)	16(2)
O(2)	45(3)	51(3)	24(2)	-3(2)	0(2)	16(2)
O(3)	126(11)	23(6)	68(8)	16(5)	8(7)	17(6)
O(3A)	112(12)	102(12)	57(9)	19(8)	-33(9)	-51(10)
O(1W)	47(3)	57(3)	29(2)	-6(2)	-5(2)	17(2)
O(2W)	39(3)	56(3)	45(3)	4(2)	4(2)	2(2)
O(3W)	450(30)	116(9)	140(10)	-38(7)	-113(13)	101(12)
S(1)	156(4)	166(4)	52(2)	28(2)	2(2)	-23(3)

Table 4C: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **6**.

	x	y	z	U(eq)
H(2A)	120	6047	7692	44
H(2B)	1241	7074	7933	44
H(5)	5757	7993	7628	51
H(7)	10379	9338	5580	61
H(8)	8207	8406	4726	54
H(12A)	-469	5284	6596	67
H(12B)	1404	4901	5830	67
H(12C)	-835	5804	5680	67
H(13)	2649	6195	4509	52
H(15)	4456	8862	4017	63
H(16)	6231	9704	2714	73
H(18)	6900	6875	1819	98
H(19)	5205	6033	3120	75
H(1W1)	7503	4442	8723	68
H(2W1)	9114	4177	9346	68
H(1W2)	606	3749	10459	73
H(2W2)	2672	3194	10628	73

APPENDIX D

Crystal structure data of [Co(sul)$_2$(2,9-dimephen)] (9)

Table 1D: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex

9.

	x	y	z	U(eq)
C(1)	4810(4)	3795(6)	9288(5)	57(2)
C(2)	5315(4)	3477(8)	10051(6)	72(3)
C(3)	5916(4)	3016(7)	9810(5)	64(2)
C(4)	6418(4)	3538(6)	9532(5)	54(2)
C(5)	6459(6)	4442(7)	9389(6)	76(3)
C(6)	7001(7)	4721(7)	9067(7)	87(3)
C(7)	7457(6)	4157(8)	8899(7)	82(3)
C(8)	7427(4)	3260(6)	9056(6)	62(2)
C(9)	6901(4)	2937(6)	9378(4)	55(2)
C(10)	6688(4)	2030(6)	9584(4)	51(2)
C(11)	6068(4)	2147(7)	9833(5)	63(2)
C(12)	5659(5)	1383(8)	10115(9)	97(4)
C(13)	6974(4)	1213(6)	9544(5)	62(2)
C(14)	7607(4)	1007(5)	9334(5)	53(2)
C(15)	8179(4)	1452(6)	9699(6)	68(2)
C(16)	8761(5)	1269(8)	9464(7)	84(3)
C(17)	8775(5)	585(9)	8863(8)	97(4)
C(18)	8226(6)	117(7)	8503(7)	86(3)
C(19)	7663(5)	302(6)	8766(5)	61(2)
C(20)	9812(16)	40(20)	8890(20)	104(8)
C(21)	3704(5)	3351(8)	6779(7)	72(3)
C(22)	3537(6)	2769(7)	6011(8)	98(4)
C(23)	3041(5)	3170(6)	5285(6)	68(2)
C(24)	2377(5)	3176(5)	5303(6)	64(2)
C(25)	2019(8)	2803(8)	5941(10)	118(5)
C(26)	1382(6)	2921(8)	5793(9)	98(4)
C(27)	1031(6)	3299(9)	5114(10)	106(4)
C(28)	1320(5)	3647(8)	4452(8)	89(3)
C(29)	2022(4)	3606(6)	4576(6)	64(2)
C(30)	2481(5)	3879(7)	4072(6)	72(3)

C(31)	3132(4)	3542(7)	4565(8)	81(3)
C(32)	3732(6)	3691(12)	4191(10)	133(5)
C(33)	2381(6)	4271(9)	3303(9)	102(4)
C(34)	1764(6)	4721(9)	2812(8)	92(3)
C(35)	1436(9)	4350(11)	2048(12)	152(7)
C(36)	905(9)	4769(15)	1594(13)	153(7)
C(37)	721(8)	5567(14)	1779(12)	133(6)
C(38)	1042(10)	5931(12)	2535(16)	162(8)
C(39)	1543(8)	5498(12)	3096(10)	135(6)
C(40)	308(17)	6370(40)	180(30)	220(30)
C(41)	3662(6)	6288(6)	7956(5)	70(3)
C(42)	4657(6)	6075(9)	7566(6)	88(4)
C(43)	4691(9)	6981(13)	7428(9)	120(6)
C(44)	4262(12)	7538(10)	7532(8)	127(8)
C(45)	3712(9)	7192(8)	7807(7)	102(5)
C(46)	3272(16)	7718(14)	7905(11)	180(12)
C(47)	2688(13)	7417(12)	8256(9)	181(12)
C(48)	2589(8)	6392(10)	8425(6)	108(5)
C(49)	3114(5)	5845(7)	8249(5)	67(3)
C(50)	2110(9)	5982(18)	8723(8)	142(8)
C(51)	2117(6)	5054(16)	8853(8)	132(7)
C(52)	2647(5)	4558(8)	8631(7)	81(3)
C(53)	5186(7)	5432(13)	7426(10)	139(7)
C(54)	2646(6)	3614(10)	8750(10)	121(5)
Co(1)	3972(1)	4365(1)	8069(1)	51(1)
F(1)	7067(5)	5636(4)	8915(7)	138(3)
F(2)	1094(5)	2625(8)	6444(8)	187(5)
N(1)	4156(4)	5724(5)	7837(4)	64(2)
N(2)	3132(3)	4960(5)	8343(4)	60(2)
O(1)	4295(3)	4111(6)	9416(4)	94(2)
O(2)	4912(3)	3810(6)	8559(4)	90(2)
O(3)	9434(11)	783(17)	7532(16)	150(9)
O(4)	3888(5)	4106(6)	6734(5)	105(3)
O(5)	3602(5)	3057(7)	7485(7)	131(3)
O(6)	-382(18)	5910(30)	1180(30)	250(20)
S(1)	9523(2)	439(8)	8471(6)	276(6)
S(2)	179(5)	6315(8)	1040(7)	284(5)

Table 2D: Bond lengths [Å] and angles [°] for complex **9**.

C(1)-O(2)	1.214(10)
C(1)-O(1)	1.231(9)
C(1)-C(2)	1.509(10)
C(2)-C(3)	1.546(12)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(11)	1.327(13)
C(3)-C(4)	1.444(13)
C(4)-C(5)	1.365(13)
C(4)-C(9)	1.407(11)
C(5)-C(6)	1.397(16)
C(5)-H(5)	0.9300
C(6)-C(7)	1.335(16)
C(6)-F(1)	1.390(12)
C(7)-C(8)	1.358(14)
C(7)-H(7)	0.9300
C(8)-C(9)	1.387(12)
C(8)-H(8)	0.9300
C(9)-C(10)	1.475(12)
C(10)-C(13)	1.360(11)
C(10)-C(11)	1.440(11)
C(11)-C(12)	1.539(14)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.462(12)
C(13)-H(13)	0.9300
C(14)-C(15)	1.386(12)
C(14)-C(19)	1.399(12)
C(15)-C(16)	1.371(13)
C(15)-H(15)	0.9300
C(16)-C(17)	1.394(15)
C(16)-H(16)	0.9300
C(17)-C(18)	1.365(16)
C(17)-S(1)	1.808(11)
C(18)-C(19)	1.354(14)

C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-S(1)	0.99(3)
C(21)-O(4)	1.190(12)
C(21)-O(5)	1.257(14)
C(21)-C(22)	1.473(15)
C(22)-C(23)	1.505(14)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(31)	1.312(15)
C(23)-C(24)	1.394(13)
C(24)-C(29)	1.391(13)
C(24)-C(25)	1.480(17)
C(25)-C(26)	1.319(18)
C(25)-H(25)	0.9300
C(26)-C(27)	1.298(17)
C(26)-F(2)	1.366(14)
C(27)-C(28)	1.409(17)
C(27)-H(27)	0.9300
C(28)-C(29)	1.444(14)
C(28)-H(28)	0.9300
C(29)-C(30)	1.425(14)
C(30)-C(33)	1.325(15)
C(30)-C(31)	1.511(13)
C(31)-C(32)	1.510(17)
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(33)-C(34)	1.520(17)
C(33)-H(33)	0.9300
C(34)-C(39)	1.353(19)
C(34)-C(35)	1.377(19)
C(35)-C(36)	1.35(2)
C(35)-H(35)	0.9300
C(36)-C(37)	1.30(2)
C(36)-H(36)	0.9300
C(37)-C(38)	1.36(2)
C(37)-S(2)	1.829(17)

C(38)-C(39)	1.39(2)
C(38)-H(38)	0.9300
C(39)-H(39)	0.9300
C(40)-S(2)	1.44(4)
C(41)-C(45)	1.370(15)
C(41)-N(1)	1.372(12)
C(41)-C(49)	1.475(14)
C(42)-N(1)	1.317(13)
C(42)-C(43)	1.37(2)
C(42)-C(53)	1.51(2)
C(43)-C(44)	1.26(2)
C(43)-H(43)	0.9300
C(44)-C(45)	1.41(2)
C(44)-H(44)	0.9300
C(45)-C(46)	1.24(3)
C(46)-C(47)	1.51(3)
C(46)-H(46)	0.9300
C(47)-C(48)	1.57(3)
C(47)-H(47)	0.9300
C(48)-C(50)	1.34(2)
C(48)-C(49)	1.438(16)
C(49)-N(2)	1.321(12)
C(50)-C(51)	1.39(3)
C(50)-H(50)	0.9300
C(51)-C(52)	1.433(19)
C(51)-H(51)	0.9300
C(52)-N(2)	1.334(13)
C(52)-C(54)	1.413(17)
C(53)-H(53A)	0.9600
C(53)-H(53B)	0.9600
C(53)-H(53C)	0.9600
C(54)-H(54A)	0.9600
C(54)-H(54B)	0.9600
C(54)-H(54C)	0.9600
Co(1)-N(2)	2.090(7)
Co(1)-N(1)	2.100(7)
Co(1)-O(4)	2.117(8)
Co(1)-O(2)	2.128(6)

Co(1)-O(1)	2.133(7)
Co(1)-O(5)	2.220(10)
O(3)-S(1)	1.55(2)
O(6)-S(2)	1.38(3)

O(2)-C(1)-O(1)	118.6(7)
O(2)-C(1)-C(2)	122.4(7)
O(1)-C(1)-C(2)	118.8(7)
C(1)-C(2)-C(3)	114.5(7)
C(1)-C(2)-H(2A)	108.6
C(3)-C(2)-H(2A)	108.6
C(1)-C(2)-H(2B)	108.7
C(3)-C(2)-H(2B)	108.7
H(2A)-C(2)-H(2B)	107.6
C(11)-C(3)-C(4)	110.2(7)
C(11)-C(3)-C(2)	128.8(10)
C(4)-C(3)-C(2)	121.0(9)
C(5)-C(4)-C(9)	121.5(9)
C(5)-C(4)-C(3)	130.7(8)
C(9)-C(4)-C(3)	107.7(8)
C(4)-C(5)-C(6)	115.7(9)
C(4)-C(5)-H(5)	122.1
C(6)-C(5)-H(5)	122.1
C(7)-C(6)-F(1)	118.5(13)
C(7)-C(6)-C(5)	123.5(10)
F(1)-C(6)-C(5)	117.9(11)
C(6)-C(7)-C(8)	121.1(11)
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-H(7)	119.5
C(7)-C(8)-C(9)	118.4(9)
C(7)-C(8)-H(8)	120.8
C(9)-C(8)-H(8)	120.8
C(8)-C(9)-C(4)	119.7(8)
C(8)-C(9)-C(10)	133.9(7)
C(4)-C(9)-C(10)	106.3(8)
C(13)-C(10)-C(11)	123.3(8)
C(13)-C(10)-C(9)	130.4(8)
C(11)-C(10)-C(9)	106.3(7)

C(3)-C(11)-C(10)	109.5(9)
C(3)-C(11)-C(12)	125.4(9)
C(10)-C(11)-C(12)	125.1(9)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-C(14)	128.6(9)
C(10)-C(13)-H(13)	115.7
C(14)-C(13)-H(13)	115.7
C(15)-C(14)-C(19)	116.4(8)
C(15)-C(14)-C(13)	123.5(8)
C(19)-C(14)-C(13)	120.0(8)
C(16)-C(15)-C(14)	122.2(8)
C(16)-C(15)-H(15)	118.9
C(14)-C(15)-H(15)	118.9
C(15)-C(16)-C(17)	118.2(9)
C(15)-C(16)-H(16)	120.9
C(17)-C(16)-H(16)	120.9
C(18)-C(17)-C(16)	121.4(9)
C(18)-C(17)-S(1)	120.8(9)
C(16)-C(17)-S(1)	117.4(10)
C(19)-C(18)-C(17)	118.8(9)
C(19)-C(18)-H(18)	120.6
C(17)-C(18)-H(18)	120.6
C(18)-C(19)-C(14)	122.7(9)
C(18)-C(19)-H(19)	118.6
C(14)-C(19)-H(19)	118.6
O(4)-C(21)-O(5)	119.7(11)
O(4)-C(21)-C(22)	121.9(11)
O(5)-C(21)-C(22)	118.2(11)
C(21)-C(22)-C(23)	114.1(8)
C(21)-C(22)-H(22A)	108.7
C(23)-C(22)-H(22A)	108.7
C(21)-C(22)-H(22B)	108.8
C(23)-C(22)-H(22B)	108.8

H(22A)-C(22)-H(22B)	107.6
C(31)-C(23)-C(24)	109.6(8)
C(31)-C(23)-C(22)	128.9(11)
C(24)-C(23)-C(22)	121.5(11)
C(29)-C(24)-C(23)	110.7(8)
C(29)-C(24)-C(25)	118.3(10)
C(23)-C(24)-C(25)	131.0(10)
C(26)-C(25)-C(24)	117.6(12)
C(26)-C(25)-H(25)	121.2
C(24)-C(25)-H(25)	121.2
C(27)-C(26)-C(25)	125.8(13)
C(27)-C(26)-F(2)	120.0(12)
C(25)-C(26)-F(2)	114.2(13)
C(26)-C(27)-C(28)	121.1(12)
C(26)-C(27)-H(27)	119.4
C(28)-C(27)-H(27)	119.4
C(27)-C(28)-C(29)	117.5(11)
C(27)-C(28)-H(28)	121.2
C(29)-C(28)-H(28)	121.2
C(24)-C(29)-C(30)	106.5(8)
C(24)-C(29)-C(28)	119.4(10)
C(30)-C(29)-C(28)	134.0(10)
C(33)-C(30)-C(29)	129.7(10)
C(33)-C(30)-C(31)	125.1(11)
C(29)-C(30)-C(31)	104.9(9)
C(23)-C(31)-C(32)	132.8(11)
C(23)-C(31)-C(30)	108.2(9)
C(32)-C(31)-C(30)	119.0(12)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.4
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(30)-C(33)-C(34)	128.4(11)
C(30)-C(33)-H(33)	115.8
C(34)-C(33)-H(33)	115.8
C(39)-C(34)-C(35)	119.2(13)

C(39)-C(34)-C(33)	121.2(12)
C(35)-C(34)-C(33)	119.5(14)
C(36)-C(35)-C(34)	119.6(16)
C(36)-C(35)-H(35)	120.2
C(34)-C(35)-H(35)	120.2
C(37)-C(36)-C(35)	123.5(16)
C(37)-C(36)-H(36)	118.3
C(35)-C(36)-H(36)	118.2
C(36)-C(37)-C(38)	116.4(16)
C(36)-C(37)-S(2)	125.8(17)
C(38)-C(37)-S(2)	116.9(18)
C(37)-C(38)-C(39)	123.6(16)
C(37)-C(38)-H(38)	118.2
C(39)-C(38)-H(38)	118.2
C(34)-C(39)-C(38)	116.6(15)
C(34)-C(39)-H(39)	121.7
C(38)-C(39)-H(39)	121.7
C(45)-C(41)-N(1)	119.1(12)
C(45)-C(41)-C(49)	125.5(12)
N(1)-C(41)-C(49)	115.3(8)
N(1)-C(42)-C(43)	120.8(15)
N(1)-C(42)-C(53)	117.0(11)
C(43)-C(42)-C(53)	122.3(14)
C(44)-C(43)-C(42)	124.3(17)
C(44)-C(43)-H(43)	117.9
C(42)-C(43)-H(43)	117.8
C(43)-C(44)-C(45)	117.0(14)
C(43)-C(44)-H(44)	121.5
C(45)-C(44)-H(44)	121.5
C(46)-C(45)-C(41)	121(2)
C(46)-C(45)-C(44)	118.9(18)
C(41)-C(45)-C(44)	120.4(15)
C(45)-C(46)-C(47)	122(2)
C(45)-C(46)-H(46)	118.7
C(47)-C(46)-H(46)	118.8
C(46)-C(47)-C(48)	119.7(14)
C(46)-C(47)-H(47)	120.1
C(48)-C(47)-H(47)	120.2

C(50)-C(48)-C(49)	118.0(15)
C(50)-C(48)-C(47)	129.6(17)
C(49)-C(48)-C(47)	112.4(16)
N(2)-C(49)-C(48)	123.0(12)
N(2)-C(49)-C(41)	118.1(8)
C(48)-C(49)-C(41)	118.9(11)
C(48)-C(50)-C(51)	121.1(15)
C(48)-C(50)-H(50)	119.5
C(51)-C(50)-H(50)	119.4
C(50)-C(51)-C(52)	117.2(14)
C(50)-C(51)-H(51)	121.4
C(52)-C(51)-H(51)	121.4
N(2)-C(52)-C(54)	120.6(10)
N(2)-C(52)-C(51)	122.3(13)
C(54)-C(52)-C(51)	117.0(13)
C(42)-C(53)-H(53A)	109.5
C(42)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
C(42)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(52)-C(54)-H(54A)	109.5
C(52)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(52)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
N(2)-Co(1)-N(1)	79.8(3)
N(2)-Co(1)-O(4)	112.3(3)
N(1)-Co(1)-O(4)	88.9(3)
N(2)-Co(1)-O(2)	147.4(3)
N(1)-Co(1)-O(2)	104.3(3)
O(4)-Co(1)-O(2)	100.2(3)
N(2)-Co(1)-O(1)	88.7(2)
N(1)-Co(1)-O(1)	108.2(3)
O(4)-Co(1)-O(1)	155.4(3)
O(2)-Co(1)-O(1)	59.1(3)
N(2)-Co(1)-O(5)	102.5(4)

N(1)-Co(1)-O(5)	145.9(3)
O(4)-Co(1)-O(5)	58.4(4)
O(2)-Co(1)-O(5)	91.9(4)
O(1)-Co(1)-O(5)	105.9(4)
C(42)-N(1)-C(41)	118.4(10)
C(42)-N(1)-Co(1)	128.5(9)
C(41)-N(1)-Co(1)	113.0(6)
C(49)-N(2)-C(52)	118.4(8)
C(49)-N(2)-Co(1)	113.7(6)
C(52)-N(2)-Co(1)	127.8(7)
C(1)-O(1)-Co(1)	90.7(5)
C(1)-O(2)-Co(1)	91.5(5)
C(21)-O(4)-Co(1)	94.2(7)
C(21)-O(5)-Co(1)	87.6(7)
C(20)-S(1)-O(3)	141(2)
C(20)-S(1)-C(17)	107(2)
O(3)-S(1)-C(17)	110.2(9)
O(6)-S(2)-C(40)	121(3)
O(6)-S(2)-C(37)	94.0(16)
C(40)-S(2)-C(37)	115.2(18)