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New mixed ligand Zn(II) complexes based on the biologically active substituted acetic acid and nitrogen donor ligands. Synthesis, crystal structure and biological applications.

مركبات جديدة تشمل معدن الزنك ثنائي الشحنة مع حمض الخليك والقواعد النيتروجينية النشطة بيولوجيا. تحضير, التركيب البلوري والتطبيقات البيولوجية

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May, 2016

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May, 2016
Shayma Kamel

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Abbreviations

^{1}H-NMR	Proton Nuclear Magnetic Resonance
^{13}C-NMR	Carbon-13 Nuclear Magnetic Resonance
G+	Gram-positive
G-	Gram-negative
2,9-dmp	2,9-Dimethyl-1,10-phenanthroline
1,10-phen	1,10-Phenanthroline
quin	Quinoline
2-ampy	2-Aminopyridine
BNPP	Bis(4-nitrophenyl) phosphate
IR	Infrared
ph	Phenyl
L	Ligand
KBr	Anhydrous potassium bromide
UV-Vis	Ultraviolet-Visible
MeOH	Methanol
DMSO	Dimethyl sulfoxide
ppt	Precipitate
h	Hour
m.p	Melting point
rt	Room Temperature
methoxy	Methoxyacetate
phenyl	phenylacetate
NMR multiplicity	s = Singlet d = Doublet t = Triplet m = Multiplet bs = Broad singlet
^{13}C{^{1}H}-NMR	^{13}C-Proton broad band decoupled NMR
IZD	Inhibition Zone Diameter

Abstract

The complexes [Zn(methoxyacetate)$_2$1,10-phenanthroline] **1,** [Zn_2 (phenylacetate)$_4$(quinoline)$_2$] **2**, [Zn (phenylacetate)$_2$(2aminopyridin)] **3**, [Zn(phenylacetate)$_2$ 1,10-phenanthroline] **4**, [Zn(phenylacetate)$_2$ 2,9-dimethyl-1,10-phenanthroline] **5** were prepared and characterized by IR-spectroscopy, UV-Visible spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, single crystal X-ray diffraction. BNPP hydrolysis of the complexes and their parent nitrogen ligands were scanned, the results showed that BNPP hydrolysis were decreased in the order: complex **2** > **4** > **3** > **1** > **5**, the results also showed that these complexes can act as a catalysts for phosphate diester hydrolysis.

In addition, anti-bacterial activities were scanned to view the effect of complexation on their activity against Gram-positive (S. epidermidis, S. aureus, E. faecalis, M. luteus and B. Subtilis) and Gram-negative (K. pneumonia, E. coli, P. Mirabilis and P. Aeruginosa) bacteria using agar well-diffusion method. Complex **1** showed high activity against G- and G+ bacteria except against E. faecalis and P. Aeruginosa. Complex **4** showed good activity against G- bacteria except against P. Aeruginosa, G+ bacteria and against E. faecalis. Complex **5** showed zero activity against G- bacteria but low activity against M. luteus, B. Subtilis bacteria and high activity against S. epidermidis and S. aureus. Complexes **2** and **3** did not show any activity against G- or G+ bacteria.

ملخص

تم تحضير المركبات المعقدة التالية:

[Zn(methoxyacetate)$_2$1,10phenanthroline] **1**, [Zn_2(phenylacetate)$_4$(quinoline)$_2$] **2**, [Zn(phenylacetate)$_2$(2aminopyridine)$_2$] **3**, [Zn(phenylacetate)$_2$1,10phenanthroline] **4**, [Zn(phenylacetate)$_2$2,9-dimethyl-1,10 phenanthroline] **5**.

ثم انه تم تشخيصها من خلال مطياف الأشعة تحت الحمراء (IR) وجهاز مطياف الأشعة فوق البنفسجية والمرئية (UV-Vis) وجهاز الرنين المغناطيسي (^{1}H, ^{13}C-NMR) وجهاز دراسة العينات أحادية البلورة باستخدام الأشعة السينية (X-ray).

تمت دراسة تحلل (*bis*-(*p*-nitrophenyl)phosphate) بواسطة المركبات **1-5** وقواعدها النيتروجينية , حيث أظهرت النتائج أن فعالية التحليل تقل حسب الترتيب التالي للمركبات :

2 > **4** > **3** > **1** > **5** ,وأظهرت النتائج أن المركبات المعقدة تعمل كمحلل جيد للفوسفات.

بالإضافة لذلك تمت دراسة الفعالية الحيوية ضد البكتيريا لمشاهدة تأثير الارتباط على الفعالية الحيوية ضد البكتيريا ايجابية غرام (S. epidermidis, S. aureus, E. ferabis, M. luteus and B. Subtilis) و بكتيريا سلبية غرام (K. pneumonia, E. coli, P. Mirabilis and P. Aeruginosa) عن طريق استخدام طريقة الانتشار المفتوحة في الاجار. المعقد الأول أظهر فعالية عالية ضد بكتيريا سلبية وايجابية غرام ماعدا ضد (E. ferabis and P. Aeruginosa) . المعقد الرابع اظهر فعالية جيده ضد بكتيريا سلبية غرام ماعدا ضد (P. Aeruginosa), وفعالية جيدة ضد بكتيريا ايجابية غرام ما عدا ضد (E. ferabis) . المعقد الخامس لم يظهر فعالية ضد بكتيريا سلبية غرام لكن فعالية ضعيفة ضد (M. luteus, B. Subtilis) و فعالية عالية ضد (S. epidemidis and S. aureus), والمعقدات الثاني والثالث لم يظهرا أي فعالية ضد بكتيريا سلبية وايجابية غرام.

1. Introduction

1.1 General principles

The metabolism and transport of the metal ions and their complexes have been studied.[1] Metals such as iron, zinc, and copper all play important roles in many of the enzymatic reactions that fuel the body's metabolism.[2]

There are four major categories for the essential chemical elements: (a) bulk elements (H, C, N, O, P, S), (b) macrominerals and ions (Na, K, Mg, Ca, Cl, PO_4^{-3}, SO_4^{-2}), (c) trace elements (Fe, Zn, Cu), and (d) ultratrace elements, involve nonmetals (F, I, Se, Si, As, B) and metals (Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li), each essential element has approximate percentages by weight for an adult human. The approximate percentages by weight of selected essential elements in the human body are shown in Table 1.1.

Table 1.1: Percentage composition of selected elements in the human body.[3]

Element	Percentage (by weight)	Element	Percentage (by weight)
Oxygen	53.6	Silicon, Magnesium	0.04
Carbon	16.0	Iron, fluorine	0.005
Hydrogen	13.4	Zinc	0.003
Nitrogen	2.4	Copper, bromine	2.0×10^{-4}
Sodium, potassium, sulfur	0.10	Selenium, manganese, arsenic, nickel	2.0×10^{-5}
Chlorine	0.09	Lead, cobalt	9.0×10^{-6}

Essentiality of these elements came from the appearance of a physical deficiency when the elements are removed from the diet. In addition, a specific biological function is associated with the element or in other meaning elements are essential if their total absence in the organism causes sharp irreversible damage.[3,4]

Elements could be deadly if they are in a lower or larger concentration (dose) than the normal concentration. Figure 1.1 shows the dose–response relationship for an essential element.

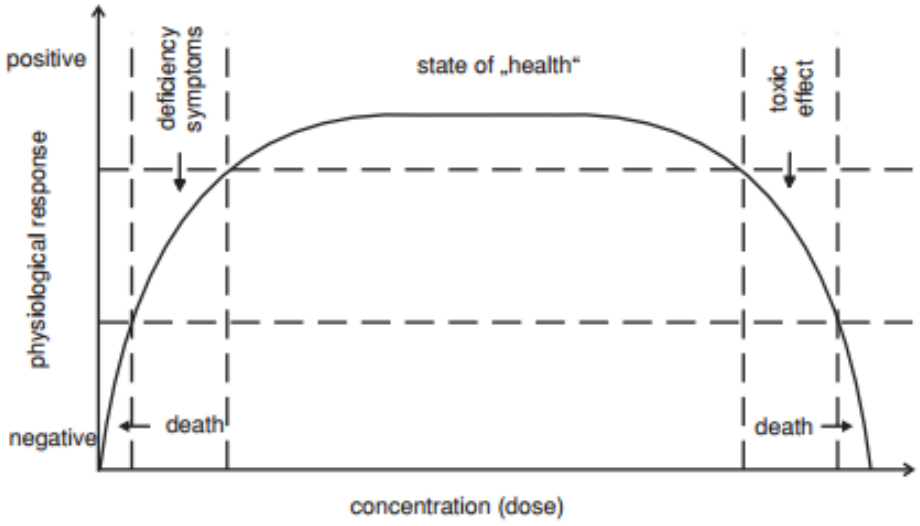


Figure 1.1: Schematic dose–response relationship (Bertrand diagram) for an essential element.[4]

1.2 Metals in biological systems

All biological activities of the metals are due to its unique characteristics such as redox activity, many coordination modes, and reactivity towards organic substrates.[5]

Living organisms store and transport transition metals to give suitable concentrations for use in metalloproteins or cofactors.[6] Many enzymes need metal ions such as (Na^{+}, K^{+}, Mg^{2+}, Ca^{+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, $Fe^{2+}$and Co^{2+}) that plays a role in the (1) stabilization of the macromolecular structure. (2) participate in cross-linking. (3) redox and non-redox catalytic roles. (4) metal metabolism and (5) affect the binding of small molecules and catalyze their reaction, where trace amounts of the metal are often enough ($< 5*10^{-5}$ g per g living substance), and the lack of these metals cause a disease such as anemia which result from the lack of iron metal.[7,8]

Many biological processes need transition metals to complete such as cell division (Fe, Co), respiration (Fe, Cu), nitrogen fixation (Fe, Mo, V), and photosynthesis (Mn, Fe).[6]

Metals complexes also can act as pharmaceuticals or drug such as trans-platinum compounds and ruthenium complexes as anticancer compounds. Gold and ruthenium complexes as antiparasitic agents, silver- and mercury-based as antibacterial agents, vanadium complexes in diabetes as insulin.[9]

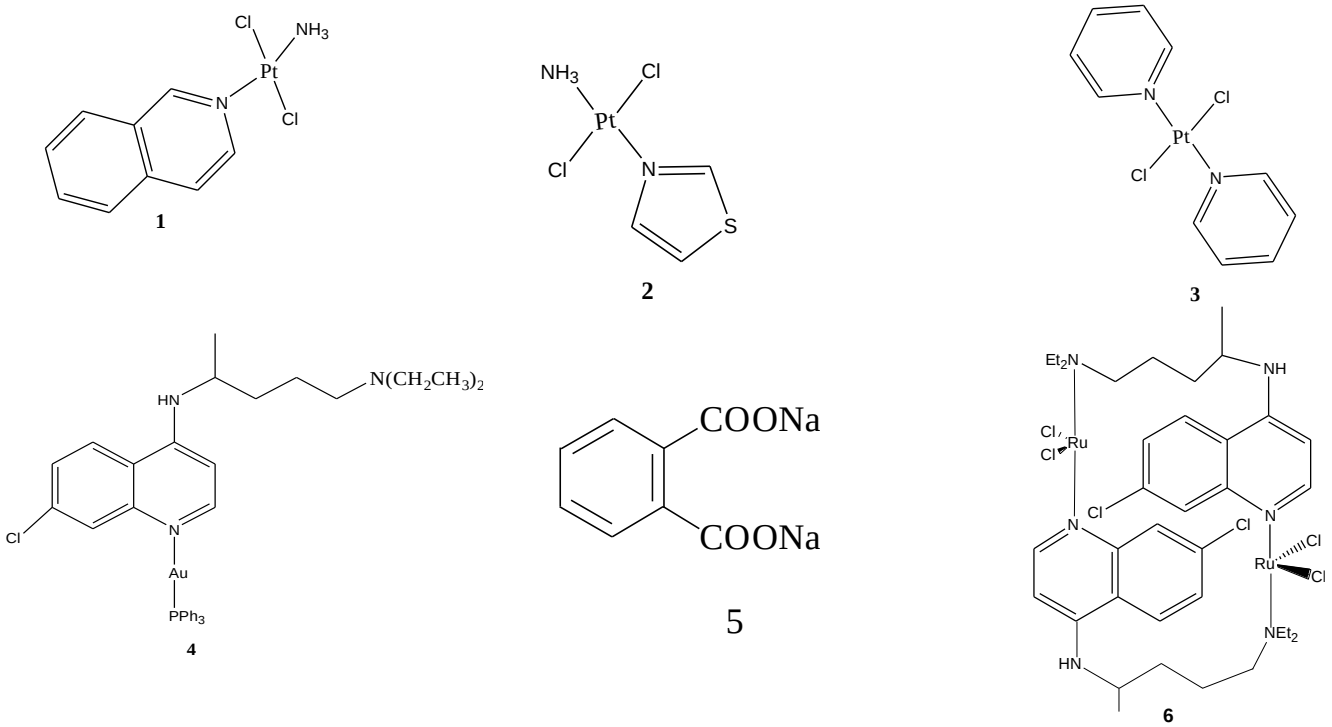


Figure 1.2: (1, 2 and 3) are trans-platinum compounds as potential anticancer compound, (4, 5, and 6) are gold, mercury and ruthenium compound respectively.[9]

1.3 Zinc in biological systems

Zinc is relatively abundant in nature and it is essential for many biological processes and must be included in the diet for optimum health. Scientists consider zinc metal as nontoxic metals since that the recommended daily allowance (RDA) of zinc for human is 8 to 15 mg more than many other essential metals, they observed that zinc does not appear to accumulate in the body with age and there are no known genetic abnormalities that result due to excessive accumulation of zinc in the body but other metals accumulation can cause this such as copper (Wilson's disease) and iron (hemochromatosis).[10] Zinc metal is the most important biometal in our body. For example, it plays

an important role in the immune system and if the percentage of zinc decrease (zinc-deficiency) the person susceptibility to a variety of pathogens increase such as oligospermia, decreased serumtestosterone in males, hyperammonemia, decreased serum thymulin activity and decreased natural killer cell activity.[10,11,12]

Zinc is the most abundant metal in biological materials. The most common site of zinc in the body is metallothionein, small protein (mw 6700) considered as primarily intracellular cytosolic molecule, where it is found in most mammalian tissues, which contains other metals such as copper, chromium, mercury and others but binds with zinc mostly and considered significant macromolecular ligand for it.[10] Zinc is also found in nucleic-acid polymerase (catalyze the formation of DNA and RNA) and transcription factors, in which its role is structural rather than catalytic, where zinc forming the peptide into multiple domains (zinc fingers) and zinc interacts with DNA and RNA and regulate their synthesis. The most interesting thing is that the zinc metal enhances the stereo-selectivity of the polymerization of nucleotides and it is needed for the optimum activity of growth hormone. On the other hand, zinc in animals and plants has no defined role, it may be keeping the structures of proteins that activate and deactivate genes.[6,13]

Zinc metal is represented in metalloenzymes of all six classes of enzymes. As a result, zinc metal is second-most plentiful transition metal in biology.[14]

Table 1.2: Representative metalloenzymes catalyzing hydrolytic and related reactions.[6]

Enzyme	Metals	Function
Carboxypeptidase	Zn^{2+}	Hydrolysis of C-terminal peptide residues
Leucine aminopeptidase	Zn^{2+}	Hydrolysis of leucine N-terminal peptide residues
Dipeptidase	Zn^{2+}	Hydrolysis of dipeptides
Neutral protease	Zn^{2+}, Ca^{2+}	Hydrolysis of peptides
Collagenase	Zn^{2+}	Hydrolysis of collagen
Phospholipase C	Zn^{2+}	Hydrolysis of phospholipids
β-lactamase II	Zn^{2+}	Hydrolysis of β-lactam ring
Thermolysin	Zn^{2+}, Ca^{2+}	Hydrolysis of peptides
Alkaline phosphatase	Zn^{2+}, Mg^{2+}	Hydrolysis of phosphate esters
Carbonic anhydrase	Zn^{2+}	Hydrolysis of CO_2
ά- Amylase	Zn^{2+}, Ca^{2+}	Hydrolysis of glucosides
Phospholipase A_2	Ca^{2+}	Hydrolysis of phospholipids
Inorganic pyrophosphatase	Mg^{2+}	Hydrolysis of pyrophosphate
ATPase	Mg^{2+}	Hydrolysis of ATP
Na^{+} -K -ATPase	Na^{+}, K^{+}	Hydrolysis of ATP with transport of cations
Mg^{2+} -Ca^{2+} -ATPase	Mg^{2+}, Ca^{2+}	
Phosphatase	Zn^{2+}, Mg^{2+}	Hydrolysis of phosphate esters
Creatine Kinase	M^{+}	Phosphorylation of creatine
Pyruvate Kinase	M^{+},M^{2+}	DePhosphorylation of phosphoenol Pyruvate
Phosphoglucomutase	Mg^{2+}	Phosphate transfer converting glucose-1- phosphate to glucose-6- phosphate
DNA polymerase	Mg^{2+} (Mn^{2+})	Polymerization of DNA with formation of phospnate esters
Alcohol dehydrogenase	Zn^{2+}	Hydride transfer from alcohols to NAD^{+}

Zinc metal also stabilizes membranes by binding with ligands in membranes which are essential for keeping the normal structural geometry of the protein and lipid components.[13]

1.3.1 Why Zinc?

First, zinc is lustrous bluish-white metal has atomic number equal 30, atomic mass 65.37 g.mol $^{-1}$ and electronic shell [Ar]$3d^{10}4s^2$, so it has two *s* electrons outside filled *d* shells.[15]

Zn^{2+} locates in the borderline region with considerable class A character. Forming stable complexes with O-donor ligands, N- and S-donor ligands, halides and CN^-, but do not form π complexes with CO, NO ligands because of the filled *d* shells. In general, Zn^{2+} has a distorted tetrahedral geometry in several enzymes where the remaining sites are occupied by carboxylate groups or sometime water molecules.[16]

1.4 Biological ligands

There are three types of biological ligands, peptides (proteins) with amino acid side chains, but not all the amino acids can act as ligands, the highest affinities for serine, cysteine, and histidine.[17] Macrocyclic (tetradentate, multidentate) chelate ligands and nucleobases (nucleic acids). Some examples on these biological ligands respectively are shown in Figure 1.3.[18]

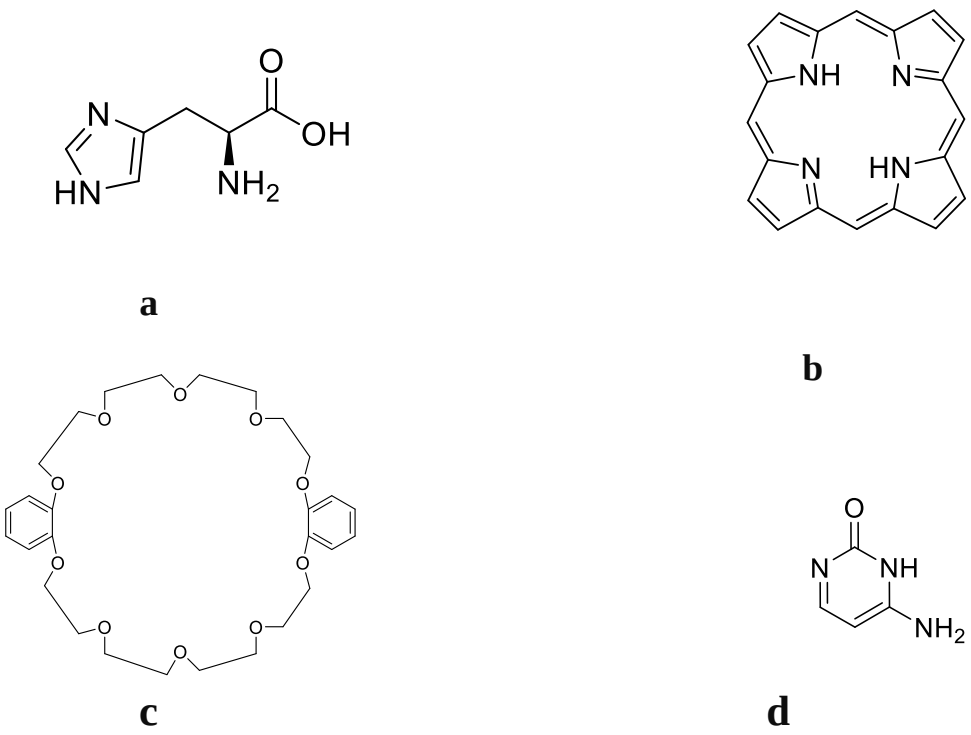


Figure 1.3: a) Histidine, **b)** Porphyrin, **c)** Dibenzol[30]crown-10 and **d)** Cytosine.[18]

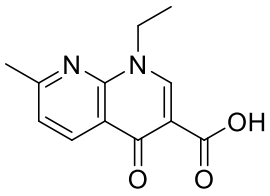
Ligands act as Lewis bases (electron donors), the donating lone pair located usually on O, N or halogen atoms of the ligand where Zn(II) interacts easily with these atoms and act as a Lewis acid as mentioned before.[19]

According to the crystal field splitting theory, ligands can be grouped in a series called spectrochemical series with the following order [20]:

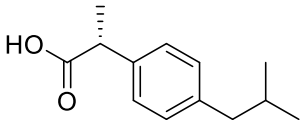
Low energy) $I^- < Br^- < S^{-2} < SCN^- < Cl^- < NO_3^- < N_3^-$, $F^- < OH^- <$ ox $< O^{-2} <$ $H_2O < NCS^- < CH_3CN < NH_3 \approx$ py $<$ en $<$ bpy $<$ phen $< NO_2^- < PPh_3 < CN^-$ $<$ CO (high energy).

1.5 Carboxylate and metal carboxylate chemistry

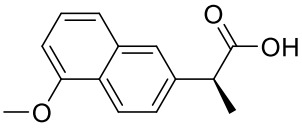
Carboxylic acids act as ligands and have many biological activities such as, anti-inflammatory like ibuprofen, naproxen and tolmetin.[21] The biological activities i,e. anti-bacterial of nalidixic acid were enhanced by complexation with metal ion.[22] However, in other similar complexes the activities were decreased.



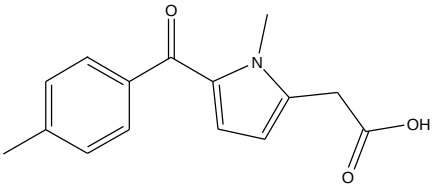
Nalidixic acid



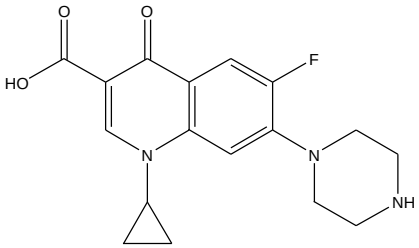
Ibuprofen



Naproxen



Tolmetin



ciprofloxacin

Figure 1.4: Carboxylic acids with biological activity.[18,19]

The activity of carboxylate ion comes from its ability to form different binding modes when it binds with metal ions, through the lone pairs on the two oxygen atoms that are separated by 120° angle, these pairs can split into syn- and anti-lone pairs.[23]

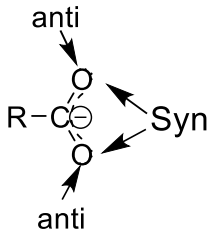
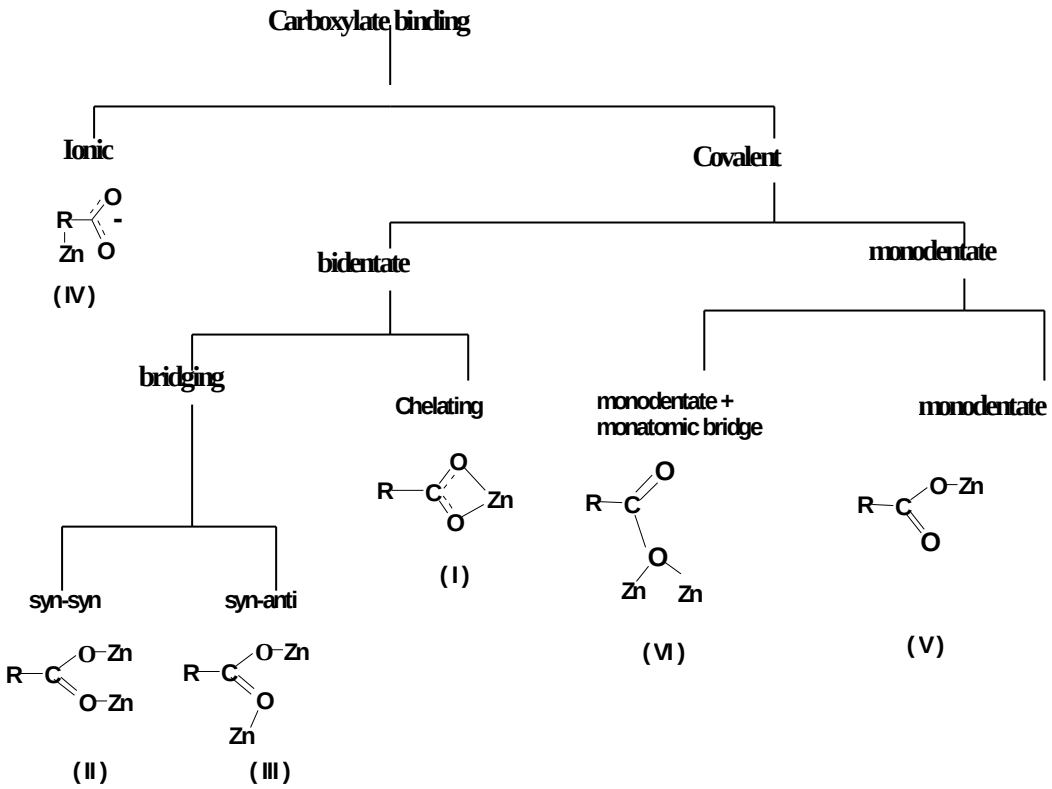


Figure 1.5: The carboxylate functional group showing syn- and anti- lone pairs of electrons on the oxygen atoms.[20]

The different types of binding modes are the following: [23,24,25]

1) Ionic: only coulombic interactions between the metal and the carboxylate anions.
2) Monodentate: The metal is coordinated to only one of the carboxylate oxygens.
3) Symmetrical bidentate chelating: Forming a chelate ring by binding with both oxygen atoms by symmetrical mode (same distance between both oxygen–metal atoms), where the O-M-O angle equal 60° (bite angle).
4) Asymmetrical bidentate chelating: Forming a chelate ring by binding with both oxygen atoms by unsymmetrical mode (different distance between both oxygen–metal atoms), where also the O-M-O angle equal 60°.
5) Syn-syn, syn-anti, anti-anti bridging: in this mode bridge forms between two metals and depending on the site of the lone pairs as in Figure 1.5 this bridge can be syn-syn, syn-anti, anti-anti. Where in the syn-syn mode there is a chance to form a short metal-metal bond.

6) Monodentate terminal bridging: this mode has the lowest possibility to occur in the complex. Scheme 1.1 illustrates all these binding modes.



Scheme 1.1: Different carboxylate binding modes with metals such as zinc.[24]

Infrared spectroscopy (IR) is one of the characterization methods that can be used to distinguish between various carboxylate binding modes and helps in structure elucidation. The most important band in the infrared spectra of metal carboxylate complexes is the strong C=O absorption band which appears in the 1760-1680 cm^{-1} range, this band disappears upon complexation between the metal center and the carboxylate group and instead two new bands appears in the 1650-1550 and 1440-1335 cm^{-1} region for the asymmetric and symmetric

(COO^-) stretching frequency, respectively. To distinguish between the binding modes of the carboxylate, the magnitude of the separation between the carboxylate stretches (Δ) are often used as a characterization method, where $\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$.[23,24]

Generally, the following order is proposed for divalent metal carboxylates:

Δ (chelating) < Δ (bridging) < Δ (ionic) < Δ (monodentate), where Δ (ionic) in 160–170 cm^{-1} range, according to this order, Δ(COO^-) bidentate chelating coordination << Δ(COO^-) sodium salt, the bidentate bridging carboxylate exists when Δ(COO^-) studied complex ≤ Δ(COO^-) sodium salt; and Δ(COO^-) monodentate coordination >> Δ(COO^-) sodium salt.[24] The binding modes of carboxylate groups based on Δ(COO^-) values, are listed in Table 1.3.[23]

Table 1.3 : Infrared spectral data (Δ(OCO)) for coordinated carboxylate ligands.[23]

Δ(OCO) (cm^{-1})	**Coordination Mode**
< 105	Symmetric chelating or short bridging
< 150	Chelating or bridging
> 200	Monodentate
160–170	Ionic

Metal carboxylates are metal salts of carboxylic acids.[26] Metal(II) carboxylate complexes with N-donor ligands have been interesting from chemical and biological aspects for the last decades, zinc heterocyclic compounds play important role in many biological systems.[27] Zinc(II) carboxylate complexes

are important for their catalytic activity, this activity is also greatly influenced by substituents.[14,28]

Because of the metals reactivity, they are tightly regulated under normal conditions and irregular metal ion concentrations are associated with various pathological disorders, like cancer. Coordination complexes, as drugs or prodrugs, became very interesting as potential anti-cancer agents. The discovery of cisplatin, *cis*-[Pt(II)$(NH_3)_2Cl_2$], was a defining event which caused the interest in platinum(II)- and other metal-containing complexes as potential new anti-cancer drugs.[29] Other metals such as zinc, copper and gold(III) complexes, tetracoordinate (square-planar geometries) gold(III) complexes have the same geometries as in cisplatin, this prompted the investigation of gold compounds as potential anti-cancer agents such gold(III) dithiocarbamate derivatives. Other metals such as arsenic, cadmium, chromium and nickel produced a wide range of toxic side-effects, like carcinogenesis.[5]

Zinc carboxylate complexes with nitrogen ligands showed anti-bacterial, anti-microbial and anti-malarial effects.[7,30]

Two carboxylic acids were chosen in the present work: phenylacetic acid which is an important class of compounds used in several industrial applications, such as flavors and fragrances in cosmetics or food. Also it plays an important role in the pharmaceutical sector as precursors or drugs. For example, phenylacetic acid can act as precursors for analgesics like

diclofenac. In addition, antibiotics on the basis of penicillin can be obtained from it.[31]

The second carboxylic acid is methoxyacetic acid which is a primary metabolite of phthalates ester that was used in many manufacture products such as electronics, building materials, plastics, textiles, adhesives, paints, deodorants and pharmaceutical products. Also, it was predicted that methoxyacetic acid has anti-cancer activity, specially prostate cancer, researchers found that methoxyacetic acid can induce apoptosis and inhibits the growth of prostate cancer cells.[32,33]

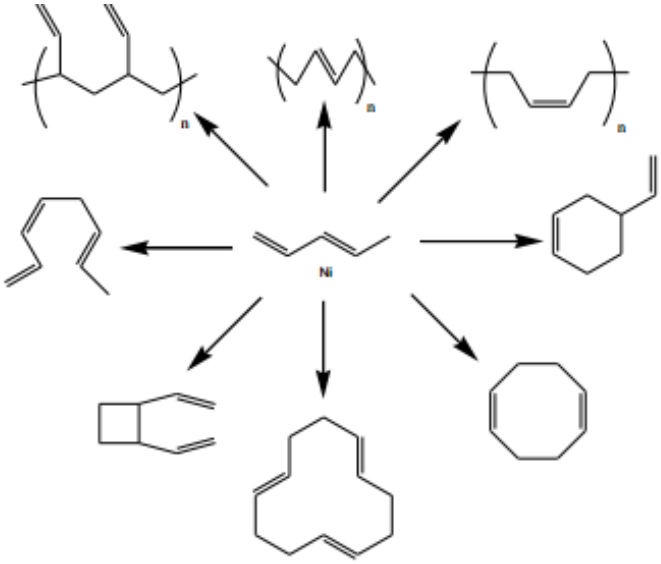
a **b**

Figure 1.6: Carboxylic acids used in the present work: **a)** Phenylacetic acid, **b)** Methoxyacetic acid.

1.6 Nitrogen-Donor ligands

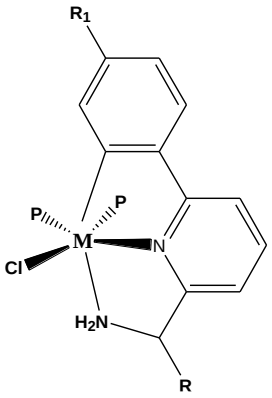
In general, ligands in metal complexes have an important roles in homogeneous catalysis i.e. nickel catalysts with butadiene ligand, polymers are formed when allyl nickel(II) complexes are used as catalysts and cyclic dimers and all cyclic trans trimers are the products when Ni(0) is the catalyst precursor as shown in Scheme 1.2.[33] Ligands classified into six categories when used in catalysis: Anionic and neutral hydrocarbyl groups, alkoxy and imido groups as anionic ligands, amines, imines and oxazolines and related

ligands, phosphine, phosphites, phosphorus amides, phospholes and related ligands, carbenes, carbon monoxide and common anions.[34]



Scheme 1.2: Effect of ligands and valence states on the selectivity in the Nickel catalyzed reaction of butadiene.[34]

There are many types of nitrogen donor ligands with biological activity applications, and they play important roles in many complexes due to the lone pairs on the nitrogen atom that leads to ease interaction with metal ion. Ru(II) and Os(II) complexes with achiral CNN-pincer ligand acted as catalyses in asymmetric transfer hydrogenation as shown in Figure 1.7.[35,36]



R = H, CH_3, t-Bu

R_1 = H, CH_3

M = Ru, Os

Figure 1.7: Example of new catalytic systems containing CNN pincer ligand.[35]

Also metal complexes with macrocyclic nitrogen ligands that enhances selectivity for binding, anions and bimetallic macrocyclic metal complexes were also prepared.[34]

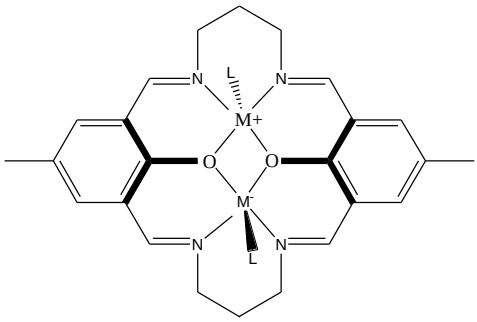
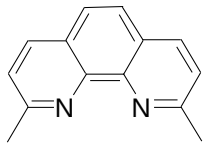


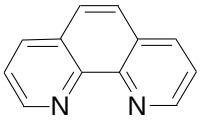
Figure 1.8: Bimetallic macrocyclic complex with phenoxy bridges (M = Cu, Ni, Co, Fe, Mn, Zn, Ni and L = Cl^-, ClO^{-4}, HSO^{-4}).[34]

Nitrogen ligands are largely available in enantiomerically pure form and they are cheap industrial chemical intermediates.[37]

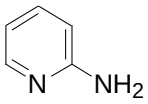
Four bioactive nitrogen base ligands were chosen in the present work: 2,9-dimethyl-1,10-phenanthroline (2,9-dmp), 1,10-phenanthroline (1,10-phen), quinoline (quin) and 2-aminopyridine (2-ampy) (Figure 1.9).



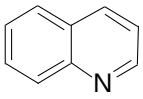
2,9-dimethyl-1,10-phenanthroline



1,10-phenanthroline



2-aminopyridine



quinoline

Figure 1.9: Nitrogen donor-ligands used in the present work.

1.7 Bis-(4-nitrophenyl) phosphate hydrolysis

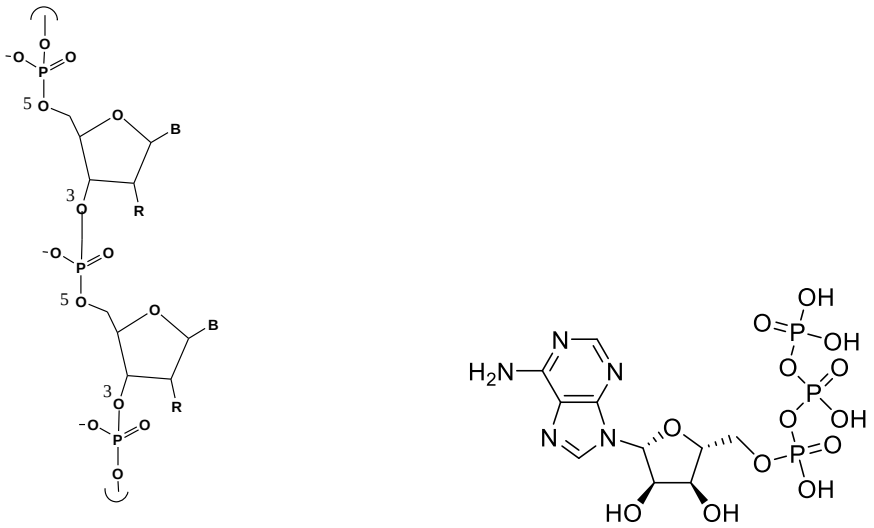
In general hydrolysis means the reaction of H_2O with organic compound as shown below.

$$RX + H_2O \longrightarrow ROH + X^- + H^+$$

Metal complexes used in this type of hydrolysis usually occurs through two types of mechanisms: (I) the metal coordinates with the hydrolysable functional group, making it more electrophilic and more easy to react with the nucleophilic this called direct polarization mechanism, this type like acid catalyzed hydrolysis of ester, where the metal acts as Lewis acid coordinating with the lone pair electrons of the oxygen atom, resulting more susceptible carbonyl group to react with the H_2O or OH^-. (II) generation of a reactive metal hydroxo species.[38]

Phosphate esters have important role in nature and in our body such as: (1) nucleic acids DNA and RNA, where the phosphate ester linkages of DNA

are very stable, with half-life of 10-100 billion years at natural pH at 25 °C, (2) the phospholipids of the lipid bilayer of the cell membrane and (3) metabolically crucial energy conduit Adenosine triphosphate (ATP), and other biologically active molecules are phosphates.[39]



a **b**

Figure 2.1: a) Structure of a di-nucleotide portion of the phosphate diesters DNA and RNA, **b)** Chemical structures of ATP.

Phosphate hydrolysis has an important role in many biological and environmental applications. For example, this hydrolysis represents the cleavage of the phosphorus bond in DNA and RNA. Rapid hydrolysis of the high stable phosphate diester bond in *bis*-(4-nitrophenyl) phosphate (BNPP) by enzymes or catalysts containing metal ion complexes have recently been acheived.[40,41]

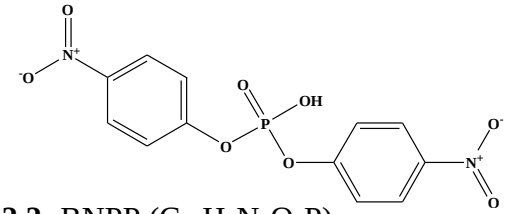


Figure 2.2: BNPP ($C_{12}H_9N_2O_8P$)**.**

Different studies showed that metals and metal complexes can act as catalysts for phosphate esters hydrolysis , for example Cu^{+2} complexes can chelate phosphate diesters in a bidentate mode and increase the rate of hydrolysis reaction.[39,42]

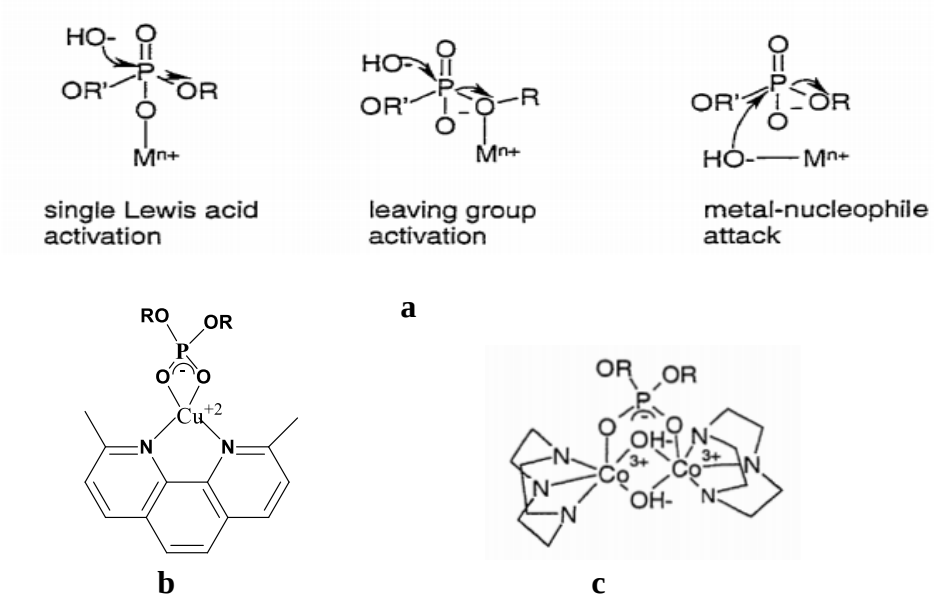


Figure 2.3: a) Modes in which phosphates are activated by metals, **b)** An example of a complex where phosphate diesters chelate the metal centre, **c)** Two metal complexes that combine double Lewis acid activation and metal-nucleophile attack.[39]

BNPP is an example of phosphate esters where many metal complexes such as lanthanide(III) complex were used as a catalyst for its hydrolysis, In 1998, Yatsimirsky *et al.*, studied this complex in the presence of bis-tris-propane buffer which considered reactive toward the hydrolysis of BNPP (La^{3+}/BTP, 25 ˚C, pH = 9.0: 2.2 x 10^{-3} s^{-l}).[39]

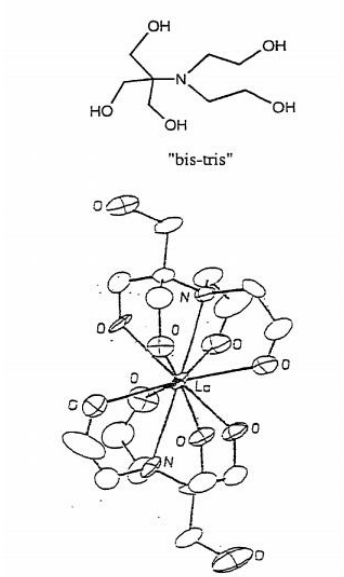
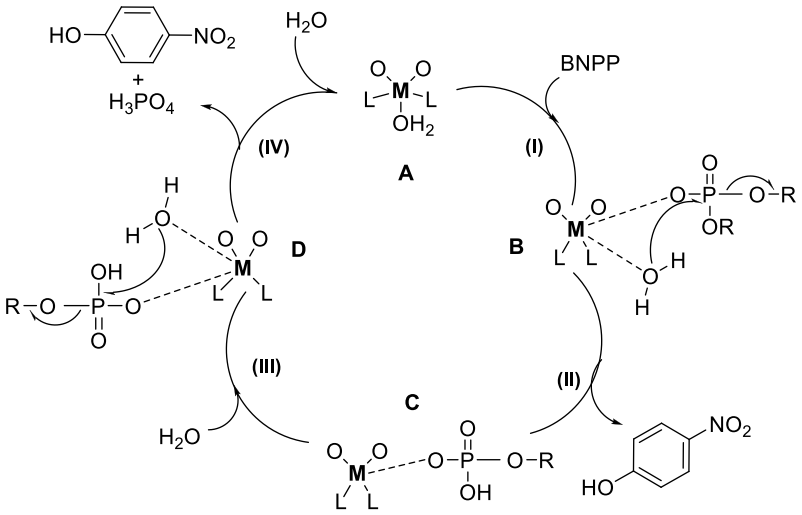


Figure 2.4: X-ray crystal structure of 1:2 La^{3+} :"bis-tris" complex.[39]

One of the possible suggested mechanisms is shown in Scheme 1.3: (1) H_2O molecule coordinate with metal complex to produce complex **A**, (2) the oxygen atom on the P=O of the substrate (BNPP) is coordinated to the complex metal ion, forming the intermediate **B**, (3) intramolecular metal hydroxide attacks the positive P atom of BNPP molecule to enhance release of the p-nitrophenol with first order-rate constant (k) for this step which is considered the key step for the hydrolysis, (4) after that H_2O coordinates again with the metal ion quickly, **D** is formed, (5) the intermediate **D** quickly loses p-nitrophenol and phosphoric acid where H_2O is bonded again to the metal(II) ion rapidly, and thus completes the catalytic cycle.[42,43,44]



Scheme 1.3: The proposed mechanism of the hydrolysis of BNPP.

1.7 Anti-bacterial activity

It is very important to control bacteria growth in different materials that are in close contact with humans, foods and others, in order to prevent risk of infections and if not treated as should be it will become a global concern.[45,46]

Millions of people died due to infections caused by microorganisms resistant to current antibiotics, as a result the anti-bacterial activity of many synthesized transition metal coordination complexes have been studied.[47,48]

The treatment of many infectious diseases is still an important and challenging problem because of several related factors like the emerging infectious

diseases and the increasing number of multi-drug resistant microbial pathogens. Metal ion complexes with heterocyclic sulfonamides such as [Cu $(L)_2$].H_2O and [$Cu(L)_2$ $(H_2O)_4$].nH_2O were reported to have anti-bacterial activity, where L = sulfamethoxazol, sulfadiazine, sulfisoxazole and sulfamethoxy pyridazine. In addition, cobalt complex with histidine ligand and metal complexes of N-methylthioformohydroxarnic acid were also reported to have activity against gram-negative Escherichia coli and gram-positive Staphylococcus aureus.[49]

Other [Co(II), Ni(II), Zn(II)] metal complexes from 2-(1'-hydroxynaphthyl)benzoxazoles and Zn(II) complexes of (4E)-4-[(2-(E)-[1-(2,4dihydroxyphenyl) ethylidene] aminoethyl)imino]pentan-2-one in a 1 : 1 metal to ligand stoichiometric ratio were prepared and their anti-bacterial activities were studied. The antibacterial activities of metal complexes depended more on the metal itself than on the geometry around it.[45,46,50]

The following five principal factors may be considered in general when the anti-bacterial activity of metal complexes is concerned:[45]

The chelate effect, bidentate ligands like quinolones, show higher anti-bacterial activity than complexes with monodentate ligands; the nature of the ligands; total charge of the complex, in general the anti-bacterial activity decreases in the order: cationic > neutral > anionic complexes; the nature of the counter ion in the case of ionic complexes and the nuclearity of the metal

center in the complex, dinuclear centers are more active than mononuclear ones.

1.8 Aim of the research

The aim of this work was to synthesize a new zinc complexes with the formula $[Zn(RCH_2COO)_n L_m]$, (n = 1, 2, ..; m = 1, 2…; R = ph, OCH_3…); L = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 2-amino pyridine, quinoline. The formula and the structure of the prepared complexes will also be determined. Moreover, the biological activity such as anti-bacteria and BNPP hydrolysis of these complexes will be investigated.

The present work reports the synthesis and spectroscopic characterization of following five complexes:

A. [Zn(methoxy acetate)$_2$1,10-phenanthroline] (**1**)

B. [Zn$_2$(phenyl acetate)$_4$(quinoline)$_2$] (**2**)

C. [Zn(phenyl acetate)$_2$(2-aminopyridine)$_2$] (**3**)

D. [Zn(phenyl acetate)$_2$1,10-phenanthroline] (**4**)

E. [Zn(phenyl acetate)$_2$2,9-dimethyl-1,10-phenanthroline] (**5**)

2. Experimental

2.1 Chemicals, materials and biological species

All chemicals and solvents are analytical reagent grade and were purchased from commercial sources. Finally, all bacteria types were obtained from Biology and Biochemistry Department at Birzeit University.

2.2 Physical measurements

Solid samples with anhydrous potassium bromide (KBr) were grounded and compressed into a disc to use them for IR spectral measurements which were recorded in the 200-4000 cm^{-1} region on TENSOR II (BRUKER) FT-IR Spectrometer. UV-Vis spectra were recorded on Agilent 8453 photodiode array (PDA) spectrophotometer in the 200-600 nm region using CH_3OH as a solvent. NMR spectra were recorded on a Varian Unity Spectrometer operating at 300 MHz for ^{1}H and ^{13}C nucleus. Melting points were determined in capillary tubes with Electrothermal apparatus and Bruker SMART APEX CCD X-ray diffractometer was used for X-ray data.

a **b**

Figure 2.5: a) TENSOR II Spectrometer and, **b)** Agilent 8453 spectrophotometer.[51,52]

2.3 Synthesis and characterization of Zinc(II) compounds

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

2.3.1 Zinc methoxyacetate 1,10-phenanthroline [Zn(methoxy)$_2$1,10-phen] (1) complex.

In (1:1) ratio sodium hydroxide (4.9 mmol, 0.20 g), and methoxyacetic acid (0.3152 g) in 50 ml of MeOH were mixed and dissolved. Then (3.5 mmol, 0.48 g) $ZnCl_2$ in minimum amount of MeOH was added and the reaction mixture was stirred for an additional 12 h. The solid product was filtered and washed with cold water and air dried to give 1 g of solid product. The prepared Zn-methoxy (2.6 mmol, 0.41 g) was dissolved in 50 ml MeOH and 1,10-phenanthroline (2.6 mmol, 0.41 g) dissolved in

minimum amount of MeOH was added to the stirred Zn-methoxy solution. Immediately a white precipitate was formed and the reaction mixture was stirred for an additional 24 h. The solution was filtrated, then the filtrate was allowed to evaporate slowly and solid crystals were obtained. Recrystallization from MeOH gave single crystals suitable for X-ray determination.

[Zn(methoxy)$_2$1,10-phen] (1): 90 % yield; m.p. 190-196 °C; ^{1}H NMR ($CDCl_3$): δ (ppm) 3.50 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 7.83 (m, 2H, CH), 7.94 (s, 2H, CH), 8.46 (d, 2H, CH, $^3J_{H-H}$ = 7.8 Hz), 9.18 (dd, 2H, CH, $^3J_{H-H}$ = 6.3 Hz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 59.01 (CH_3), 71.21 (CH_2), 124.25 (CH), 124.29 (CH), 126.79 (CH), 128.80 (CH), 149.97 (CH), 150.01 (CH) 173.84 (C=O); IR (cm^{-1}, KBr): 3046, 2995, 1597.1, 1514.22, 1425.9, 1342, 1101, 849.01, 726.37; UV-Vis (MeOH, λ (nm)): 271, 292.

2.3.2 Zinc phenylacetate complex.

Sodium hydroxide (1.0 mmol, 1.5 g), and phenylacetic acid (1.0 mmol, 5.0 g) in 100 ml of MeOH were mixed, stirred for 3 h. Then the solvent was evaporated to give a needle solid which was re-dissolved in MeOH and $ZnCl_2$ (1.0 mmol, 5.0 g) in 15 ml of MeOH was added to it with stirring. The reaction mixture was stirred for additional 12 h; the obtained white precipitate was then filtered, washed with cold water and air dried

to give 4.4 g of solid product. 89 % yield; m.p. > 200 °C; ^{1}H NMR ($CDCl_3$): δ (ppm) 3.39 (s, 2H, CH_2), 7.21 (s, 5H, CH); $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ (ppm) 43.11 (CH_2), 126.21 (CH), 128.31 (CH), 129.69 (CH), 137.91 (C),176.98 (C=O); IR(cm^{-1}, KBr): 3444, 2350, 1531, 1439, 1391, 723; UV-Vis (MeOH, λ (nm)): 214, 259, 265.

2.3.3 Zinc phenylacetate quinoline complex $[Zn_2(phenyl)_4(quin)_2]$ (2).

Zn-phenyl (2.0 mmol, 0.40 g) was dissolved in 50 ml MeOH (insoluble) and quinoline (4.0 mmol, 0.52 g) dissolved in minimum amount of MeOH was added to the Zn-phenyl solution with stirring. The reaction mixture was stirred for additional 12 h, dichloromethane was then added until the solution became clear, and the solution was allowed to evaporate slowly to give solid crystals suitable for X-ray determination.

$[Zn_2(phenyl)_4(quin)_2]$ (2): 87 % yield; m.p. = 144 °C; ^{1}H NMR (DMSO): δ (ppm) 3.39 (s, 2H, CH_2), 7.22 (bs, 5H, CH), 7.56 (m, 2H, CH), 7.75 (m, 1H, CH), 7.98 (m, 2H ,CH), 8.35 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 8.88 (bs, 1H, CH); $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ (ppm) 43.99 (CH_2), 122.68 (CH), 126.97 (CH), 127.81 (CH), 129.10 (C), 129.32 (C), 129.99 (CH), 130.48 (CH), 130.80 (CH), 137.47 (C),138.74 (CH), 151.82 (CH), 177.64 (C=O); IR (cm^{-1}, KBr): 3027, 2362, 1946, 1588, 1403, 1316, 809; UV-Vis (MeOH, λ (nm)): 276, 287.

2.3.4 Zinc phenylacetate 2-aminopyridine complex [Zn(phenyl)$_2$(2-ampy)$_2$] (3).

Zn-phenyl (2.0 mmol, 0.40 g) was dissolved in 50 ml MeOH (insoluble) and 2-aminopyridine (4 mmol, 0.38 g) dissolved in minimum amount of MeOH was then added to the Zn-phenyl solution with stirring, then the clear reaction mixture was stirred for additional 7 h, the solution was allowed to evaporate to give solid crystals. Recrystallization from CH_2Cl_2 gave single crystals suitable for X-ray determination.

[Zn(phenyl)$_2$ (2-ampy)$_2$] (3). 77% yield; m.p. = 147-149 °C; ^{1}H NMR ($CDCl_3$): δ (ppm) 3.64 (s, 2H, CH_2), 5.78 (s, 2H, NH_2), 6.39 (d,1H, CH, $^3J_{H-H}$ = 8.4 Hz), 6.47 (t, 1H, CH, $^3J_{H-H}$ = 12.9 Hz), 7.20 (m, 1H,CH), 7.26 (m,5H,CH), 7.37 (m, 1H, CH), 7.74 (d, 1H, CH, $^3J_{H-H}$ = 5.4 Hz);^{13}C{^{1}H}-NMR($CDCl_3$): δ (ppm) 43.60 (CH_2), 111.43 (CH), 112.96 (CH), 122.96 (CH), 126.10 (CH), 128.18 (CH), 129.52 (CH), 137.16 (C), 139.73 (CH), 145.97 (CH), 159.05 C(NH_2), 178.52 (C=O); IR (cm^{-1}, KBr): 3341, 3227, 3024, 2700, 1619, 1567, 1499, 1360, 1271, 1159, 851, 698, 661; UV-Vis (MeOH, λ (nm)): 296.

2.3.5 Zinc phenylacetate 1,10-phenanthroline complex [Zn(phenyl)$_2$1,10-phen](4).

Zn-phenyl (2,0 mmol, 0.40 g) was dissolved in 50 ml MeOH (insoluble) and 1,10-phenanthroline (2.0 mmol, 0.36 g) dissolved in minimum

amount of MeOH was then added to the Zn-phenyl solution with stirring. The clear solution of the reaction mixture was stirred for additional 7 h then was allowed to evaporate and solid crystals were obtained. Recrystallization from MeOH gave single crystals suitable for X-ray determination.

[Zn(phenyl)$_2$1,10-phen](4). 85% yield; m.p. = 101 °C; ^{1}H NMR ($CDCl_3$): δ (ppm) 3.63 (s, 2H, CH_2), 7.19 (m, 5H, CH), 7.68 (t, 2H, CH, $^3J_{H\text{-}H}$ =12.6 Hz), 7.76 (s, 2H, CH), 8.32 (d, 2H, CH, $^3J_{H\text{-}H}$ = 8.1 Hz), 9.05 (d, 2H, CH, $^3J_{H\text{-}H}$ =4.8 Hz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 43.43 (CH_2), 124.28 (CH), 125.03 (CH), 126.04(CH), 126.58 (CH), 128.11(CH), 128.45 (C), 129.39 (CH), 137.06 (C), 138.85 (CH), 150.12 (CH), 180.59 (C=O) ; IR (cm^{-1}, KBr): 1998, 1515, 1223, 1144, 1100, 853; UV-Vis (MeOH, λ (nm)): 277, 292, 325.

2.3.6 Zinc phenylacetate 2,9-dimethyl-1,10-phenanthroline complex [Zn(phenyl)$_2$2,9-dmp] (5)

Zn-phenyl (2.0 mmol, 0.40 g) dissolved in 50 ml MeOH (insoluble) and 2,9-dmp (2.0 mmol, 0.45 g) dissolved in minimum amount of MeOH were mixed and the reaction mixture was stirred for 3 h, the solid product was then filtrated and collected. Recrystallization from MeOH gave crystals suitable for X-ray determination.

[Zn(phenyl)$_2$ 2,9-dmp] (5). 79 % yield; m.p. = 159-165 °C; ^{1}H NMR ($CDCl_3$): δ (ppm) 2.99 (s, 3H, CH_3), 3.66 (s, 2H, CH_2), 7.15 (t,2H, CH, $^3J_{H\text{-}H}$ = 15.6 Hz), 7.21 (d, 2H, CH, $^3J_{H\text{-}H}$ = 6.9 Hz), 7.28 (d, 2H, CH, $^3J_{H\text{-}H}$ = 7.2 Hz), 7.54 (d, 2H, CH, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.64 (s, 2H, CH), 8.19 (d, 2H, CH, $^3J_{H\text{-}H}$ = 8.4 Hz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 24.78 (CH_3), 43.05 (CH_2), 125.55 (CH), 125.99 (CH), 126.25 (C), 126.86 (CH), 128.10 (CH), 129.35 (CH), 137.35 (C), 139.09 (CH), 140.1 9 (C), 160.73 (C), 179.04 (C=O); IR (cm^{-1}, KBr): 3027, 2800, 1500, 1450, 1340, 1221, 861; UV-Vis (MeOH, λ (nm)): 201, 231 269.

2.4 X-ray crystallography

Single crystals suitable for X-ray measurements of the complexes **(1)**, **(2)** **(3)**, **(4)** and **(5)** were attached to a glass fiber, with epoxy glue, and transferred to a Bruker SMART APEX CCD X-ray diffractometer system controlled by a Pentium-based PC running the SMART software package.[53] The crystal was mounted on the three-circle goniometer with χ fixed at +54.76°. The Mo Kα radiation (λ = 0.71073 A) diffracted graphite-monochromated was detected on a phosphor screen held at a distance of 6.0 cm from the crystal operating at -43 °C. A detector array of 512 X 512 pixels, with a pixel size of approximately 120 μm, was employed for data collection. The detector centroid and crystal-to-

detector distance were calibrated from a least-squares analysis of the unit cell parameters of a carefully centered YLID reference crystal.

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, all these after The crystal of the compound centered within the X-ray beam. In order 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. Then four distinct shells were the data frames were collected, and when these shells combined, it is measured more than 1.3 hemispheres of intensity data with a maximum 2θ of 46.5°. Then there was another PC computer which the raw data frames transferred to it, to integrate by the 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 integrated intensities for the four shells of data were merged to one reflection file. Then any outlier reflections rejected by the filtration the data file. 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 1.4, 1.5, and 1.6.[54]

Table 1.4: Structure refinement and crystal data for compounds (**1**) and (**2**).

	Complex (1)	**Complex (2)**
Empirical formula	C18 H22 N2 O8 Zn	C50 H42 N2 O8 Zn2
Formula weight	459.75	929.60
Temperature	295(2) K	296(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions	a = 14.287(2) Å α = 90°. b = 10.137(1) Å β = 104.011(2)°. c = 28.861(4) Å γ = 90°.	a = 8.464(2) Å α= 95.179(3)°. b = 11.165(2) Å β= 108.293(3) . c = 12.160(3) Å γ = 93.175(3)°.
Volume	4055.2(9) $Å^3$	1082.4(4) $Å^3$
Z	8	1
Density (calculated)	1.506 Mg/m^3	1.426 Mg/m^3
Absorption coefficient	1.259 mm^{-1}	1.166 mm^{-1}
F(000)	1904	480
Crystal size	0.40 x 0.29 x 0.14 mm^3	0.52 x 0.51 x 0.40 mm^3
Theta range for data collection	2.49 to 28.03°.	2.41 to 26.00°.
Index ranges	-18<=h<=18,-13<=k<=13, -38<=l<=37	-10<=h<=10,-13<=k<=13, -14<=l<=14
Reflections collected	22840	10335
Independent reflections	4880 [R(int) = 0.0268]	4095 [R(int) = 0.0323]
Completeness to theta = 28.03°	98.9 %	96.1 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8435 and 0.6329	0.6527 and 0.5823
Data / restraints / parameters	4880 / 0 / 264	4095 / 0 / 280
Goodness-of-fit on F^2	1.199	1.140
Final R indices [I > 2sigma (I)]	R1 = 0.0508, wR2 = 0.116	R1 = 0.0546, wR2 = 0.1662
R indices (all data)	R1 = 0.0562, wR2 = 0.1191	R1 = 0.0583, wR2 = 0.1675
Largest diff. peak and hole	0.478 and -0.400 e.$Å^{-3}$	1.274 and -0.362 e.$Å^{-3}$

a $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$ and $wR2 = \{\sum[w(F02 - Fc2)2] / \sum[w(Fo2)2]\}1/2$

Table 1.5: Structure refinement and crystal data for compounds (**3**) and (**4**).

	Complex (3)	**Complex (4)**
Empirical formula	C26 H26 N4 O4 Zn	C28 H22 N2 O5 Zn
Formula weight	523.88	531.85
Temperature	293(1) K	293(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/c
Unit cell dimensions	a= 10.877(2)Å α = 87.918(4)°. b = 11.204(2) Å β= 74.302(4)°. c = 11.461(3) Å γ = 75.807(4)°.	a = 10.589(1) Å α = 90°. b = 11.165(2) Å β = 97.681(2)°. c = 12.160(3) Å γ = 90°.
Volume	1302.9(5) $Å^3$	2438.3(6) $Å^3$
Z	2	4
Density (calculated)	1.335 Mg/m^3	1.449 Mg/m^3
Absorption coefficient	0.980 mm^{-1}	1.049 mm^{-1}
F(000)	544	1096
Crystal size	0.36 x 0.36 x 0.13 mm^3	0.36 x 0.29 x 0.26 mm^3
Theta range for data collection	2.39 to 28.01°.	2.20 to 27.00°.
Index ranges	-14<=h<=14, -14<=k<=14, -15<=l<=14	-13<=h<=13, -23<=k<=23, - 16<=l<=16
Reflections collected	15064	26565
Independent reflections	6067 [R(int) = 0.0258]	5314 [R(int) = 0.0306]
Completeness to theta = 28.03°	96.4 %	99.8 %
Absorption correction	Multi-scan	Semi-empirical from equivalents
Max. and min. transmission	0.8832 and 0.7193	0.7720 and 0.7038
Data / restraints / parameters	6067 / 4 / 332	5314 / 0 / 325
Goodness-of-fit on F^2	1.122	1.197
Final R indices [I > 2sigma (I)]	R1 = 0.0591, wR2 = 0.1440	R1 = 0.0519, wR2 = 0.1213
R indices (all data)	R1 = 0.0722, wR2 = 0.1514	R1 = 0.0576, wR2 = 0.1244
Largest diff. peak and hole	0.526 and -0.397 $e.Å^{-3}$	0.533 and -0.439 $e.Å^{-3}$

Table 1.6: Structure refinement and crystal data for compound (**5**)

	Complex (5)
Empirical formula	C30 H27 N2 O4.50 Zn
Formula weight	552.91
Temperature	296(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 29.017(6) Å α = 90°. b = 12.615(2) Å β = 100.401(2) °. c = 14.667(3) Å γ = 90°.
Volume	5280(2) $Å^3$
Z	8
Density (calculated)	1.391 Mg/m^3
Absorption coefficient	0.971 mm^{-1}
F(000)	2296
Crystal size	0.42 x 0.16 x 0.10 mm^3
Theta range for data collection	2.68 to 27.00°.
Index ranges	-36<=h<=36, -14<=k<=16, -18<=l<=18
Reflections collected	19220
Independent reflections	5684 [R(int) = 0.0581]
Completeness to theta = 28.03°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9092 and 0.6859
Data / restraints / parameters	5684 / 0 / 341
Goodness-of-fit on F^2	0.851
Final R indices [I > 2sigma (I)]	R1 = 0.0546, wR2 = 0.1425
R indices (all data)	R1 = 0.1619, wR2 = 0.1740
Largest diff. peak and hole	0.270 and -0.324 e.$Å^{-3}$

2.5 BNPP hydrolysis

Optimum concentrations and conditions for the BNPP hydrolysis were chosen by running different UV-visible kinetic experiments and the best absorbance versus time plots were used to determine the optimum conditions.

The following conditions were used for all hydrolysis reactions:

HEPES "4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid") buffer with concentration of 50 μM was prepared by dissolving the appropriate amount in minimum amount of deionized water, then controlling the pH to 7.91 using HCl or NaOH and the final volume was adjusted to 100 ml. (0.036 g) of BNPP was dissolved in the prepared buffer to obtain a certain concentration of 1.0×10^{-3} M. The desired complex concentration was prepared using methanol as a solvent, the two solutions were kept in a water bath at 25 ˚C for 10 minutes, then (1.5 ml) of the two solutions were mixed in a quartz cell at 25 ˚C, the rate of release of p-nitrophenol was directly measured using UV-Vis spectrophotometer at λ = 400 nm and an extinction coefficient of 13400 $Lmol^{-1}cm^{-1}$. The concentration effect of BNPP solution on the hydrolysis process was measured by preparing 10^{-4}, 10^{-5} M solutions and the rate of hydrolysis was calculated.[42]

2.6 Anti-bacterial activity

Zn(II) complexes (**1-5**) were screened against nine kinds of bacteria, G^+ bacteria (S. aureus, M. luteus, E. faecalis, S. epidermidis and B. Subtilis) and G^- bacteria (K. pneumoniae, P. mirabilis, P. aeruginosa and E. coli) using agar diffusion method as shown in Figure 2.6, where in this method single bacterial colonies dissolved in sterile saline until the suspended cells reached the turbidity of McFarland 0.5 Standard. Then 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. Zn complexes were dissolved in DMSO in concentrations equal to 6 mg/ml, then 25 μL of the test samples were introduced in the respective wells. DMSO solvent was used as negative control while gentamycin (G) and erythromycin (E) was used as positive control. 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 error.[55,27]

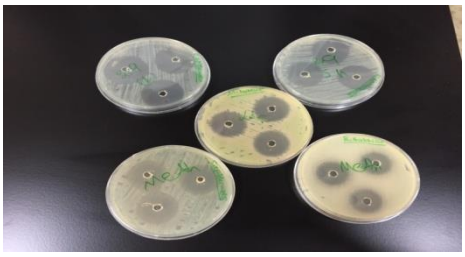


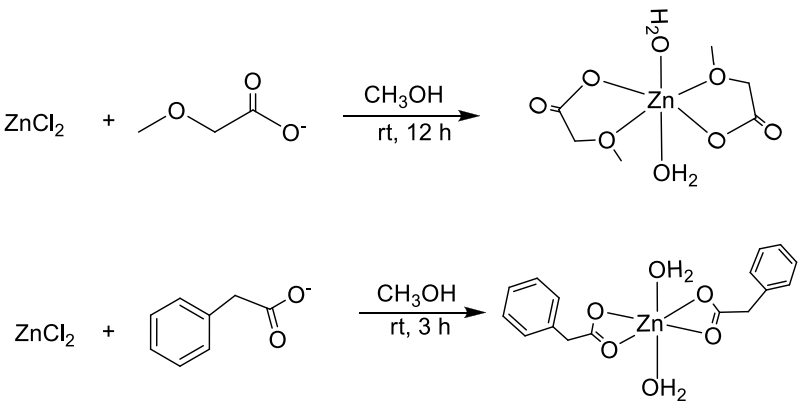
Figure 2.6: Agar diffusion**.**

3. Results and discussion

3.1 Synthesis of Zn(II) complexes

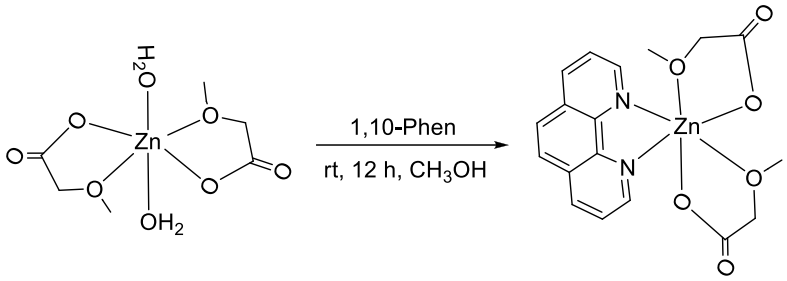
1 equivalent of $ZnCl_2$ was reacted with 1 equivalent of sodium methoxyacetate and sodium phenylacetate in methanol to give $[Zn(methoxy)_2(H_2O)_2]$ and $[Zn(phen)_2(H_2O)_2]$, respectively as shown in Scheme 1.3.

Scheme 1.3: Synthesis and proposed structure of zinc(II) complexes.



Different nitrogen donor ligands were mixed with the synthesized zinc methoxy and zinc phenyl acetate and their structures are shown in Scheme 1.5 and Scheme 1.6, the proposed structures are also supported by their single crustal X-ray structure determination.

Scheme 1.5: Synthesis and proposed structure of zinc(II) complex **1**.



Scheme 1.6: Synthesis and proposed structure of zinc(II) complexes **2-5**.

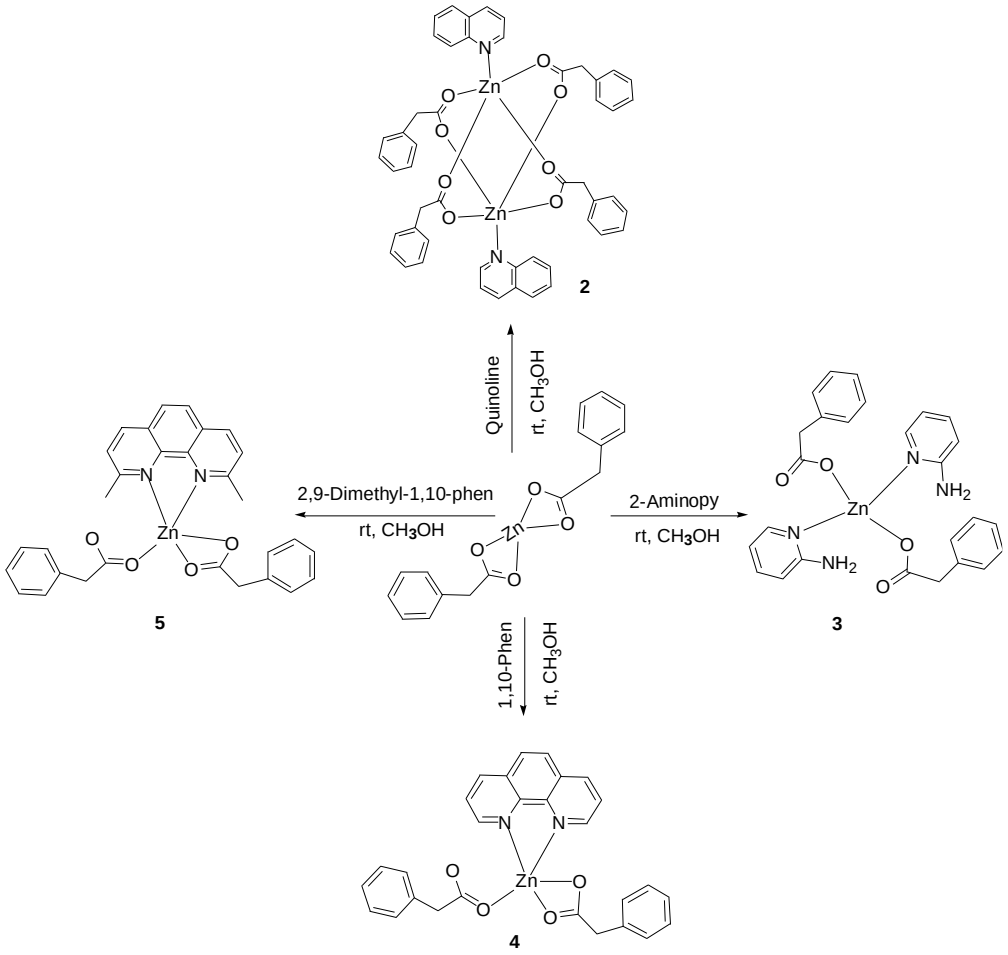
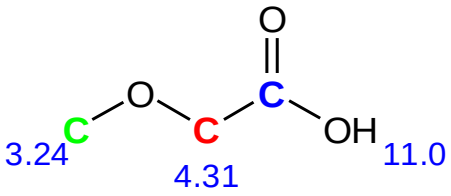


Table 1.7: Physical properties and yield of Zinc(II) compounds.

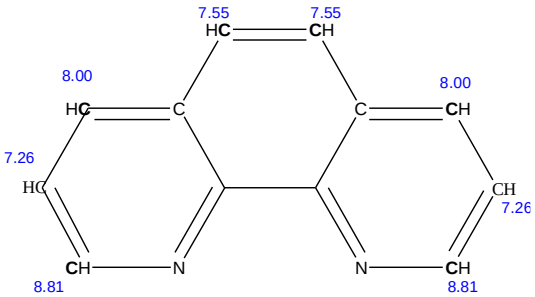
Compounds	%Yield	m.p (°C)	Solubility
1	90	190-196	Hot CH_3OH, DMSO
2	87	144	DMSO,CH_2Cl_2
3	77	147-149	$CHCl_3$, CH_3OH, $CH_3C(O)CH_3$, DMSO
4	85	101	$CHCl_3$, CH_3OH
5	79	159-165	CH_3OH, $CH_3C(O)CH_3$, DMSO

3.2 ^{1}H and ^{13}C Nuclear Magnetic Resonance

The ^{1}H and ^{13}C NMR spectral data of complex **1** and Zn-methoxyacetate and methoxyacetic acid[56] are reported in Table 3.2. The relation intensities of ^{1}H NMR signals are in according with the proposed structure. Due to complex formation, change in the resonance chemical shift takes place, where comparison of the ^{1}H NMR spectra of **1** and Zn-methoxy showed a downfield shift in complex **1**, this deshielding effect causes by the donation of electrons from the carboxylate group to the zinc ion through σ bond. 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.



Methoxyacetic acid (ChemDraw data)



1,10-phenanthroline (ChemDraw data)

As shown in Table 1.8 to Table 2.1 slight upfield and downfield shifts in methoxyacetic acid and phenylacetic acid were observed due to complexation with Zn metal or/and nitrogen donor ligands.

Table 1.8: ^{1}H-NMR and ^{13}CNMR spectral data of complex **1** and Zn-methoxyacetate and methoxyacetic acid.

^{1}H NMR		
Complex **1**	Zn-methoxy	H- methox
-	-	11.00 (OH)
3.50 (s, 3H, CH_3)	3.90 (s, 2H, CH_2)	4.12 (s, 2H, CH_2)
4.03 (s, 2H, CH_2)	3.25 (s, 3H, CH_3)	3.48 (s, 3H, CH_3)
7.83 (m, 2H, CH)		
7.94 (s, 2H, CH)		
8.46 (d, 2H, CH, $^{3}J_{H-H}$ = 7.8 Hz)		
9.18 (dd, 2H, CH, $^{3}J_{H-H}$ = 6.3 Hz)		

Table 1.8: Continued

^{13}C NMR		
Complex **1**	Zn-methoxy	H-methox
173.84 C=O	174.02 C=O	174.83 C=O
71.21 CH_2	71.44 CH_2	69.33 CH_2
59.01 CH_3	58.25 CH_3	59.35 CH_3
150.01 CH		
149.97 CH		
128.80 CH		
126.79 CH		
124.29 CH		
124.25 CH		

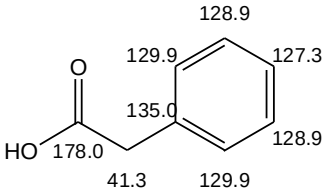
Table 1.9: ^{1}H-NMR and ^{13}C NMR spectral data of complex **2**, Zn-phenylacetate and phenylacetic acid

^{1}H NMR		
Complex **2**	Zn-phenyl	Hphenyl
-	-	11.00 (OH)
3.39 (s, 2H, CH_2)	3.39 (s, 2H, CH_2)	3.49 (s, 2H, CH_2)
7.22 (bs, 5H, CH)	7.21 (s, 5H, CH)	7.32 to 7.25 (s, 5H, CH)
7.56 (m, 2H, CH)		
7.75 (m, 1H, CH)		
7.98 (m, 2H, CH)		
8.35 (d, 1H, CH, 3JH-H = 8.1 Hz)		
8.88 (bs, 1H, CH)		

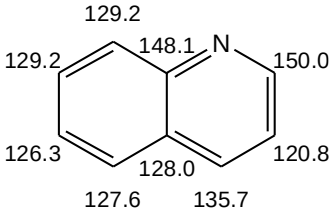
Table 1.9: Continued

^{13}C NMR		
Complex **2**	Zn- phenyl	Hphenyl
177.64 C=O	176.98 C=O	178.00 C=O
43.99 CH_2	43.11 CH_2	41.30 CH_2
151.82 CH	137.91 CH	137.35 CH
138.74 CH	129.69 CH	139.09 CH
137.47 CH	128.31 CH	128.90 CH
130.80 CH	126.21 CH	127.30 CH
129.99 CH		
129.32 CH		
129.10(CH)		
127.81(CH)		
126.97(CH)		
122.68(CH)		

Phenylacetic acid (ChemDraw data)



Quinoline (ChemDraw data)



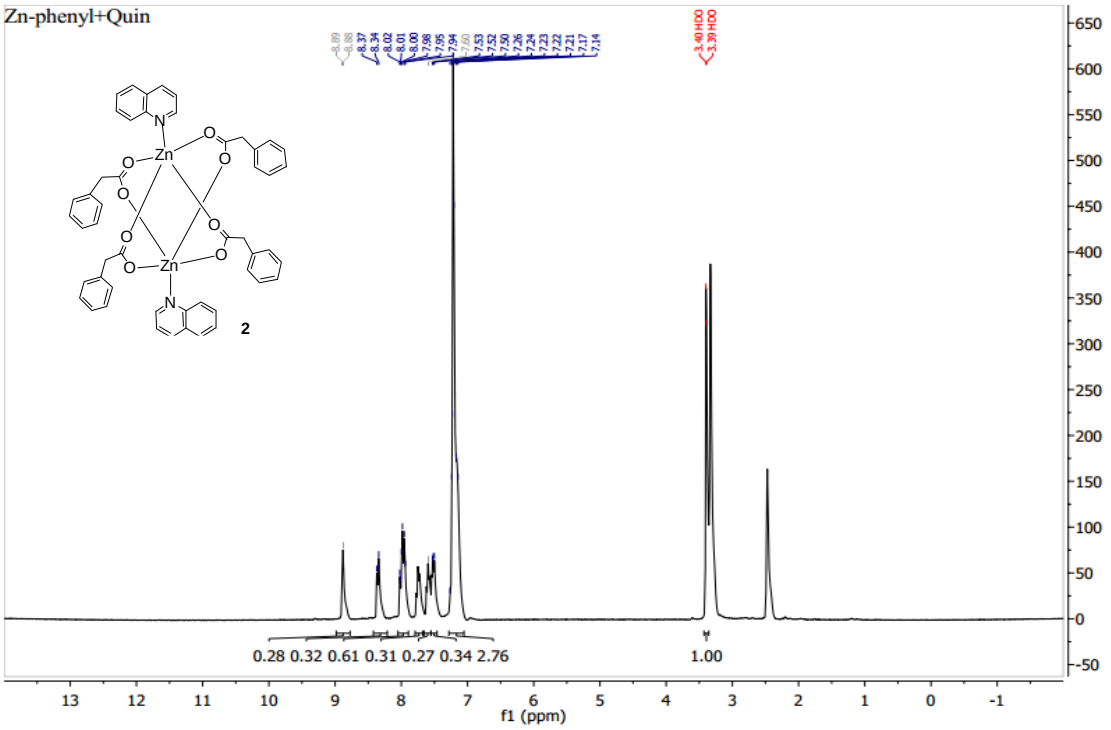
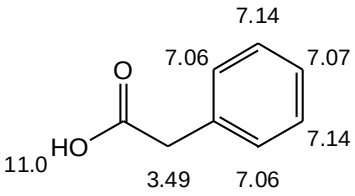


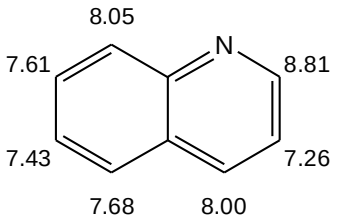
Figure 2.7: ^{1}H-NMR spectra of complex **2**

Table 2.1: ^{1}H-NMR and ^{13}C NMR spectral data of complexes **3- 5**

^{1}H NMR		
Complex **3**	Complex **4**	Complex **5**
3.64 (s, 2H, CH_2)	-	-
5.78 (s,1H, NH_2)	3.63 (s, 2H, CH_2)	2.99 (s, 3H,CH_3)
6.39 (d, 1H, CH, 3J-H-H = 8.4 Hz)	7.19 (m, 5H, CH)	3.66 (s, 2H, CH2)
6.47 (t, 1H, CH, 3JH-H = 12.9 Hz)	7.68 (t, 2H, CH, $^{3}J_{H-H}$ = 12.6 Hz)	7.15 (t,1H,CH, $^{3}J_{H-H}$ = 15.6 Hz)
7.20 (m,1H, CH)	7.76 (s, 2H, CH)	7.21(d,2H,CH, $^{3}J_{H-H}$ = 6.9Hz)
7.26 (m, 5H, CH)	8.32 (d, 2H, CH, $^{3}J_{H-H}$ = 8.1 Hz)	7.28 (d, 2H, CH, $^{3}J_{H-H}$ = 7.2Hz)
7.37 (m, 1H, CH)	9.05 (d, 2H, CH,$^{3}J_{H-H}$ = 4.8 Hz)	7.54 (d, 2H, CH, $^{3}J_{H-H}$ = 8.4Hz)
7.74 (d, 1H, CH, $^{3}J_{H-H}$ = 5.4 Hz)		7.64 (s, 2H, CH)
		8.19 (d,1H, CH, $^{3}J_{H-H}$ = 8.4Hz)



Phenylacetic acid (ChemDraw date)



Quinoline (ChemDraw data**)**

Table 2.1: Continued

^{13}C NMR		
Complex **3**	Complex **4**	Complex **5**
178.52 C=O	180.59 C=O	179.04 C=O
43.60 CH_2	43.43 CH_2	43.05 CH_2
137.16 C	137.06 C	137.35 C
129.52 CH	138.85 C	129.35 CH
128.18 CH	128.45 C	128.10 CH
126.10 CH	129.39 CH	126.86 CH
159.05 C(NH_2)	126.58(CH)	160.73(C)
145.97(CH)	125.03(CH)	140.19(C)
139.73(CH)	128.11(CH)	139.09(CH)
137.16(CH)	126.04(CH)	126.25(C)
122.96(CH)	150.12(CH)	125.99(CH)
111.43(CH)	124.28(CH)	125.55(CH)
		24.78(CH_3)

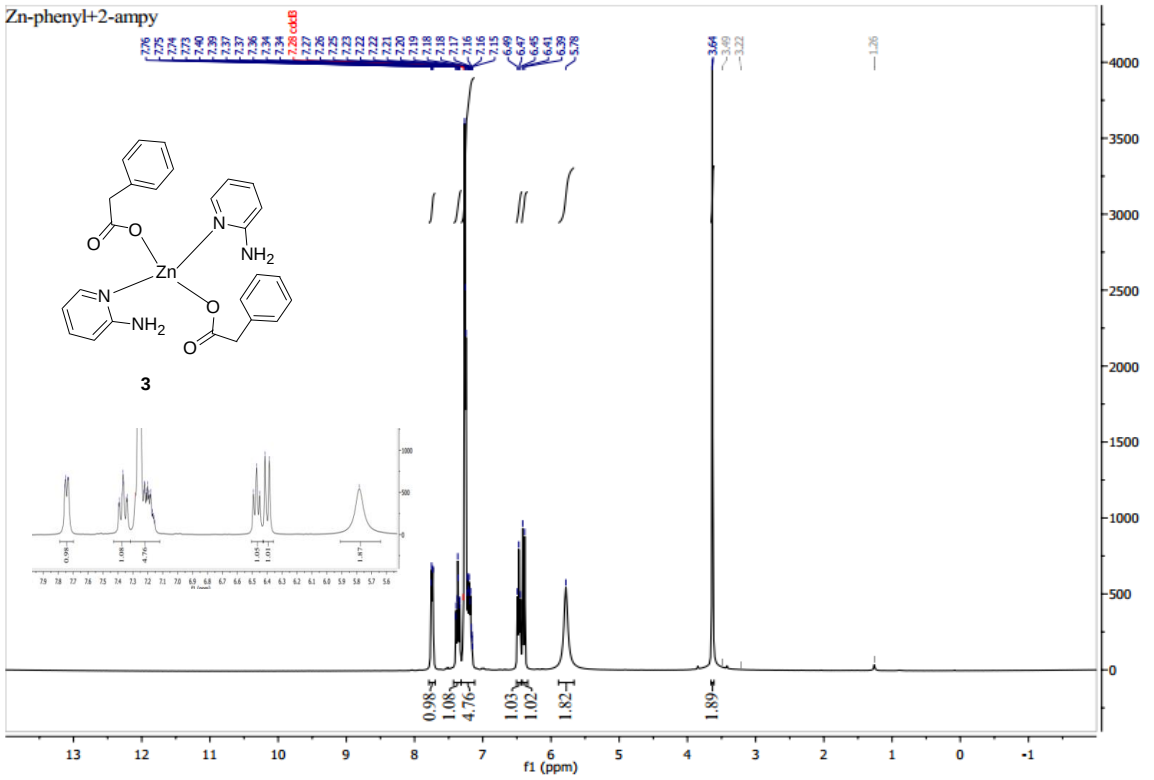


Figure 2.8: ^{1}H-NMR spectra of complex **3**

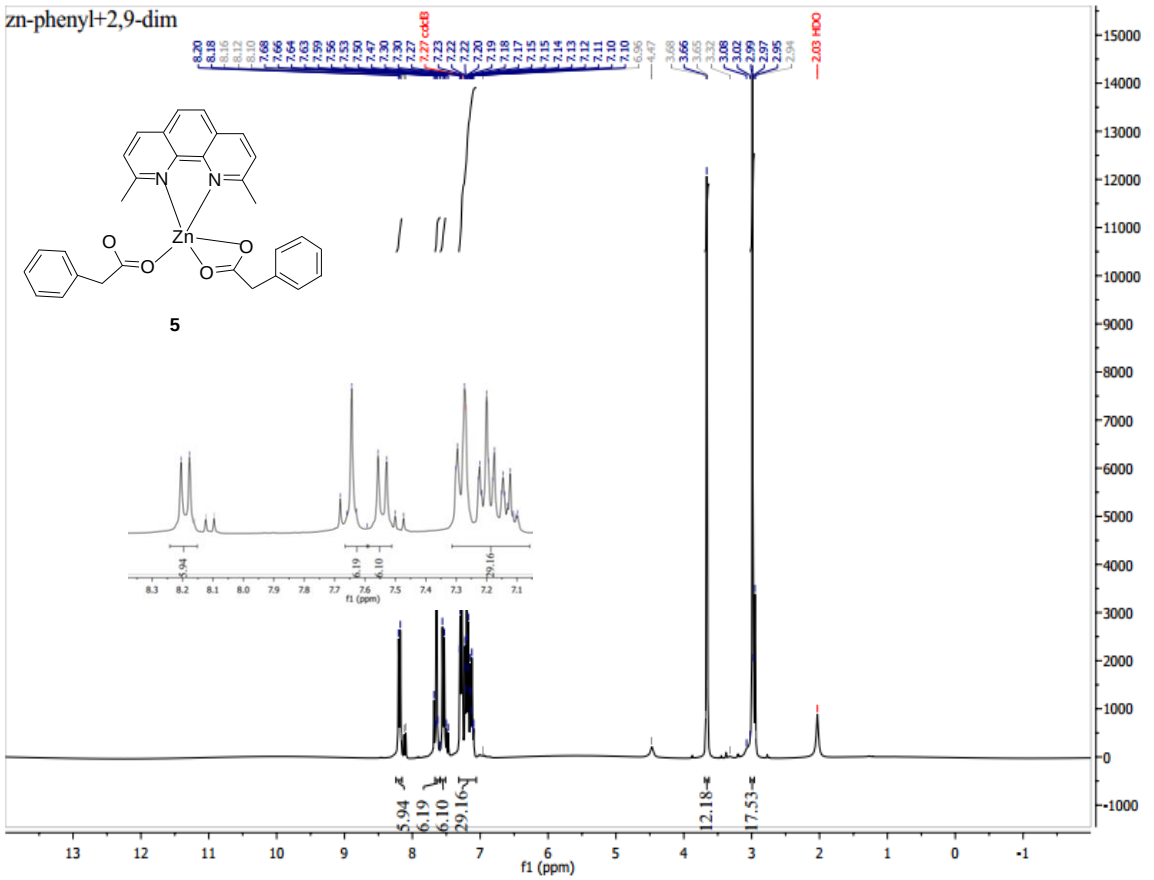


Figure 2.9: ^{1}H-NMR spectra of complex **5**

3.3 IR spectroscopy

IR spectroscopy is a functional group technique which plays an important role in structure elucidation. Infrared spectral data of sodium methoxyacetate and complex **1** and of sodium phenylacetate and complexes **2-5** in the 400-4000 cm^{-1} range as KBr pellet are summarized Table 3.31 and Table 3.32, respectively.

In metal carboxylate complexes, the major characteristic of the IR spectra is the frequency of the υ asymmetric (υ_{as}) and υ symmetric (υ_s) of carbonyl (COO^-) stretching vibrations and the difference between them $\Delta\upsilon(COO^-)$. The frequency of these bands depends upon the coordination mode of the carboxylate ligand. Monodentate complexes exhibit $\Delta\upsilon(COO^-)$ values that are much greater than the ionic complexes. Chelating (bidentate) complexes exhibit $\Delta\upsilon(COO^-)$ values that are significantly less than the ionic values. $\Delta\upsilon(COO^-)$ values for bridging complexes are greater than those of chelating complexes, and close to the ionic values.[57]

The stretching vibrations for sodium phenylacetate $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ have been observed at 1562.2 cm^{-1} and 1387.1 cm^{-1}, respectively and ($\Delta\upsilon COO^-$) = 175.1 cm^{-1}. For sodium methoxyacetate $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ have been observed at 1610.9 cm^{-1} and 1427.4 cm^{-1}, respectively and ($\Delta\upsilon COO^-$) = 183.5 cm^{-1}.

In complex **1**; $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ are observed at 1597.1 cm^{-1} and 1425.9 cm^{-1}, respectively, with $\Delta\upsilon COO^-$ = 171.2 cm^{-1} which is less than in sodium methoxyacetate supporting a bidentate (chelating) coordination mode. The O-H vibration frequency at 3440 cm^{-1} indicates the presence of water molecules in the crystal structure. Generally, the *v*(M-O) and *v*(M-N) for metal complexes appear as weak bands in the range of (430-474) cm^{-1} and (524- 576) cm^{-1}, respectively.[58] These bands for complexes **1-5** were shown in Table 2.2 and 2.3 respectively.

Table 2.2: Summary of principle peaks in the IR spectra of sodium methoxyacetate and complex **1** in (cm^{-1}).

Assignments	Na (methoxy)	Complex **1**
$v(C\text{-}H)_{aliph}$	2940,2829	-
$v\ (C\text{-}H)_{ar}$	-	3046, 2995
v(C-O)	1208, 1110	1101
γ(C-H)	932	849.01
δ(C-H)	1333	1514.22
$\nu_{as}(COO\text{-})$	1610.9	1597.1
$\nu_s(COO\text{-})$	1427.4	1425.9
$\Delta_v(COO\text{-})$	183.5	171.2
v(ring)	-	726.37
v(ring) + *δ*(C-H)	-	1342
ν(Zn-O)	-	430

In complex **2**; $\Delta\upsilon COO^-$ = 132.3 cm^{-1} which is less than in sodium phenylacetate supporting a bidentate (*syn-syn* bridging) coordination mode. For complex **3** $\Delta\upsilon COO^-$ = 199 cm^{-1} > $\Delta\upsilon COO^-_{(Na\ phenyl)}$ so

monodentate coordination mode is expected. In complex **4**; $\Delta\upsilon COO^{-}$ = 139.5 cm^{-1} < $\Delta\upsilon COO^{-}_{(Na\ phenyl)}$ so bidentate coordination mode, but according to X-ray structure determination the coordination mode was bidentate for the first carboxylate group and monodentate for the second one. Complex **5** with $\Delta\upsilon COO^{-}$ = 226 cm^{-1} >> $\Delta\upsilon COO^{-}_{(Na\ phenyl)}$ demonstrate monodentate coordination mode. All previously mentioned coordination modes of complexes **1-5** are in good agreement with their X-ray structure determination.

Table 2.3: Summary of principle peaks in the IR spectra of complexes **2-5** in (cm^{-1}).

Assignments	Na-phenyl	Complex **2**	Complex **3**	Complex **4**	Complex **5**
$\nu(C\text{-}H)_{ar}$	3025	3027	3024	3057	3027
$\gamma(C\text{-}H)$	933,710	809	851	853	861
$\nu(C\text{-}H)_{alph}$	2000	2362,1946	2700	1998	2800
$\nu_{as}(N\text{-}H)$	-	-	3341	-	-
$\nu_{s}(N\text{-}H)$	-	-	3227	-	-
$\delta(NH_2)$	-	-	1619	-	-
(N-H) wagging	-	-	661,698	-	-
$\nu(C\text{-}NH_2)$	-	-	1271	-	-
$\nu(C\text{-}C)_{ring}$	1496	1588	1159	1223	1450
$\nu(C\text{-}C)_{ring}$+ $\delta(CH)$	1281,1186	1316	1499,1360	1144,1100	1340,1221
$\nu(C\text{-}N)$	-	1403	1567	1515	1500
$\nu(Zn\text{-}O)$	-	483	459	421	400
$\nu(Zn\text{-}N)$	-	561	527	580	550

3.4 Electronic absorption spectroscopy

Zn(II) complexes with a spatial configuration of d^{10} and completely filled *d* orbital's have no *d-d* electronic transition bands. From the results tabulated in Table 2.4 and Table 2.5, no ligand to metal charge transfer "LMCT" can be observed due to filled *d* orbital's. The bands are assigned to MLCT charge transfer and intraligand transition e.g., π-π^* transition , the spectra of the complexes are similar to those of nitrogen parent ligands with very small shifts caused by zinc coordination. MLCT bands were observed around (201-296 nm) with ϵ values around 3000 $Lmol^{-1}cm^{-1}$.[59,60]

Table 2.4: UV-visible spectral data for the prepared complexes.

Compounds	λ_{max} (nm)	Є (Lmol^{-1}cm^{-1})
Zn-phenyl	214 259 265	2280.3 202.9 203.68
Zn-methoxy	271 292	1454.2 565.02
1	271 292	49119 14563
2	276 287	5606.4 5359.8
3	296	7864.7
4	277 292 325	27471 19379 1594.4
5	201 231 269	23816 53062 31408

Table 2.5: UV-visible spectral data for pure N-ligands.

Ligands	λ_{max} (nm)	ϵ(Lmol^{-1}cm^{-1})
1,10-phen **(1*10^{-5} M)**	266.0 225.0	45919 45488
quin **(1*10^{-5} M)**	204.0 225.0 276.0	44107 41442 3605.9
2-ampy **(1*10^{-4} M)**	234.0 291.0 200.0	11479 5569.5 5269.4
2,9-dmp **(1*10^{-5} M)**	272.0 231.0	184090 58280

3.5 X-ray crystallography

The crystal structures of complexes **1-5** were determined, suitable crystals were obtained by recrystallization from MeOH for **1**, **4** and **5** and from CH_2Cl_2 for **3**, whereas suitable crystals for complex **2** were obtained directly from the reaction solution. Selected bond angles (°) and bond distances (Å) are listed in Tables 2.6-3.3 respectively. Crystallographic information files (CIF) are given in the Appendices.

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

Figure 3.1 shows the crystal structure of complex **1** with two bidentate methoxyacetate groups and one bidentate 1,10-phen ligand, both ligands formed stable five member ring with Zn metal center.

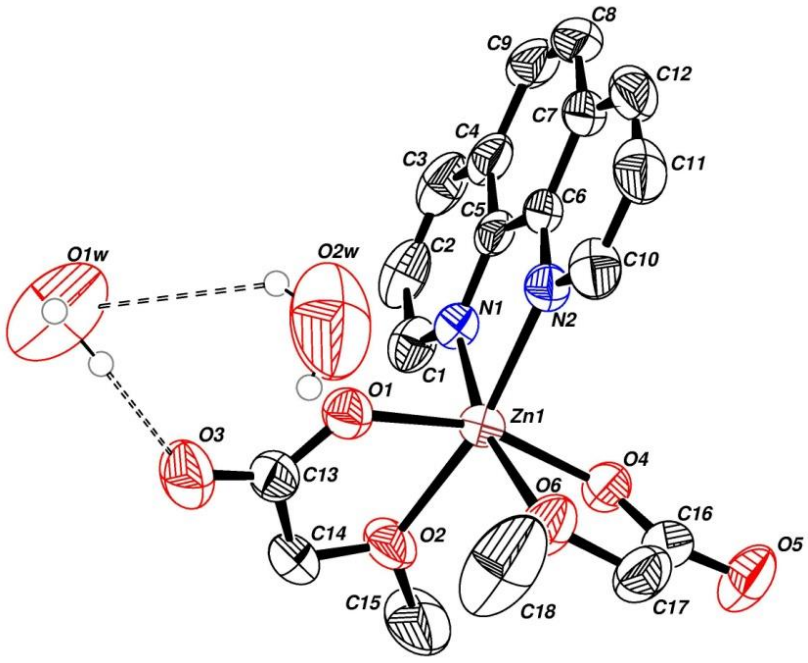


Figure 3.1: Molecular structure of compound **1** showing the labeling atom scheme.

Further stability of the crystal lattice was gained by the intramolecular hydrogen bonding between the two water molecules and the carbonyl oxygen atom of one methoxyacetate groups as represented by the dashed lines which occurs within one single molecule.[61]

In addition, both intramolecular and intermolecular hydrogen bonding play a crucial role in the enhancement of complex stability, for example, H-bonds give conformational stability of protein and other complex structures.[62,63] Hemilability is the most interesting property of this compound which refer to polydentate chelate ligand containing two types of bonding groups (hard and soft).[64]

The bond distances of O-Zn (2.0269(19) Å, 2.155(2) Å, 2.0253(19) Å and 2.201(2) Å) are similar to previously reported values (1.84–2.33 Å).[65] N-Zn bond distances (2.128(2) Å and 2.115(2) Å) are also similar to previously reported values i.e. (2.097 Å).[66]

Table 2.6: Selected bond angles (°) and bond distances (Å) of **1.**

Bond distance (Å)		Bond angle (Å)	
N(1)-Zn(1)	2.128(2)	N(1)-Zn(1)-N(2)	79.11(9)
N(2)-Zn(1)	2.115(2)	O(4)-Zn(1)-N(2)	99.33(8)
O(1)-Zn(1)	2.0269(19)	N(1)-Zn(1)-O(1)	101.79(8)
O(2)-Zn(1)	2.155(2)	O(2)-Zn(1)-O(1)	76.93(8)
O(4)-Zn(1)	2.0253(19)	O(2)-Zn(1)-O(6)	94.62(10)
O(6) -Zn(1)	2.201(2)	O(4)-Zn(1)-O(6)	76.00(8)
C(1)-N(1)	1.328(4)	C(1)-N(1)-C(5)	118.5(2)
C(5)-N(1)	1.355(3)	C(1)-N(1)-Zn(1)	129.1(2)
C(6)-N(2)	1.347(4)	C(5)-N(1)-Zn(1)	112.34(17)
C(10)-N(2)	1.334(4)	C(6)-N(2)-C(10)	118.4(2)
C(13)-O(1)	1.269(4)	C(10)-N(2)-Zn(1)	128.7(2)
C(14)-O(2)	1.416(4)	C(6)-N(1)-Zn(1)	112.89(18)
C(15)-O(2)	1.422(4)	Zn(1)-O(1)-C(13)	120.22(19)
C(16)-O(4)	1.265(4)	C(14)-O(2)-Zn(1)	114.54(17)
C(17)-O(6)	1.418(4)	C(15)-O(2)-Zn(1)	130.0(2)
C(18)-O(6)	1.403(4)	C(14)-O(2)-C(15)	113.8(3)
		Zn(1)-O(4)-C(16)	121.84(19)
		Zn(1)-O(6)-C(17)	113.77(18)
		Zn(1)-O(6)-C(18)	130.8(2)
		C(17)-O(6)-C(18)	114.3(3)

Complex **1** adopted slightly distorted octahedral geometry around the central Zn(II) cation due to unsymmetrical bond angles. O(4)-Zn(1)-O(6) = 76.00(8)˚, O(2)-Zn(1)-O(6) = 94.62(10)˚, O(2)-Zn(1)-O(1) = 76.93(8)˚, O(1)-Zn(1)-N(1) = 101.79(8)˚ and O(4)-Zn(1)-N(2) = 99.33(8)˚, N(1)-Zn(1)-N(2) = 79.11(9)˚.

Table 2.7 shows the H-bond distances in (Å), where these bonds are between O(3), O(4) and O(5) of the methoxyacetate with H of water molecules.

Table 2.7: Hydrogen bonds in complex **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2W)-H(2W2)...O(5)#1	0.87	2.62	3.035(6)	110.8
O(1W)-H(2W1)...O(4)#1	0.93	2.02	2.914(4)	161.2
O(1W)-H(1W1)...O(3)	0.90	2.00	2.900(5)	173.1

Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z

3.5.2 X-ray crystal structure of $Zn_2(phenyl)_4(quin)_2]$ (2)

The binuclear crystal structure of complex **2** is shown in Figure 3.2 in which two Zn(II) cations are bounded to four bidentate phenylacetate groups in (*syn-syn*) bridging coordination mode and two monodentate quin groups.

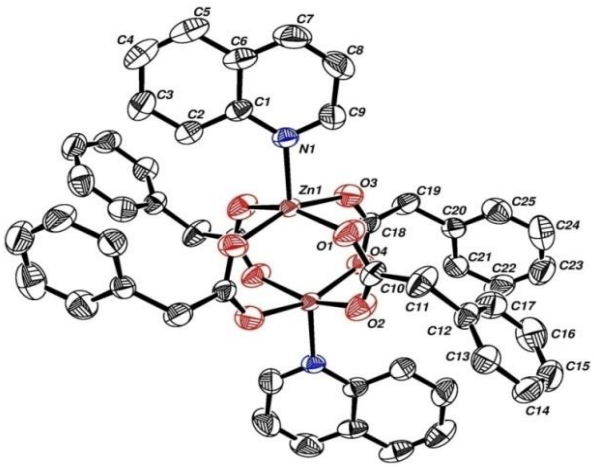


Figure 3.2: Molecular structure of compound **2** showing the labeling atom scheme.

The bond distances of O(1)-Zn(1) 2.060(4) Å, O(2)-Zn(1)#1 2.039(4) Å, O(3)-Zn(1) 2.057(4) Å, O(4)-Zn(1)# 12.026(4) Å. The coordination

distances of N(1)-Zn(1) 2.064(4) Å. Selected bond distances and bond angles are listed in Table 2.8.

Table 2.8: Selected bond distances (Å) and bond angles (°) of **2.**

Bond distance (Å)		Bond angle (°)	
N(1)-Zn(1)	2.064(4)	O(1)-Zn(1)-O(3)	85.7(2)
Zn(1)-Zn(1)#1	2.9773(12)	O(1)-Zn(1)-N(1)	96.35(17)
O(1)-Zn(1)	2.060(4)	N(1)-Zn(1)-O(3)	97.07(16)
O(2)-Zn(1)#1	2.039(4)	O(4)#1-Zn(1)-N(1)	104.37(17)
O(3)-Zn(1)	2.057(4)	O(2)#1-Zn(1)-N(1)	104.97(17)
O(4)-Zn(1)#1	2.026(4)	(2)#1-Zn(1)-Zn(1)#1	80.64(12)
C(1)-N(1)	1.368(6)	O(1)-Zn(1)-Zn(1)#1	77.81(12)
C(9)-N(1)	1.308(7)	O(3)-Zn(1)-Zn(1)#1	78.25(11)
C(10)-O(1)	1.246(6)	(4)#1-Zn(1)-Zn(1)#1	80.18(12)
C(18)-O(3)	1.236(6)	C(9)-N(1)-Zn(1)	115.5(4)
C(21)-O(3)		C(1)-N(1)-Zn(1)	126.2(4)
		C(9)-N(1)-C(1)	
		C(10)-O(1)-Zn(1)	129.0(4)
		C(10)-O(2)-Zn(1)#1	126.3(4)
		C(18)-O(3)-Zn(1)	128.7(4)

Complex **2** adopted slightly distorted square based pyramidal geometry around the central Zn(II) centers with O(1)-Zn(1)-O(3) = 85.7(2)˚, O(1)-Zn(1)-N(1) = 96.35(17)˚, N(1)-Zn(1)-O(3) = 97.07(16)˚, O(4)#1-Zn(1) N(1) = 104.37(17)˚, O(2)#1-Zn(1)-N(1) = 104.97 (17)˚, O(2)#1-Zn(1)-Zn(1)#1 = 80.64(12)˚ and O(4)#1-Zn(1)-Zn(1)#1 = 80.18(12)˚.

3.5.3 X-ray crystal structure of [Zn(phenyl)$_2$ (2-ampy)$_2$] (3)

As shown in Figure 3.3, the Zn(II) cation is bounded to two monodentate phenylacetate and two monodentate 2-ampy ligands. The Zn(1)-O(1) of 1.942(2) Å and Zn(1)-O(3) 1.9359(19) Å and Zn(1)-N(1) 2.056(3) Å and Zn(1)-N(3) 2.048(2) Å bond distances are obtained. Selected bond distances and bond angles are listed in Table 2.9.

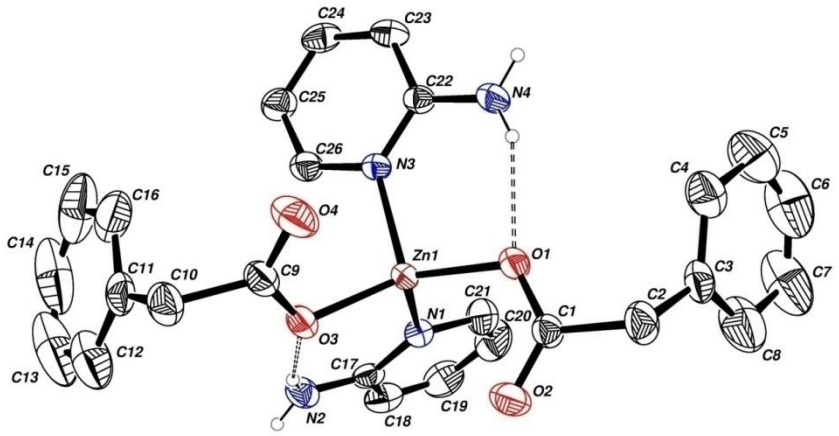


Figure 3.3: Molecular structure of compound **3** showing the labeling atom scheme.

Table 2.9: Selected bond distances (Å) and bond angles (°) of **3.**

Bond distance (Å)		Bond angle (°)	
N(1)-Zn(1)	2.056(3)	N(1)-Zn(1)-N(3)	99.19(10)
N(3)-Zn(1)	2.048(2)	O(1)-Zn(1)-N(1)	108.34(10)
O(1)-Zn(1)	1.942(2)	N(3)-Zn(1)-O(3)	106.05(9)
O(3)-Zn(1)	1.9359(19)	O(1)-Zn(1)-O(3)	129.09(10)
O(1)-C(1)	1.206(4)	O(1)-Zn(1)-N(3)	105.53(9)
O(3)-C(9)	1.275(4)	C(17)-N(1)-Zn(1)	126.9(2)
C(17)-N(1)	1.359(4)	C(21)-N(1)-Zn(1)	115.1(3)
C(21)-N(1)	1.344(4)	C(21)-N(1)-C(17)	117.8(3)
C(22)-N(3)	1.348(4)	C(22)-N(3)-Zn(1)	127.8(2)
C(26)-N(3)	1.358(4)	C(26)-N(3)-Zn(1)	113.66(19)
		C(26)-N(3)-C(22)	118.5(2)
		C(1)-O(1)-Zn(1)	115.25(18)
		C(9)-O(3)-Zn(1)	116.28(19)

Complex **3** adopted slightly distorted tetrahedral geometry around the central Zn(II) center. O(1)-Zn(1)-O(3) = 129.09(10)˚, N(1)-Zn(1)-N(3) = 99.19(10)˚, N(1)-Zn(1)-O(1) = 108.34(10)˚,N(3)-Zn(1)-O(3) = 106.05(9)

Table 3.1: Hydrogen bonds for complex **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(1N2)...O(2)#1	0.819(10)	2.112(11)	2.931(4)	179(3)
N(2)-H(2N2)...O(3)	0.815(10)	2.090(15)	2.873(4)	161(3)
N(4)-H(1N4)...O(4)#2	0.811(10)	2.194(15)	2.971(4)	160(3)
N(4)-H(2N4)...O(1)	0.817(10)	2.140(17)	2.901(4)	155(3)

3.5.4 X-ray crystal structure of [Zn(phenyl)$_2$1,10-phen] (4)

The atomic scheme and atom connectivity for complex **4** are shown in Figure 3.4, in which Zn(II) is covalently bonded to one monodentate phenylacetate group, one bidentate phenylacetate and one bidentate 1,10-phen ligands. Selected interatomic distances and angles are found in Table 3.2.

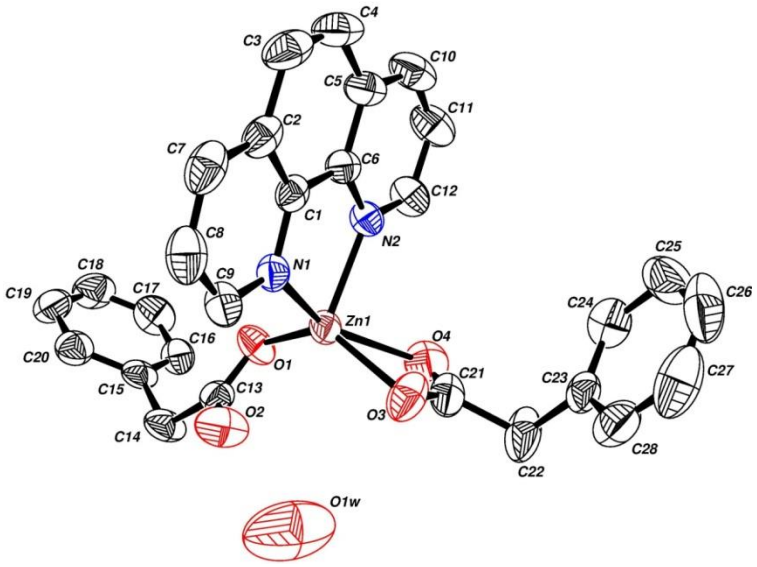


Figure 3.4: Molecular structure o f compound **4** showing the labeling atom scheme.

Table 3.2: Selected bond distances (Å) and angles bond (°) of **4.**

Bond distance (Å)		Bond angle (°)	
N(1)-Zn(1)	2.106(2)	N(1)-Zn(1)-N(2)	79.40(8)
N(2)-Zn(1)	2.096(2)	O(1)-Zn(1)-N(2)	109.19(8)
O(1)-Zn(1)	1.9768(19)	N(1)-Zn(1)-O(3)	104.10(8)
O(3)-Zn(1)	2.011(2)	O(3)-Zn(1)-O(4)	58.56(10)
O(4)-Zn(1)	2.392(2)	C(9)-N(1)-C(1)	118.3(2)
C(1)-N(1)	1.358(3)	C(9)-N(1)-Zn(1)	129.07(19)
C(9)-N(1)	1.321(3)	C(1)-N(1)-Zn(1)	112.58(16)
C(6)-N(2)	1.357(3)	C(6)-N(2)-Zn(1)	112.90(17)
C(12)-N(2)	1.325(4)	C(12)-N(2)-Zn(1)	128.5(2)
C(13)-O(1)	1.257(3)	C(13)-O(1)-Zn(1)	104.18(17)
C(21)-O(3)	1.264(4)	O(4)-Zn(1)-N(2)	85.87(8)
C(21)-O(4)	1.230(4)	C(21)-O(3)-Zn(1)	98.1(2)
		C(21)-O(4)-Zn(1)	81.41(19)

Complex **4** adopted slightly distorted trigonal bipyramidal geometry around the central Zn(II) center with O(3)-Zn(1)-O(4) = 58.56(10)˚, N(1)-Zn(1)-N(2) = 79.40(8)˚, N(1)-Zn(1)-O(3) = 104.10(8)˚, O(1)-Zn(1)-N(2) = 109.19(8)˚.

3.5.5 X-ray crystal structure of [Zn(phenyl)$_2$(2,9-dmp)] (5)

The atomic scheme and atom connectivity for complex **5** are shown in Figure 3.5, in which Zn(II) is covalently bonded to one monodentate phenylacetate group, one bidentate phenylacetate and one bidentate 2,9-dmp ligands. Selected interatomic distances and angles are found in Table 3.3. Complex **5** adopted slightly distorted trigonal bipyramidal geometry around the central Zn(II) cation O(1)-Zn(1)-O(4) = 111.81(19)˚, N(1)-

Zn(1)-N(2) = 80.8(3)˚, O(1)-Zn(1)-N(2) = 110.45(16)˚, N(1)-Zn(1)-O(3) = 100.1˚(2).

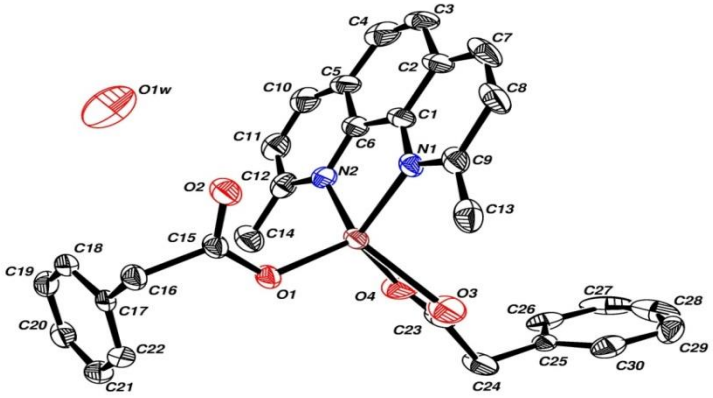


Figure 3.5: Molecular structure o f compound **5** showing the labeling atom scheme.

Table 3.3: Selected bond distances (Å) and bond angles (°) of **5.**

Bond distance (Å)		Bond angle (°)	
N(1)-Zn(1)	2.062(4)	N(1)-Zn(1)-N(2)	80.8(3)
N(2)-Zn(1)	2.077(5)	O(1)-Zn(1)-N(2)	110.45(16)
O(1)-Zn(1)	1.911(3)	N(1)-Zn(1)-O(3)	100.1(2)
O(3)-Zn(1)	2.278(6)	O(1)-Zn(1)-O(4)	111.81(19)
O(4)-Zn(1)	2.092(5)	C(9)-N(1)-C(1)	121.6(7)
C(1)-N(1)	1.376(8)	C(9)-N(1)-Zn(1)	127.2(6)
C(9)-N(1)	1.312(8)	C(1)-N(1)-Zn(1)	111.1(4)
C(6)-N(2)	1.352(7)	C(6)-N(2)-Zn(1)	113.7(6)
C(12)-N(2)	1.338(8)	C(12)-N(2)-Zn(1)	127.6(5)
C(15)-O(1)	1.242(5)	C(15)-O(1)-Zn(1)	120.0(3)
C(23)-O(3)	1.173(12)	O(4)-Zn(1)-O(3)	55.5(2)
C(23)-O(4)	1.211(12)	C(23)-O(3)-Zn(1)	89.1(7)
		C(23)-O(4)-Zn(1)	97.2(6)

3.6 BNPP Hydrolysis

The ability of metal complexes for phosphate diester hydrolysis was studied in the present work**.** The initial rate of the hydrolysis was determined by measuring the absorption of 4-nitrophenolate ion at 400 nm and various plots of absorbance versus time were obtained, the plot shown in Figure 3.6 is one representative example. The prepared complexes were used as catalysts for the phosphate diester group hydrolysis. The results showed good trend and rates in the BNPP hydrolysis process by **1-5** complexes. Moreover, Michaelies-Menten equation was used for calculating the initial rate against different concentrations of BNPP and the results are summarized in Table 3.4.

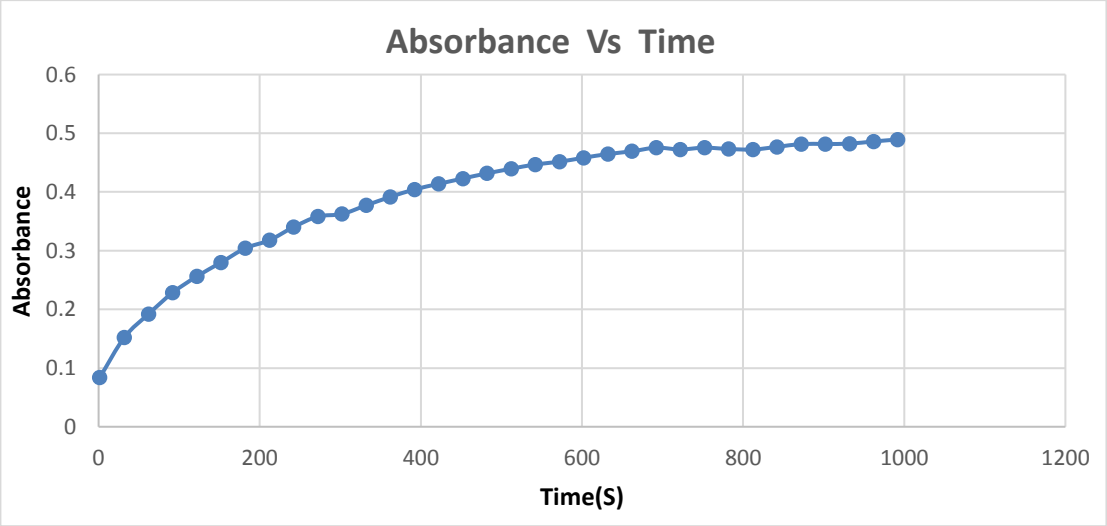


Figure 3.6: BNPP hydrolysis by complex **2** at pH = 7.91, 25 °C and [complex] = 1×10^{-4} M.

The results showed that the rate of BNPP hydrolysis was decreased in the following order: complex **2** > **4** > **3** > **1** > **5**.

Table 3.4: Kinetic parameters of the BNPP hydrolysis by complexes [**1-5**] 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, Km mol L^{-1}	Catalytic rate constant, Kcat[a] s^{-1}	2-order rate constant[b], K[BNPP] L\mol^{-1} s^{-1}
Complex **1**(1×10^{-3} M)					
1×10^{-3}	3.1×10^{-4}	3.16×10^{-4}	6.9×10^{-6}	0.316	4.5×10^{4}
1×10^{-4}	3×10^{-4}				
1×10^{-5}	1.8×10^{-4}				
Complex **2** (1×10^{-4} M)					
1×10^{-3}	9.4×10^{-4}	9.5×10^{-4}	1.5×10^{-5}	9.487	6.2×10^{5}
1×10^{-4}	8.1×10^{-4}				
1×10^{-5}	3.6×10^{-4}				
Complex **3** (1×10^{-3} M)					
1×10^{-3}	5.2×10^{-4}	5.1×10^{-4}	3.1×10^{-6}	0.513	1.7×10^{5}
1×10^{-4}	4.9×10^{-4}				
1×10^{-5}	3.8×10^{-4}				
Complex **4** (1×10^{-4} M)					
1×10^{-3}	3×10^{-4}	3×10^{-4}	9.6×10^{-6}	2.999	3.1×10^{5}
1×10^{-4}	2.7×10^{-4}				
1×10^{-5}	1.5×10^{-4}				
Complex **5** (1×10^{-3} M)					
1×10^{-3}	5.2×10^{-4}	5.3×10^{-4}	1.2×10^{-5}	0.526	4.3×10^{4}
1×10^{-4}	4.7×10^{-4}				
1×10^{-5}	2.4×10^{-4}				

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

3.7 Antibacterial activity

As mentioned in Section 2.6 the anti-bacterial activities of the synthesized zinc complexes were screened against different types of gram-negative bacteria (K. pneumonia, E. coli, P. Mirabilis and P. Aeruginosa) and gram-positive bacteria (S. epidermidis, S. aureus, E. ferabis, M. luteus and B. Subtilis) to show the effect of complexation on anti-bacteria activity. The average IZD inhibition zone diameters of three trials of the complexes were measured and stated as average ± standard error and summarized in Table 3.5.

$ZnCl_2$, Zn-phenyl and Zn-methoxyacetate did not show any anti-bacterial activity against all tested micro-organisms. DMSO was used as negative control to resist any tested microorganisms, whereas gentamicin was used as positive control for both G- and G+ bacteria.

The complexes **2** and **3** showed no activity against all tested bacterial species. Complex **1** showed high activity against G- or G+ bacteria except against E. ferabis and P. Aeruginosa. Complex **4** showed good activity against G- bacteria except P. Aeruginosa, and against G+ bacteria except E. ferabis. Complex **5** showed zero activity against G- bacteria but low activity against M. luteus, B. Subtilis bacteria and high activity against S. epidemidis and S. aureus.

Table 3.5: Anti-bacterial activity data of complexes **1-5**.

Compounds	***B. Subtilis*** **G+**	***S. epidermidis*** **G+**	***S. aureus*** **G+**	***E. faecalis*** **G+**	***M.luteus*** ***G+***
Zn- phenyl	-	-	-	-	-
Zn-methoxy	-	-	-	-	-
$ZnCl_2$	-	-	-	-	-
DMSO	-	-	-	-	-
G	29.3 ± 4.4	34.7± 1.4	29.3 ± 3.2	16.3 ± 0.9	34.7 ± 3.4
E	36.0 ± 2.1	45.0 ± 0.7	41.3 ± 1.4	-	40.0 ± 0.1
1	20.6 ± 1.1	28.7 ± 1.1	27.0 ± 0.8	-	27.6 ± 1.1
2	-	-	-	-	-
3	-	-	-	-	-
4	20.0 ± 0.9	29.6 ± 0.6	19.7 ± 0.5	-	25.3 ± 0.6
5	16.0 ± 1.7	30.6 ± 1.1	20.3 ± 0.5	-	14.6 ± 0.6
1,10-phen (pure)	32.7 ± 1.2	16.3 ± 0.8	16.8 ± 0.3	19.0 ± 0.8	35.7 ± 0.3

Table 3.5: Continued

Compounds	***K. pneumonia*** ***G-***	***P. Mirabilis*** ***G-***	***E. coli*** **G-**	***P. Aeruginosa*** ***G-***
Zn- phenyl	-	-	-	-
Zn-methoxy	-	-	-	-
$ZnCl_2$	-	-	-	-
DMSO	-	-	-	-
G	34.7 ± 3.4	27.0 ± 1.0	25.3 ± 0.9	20.0 ± 1.8
E	21.5 ± 0.5	17.3 ± 0.9	24.0 ± 1.6	21.7 ± 3.3
1	24.3 ± 0.6	25.6 ± 1.4	22.3 ± 1.5	-
2	-	-	-	-
3	-	-	-	-
4	20.6 ± 1.1	24.6 ± 0.6	24.0 ± 1.4	-
5	-	-	-	-
1,10-phen (pure)	32.0 ± 1.0	33.0 ± 0.6	31.0 ± 0.6	-

4. Conclusion

Five new Zn(II) complexes with phenylacetic acid and methoxyacetic acid in the presence of the following nitrogen donor ligands; 1,10-phen, quin, 2-ampy and 2,9-dmp have been synthesized and characterized. IR, UV-Vis, ^{1}H and $^{13}C\{^{1}H\}$-NMR spectroscopic techniques were used to study and characterize the new complexes. X-ray single crystal diffraction measurements were also determined for complexes **1-5** as an additional strong evidence for their structure elucidation. Different metal geometries and carboxylate coordination modes have been obtained and proved. The structure of complex **1** revealed slightly distorted octahedral geometry with two bidentate methoxy ligands and one bidentate 1,10-phen ligand bonded to the Zn(II) center. In complex **2**, slightly distorted square based pyramidal geometry of the binuclear Zn units was obtained with four phenyl bridging bidentate ligands and two monodentate quin ligands were bonded to the two Zn(II) catinos. The structure of complex **3** revealed slightly distorted tetrahedral geometry which consists of two monodentate phenylacetate groups and two monodentate 2-ampy ligands. Complexes **4** and **5** showed similar distorted trigonal bipyramidal geometries with one monodentate, one bidentate phenylacetate groups and one bidentate 1,10-phen or 2,9-dmp ligand, respectively. The obtained results from the kinetic experiments showed

that these complexes can act as potent BNPP hydrolysis, these activities were decreased in the order: complex **2** > **4** > **3** > **1** > **5**. Complex **1** showed high activity against G- and G+ bacteria except against E. faecalis and P. Aeruginosa. Complex **4** showed good activity against G- bacteria except against P. Aeruginosa, G+ bacteria except against E. faecalis. Complex **5** showed no activity against G- bacteria but low activity against M. luteus, B. Subtilis bacteria and high activity against S. epidermidis and S. aureus. Complexes **2** and **3** did not show any activity against G- or G+ bacteria.

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6. Appendices

Appendix A

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

Table 1A .Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

x	y	z	U(eq)	
C(1)	-153(2)	3321(3)	659(1)	50(1)
C(2)	-807(2)	3020(3)	223(1)	63(1)
C(3)	-503(3)	3062(3)	-187(1)	64(1)
C(4)	449(2)	3414(3)	-178(1)	52(1)
C(5)	1054(2)	3716(2)	271(1)	40(1)
C(6)	2037(2)	4110(2)	303(1)	40(1)
C(7)	2382(3)	4205(3)	-115(1)	53(1)
C(8)	1746(3)	3879(3)	-562(1)	68(1)
C(9)	836(3)	3498(3)	-592(1)	67(1)
C(10)	3510(2)	4751(3)	771(1)	53(1)
C(11)	3903(3)	4853(3)	377(1)	63(1)
C(12)	3341(3)	4590(3)	-63(1)	63(1)
C(13)	1132(2)	6424(3)	1660(1)	49(1)
C(14)	721(2)	5370(3)	1926(1)	55(1)
C(15)	664(4)	3050(4)	2036(2)	103(2)
C(16)	2984(2)	1866(3)	1748(1)	50(1)
C(17)	3613(3)	2954(3)	2016(1)	62(1)
C(18)	3629(4)	5256(5)	2161(2)	129(3)
N(1)	756(2)	3656(2)	682(1)	39(1)
N(2)	2597(2)	4395(2)	738(1)	40(1)
O(1)	1649(2)	6059(2)	1382(1)	47(1)
O(2)	934(2)	4105(2)	1770(1)	58(1)
O(3)	931(2)	7574(2)	1731(1)	77(1)
O(4)	2221(1)	2198(2)	1446(1)	46(1)
O(5)	3264(2)	724(2)	1836(1)	76(1)
O(6)	3213(2)	4207(2)	1865(1)	59(1)
O(1W)	858(3)	10022(4)	1203(2)	130(2)
O(2W)	3061(3)	8161(4)	1277(2)	159(2)
Zn(1)	1881(1)	4114(1)	1291(1)	38(1)

Table 2 A. Bond lengths [Å] and angles [°] for complex **1**

C(1)-N(1)	1.328(4)
C(1)-C(2)	1.407(5)
C(1)-H(1)	0.9300
C(2)-C(3)	1.357(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.400(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.404(4)
C(4)-C(9)	1.434(5)
C(5)-N(1)	1.355(3)
C(5)-C(6)	1.442(4)
C(6)-N(2)	1.347(4)
C(6)-C(7)	1.410(4)
C(7)-C(12)	1.397(5)
C(7)-C(8)	1.426(5)
C(8)-C(9)	1.340(6)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-N(2)	1.334(4)
C(10)-C(11)	1.389(4)
C(10)-H(10)	0.9300
C(11)-C(12)	1.354(5)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-O(3)	1.229(4)
C(13)-O(1)	1.269(4)
C(13)-C(14)	1.514(5)
C(14)-O(2)	1.416(4)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-O(2)	1.422(4)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-O(5)	1.231(4)

C(16)-O(4)	1.265(4)
C(16)-C(17)	1.511(5)
C(17)-O(6)	1.418(4)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-O(6)	1.403(4)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
N(1)-Zn(1)	2.128(2)
N(2)-Zn(1)	2.115(2)
O(1)-Zn(1)	2.0269(19)
O(2)-Zn(1)	2.155(2)
O(4)-Zn(1)	2.0253(19)
O(6)-Zn(1)	2.201(2)
O(1W)-H(1W1)	0.9044
O(1W)-H(2W1)	0.9281
O(2W)-H(1W2)	0.8843
O(2W)-H(2W2)	0.8680

N(1)-C(1)-C(2)	122.0(3)
N(1)-C(1)-H(1)	119.0
C(2)-C(1)-H(1)	119.0
C(3)-C(2)-C(1)	119.3(3)
C(3)-C(2)-H(2)	120.4
C(1)-C(2)-H(2)	120.4
C(2)-C(3)-C(4)	120.4(3)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	116.8(3)
C(3)-C(4)-C(9)	124.5(3)
C(5)-C(4)-C(9)	118.7(3)
N(1)-C(5)-C(4)	122.9(3)
N(1)-C(5)-C(6)	117.6(2)
C(4)-C(5)-C(6)	119.4(3)
N(2)-C(6)-C(7)	122.0(3)
N(2)-C(6)-C(5)	117.9(2)
C(7)-C(6)-C(5)	120.0(3)

C(12)-C(7)-C(6)	117.6(3)
C(12)-C(7)-C(8)	123.7(3)
C(6)-C(7)-C(8)	118.7(3)
C(9)-C(8)-C(7)	121.3(3)
C(9)-C(8)-H(8)	119.3
C(7)-C(8)-H(8)	119.3
C(8)-C(9)-C(4)	121.9(3)
C(8)-C(9)-H(9)	119.1
C(4)-C(9)-H(9)	119.1
N(2)-C(10)-C(11)	122.8(3)
N(2)-C(10)-H(10)	118.6
C(11)-C(10)-H(10)	118.6
C(12)-C(11)-C(10)	119.2(3)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(7)	120.0(3)
C(11)-C(12)-H(12)	120.0
C(7)-C(12)-H(12)	120.0
O(3)-C(13)-O(1)	125.2(3)
O(3)-C(13)-C(14)	116.7(3)
O(1)-C(13)-C(14)	118.1(3)
O(2)-C(14)-C(13)	109.8(2)
O(2)-C(14)-H(14A)	109.7
C(13)-C(14)-H(14A)	109.7
O(2)-C(14)-H(14B)	109.7
C(13)-C(14)-H(14B)	109.7
H(14A)-C(14)-H(14B)	108.2
O(2)-C(15)-H(15A)	109.5
O(2)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
O(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(5)-C(16)-O(4)	125.1(3)
O(5)-C(16)-C(17)	117.2(3)
O(4)-C(16)-C(17)	117.7(3)
O(6)-C(17)-C(16)	110.6(2)
O(6)-C(17)-H(17A)	109.5

C(16)-C(17)-H(17A)	109.5
O(6)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	108.1
O(6)-C(18)-H(18A)	109.5
O(6)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(6)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(1)-N(1)-C(5)	118.5(2)
C(1)-N(1)-Zn(1)	129.1(2)
C(5)-N(1)-Zn(1)	112.34(17)
C(10)-N(2)-C(6)	118.4(2)
C(10)-N(2)-Zn(1)	128.7(2)
C(6)-N(2)-Zn(1)	112.89(18)
C(13)-O(1)-Zn(1)	120.22(19)
C(14)-O(2)-C(15)	113.8(3)
C(14)-O(2)-Zn(1)	114.54(17)
C(15)-O(2)-Zn(1)	130.0(2)
C(16)-O(4)-Zn(1)	121.84(19)
C(18)-O(6)-C(17)	114.3(3)
C(18)-O(6)-Zn(1)	130.8(2)
C(17)-O(6)-Zn(1)	113.77(18)
H(1W1)-O(1W)-H(2W1)	110.8
H(1W2)-O(2W)-H(2W2)	109.6
O(4)-Zn(1)-O(1)	160.45(8)
O(4)-Zn(1)-N(2)	99.33(8)
O(1)-Zn(1)-N(2)	95.18(8)
O(4)-Zn(1)-N(1)	93.79(8)
O(1)-Zn(1)-N(1)	101.79(8)
N(2)-Zn(1)-N(1)	79.11(9)
O(4)-Zn(1)-O(2)	90.49(8)
O(1)-Zn(1)-O(2)	76.93(8)
N(2)-Zn(1)-O(2)	168.11(9)
N(1)-Zn(1)-O(2)	93.64(9)
O(4)-Zn(1)-O(6)	76.00(8)
O(1)-Zn(1)-O(6)	89.99(8)

N(2)-Zn(1)-O(6)	94.26(9)
N(1)-Zn(1)-O(6)	166.90(8)
O(2)-Zn(1)-O(6)	94.62(10)

Symmetry transformations used to generate equivalent atoms:

Table 3 A . Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **1**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	45(2)	40(1)	65(2)	6(1)	11(1)	-1(1)
C(2)	45(2)	38(2)	93(3)	5(2)	-4(2)	-3(1)
C(3)	67(2)	41(2)	66(2)	-5(2)	-18(2)	5(1)
C(4)	71(2)	34(1)	43(2)	-2(1)	-4(1)	14(1)
C(5)	53(2)	27(1)	38(1)	1(1)	5(1)	10(1)
C(6)	55(2)	30(1)	40(1)	4(1)	18(1)	12(1)
C(7)	80(2)	39(1)	47(2)	8(1)	30(2)	21(1)
C(8)	110(3)	59(2)	38(2)	5(1)	26(2)	31(2)
C(9)	103(3)	56(2)	33(2)	-3(1)	-2(2)	26(2)
C(10)	50(2)	43(2)	69(2)	2(1)	22(1)	-2(1)
C(11)	62(2)	48(2)	91(3)	12(2)	43(2)	3(2)
C(12)	83(2)	47(2)	78(2)	16(2)	54(2)	17(2)
C(13)	54(2)	49(2)	40(1)	-7(1)	7(1)	6(1)
C(14)	65(2)	59(2)	47(2)	-5(1)	25(1)	8(2)
C(15)	155(5)	72(3)	118(4)	27(3)	102(4)	12(3)
C(16)	56(2)	53(2)	43(2)	7(1)	14(1)	7(1)
C(17)	63(2)	62(2)	51(2)	4(2)	-5(2)	11(2)
C(18)	134(4)	73(3)	128(4)	-27(3)	-72(4)	0(3)
N(1)	41(1)	36(1)	40(1)	3(1)	9(1)	2(1)
N(2)	43(1)	37(1)	43(1)	2(1)	15(1)	3(1)
O(1)	54(1)	41(1)	47(1)	0(1)	17(1)	1(1)
O(2)	81(2)	48(1)	60(1)	5(1)	45(1)	4(1)
O(3)	104(2)	51(1)	82(2)	-11(1)	37(2)	12(1)
O(4)	47(1)	43(1)	45(1)	1(1)	7(1)	2(1)
O(5)	85(2)	52(1)	82(2)	15(1)	0(1)	17(1)
O(6)	59(1)	49(1)	56(1)	-5(1)	-11(1)	1(1)

O(1W)	102(3)	102(3)	152(4)	26(2)	-33(2)	-35(2)
O(2W)	138(3)	110(3)	271(6)	30(3)	131(4)	6(3)
Zn(1)	41(1)	40(1)	33(1)	1(1)	11(1)	2(1)

Table 4A . Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex 1.

	x	y	z	U(eq)
H(1)	-363	3284	939	60
H(2)	-1442	2795	216	75
H(3)	-929	2856	-476	77
H(8)	1968	3933	-839	81
H(9)	443	3281	-889	80
H(10)	3901	4939	1072	63
H(11)	4544	5100	414	75
H(12)	3593	4664	-330	76
H(14A)	998	5457	2266	66
H(14B)	28	5479	1868	66
H(15A)	1022	3109	2363	155
H(15B)	802	2224	1904	155
H(15C)	-13	3104	2020	155
H(17A)	3670	2852	2356	74
H(17B)	4254	2891	1959	74
H(18A)	3649	5041	2487	194
H(18B)	3250	6038	2071	194
H(18C)	4272	5406	2127	194
H(1W1)	934	9268	1376	195
H(2W1)	1393	10564	1299	195
H(1W2)	2548	8564	1101	239
H(2W2)	3068	8246	1577	239

Appendix B

6.2 Crystal structure data of $[Zn_2(phenyl)_4(quin)_2]$ (2)

Table 1B.Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) For complex 2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6697(6)	8989(4)	5986(5)	40(1)
C(2)	6377(8)	8758(5)	7021(5)	55(2)
C(3)	6570(11)	9683(6)	7882(6)	73(2)
C(4)	7071(10)	10867(6)	7745(8)	78(2)
C(5)	7386(9)	11115(6)	6767(7)	67(2)
C(6)	7227(7)	10175(5)	5858(6)	50(1)
C(7)	7521(10)	10370(6)	4816(7)	71(2)
C(8)	7331(11)	9444(7)	3984(7)	77(2)
C(9)	6811(9)	8288(6)	4180(6)	60(2)
C(10)	7292(6)	4397(5)	4131(5)	42(1)
C(11)	8599(8)	4107(6)	3554(6)	60(2)
C(12)	8161(7)	2989(5)	2691(5)	44(1)
C(13)	9242(7)	2083(5)	2813(5)	50(1)
C(14)	8894(9)	1072(6)	2018(6)	59(2)
C(15)	7484(10)	952(6)	1082(6)	66(2)
C(16)	6403(9)	1830(8)	933(6)	70(2)
C(17)	6727(8)	2847(6)	1737(6)	60(2)
C(18)	3081(7)	5159(5)	2914(4)	40(1)
C(19)	1889(9)	5290(5)	1701(5)	58(2)
C(20)	1936(7)	4331(5)	752(4)	42(1)
C(21)	1160(8)	3194(6)	639(5)	56(2)
C(22)	1178(10)	2342(6)	-260(6)	72(2)
C(23)	1974(12)	2603(8)	-1030(7)	80(2)
C(24)	2742(10)	3721(9)	-926(7)	82(2)
C(25)	2735(9)	4585(7)	-38(6)	63(2)
N(1)	6495(5)	8056(4)	5129(4)	39(1)
O(1)	7243(6)	5488(4)	4429(4)	61(1)
O(2)	6404(5)	3552(4)	4286(4)	59(1)

O(3)	3955(6)	6077(4)	3465(3)	58(1)
O(4)	3067(6)	4144(4)	3277(3)	58(1)
Zn(1)	5601(1)	6300(1)	5137(1)	33(1)

Table 2B. Bond lengths [Å] and angles [°] for complex 2.

C(1)-N(1)	1.368(6)
C(1)-C(2)	1.411(8)
C(1)-C(6)	1.412(8)
C(2)-C(3)	1.367(8)
C(2)-H(2)	0.9300
C(3)-C(4)	1.405(11)
C(3)-H(3)	0.9300
C(4)-C(5)	1.346(11)
C(4)-H(4)	0.9300
C(5)-C(6)	1.422(9)
C(5)-H(5)	0.9300
C(6)-C(7)	1.400(10)
C(7)-C(8)	1.344(10)
C(7)-H(7)	0.9300
C(8)-C(9)	1.406(9)
C(8)-H(8)	0.9300
C(9)-N(1)	1.308(7)
C(9)-H(9)	0.9300
C(10)-O(2)	1.238(7)
C(10)-O(1)	1.246(6)
C(10)-C(11)	1.519(7)
C(11)-C(12)	1.505(8)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(17)	1.381(9)
C(12)-C(13)	1.388(8)
C(13)-C(14)	1.373(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.356(10)
C(14)-H(14)	0.9300
C(15)-C(16)	1.363(11)
C(15)-H(15)	0.9300
C(16)-C(17)	1.384(10)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(18)-O(3)	1.236(6)

C(18)-O(4)	1.253(7)
C(18)-C(19)	1.529(7)
C(19)-C(20)	1.513(8)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-C(21)	1.372(8)
C(20)-C(25)	1.377(9)
C(21)-C(22)	1.387(9)
C(21)-H(21)	0.9300
C(22)-C(23)	1.356(11)
C(22)-H(22)	0.9300
C(23)-C(24)	1.352(12)
C(23)-H(23)	0.9300
C(24)-C(25)	1.383(11)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
N(1)-Zn(1)	2.064(4)
O(1)-Zn(1)	2.060(4)
O(2)-Zn(1)#1	2.039(4)
O(3)-Zn(1)	2.057(4)
O(4)-Zn(1)#1	2.026(4)
Zn(1)-O(4)#1	2.026(4)
Zn(1)-O(2)#1	2.039(4)
Zn(1)-Zn(1)#1	2.9773(12)

N(1)-C(1)-C(2)	119.2(5)
N(1)-C(1)-C(6)	121.4(5)
C(2)-C(1)-C(6)	119.3(5)
C(3)-C(2)-C(1)	119.7(6)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	120.8(7)
C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(5)-C(4)-C(3)	120.8(6)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	120.2(6)

C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(7)-C(6)-C(1)	117.7(6)
C(7)-C(6)-C(5)	123.2(6)
C(1)-C(6)-C(5)	119.1(6)
C(8)-C(7)-C(6)	120.3(6)
C(8)-C(7)-H(7)	119.8
C(6)-C(7)-H(7)	119.8
C(7)-C(8)-C(9)	118.6(7)
C(7)-C(8)-H(8)	120.7
C(9)-C(8)-H(8)	120.7
N(1)-C(9)-C(8)	123.7(6)
N(1)-C(9)-H(9)	118.1
C(8)-C(9)-H(9)	118.1
O(2)-C(10)-O(1)	125.9(5)
O(2)-C(10)-C(11)	118.5(5)
O(1)-C(10)-C(11)	115.6(5)
C(12)-C(11)-C(10)	115.2(5)
C(12)-C(11)-H(11A)	108.5
C(10)-C(11)-H(11A)	108.5
C(12)-C(11)-H(11B)	108.5
C(10)-C(11)-H(11B)	108.5
H(11A)-C(11)-H(11B)	107.5
C(17)-C(12)-C(13)	117.9(5)
C(17)-C(12)-C(11)	121.9(6)
C(13)-C(12)-C(11)	120.2(6)
C(14)-C(13)-C(12)	121.2(6)
C(14)-C(13)-H(13)	119.4
C(12)-C(13)-H(13)	119.4
C(15)-C(14)-C(13)	120.0(6)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.2(6)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	120.5(6)
C(15)-C(16)-H(16)	119.8
C(17)-C(16)-H(16)	119.8

C(12)-C(17)-C(16)	120.3(6)
C(12)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
O(3)-C(18)-O(4)	125.5(5)
O(3)-C(18)-C(19)	116.8(5)
O(4)-C(18)-C(19)	117.7(5)
C(20)-C(19)-C(18)	114.8(4)
C(20)-C(19)-H(19A)	108.6
C(18)-C(19)-H(19A)	108.6
C(20)-C(19)-H(19B)	108.6
C(18)-C(19)-H(19B)	108.6
H(19A)-C(19)-H(19B)	107.5
C(21)-C(20)-C(25)	118.1(6)
C(21)-C(20)-C(19)	121.1(6)
C(25)-C(20)-C(19)	120.8(6)
C(20)-C(21)-C(22)	120.0(6)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(23)-C(22)-C(21)	121.3(7)
C(23)-C(22)-H(22)	119.3
C(21)-C(22)-H(22)	119.3
C(24)-C(23)-C(22)	119.1(7)
C(24)-C(23)-H(23)	120.4
C(22)-C(23)-H(23)	120.4
C(23)-C(24)-C(25)	120.5(7)
C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7
C(20)-C(25)-C(24)	121.0(7)
C(20)-C(25)-H(25)	119.5
C(24)-C(25)-H(25)	119.5
C(9)-N(1)-C(1)	118.2(5)
C(9)-N(1)-Zn(1)	115.5(4)
C(1)-N(1)-Zn(1)	126.2(4)
C(10)-O(1)-Zn(1)	129.0(4)
C(10)-O(2)-Zn(1)#1	126.3(4)
C(18)-O(3)-Zn(1)	128.7(4)
C(18)-O(4)-Zn(1)#1	127.3(4)
O(4)#1-Zn(1)-O(2)#1	88.9(2)

O(4)#1-Zn(1)-O(3)	158.42(16)
O(2)#1-Zn(1)-O(3)	87.9(2)
O(4)#1-Zn(1)-O(1)	89.5(2)
O(2)#1-Zn(1)-O(1)	158.34(17)
O(3)-Zn(1)-O(1)	85.7(2)
O(4)#1-Zn(1)-N(1)	104.37(17)
O(2)#1-Zn(1)-N(1)	104.97(17)
O(3)-Zn(1)-N(1)	97.07(16)
O(1)-Zn(1)-N(1)	96.35(17)
O(4)#1-Zn(1)-Zn(1)#1	80.18(12)
O(2)#1-Zn(1)-Zn(1)#1	80.64(12)
O(3)-Zn(1)-Zn(1)#1	78.25(11)
O(1)-Zn(1)-Zn(1)#1	77.81(12)
N(1)-Zn(1)-Zn(1)#1	172.69(13)

Symmetry transformations used to generate equivalent atoms:

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

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(3)	32(2)	44(3)	-1(2)	4(2)	2(2)
C(2)	72(4)	37(3)	52(3)	-3(2)	19(3)	-5(3)
C(3)	100(6)	58(4)	59(4)	-15(3)	29(4)	-5(4)
C(4)	90(6)	47(4)	89(6)	-26(4)	28(5)	-2(4)
C(5)	63(4)	34(3)	92(5)	-5(3)	11(4)	1(3)
C(6)	43(3)	32(3)	65(4)	5(2)	3(3)	0(2)
C(7)	81(5)	46(4)	81(5)	16(3)	18(4)	-13(3)
C(8)	105(6)	67(5)	64(4)	14(4)	38(4)	-20(4)
C(9)	81(5)	50(3)	49(3)	0(3)	27(3)	-11(3)
C(10)	36(3)	42(3)	45(3)	-6(2)	12(2)	6(2)
C(11)	50(3)	52(4)	82(5)	-19(3)	35(3)	-5(3)
C(12)	42(3)	43(3)	51(3)	-5(2)	24(2)	-2(2)
C(13)	41(3)	55(3)	55(3)	2(3)	19(3)	6(3)
C(14)	68(4)	45(3)	74(4)	2(3)	36(4)	12(3)

C(15)	86(5)	58(4)	59(4)	-12(3)	37(4)	-6(4)
C(16)	62(4)	90(5)	45(3)	-2(3)	2(3)	-6(4)
C(17)	57(4)	60(4)	62(4)	11(3)	16(3)	14(3)
C(18)	45(3)	37(3)	33(2)	0(2)	5(2)	9(2)
C(19)	73(4)	42(3)	41(3)	-1(2)	-9(3)	17(3)
C(20)	43(3)	41(3)	32(2)	5(2)	-3(2)	4(2)
C(21)	65(4)	51(3)	47(3)	3(3)	15(3)	-8(3)
C(22)	90(5)	44(4)	65(4)	-9(3)	8(4)	-2(3)
C(23)	105(6)	77(5)	54(4)	-9(4)	20(4)	27(5)
C(24)	78(5)	120(8)	57(4)	14(4)	32(4)	20(5)
C(25)	61(4)	64(4)	60(4)	11(3)	14(3)	-7(3)
N(1)	41(2)	30(2)	41(2)	4(2)	9(2)	0(2)
O(1)	67(3)	45(2)	85(3)	-1(2)	46(3)	10(2)
O(2)	55(2)	49(2)	84(3)	-6(2)	40(2)	0(2)
O(3)	69(3)	42(2)	43(2)	2(2)	-5(2)	-5(2)
O(4)	76(3)	40(2)	41(2)	6(2)	-7(2)	3(2)
Zn(1)	38(1)	25(1)	33(1)	-1(1)	9(1)	1(1)

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

	x	y	z	U(eq)
H(2)	6035	7979	7118	66
H(3)	6369	9528	8567	88
H(4)	7185	11486	8337	94
H(5)	7709	11903	6686	80
H(7)	7851	11143	4698	85
H(8)	7538	9567	3293	92
H(9)	6684	7651	3602	72
H(11A)	8792	4789	3157	72
H(11B)	9638	4016	4157	72
H(13)	10220	2163	3446	60
H(14)	9625	468	2120	71
H(15)	7254	270	540	80

H(16)	5441	1745	288	84
H(17)	5976	3436	1633	72
H(19A)	759	5271	1736	70
H(19B)	2155	6074	1488	70
H(21)	622	2994	1165	67
H(22)	634	1578	-336	86
H(23)	1991	2020	-1622	96
H(24)	3280	3911	-1456	98
H(25)	3277	5348	26	76

Appendix C

6.3 Crystal structure data of [Zn(phenyl)$_2$ (2-ampy)$_2$] (3)

Table 1C.Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) For complex 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

U(eq)	z	y	x	
54(1)	3874(3)	1091(3)	1130(3)	C(1)
81(1)	3273(4)	-36(4)	998(4)	C(2)
72(1)	2023(3)	-327(3)	1889(4)	C(3)
99(1)	1871(4)	-1040(4)	3141(5)	C(4)
140(2)	740(6)	-1343(6)	4034(7)	C(5)
164(3)	-205(6)	-889(8)	3657(11)	C(6)
174(4)	-173(6)	-178(7)	2490(11)	C(7)
159(3)	1010(6)	89(6)	1559(9)	C(8)
64(1)	7167(3)	2622(3)	1777(3)	C(9)

80(1)	8382(3)	3298(4)	1311(4)	C(10)
78(1)	8361(3)	4388(4)	1903(4)	C(11)
136(2)	8495(5)	5551(5)	1146(8)	C(12)
215(7)	8477(9)	6595(10)	1698(15)	C(13)
197(7)	8287(8)	6271(10)	2982(16)	C(14)
181(4)	8143(6)	5165(11)	3837(9)	C(15)
120(2)	8184(4)	4182(7)	3240(6)	C(16)
58(1)	3871(3)	5220(3)	1734(3)	C(17)
82(1)	2988(4)	6126(4)	1776(4)	C(18)
103(2)	1818(5)	5784(5)	2285(5)	C(19)
110(2)	1476(4)	4571(6)	2747(5)	C(20)
85(1)	2351(3)	3708(4)	2697(4)	C(21)
50(1)	4040(2)	1318(3)	5387(3)	C(22)
67(1)	4068(3)	1272(3)	6680(3)	C(23)
74(1)	4601(4)	2201(3)	6934(3)	C(24)
75(1)	5139(4)	3199(3)	5911(4)	C(25)
65(1)	5094(3)	3206(3)	4677(3)	C(26)
57(1)	3541(2)	4006(2)	2210(2)	N(1)
68(1)	5038(3)	5535(3)	1280(3)	N(2)
50(1)	4550(2)	2288(2)	4395(2)	N(3)
66(1)	3481(3)	423(3)	5123(3)	N(4)
68(1)	3888(2)	1106(2)	2287(2)	O(1)
84(1)	4329(3)	1899(2)	173(2)	O(2)
62(1)	6284(2)	3253(2)	1499(2)	O(3)
96(1)	7058(3)	1546(3)	2392(3)	O(4)

49(1) 4676(1) 2551(1) 2432(1) Zn(1)

Table 2C. Bond lengths [Å] and angles [°] for complex 3.

C(1)-O(2)	1.206(4)
C(1)-O(1)	1.266(4)
C(1)-C(2)	1.515(4)
C(2)-C(3)	1.492(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(8)	1.340(6)
C(3)-C(4)	1.368(6)
C(4)-C(5)	1.388(7)
C(4)-H(4)	0.9300
C(5)-C(6)	1.304(10)
C(5)-H(5)	0.9300
C(6)-C(7)	1.314(11)
C(6)-H(6)	0.9300
C(7)-C(8)	1.446(9)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
C(9)-O(4)	1.219(4)
C(9)-O(3)	1.275(4)
C(9)-C(10)	1.509(5)
C(10)-C(11)	1.511(6)

C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.348(7)
C(11)-C(16)	1.374(7)
C(12)-C(13)	1.437(14)
C(12)-H(12)	0.9300
C(13)-C(14)	1.312(17)
C(13)-H(13)	0.9300
C(14)-C(15)	1.339(14)
C(14)-H(14)	0.9300
C(15)-C(16)	1.403(9)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-N(2)	1.322(4)
C(17)-N(1)	1.359(4)
C(17)-C(18)	1.407(5)
C(18)-C(19)	1.336(6)
C(18)-H(18)	0.9300
C(19)-C(20)	1.360(7)
C(19)-H(19)	0.9300
C(20)-C(21)	1.367(6)
C(20)-H(20)	0.9300
C(21)-N(1)	1.344(4)
C(21)-H(21)	0.9300
C(22)-N(4)	1.336(4)

C(22)-N(3)	1.348(4)
C(22)-C(23)	1.404(4)
C(23)-C(24)	1.345(5)
C(23)-H(23)	0.9300
C(24)-C(25)	1.392(5)
C(24)-H(24)	0.9300
C(25)-C(26)	1.355(5)
C(25)-H(25)	0.9300
C(26)-N(3)	1.358(4)
C(26)-H(26)	0.9300
N(1)-Zn(1)	2.056(3)
N(2)-H(1N2)	0.819(10)
N(2)-H(2N2)	0.815(10)
N(3)-Zn(1)	2.048(2)
N(4)-H(1N4)	0.811(10)
N(4)-H(2N4)	0.817(10)
O(1)-Zn(1)	1.942(2)
O(3)-Zn(1)	1.9359(19)

O(2)-C(1)-O(1)	123.3(3)
O(2)-C(1)-C(2)	120.8(3)
O(1)-C(1)-C(2)	115.9(3)
C(3)-C(2)-C(1)	114.0(3)
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(8)-C(3)-C(4)	116.3(5)
C(8)-C(3)-C(2)	124.3(5)
C(4)-C(3)-C(2)	119.4(4)
C(3)-C(4)-C(5)	122.9(5)
C(3)-C(4)-H(4)	118.5
C(5)-C(4)-H(4)	118.5
C(6)-C(5)-C(4)	117.5(7)
C(6)-C(5)-H(5)	121.2
C(4)-C(5)-H(5)	121.2
C(5)-C(6)-C(7)	125.1(8)
C(5)-C(6)-H(6)	117.5
C(7)-C(6)-H(6)	117.5
C(6)-C(7)-C(8)	116.5(6)
C(6)-C(7)-H(7)	121.8
C(8)-C(7)-H(7)	121.8
C(3)-C(8)-C(7)	121.6(7)
C(3)-C(8)-H(8)	119.2
C(7)-C(8)-H(8)	119.2
O(4)-C(9)-O(3)	123.4(3)
O(4)-C(9)-C(10)	121.0(3)
O(3)-C(9)-C(10)	115.6(3)
C(9)-C(10)-C(11)	111.6(3)

C(9)-C(10)-H(10A)	109.3
C(11)-C(10)-H(10A)	109.3
C(9)-C(10)-H(10B)	109.3
C(11)-C(10)-H(10B)	109.3
H(10A)-C(10)-H(10B)	108.0
C(12)-C(11)-C(16)	119.9(6)
C(12)-C(11)-C(10)	121.1(5)
C(16)-C(11)-C(10)	118.9(4)
C(11)-C(12)-C(13)	121.6(8)
C(11)-C(12)-H(12)	119.2
C(13)-C(12)-H(12)	119.2
C(14)-C(13)-C(12)	112.2(10)
C(14)-C(13)-H(13)	123.9
C(12)-C(13)-H(13)	123.9
C(13)-C(14)-C(15)	131.9(14)
C(13)-C(14)-H(14)	114.1
C(15)-C(14)-H(14)	114.1
C(14)-C(15)-C(16)	113.3(9)
C(14)-C(15)-H(15)	123.3
C(16)-C(15)-H(15)	123.3
C(11)-C(16)-C(15)	121.0(7)
C(11)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
N(2)-C(17)-N(1)	118.8(3)
N(2)-C(17)-C(18)	120.6(3)

N(1)-C(17)-C(18)	120.5(3)
C(19)-C(18)-C(17)	119.4(4)
C(19)-C(18)-H(18)	120.3
C(17)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	120.6(4)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(19)-C(20)-C(21)	118.9(4)
C(19)-C(20)-H(20)	120.5
C(21)-C(20)-H(20)	120.5
N(1)-C(21)-C(20)	122.8(4)
N(1)-C(21)-H(21)	118.6
C(20)-C(21)-H(21)	118.6
N(4)-C(22)-N(3)	118.9(3)
N(4)-C(22)-C(23)	120.8(3)
N(3)-C(22)-C(23)	120.3(3)
C(24)-C(23)-C(22)	120.0(3)
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	120.0(3)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.0
C(26)-C(25)-C(24)	118.1(3)
C(26)-C(25)-H(25)	120.9
C(24)-C(25)-H(25)	120.9

C(25)-C(26)-N(3)	123.2(3)
C(25)-C(26)-H(26)	118.4
N(3)-C(26)-H(26)	118.4
C(21)-N(1)-C(17)	117.8(3)
C(21)-N(1)-Zn(1)	115.1(3)
C(17)-N(1)-Zn(1)	126.9(2)
C(17)-N(2)-H(1N2)	118(2)
C(17)-N(2)-H(2N2)	119(2)
H(1N2)-N(2)-H(2N2)	121(3)
C(22)-N(3)-C(26)	118.5(2)
C(22)-N(3)-Zn(1)	127.8(2)
C(26)-N(3)-Zn(1)	113.66(19)
C(22)-N(4)-H(1N4)	119(3)
C(22)-N(4)-H(2N4)	123(2)
H(1N4)-N(4)-H(2N4)	117(3)
C(1)-O(1)-Zn(1)	115.25(18)
C(9)-O(3)-Zn(1)	116.28(19)
O(3)-Zn(1)-O(1)	129.09(10)
O(3)-Zn(1)-N(3)	106.05(9)
O(1)-Zn(1)-N(3)	105.53(9)
O(3)-Zn(1)-N(1)	104.77(10)
O(1)-Zn(1)-N(1)	108.34(10)
N(3)-Zn(1)-N(1)	99.19(10)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	51(2)	51(2)	59(2)	-7(1)	-10(1)	-16(1)
C(2)	71(2)	75(2)	100(3)	-29(2)	-9(2)	-33(2)
C(3)	103(3)	49(2)	71(2)	-9(2)	-29(2)	-21(2)
C(4)	105(4)	98(3)	83(3)	-18(2)	-9(2)	-20(3)
C(5)	134(5)	135(5)	119(5)	-22(4)	8(4)	-17(4)
C(6)	271(11)	124(6)	85(4)	8(4)	-14(5)	-65(6)
C(7)	307(12)	110(5)	79(4)	7(3)	-53(6)	-3(6)
C(8)	241(8)	104(4)	125(5)	-17(3)	-97(5)	28(5)
C(9)	57(2)	65(2)	59(2)	-8(2)	-5(1)	-8(2)
C(10)	87(3)	92(3)	52(2)	-5(2)	-7(2)	-14(2)
C(11)	102(3)	93(3)	38(2)	-5(2)	-17(2)	-21(2)
C(12)	211(7)	86(4)	85(3)	-6(3)	-22(4)	-8(4)
C(13)	380(20)	110(6)	94(5)	-18(4)	-11(9)	2(10)
C(14)	360(20)	142(9)	79(5)	-14(5)	-13(9)	-91(11)
C(15)	189(8)	320(13)	76(4)	-12(6)	-14(4)	-165(9)
C(16)	119(4)	177(6)	81(3)	-12(3)	-37(3)	-56(4)
C(17)	39(1)	58(2)	80(2)	3(2)	-22(1)	-13(1)
C(18)	68(2)	73(2)	109(3)	22(2)	-34(2)	-20(2)
C(19)	108(4)	111(4)	104(4)	38(3)	-48(3)	-34(3)
C(20)	125(4)	151(5)	60(2)	15(3)	-28(2)	-40(4)
C(21)	89(3)	101(3)	61(2)	-8(2)	-19(2)	-17(2)

C(22)	43(1)	55(2)	48(1)	5(1)	-7(1)	-9(1)
C(23)	42(2)	65(2)	82(2)	9(2)	-9(2)	-4(1)
C(24)	48(2)	79(2)	103(3)	16(2)	-30(2)	-21(2)
C(25)	65(2)	70(2)	101(3)	-2(2)	-33(2)	-23(2)
C(26)	53(2)	62(2)	82(2)	-7(2)	-21(2)	-10(1)
N(1)	51(1)	62(2)	56(1)	-4(1)	-17(1)	-8(1)
N(2)	62(2)	47(2)	89(2)	-10(2)	-14(2)	-9(1)
N(3)	40(1)	52(1)	56(1)	-4(1)	-12(1)	-7(1)
N(4)	45(2)	64(2)	77(2)	-17(1)	-9(1)	1(1)
O(1)	50(1)	62(1)	89(2)	-29(1)	-19(1)	-6(1)
O(2)	51(1)	69(2)	122(2)	-24(1)	-13(1)	-4(1)
O(3)	60(1)	65(1)	50(1)	-11(1)	-9(1)	1(1)
O(4)	99(2)	70(2)	92(2)	-3(1)	-11(2)	13(2)
Zn(1)	41(1)	49(1)	54(1)	-13(1)	-12(1)	-4(1)

Table 4C. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

For complex 3.

	x	y	z	U(eq)
H(2A)	1183	-740	3773	97
H(2B)	94	91	3238	97
H(4)	3406	-1334	2556	119
H(5)	4870	-1852	660	168
H(6)	4260	-1083	-961	197
H(7)	2275	137	-873	209
H(8)	710	560	1070	191
H(10A)	1552	2737	8994	97
H(10B)	358	3581	8603	97
H(12)	244	5680	8601	163
H(13)	1202	7407	8588	258
H(14)	3369	6930	8244	237
H(15)	4737	5060	8028	217
H(16)	3757	3378	8090	144
H(18)	1452	6956	3218	98
H(19)	2324	6380	1231	124
H(20)	3092	4332	661	132
H(21)	3012	2880	2113	102
H(23)	7361	600	3718	80

H(24)	7792	2175	4611	89
H(25)	6070	3844	5519	90
H(26)	3991	3871	5452	78
H(1N2)	870(30)	6248(13)	5220(30)	56(9)
H(2N2)	1240(30)	4990(20)	5530(20)	52(9)
H(1N4)	5700(30)	-199(19)	3250(30)	66(10)
H(2N4)	4373(15)	390(30)	3510(30)	55(9)

Appendix D

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

Table 1A. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex 4 U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5224(2)	-608(1)	1286(2)	37(1)
C(2)	4567(3)	-969(1)	398(2)	45(1)
C(3)	3222(3)	-1079(2)	356(3)	58(1)
C(4)	2588(3)	-840(2)	1143(3)	59(1)
C(5)	3230(3)	-465(2)	2051(2)	47(1)
C(6)	4547(2)	-354(1)	2122(2)	38(1)
C(7)	5272(3)	-1190(2)	-410(3)	55(1)
C(8)	6550(3)	-1048(2)	-304(2)	58(1)
C(9)	7133(3)	-689(2)	607(2)	48(1)
C(10)	2617(3)	-180(2)	2886(3)	62(1)
C(11)	3295(3)	178(2)	3714(3)	65(1)
C(12)	4601(3)	267(2)	3720(2)	53(1)
C(13)	9173(2)	-649(1)	3545(2)	43(1)
C(14)	10214(3)	-1072(2)	4230(3)	57(1)

C(15)	9772(2)	-1628(2)	4966(2)	45(1)
C(16)	9397(3)	-1438(2)	5936(3)	56(1)
C(17)	9005(3)	-1959(2)	6606(3)	71(1)
C(18)	9016(3)	-2676(2)	6329(3)	73(1)
C(19)	9406(3)	-2873(2)	5379(3)	67(1)
C(20)	9775(3)	-2352(2)	4700(3)	55(1)
C(21)	7389(3)	1426(2)	3150(3)	60(1)
C(22)	7449(4)	2245(2)	3112(4)	88(1)
C(23)	6297(3)	2556(1)	2419(2)	48(1)
C(24)	5115(3)	2533(2)	2738(3)	62(1)
C(25)	4064(4)	2807(2)	2083(4)	84(1)
C(26)	4204(5)	3109(2)	1119(4)	90(2)
C(27)	5363(6)	3139(2)	813(3)	86(1)
C(28)	6402(4)	2866(2)	1444(3)	66(1)
N(1)	6496(2)	-474(1)	1386(2)	37(1)
N(2)	5218(2)	7(1)	2953(2)	40(1)
O(1)	8141(2)	-534(1)	3908(2)	53(1)
O(2)	9379(2)	-411(2)	2673(2)	68(1)
O(3)	7545(2)	1084(1)	2306(2)	63(1)
O(4)	7173(2)	1112(1)	3971(2)	71(1)
O(1W)	9947(4)	635(3)	1108(4)	156(2)
Zn(1)	7163(1)	87(1)	2811(1)	38(1)

Table 2A. Bond lengths [Å] and angles [°] for complex 4.

C(1)-N(1)	1.358(3)
C(1)-C(2)	1.402(4)
C(1)-C(6)	1.428(4)
C(2)-C(7)	1.399(5)
C(2)-C(3)	1.433(4)
C(3)-C(4)	1.341(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.426(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.400(4)
C(5)-C(10)	1.407(5)
C(6)-N(2)	1.357(3)
C(7)-C(8)	1.368(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.394(4)
C(8)-H(8)	0.9300
C(9)-N(1)	1.321(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.355(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.391(4)
C(11)-H(11)	0.9300
C(12)-N(2)	1.325(4)
C(12)-H(12)	0.9300
C(13)-O(2)	1.226(3)
C(13)-O(1)	1.257(3)
C(13)-C(14)	1.522(4)
C(14)-C(15)	1.499(4)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.376(4)
C(15)-C(20)	1.381(4)
C(16)-C(17)	1.379(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.373(5)
C(17)-H(17)	0.9300

C(18)-C(19)	1.363(5)
C(18)-H(18)	0.9300
C(19)-C(20)	1.377(5)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-O(4)	1.230(4)
C(21)-O(3)	1.264(4)
C(21)-C(22)	1.519(4)
C(22)-C(23)	1.513(4)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(24)	1.365(4)
C(23)-C(28)	1.370(5)
C(24)-C(25)	1.388(5)
C(24)-H(24)	0.9300
C(25)-C(26)	1.360(6)
C(25)-H(25)	0.9300
C(26)-C(27)	1.335(7)
C(26)-H(26)	0.9300
C(27)-C(28)	1.364(6)
C(27)-H(27)	0.9300
C(28)-H(28)	0.9300
N(1)-Zn(1)	2.106(2)
N(2)-Zn(1)	2.096(2)
O(1)-Zn(1)	1.9768(19)
O(2)-O(1W)	2.878(4)
O(3)-Zn(1)	2.011(2)
O(4)-Zn(1)	2.392(2)

N(1)-C(1)-C(2)	122.8(2)
N(1)-C(1)-C(6)	117.5(2)
C(2)-C(1)-C(6)	119.7(2)
C(7)-C(2)-C(1)	117.3(3)
C(7)-C(2)-C(3)	123.8(3)
C(1)-C(2)-C(3)	118.8(3)
C(4)-C(3)-C(2)	121.2(3)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4

C(3)-C(4)-C(5)	121.1(3)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(6)-C(5)-C(10)	116.8(3)
C(6)-C(5)-C(4)	119.1(3)
C(10)-C(5)-C(4)	124.0(3)
N(2)-C(6)-C(5)	122.5(3)
N(2)-C(6)-C(1)	117.6(2)
C(5)-C(6)-C(1)	119.9(2)
C(8)-C(7)-C(2)	119.4(3)
C(8)-C(7)-H(7)	120.3
C(2)-C(7)-H(7)	120.3
C(7)-C(8)-C(9)	119.7(3)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
N(1)-C(9)-C(8)	122.5(3)
N(1)-C(9)-H(9)	118.8
C(8)-C(9)-H(9)	118.8
C(11)-C(10)-C(5)	120.3(3)
C(11)-C(10)-H(10)	119.8
C(5)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	119.1(3)
C(10)-C(11)-H(11)	120.5
C(12)-C(11)-H(11)	120.4
N(2)-C(12)-C(11)	122.7(3)
N(2)-C(12)-H(12)	118.7
C(11)-C(12)-H(12)	118.7
O(2)-C(13)-O(1)	122.0(2)
O(2)-C(13)-C(14)	119.1(3)
O(1)-C(13)-C(14)	118.8(2)
C(15)-C(14)-C(13)	116.1(2)
C(15)-C(14)-H(14A)	108.3
C(13)-C(14)-H(14A)	108.3
C(15)-C(14)-H(14B)	108.3
C(13)-C(14)-H(14B)	108.3
H(14A)-C(14)-H(14B)	107.4
C(16)-C(15)-C(20)	118.2(3)
C(16)-C(15)-C(14)	121.4(3)

C(20)-C(15)-C(14)	120.4(3)
C(15)-C(16)-C(17)	120.5(3)
C(15)-C(16)-H(16)	119.8
C(17)-C(16)-H(16)	119.8
C(18)-C(17)-C(16)	120.5(3)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(19)-C(18)-C(17)	119.6(3)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(18)-C(19)-C(20)	119.9(3)
C(18)-C(19)-H(19)	120.0
C(20)-C(19)-H(19)	120.0
C(19)-C(20)-C(15)	121.3(3)
C(19)-C(20)-H(20)	119.4
C(15)-C(20)-H(20)	119.4
O(4)-C(21)-O(3)	121.7(3)
O(4)-C(21)-C(22)	120.7(4)
O(3)-C(21)-C(22)	117.5(4)
C(23)-C(22)-C(21)	111.3(3)
C(23)-C(22)-H(22A)	109.4
C(21)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22B)	109.4
C(21)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
C(24)-C(23)-C(28)	117.5(3)
C(24)-C(23)-C(22)	121.3(3)
C(28)-C(23)-C(22)	121.1(3)
C(23)-C(24)-C(25)	120.6(3)
C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7
C(26)-C(25)-C(24)	120.2(4)
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9
C(27)-C(26)-C(25)	119.2(4)
C(27)-C(26)-H(26)	120.4
C(25)-C(26)-H(26)	120.4
C(26)-C(27)-C(28)	121.2(4)

C(26)-C(27)-H(27)	119.4
C(28)-C(27)-H(27)	119.4
C(27)-C(28)-C(23)	121.2(4)
C(27)-C(28)-H(28)	119.4
C(23)-C(28)-H(28)	119.4
C(9)-N(1)-C(1)	118.3(2)
C(9)-N(1)-Zn(1)	129.07(19)
C(1)-N(1)-Zn(1)	112.58(16)
C(12)-N(2)-C(6)	118.6(2)
C(12)-N(2)-Zn(1)	128.5(2)
C(6)-N(2)-Zn(1)	112.90(17)
C(13)-O(1)-Zn(1)	104.18(17)
C(13)-O(2)-O(1W)	158.3(3)
C(21)-O(3)-Zn(1)	98.1(2)
C(21)-O(4)-Zn(1)	81.41(19)
O(1)-Zn(1)-O(3)	130.14(9)
O(1)-Zn(1)-N(2)	109.19(8)
O(3)-Zn(1)-N(2)	109.43(9)
O(1)-Zn(1)-N(1)	112.97(9)
O(3)-Zn(1)-N(1)	104.10(8)
N(2)-Zn(1)-N(1)	79.40(8)
O(1)-Zn(1)-O(4)	94.45(9)
O(3)-Zn(1)-O(4)	58.56(10)
N(2)-Zn(1)-O(4)	85.87(8)
N(1)-Zn(1)-O(4)	151.85(8)

Symmetry transformations used to generate equivalent atoms:

Table 4A. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex 4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42(1)	29(1)	37(1)	7(1)	-3(1)	1(1)
C(2)	56(2)	34(1)	41(1)	6(1)	-10(1)	-4(1)
C(3)	59(2)	50(2)	57(2)	10(1)	-19(2)	-17(1)
C(4)	42(2)	64(2)	65(2)	21(2)	-12(1)	-17(1)
C(5)	37(1)	52(2)	50(2)	20(1)	0(1)	-5(1)
C(6)	36(1)	38(1)	39(1)	10(1)	-1(1)	0(1)
C(7)	77(2)	39(2)	44(2)	-4(1)	-10(2)	1(1)
C(8)	77(2)	52(2)	44(2)	-7(1)	8(2)	15(2)
C(9)	48(2)	45(2)	52(2)	-2(1)	6(1)	10(1)
C(10)	39(2)	83(2)	67(2)	26(2)	11(1)	2(2)
C(11)	49(2)	89(2)	58(2)	8(2)	17(2)	11(2)
C(12)	51(2)	64(2)	43(2)	-1(1)	9(1)	7(1)
C(13)	35(1)	38(1)	53(2)	5(1)	-5(1)	-3(1)
C(14)	32(1)	66(2)	72(2)	28(2)	3(1)	7(1)
C(15)	26(1)	53(2)	52(2)	13(1)	-3(1)	3(1)
C(16)	52(2)	51(2)	65(2)	5(2)	5(1)	6(1)
C(17)	71(2)	86(3)	57(2)	9(2)	16(2)	4(2)
C(18)	68(2)	66(2)	85(3)	25(2)	15(2)	-9(2)
C(19)	57(2)	48(2)	92(3)	2(2)	2(2)	-10(2)
C(20)	45(2)	62(2)	56(2)	-4(2)	1(1)	-1(1)
C(21)	50(2)	44(2)	75(2)	-10(2)	-30(2)	6(1)
C(22)	84(3)	40(2)	122(3)	-17(2)	-50(2)	5(2)
C(23)	55(2)	31(1)	56(2)	-9(1)	-4(1)	-1(1)
C(24)	82(2)	58(2)	48(2)	-3(1)	16(2)	3(2)
C(25)	55(2)	82(3)	118(4)	-27(3)	20(2)	14(2)
C(26)	110(4)	59(2)	88(3)	-10(2)	-37(3)	32(2)
C(27)	152(5)	53(2)	51(2)	9(2)	4(2)	5(3)
C(28)	79(2)	46(2)	76(2)	-8(2)	28(2)	-11(2)
N(1)	39(1)	33(1)	39(1)	-1(1)	2(1)	4(1)
N(2)	37(1)	43(1)	39(1)	1(1)	2(1)	4(1)
O(1)	40(1)	67(1)	52(1)	10(1)	1(1)	17(1)
O(2)	51(1)	89(2)	62(1)	32(1)	1(1)	-3(1)
O(3)	82(2)	43(1)	60(1)	-5(1)	-11(1)	-6(1)

O(4)	63(1)	74(2)	70(2)	-12(1)	-9(1)	1(1)
O(1W)	122(3)	184(4)	152(4)	98(3)	-21(3)	-45(3)
Zn(1)	35(1)	37(1)	40(1)	0(1)	-3(1)	3(1)

Table 5A. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex 4.

	x	y	z	U(eq)
H(3)	2779	-1320	-229	69
H(4)	1715	-919	1096	71
H(7)	4876	-1432	-1013	66
H(8)	7028	-1190	-837	69
H(9)	8003	-596	669	58
H(10)	1742	-238	2869	75
H(11)	2894	362	4271	77
H(12)	5059	519	4285	63
H(14A)	10731	-1312	3754	69
H(14B)	10760	-732	4662	69
H(16)	9408	-955	6141	67
H(17)	8731	-1823	7251	85
H(18)	8759	-3026	6787	87
H(19)	9423	-3358	5189	80
H(20)	10031	-2491	4050	66
H(22A)	7491	2437	3835	106
H(22B)	8216	2392	2825	106
H(24)	5012	2332	3400	75
H(25)	3262	2784	2305	101
H(26)	3502	3292	678	108
H(27)	5464	3349	157	103
H(28)	7197	2892	1208	79

Appendix E

6.5 Crystal structure data of [Zn(phenyl)2 (2,9-dmp)] (5)

Table 1E .Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) For complex 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1W)	0	2531(8)	-2500	305(6)
C(1)	76(2)	2711(9)	1221(3)	134(3)
C(2)	-389(2)	2623(10)	1366(3)	165(4)
C(3)	-622(3)	3674(10)	1430(5)	172(4)
C(4)	-413(4)	4597(11)	1393(5)	208(5)
C(5)	48(3)	4709(11)	1206(4)	165(4)
C(6)	288(2)	3735(9)	1135(3)	137(3)
C(7)	-583(3)	1679(14)	1427(5)	223(8)
C(8)	-333(3)	792(9)	1328(4)	180(4)
C(9)	157(2)	861(9)	1207(3)	132(2)
C(10)	299(5)	5589(9)	1100(5)	177(3)
C(11)	733(4)	5580(9)	932(4)	170(3)
C(12)	946(3)	4615(8)	853(4)	136(2)
C(13)	436(2)	-82(6)	1145(4)	153(2)
C(14)	1432(2)	4568(5)	639(4)	160(2)
C(15)	1010(2)	1982(4)	-841(3)	112(2)
C(16)	1249(2)	1979(4)	-1685(3)	111(2)
C(17)	1613(2)	2833(5)	-1625(3)	94(1)
C(18)	1489(2)	3814(6)	-1952(3)	109(2)
C(19)	1809(3)	4611(6)	-1882(4)	135(2)
C(20)	2254(3)	4446(7)	-1475(4)	141(2)
C(21)	2395(2)	3463(8)	-1159(4)	146(2)
C(22)	2072(2)	2649(5)	-1236(4)	131(2)
C(23)	1642(2)	1704(12)	2410(4)	169(4)
C(24)	2055(2)	1534(8)	3203(3)	225(4)
C(25)	1915(1)	1645(7)	4110(3)	91(1)
C(26)	1923(2)	2559(6)	4581(8)	148(3)
C(27)	1807(4)	2631(12)	5539(14)	258(10)
C(28)	1689(4)	1753(15)	5720(8)	237(11)

C(29)	1658(3)	809(11)	5382(9)	215(6)
C(30)	1783(2)	793(7)	4522(7)	146(2)
N(1)	335(2)	1810(6)	1158(2)	111(2)
N(2)	731(2)	3700(5)	968(2)	115(1)
O(1)	1262(1)	1889(3)	-65(2)	120(1)
O(2)	591(2)	2096(4)	-924(2)	183(2)
O(3)	1416(2)	1002(5)	2045(3)	193(3)
O(4)	1538(2)	2595(5)	2145(4)	189(3)
Zn(1)	1012(1)	2183(1)	1028(1)	111(1)

Table 2E. Bond lengths [Å] and angles [°] for complex 5.

O(1W)-O(2)	2.674(4)
C(1)-N(1)	1.376(8)
C(1)-C(2)	1.406(8)
C(1)-C(6)	1.446(9)
C(2)-C(7)	1.326(14)
C(2)-C(3)	1.499(12)
C(3)-C(4)	1.318(12)
C(4)-C(5)	1.420(12)
C(5)-C(10)	1.352(12)
C(5)-C(6)	1.425(10)
C(6)-N(2)	1.352(7)
C(7)-C(8)	1.356(16)
C(8)-C(9)	1.466(9)
C(9)-N(1)	1.312(8)
C(9)-C(13)	1.452(8)
C(10)-C(11)	1.326(10)
C(11)-C(12)	1.381(10)
C(12)-N(2)	1.338(8)
C(12)-C(14)	1.499(9)
C(15)-O(2)	1.211(5)
C(15)-O(1)	1.242(5)
C(15)-C(16)	1.523(6)

C(16)-C(17)	1.500(6)
C(17)-C(18)	1.351(6)
C(17)-C(22)	1.372(7)
C(18)-C(19)	1.361(7)
C(19)-C(20)	1.337(7)
C(20)-C(21)	1.361(8)
C(21)-C(22)	1.380(8)
C(23)-O(3)	1.173(12)
C(23)-O(4)	1.211(12)
C(23)-C(24)	1.526(7)
C(24)-C(25)	1.468(6)
C(25)-C(30)	1.323(8)
C(25)-C(26)	1.341(8)
C(26)-C(27)	1.506(17)
C(27)-C(28)	1.20(2)
C(28)-C(29)	1.288(14)
C(29)-C(30)	1.373(11)
N(1)-Zn(1)	2.062(4)
N(2)-Zn(1)	2.077(5)
O(1)-Zn(1)	1.911(3)
O(3)-Zn(1)	2.278(6)
O(4)-Zn(1)	2.092(5)

N(1)-C(1)-C(2)	119.8(9)
N(1)-C(1)-C(6)	119.0(6)
C(2)-C(1)-C(6)	121.2(9)
C(7)-C(2)-C(1)	120.7(10)
C(7)-C(2)-C(3)	126.0(8)
C(1)-C(2)-C(3)	113.3(10)
C(4)-C(3)-C(2)	124.3(10)
C(3)-C(4)-C(5)	123.5(12)
C(10)-C(5)-C(4)	130.5(13)
C(10)-C(5)-C(6)	114.8(9)
C(4)-C(5)-C(6)	114.7(10)
N(2)-C(6)-C(5)	122.3(9)
N(2)-C(6)-C(1)	114.8(8)
C(5)-C(6)-C(1)	122.9(8)
C(2)-C(7)-C(8)	119.5(9)

C(7)-C(8)-C(9)	120.9(11)
N(1)-C(9)-C(13)	121.0(7)
N(1)-C(9)-C(8)	117.5(8)
C(13)-C(9)-C(8)	121.6(9)
C(11)-C(10)-C(5)	124.4(11)
C(10)-C(11)-C(12)	118.6(10)
N(2)-C(12)-C(11)	121.5(8)
N(2)-C(12)-C(14)	118.1(8)
C(11)-C(12)-C(14)	120.4(9)
O(2)-C(15)-O(1)	121.2(4)
O(2)-C(15)-C(16)	121.0(5)
O(1)-C(15)-C(16)	117.7(4)
C(17)-C(16)-C(15)	111.6(4)
C(18)-C(17)-C(22)	118.6(5)
C(18)-C(17)-C(16)	119.8(5)
C(22)-C(17)-C(16)	121.5(6)
C(17)-C(18)-C(19)	121.0(6)
C(20)-C(19)-C(18)	120.6(7)
C(19)-C(20)-C(21)	120.0(7)
C(20)-C(21)-C(22)	119.5(6)
C(17)-C(22)-C(21)	120.1(6)
O(3)-C(23)-O(4)	117.8(7)
O(3)-C(23)-C(24)	122.7(12)
O(4)-C(23)-C(24)	119.5(11)
C(25)-C(24)-C(23)	111.6(4)
C(30)-C(25)-C(26)	116.3(6)
C(30)-C(25)-C(24)	119.1(9)
C(26)-C(25)-C(24)	124.5(9)
C(25)-C(26)-C(27)	123.1(9)
C(28)-C(27)-C(26)	105.7(13)
C(27)-C(28)-C(29)	140.3(18)
C(28)-C(29)-C(30)	110.8(11)
C(25)-C(30)-C(29)	123.6(8)
C(9)-N(1)-C(1)	121.6(7)
C(9)-N(1)-Zn(1)	127.2(6)
C(1)-N(1)-Zn(1)	111.1(4)
C(12)-N(2)-C(6)	118.5(7)
C(12)-N(2)-Zn(1)	127.6(5)

C(6)-N(2)-Zn(1)	113.7(6)
C(15)-O(1)-Zn(1)	120.0(3)
C(15)-O(2)-O(1W)	126.0(3)
C(23)-O(3)-Zn(1)	89.1(7)
C(23)-O(4)-Zn(1)	97.2(6)
O(1)-Zn(1)-N(1)	123.10(15)
O(1)-Zn(1)-N(2)	110.45(16)
N(1)-Zn(1)-N(2)	80.8(3)
O(1)-Zn(1)-O(4)	111.81(19)
N(1)-Zn(1)-O(4)	123.75(19)
N(2)-Zn(1)-O(4)	91.7(2)
O(1)-Zn(1)-O(3)	101.20(16)
N(1)-Zn(1)-O(3)	100.1(2)
N(2)-Zn(1)-O(3)	141.49(17)
O(4)-Zn(1)-O(3)	55.5(2)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1W)	321(13)	297(10)	247(11)	0	-83(10)	0
C(1)	73(3)	278(9)	48(2)	-16(4)	2(2)	9(5)
C(2)	73(3)	363(12)	58(3)	-10(5)	7(2)	24(6)
C(3)	84(4)	345(15)	81(4)	-34(7)	1(3)	38(7)
C(4)	175(11)	359(17)	74(4)	-42(7)	-17(5)	79(9)
C(5)	105(6)	313(13)	71(3)	-23(6)	2(3)	62(7)
C(6)	91(4)	260(10)	52(3)	-12(4)	-6(2)	8(6)
C(7)	96(6)	510(20)	66(4)	-10(7)	18(4)	-95(10)
C(8)	108(6)	357(15)	76(4)	-3(5)	20(4)	-88(6)
C(9)	108(5)	227(9)	58(3)	5(4)	1(3)	-30(5)
C(10)	182(9)	249(11)	86(4)	-27(6)	-8(5)	25(8)
C(11)	187(8)	222(11)	88(4)	-24(5)	-13(5)	-13(8)
C(12)	170(7)	155(7)	72(3)	-16(4)	-7(4)	0(6)
C(13)	162(6)	204(7)	91(4)	14(4)	18(4)	-54(5)
C(14)	148(5)	205(7)	132(5)	-19(4)	36(4)	-46(5)
C(15)	89(3)	174(5)	73(3)	-1(3)	14(3)	-24(3)
C(16)	118(4)	145(5)	74(3)	-7(3)	26(2)	-5(3)
C(17)	97(3)	133(4)	56(2)	7(3)	25(2)	7(4)
C(18)	106(4)	147(5)	77(3)	4(4)	24(3)	12(4)
C(19)	165(6)	155(6)	89(4)	9(4)	31(4)	8(6)
C(20)	141(6)	182(8)	108(4)	2(5)	43(4)	-33(5)
C(21)	82(4)	232(8)	123(5)	22(5)	15(3)	-3(5)
C(22)	107(4)	173(6)	117(4)	33(4)	34(3)	33(4)
C(23)	76(4)	364(15)	64(4)	-10(6)	10(3)	42(6)
C(24)	97(4)	507(14)	65(3)	2(5)	-2(3)	77(6)
C(25)	66(2)	123(5)	77(3)	2(4)	-3(2)	9(3)
C(26)	100(4)	115(6)	205(8)	-12(6)	-37(5)	19(3)
C(27)	112(7)	316(18)	310(17)	-193(15)	-64(8)	77(9)
C(28)	121(8)	450(30)	130(7)	-138(14)	-8(5)	47(14)
C(29)	121(5)	304(16)	203(10)	147(11)	-17(7)	-22(8)
C(30)	118(5)	135(6)	168(7)	3(5)	-23(4)	6(4)
N(1)	89(3)	187(5)	56(2)	5(3)	8(2)	-26(3)
N(2)	99(3)	176(5)	64(2)	-6(3)	-5(2)	5(3)
O(1)	92(2)	197(4)	71(2)	5(2)	18(2)	-2(2)

O(2)	101(3)	359(7)	86(2)	-5(3)	7(2)	-19(3)
O(3)	122(3)	341(8)	108(3)	-18(4)	-3(3)	7(4)
O(4)	122(4)	295(7)	132(4)	-19(4)	-29(3)	16(4)
Zn(1)	71(1)	196(1)	64(1)	1(1)	8(1)	-12(1)

Table 4E. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) For complex 5 .

	x	y	z	U(eq)
H(3)	-934	3675	1500	206
H(4)	-576	5207	1495	249
H(7)	-888	1627	1536	267
H(8)	-474	131	1338	216
H(10)	158	6244	1148	212
H(11)	890	6211	868	204
H(13A)	535	-97	554	229
H(13B)	252	-701	1209	229
H(13C)	707	-72	1630	229
H(14A)	1613	5151	933	240
H(14B)	1416	4610	-20	240
H(14C)	1578	3913	865	240
H(16A)	1396	1295	-1732	133
H(16B)	1015	2082	-2240	133
H(18)	1180	3945	-2228	131
H(19)	1717	5277	-2120	162
H(20)	2467	5004	-1408	170
H(21)	2706	3340	-894	176
H(22)	2166	1975	-1023	157
H(24A)	2184	831	3153	270
H(24B)	2298	2047	3153	270
H(26)	2004	3177	4303	178
H(27)	1823	3229	5914	310
H(28)	1587	1758	6285	284

H(29)	1564	217	5679	258
H(30)	1775	147	4213	176