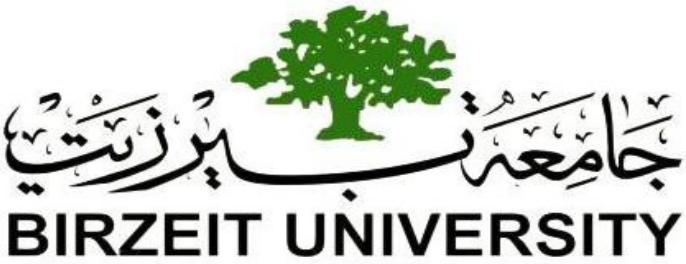

Faculty of Graduate Studies

Master Program in Applied Chemistry

Synthesis, Characterization, and Biological Activity of Novel Mixed Ligand Complexes of Zinc(II) Diclofenac or Indomethacin with Nitrogen Based Ligands

تحضير وتشخيص ودراسة الفعالية الحيوية لمركبات تحتوي أيون الزنك الثنائي والدكلوفيناك أو الاندوميثاسين وقواعد نيتروجينية

This Thesis was Submitted in Partial Fulfillment of the Requirements for the Degree of Master in Applied Chemistry, at Faculty of Graduate Studies, at Birzeit University, Ramallah, Palestine.

By

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Under supervision of

Dr. Hijazi Abu Ali

June, 2014

Synthesis, Characterization, and Biological Activity of Novel Mixed Ligand Complexes of Zinc(II) Diclofenac and Indomethacin with Nitrogen Based Ligands

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Baha'a, H. Jabali

DEDICATION

To my parents with love and gratitude

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ABBREVATIONS

Diclo	Diclofenac
Indo	Indomethacin
apy	2-amino pyridine
amp	2-aminomethyl pyridine
pico	3-picoline
phen	1,10-phenanthroline
dmph	2,9-dimethyl-1,10-phenanthroline
admp	2-aminodimethyl pyrimidine
DMSO	dimethyl sulfoxide
DMF	dimethyl formamind
h	hour
m.p.	melting point
^{1}H-NMR	proton nuclear magnetic resonance
^{13}C{H}-NMR	proton decoupled carbon nuclear magnetic resonance
UV-Vis	Ultraviolet-Visible
IR	Infra Red
s	singlet
d	doublet
m	multiplet
ppt	precipitate

ABSTRACT

Fourteen novel Zn(II) complexes, $[Zn_2(diclo)_2(H_2O)_2]$ **(1)**, $[Zn_2(Indo)_4]$ **(2)**, $[Zn(diclo)_4(pico)_2]$ **(3)**, $[Zn_2(indo)_4(pico)_2]$ **(4)**, $[Zn(diclo)_2(apy)_2]$ **(5)**, $[Zn(indo)_2(apy)_2]$ **(6)**, $[Zn(diclo)_2(ampy)]$ **(7)**, $[Zn(indo)_2(ampy)]$ **(8)**, $[Zn(diclo)_2(phen)]$ **(9)** $[Zn(diclo)_2(phen)]$ **(9)**, $[Zn(indo)_2(phen)]$ **(10)**, $[Zn(diclo)_2(dmph)]$ **(11)**, $[Zn(indo)_2(dmph)]$ **(12)**, $[Zn(diclo)_2(admp)_2]$ **(13)**, $[Zn(indo)_2(admp)_2]$ **(14),** were synthesized and characterized by means of IR, ^{1}H-NMR, ^{13}C{H}-NMR and UV-Vis spectrometry. The crystal structures of complexes **(1)**, **(4)**, **(5)**, **(11)** were determined by single crystal X-ray diffraction. Melting point and solubility of the synthesized complexes were determined.

The *in-vitro* anti-bacterial activity of the synthesized complexes was screened using agar diffusion assay against two strains of Gram-negative bacteria (*Escherichia coli, Pseudomonas aeruginosa*), and two strains of Gram-positive bacteria (*Staphylococcus aureus, Listeria monocytogenes*), the results showed higher activity against *Pseudomonas aeruginosa* and *Staphylococcus aureus*, in comparison with diclofenac, indomethacin and free nitogen ligands.

ملخص

يعرض هذا البحث تحضير أربعة عشر مركبا جديدا من مركبات الزنك الثنائي الشحنة وهي:

$[Zn_2(diclo)_2(H_2O)_2]$ **(1)**, $[Zn_2(Indo)_4]$ **(2)**, $[Zn(diclo)_4(pico)_2]$ **(3)**, $[Zn_2(indo)_4(pico)_2]$ **(4)**, $[Zn(diclo)_2(apy)_2]$ **(5)**, $[Zn(indo)_2(apy)_2]$ **(6)**, $[Zn(diclo)_2(ampy)]$ **(7)**, $[Zn(indo)_2(ampy)]$ **(8)**, $[Zn(diclo)_2(phen)]$ **(9)** $[Zn(diclo)_2(phen)]$ **(9)**, $[Zn(indo)_2(phen)]$ **(10)**, $[Zn(diclo)_2(dmph)]$ **(11)**, $[Zn(indo)_2(dmph)]$ **(12)**, $[Zn(diclo)_2(admp)_2]$ **(13)**, $[Zn(indo)_2(admp)_2]$ **(14)**,

حيث تمت دراسة هذه المركبات وتشخيصها بواسطة مطياف الأشعة تحت الحمراء (IR) وجهاز الرنين النووي المغناطيسي(الهيدروجيني 1 والكربوني 13)، بالإضافة إلى مطياف الأشعة فوق االبنفسجية والمرئية (UV-Vis)، إضافة إلى ذلك تم تحديد البنية البلورية للمركبات **(1)**، **(4)**، **(5)**، **(11)** عن طريق جهاز دراسة العينات وحيدة البلورة باستخدام الأشعة السينية.

تمت دراسة التأثير البيولوجي للمركبات بواسطة طريقة الانتشار في الآجار على نوعين من البكتيريا سالبة صبغة غرام وهي بسيدومونس اريجينوزا و اشريشيا كولاي، بالضافة إلى نوعين من البكتيرا موجبة صبغة غرام وهي ستافيلوكوكس اوريس ولستيريا مونوسيتوجنيس، حيث وجد أن هذه المركبات فعالة ضد نوعين من البكتيريا، وهي بسيدومونس اريجينوزا وستافيلوكوكس اوريس. وأظهرت النتائج زيادة في فعالية هذه المركبات بالمقارنة مع الدكلوفيناك والاندوميثاسين والقواعد النيتروجينية الحرة.

1. Introduction

1.1 Metal ions in biological systems

The importance of metal ions in biology, environment and medicine has become increasingly evident over the last 25 years[1]. As analytical methods and techniques for determining molecular structure have become more sophisticated, so the awareness that a small detail in a structure may have a major role in its function. It had become increasingly apparent that such a small detail might be a metal ion[2].

Metal ions in biological systems function in a number of different ways. Some metal ions have structural role (zinc(II) in zinc fingers) or catalytic (zinc(II) in carbonic anhydrase), some others operate as electron carriers (iron ions in cytochromes), facilitators of oxygen transport (iron ions in hemoglobin), triggers protein activity (calcium ions)[1,3]. Metal ions may serve multiple functions, depending on their location within the biological system, so their classification are somewhat arbitrary and/or overlapping.

Chemical elements essential to life aspects can be classified into four major categories[3]:

(1) Bulk elements (H, C, N, O, P, S)

(2) Macrominerals and ions (Na, K, Mg, Ca, Cl, PO_4^{-3}, SO_4^{-2})

(3) Trace elements (Fe, Zn, Cu)

(4) Ultratrace elements, comprised of nonmetals (F, I, Se, Si, As, B) and metals (Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li).

1.2 Biological systems and zinc

Zinc (II) is one of the most abundant essential elements in the human body. It is found in all body tissues[4], an average adult has about 3 g of Zn(II)[5]. It is essential in fundamental biological processes, required for the growth and differentiation of all types of life[6], it can play a catalytic, cocatalytic, or structural role[5,7]. It is an essential cofactor in many metabolic enzymes and regulatory proteins[8,9].

Many enzymes have been identified that are known to require zinc(II) for their function[10]. It has representatives in each of the International Union of Biochemists (IUB) classes of enzymes: oxidoreductases, hydrolases, lyases, isomerases, ligases[11]. Indeed zinc is the only metal encountered in each class, too many basis behind this extensive participation of zinc in fundamental biological processes, as it is nontoxic[12], its physical and chemical properties including stable association with macromolecules, and its coordination flexibility, makes it highly adaptable to meet the needs for proteins and enzymes that carry out diverse biological functions[10].

Because zinc(II) required by numerous proteins and enzymes, zinc homeostasis is highly regulated in all cells and organisms to optimize availability. Excess zinc is toxic, but unlike some other metals, its toxicity is not directly attributable to redox activity. But, it appears that excess zinc may compete for the protein binding sites of other metals and thereby interfere with the normal functions of these metalloproteins[13,14].

1.3 Bioinorganic chemistry of zinc(II)

The inherent chemical potential of zinc(II) is not exceptional compared with those of other metal ions[15]. Unlike other first row transition metal ions, (Zn(II) is stable under physiological conditions with filled *d* orbital (d^{10}), so it does not participate in redox reactions, but rather function as Lewis acid to accept a pair of electrons[16].

Under biological conditions, the stability of Zn(II) and lack of redox activity, makes zinc ion an ideal metal cofactor for reactions that require a redox-stable ion to function as Lewis acid catalyst[17], such as proteolysis and hydration of carbon dioxide[15]. Due to the filled *d* shell, Zn(II) has zero value of ligand-field stabilization energy in all geometries and hence no geometry is inherently more stable than others[18]. Hence, making it easy to change between accessible geometries lacking the energetic barrier; altering the reactivity of zinc metalloenzyme. The most often observed binding geometry in all studied zinc metalloprotreins are a slightly distorted tetrahedral[15], which enhances both the Lewis acidity of the zinc center and the acidity of the coordinated water molecules[5]. Another important properties of Zn(II) that makes it well suited as catalytic cofactor is that ligand exchange is rapid (labile) allowing for the rapid product dissociation required for efficient turnover[15].

Zinc is classified as borderline metal in term of hard and soft acids and basis, meaning that Zn(II) does not consistently act either as hard (not very polarizable) or soft (highly polarizable), and does not have strong preference for coordinating with

either oxygen, nitrogen or sulfur atoms[19]. This features of zinc chemistry is doubtless important in the catalytically active and structural sites of zinc enzymes in which complexation with O-, N-, and S-containing groups from amino acid side chains readily occurs[20].

To introduce functions mediated by metal ions it is therefore necessary to identify the principal liganding residues for the chosen metal, the required architecture of the metal-ligand complex and sites within the target protein that could accommodate such sites. In protein zinc-binding sites, the zinc ion is coordinated by different combinations of protein side chains, including nitrogen of histidine, oxygen of aspartate or glutamate and sulfur of cysteine[21] (Figure 1.1).

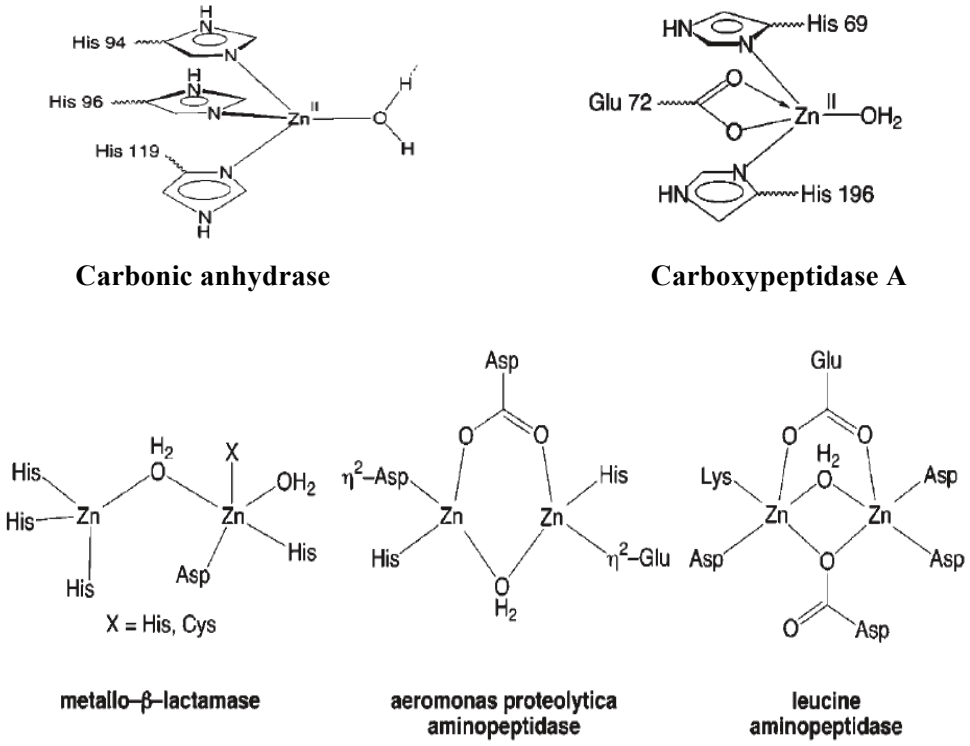


Figure 1.1: Different active sites of zinc enzymes[5].

In catalytic sites, zinc generally forms complexes with water and any three nitrogen, oxygen and sulfur donors with His being the predominant amino acid chosen. Water is always a ligand to such sites (Figure 1.2).

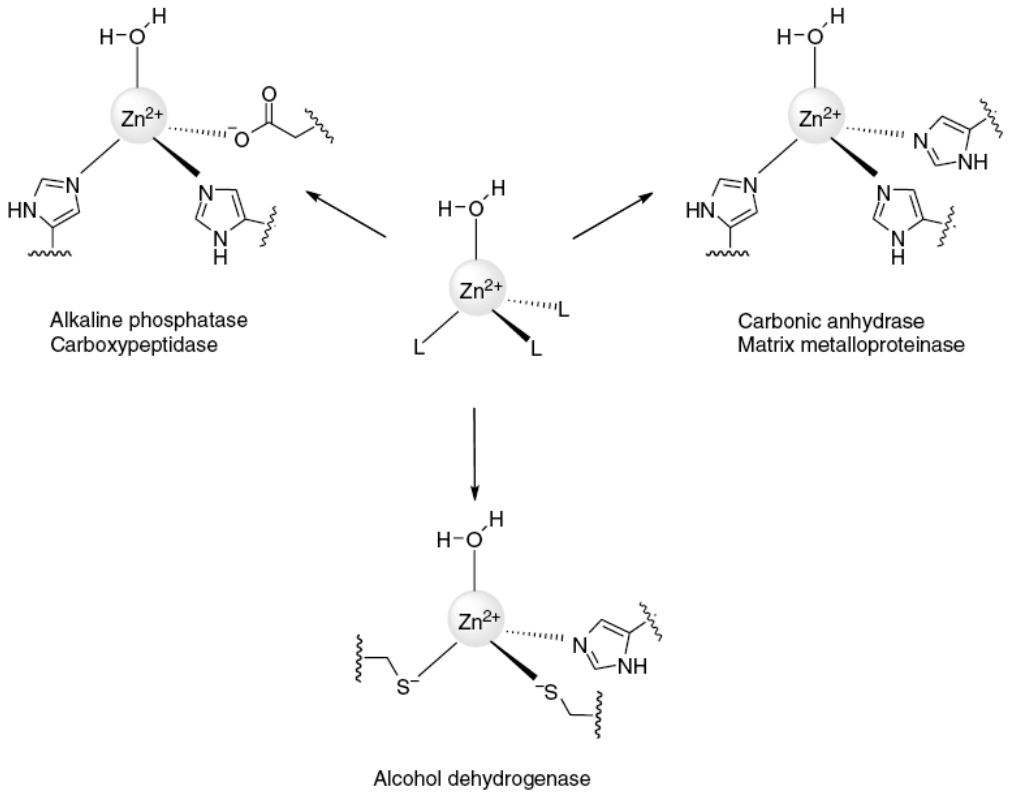


Figure 1.2: Catalytic binding sites of some representative metalloenzymes [14].

Structural zinc sites have four protein ligands and no bound water molecule. Cys is the preferred ligand in such sites (Figure 1.3).

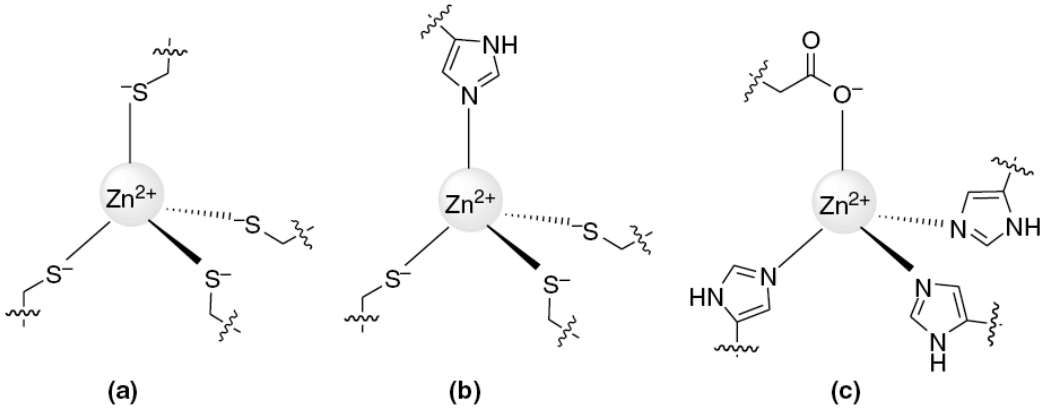


Figure 1.3: Structural zinc binding sites in metalloenzymes: (a) four Cys residues coordinated to the metal center; (b) 3 Cys + 1 His; (c) 3 His + 1 Asp/Glu residue coordinated to Zn(II)[14].

Co-catalytic sites contain two or three metals in close proximity with two of the metals bridged by a side chain moiety of a single amino acid residue, such as Asp, Glu or His and sometimes a water molecule. Asp and His are the preferred amino acids for these sites. No Cys ligands are found in such sites. The zinc ion can be bridged with another zinc ion or with another metal ion, such as Cu(II). For example, in Cu–Zn superoxide dismutases (SOD)[8,22,23].

It is known that the metal coordination number is a key determinant of the structure and properties of metal complexes, and plays an important role in metal selectivity in certain metalloproteins[24].

1.4 Zinc compounds and biological activity

Recently, the medicinal application of metal complexes has been a subject of great interest[25]. Zinc-containing enzymes are considered an attractive target for drug therapy, and their inhibitors are included in the armamentarium of modern medicine against human diseases such as cardiovascular, neurological, infectious and metabolic diseases as well as cancer[26].

Apart from the huge success of platinum based drugs, some other metal compounds such as titanium and ruthenium complexes have shown some potential for chemotherapy. The toxicity of metallo-drugs is problematic; therefore, it is proposed that drugs based on essential metals may be less toxic[27].

Zinc ions possess some anti-bacterial effects, and one research direction for inorganic anti-bacterial agents is to enhance the anti-bacterial ability of Zn(II) through adding the additives[28], like N-based ligands, carboxylate containing compounds as diclofenac or indomethacin.

Of the 20 amino acids present in proteins and enzymes, only a relatively small number are potential metal ligands. The ligand groups, which are encountered most often, are the thiolate of Cys, the imidazole of His, the carboxylates of Glu and Asp, and the phenolate of Tyr. Metal ions can also bind to peptide bonds, through the carbonyl or the deprotonated amide nitrogen, and to the terminal amino and carboxyl groups of the protein[29]. N-, O- and S-donor groups, are of great interest for synthesis of biologically active complexes, or models of metalloenzymes and proteins.

Zinc carboxylates are of great interest owing to their role in biochemical systems, catalysis, and material chemistry[30]. This can be accredited to the versatility of the $RCOO^-$ moiety and the wide range of coordination modes that it can adopt. Carboxylate ligand can coordinate to metal cation in a variety of ways including ionic bond, monodentate coordination, and bidentate coordination that also occur in two forms, chelating and bridging. Bidentate chelating or bridging groups can occur in many different ways with respect to syn- and anti- mode of coordination, with the stronger syn- binding mode than anti- as the syn- pair of electrons on oxygen of caroxylate group are more basic than the anti- one[31-35]. Figure 1.4 shows the various modes of interaction that can be differentiated based on their IR spectra upon complexation.

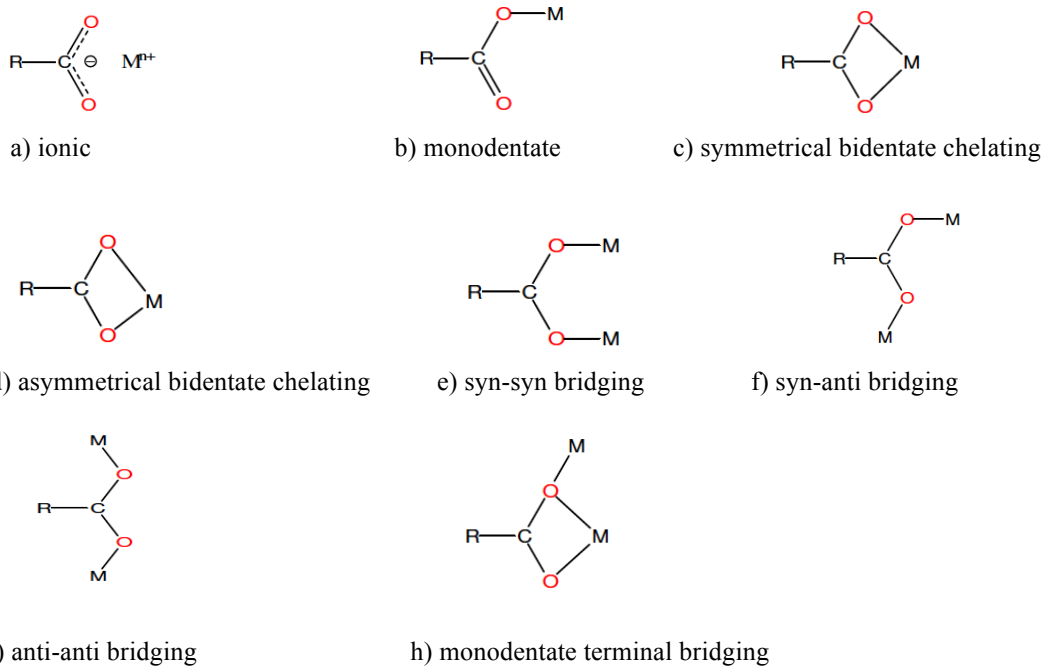


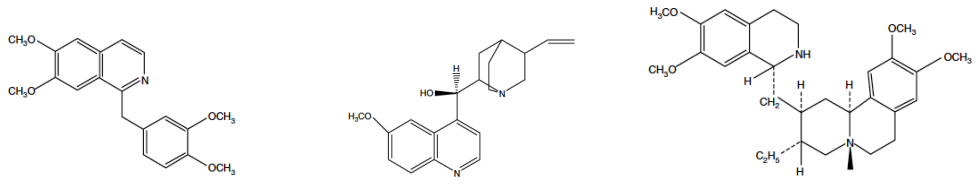
Figure 1.4: Coordination modes of carboxylate groups[36].

The position of the strong C=O absorption band in the carboxylic acid group of the free carboxylic acid occurs at *ca.* 1760-1680 cm^{-1}. Upon complexation to a metal center, this ν(C=O) band is red-shifted and splits to two new bands, asymmetric ($\nu(COO^-)_{asym}$) and symmetric ($\nu(COO^-)_{sym}$) stretches appear in the regions 1650-1550 and 1440-1335 cm^{-1}, respectively[36,37].

The magnitude of the separation between asymmetric and symmetric bands $\Delta\nu(COO^-)$ cm^{-1} has been used as spectroscopic criterion in determination of the carboxylate coordination mode, generally the following order is proposed for divalent metal carboxylates[36]:

$\Delta\nu$ (COO^-)monodentate > $\Delta\nu(COO^-)$ionic > $\Delta\nu(COO^-)$ bridging > $\Delta\nu(COO^-)$ chelating

Nitrogen-containing compounds are used as structural components of pharmaceuticals and agrochemicals due to their high biological activities. These nitrogen containing compounds especially with heterocyclic ring play an important role in biological systems and found in vitamins, enzymes, metalloproteins and nucleic acids[38]. Another reason for this vital interest arises from natural occurrence; as many natural drugs like papaverine, quinine, emetine (Figure 1.5), theobromine and theophylline are nitrogen heterocyclic compounds[39].



a) papavirine b) quinine c) emetine

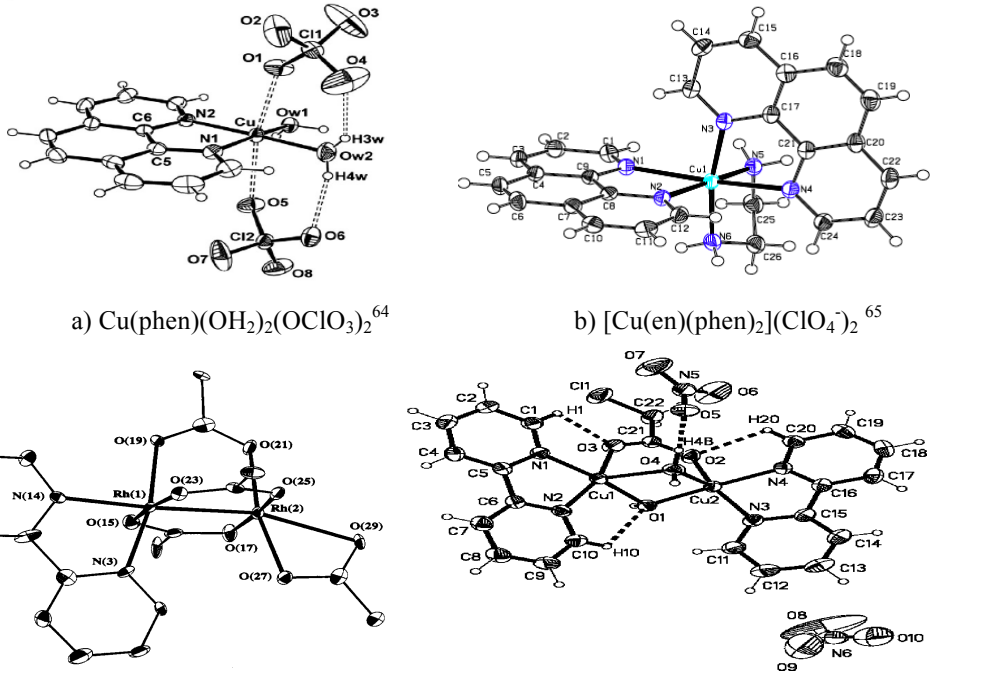
Figure 1.5: Natural nitrogen containing heterocyclic compounds[40].

Among the nitrogen containing compounds, pyridine derivatives play significant role in many biological systems as the component of several vitamins, nucleic acids, enzymes and proteins[41,42], also its bases are used in various applications as herbicides, insecticides, pharmaceuticals, as it have several biological activities like anti-microbial, anti-bacterial, anti-tumor effects, and anti-malarial activity[42-44], Anti-chagasic, anti-diabetic, anti-oxidant, anti-dote also have been reported[45].

Another important nitrogen containing compounds are pyrazine, piperidine, pyrrole, pyrrolidine, indole, and imidazole derivatives are highly valuable intermediates for the production of pharmaceuticals and agrochemicals. For example, 2-methylpyrazine is used as raw material of anti-tuberculosis drug, and pyrole is biologically important as it is found in heme, chlorophyll and many alkaloidal compounds[46].

1,10-Phenanthroline, 2,2′-bipyridine and their substituted derivatives, both in the metal-free state and as ligands coordinated to transition metals, disturb the functioning of a wide variety of biological systems[27]. When the metal-free N, N-chelating bases are found to be bioactive as it exhibit anti-bacterial[47-49], anti-fungal[50], anti-microbial[51-54], anti-viral[55,56] and anti-tumor[57-59] activities, it is usually assumed that the sequestering of trace metals is involved, and that the resulting metal complexes are the actual active species[60,61].

The ligands 2,2'-bipyridine, and 1,l0-phenanthroline are known to form tris, bis, and mono complexes with transition metal ions (Figure 1.6).



a) $Cu(phen)(OH_2)_2(OClO_3)_2$ [64] b) $[Cu(en)(phen)_2](ClO_4^-)_2$ [65]

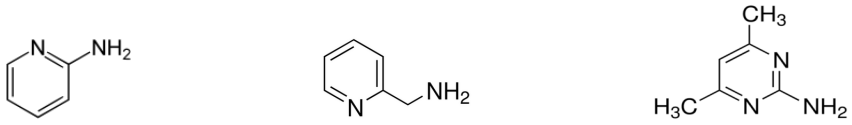
c) $Rh_2(OAc)_4(bpy)$ [66] d)$[Cu_2(ClCH_2COO)(2,2\text{-}bpy)_2(OH)(H_2O)](NO_3)_2$ [67]

Figure 1.6: 2,2'-bipyridine, and 1,l0-phenanthroline metal complexes.

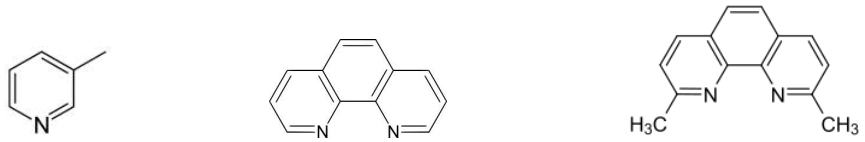
Whereas the former two types are well known, few examples of the mono complexes have been isolated, though dissociation studies have suggested their presence in aqueous solution[62]. 2,4-Bipyridyl ammonium salts are effective agents against most *S. aureus* strains[63]

Pyrimidine ring has received a significant attention owing to its diverse range of biological properties[68]. Furthermore, several important sulfa drugs are pyrimidine derivatives namely sulfadiazine, sulfamerazine and sulfadiamine[69,70].

Six biologically important nitrogen donor ligands are chosen in the present work: 2-aminopyridine, 2-aminomethylpyridine, 3-picoline, 1,10-phenanthrolone, 2,9-dimethyl-1,10-phenanthroline, 4,6-dimethyl pyrimidine (Figure 1.7).



a) 2-aminopyridine b) 2-aminomethyl pyridine c) 2-amino-4,6-dimethyl pyrimidine



c) 3-picoline e) 1,10-phenanthrolone f) 2,9-dimethyl-1,10-phenanthroline

Figure 1.7: Chemical structures of N-donor ligands used in this research.

Due to their remarkable anti-neoplastic activity against variety of tumors[71], in addition to their applicable antifungal[72] and antibacterial[73] activities, the coordination chemistry of nitrogen-sulfur donor ligands such as substituted thiosemicarbazides[74] dithiocarbazates[75] and thiosemicarbazones[76-78] are of great interest. The investigation of complexes of thiosemicarbazones gave promising results.

Interesting metal(II) complexes were obtained with derivatives of isoflavones[79], 4'-methoxy-5,7-dihydroxy-isoflavone ligand (Figure 1.8). Here, the zinc(II) complex showed a moderate anti-tumor activity *in-vitro*. However, the complex was more active than the free ligand and the metal ion. On the other hand, compared to the chemotherapeutic drug cisplatin, the complex was less active.

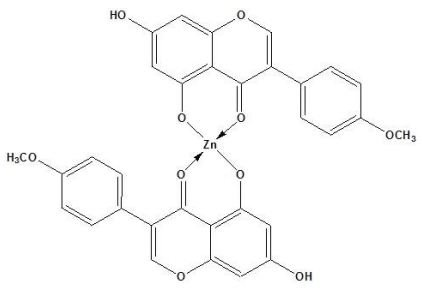


Figure 1.8: Zinc(II) complex of 4'-methoxy-5,7-dihydroxy-isoflavone[79]

Zinc(II) carboxylate complexes appeared to have good anti-bacterial activity; e.g., a strong inhibition was noticed against *E. coli* and *S. aureus*[80]. Zinc(II) complexes of known anti-microbial activity, such as anti-bacterial activity have been achieved; e.g. the interaction between zinc and the gyrase inhibitor ciprofloxacin and various nitrogen-donor ligands have been studied and the complexes were found to possess more potent activity than the parent drugs alone[81].

Zinc(II) complexes of sulfa drugs, such as sulfadiazine and sulfamerazine also proved to be effective anti-fungal agents against *Aspergillus* and *Candida* species[82]. Zinc(II) complexes with amino acids have been developed with anti-microbial activity. The anti-bacterial activity of zinc(II) complex with S-phenylalaninato ligand was 10-fold greater than the simple metal salt (Figure 1.9). A very good inhibitor activity was also found by the yeast *Candida albicans*[83].

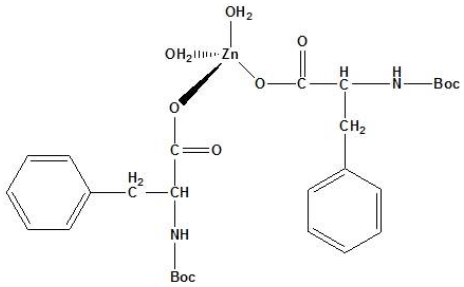


Figure 1.9: The proposed structure of the zinc(II) complex of N-benzyloxycarbonyl-(s)-phenylalanine[83]

Another zinc(II) complex (Figure 1.10) containing N-donor ligand, 2,6-bis(benzimidazol-2yl) pyridine also has strong anti-microbial activities[84].

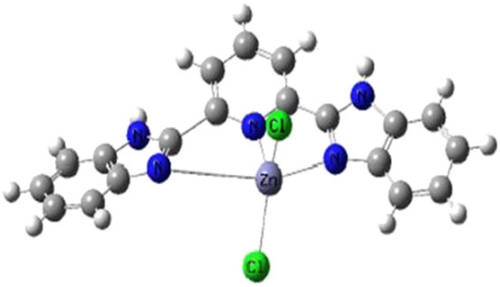


Figure 1.10: [Zn**(**2,6-Bis(benzimidazol-2-yl)pyridine**)**Cl_2**]** complex[84].

Zinc pyrithione is a good example of an agent with anti-bacterial and anti-fungal activity. In the form of bis(N-oxopyridine-2-thionato)zinc(II) (Figure 1.11), the drug inhibits the membrane transport processes by blocking the proton pump in fungi. However, it was shown that at low concentration of the agent fungi are able to inactivate pyrithione [85].

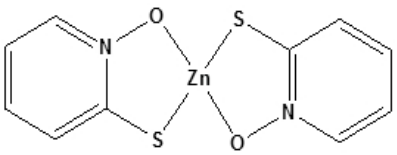
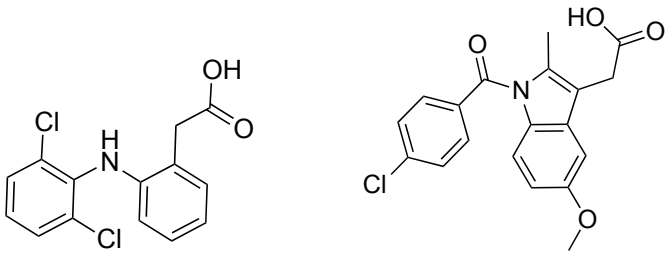


Figure 1.11: Structure of zinc pyrithione[85].

1.5 Dicolfenac and Indomethacin

Dicolfenac and indomethacin are non-steroidal anti-inflammatory drugs (NSAIDs). NSAIDs are the most frequently used analgesic, anti-inflammatory and anti-pyretic agents. NSAIDs act by inhibiting the cyclo-oxygenase (COX)-mediated production of prostaglandins. They have also exhibited anti-tumorigenic activity by reducing the number and size of carcinogen-induced colon tumors, or through inducing the apoptosis of several cancer cell lines. The chemical classes of NSAIDs comprise salicylate derivatives, phenylalkanoic acids, oxicams, anthranilic acids, sulfonamides and furanones[86].

Indomethacin, [1-(4-chlorobenzoyl)-5-methoxy-2- methyl-1-H-indole-3-acetic acid], and Diclofenac, sodium salt of [2-[(2,6-dichlorophenyl) amino]phenyl] acetic acid] (Figure 1.12), belong to phenylalkanoic acids, are a potent NSAIDs for the treatment of inflammatory conditions, such as rheumatoid arthritis, osteoarthritis, and ankylosing spondilytis, in addition to analgesic and anti-pyretic activity[87-90].



Indomethacin Diclofenac

Figure 1.12: Structure of indomethacin and diclofenac[90].

It has been suggested that the anti-inflammatory activity of NSAIDs is enhanced by coordination with metals[91,92], it was reported that Cu-complexes of these

anti-inflammatory drugs were more active in animal models than their parent inorganic Cu(II) salt or the parent NSAIDs. The pharmacological activity was proposed to be due to the inherent physico-chemical properties of the complex itself rather than just that of its constituents[90].

Several complexes of NSAIDs have been synthesized and tested for their biological and pharmacological activity, $[Cu(diclo)_2(H_2O)]_2$ (Figure 1.13), $[Cu(diclo)_2(H_2O)].2H_2O$, $[Pd(diclo)_2].2H_2O$, $[Fe(diclo)_2(H_2O)]$, $[Ni(diclo)_2(H_2O)].2H_2O$ and $[Co(diclo)_2(H_2O)].2H_2O$ complexes of diclofenac exhibit very promising anti-inflammatory activity and act as anti-oxidant compounds, a property that is absent from diclofenac.

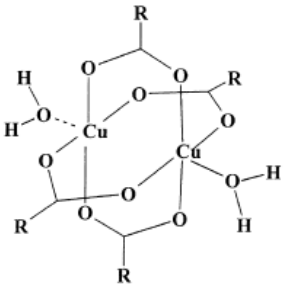


Figure 1.13: Structure of $[Cu(diclo)_2(H_2O)]_2$

Almost all the complexes of diclofenac tested showed high anti-inflammatory activity at molecular concentrations much lower than that of diclofenac[91,93]. It was found that diclofenac Ni(II) complexes have leishmanicidal activity[93].

Although diclofenac is usually well tolerated by patients, it has side effects, particularly those related to the gastrointestinal tract. It has been demonstrated that

Zn(II) possesses an anti-ulcerogenic profile[94,95] besides having its own anti-arthritic effects[96].

Many experimental and clinical studies have demonstrated that zinc compounds may be useful to treat or prevent gastric ulcers[97-101]. Rodrigues de la Serna and Díaz- Rubio[102] showed that zinc acexamate markedly reduced the severity of gastric lesions induced by piroxicam, in patients. The search for medicines that associate anti-inflammatory and gastroprotective effects is important because it could avoid the co-administration of two drugs. Tagliati *et al*.[(103)] were the first to evaluate the anti-inflammatory activity and the incidence of gastric lesions induced by piroxicam, complexed with zinc in rats. The anti-inflammatory activity of piroxicam was not changed when the drug was used as zinc complex, but the severity of gastric lesions was reduced in the group treated with the zinc complex. Similar results have been reported for zinc-tenoxicam[104], zinc- acetylsalisylic acid[105] and zinc naproxen[106].

Santos et al. showed that zinc-diclofenac complex had the same anti-inflammatory and anti-nociceptive effects as diclofenac. But at the same time zinc diclofenac complex has reduces the severity of gastric lesions induced by diclofenac alone[107]. However, Abou-Mohamed *et al*.[108] have demonstrated that the simultaneous administration of diclofenac plus zinc sulfate induces a higher inhibition of carrageenin induced edema than diclofenac alone, this results may be due to the differences in dose (25mg/kg) of the zinc compound used by Abou-Mohamed et al. which approximately eight times higher than that used by Santos et al.

Singla et al.[109] reported that zinc-indomethacin complex have higher anti-

inflammatory activity than that of indomethacin alone and also it has lower ulcerogenic activity.

1.6 Aim of the research

The main purpose of this research is to synthesize, characterize, and to determination *In-vitro* the anti-microbial activity of new mixed ligands zinc(II) complexes of diclofenac and indomethacin.

2. Experimental

2.1 Chemicals, materials and biological species

All chemicals and solvents were purchased from commercial sources and, unless specified, were used without further purification. Bacterial species: *Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa,* and *Listeria monocytogenes* were kindly obtained from Biology and Biochemistry Department at Birzeit University.

2.2 Physical measurements

Infrared (IR) spectra were recorded in 450-4000 cm^{-1} region, as (KBr) pellets, by means of Perkin Elmer FT-IR spectrometer (2004).

NMR spectra were recorded on a Varian unity spectrometer operating at 300 MHz for ^{1}H measurements and at 75 MHz for $^{13}C\{^{1}H\}$ measurements. Spectra were recorded on deuterated chloroform ($CDCl_3$) unless otherwise stated. Chemical shifts were given in ppm down field from the internal standard Me_4Si and coupling constants are given in Hz.

UV-Vis measurements were recorded on a Hewlett Packard 8453 photo diode-array spectrometer in the 200–800 nm region using DMSO as solvents.

Melting points were determined in capillary tube with MPA120 EZ-melt apparatus.

2.3 Synthesis and characterization of Zn(II) complexes

The synthesis of all Zn(II) complexes were conducted at ambient conditions.

2.3.1 Zinc diclofenac complex, $[Zn(diclo)_2(H_2O)_2]$ (1)

Diclofenac sodium (3.52 g, 11.9 mmol) in 100 ml of water was added with stirring to $ZnCl_2$ (0.81 g, 6 mmol) in 50 ml of water. Immediately a white ppt was formed and the reaction mixture was kept stirring for and additional 3 h. the ppt was then filtered, washed with cold water and air dried to give 3.73 g of solid product. Suitable crystals for X-ray structural analysis were obtained by recrystallization from 4:1 mixture of CH_3OH and DMSO.

Yield 86%; m.p. 252 $^{\circ}$C (decompose); IR (cm^{-1}, KBr): 3283, 3075, 2975, 2928, 1578, 1511, 1474, 1454, 1399, 1303, 1249, 1201, 1154, 1089, 1046, 870, 839, 770, 749, 716, 674, 613, 546, 476; ^{1}H-NMR (δ, DMSO): 3.57 (s, 2H, CH_2), 6.29 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 9 Hz), 6.82 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 12 Hz), 7.00 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 11.25 Hz), 7.07 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 13.5 Hz), 7.12 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 6 Hz), 7.43 (d, 2H, CH, $^{3}J_{H\text{-}H}$ = 9 Hz), 8.29 (s, 1H, NH); $^{13}C\{^{1}H\}$-NMR (δ, DMSO): 40.00 (CH_2), 116.70 (CH), 121.17 (CH), 125.00 (CH), 127.00 (C), 127.20 ($2CH_2$), 129.34 (CH), 129.48 (2C), 130.95 (CH), 137.94 (C), 143.22 (C), 177.70 (C=O); UV-Vis (DMSO, λ (nm)): 284.

2.3.2 Zinc indomethacin complex, $[Zn_2(indo)_4]$ (2)

Indomethacin sodium salt (3.52 g, 9.8 mmol) dissolved in 100 ml of water was added gradually with stirring to $ZnCl_2$ (0.67 g, 4.9 mmol) in 50 ml of water. Immediately a precipitate was formed, the reaction mixture was kept stirring for an additional 3 h. the precipitate was then filtered, washed with cold water, and air dried to give 2.77 g of solid product.

Yield 66%; m.p. 190 °C (decompose); IR (cm^{-1}, KBr): 3404, 2970, 2923, 2850, 1681, 120, 1610, 1587, 1465, 1437, 1401, 1353, 1330, 1285, 1234, 1150, 1091, 1068, 1032, 1016, 916, 845, 797, 756, 603, 485; ^{1}H-NMR (δ, DMSO): 2.15 (s, 3H, CH_3), 3.41 (s, 2H, CH_2), 3.71 (s, 3H, CH_3), 6.64 (d, 1H, CH, $^3J_{H\text{-}H}$ = 9 Hz), 6.67 (d, 1H, CH, $^3J_{H\text{-}H}$ = 6.5 Hz), 6,90 (s, 1H, CH), 7.62 (d, 4H, 4CH); $^{13}C\{^1H\}$-NMR (δ, DMSO): 13.8 (CH_3), 31.68 (CH_2), 55.71 (CH_3), 102.46 (CH), 111.53 (CH), 114.86 (C), 116.43 (CH), 129.45 (2CH), 130.65 (C), 131.50 (C), 131.71 (2CH), 134.55 (C), 134.78 (C), 137.88 (C), 155.86 (C), 168.24 (C), 176.32 (C); UV-Vis (DMSO, λ (nm)): 319.

2.3.3 Zinc diclofenac 3-picoline, $[Zn(diclo)_4(pico)_2]$ (3)

3-Picoline (0.15 g, 1.6 mmol) was dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of $[Zn_2(diclo)_4]$ (0.5 g, 0.4 mmol). The reaction mixture was kept stirring for an additional 3 h, the precipitate was then filtered, washed with ether and air dried to give 0.37 g of solid product.

Yield 57%; m.p. 118-120 °C; IR (cm^{-1}, KBr): 3251, 3083, 3040, 2977, 2927, 1605, 1579, 1551, 1510, 1497, 1469, 1453, 1432, 1415, 1403, 1303, 1291, 1248, 1198,

1154, 1170, 1130, 1087, 1065, 1047, 943, 867, 839, 795, 768, 747, 716, 700, 782, 658, 613, 547, 534, 513, 463; ^{1}H-NMR (δ, $CDCl_3$): 2.14 (s, 3H, CH_3), 3.74 (s, 2H, CH_2), 6.41 (d, 1H, $^{3}J_{H\text{-}H}$ = 6 Hz), 6.83 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 6.88 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 7.8 Hz), 7.00 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 6.3 Hz), 7.06 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 7.17 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 5.4 Hz), 7.25 (m, 1H, $CH_{(pico)}$) 7.35 (s, 1H, NH), 7.51 (d, 1H, $CH_{(pico)}$, $^{3}J_{H\text{-}H}$ = 6Hz), 8.12 (d, 1H, $CH_{(pico)}$), 8.22 (s, 1H, $CH_{(pico)}$); UV-Vis (DMSO, λ (nm)): 270, 283.

2.3.4 Zinc indomethacin 3-picoline, $[Zn_2(indo)_4(pico)_2]$ (4)

3-Picoline (0.12 g, 1.3 mmol) was dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of $[Zn_2(indo)_4]$ (0.5 g, 0.32 mmol). The reaction mixture was kept stirring for an additional 3 h which was then left to evaporate at room temperature, the sticky residue was then washed with petroleum ether and air dried to give 0.31 g of solid product. Suitable crystals for X-ray structural analysis were obtained by recrystallization from acetone.

Yield 50%; m.p. 186-188 °C; IR (cm^{-1}, KBr): 3462, 3109, 3078, 2966, 2923, 2841, 1682, 1620, 1614, 1588, 1575, 1479, 1456, 1394, 1369, 1309, 1259, 1234, 1220, 1146, 1089, 1067, 1032, 1013, 924, 905, 860, 845, 831, 800, 790, 756, 720, 701, 674, 568, 612, 549, 480; ^{1}H-NMR (δ, DMSO) 2.12 (s, 3H, $CH_{3(pico)}$) 2.21 (s, 3H, CH_3), 3.63 (s, 2H, CH_2), 3.63 (s, 3H, CH_3), 6.56 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 9 Hz), 6.87 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 9.3 Hz), 6.94 (s, 1H, CH), 77.20 (m, 1H, $CH_{(pico)}$, $^{3}J_{H\text{-}H}$ = 12.6 Hz), 7.40 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 8.4 Hz), 7.55 (d, 1H, $CH_{(pico)}$), 7.58 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 9 Hz),

8.09 (s, 1H, $CH_{(pico)}$), 8.11 (d, 1H, $CH_{(pico)}$ $^{3}J_{H\text{-}H}$ = 6 Hz); $^{13}C\{^{1}H\}$-NMR (δ, DMSO): 13.43 (CH_3), 18.31 ($CH_{3(pico)}$), 31.74 (CH_2), 55.46 (CH_3), 101.68 (CH), 111.38 (CH), 114.75 (C), 114.90 (CH), 124.31 ($CH_{(pico)}$), 128.92 (2CH), 130.90 (C), 131.04 (C), 131.30 (2CH), 134.10 (C), 135.00 (C), 135.10 (C), 138.97 (C), 139.76 ($CH_{(pico)}$), 146.23 ($CH_{(pico)}$), 149.09 ($CH_{(pico)}$), 155.80 (C), 168.24 (C), 179.17 (C); UV-Vis (DMSO, λ (nm)): 268, 319.

2.3.5 Zinc diclofenac 2-amino pyridine, $[Zn(diclo)_2(apy)_2]$ (5)

2-Aminopyridine (0.15 g, 1.6 mmol) was dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of $[Zn_2(diclo)_4]$ (0.5 g, 0.4 mmol). The reaction mixture was kept stirring for an additional 3 h, then left to evaporate at room temperature, to give 0.47 g of solid product. Suitable crystals for X-ray structural analysis were obtained by recrystallization from acetone.

Yield 72%; m.p. 184-185 °C; IR (cm^{-1}, KBr): 3440, 3315, 3210, 3060, 3017, 2940, 2860, 653, 1619, 1611, 1587, 1565, 1510, 1498, 1470, 1452, 178, 1333, 1302, 1273, 1157, 19011, 853, 768, 740, 719, 666, 582, 520; ^{1}H-NMR (δ, $CDCl_3$): 3.82 (s, 2H, CH_2), 5.80 (s, 2H, $NH_{2(apy)}$), 6.44 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 8.4 Hz), 6.87 (m, 2H, CH, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 6.90 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 6.86 (d, 1H, $CH_{(apy)}$, $^{3}J_{H\text{-}H}$ = 8.4 Hz), 6.89 (m, 1H, $CH_{(apy)}$, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 7.23 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 1.8 Hz), 7.06 (m, 1H, CH, $^{3}J_{H\text{-}H}$ = 17.1 Hz), 7.26 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 7.36 (m, 1H, $CH_{(apy)}$, $^{3}J_{H\text{-}H}$ = 3.9 Hz), 7.70 (s, 1H, NH) 7.71 (d, 1H, $CH_{(apy)}$, $^{3}J_{H\text{-}H}$ = 5.4 Hz); $^{13}C\{^{1}H\}$-NMR (δ, $CDCl_3$): 41.30 (CH_2), 111.57 ($CH_{(apy)}$), 113.14 ($CH_{(apy)}$), 117.05 (CH), 121.09 (CH),

123.54 (CH), 126.42 (C), 126.92 (2CH), 128.66 (CH), 129.72 (2CH), 130.86 (CH), 138.05 (C), 139.90 ($CH_{(apy)}$), 142.98 (C), 145.88 ($CH_{(apy)}$), 159.02 ($C_{(apy)}$), 179.38 (C); UV-Vis (DMSO, λ (nm)): 291.

2.3.6 Zinc indomethacin 2-amino pyridine, $[Zn(indo)_2(apy)_2]$ (6)

2-Aminopyridine (0.17 g, 1.8 mmol) was dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of $[Zn_2(indo)_4]$ (0.7 g, 0.45 mmol). The reaction mixture was kept stirring for an additional 3 h, then left to evaporate at room temperature, to give 0.52 g of solid product.

Yield 60%; m.p. 95 °C (decompose); IR (cm^{-1}, KBr): 3337, 3227, 3113, 3082, 2932, 2925, 2841, 1677, 1620, 1592, 1565, 1498, 1477, 1454, 1450, 1398, 1354, 1326, 1287, 1258,1228, 1177, 1148, 1086, 1068, 1033, 1014, 994, 917, 831, 799, 769, 754, 667, 603, 481; ^{1}H-NMR (δ, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.59 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 6.04 (s, $NH_{(apy)}$), 6.33 (d, 1H, $CH_{(apy)}$, $^3J_{H\text{-}H}$ = 9.6 Hz), 6.37 (m, 1H, $CH_{(apy)}$, $^3J_{H\text{-}H}$ = 12.9 Hz), 6.59 (d, 1H, CH, $^3J_{H\text{-}H}$ = 11.7 Hz), 6.87 (d, 1H, CH, $^3J_{H\text{-}H}$ = 9.6 Hz), 6.97 (s, 1H, CH), 7.31 (m, 1H, $CH_{(apy)}$, $^3J_{H\text{-}H}$ = 15.9 Hz), 7.39 (d, 2H, 2CH, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.59 (d, 2H, 2CH, $^3J_{H\text{-}H}$ = 8.7 Hz), 7.63 (d, 1H, $CH_{(apy)}$, $^3J_{H\text{-}H}$ 4.5Hz); $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 13.42 (CH_3), 31.94 (CH_2), 55.60 (CH_3), 101.77 (CH), 111.28 (CH), 111.62 ($CH_{(apy)}$), 112.61 (C), 114.75 (CH), 115.49 ($CH_{(apy)}$), 129.03 (2CH), 130.79 (C), 131.14 (C), 131.35 (2CH), 134.04 (C), 135.12 (C), 139.03 ($CH_{(apy)}$), 140.09 (C), 144.61 ($CH_{(apy)}$), 155.83 (C), 158.51 ($C_{(apy)}$), 168.43 (C), 177.59 (C); UV-Vis (DMSO, λ (nm)): 274, 319.

2.3.7 Zinc diclofenac 2-aminomethyl pyridine, [Zn(diclo)$_2$(ampy)] (7)

2-Aminomethyl pyridine (0.0886 g, 0.819 mmol) was dissolved in 20 ml of acetone and gradually added to 100 of stirred acetone solution of [Zn_2(diclo)$_4$] (0.5 g, 4.09 mmol). The reaction mixture was kept stirring for an additional 3 h, then filtered, washed with acetone and air dried to give 0.45 g of solid product.

Yield 76%; m.p. 237-241 $^{\circ}$C; IR (cm^{-1}, KBr): 3477, 3330, 3233, 3091, 3041, 2914, 2938, 2864, 1663, 1614, 1578, 1562, 1502, 1467, 1453, 1407, 1379, 1307, 1275, 1219, 1195, 1157, 1093, 1055, 1031, 948, 872, 841, 767, 758, 745, 719, 653, 531.

^{1}H-NMR (δ, $CDCl_3$): 2.16 (s, 2H, $CH_{2(ampy)}$), 3.82 (s, 2H, CH_2), 5.75 (s, 2H, $NH_{2(ampy)}$), 6.39 (d, 1H, CH, $^3J_{H-H}$ = 8.7 Hz), 6.45 (m, 2H, 2CH, $^3J_{H-H}$ = 7.8 Hz), 6.86 (m, 1H, CH, $^3J_{H-H}$ = 8.4 Hz), 6.89 (d, 1H, CH, $^3J_{H-H}$ = 8.1 Hz), 7.04 (m, 1H, $CH_{(ampy)}$, $^3J_{H-H}$ = 15.3 Hz), 7.22 (d, 2H, 2CH, $^3J_{H-H}$ = 8.4 Hz), 7.25 (d, 1H, $CH_{(ampy)}$, $^3J_{H-H}$ = 8.4 Hz), 7.36 (m, 1H, $CH_{(ampy)}$, $^3J_{H-H}$ = 15 Hz), 7.72 (d, 1H, $CH_{(ampy)}$, $^3J_{H-H}$ = 6.6 Hz), 7.74 (s, 1H, NH); ^{13}C{^{1}H}-NMR (δ, $CDCl_3$): 30.92 (CH_2), 41.30 ($CH_{2(ampy)}$), 111.45 (CH), 113.14 (CH), 117.70 (CH), 121.08 ($CH_{(ampy)}$), 123.49 ($CH_{(ampy)}$), 126.50 (C), 126.88 (2CH), 128.65 (CH), 129.73 (2CH), 130.83 (CH), 138.11 (C), 139.85 ($CH_{(ampy)}$), 143.00 (C), 146.08 ($CH_{(ampy)}$), 159.08 ($C_{(ampy)}$), 179.25 (C); UV-Vis (DMSO, λ (nm)): 268, 287.

2.3.8 Zinc indomethacin 2-aminomethyl pyridine, [Zn(indo)$_2$(ampy)] (8)

2-Aminomethyl pyridine (0.097 g, 0.899 mmol) dissolved in 20 ml of acetone was gradually added to 100 ml of stirred acetone solution of [Zn_2(indo)$_4$] (0.7 g, 0.45

mmol). The reaction mixture was kept stirring for an additional 3 h, then left to evaporate to give 0.62 g of solid product.

Yield 78%; m.p. 117-120 °C; IR (cm^{-1}, KBr): 3432, 3337, 3278, 3114, 3091, 2940, 2925, 2852, 1682, 1620, 1609, 1590, 1565, 1477, 1460, 1440, 1397, 1356, 1319, 1258, 1222, 1177, 1146, 1987, 1068, 1033, 1014, 922, 833,754, 668, 480; ^{1}H-NMR (δ, $CDCl_3$): 2.19 38 (s, 3H, CH_3), 2.19 (s, 2H, $CH_{2(ampy)}$), 3.54 (s, 2H, CH_2), 3.68 (s, 3H, CH_3), 3.93 (s, 2H, $NH_{2(ampy)}$), 6.59 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 12 Hz), 6.86 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 10 Hz), 6.90 (s, 1H, CH), 7.10 (d, H, $CH_{(ampy)}$, $^{3}J_{H\text{-}H}$ = 9 Hz), 7.18 (t, H, $CH_{(ampy)}$, $^{3}J_{H\text{-}H}$ = 15 Hz), 7.40 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 10 Hz), 7.59 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 10 Hz), 7.74 (m, H, $CH_{(ampy)}$, $^{3}J_{H\text{-}H}$ = 15 Hz), 8.35 (d, H, $CH_{(ampy)}$, $^{3}J_{H\text{-}H}$ = 9Hz); $^{13}C\{^{1}H\}$-NMR (δ, $CDCl_3$): 13.43 (CH_3), 32.09 (CH_2), 42.88 ($CH_{2(ampy)}$), 55.58 (CH_3), 101.87 (CH), 111.07 (CH), 114.78 (C), 115.86 (CH), 122.54 ($CH_{(ampy)}$), 123.45 ($CH_{(ampy)}$), 129.00 (2CH), 130.80 (C), 131.06 (C), 131.44 (2CH), 134.14 (C), 134.89 (C), 138.92 ($CH_{(ampy)}$), 139.09 (C), 147.39 ($CH_{(ampy)}$), 155.78 (C), 156.59 ($C_{(ampy)}$), 168.34 (C), 178.11 (C); UV-Vis (DMSO, λ (nm)): 265, 320.

2.3.9 Zinc diclofenac 1,10-phenanthroline, $[Zn(diclo)_2(phen)]$ (9)

1,10-Phenanthroline (0.35 g, 1.94 mmol) dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of $[Zn_2(diclo)_4]$ (1.4 g, 1.146 mmol), The reaction mixture was kept stirring for an additional 3 h, then filtrated, washed and air dried to give 1.31 g of solid product.

Yield 75%; m.p. 273 °C (decompose); IR (cm^{-1}, KBr): 3436, 3244, 3096, 3057, 2982,

2915, 2857, 1600, 1586, 1574, 1559, 1515, 1476, 1453, 1426, 1400, 1305, 1287, 1193, 1168, 1105, 1045; ^{1}H-NMR (δ, DMSO): 3.49 (s, 2H, CH_2), 6.20 (d, 1H, CH, $^{3}J_{H-H}$ = 9 Hz), 6.77 (m, 1H, CH, $^{3}J_{H-H}$ = 12 Hz), 6.97 (m, 1H, CH), 7.02 (m, 1H, CH), 7.05 (d, 1H, CH), 7.37 (d, 2H, 2CH, $^{3}J_{H-H}$ = 9 Hz), 7.88 (m, 2H, $2CH_{(phen)}$), 8.17 (s, 2H, $2CH_{(phen)}$), 8.39 (s, 1H, NH), 8.74 (d, 2H, $2CH_{(phen)}$, $^{3}J_{H-H}$ = 10 Hz), 8.94 (d, 2H, $2CH_{(phen)}$); UV-Vis (DMSO, λ (nm)): 267; 290.

2.3.10 Zinc indomethacin 1,10-phenanthroline, [Zn(indo)$_2$(phen)] (10)

1,10-Phenanthroline (0.35 g, 1.94 mmol) dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of [Zn_2(indo)$_4$] (1.5 g, 0.963 mmol). The reaction mixture was kept stirring for an additional 3 h, then to evaporate to give 1.48 g of solid product.

Yield 80%; m.p. 248 °C (decompose); IR (cm^{-1}, KBr): 3467, 3093, 3068, 2995, 2973, 2922, 1677, 1625, 1608, 1590, 1520, 1475, 1460, 1430, 1429, 1396, 1366, 1316, 1255, 1220, 1194, 1147, 1106, 1085, 1073, 1038, 1010, 922, 907, 871, 856, 829, 795, 753, 727, 715, 681, 645, 600, 584, 566, 546, 480; ^{1}H-NMR (δ, DMSO): 2.23 (s, 3H, CH_3), 3.58 (s, 2H, CH_2), 3.65 (s, 3H, CH_3) 6.54 (d, 1H, CH, $^{3}J_{H-H}$ = 9 Hz), 6.85 (d, 1H, CH, $^{3}J_{H-H}$ = 9 Hz), 6.88 (s, 1H, CH), 7.15 (d, 2H, 2CH, $^{3}J_{H-H}$ = 12 Hz), 7.57 (d, 2H, 2CH, $^{3}J_{H-H}$ = 9 Hz), 7.67 (t, $2CH_{(phen)}$), 8.37 (d, 1H, $2CH_{(phen)}$, $^{3}J_{H-H}$ = 9Hz), 7.83 (s, $2CH_{(phen)}$), 9.05 (d, $2CH_{(phen)}$); $^{13}C\{^{1}H\}$-NMR (δ, DMSO): 13.55 (CH_3), 31.16 (CH_2), 55.46 (CH_3), 101.69(CH), 111.27 (CH), 114.71 (C), 115.53 (CH), 125.01 ($2CH_{(phen)}$), 126.61 ($2CH_{(phen)}$), 128.71 ($2CH_{(phen)}$), 128.96 (2CH), 130.80 (C), 131.01

(C), 131.20 (2CH), 133.40 (C), 135.00 (C), 135.00 ($2CH_{(phen)}$), 138.82 (C), 146.25 ($2C_{(phen)}$), 150.00 ($2CH_{(phen)}$), 155.66 (C), 168.23 (C), 180.16 (C); UV-Vis (DMSO, λ (nm)): 267, 318.

2.3.11 Zinc diclofenac 2,9-dimethyl-1,10-phenanthroline, $[Zn(diclo)_2(dmph)]$ (11)

2,9-Dimethyl-1,10-phenanthroline (0.17 g, 0.816 mmol) dissolved in 20 ml of acetone was gradually added to 100 ml of stirred acetone solution of $[Zn_2(diclo)_4]$ (0.5 g, 0.409 mmol), The reaction mixture was kept stirring for an additional 3 h which was then filtered washed with actone and air deried to give 0.51 g of solid product. Suitable crystals for X-ray structural analysis were obtained by recrystallization from 1:1 mixture of CH_2Cl_2 CH_3OH.

Yield 76%; m.p. 255 °C (decompose); IR (cm^{-1}, KBr): 3475, 3248, 3076, 2945, 2922, 2841, 1617, 1600, 1588, 1575, 1561, 1510, 1474, 1453, 1425, 1379, 1307, 1284, 1250, 1195, 1153, 1092, 1046, 955; ^{1}H-NMR (δ, $CDCl_3$): 2.91 (s, 6H, $2CH_{3(dmph)}$), 3.78 (s, 2H, CH_2), 6.41 (d, 1H, CH, $^3J_{H\text{-}H}$ = 7.8 Hz), 6.80 (m, 1H, CH, $^3J_{H\text{-}H}$ = 12.9 Hz), 6.86 (m, 1H, CH, $^3J_{H\text{-}H}$ = 15.9 Hz), 7.00 (m, 1H, CH, $^3J_{H\text{-}H}$ = 15.3 Hz), 7.15 (d, 1H, CH, $^3J_{H\text{-}H}$ = 7.2 Hz), 7.20 (d, 2H, 2CH, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.61 (d, 2H, $2CH_{(dmph)}$ $^3J_{H\text{-}H}$ = 8.4 Hz), 7.82 (s, 2H, $2CH_{(dmph)}$), 8.00 (s, 1H, NH), 8.32 (d, 2H, $2CH_{(dmph)}$ $^3J_{H\text{-}H}$ = 8.4 Hz); $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 24.77 ($CH_{3(dmph)}$), 40.75 (CH_2), 117.16 (CH), 120.96 (CH), 123.19 ($2CH_{(dmph)}$), 125.69 (C), 126.31 ($2CH_{(dmph)}$), 126.73 (2CH), 126.94 ($2C_{(dmph)}$), 128.60 (CH), 129.46 (2CH), 130.71 (CH), 139.06 (C), 140.31 ($2CH_{(dmph)}$), 142.96 (C), 150.59 ($2C_{(dmph)}$), 160.91 ($2C_{(dmph)}$), 190.96 (C); UV-Vis (DMSO, λ (nm)): 273, 284.

2.3.12 Zinc indomethacin 2,9-dimethyl-1,10-phenanthroline, [Zn(indo)$_2$(dmph)] (12)

2,9-Dimethyl-1,10-phenanthroline (0.187 g, 0.899 mmol) dissolved in 20 ml of acetone was gradually added to 100 ml of stirred acetone solution of [Zn_2(diclo)$_4$] (0.7 g, 0.449 mmol). The reaction mixture was kept stirring for an additional 3 h, which was then filtered washed with actone to give 0.83 g of solid product.

Yield 94%; m.p. 235-237 $^{\circ}$C; IR (cm^{-1}, KBr): 3435, 3080, 2961, 2926, 2830, 1666, 1625, 1613, 1590, 1510, 1480, 1458, 1427, 1391,1371, 1354, 1330, 1288, 1252, 1227, 1216, 1177, 1149, 1088, 1076, 1038, 1013, 926, 859, 846, 838, 787, 756, 737, 729, 719, 691, 674, 649, 625, 611, 570, 551, 487, 462; ^{1}H-NMR (δ, $CDCl_3$): 2.26 (s, 3H, CH_3), 2.91 (s, 3H, $CH_{3(dmph)}$), 3.58 (s, 2H, CH_2), 3.65 (s, 3H, CH_3), 6.56 (d, 1H, CH, $^{3}J_{H-H}$ = 8.7 Hz), 6.85 (d, 1H, CH, $^{3}J_{H-H}$ = 9.9 Hz), 6.90 (s, 1H, CH), 7.27 (d, 2H, $CH_{(dmph)}$ $^{3}J_{H-H}$ 7.8Hz), 7.42 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8.1 Hz), 7.61 (d, 2H, 2CH, $^{3}J_{H-H}$ = 8.4 Hz), 7.82 (s, 1H, $CH_{(dmph)}$), 8.32 (d, 2H, $CH_{(dmph)}$ $^{3}J_{H-H}$ = 8.1 Hz). $^{13}C\{^{1}H\}$-NMR (δ, $CDCl_3$): 13.60 (CH_3), 24.68 ($2CH_{3(dmph)}$), 31.70 (CH_2), 55.41 (CH_3), 101.62 (CH), 111.30 (CH), 114.73 (C), 116.01 (CH), 125.63 ($2CH_{(dmph)}$), 126.31 (2CH), 126.89 ($2CH_{(dmph)}$), 128.97 ($2C_{(dmph)}$), 130.77 (CH), 130.77 (CH), 131.03 (2CH), 131.46 (C), 134.26 (C), 134.78 ($2CH_{(dmph)}$), 138.8 (C), 139.10 ($2C_{(dmph)}$), 155.65 (C), 160.68 ($2C_{(dmph)}$), 168.28 (C), 178.11 (C); UV-Vis (DMSO, λ (nm)): 271, 319.

2.3.13 Zinc diclofenac 2-amino-4,6-dimethylpyrimidine, [Zn(diclo)$_2$ (admp)] (13)

2-Amino-4,6-dimethylpyrimidine (0.2 g, 1.62 mmol) dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of [$Zn_2(diclo)_4$] (0.5 g, 0.409 mmol). The reaction mixture was kept stirring for an additional 3 h, then left to evaporate to give 0.42 g of solid product.

Yield 60%; m.p. 155 °C (decompose); IR (cm^{-1}, KBr): 3447, 3369, 3182, 3080, 3034, 2975, 2927, 2845, 1673, 1621, 1605, 1591, 1565, 1538, 1451, 1400, 1368, 1304, 1196, 1155, 1094, 1049, 947; ^{1}H-NMR (δ, $CDCl_3$): 2.50 (s, 6H, $2CH_{3(admp)}$), 3.70 (s, 2H, CH_2), 3.93 (s, 2H, $NH_{2(admp)}$) 6.65 (d, 1H, CH, $^3J_{H-H}$ = 9 Hz), 6.71(s, 1H, $CH_{(admp)}$), 7.17 (m, 1H, CH, $^3J_{H-H}$ = 15 Hz), 7.36 (m, 1H, CH, $^3J_{H-H}$ = 14.4 Hz), 7.43 (m, 1H, CH, $^3J_{H-H}$ = 17.28 Hz), 7.52 (d, 1H, CH, $^3J_{H-H}$ = 7.7 Hz), 7.79 (d, 2H, 2CH, $^3J_{H-H}$ = 9 Hz), 8.85 (s, 1H, NH); $^{13}C\{^1H\}$-NMR(δ, $CDCl_3$): 23.72 ($2CH_{3(admp)}$), 40.00 (CH_2), 109.08 ($CH_{(admp)}$), 116.67 (CH), 121.14 (CH), 124.90 (CH), 127.10 (C), 127.30 (2CH), 129.32 (CH), 129.45 (2CH), 131.20 (CH), 137.93 (C), 143.20 (C), 163.72 ($2C_{(admp)}$), 167.17 ($2C_{(admp)}$), 177.63 (C); UV-Vis (DMSO, λ (nm)): 285.

2.3.14 Zn indomethacin 2-amino-4,6-dimethylpyrimidine, [Zn (indo)$_2$(admp)] (14)

2-Amino-4,6-dimethylpyrimidine (0.158 g, 1.28 mmol) dissolved in 20 ml of acetone and gradually added to 100 ml of stirred acetone solution of [$Zn_2(indo)_4$] (0.5 g, 0.321 mmol). The reaction mixture was kept stirring for an additional 3 h, then left to evaporate to give 0.59 g of solid product.

Yield 90%; m.p. 115-118 °C; IR (cm^{-1}, KBr): 3421, 3330, 3152, 3000, 2957, 2925,

2852, 1677, 1658, 1620, 1612, 1596, 1570, 1468, 1437, 1398, 1356, 1332, 1285, 1235, 1212, 1151, 1091, 1071, 1034, 1015, 994, 954, 916, 845, 823, 793, 769, 753, 601, 564, 484; ^{1}H-NMR (δ, $CDCl_3$): 2.31 (s, 3H, CH_3), 2.31 (s, 6H, $2CH_{3(admp)}$), 3.29 (s, 2H, CH_2), 3.69 (s, 3H, CH_3), 5.58 (s, 2H, $NH_{2(admp)}$), 6.36 (s, 1H, $CH_{(admp)}$), 7.00 (s, 1H, CH), 6.69 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 8.7 Hz), 6.92 (d, 1H, CH, $^{3}J_{H\text{-}H}$ = 8.7 Hz), 7.54 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 6.9 Hz), 7.72 (d, 2H, 2CH, $^{3}J_{H\text{-}H}$ = 6.9 Hz); $^{13}C\{^{1}H\}$-NMR(δ, $CDCl_3$): 13.45 (CH_3), 23.67 ($2CH_{3(admp)}$), 32.02 (CH_2), 55.73 (CH_3), 101.70 (CH), 110.79 ($CH_{(admp)}$), 111.50 (CH), 114.75 (C), 114.91 (CH), 129.24 (2CH), 130.88 (C), 131.34 (C), 131.95 (2CH), 134.16 (C), 135.55 (C), 139.29 (C), 156.03 (C), 162.47 ($C_{(admp)}$), 168.14 (C), 168.49 ($2C_{(admp)}$), 178.10 (C); UV-Vis (DMSO, λ (nm)): 271, 322.

2.4 X-ray Crystallography

Single crystal suitable for x-ray measurments for the complexes **(1), (4), (5)** and **(11)** 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, (SMART-NT V5.6, Bruker AXS GMBH, Karlsruhe, Germany). The crystal was mounted on a three-circle goniometer with χ fixed at +54.76°. The diffracted graphite-monochromated Mo Kα radiation λ = 0.71073 A) 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.

After the crystal of the complex had been carefully optically centered within the X-ray beam, a series of 30 data frames measured at 0.3° increments of ω were collected with three different θ and φ values to assess the overall crystal quality and to calculate a preliminary unit cell. For the collection of the intensity data, the detector was positioned at a θ value of -28° and the intensity images were measured at 0.3° intervals of ω for duration of 20 sec. each. The data frames were collected in four distinct shells which, when combined, measured more than 1.3 hemispheres of intensity data with a maximum θ of 46.5°.

Immediately after collection, the raw data frames were transferred to a second PC computer for integration by the SAINT program package (SAINT-NT V5.0, BRUKER AXS GMBH, Karlsruhe, Germany). The background frame information was updated according to the equation B' = (7B+C)/8, where B' is the update pixel value, B is the background pixel value before updating, and C is the pixel value in the current frame. The integration was also corrected for distortion induced by the detector. In addition, pixels that reside outside the detector active area or behind the beam stop were masked during frame integration. The integrated intensities for the four shells of data were merged to one reflection file. The data file was filtered to reject outlier reflections. The rejection of a reflection was based on the disagreement between the intensity of the reflection and the average intensity of the symmetry equivalents to which the reflection belongs. In the case of strong reflections

(I>99σ(I)), which contain only two equivalents, the larger of the two equivalents was retained. The structure was solved and refined by the SHELXTL software package (SHELXTL-NT V6.1, BRUKER AXS GMBH, Karlsruhe, Germany).

Crystal data and more details of the data collections and refinements are summarized in Tables 2.1 & 2.2.

Table 2.1: Crystal data and structure refinement for complexes **(1)** and $[Zn(diclo)_2(DMSO)_2]$.

	Complex **(1)**	
Empirical formula	$C_{57}H_{52}C_{l8}N_4O_{13}Zn_2$	$C_{32}H_{32}Cl_4N_2O_6S_2Zn$
Formula weight	1415.37	811.89
Temperature	295(1) K	293(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	Pna2(1)	Pbcn
Unit cell dimensions	a = 33.707(3) Å α= 90°.	a = 12.147(1) Å α= 90°.
	b = 9.6250(7) Å β= 90°.	b = 11.472(1) Å β= 90°.
	c = 9.6042(7) Å γ= 90°.	c = 25.121(3) Å γ = 90°.
Volume	3115.9(4) $Å^3$	3500.6(6) $Å^3$
Z	2	4
Density (calculated)	1.509 Mg/ m^3	1.540 Mg/ m^3
Absorption coefficient	1.177 mm^{-1}	1.172 mm^{-1}
F(000)	1444	1664
Crystal size	0.33 x 0.28 x 0.17 mm^3	0.40 x 0.24 x 0.08 mm^3
Theta range for data collection	2.44 to 26.99°.	2.93 to 28.00°.
Index ranges	-43<=h<=43, -12<=k<=12, -12<=l<=12	-15<=h<=16, -15<=k<=15, -32<=l<=33
Reflections collected	33475	28629
Independent reflections	6799 [R(int) = 0.0296]	4205 [R(int) = 0.0360]
Completeness to theta = 26.99°	99.9 %	99.5 %
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	0.8250 and 0.6974	0.9121 and 0.6514
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6799 / 1 / 390	4205 / 0 / 215
Goodness-of-fit on F^2	1.209	1.093
Final R indices [a] [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1385	R1 = 0.0417, wR2 = 0.0936
R indices (all data)	R1 = 0.0538, wR2 = 0.1403	R1 = 0.0508, wR2 = 0.0976
Absolute structure parameter	0.320(16)	
Largest diff. peak and hole	1.003 and -0.311 e. $Å^{-3}$	0.631 and -0.254 e. $Å^{-3}$

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

Table 2.2: Crystal data and structure refinement for complexes **(4)**, **(5)** and **(11)**.

	Complex **(4)**	Complex **(5)**	Complex **(11)**
Empirical formula	$C_{88}H_{74}C_{l4}N_6O_{16}Zn_2$	$C_{39.50}H_{35}C_{l4}N_6O_{4.50}Zn$	$C_{84}H_{66}C_{l8}N_8O_9Zn_2$
Formula weight	1744.07	872.91	1745.79
Temperature	293(1) K	295(1) K	173(1) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Unit cell dimensions	a = 11.4602(8) Å α= 97.226(1)°	a = 8.3725(6) Å α= 93.720(1)°	a = 12.213(1) Å α= 71.108(2)°
	b = 14.454(1) Å β= 98.253(1)°	b = 11.0190(8) Å β= 98.353(1)°	b = 15.515(1) Å β= 75.432(2)°
	c = 26.546(2) Å γ = 109.530(1)°	c = 23.477(2) Å γ = 94.552(1)°	c = 22.987(2) Å γ = 70.367(1)°
Volume	4029.7(5) $Å^3$	2129.7(3) $Å^3$	3831.5(6) $Å^3$
Z	2	2	2
Density (calculated)	1.437 Mg/ m^3	1.361 Mg/ m^3	1.513 Mg/ m^3
Absorption coefficient	0.800 mm^{-1}	0.874 mm^{-1}	0.971 mm^{-1}
F(000)	1800	896	1788
Crystal size	0.33 x 0.24 x 0.13 mm^3	0.22 x 0.15 x 0.11 mm^3	0.29 x 0.26 x 0.12 mm^3
Theta range for data collection	1.93 to 27.00°.	1.86 to 27.00°.	1.44 to 27.00°.
Index ranges	-14<=h<=14, -18<=k<=18, -33<=l<=33	-10<=h<=10, -14<=k<=14, -29<=l<=29	-15<=h<=15, -19<=k<=19, -29<=l<=29
Reflections collected	44916	23393	42526
Independent reflections	17396 [R(int) = 0.0325]	9161 [R(int) = 0.0332]	16545 [R(int) = 0.0421]
Completeness to theta = 26.99°	98.9 %	98.6 %	98.8 %
Absorption correction	Multi-scan	None	Semi-empirical from equivalents
Max. and min. transmission	0.9031 and 0.7781	0.9099 and 0.8309	0.8924 and 0.7660
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	17396 / 0 / 1055	9161 / 8 / 535	16545 / 1 / 1011
Goodness-of-fit on F^2	1.282	1.242	1.281
Final R indices[a] [I>2sigma(I)]	R1 = 0.0741, wR2 = 0.1489	R1 = 0.0976, wR2 = 0.2436	R1 = 0.0807, wR2 = 0.1791
R indices (all data)	R1 = 0.0861, wR2 = 0.1541	R1 = 0.1089, wR2 = 0.2506	R1 = 0.0926, wR2 = 0.1848
Largest diff. peak and hole	0.603 and -0.420 e.$Å^{-3}$	1.305 and -0.698 e.$Å^{-3}$	1.490 and -0.540 e.$Å^{-3}$

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

2.5 Anti-bacterial activity

Agar diffusion method[110] were used for screening the antibacterial activity of the synthesized zinc complexes. Different gram-positive (*Staphylococcus aureus, Listeria monocytogenes*) and gram-negative bacteria (*Escherichia coli, Pseudomonas aeruginosa*) were used in this study.

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

3. Results and discussion

3.1 Synthesis of Zn complexes

The reaction of 1:2 molar ratio of $ZnCl_2$ with diclofenac sodium (Figure 3.1) or indomethacin sodium (Figure 3.2) in aqueous medium afforded the complexes, $[Zn(diclo)_2(H_2O)_2]$ **(1)** and $[Zn_2(Indo)_4]$ **(2)**, respectively, as solid products.

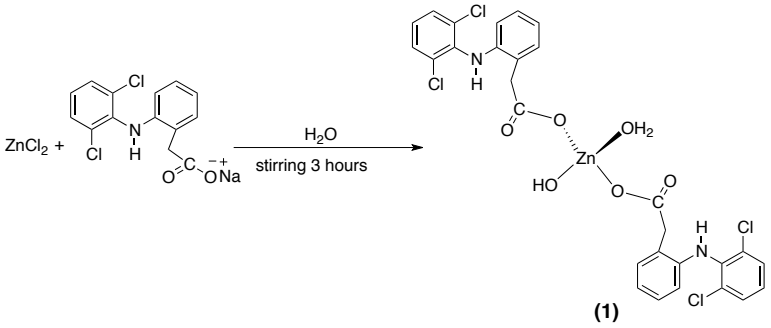


Figure 3.1: Synthesis of Zn diclofenac complex **(1)**

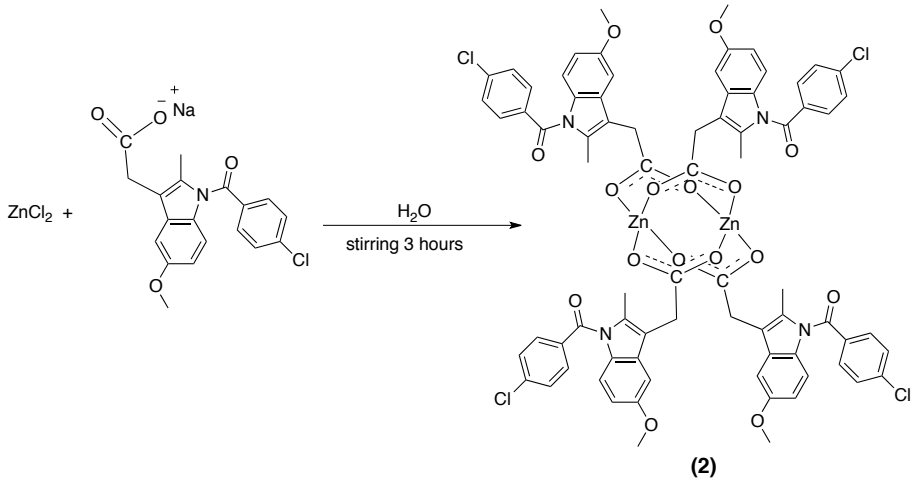
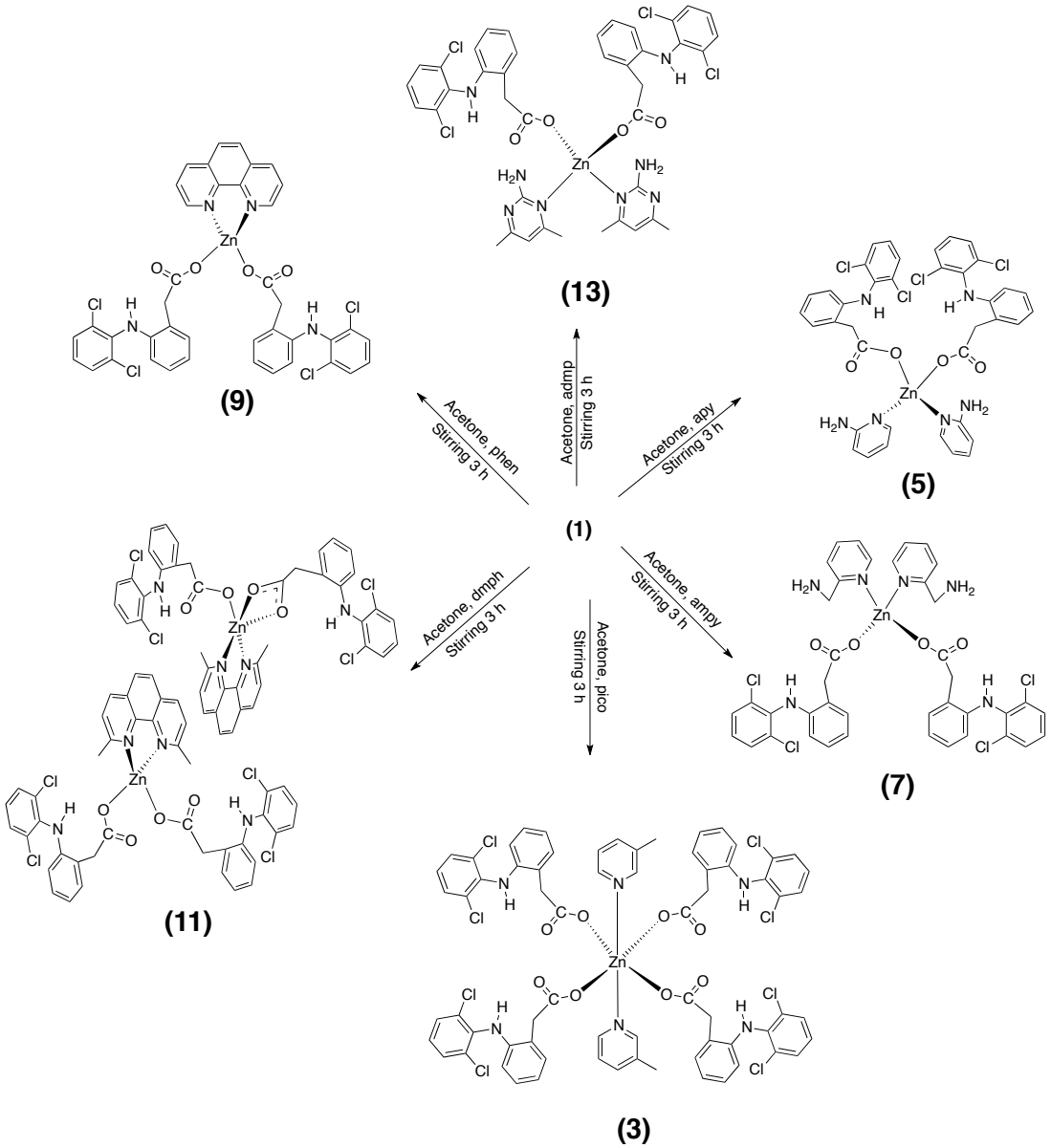


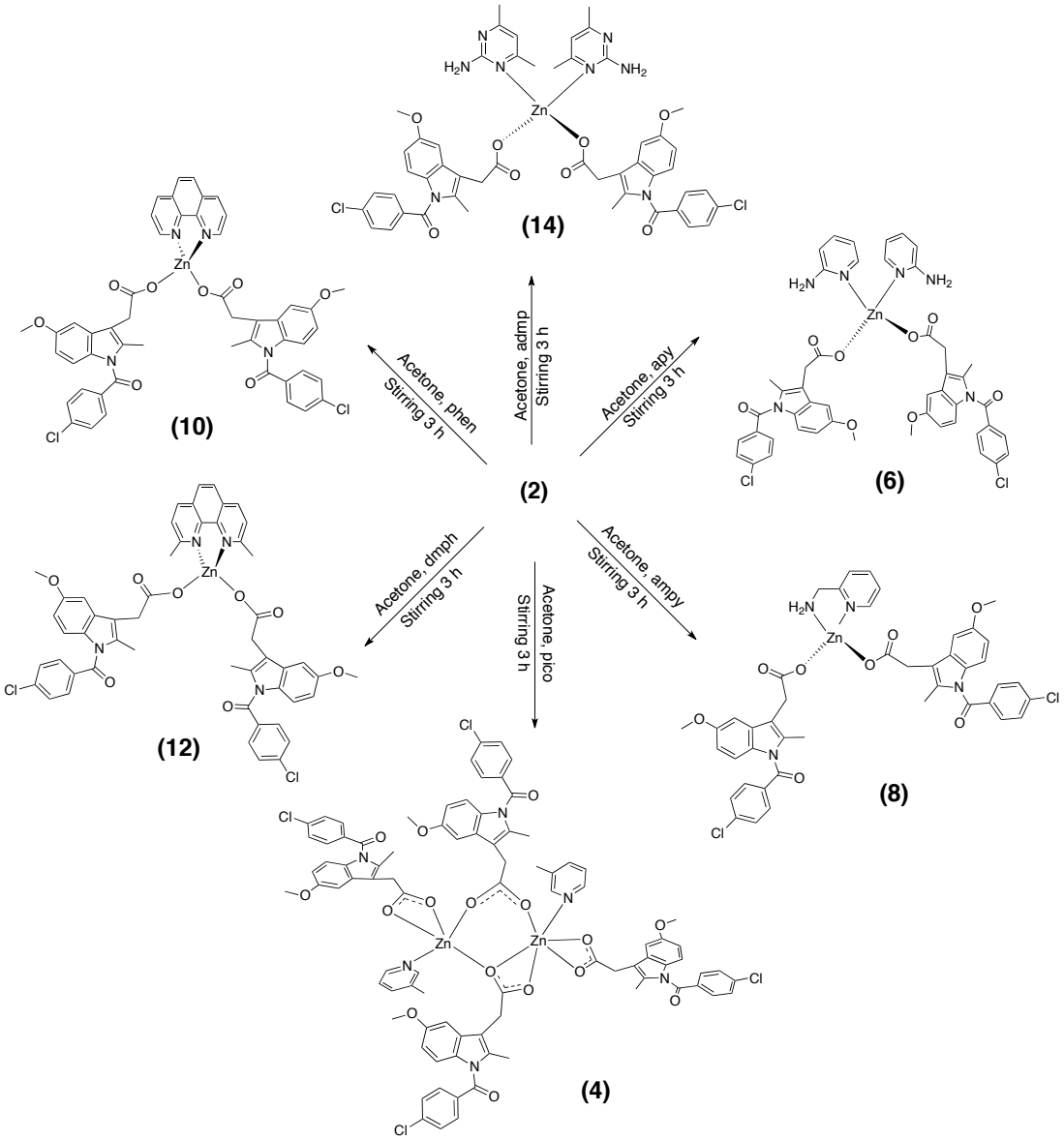
Figure 3.2: Synthesis of Zn indomethacin complex **(2)**

A series of novel mixed ligand zinc complexes have been synthesized by reacting zinc diclofenac complex or zinc indomethacin complex with the corresponding N-donor ligand. The proposed structures for these complexes are shown in Schemes (3.1 and 3.2).

Scheme 3.1: Proposed molecular structure of zinc diclofenac complexes.



Scheme 3.2: Proposed molecular structure of zinc indomethacin complexes.



Complexes **(4)**, **(5)**, **(6)**, **(8)**, **(10)**, **(13)** and **(14)** are soluble in reaction solvent (acetone), but the others are insoluble. Melting point, % yield, and solubility of the synthesized complexes were presented in (Table 3.1).

Table 3.1: Physical properties of zinc diclofenac and zinc indomethacin complexes.

Complex	m.p. (°C)	% Yield	Solubility
$[Zn_2(diclo)_2(H_2O)_2]$ **(1)**	252[a]	86	Methanol, ethanol, acetone, dichloromethane, hot DMSO
$[Zn_2(Indo)_4]$ **(2)**	190[a]	66	Acetone, chloroform, hot DMSO
$[Zn(diclo)_4(pico)_2]$ **(3)**	118-120	57	Methanol, ethanol, dichloromethane, chloroform, DMSO
$[Zn_2(indo)_4(pico)_2]$ **(4)**	186-188	50	Acetone, dichloromethane, chloroform, DMSO
$[Zn(diclo)_2(apy)_2]$ **(5)**	184-185	72	Acetone, chloroform, DMF, DMSO
$[Zn(indo)_2(apy)_2]$ **(6)**	95[a]	60	Acetone, dichloromethane, DMF, DMSO
$[Zn(diclo)_2(ampy)]$ **(7)**	237-241	76	Chloroform, dichloromethane, DMF, DMSO
$[Zn(indo)_2(ampy)]$ **(8)**	117-120	78	Methanol, ethanol, acetone, chloroform, dichloromethane, acetonitrile, DMF, DMSO
$[Zn(diclo)_2(phen)]$ **(9)**	273[a]	75	Hot DMSO
$[Zn(indo)_2(phen)]$ **(10)**	248[a]	80	Dichloromethane, chloroform, hot acetone, hot DMSO
$[Zn(diclo)_2(dmph)]$ **(11)**	255[a]	76	Chloroform, dichloromethane, hot DMSO
$[Zn(indo)_2(dmph)]$ **(12)**	235-237	94	Chloroform, dichloromethane, hot DMSO
$[Zn(diclo)_2(admp)_2]$ **(13)**	155[a]	60	Acetone, chloroform, dichloromethane, DMSO
$[Zn(indo)_2(admp)_2]$ **(14)**	115-118	90	Acetone, chloroform, dichloromethane, DMSO and acetonitrile

a: decomposition

3.2 Infrared spectral results

It is known that IR spectroscopy is a useful tool for predicting the structure of chemical compounds or it might provide a clue about the present functional groups, and their binding modes.

For metal complexes that contains carboxylate groups directly coordinated to metal, the major characteristic frequency in IR spectra is the symmetric and asymmetric stretching vibration and the separation between them $\Delta\nu(COO^{-})$, The frequency of these bands greatly affected by the coordination mode between the ligand and the metal. As mentioned earlier, $\Delta\nu(COO^{-})$ is much greater for monodentate binding mode than for ionic binding mode, while it is much less than ionic for chelating binding mode, while for bridging binding mode it is greater than chelating and less or so close to that of ionic binding mode[111].

IR spectral data such as assignments frequency of the principal peaks and comparasion with the free parent ligands; diclofenac sodium, indomethacin sodium and nitrogen donor ligands, are summarized in Tables 3.2 - 3.5 below

The assignment of selected IR vibration peaks of diclofenac sodium and zinc diclofenac complex are presented in Table 3.2. The asymmetric and symmetric stretching frequency of carboxylate groups of the diclofenac sodium occur at 1556 cm^{-1} and 1405 cm^{-1}, respectively, and $\Delta\nu(COO^{-})$ = 151 cm^{-1}, while for the zinc diclofenac complex **(1)** $\Delta\nu(COO^{-})$ = 173 cm^{-1}, indicating mondentate coordination mode, as also confirmed by single crystal structure determination of complex **(1)**.

Table 3.2: Principal IR vibrational frequencies for diclofenac sodium and complex **(1),** (cm^{-1}).

Assignments	Diclofenac sodium	Zinc diclofenac **(1)**
ν(N-H)	3400 3280	3283
$\nu(C\text{-}H)_{ar}$	3070 3020	3075 3035
$\nu(C\text{-}H)_{aliph}$	2960 2920	2975 2928
ν(ring)	1590 1450	1578 1454
δ(N-H)	1500	1511, 1500
$\delta(CH_2)$	1475	1474
$\nu_{as}(COO^-)$	**1556**	**1572**
$\nu_{s}(COO^-)$	**1405**	**1399**
$\Delta_{\nu}(COO^-)$	**151**	**173**

As shown in Table 3.3 below $\Delta\nu(COO^-)$ for indomethacin sodium was 190 cm^{-1} while that for complex **(2)** was 186 cm^{-1}, indicating bridging binding mode, as shown by Zhou Q. *et al*[112].

Table 3.3: Principal IR vibrational frequencies for indomethacin sodium and complex **(2),** (cm^{-1}).

Assignments	Indomethacin	Zinc indomethacin **(2)**
$\nu(C\text{-}H)_{ar}$	3015	3005
$\nu(C\text{-}H)_{aliph}$	2995 2977	2970 2923
Amide I band	1678	1681
ν(ring)	1535 1440	1575 1465
$\delta(CH_2)$	1467	1475
$\delta(CH_3)$	1437	1437
$\nu_{as}(COO^-)$	**1590**	**1587**
$\nu_{s}(COO^-)$	**1400**	**1401**
$\Delta_{\nu}(COO^-)$	**190**	**186**

The IR stretching vibration frequencies and $\Delta\nu(COO^-)$ for of zinc diclofenac complexes and zinc indomethacin complexes are summarized in Tables 3.4 and 3.5, respectively.

Table 3.4: Assignments of principal IR vibrational frequencies for zinc diclofenac complexes and $\Delta\nu(COO^-)$, (cm^{-1}).

Assignments	**(3)**	**(5)**	**(7)**	**(9)**	**(11)**	**(13)**
ν(N-H)	3251	3440 3315 3210	3477 b 3332 3232	3436 b 3244	3475 b 3248	3447 3369 3182
$\nu(C\text{-}H)_{ar}$	3082 3040	3060 3017	3091 3041	3096 3057	3076	3080 3034
$\nu(C\text{-}H)_{aliph}$	2977 2927	2940 2860	2914 2938 2864	2982 2915 2857	2945 2922 2841	2975 2927 2845
ν(ring)	1579 1551 1497 1450	1619(C=N) 1611 1565 1498 1452	1613 1590 1562 1492 1453	1586 1574 1559 1517 1450	1575 1561 1504 1453	1621 (C=N) 1591 1565 1540 1451
δ(N-H)	1510	1587 1510	1578 1503	1515	1510	1511
$\delta(CH_2)$	1469	1470	1495	1476	1474	1476
$\delta(CH_3)$	1432				1425	1428
$\nu_{as}(COO^-)$	**1604**	**1653**	**1663**	**1600**	**1617**	**1673**
$\nu_s(COO^-)$	**1403**	**1378**	**1407**	**1400**	**1379**	**1400**
$\Delta\nu(COO^-)$	**201**	**275**	**256**	**200**	**238**	**273**

Table 3.5: Assignments of principal IR peaks for zinc indomethacin complexes and $\Delta\nu(COO^-)$, (cm^{-1}).

Assignments	**(4)**	**(6)**	**(8)**	**(10)**	**(12)**	**(14)**
ν(N-H)		3337 3227	3432 3337 3278			3421 3330 3152
$\nu(C\text{-}H)_{ar}$	3119 3078	3113 3082	3114 3091	3093 3068	3080	3000
$\nu(C\text{-}H)_{aliph}$	2966 2923 2841	2932 2925 2841	2940 2925 2852	2995 2973 2922	2961 2926 2830	2957 2925 2852
Amide I band	1682	1677	1682	1677	1667	1658
νC=C	1620	1620	1620	1625	1613	1620
ν(ring)	1588 1575 1479 1369	1592 1498 1354 1326	1590 1440 1356 1322	1597 1586 1519 1428	1591 1510 1427 1400	1612 (C=N) 1596 1375
δ(N-H)		1565	1565			1570
$\delta(CH_2)$	1460	1477	1477	1475	1480	1468
$\delta(CH_3)$	1456	1454	1460	1460	1458	1437
$\nu_{as}(COO^-)$	**1614**	**1609**	**1606**	**1608**	**1625**	**1677**
$\nu_s(COO^-)$	**1394**	**1398**	**1397**	**1396**	**1371**	**1399**
$\Delta\nu(COO^-)$	**220**	**211**	**209**	**212**	**254**	**278**

In all zinc diclofenac and zinc indomethacin complexes $\Delta\nu(COO^-)$ are greater than $\Delta\nu(COO^-)$ in the sodium salt indicating monodentate coordination modes.

In complexes **(5)**, **(6)**, **(7)**, **(8)**, **(13)**, **(14)**, the symmetric and asymmetric N-H stretching frequency were shifted to lower energy due to coordination of N-donor ligand to metal, and due to formation of hydrogen bonds.

For complex **(5)**, the primary amino group streches asymmetrically and symmetrically at 3440 and 3315 cm^{-1}, respectively, with $\Delta\nu$(N-H) = 125 cm^{-1} which was less than that of free ligand as $\Delta\nu$(N-H) = 276 cm^{-1}indicating the presence of hydrogen bonding in complex **(5)**. However in complex **(6)** the asymmetric and symmetric ν(N-H) of the primary amino group occurs at 3337 and 3227 cm^{-1}, respectively, with $\Delta\nu$(N-H) = 110 $cm^{-1,}$ which is less than that of free ligand, $\Delta\nu$(N-H) = 276 cm^{-1}, indicating hydrogen bonding.

For complex **(7)** primary amino group stretches asymetrically and symmetrically at 3477 and 3332 cm^{-1}, respectively, $\Delta\nu$(N-H) = 145 cm^{-1}, which is less than that of free ligand , $\Delta\nu$(N-H) = 174 cm^{-1}, indicating hydrogen bonding. The same conclusion for complex **(8)**, as $\Delta\nu$(N-H) = 95 cm^{-1}.

In complex **(13)**, ν_{as}(N-H) and ν_s(N-H) of 2-amino-4,6-dimethyl pyrimidine are 3447 and 3182 cm^{-1}, respectively. Some peaks are broad, and others are shifted to lower frequency, indicating the presence of hydrogen bonding. The same results can be concluded for complex **(14)**, with two amino group ν(N-H) frequencies, 3421 and 3152 cm^{-1}, which are broad and shifted to a lower frequency.

3.3 Electronic absorption spectral results

Electronic absorption measurements in the range of 200-800 nm for **1-14** complexes were performed in DMSO. The maximum absorptions were similar to those of free parent ligands, except small shift in the maximas as a result of their coordination to the zinc metal ion. No *d-d* transition or ligand to metal charge transfer are expected for a d^{10} Zn(II) complexes, the only possible transitions are metal to ligand charge transfer and transfers among the ligands itself; π-π* or non bonding-π*.

Table 3.6: UV-Vis spectral data for complexes **1-14**

Complex	**UV-Vis λ max (nm)**
$[Zn_2(diclo)_2\ (H_2O)_2]$ **(1)**	284
$[Zn_2(Indo)_4]$ **(2)**	319
$[Zn(diclo)_4(pico)_2]$ **(3)**	283, 270
$[Zn_2(indo)_4(pico)_2]$ **(4)**	319, 268
$[Zn(diclo)_2(apy)_2]$ **(5)**	291
$[Zn(indo)_2(apy)_2]$ **(6)**	319, 274
$[Zn(diclo)_2(ampy)]$ **(7)**	287, 268
$[Zn(indo)_2(ampy)]$ **(8)**	320, 265
$[Zn(diclo)_2(phen)]$ **(9)**	290, 267
$[Zn(indo)_2(phen)]$ **(10)**	318, 267
$[Zn(diclo)_2(dmph)]$ **(11)**	284, 273
$[Zn(indo)_2(dmph)]$ **(12)**	319, 271
$[Zn(diclo)_2(admp)_2]$ **(13)**	285
$[Zn(indo)_2(admp)_2]$ **(14)**	322, 271

3.4 ^{1}H and ^{13}C{^{1}H}NMR spectral results

^{1}H-NMR and ^{13}C{^{1}H}-NMR spectral data of complexes **1-14** in addition to their parent ligands are listed in Tables 3.7 – 3.20 (Appendix A)

Shifts in the ^{1}H-NMR and ^{13}C{1H}-NMR ligand's responses have been observed due to complexation to Zn(II).

Integration parameter has been used to assist in the assignment of ^{1}H-NMR resonances and prediction of the coordination sphere and stoichiometric. In which the ratio between the carboxylate groups complexes and N-based ligands in complexes **(5)**, **(6)**, **(7)**, **(13), (14)** was 1:1, while it was 2:1 in **(3)**, **(4)**, **(8)**, **(9)**, **(10)**, **(11)**, **(12)**

From the IR spectral analysis we may conclude that for complexes **3-14** the carboxylate groups are monodentatelly coordinated to Zn(II). However, based on ^{1}H-NMR results, complexes with 1:1 stoichiometric ratio between the carboxylate groups and nitrogen based ligands force the complex to adopt tetrahedral arrangement. Complexes with 2:1 molar ratio between carboxylate groups and bidentate nitrogen based ligands adopted tetrahedral arrangement around the central Zn(II) cation. Whereas, 2:1 molar ratio between carboxylate groups and monodintate nitrogen based ligands adopted octahedral or square pyramidal arrangement.

3.5 X-Ray crystal structure analysis

The crystal structures of complexes **(1)**, **(4)**, **(5)** and **(11)** have been determined, suitable crystals were obtained by recrystallization from 4:1 mixture of CH_3OH and DMSO for **(1)**, for **(4)** and (**5)** from acetone, and for **(11)** from 1:1 mixture of CH_2Cl_2 and CH_3OH.

Crystal data and parameters for data collection are reported in Tables 2.1 and 2.2. The complete crystallographic information files (CIF) are given in the Appendices B-F in the attached CD.

3.5.1 Crystal structure of $[Zn(diclo)_2(H_2O)_2]$ (1)

An ORTEP diagram with the labeling scheme of $[Zn(diclo)_2(H_2O)_2]$ complex is shown in Figure 3.3 selected inter-atomic distances and angles are found in Table 3.21.

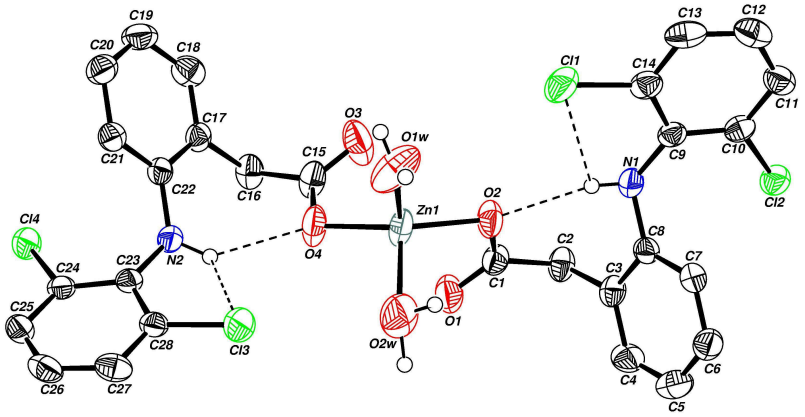


Figure 3.3: ORTEP view of molecular structure of $[Zn(diclo)_2(H_2O)_2]$ **(1)**.

The mononuclear $[Zn(diclo)_2(H_2O)_2]$ complex crystallizes in orthorhombic crystal system and Pna2(1) space group. The asymmetric unit consist of one Zn(II), two diclofenac, and two coordinated water molecules. Zn(II) is coordinated by two carboxylate oxygen atoms from two different diclofenac molecules (O2 and O4) and two water molecules (O1W and O2W) making distorted tetrahedral environment. This distortion exemplified by the angles; O(2)-Zn(1)-O(4) = 133.98, (14) O(2)-Zn(1)-O(1W) = 106.31(16), O(4)-Zn(1)-O(1W) = 106.42(17), O(2)-Zn(1)-O(2W) = 105.43(17), O(4)-Zn(1)-O(2W) = 102.28(15), O(1W)-Zn(1)-O(2W) = 96.1(2).

Tbale 3.21: Selected bond distances (Å) and angles (°) for complex (**1)**

Bond distance (Å)		Bond angle (°)	
C(1)-O(1)	1.232(5)	O(1)-C(1)-O(2)	120.9(4)
C(1)-O(2)	1.282(5)	O(3)-C(15)-O(4)	121.7(4)
C(15)-O(3)	1.214(6)	O(2)-Zn(1)-O(4)	133.98(14)
C(15)-O(4)	1.255(5)	O(2)-Zn(1)-O(1W)	106.31(16)
O(2)-Zn(1)	1.945(2)	O(4)-Zn(1)-O(1W)	106.42(17)
O(4)-Zn(1)	1.951(3)	O(2)-Zn(1)-O(2W)	105.43(17)
O(1W)-Zn(1)	1.989(4)	O(4)-Zn(1)-O(2W)	102.28(15)
O(2W)-Zn(1)	2.048(4)	O(1W)-Zn(1)-O(2W)	96.1(2)

The O(2)-Zn(1) and O(4)-Zn(1) bond lengths are 1.945(2) Å and 1.951(3) Å, respectively, which are in accord with similar bond between Cu(II) and diclofenac, 1.9342(2) Å[128], 1.9446(15) Å[129], (1.941-2.1934) Å[130]. Further more, these values are in the range of Zn-O distances of monodentate acetate complexes (1.84-2.33 Å)[131].

The carboxylate groups are monodentatelly coordinated to Zn(II) , which is ensured by the significant difference in the bond length of coordinated C(1)-O(2) =

1.282(5) Å and C(15)-O(4) = 1.255(5) Å and free C(1)-O(1) = 1.232(5) Å, C(15)-O(3) = 1.214(6) Å, oxygen atoms of diclofenac carboxylate groups.

Hydrogen bonding for complex **(1)** summarized in Table 3.22, shows that there are intermolecular hydrogen bonding, O(2W)-H(2W2)...O(5)$^{\#1}$ = 2.56, O(2W)-H(1W2)...O(3)$^{\#2}$ = 2.27, O(1W)-H(1W1)...O(1)$^{\#3}$ = 1.89, O(5)-H(1O5)...O(3)$^{\#2}$ = 2.05 that occur between four different molecules of complex **(1)** and intramolecular hydrogen bonding, O(1W)-H(2W1)...O(5) = 1.86, N(2)-H(1N2)...Cl(3) = 2.45, N(2)-H(1N2)...O(4) = 2.24, N(1)-H(1N1)...Cl(1) = 2.75, N(1)-H(1N1)...O(2) = 2.18, these hydrogen bonding stabilizes and affect the geometry of the complex.

Table 3.22: Hydrogen bonds for complex **(1)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2W)-H(2W2)...O(5)#1	1.04	2.56	3.57(2)	165.5
O(2W)-H(1W2)...O(3)#2	0.81	2.27	2.707(5)	114.7
O(1W)-H(2W1)...O(5)	0.84	1.86	2.665(9)	160.9
O(1W)-H(1W1)...O(1)#3	0.81	1.89	2.672(6)	162.8
O(5)-H(1O5)...O(3)#2	0.85	2.05	2.898(19)	178.8
N(2)-H(1N2)...Cl(3)	0.89	2.45	2.995(4)	120.3
N(2)-H(1N2)...O(4)	0.89	2.24	2.957(4)	137.6
N(1)-H(1N1)...Cl(1)	0.81	2.75	2.982(4)	98.7
N(1)-H(1N1)...O(2)	0.81	2.18	2.967(4)	165.6
Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,z+1/2 #2 -x+1/2,y+1/2,z+1/2 #3 -x+1/2,y+1/2,z-1/2				

In attempts to crystallize [Zn(diclo)$_2$(admp)$_2$] **(13)**, in 3:1 mixture of CH_3OH : DMSO, a new [Zn(diclo)$_2$(DMSO)$_2$] complex was obtained, (Figure 3.4).

An ORTEP diagram with the labeling scheme of $[Zn(diclo)_2(DMSO)_2]$ complex is shown in Figure 3.4 selected inter-atomic distances and angles are found in Table 3.23.

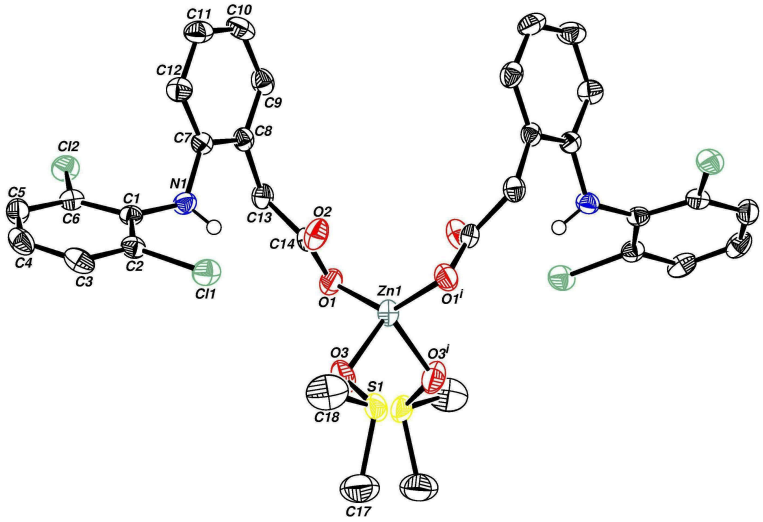


Figure 3.4: ORTEP view of molecular structure of **$[Zn(diclo)_2(DMSO)_2]$**.

The mononuclear $[Zn(diclo)_2(DMSO)_2]$ complex crystallizes in orthorhombic crystal system and Pbcn space group. The symmetric unit consist of one Zn(II), two monodentate diclofenac groups, and two DMSO molecules making distorted tetrahedral environment. Zn-O distances were in the range 2.0376 – 2.0457 Å which is in accordance with similar bond lenghts[131].

Tbale 3.23: Selected bond distances (Å) and angles (°) for complex $Zn(diclo)_2(DMSO)_2]$.

Bond distance (Å)		Bond angle (°)	
O(1)-Zn(1)	2.0376(17)	O(1)-Zn(1)-O(3)	110.03(7)
Zn(1)-O(1)#1	2.0376(17)	O(1)#1-Zn(1)-O(1)	138.54(9)
O(2)-Zn(1)	2.3459(17)	O(1)#1-Zn(1)-O(3)#1	110.03(7)
Zn(1)-O(2)#1	2.3459(17)	O(1)#1-Zn(1)-O(3)	97.91(7)
O(3)-Zn(1)	2.0457(16)	O(1)-Zn(1)-O(3)#1	97.91(7)
Zn(1)-O(3)#1	2.0457(16)	O(3)-Zn(1)-O(3)#1	94.60(11)
C(14)-O(2)	1.242(3)		
C(14)-O(1)	1.273(3)		
O(3)-S(1)	1.5196(17)		

3.5.2 Crystal structure of $[Zn_2(indo)_4(pico)_2]$ (4)

An ORTEP diagram with the labeling scheme of $[Zn_2(indo)_4(pico)_2]$ complex is shown in Figure 3.5.

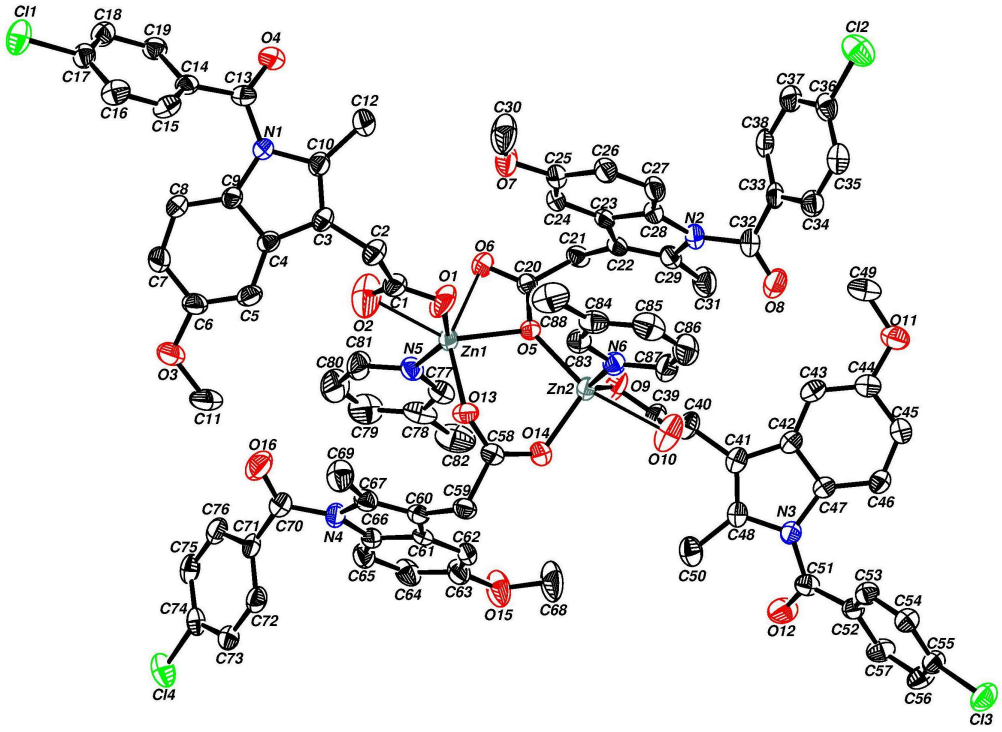


Figure 3.5: ORTEP view of molecular structure of $[Zn_2(indo)_4(pico)_2]$ **(4).**

Selected inter-atomic distances and angles are found in Table 3.24 and Table 3.25, respectively. The dinuclear $[Zn_2(indo)_4(pico)_2]$ complex crystallizes in triclinic crystal system and P-1 space group.

The binuclear complex consists of two Zn(II) centers, Zn1 center that is N_1O_5 hexacoordinated, and Zn2 center that is N_1O_4 pentacoordinated. The binuclear complex contains two 3-picoline molecules, in which one 3-picoline molecule coordinated to Zn1 center and the other coordinated to Zn2 center through pyridyl

nitrogen atom. Also the complex contains four indomethacin molecules, two of them coordinated in bidentate chelating to Zn(II) cation; one indomethacin molecule to each one of the Zn(II) center, the third indomethacin molecule coordinated to Zn(II) centers in a syn-syn bridging binding mode, while the fourth indomethacin molecule coordinated in monodentate terminal bidging binding mode.

Table 2.24: Selected bond distances Å for complex **(4)**

Bond distance Å		Bond distance Å	
N(5)-Zn(1)	2.027(3)	C(1)-O(2)	1.209(5)
N(6)-Zn(2)	2.031(3)	C(1)-O(1)	1.241(5)
O(1)-Zn(1)	1.995(3)	C(20)-O(6)	1.219(4)
O(2)-Zn(1)	2.403(3)	C(20)-O(5)	1.289(4)
O(5)-Zn(2)	2.025(2)	C(39)-O(10)	1.224(4)
O(5)-Zn(1)	2.081(2)	C(39)-O(9)	1.248(4)
O(6)-Zn(1)	2.381(3)	C(58)-O(13)	1.246(4)
O(9)-Zn(2)	1.979(3)	C(58)-O(14)	1.256(4)
O(10)-Zn(2)	2.386(3)		
O(13)-Zn(1)	2.035(2)		
O(14)-Zn(2)	1.974(2)		

Zn-O bond distances are between of 1.974-2.403 Å, as it is reported by (Kremer-Aach et al., 1997) in which Zn-O distances of bidentate carboxylates varies over a wide range and different values as 1.932 and 2.460 Å showing a greatest asymmetry in this binding mode to metals[131], Zn-O of bridging indomethacin are within 1.975-2.081 Å which is in accordance with similar bonds of ($Zn_2(indo)_4L_2$) complexes[112] that occur in the range of 2.038 Å.

Zn-N bond distance are N(5)-Zn(1) = 2.027(3) and N(6)-Zn(2) = 2.031(3) which is in agreement with other Zn-N bond length = 2.055 A in [$Zn_3(bba)_6(3\text{-pic})_2$] Complex[132].

Selected bond angles presented in Table 3.25 shows that the geometries around Zn1 and Zn2 centers, respectively, are distorted octahedral and distorted trigonal bi-pyramidal as a results of formation of four membered rings and bridging ligands between these two centers.

Table 2.25: Selected bond angles (°) for complex **(4)**

Bond angle (°)		Bond angle (°)	
O(1)-Zn(1)-N(5)	149.36(13)	O(14)-Zn(2)-O(9)	109.73(12)
O(1)-Zn(1)-O(13)	94.05(12)	O(14)-Zn(2)-O(5)	102.11(10)
N(5)-Zn(1)-O(13)	96.47(11)	O(9)-Zn(2)-O(5)	95.56(10)
O(1)-Zn(1)-O(5)	100.97(11)	O(14)-Zn(2)-N(6)	109.15(11)
N(5)-Zn(1)-O(5)	107.90(11)	O(9)-Zn(2)-N(6)	134.79(13)
O(13)-Zn(1)-O(5)	88.98(9)	O(5)-Zn(2)-N(6)	98.02(10)
O(1)-Zn(1)-O(6)	96.39(13)	O(14)-Zn(2)-O(10)	98.26(11)
N(5)-Zn(1)-O(6)	90.81(11)	O(9)-Zn(2)-O(10)	57.89(10)
O(13)-Zn(1)-O(6)	145.91(9)	O(5)-Zn(2)-O(10)	151.02(10)
O(5)-Zn(1)-O(6)	57.20(8)	N(6)-Zn(2)-O(10)	94.49(11)
O(1)-Zn(1)-O(2)	56.97(12)	Zn(2)-O(5)-Zn(1)	123.26(10)
N(5)-Zn(1)-O(2)	92.68(12)	O(2)-C(1)-O(1)	120.6(4)
O(13)-Zn(1)-O(2)	116.22(14)	O(6)-C(20)-O(5)	118.2(3)
O(5)-Zn(1)-O(2)	145.74(12)	O(10)-C(39)-O(9)	120.1(3)
O(6)-Zn(1)-O(2)	96.54(13)	O(13)-C(58)-O(14)	125.3(3)

3.5.3 Crystal structure of $[Zn(diclo)_2(apy)_2]$ (5)

An ORTEP diagram with the labeling scheme of $[Zn(diclo)_2(apy)_2]$ complex is shown in Figure 3.6.

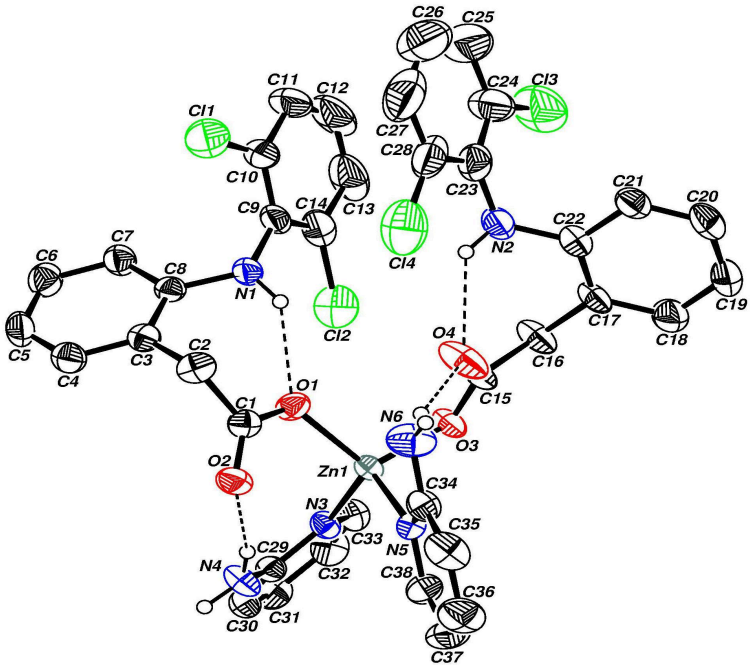


Figure 3.6: ORTEP view of molecular structure of $[Zn(diclo)_2(dapy)_2]$ **(5).**

Selected inter-atomic distances and angles are found in Table 3.26 .

Table 3.26: Selected bond distances Å and angles (°) for complex (**5**)

Bond distance Å		Bond angle (°)	
C(1)-O(2)	1.230(6)	O(2)-C(1)-O(1)	124.6(5)
C(1)-O(1)	1.284(6)	O(4)-C(15)-O(3)	123.7(5)
C(15)-O(4)	1.216(7)	O(1)-Zn(1)-O(3)	112.00(16)
C(15)-O(3)	1.279(6)	O(1)-Zn(1)-N(5)	111.96(16)
N(3)-Zn(1)	2.037(4)	O(3)-Zn(1)-N(5)	111.17(17)
N(5)-Zn(1)	2.016(4)	O(1)-Zn(1)-N(3)	111.03(17)
O(1)-Zn(1)	1.949(4)	O(3)-Zn(1)-N(3)	100.92(17)
O(3)-Zn(1)	1.956(4)	N(5)-Zn(1)-N(3)	109.23(17)

The mononuclear [Zn(diclo)2(dmph)] complex crystallizes in triclinic crystal system and P-1 space group. The asymmetric unit consist of one Zn(II), two diclofenac, and two 2-aminopyridine molecules. Zn(II) is tetrahedraly coordinated by two carboxylate oxygen atoms from two different diclofenac molecules (O1 and O3) and two nitrogen atoms from two 2-aminopyridine molecules. The tetrahedral environment is slightly distorted as exemplified by the angles; O(1)-Zn(1)-O(3) = 112.00(16), O(1)-Zn(1)-N(5) = 111.96(16), O(3)-Zn(1)-N(5) = 111.17(17) O(1)-Zn(1)-N(3) = 111.03(17), O(3)-Zn(1)-N(3) = 100.92(17), N(5)-Zn(1)-N(3) = 109.23(17).

The bond length of O(1)-Zn(1) and O(3)-Zn(1), are 1.949(4), 1.956(4), respectively, similar to that of $[Zn(diclo)_2(H_2O)_2]$ **(1)**, mentioned above, and in accords with similar bonds between Cu(II) and diclofenac, 1.9342(2) Å[128], 1.9446(15) Å1[129], (1.941-2.1934) Å[130]. In addition N(3)-Zn(1) , N(5)-Zn(1), bond distances are 2.037(4), 2.016(4) which are is the same range of similar bonds between zinc and 2-aminopyridine in other complexes, 2.052Å[133], 2.068 Å[134], (2.0643-2.726) Å[135].

C-O bond length of coordinated oxygens C(1)-O(1) = 1.284(6), C(15)-O(3) = 1.279(6) are longer than that of free ones C(1)-O(2) = 1.230(6), C(15)-O(4) = 1.216(7), respectively, indicating that diclofenac molecules are monodintately coordinated to Zn(II) center. That is also confirmed by IR results as $\Delta\nu(COO^-)$ for ionic diclofenac is 151 while it is for complexed one is 275 which is much greater

indicating monodentate binding mode.

Hydrogen bonding for complex **(5)**, are shown in Table 3.27. The data show only one intermolecular hydrogen bonding N(4)-H(2N4)...O(2)$^{\#1}$ = 2.12(3), and five intramolecular hydrogen bonds. This inter- and intra-molecular hydrogen bonding affects the stability and geometry of the complex.

Table 3.27: Hydrogen bonds for complex **(5)** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D...A)	<(DHA)
N(6)-H(1N6)...O(4)	0.851(10)	2.06(2)	2.896(8)	169(9)
N(4)-H(2N4)...O(2)#1	0.850(10)	2.12(3)	2.918(6)	156(7)
N(4)-H(1N4)...O(2)	0.851(10)	2.05(2)	2.882(7)	167(8)
N(2)-H(1N2)...Cl(4)	0.851(10)	2.52(5)	2.968(6)	114(5)
N(2)-H(1N2)...O(4)	0.851(10)	2.21(4)	2.881(7)	136(5)
N(1)-H(1N1)...O(1)	0.850(10)	2.16(4)	2.887(6)	143(6)
Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z				

3.5.4 Crystal structure of [Zn(diclo)$_2$(dmph)] (11)

An ORTEP diagram with the labeling scheme of [Zn(diclo)$_2$(dmph)] complex is shown in Figure 3.7.

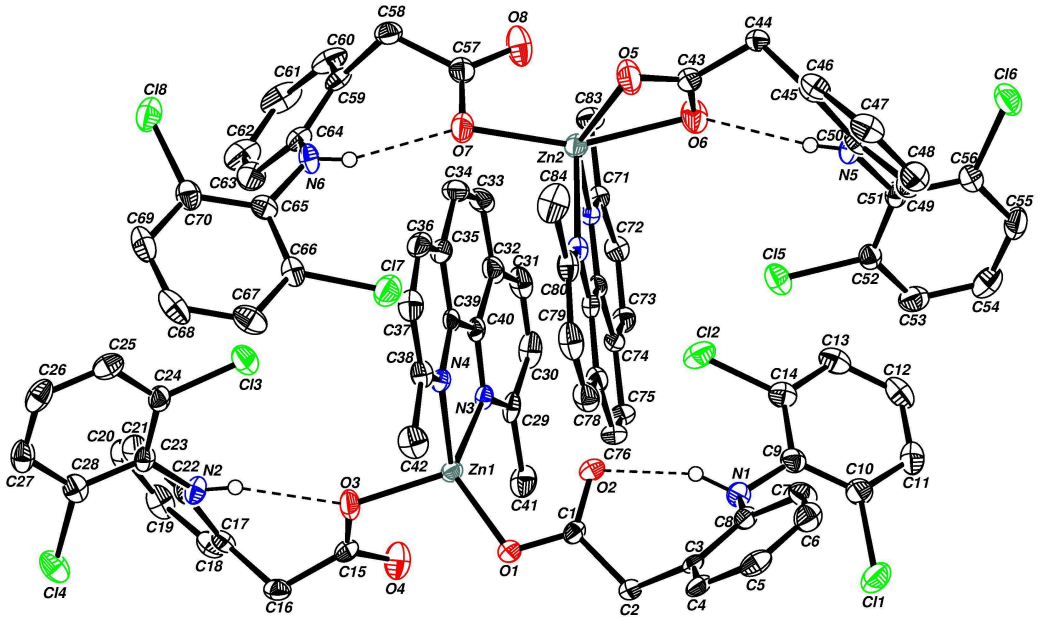


Figure 3.7: ORTEP view of molecular structure of [Zn(diclo)$_2$(dmph)] **(11)**.

Selected inter-atomic distances and angles are found in Tables 3.28 and 3.29 respectively.

Table 3.28: Selected bond distances Å for complex **(11)**

Distance Å		Distance Å	
N(3)-Zn(1)	2.066(4)	N(7)-Zn(2)	2.113(4)
N(4)-Zn(1)	2.072(4)	N(8)-Zn(2)	2.112(4)
O(1)-Zn(1)	1.946(3)	O(5)-Zn(2)	2.113(4)
O(3)-Zn(1)	2.010(3)	O(6)-Zn(2)	2.222(4)
		O(7)-Zn(2)	2.104(4)
		O(8)-Zn(2)	2.281(5)

The mononuclear [Zn(diclo)$_2$(dmph)] complex crystallizes in triclinic crystal system and P-1 space group. For the two molecules per unit cell, there is one center Zn(1) cation, that is N_2O_2 tetracoordinated to two diclofenac, and one 2,9-dimethyl-1,10-phenanthroline molecule, producing tetrahedral environment. The other center Zn(2) is N_2O_3 pentacoordenated to two diclofenac, and one 2,9-dimethyl-1,10-phenanthroline molecule, producing distorted trigonal bipyramidal environment. For N_2O_3 pentacoordenation in which one carboxylate group is bidentate to Zn(II) is not very common in Zn(II) chemistry[131].

For Zn(1) and Zn(2) centers, the bidentate 2,9 dimethyl-1,10-phenanthroline ligand bound symmetrically with bond distances N(3)-Zn(1) = 2.066(4) Å, N(4)-Zn(1) = 2.072 Å, N(7)-Zn(1) = 2.113(4) Å, N(8)-Zn(1) = 2.112(4) Å. These distances are in the range of other Zn(II) 2,9 dimethyl-1,10-phenanthroline complexes[131, 136-138].

Two diclofenac molecules coordinated monodentatelly to Zn(1) center with Zn-O distances O(1)-Zn(1) = 1.946(3) Å, O(3)-Zn(1) = 2.010(3) Å, again this values are in the range of Zn-O distances of monodentate acetate complexes (1.84-2.33 Å)[131]. While for Zn(2) center; one of the diclofenac molecules is coordinated in a bidentate chelate fashion to Zn(2), and the other molecule coordinated monodentatelly to the same Zn(2) center. Zn-O distances for bidentate ligand are O(5)-Zn(2) = 2.113(4) Å, O(6)-Zn(2) = 2.222(4) Å, which are comparable to (1.941-2,1934) Å Cu-O bond distances in [Cu(diclo)$_2$(4-pico)$_2$] octahedral complex[130]. In addition they are in the range of Zn-O distances of bidentate acetate complexes

(1.932-2.460 Å)[131]. While that distance for monodentate is O(7)-Zn(2) = 2.104(4), which is also in the respective range.

For Zn(1) center all angles are within the expected range for distorted tetrahedral except that for N(3)-Zn(1)-N(4) = 81.53(15) (°) and resulted from rigidity of the dmph ligand that forms a five-membered ring upon chelation to metal.

Table 3.29: Selected bond angles (°)for complex **(11)**

Bond angle (°)		Bond angle (°)	
O(2)-C(1)-O(1)	121.5(4)	O(5)-C(43)-O(6)	120.3(5)
O(4)-C(15)-O(3)	121.1(5)	O(8)-C(57)-O(7)	120.3(5)
O(1)-Zn(1)-O(3)	106.06(15)	O(7)-Zn(2)-N(8)	95.27(14)
O(1)-Zn(1)-N(3)	125.41(15)	O(7)-Zn(2)-O(5)	105.13(16)
O(3)-Zn(1)-N(3)	120.81(15)	N(8)-Zn(2)-O(5)	101.58(16)
O(1)-Zn(1)-N(4)	119.55(15)	O(7)-Zn(2)-N(7)	108.38(16)
O(3)-Zn(1)-N(4)	98.16(15)	N(8)-Zn(2)-N(7)	80.34(14)
N(3)-Zn(1)-N(4)	81.63(15)	O(5)-Zn(2)-N(7)	146.12(14)
		O(7)-Zn(2)-O(6)	156.99(15)
		N(8)-Zn(2)-O(6)	104.47(15)
		O(5)-Zn(2)-O(6)	59.74(14)
		N(7)-Zn(2)-O(6)	86.82(13)
		O(7)-Zn(2)-O(8)	58.61(14)
		N(8)-Zn(2)-O(8)	153.52(14)
		O(5)-Zn(2)-O(8)	90.47(17)
		N(7)-Zn(2)-O(8)	102.62(15)
		O(6)-Zn(2)-O(8)	101.97(15)

For Zn(2) center the rigidity of the four-membered ring and the five-membered ring formed upon chelation of the two oxygen atoms of diclofenac and the two nitrogen of dmph lingand, respectively to Zn(II) results in deviation in trigonal bi-pyramidal bond angles, in which O(5)-Zn(2)-O(6) angle is 59.74(14) (°) and N(8)-

Zn(2)-N(7) angle is 80.34(14) (°). The values of other angles are shown in Table 3.23.

Table 3.30 shows hydrogen bonding for complex **(11)**, as there is one intermolecular hydrogen bonding O(1W)-H(2W)...O(1)$^{\#1}$ = 2.15(3) results from water molecule present in crystal and five intramolecular hydrogen bonding.

Table 3.30: Hydrogen bonds for complex **(11)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(2W)...O(1)#1	0.91(2)	2.15(3)	3.009(6)	157(6)
O(1W)-H(1W)...O(4)	0.90(7)	2.12(7)	2.977(7)	158(6)
N(2)-H(2N)...O(3)	0.75	2.21	2.914(5)	155.8
N(1)-H(1N)...O(2)	0.89	2.00	2.821(5)	152.0
N(6)-H(6N)...O(7)	0.74	2.13	2.833(5)	159.3
N(5)-H(5N)...O(6)	0.74	2.17	2.905(5)	169.1
Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1				

3.6 *In-vitro* antibacterial activity

Agar diffusion method[110] was used for screening the anti-bacterial activity of the synthesized zinc complexes, **(1-14)**. Different gram positive (*Staphylococcus aureus, Listeria monocytogenes*) and gram negative (*Escherichia coli, Pseudomonas aeruginosa*) bacteria were tested. The results (the average of two trails ± standard deviation) are summarized in Table 3.31.

Single bacterial colonies dissolved in sterile saline until the suspended cells reached the turbidity of McFarland 0.5 Standard. The bacterial inoculum was spread on the surface of the Muller Hinton nutrient agar by means of a sterile cotton swab. Sterile glassy borer were used for making a 6 mm in diameter wells in the agar plate. Zinc complexes were dissolved in DMSO in two concentrations (8 mg/ml) and (4 mg/ml), and then 50 μL of the test samples were introduced in the respective wells. DMSO used as negative control while gentamycin used as positive control. The plates were incubated immediately at 37 °C for 24 h. The anti-bacterial activity was determined by measuring inhibition zone diameter (IZD) in millimeter (mm). The results were summarized in Table 3.31 are the average of two trials and are stated as average ± standard deviation.

Table 3.31: *In-vitro* anti-bacterial activity (IZD) in mm for complexes **(1-14)** ant their parent ligands.

Compound	Concentration	*P. aeruginosa*	*E. coli*	*S. aureus*	*L. monocytogenes*
diclofenac sodium	8mg/ml	11.5 ± 0.5	-	11.0 ± 1.0	-
	4mg/ml	11.0 ± 1.0	-	11.5 ± 0.5	-
(1)	8mg/ml	23.0 ± 1.0	-	15.5 ± 2.5	-
	4mg/ml	14.5 ± 2.5	-	19.0 ± 1.0	-
Indomethacin	8mg/ml	13.5 ± 0.5	-	11.5 ± 0.5	-
	4mg/ml	-	-	-	-
(2)	8mg/ml	20.5 ± 0.5	-	12.0 ± 0.0	-
	4mg/ml	15.0 ± 3.0	-	15.5 ± 0.5	-
3-picpline	8mg/ml	-	-	-	-
	4mg/ml	-	-	-	-
(3)	8mg/ml	22.0 ± 0.0	-	14.0 ± 1.0	-
	4mg/ml	15.5 ± 2.5	-	18.0 ± 0.0	-
(4)	8mg/ml	12.0 ± 0.0	-	15.0 ± 1.0	-
	4mg/ml	11.0 ± 1.0	-	11.5 ± 0.5	-
2-aminopyridine	8mg/ml	-	-	-	-
	4mg/ml	-	-	-	-
(5)	8mg/ml	14.0 ± 2.0	-	19.5 ± 0.5	-
	4mg/ml	12.0 ± 2.0	-	15.0 ± 1.0	-
(6)	8mg/ml	17.0 ± 1.0	-	11.5 ± 0.5	-
	4mg/ml	13.5 ± 0.5	-	-	-
2-aminomethyl pyridine	8mg/ml	-	-	-	-
	4mg/ml	-	-	-	-
(7)	8mg/ml	21.0 ± 1.0	-	16.5 ± 0.5	-
	4mg/ml	14.5 ± 4.5	-	14.0 ± 0.0	-
(8)	8mg/ml	21.0 ± 2.0	-	11.5 ± 0.5	-
	4mg/ml	13.0 ± 0.0	-	12.0 ± 1.0	-
1,10-phenanthroline	8mg/ml	35.5 ± 0.5	42.0 ± 2.0	38.5 ± 0.5	36.5 ± 0.5
	4mg/ml	28.0 ± 1.0	39.0 ± 2.0	35.0 ± 1.0	34.5 ± 0.5
(9)	8mg/ml	-	11.5 ± 0.5	11.5 ± 0.5	12.0 ± 1.0
	4mg/ml	-	13.0 ± 1.0	12.5 ± 1.5	12.5 ± 0.5
(10)	8mg/ml	-	22.5 ± 1.5	20.5 ± 0.5	22.0 ± 1.0
	4mg/ml	-	20.5 ± 1.5	17.5 ± 0.5	18.5 ± 0.5
2,9-dimethyl-1,10-phenanthroline	8mg/ml	10.5 ± 0.5	-	30.0 ± 0.0	-
	4mg/ml	11.0 ± 1.0	-	30.0 ± 1.0	-
(11)	8mg/ml	12.5 ± 2.5	-	15.5 ± 1.5	-
	4mg/ml	11.0 ± 1.0	-	18.0 ± 1.0	-
(12)	8mg/ml	11.5 ± 1.5	-	15.0 ± 0.0	-
	4mg/ml	11.5 ± 1.5	-	23.0 ± 2.0	-
2-amino-4,6-dimethylpyrimidine	8mg/ml	12.5 ± 0.5	-	-	-
	4mg/ml	-	-	-	-
(13)	8mg/ml	22.0 ± 2.0	-	13.0 ± 1.0	-
	4mg/ml	14.5 ± 2.5	-	16.5 ± 0.5	-
(14)	8mg/ml	-	-	12.5 ± 0.5	-
	4mg/ml	-	-	-	-
$ZnCl_2$	8mg/ml	-	-	-	-
DMSO	8mg/ml	-	-	-	-
Gentamycin	2mg/ml	35	41	36	40

It is obvious that neither DMSO nor $ZnCl_2$ has any activity against the tested bacteria. Positive control has activity against all tested bacteria. And all tested zinc complexes have no bacterial activity against *E. coli* (Gram-negative) and *L. monocytogenes* (Gram-positive) bacteria, except 1,10-phenanthroline ligand and their complexes **(9)** and **(10)**, which showed anti-bacterial activity against all tested bacteria except *P. aeruginosa*. Mainly it is known that 1,10-phenanthroline has significant anti-bacterial activity, making its complexes as a good choice for biological activity screening.

Minimum inhibitory concentration (MIC) tests using the broth dilution method were also conducted against only the two types of bacteria *P. aeruginosa*, *S. aureus*, that was affected by the tested complexes **(1-14)**, to domenstrate the effect of complexation on their activity. The results were presented in Table 3.32.

For complexes **(1)** and **(2)** the anti-bacterial activity increases upon complexation, as the IZD of diclofenac increase from about 12 mm to the range of 16-23 mm for complex **(1)**, and that for indomethacin increase form the range of 12-14 mm to the range of 12-20 mm for complex **(2)**, (Figure 3.8).

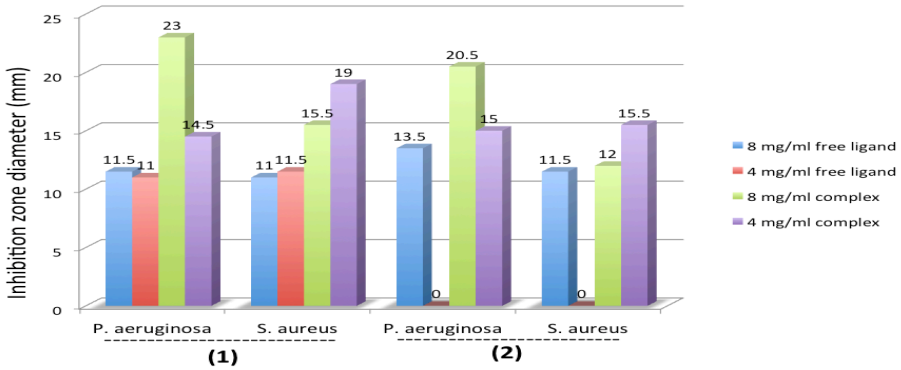


Figure 3.8: Inhibition zone diameter in mm for complexes **(1)** and **(2)** and their parent ligands

MIC tests showed that MIC value for both complexes **(1)** and **(2)** are lower than that of corresponding free ligands, indicating that complexation enhances their anti-bacterial activity.

Table 3.32: Minimum inhibitory concentration (MIC) in mg for the synthesized complexes.

Compound*	***P aregenosa***	***S aureus***
Diclofenac sodium	2	4
(1)	1	2
Indomethacin	8	8
(2)	1	2
3-picpline	>8	>8
(3)	1	1
(4)	2	2
2-aminopyridine	>8	>8
(5)	2	0.5
(6)	1	8
2-aminomethyl pyridine	>8	>8
(7)	2	1
(8)	1	2
1,10-phenanthroline	0.25	0.125
(9)	>8	2
(10)	>8	1
2,9-dimethyl-1,10-phenanthroline	4	1
(11)	4	2
(12)	4	1
2-amino-4,6-dimethylpyrimidine	8	>8
(13)	2	0.5
(14)	>8	8

>: highest tested concentration of tested sample is inactive.

For complexes **(3-8)**, **(13)** and **(14)**, at testing concentration, the parent ligands are inactive against the tested bacteria, while the product of their complexation with **(1)** or **(2)** are active (Figure 3.9), but as their activities, (IZD) values, are close to that of the corresponding zinc indomethacin or zinc diclofenac before complexation with the N-donor (3-picoline, 2-amino pyridine, 2-aminomethyl pyridine or 2-amino-4,6-dimethyl pyrimidine) ligand, indicating that the anti-bacterial activity of complexes **(1)** and **(2)** is not affected by the addition of N-donor ligands.

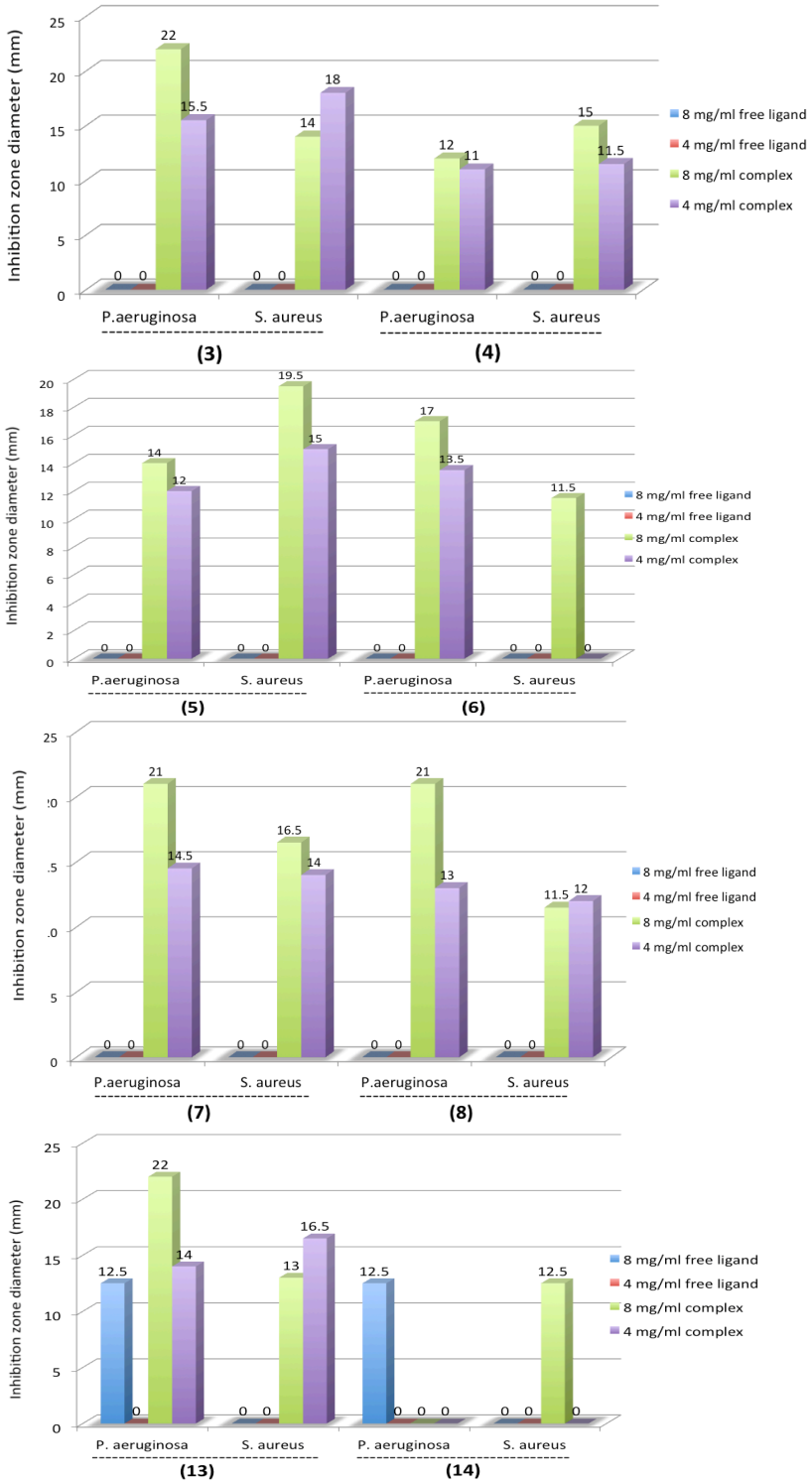


Figure 3.9: Inhibition zone diameter in mm for complexes **(3-8)**, **(13)** and **(14)** and their parent ligands.

In addition, for **(3-8)**, **(13)** and **(14)**, complexes MIC results confirm the above conclusions, as the MIC value for complexes was lower than that of the corresponding free ligands.

The increased bacterial activity could be resulted from increasing content of diclofenac and indomethacin and not due to complexation effect. Based on it's structure each mole of complex **(1)** contains two moles of diclofenac, and each mole of complex **(2)** contains four moles of indomethacin based on the proposed structure for complex **(2)**. So the increase in amount of diclofenac and indomethacin was logically to encounter with an increase in their effect.

According to Table 3.31, the complexation of 1,10-phenanthroline with zinc indomethacin or zinc diclofenac reduces it's anti-bacterial activity from 38 mm in average against all tested bacteria to 12 mm in average for complex **(9)**, and to 22mm in average for complex **(10)**, (Figure 3.10).

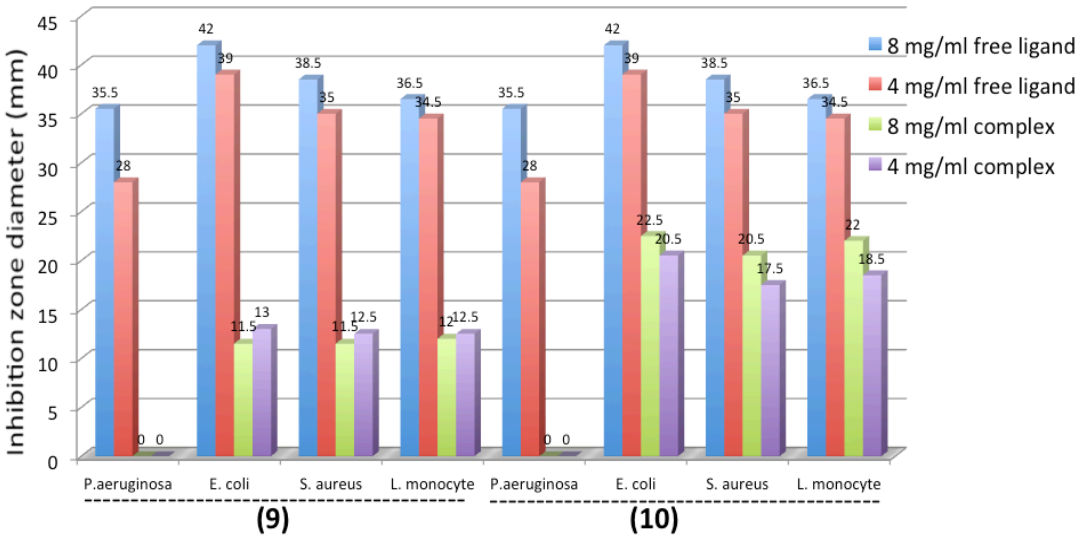


Figure 3.10: Inhibition zone diameter in mm for complexes **(9)** and **(10)** and their parent ligands.

MIC value for both complexes **(9)**, **(10)** is higher than that of free ligand against both types of tested bacteria, indicating that complexation of 1,10-phenanthroline to complexes **(1)** and **(2)**, respectively, reduces it's anti-bacterial activity.

The activity of 2,9-dimethyl-1,10-phenanthroline against *S. aureus*, reduced from 30 mm to 15.5 mm in average upon complexation with **(1)** and **(2)** producing **(11)** and **(12)** complexes. While that against *P. aeruginosa* increased slightly from 11 mm to 13mm in average upon complexation with **(1)** and **(2)**. MIC value for **(11)** and **(12)** against *P. aeruginosa* doesn't differ from that of free ligand. While it is higher for (**11)** and **(12)** against *S. aureus* than that of free ligand, indicating the negative effect of complexation of this ligand on it's anti-bacterial activity. These differences in activity and MIC values between *P. aeruginosa* and *S. aureus*, were attributed to differences in cell wall structure between gram –ve and gram +ve bacterial types.

Concentration of 4mg/ml also screened to deduce the effect of concentration on anti-bacterial activity. Table 3.31 shows that the activity of all complexes against all tested bacteria reduced by decreasing the concentration, except that complexes **(1)**, **(2)**, **(3)**, **(11)**, **(12)**, **(13)** showed higher activities against *S. aureus* by reducing concentration from 8 mg/ml to 4 mg/ml, that might be explained by product inhibition theory of bacterial enzymes; a type of enzyme inhibition where the product of an enzyme reaction binds to the enzyme and inhibits its activity.

Conclusion

Different mixed ligands of zinc complexes have been synthesized to enhance the biological activity for the parent components of the target compounds due to complexation.

IR, ^{1}H-NMR, ^{13}C{H}-NMR, UV-Vis, and X-ray crystallography spectrometric techniques were used to characterize and study the newly synthesized mixed ligand complexes of Zn(II) diclofenac or indomethacin with N-donor ligands; $[Zn_2(diclo)_2(H_2O)_2]$ **(1)**, $[Zn_2(Indo)_4]$ **(2)**, $[Zn(diclo)_4(pico)_2]$ **(3)**, $[Zn_2(indo)_4(pico)_2]$ **(4)**, $[Zn(diclo)_2(apy)_2]$ **(5)**, $[Zn(indo)_2(apy)_2]$ **(6)**, $[Zn(diclo)_2(ampy)]$ **(7)**, $[Zn(indo)_2(ampy)]$ **(8)**, $[Zn(diclo)_2(phen)]$ **(9),** $[Zn(diclo)_2(phen)]$ **(9)**, $[Zn(indo)_2(phen)]$ **(10)**, $[Zn(diclo)_2(dmph)]$ **(11)**, $[Zn(indo)_2(dmph)]$ **(12)**, $[Zn(diclo)_2(admp)_2]$ **(13)**, $[Zn(indo)_2(admp)_2]$ **(14)**.

Single-crystal X-ray diffraction was used to determine crystal structure of the complexes **(1)**, **(4)**, **(5)** and **(11)**. Structures **(1)** and **(5)** were distorted tetrahedral mononuclear complexes, with two monodentate diclofenac groups and two water molecules, and two monodentate diclofenac groups and two 2-aminopyridine groups, respectively. Complex **(4)** was binuclear with two 3-picoline groups one for each Zn(II) centre, and four indomethacin molecules, two of them were bidentate chelating, one was bidentate bridging, and the other was monodentate terminal bridging. While complex **(11)** was dimer of two $[Zn(diclo)_2(dmph)]$ molecules, one of them was distorted trigonal bipyramidal with one monodintate dicolfenac and one

bindentate chelating, and one bidentate chelating 2,9-dimethyl-1,10-phenanthroline group. For the other [Zn(diclo)$_2$(dmph)], two dicolfenac groups were both monodentate, and 2,9-dimethyl 1,10-phenanthroline group was bidentate chelating.

Depending on characterization techniques and similar published complexes, the structure of the other complexes was proposed; complex **(2)** was binuclear paddle wheel structure with four bidentate indomethacin groups. Complexes **(3)** and **(13)** were adopted octahedral structures with four monodentate diclofenac groups for each, and two 3-picoline groups for **(3)** and two 2-amino-4,6-dimethyl groups for **(13)**. While the proposed structure for complexes **(6-10)**, **(12)** and **(14)** were tetrahedral.

We anticipated that the anti-bacterial activity would increase due to complexation, however, from the anti-bacterial activity results some of the complexes showed lower activity than their parent ligands

Most of the complexes showed anti-bacterial effects against *P. aeruginosa,* and *S aureus* while they were inactive toward *E coli* and *L monocytogenes*. Complexes **(1-8)**, **(13)**, showed higher activity upon complexation against *P. aeruginosa,* and *S. aureus* than their parent ligangs, complex **(14)** showed higher activity against *S aureus* and no activity against *P. aeruginosa.* 1,10-phenanthroline complexes **(9)** and **(10),** showed decreased activity upon complexeation against all tested bacteria, except *P. aeruginosa* it was inactive. Complexes **(11)** and **(12)** showed dereased activity against *S. aureus*, but their activity didn't affected by complection against *P. aeruginosa.*

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Appendices

Appendix A: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complexes **1-14** and their parent ligands are listed in Tables 3.7-3.20.

Table 3.7: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(1)** parent ligand.

^{1}H-NMR		^{13}C{^{1}H}-NMR	
Diclo[113]	Complex **(1)**	Diclo	Complex **(1)**
3.43 s	3.57 s	39.40	40.00
6.25 d	6.29 (d, 1H, $^{3}J_{H-H}$ 9 Hz)	118.70	116.70
6.75 m	6.82 (m, 1H, $^{3}J_{H-H}$ 12 Hz)	119.50	121.17
6.94 m	7.00 (m, 1H, $^{3}J_{H-H}$ 11,25 Hz)	121.10	125.00
7.07 m	7.07 (m, 1H, $^{3}J_{H-H}$ 13.5 Hz)	125.20	127.00
7.08 d	7.12 (d, 1H, $^{3}J_{H-H}$ 6 Hz)	127.90	127.20
7.45 d	7.43 (d, 2H, $^{3}J_{H-H}$ 9 Hz)	128.50	129.34
10.15 s	8.29 s	129.40	129.48
		130.70	130.95
		135.40	137.94
		139.30	143.22
		176.30	177.70

Table 3.8: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(2)** parent ligand.

^{1}H-NMR		^{13}C{^{1}H}-NMR	
Indo[114]	Complex **(2)**	Indo[115]	Complex **(2)**
2.38 s	2.15 s	13.28	13.80
3.67 s	3.41 s	29.98	31.68
3.82 s	3.71 s	55.75	55.71
6.67 d	6.64 (d, 1H, $^{3}J_{H-H}$, 9 Hz)	101.31	102.46
6.85 d	6.67 (d, 1H, $^{3}J_{H-H}$ 6.5 Hz)	111.72	111.53
6.94 s	6.90 s	111.81	114.86
7.46 d	7.62 d	115.00	116.43
7.65 d	7.62 d	129.14	129.45
		130.47	130.65
		130.82	131.50
		131.19	131.71
		133.83	134.55
		136.26	134.78
		139.36	137.88
		156.11	155.86
		168.28	168.24
		176.47	176.32

Table 3.9: ^{1}H-NMRspectral data of complex **(3)** parent ligands

^{1}H-NMR		
Diclo	pico[116]	Complex **(3)**
3.43 s		3.74 s
6.25 d		6.41 (d, 1H, $^{3}J_{H-H}$ 6 Hz)
6.75 m		6.83 (m, 1H, $^{3}J_{H-H}$ 8.1 Hz)
6.94 m		6.88 (m, 1H, $^{3}J_{H-H}$ 7.8 Hz)
7.07 m		7.00 (m, 1H, $^{3}J_{H-H}$ 6.3 Hz)
7.08 d		7.06 (d, 1H, $^{3}J_{H-H}$ 8.1 Hz)
7.45 d		7.17 (d, 1H, $^{3}J_{H-H}$ 5.4 Hz)
10.15 s		7.35 s
	2.32 s	2.14 s
	7.16 m	7.25 m,
	7.46 d	7.51 (d, 1H $^{3}J_{H-H}$ 6 Hz)
	8.42 d	8.12 d
	8.44 s	8.22 s

Table 3.10: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(4)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Indo	pico[117]	Complex **(4)**	Indo	pico[118]	Complex **(4)**
2.38 s		2.21 s	13.28		13.43
3.69 s		3.63 s	29.98		31.74
3.82 s		3.63 s	55.75		55.46
6.67 d		6.56 (d, 1H, $^{3}J_{H-H}$ 9 Hz)	101.31		101.68
6.85 d		6.87 (d, 1H, $^{3}J_{H-H}$ 9.3 Hz)	111.72		111.38
6.94 s		6.94 s	111.81		114.75
7.46 d		7.40 (d, 2H, $^{3}J_{H-H}$ 8.4 Hz)	115.00		114.90
7.65 d		7.58 (d, 2H, $^{3}J_{H-H}$ 9 Hz)	129.14		128.92
	2.32 s	2.12 s	130.47		130.90
	7.16 m	7.20 (m, 1H, $^{3}J_{H-H}$12.6 Hz)	130.82		131.04
	7.46 d	7.55 d	131.19		131.30
	8.42 s	8.09 s	133.83		134.10
	8.44 d	8.11 (d, 1H, $^{3}J_{H-H}$ 6 Hz)	136.26		135.00
			139.36		138.97
			156.11		155.80
			168.28		168.24
			176.47		179.17
				18.00	18.31
				123.00	124.31
				133.90	135.10
				136.80	139.76
				147.30	146.23
				150.10	149.09

Table 3.11: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(5)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Diclo	apy[119]	Complex **(5)**	Diclo	apy[120]	Complex **(5)**
3.43 s		3.82 s	39.40		41.30
6.25 d		6.44 (d, 1H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	118.70		117.05
6.75 m		6.87 (m, 1H, $^{3}J_{H\text{-}H}$ 8.1 Hz)	119.50		121.09
6.94 m		6.90 (m, 1H, $^{3}J_{H\text{-}H}$ 9.6 Hz)	121.10		123.54
7.07 m		7.06 (m, 1H, $^{3}J_{H\text{-}H}$ 17.1 Hz)	125.20		126.42
7.08 d		7.23 (d, 1H, $^{3}J_{H\text{-}H}$ 1.8 Hz)	127.90		126.92
7.45 d		7.26 (d, 2H, $^{3}J_{H\text{-}H}$ 8.1 Hz)	128.50		128.66
10.15 s		7.70 s	129.40		129.72
	4.63 s	5.80 s	130.70		130.86
	6.47 d	6.86 (d, 1H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	135.40		138.05
	6.61 m	6.89 (m, 1H, $^{3}J_{H\text{-}H}$ 8.1 Hz)	139.30		142.98
	7.38 m	7.36 (m, 1H, $^{3}J_{H\text{-}H}$ 3.9 Hz)	176.30		179.38
	8.05 d	7.71 (d, 1H, $^{3}J_{H\text{-}H}$ 5.4 Hz)		108.66	111.57
				113.67	113.14
				137.60	139.9
				147.98	145.88
				158.85	159.02

Table 3.12: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(6)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Indo	apy	Complex **(6)**	Indo	apy	Complex **(6)**
2.38 s		2.22 s	13.28		13.42
3.69 s		3.59 s	29.98		31.94
3.82 s		3.70 s	55.75		55.60
6.67 d		6.59 (d, 1H, $^{3}J_{H\text{-}H}$ 11.7 Hz)	101.31		101.77
6.85 d		6.87 (d, 1H, $^{3}J_{H\text{-}H}$ 9.6 Hz)	111.72		111.28
6.94 s		6.97 s	111.81		112.61
7.46 d		7.39 (d, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	115.00		114.75
7.65 d		7.59 (d, 2H, $^{3}J_{H\text{-}H}$ 8.7 Hz)	129.14		129.03
	4.63 s	6.04 s	130.47		130.79
	6.47 d	6.33 (d, 1H, $^{3}J_{H\text{-}H}$ 9.6 Hz)	130.82		131.14
	6.61 m	6.37 (m, 1H, $^{3}J_{H\text{-}H}$ 12.9 Hz)	131.19		131.35
	7.38 m	7.31 (m, 1H, $^{3}J_{H\text{-}H}$ 15.9 Hz)	133.83		134.04
	8.05 d	7.63 (d, 1H, $^{3}J_{H\text{-}H}$ 4.5 Hz)	136.26		135.12
			139.36		140.09
			156.11		155.83
			168.28		168.43
			176.47		177.59
				108.66	111.62
				113.67	115.49
				137.60	139.03
				147.98	144.61
				158.85	158.51

Table 3.13: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(7)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Diclo	ampy[121]	Complex **(7)**	Diclo	ampy[122]	Complex **(7)**
3.43 s		3.82 s	39.40		30.92
6.25 d		6.39 (d, 1H, $^{3}J_{H\text{-}H}$ 8.7 Hz)	118.70		111.45
6.75 m		6.45 (m, 1H, $^{3}J_{H\text{-}H}$ 7.8 Hz)	119.50		113.14
6.94 m		6.45 (m, 1H, $^{3}J_{H\text{-}H}$ 7.8 Hz	121.10		117.70
7.07 m		6.86 (m, 1H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	125.20		126.50
7.08 d		6.89 (d, 1H, $^{3}J_{H\text{-}H}$ 8.1 Hz)	127.90		126.88
7.45 d		7.22 (d, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	128.50		128.65
10.15 s		7.74 s	129.40		129.73
	1.84 s	2.16 s	130.70		130.83
	3.97 s	5.75 s	135.40		138.11
	7.15 m	7.04 (m, 1H, $^{3}J_{H\text{-}H}$ 15.3 Hz)	139.30		143.00
	7.26 d	7.25 (d, 1H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	176.30		179.25
	7.62 m	7.36 (m, 1H, $^{3}J_{H\text{-}H}$ 15 Hz)		47.76	41.30
	8.55 d	7.72 (d, 1H, $^{3}J_{H\text{-}H}$ 6.6 Hz)		121.09	121.08
				121.64	123.49
				136.39	139.85
				149.14	146.08
				162.07	159.08

Table 3.14: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(8)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Indo	ampy	Complex **(8)**	Indo	ampy	Complex **(8)**
2.38 s		2.19 s	13.28		13.43
3.69 s		3.54 s	29.98		32.09
3.82 s		3.68 s	55.75		55.58
6.67 d		6.59 (d, 1H, $^{3}J_{H\text{-}H}$ 12 Hz)	101.31		101.87
6.85 d		6.86 (d, 1H, $^{3}J_{H\text{-}H}$ 10 Hz)	111.72		111.07
6.94 s		6.90 s	111.81		114.78
7.46 d		7.40 (d, 2H, $^{3}J_{H\text{-}H}$ 10 Hz)	115.00		115.86
7.65 d		7.59 (d, 2H, $^{3}J_{H\text{-}H}$ 10 Hz)	129.14		129.00
	1.84 s	2.19 s	130.47		130.80
	3.97 s	3.93 s	130.82		131.06
	7.15 m	7.18 (m, H, $^{3}J_{H\text{-}H}$ 15 Hz)	131.19		131.44
	7.26 d	7.10 (d, H, $^{3}J_{H\text{-}H}$ 9 Hz)	133.83		134.14
	7.62 m	7.74 (m, H, $^{3}J_{H\text{-}H}$ 15 Hz)	136.26		134.89
	8.55 d	8.35 (d, H, $^{3}J_{H\text{-}H}$ 9 Hz)	139.36		139.09
			156.11		155.78
			168.28		168.34
			176.47		178.11
				47.76	42.88
				121.09	122.54
				121.64	123.45
				136.39	138.92
				149.14	147.39
				162.07	156.59

Table 3.15: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(9)** parent ligands.

^{1}H-NMR		
Diclo	phen[123]	Complex **(9)**
3.43 s		3.49 s
6.25 d		6.20 (d, 1H, $^{3}J_{H\text{-}H}$ 9 Hz)
6.75 m		6.77 (m, 1H, $^{3}J_{H\text{-}H}$ 12 Hz)
6.94 m		6.97 m
7.07 m		7.02 m
7.08 d		7.05 d
7.45 d		7.37 (d, 2H, $^{3}J_{H\text{-}H}$ 9 Hz)
10.15 s		8.39 s
	7.58 m	7.88 m
	8.20 s	8.17 s
	8.22 d	8.74 (d, 2H, $^{3}J_{H\text{-}H}$ 10 Hz)
	9.18 d	8.94 d

Table 3.16: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(10)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Indo	phen	Complex **(10)**	Indo	phen[123]	Complex **(10)**
2.38 s		2.23 s	13.28		13.55
3.69 s		3.58 s	29.98		31.16
3.82 s		3.65 s	55.75		55.46
6.67 d		6.54 (d, 1H, $^{3}J_{H\text{-}H}$ 9 Hz)	101.31		101.69
6.85 d		6.85 (d, 1H, $^{3}J_{H\text{-}H}$ 9 Hz)	111.72		111.27
6.94 s		6.88 s	111.81		114.71
7.46 d		7.15 (d, 1H, $^{3}J_{H\text{-}H}$ 12 Hz)	115.00		115.53
7.65 d		7.57 (d, 1H, $^{3}J_{H\text{-}H}$ 9 Hz)	129.14		128.96
	7.58 m	7.40 m	130.47		130.80
	8.20 d	8.37 (d, 1H, $^{3}J_{H\text{-}H}$ 9 Hz)	130.82		131.01
	8.22 s	7.83 s	131.19		131.20
	9.18 d	9.05 d	133.83		133.40
			136.26		135.00
			139.36		138.82
			156.11		155.66
			168.28		168.23
			176.47		180.16
				122.90	125.01
				126.35	126.61
				128.46	128.71
				135.81	135.00
				146.10	146.25
				150.12	150.00

Table 3.17: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(11)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Diclo	dmph[124]	Complex **(11)**	Diclo	dmph[125]	Complex **(11)**
3.43 s		3.78 s	39.40		40.75
6.25 d		6.41 (d, 1H, $^{3}J_{H\text{-}H}$ 7.8 Hz)	118.70		117.16
6.75 m		6.80 (m, 1H, $^{3}J_{H\text{-}H}$ 12.9 Hz)	119.50		Not observed
6.94 m		6.86 (m, 1H, $^{3}J_{H\text{-}H}$ 15.9 Hz)	121.10		120.96
7.07 m		7.00 (m, 1H, $^{3}J_{H\text{-}H}$ 15.3 Hz)	125.20		125.69
7.08 d		7.15 (d, 1H, $^{3}J_{H\text{-}H}$ 7.2 Hz)	127.90		126.73
7.45 d		7.20 (m, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	128.50		128.60
10.15 s		8.00 s	129.40		129.46
	2.53 s	2.91 s	130.70		130.71
	7.12 d	7.61 (d, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	135.40		139.06
	7.92 s	7.82 s	139.30		142.96
	8.32 d	8.32 (d, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	176.30		190.96
				25.79	24.77
				123.44	123.19
				125.40	126.31
				126.78	126.94
				136.23	140.31
				145.27	150.59
				159.23	160.91

Table 3.18: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(12)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Indo	dmph	Complex **(12)**	Indo	dmph	Complex **(12)**
2.38 s		2.26 s	13.28		13.60
3.69 s		3.58 s	29.98		31.70
3.82 s		3.65 s	55.75		55.41
6.67 d		6.56 (d, 1H, $^{3}J_{H\text{-}H}$ 8.7 Hz)	101.31		101.62
6.85 d		6.85 (d, 1H, $^{3}J_{H\text{-}H}$ 9.9 Hz)	111.72		111.30
6.94 s		6.90 s	111.81		114.73
7.46 d		7.42 (d, 2H, $^{3}J_{H\text{-}H}$ 8.1 Hz)	115.00		116.01
7.65 d		7.61 (d, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	129.14		126.31
	2.53	2.91 s	130.47		130.77
	7.12	7.61 (d, 2H, $^{3}J_{H\text{-}H}$ 8.4 Hz)	130.82		130.77
	7.92	7.82 s	131.19		131.03
	8.32	8.32 (d, 2H, $^{3}J_{H\text{-}H}$ 8.1 Hz)	133.83		131.46
			136.26		134.26
			139.36		138.8
			156.11		155.65
			168.28		168.28
			176.47		178.11
				25.79	24.68
				123.44	125.63
				125.40	126.89
				126.78	128.97
				136.23	134.78
				145.27	139.10
				159.23	160.68

Table 3.19: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(13)** parent ligands.

1H-NMR			^{13}C{^{1}H}-NMR		
Diclo	admp[126]	Complex **(13)**	diclo	admp[127]	Complex **(13)**
3.43 s		3.70 s	39.40		40.00
6.25 d		6.65 (d, 1H, $^{3}J_{H\text{-}H}$ 9 Hz)	118.70		116.67
6.75 m		7.17 (t, 1H, $^{3}J_{H\text{-}H}$ 15 Hz)	119.50		121.14
6.94 m		7.36 (t, 1H, $^{3}J_{H\text{-}H}$ 14.4 Hz)	121.10		124.90
7.07 m		7.43 (t, 1H, $^{3}J_{H\text{-}H}$ 17.28 Hz)	125.20		127.10
7.08 d		7.52 (d, 1H, $^{3}J_{H\text{-}H}$ 7.7 Hz)	127.90		127.30
7.45 d		7.79 (d, 2H, $^{3}J_{H\text{-}H}$ 9 Hz)	128.50		129.32
10.15 s		8.85 s	129.40		129.45
	2.28 s	2.50 s	130.70		131.20
	5.84 s	3.93 s	135.40		137.93
	6.35 s	6.71 s	139.30		143.20
			176.30		177.63
				23.64	23.72
				110.36	109.08
				163.10	163.72
				167.74	167.17

Table 3.20: ^{1}H-NMR and ^{13}C{1H}-NMR spectral data of complex **(14)** parent ligands.

^{1}H-NMR			^{13}C{^{1}H}-NMR		
Indo	admp	Complex **(14)**	Indo	admp	Complex **(14)**
2.38 s		2.31 s	13.28		13.45
3.69 s		3.29 s	29.98		32.02
3.82 s		3.69 s	55.75		55.73
6.67 d		6.69 (d, 1H, $^{3}J_{H\text{-}H}$ 8.7 Hz)	101.31		101.70
6.85 d		6.92 (d, 1H, $^{3}J_{H\text{-}H}$ 8.7 Hz)	111.72		111.50
6.94 s		7.00 s	111.81		114.75
7.46 d		7.54 (d, 2H, $^{3}J_{H\text{-}H}$ 6.9 Hz)	115.00		114.91
7.65 d		7.72 (d, 2H, $^{3}J_{H\text{-}H}$ 6.9 Hz)	129.14		129.24
	2.28 s	2.31 s	130.47		130.88
	5.84 s	5.58 s	130.82		131.34
	6.35 s	6.36 s	131.19		131.95
			133.83		134.16
			136.26		135.55
			139.36		139.29
			156.11		156.03
			168.28		168.14
			176.47		178.10
				23.64	23.67
				110.36	110.79
				163.10	162.47
				167.74	168.49

Appendix B: Crystal structure data for $[Zn(diclo)_2(H_2O)_2]$ **(1)**

Table 1: Crystal data and structure refinement for complex **(1)**.

Empirical formula	C57 H52 Cl8 N4 O13 Zn2	
Formula weight	1415.37	
Temperature	295(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 33.707(3) Å	α= 90°.
	B = 9.6250(7) Å	β= 90°.
	C = 9.6042(7) Å	γ = 90°.
Volume	3115.9(4) $Å^3$	
Z	2	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	1.177 mm^{-1}	
F(000)	1444	
Crystal size	0.33 x 0.28 x 0.17 mm^3	
Theta range for data collection	2.44 to 26.99°.	
Index ranges	-43<=h<=43, -12<=k<=12, -12<=l<=12	
Reflections collected	33475	
Independent reflections	6799 [R(int) = 0.0296]	
Completeness to theta = 26.99°	99.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.8250 and 0.6974	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6799 / 1 / 390	
Goodness-of-fit on F^2	1.209	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1385	
R indices (all data)	R1 = 0.0538, wR2 = 0.1403	
Absolute structure parameter	0.320(16)	
Largest diff. peak and hole	1.003 and -0.311 $e.Å^{-3}$	

Table 2: 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)	3006(1)	4034(4)	10457(4)	37(1)
C(2)	3403(1)	3363(4)	10722(5)	40(1)
C(3)	3677(1)	4321(4)	11509(4)	35(1)
C(4)	3707(1)	4227(4)	12959(5)	44(1)
C(5)	3954(1)	5067(5)	13704(5)	49(1)
C(6)	4177(1)	6067(4)	13019(5)	42(1)
C(7)	4149(1)	6207(5)	11594(4)	36(1)
C(8)	3907(1)	5325(4)	10823(4)	31(1)
C(9)	4157(1)	6118(4)	8534(4)	32(1)
C(10)	4567(1)	5850(4)	8607(4)	34(1)
C(11)	4836(1)	6547(4)	7778(5)	41(1)
C(12)	4708(2)	7484(5)	6791(5)	48(1)
C(13)	4308(2)	7711(5)	6633(5)	49(1)
C(14)	4039(1)	7048(4)	7498(4)	39(1)
C(15)	1979(1)	4176(4)	8179(5)	42(1)
C(16)	1606(1)	3406(4)	7752(5)	40(1)
C(17)	1334(1)	4351(4)	6933(4)	33(1)
C(18)	1332(1)	4288(4)	5503(5)	45(1)
C(19)	1078(1)	5122(5)	4699(5)	48(1)
C(20)	832(1)	6045(5)	5356(5)	44(1)
C(21)	834(1)	6147(4)	6809(4)	34(1)
C(22)	1081(1)	5298(4)	7609(4)	31(1)
C(23)	806(1)	6079(4)	9860(4)	30(1)
C(24)	396(1)	5861(3)	9774(4)	31(1)
C(25)	124(1)	6596(4)	10551(4)	40(1)
C(26)	253(1)	7538(5)	11512(5)	45(1)
C(27)	654(1)	7733(4)	11714(5)	43(1)
C(28)	923(1)	7014(4)	10909(4)	33(1)
C(29)	2138(3)	10559(10)	10231(18)	84(5)
Cl(1)	3536(1)	7363(1)	7252(1)	60(1)
Cl(2)	4750(1)	4585(1)	9706(1)	42(1)
Cl(3)	1426(1)	7266(1)	11200(1)	54(1)

Cl(4)	211(1)	4593(1)	8647(1)	42(1)
N(1)	3877(1)	5427(4)	9362(4)	38(1)
N(2)	1080(1)	5346(4)	9067(3)	36(1)
O(1)	2697(1)	3617(4)	11001(4)	59(1)
O(2)	3005(1)	5099(3)	9655(4)	48(1)
O(3)	2287(1)	4057(4)	7539(5)	73(1)
O(4)	1950(1)	4958(4)	9219(4)	57(1)
O(5)	2520(3)	10010(12)	9758(19)	164(8)
O(1W)	2484(1)	7550(4)	8490(5)	83(2)
O(2W)	2374(1)	6735(5)	11484(5)	76(1)
Zn(1)	2465(1)	5802(1)	9593(1)	45(1)

Table 3: Bond lengths [Å] and angles [°] for complex **(1)**.

C(1)-O(1)	1.232(5)
C(1)-O(2)	1.282(5)
C(1)-C(2)	1.507(5)
C(2)-C(3)	1.509(6)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.399(6)
C(3)-C(8)	1.402(6)
C(4)-C(5)	1.363(7)
C(4)-H(4)	0.9300
C(5)-C(6)	1.387(7)
C(5)-H(5)	0.9300
C(6)-C(7)	1.378(6)
C(6)-H(6)	0.9300
C(7)-C(8)	1.392(6)
C(7)-H(7)	0.9300
C(8)-N(1)	1.410(5)
C(9)-C(14)	1.397(5)
C(9)-N(1)	1.402(5)
C(9)-C(10)	1.408(5)
C(10)-C(11)	1.380(6)
C(10)-Cl(2)	1.726(4)
C(11)-C(12)	1.378(7)
C(11)-H(11)	0.9300
C(12)-C(13)	1.372(7)
C(12)-H(12)	0.9300
C(13)-C(14)	1.387(6)
C(13)-H(13)	0.9300
C(14)-Cl(1)	1.737(4)
C(15)-O(3)	1.214(6)
C(15)-O(4)	1.255(5)
C(15)-C(16)	1.515(5)
C(16)-C(17)	1.512(6)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700

C(17)-C(18)	1.375(6)
C(17)-C(22)	1.408(5)
C(18)-C(19)	1.405(7)
C(18)-H(18)	0.9300
C(19)-C(20)	1.367(7)
C(19)-H(19)	0.9300
C(20)-C(21)	1.400(6)
C(20)-H(20)	0.9300
C(21)-C(22)	1.397(5)
C(21)-H(21)	0.9300
C(22)-N(2)	1.401(5)
C(23)-N(2)	1.391(5)
C(23)-C(24)	1.401(5)
C(23)-C(28)	1.407(5)
C(24)-C(25)	1.377(5)
C(24)-Cl(4)	1.746(4)
C(25)-C(26)	1.365(6)
C(25)-H(25)	0.9300
C(26)-C(27)	1.381(7)
C(26)-H(26)	0.9300
C(27)-C(28)	1.375(6)
C(27)-H(27)	0.9300
C(28)-Cl(3)	1.737(4)
C(29)-O(5)	1.464(15)
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
N(1)-H(1N1)	0.8055
N(2)-H(1N2)	0.8856
O(2)-Zn(1)	1.945(2)
O(4)-Zn(1)	1.951(3)
O(5)-H(2W1)	1.8558
O(5)-H(1O5)	0.8505
O(1W)-Zn(1)	1.989(4)
O(1W)-H(1W1)	0.8056
O(1W)-H(2W1)	0.8410
O(2W)-Zn(1)	2.048(4)

O(2W)-H(1W2)	0.8056
O(2W)-H(2W2)	1.0382
Zn(1)-H(1W2)	2.1379

O(1)-C(1)-O(2)	120.9(4)
O(1)-C(1)-C(2)	122.6(4)
O(2)-C(1)-C(2)	116.5(4)
C(1)-C(2)-C(3)	111.5(3)
C(1)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2B)	109.3
C(3)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-C(8)	118.3(4)
C(4)-C(3)-C(2)	120.2(4)
C(8)-C(3)-C(2)	121.6(4)
C(5)-C(4)-C(3)	121.8(4)
C(5)-C(4)-H(4)	119.1
C(3)-C(4)-H(4)	119.1
C(4)-C(5)-C(6)	119.6(4)
C(4)-C(5)-H(5)	120.2
C(6)-C(5)-H(5)	120.2
C(7)-C(6)-C(5)	120.1(4)
C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(6)-C(7)-C(8)	120.6(4)
C(6)-C(7)-H(7)	119.7
C(8)-C(7)-H(7)	119.7
C(7)-C(8)-C(3)	119.6(4)
C(7)-C(8)-N(1)	121.9(4)
C(3)-C(8)-N(1)	118.5(4)
C(14)-C(9)-N(1)	121.0(4)
C(14)-C(9)-C(10)	115.7(4)
N(1)-C(9)-C(10)	123.1(3)
C(11)-C(10)-C(9)	121.8(4)
C(11)-C(10)-Cl(2)	117.5(3)
C(9)-C(10)-Cl(2)	120.7(3)

C(12)-C(11)-C(10)	120.6(4)
C(12)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7
C(13)-C(12)-C(11)	119.2(4)
C(13)-C(12)-H(12)	120.4
C(11)-C(12)-H(12)	120.4
C(12)-C(13)-C(14)	120.2(4)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(13)-C(14)-C(9)	122.3(4)
C(13)-C(14)-Cl(1)	118.5(3)
C(9)-C(14)-Cl(1)	119.2(3)
O(3)-C(15)-O(4)	121.7(4)
O(3)-C(15)-C(16)	121.9(4)
O(4)-C(15)-C(16)	116.4(4)
C(17)-C(16)-C(15)	110.4(3)
C(17)-C(16)-H(16A)	109.6
C(15)-C(16)-H(16A)	109.6
C(17)-C(16)-H(16B)	109.6
C(15)-C(16)-H(16B)	109.6
H(16A)-C(16)-H(16B)	108.1
C(18)-C(17)-C(22)	119.1(4)
C(18)-C(17)-C(16)	119.8(4)
C(22)-C(17)-C(16)	121.1(4)
C(17)-C(18)-C(19)	121.8(4)
C(17)-C(18)-H(18)	119.1
C(19)-C(18)-H(18)	119.1
C(20)-C(19)-C(18)	119.1(4)
C(20)-C(19)-H(19)	120.4
C(18)-C(19)-H(19)	120.4
C(19)-C(20)-C(21)	120.2(4)
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-H(20)	119.9
C(22)-C(21)-C(20)	120.7(4)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(21)-C(22)-N(2)	122.0(4)

C(21)-C(22)-C(17)	119.1(4)
N(2)-C(22)-C(17)	118.9(4)
N(2)-C(23)-C(24)	123.2(3)
N(2)-C(23)-C(28)	122.1(3)
C(24)-C(23)-C(28)	114.4(3)
C(25)-C(24)-C(23)	123.2(3)
C(25)-C(24)-Cl(4)	117.3(3)
C(23)-C(24)-Cl(4)	119.5(3)
C(26)-C(25)-C(24)	119.8(4)
C(26)-C(25)-H(25)	120.1
C(24)-C(25)-H(25)	120.1
C(25)-C(26)-C(27)	119.8(4)
C(25)-C(26)-H(26)	120.1
C(27)-C(26)-H(26)	120.1
C(28)-C(27)-C(26)	119.8(4)
C(28)-C(27)-H(27)	120.1
C(26)-C(27)-H(27)	120.1
C(27)-C(28)-C(23)	122.7(4)
C(27)-C(28)-Cl(3)	118.8(3)
C(23)-C(28)-Cl(3)	118.5(3)
O(5)-C(29)-H(29A)	109.5
O(5)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
O(5)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(9)-N(1)-C(8)	123.3(3)
C(9)-N(1)-H(1N1)	130.4
C(8)-N(1)-H(1N1)	98.3
C(23)-N(2)-C(22)	124.4(3)
C(23)-N(2)-H(1N2)	104.8
C(22)-N(2)-H(1N2)	122.5
C(1)-O(2)-Zn(1)	107.4(2)
C(15)-O(4)-Zn(1)	109.1(3)
C(29)-O(5)-H(2W1)	119.5
C(29)-O(5)-H(1O5)	92.1
H(2W1)-O(5)-H(1O5)	102.0

Zn(1)-O(1W)-H(1W1)	131.0
Zn(1)-O(1W)-H(2W1)	129.8
H(1W1)-O(1W)-H(2W1)	99.0
Zn(1)-O(2W)-H(1W2)	85.2
Zn(1)-O(2W)-H(2W2)	132.4
H(1W2)-O(2W)-H(2W2)	106.0
O(2)-Zn(1)-O(4)	133.98(14)
O(2)-Zn(1)-O(1W)	106.31(16)
O(4)-Zn(1)-O(1W)	106.42(17)
O(2)-Zn(1)-O(2W)	105.43(17)
O(4)-Zn(1)-O(2W)	102.28(15)
O(1W)-Zn(1)-O(2W)	96.1(2)
O(2)-Zn(1)-H(1W2)	88.8
O(4)-Zn(1)-H(1W2)	124.2
O(1W)-Zn(1)-H(1W2)	87.1
O(2W)-Zn(1)-H(1W2)	22.1

Symmetry transformations used to generate equivalent atoms:

Table 4: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **(1)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(2)	39(2)	40(2)	2(2)	-7(2)	-4(2)
C(2)	33(2)	34(2)	53(2)	6(2)	-7(2)	1(2)
C(3)	31(2)	30(2)	43(2)	5(2)	-5(2)	8(1)
C(4)	48(2)	44(2)	39(2)	17(2)	5(2)	3(2)
C(5)	62(3)	52(3)	34(2)	0(2)	-2(2)	11(2)
C(6)	39(2)	48(2)	41(2)	-9(2)	-3(2)	6(2)
C(7)	30(2)	41(2)	38(2)	0(2)	1(2)	-2(2)
C(8)	28(2)	35(2)	31(2)	2(2)	2(1)	5(1)
C(9)	36(2)	35(2)	25(2)	-5(1)	-2(1)	-2(1)
C(10)	43(2)	32(2)	29(2)	-3(2)	-4(2)	-1(1)
C(11)	42(2)	44(2)	38(2)	-6(2)	7(2)	-4(2)
C(12)	59(3)	44(2)	41(2)	0(2)	13(2)	-9(2)
C(13)	76(3)	40(2)	31(2)	6(2)	0(2)	1(2)
C(14)	46(2)	40(2)	31(2)	-5(2)	-2(2)	6(2)
C(15)	34(2)	38(2)	55(3)	-18(2)	-11(2)	8(2)
C(16)	35(2)	31(2)	53(2)	-12(2)	-2(2)	5(2)
C(17)	29(2)	34(2)	36(2)	-4(2)	-3(1)	-5(1)
C(18)	49(2)	42(2)	43(2)	-8(2)	5(2)	-4(2)
C(19)	57(2)	58(2)	28(2)	-4(2)	1(2)	-8(2)
C(20)	44(2)	50(2)	38(2)	7(2)	-5(2)	-7(2)
C(21)	33(2)	33(2)	36(2)	-1(2)	1(2)	-1(2)
C(22)	28(2)	34(2)	32(2)	-1(2)	-1(1)	-3(1)
C(23)	32(2)	33(2)	26(2)	5(1)	1(1)	2(1)
C(24)	34(2)	35(2)	23(2)	-1(2)	1(2)	-3(1)
C(25)	34(2)	48(2)	37(2)	5(2)	5(2)	7(2)
C(26)	49(2)	47(2)	38(2)	4(2)	16(2)	11(2)
C(27)	57(3)	37(2)	35(2)	-7(2)	9(2)	-2(2)
C(28)	35(2)	38(2)	27(2)	2(2)	3(1)	-4(2)
C(29)	44(5)	40(5)	169(15)	-29(7)	-42(7)	11(4)
Cl(1)	53(1)	77(1)	50(1)	5(1)	-15(1)	17(1)
Cl(2)	41(1)	46(1)	39(1)	2(1)	-4(1)	8(1)
Cl(3)	43(1)	73(1)	48(1)	-13(1)	-4(1)	-13(1)

Cl(4)	36(1)	47(1)	43(1)	-5(1)	-2(1)	-8(1)
N(1)	28(1)	47(2)	37(2)	4(1)	-4(1)	-5(1)
N(2)	29(2)	49(2)	30(2)	-5(1)	-2(1)	6(1)
O(1)	34(2)	76(2)	68(2)	25(2)	-3(2)	-7(2)
O(2)	28(1)	49(2)	65(2)	20(2)	-6(2)	3(1)
O(3)	37(2)	93(3)	89(3)	-45(2)	11(2)	-4(2)
O(4)	28(1)	72(2)	70(3)	-31(2)	-12(1)	6(1)
O(5)	123(8)	101(7)	269(17)	-140(10)	-142(10)	81(6)
O(1W)	117(4)	50(2)	81(3)	-1(2)	-44(3)	21(2)
O(2W)	63(2)	88(3)	78(3)	-34(2)	-10(2)	-12(2)
Zn(1)	29(1)	51(1)	57(1)	-6(1)	-14(1)	5(1)

Table 5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **(1)**.

	x	y	z	U(eq)
H(2A)	3524	3114	9840	48
H(2B)	3364	2517	11254	48
H(4)	3554	3572	13427	53
H(5)	3973	4971	14665	59
H(6)	4346	6644	13522	51
H(7)	4293	6897	11144	44
H(11)	5106	6382	7886	49
H(12)	4889	7957	6239	58
H(13)	4218	8311	5944	59
H(16A)	1677	2607	7188	48
H(16B)	1469	3073	8576	48
H(18)	1503	3676	5055	54
H(19)	1076	5048	3734	57
H(20)	664	6607	4834	53
H(21)	669	6786	7247	41
H(25)	-146	6452	10420	48
H(26)	70	8046	12031	54
H(27)	744	8348	12391	51
H(29A)	1990	10899	9446	127
H(29B)	2182	11305	10876	127
H(29C)	1990	9835	10682	127
H(1N1)	3639	5393	9298	56
H(1N2)	1302	5364	9563	54
H(1O5)	2580	9734	10572	246
H(1W1)	2428	7703	7689	124
H(2W1)	2533	8367	8748	124
H(1W2)	2594	7044	11383	115
H(2W2)	2363	6348	12492	115

Table 6: Hydrogen bonds for complex **(1)** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O(2W)-H(2W2)…O(5)#1	1.04	2.56	3.57(2)	165.5
O(2W)-H(1W2)…O(3)#2	0.81	2.27	2.707(5)	114.7
O(1W)-H(2W1)…O(5)	0.84	1.86	2.665(9)	160.9
O(1W)-H(1W1)…O(1)#3	0.81	1.89	2.672(6)	162.8
O(5)-H(1O5)…O(3)#2	0.85	2.05	2.898(19)	178.8
N(2)-H(1N2)…Cl(3)	0.89	2.45	2.995(4)	120.3
N(2)-H(1N2)…O(4)	0.89	2.24	2.957(4)	137.6
N(1)-H(1N1)…Cl(1)	0.81	2.75	2.982(4)	98.7
N(1)-H(1N1)…O(2)	0.81	2.18	2.967(4)	165.6

Symmetry transformations used to generate equivalent atoms:

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

#3 –x+1/2,y+1/2,z-1/2

Appendix C: Crystal structure data for $[Zn_2(indo)_4(pico)_2]$ **(4)**

Table 1: Crystal data and structure refinement for complex **(4)**.

Empirical formula	C88 H74 Cl4 N6 O16 Zn2	
Formula weight	1744.07	
Temperature	293(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4602(8) Å	α= 97.226(1)°.
	b = 14.454(1) Å	β= 98.253(1)°.
	c = 26.546(2) Å	γ = 109.530(1)°.
Volume	4029.7(5) $Å^3$	
Z	2	
Density (calculated)	1.437 Mg/m^3	
Absorption coefficient	0.800 mm^{-1}	
F(000)	1800	
Crystal size	0.33 x 0.24 x 0.13 mm^3	
Theta range for data collection	1.93 to 27.00°.	
Index ranges	-14<=h<=14, -18<=k<=18, -33<=l<=33	
Reflections collected	44916	
Independent reflections	17396 [R(int) = 0.0325]	
Completeness to theta = 27.00°	98.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9031 and 0.7781	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17396 / 0 / 1055	
Goodness-of-fit on F^2	1.282	
Final R indices [I>2sigma(I)]	R1 = 0.0741, wR2 = 0.1489	
R indices (all data)	R1 = 0.0861, wR2 = 0.1541	
Largest diff. peak and hole	0.603 and -0.420 $e.Å^{-3}$	

Table 2: 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)	4804(4)	9198(3)	6357(2)	48(1)
C(2)	4131(4)	9208(3)	5825(1)	47(1)
C(3)	4228(3)	10217(3)	5705(1)	39(1)
C(4)	5339(3)	10950(3)	5610(1)	36(1)
C(5)	6596(3)	11004(3)	5665(1)	45(1)
C(6)	7487(3)	11851(3)	5585(2)	50(1)
C(7)	7155(4)	12657(3)	5467(2)	53(1)
C(8)	5926(3)	12619(3)	5414(1)	44(1)
C(9)	5013(3)	11745(2)	5473(1)	36(1)
C(10)	3271(3)	10569(3)	5636(1)	42(1)
C(11)	9186(5)	11306(4)	5841(2)	91(2)
C(12)	1946(4)	10104(3)	5704(2)	73(1)
C(13)	2995(3)	12088(3)	5372(1)	43(1)
C(14)	3356(3)	12766(3)	4996(1)	38(1)
C(15)	3670(4)	12462(3)	4535(1)	46(1)
C(16)	3903(4)	13075(3)	4179(1)	50(1)
C(17)	3821(3)	14006(3)	4288(1)	43(1)
C(18)	3520(4)	14327(3)	4740(2)	47(1)
C(19)	3281(3)	13701(3)	5098(1)	43(1)
C(20)	3883(3)	8281(2)	7761(1)	36(1)
C(21)	2841(3)	7825(3)	8038(1)	40(1)
C(22)	1858(3)	6871(2)	7735(1)	35(1)
C(23)	1189(3)	6744(2)	7214(1)	35(1)
C(24)	1319(3)	7357(3)	6847(1)	39(1)
C(25)	548(3)	6999(3)	6363(2)	45(1)
C(26)	-359(3)	6035(3)	6243(1)	45(1)
C(27)	-495(3)	5410(3)	6602(1)	44(1)
C(28)	275(3)	5776(2)	7087(1)	39(1)
C(29)	1386(3)	6009(3)	7908(1)	43(1)
C(30)	-24(5)	7331(4)	5521(2)	91(2)
C(31)	1702(4)	5769(3)	8433(2)	64(1)
C(32)	-279(4)	4323(3)	7553(2)	52(1)

C(33)	-1638(3)	3941(3)	7310(1)	44(1)
C(34)	-2220(4)	2967(3)	7045(2)	50(1)
C(35)	-3504(4)	2592(3)	6841(2)	51(1)
C(36)	-4191(4)	3193(3)	6910(1)	47(1)
C(37)	-3640(4)	4157(3)	7186(2)	50(1)
C(38)	-2365(4)	4524(3)	7378(2)	49(1)
C(39)	4885(3)	5928(3)	8583(1)	41(1)
C(40)	5003(4)	5837(3)	9148(1)	46(1)
C(41)	4991(3)	4861(2)	9277(1)	39(1)
C(42)	3908(3)	4063(2)	9351(1)	36(1)
C(43)	2654(4)	3977(3)	9331(1)	43(1)
C(44)	1842(3)	3150(3)	9464(1)	43(1)
C(45)	2260(3)	2405(3)	9615(1)	44(1)
C(46)	3489(3)	2473(3)	9635(1)	41(1)
C(47)	4318(3)	3304(2)	9491(1)	35(1)
C(48)	6014(3)	4587(2)	9375(1)	39(1)
C(49)	74(4)	3677(4)	9298(2)	80(2)
C(50)	7326(4)	5130(3)	9314(2)	56(1)
C(51)	6472(3)	3193(3)	9715(1)	43(1)
C(52)	6103(3)	2090(3)	9591(1)	39(1)
C(53)	5289(3)	1513(3)	9140(1)	41(1)
C(54)	5074(3)	509(3)	9010(1)	43(1)
C(55)	5661(4)	77(3)	9347(1)	44(1)
C(56)	6456(4)	628(3)	9802(2)	55(1)
C(57)	6680(4)	1636(3)	9921(1)	50(1)
C(58)	7006(3)	7297(2)	7273(1)	35(1)
C(59)	8298(3)	7353(3)	7182(1)	41(1)
C(60)	9265(3)	8376(2)	7394(1)	37(1)
C(61)	10008(3)	8684(2)	7910(1)	36(1)
C(62)	9983(3)	8199(3)	8332(1)	44(1)
C(63)	10799(4)	8707(3)	8790(2)	53(1)
C(64)	11624(4)	9683(3)	8830(2)	56(1)
C(65)	11657(3)	10173(3)	8422(2)	48(1)
C(66)	10848(3)	9659(3)	7956(1)	39(1)
C(67)	9607(3)	9158(3)	7147(1)	42(1)
C(68)	9925(5)	7411(4)	9253(2)	100(2)
C(69)	9123(4)	9204(3)	6601(2)	65(1)

C(70)	11163(4)	10923(3)	7370(2)	51(1)
C(71)	12522(4)	11438(3)	7605(1)	44(1)
C(72)	13348(4)	10938(3)	7558(2)	48(1)
C(73)	14618(4)	11410(3)	7753(1)	46(1)
C(74)	15052(3)	12388(3)	8004(1)	44(1)
C(75)	14258(4)	12909(3)	8056(1)	48(1)
C(76)	12995(4)	12436(3)	7847(2)	50(1)
C(77)	7406(4)	9591(3)	8191(2)	51(1)
C(78)	8397(4)	10247(4)	8575(2)	62(1)
C(79)	9058(5)	11144(4)	8450(2)	81(2)
C(80)	8736(5)	11362(3)	7980(2)	83(2)
C(81)	7735(4)	10676(3)	7624(2)	61(1)
C(82)	8717(5)	9967(5)	9089(2)	90(2)
C(83)	3298(4)	5857(3)	6671(1)	45(1)
C(84)	2430(4)	5272(3)	6238(2)	52(1)
C(85)	1737(4)	4309(3)	6275(2)	64(1)
C(86)	1927(4)	3961(3)	6725(2)	66(1)
C(87)	2822(4)	4591(3)	7137(2)	52(1)
C(88)	2282(5)	5696(4)	5755(2)	79(2)
Cl(1)	4113(1)	14792(1)	3840(1)	70(1)
Cl(2)	-5794(1)	2739(1)	6653(1)	72(1)
Cl(3)	5406(1)	-1187(1)	9185(1)	64(1)
Cl(4)	16656(1)	12965(1)	8272(1)	65(1)
N(1)	3708(3)	11496(2)	5471(1)	39(1)
N(2)	396(3)	5322(2)	7523(1)	44(1)
N(3)	5628(3)	3622(2)	9500(1)	39(1)
N(4)	10601(3)	9963(2)	7477(1)	44(1)
N(5)	7074(3)	9795(2)	7731(1)	43(1)
N(6)	3506(3)	5536(2)	7113(1)	40(1)
O(1)	4487(3)	8384(2)	6505(1)	74(1)
O(2)	5620(4)	9928(3)	6628(1)	101(1)
O(3)	8747(3)	12011(3)	5631(1)	78(1)
O(4)	2081(3)	12035(2)	5563(1)	68(1)
O(5)	4520(2)	7760(2)	7599(1)	37(1)
O(6)	4138(3)	9126(2)	7672(1)	59(1)
O(7)	753(3)	7639(2)	6016(1)	65(1)
O(8)	223(3)	3843(2)	7782(1)	76(1)

O(9)	4920(3)	6756(2)	8481(1)	60(1)
O(10)	4749(3)	5239(2)	8234(1)	72(1)
O(11)	593(3)	2985(2)	9479(1)	59(1)
O(12)	7495(3)	3718(2)	9974(1)	67(1)
O(13)	6505(2)	7803(2)	7035(1)	43(1)
O(14)	6515(2)	6741(2)	7571(1)	48(1)
O(15)	10859(3)	8331(3)	9239(1)	83(1)
O(16)	10569(3)	11274(2)	7088(1)	76(1)
Zn(1)	5609(1)	8770(1)	7204(1)	36(1)
Zn(2)	4811(1)	6493(1)	7722(1)	37(1)

Table 3: Bond lengths [Å] and angles [°] for complex **(4)**.

C(1)-O(2)	1.209(5)
C(1)-O(1)	1.241(5)
C(1)-C(2)	1.515(5)
C(2)-C(3)	1.502(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(10)	1.355(5)
C(3)-C(4)	1.438(5)
C(4)-C(9)	1.394(4)
C(4)-C(5)	1.402(5)
C(5)-C(6)	1.371(5)
C(5)-H(5)	0.9300
C(6)-O(3)	1.369(4)
C(6)-C(7)	1.397(5)
C(7)-C(8)	1.377(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.390(5)
C(8)-H(8)	0.9300
C(9)-N(1)	1.415(4)
C(10)-N(1)	1.413(4)
C(10)-C(12)	1.489(5)
C(11)-O(3)	1.417(5)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-O(4)	1.212(4)
C(13)-N(1)	1.390(4)
C(13)-C(14)	1.490(5)
C(14)-C(19)	1.379(5)
C(14)-C(15)	1.386(5)
C(15)-C(16)	1.368(5)
C(15)-H(15)	0.9300

C(16)-C(17)	1.378(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.364(5)
C(17)-Cl(1)	1.737(4)
C(18)-C(19)	1.385(5)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-O(6)	1.219(4)
C(20)-O(5)	1.289(4)
C(20)-C(21)	1.500(5)
C(21)-C(22)	1.496(5)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(29)	1.350(5)
C(22)-C(23)	1.439(5)
C(23)-C(24)	1.387(5)
C(23)-C(28)	1.404(5)
C(24)-C(25)	1.380(5)
C(24)-H(24)	0.9300
C(25)-O(7)	1.375(4)
C(25)-C(26)	1.395(5)
C(26)-C(27)	1.385(5)
C(26)-H(26)	0.9300
C(27)-C(28)	1.381(5)
C(27)-H(27)	0.9300
C(28)-N(2)	1.410(4)
C(29)-N(2)	1.406(5)
C(29)-C(31)	1.501(5)
C(30)-O(7)	1.405(5)
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600
C(31)-H(31A)	0.9600
C(31)-H(31B)	0.9600
C(31)-H(31C)	0.9600
C(32)-O(8)	1.207(5)
C(32)-N(2)	1.411(4)

C(32)-C(33)	1.480(5)
C(33)-C(34)	1.382(5)
C(33)-C(38)	1.382(5)
C(34)-C(35)	1.385(6)
C(34)-H(34)	0.9300
C(35)-C(36)	1.366(5)
C(35)-H(35)	0.9300
C(36)-C(37)	1.379(5)
C(36)-Cl(2)	1.730(4)
C(37)-C(38)	1.369(5)
C(37)-H(37)	0.9300
C(38)-H(38)	0.9300
C(39)-O(10)	1.224(4)
C(39)-O(9)	1.248(4)
C(39)-C(40)	1.514(5)
C(40)-C(41)	1.490(5)
C(40)-H(40A)	0.9700
C(40)-H(40B)	0.9700
C(41)-C(48)	1.360(5)
C(41)-C(42)	1.441(5)
C(42)-C(43)	1.393(5)
C(42)-C(47)	1.399(4)
C(43)-C(44)	1.370(5)
C(43)-H(43)	0.9300
C(44)-O(11)	1.377(4)
C(44)-C(45)	1.396(5)
C(45)-C(46)	1.372(5)
C(45)-H(45)	0.9300
C(46)-C(47)	1.396(5)
C(46)-H(46)	0.9300
C(47)-N(3)	1.411(4)
C(48)-N(3)	1.415(4)
C(48)-C(50)	1.488(5)
C(49)-O(11)	1.423(5)
C(49)-H(49A)	0.9600
C(49)-H(49B)	0.9600
C(49)-H(49C)	0.9600

C(50)-H(50A)	0.9600
C(50)-H(50B)	0.9600
C(50)-H(50C)	0.9600
C(51)-O(12)	1.210(4)
C(51)-N(3)	1.405(4)
C(51)-C(52)	1.486(5)
C(52)-C(53)	1.380(5)
C(52)-C(57)	1.381(5)
C(53)-C(54)	1.376(5)
C(53)-H(53)	0.9300
C(54)-C(55)	1.375(5)
C(54)-H(54)	0.9300
C(55)-C(56)	1.372(5)
C(55)-Cl(3)	1.737(4)
C(56)-C(57)	1.379(5)
C(56)-H(56)	0.9300
C(57)-H(57)	0.9300
C(58)-O(13)	1.246(4)
C(58)-O(14)	1.256(4)
C(58)-C(59)	1.511(5)
C(59)-C(60)	1.499(5)
C(59)-H(59A)	0.9700
C(59)-H(59B)	0.9700
C(60)-C(67)	1.352(5)
C(60)-C(61)	1.434(5)
C(61)-C(62)	1.393(5)
C(61)-C(66)	1.395(5)
C(62)-C(63)	1.371(5)
C(62)-H(62)	0.9300
C(63)-O(15)	1.374(4)
C(63)-C(64)	1.392(6)
C(64)-C(65)	1.366(5)
C(64)-H(64)	0.9300
C(65)-C(66)	1.386(5)
C(65)-H(65)	0.9300
C(66)-N(4)	1.415(4)
C(67)-N(4)	1.411(5)

C(67)-C(69)	1.493(5)
C(68)-O(15)	1.409(6)
C(68)-H(68A)	0.9600
C(68)-H(68B)	0.9600
C(68)-H(68C)	0.9600
C(69)-H(69A)	0.9600
C(69)-H(69B)	0.9600
C(69)-H(69C)	0.9600
C(70)-O(16)	1.209(4)
C(70)-N(4)	1.406(5)
C(70)-C(71)	1.482(5)
C(71)-C(72)	1.381(5)
C(71)-C(76)	1.390(5)
C(72)-C(73)	1.372(5)
C(72)-H(72)	0.9300
C(73)-C(74)	1.374(5)
C(73)-H(73)	0.9300
C(74)-C(75)	1.372(5)
C(74)-Cl(4)	1.740(4)
C(75)-C(76)	1.372(6)
C(75)-H(75)	0.9300
C(76)-H(76)	0.9300
C(77)-N(5)	1.327(5)
C(77)-C(78)	1.389(6)
C(77)-H(77)	0.9300
C(78)-C(79)	1.374(7)
C(78)-C(82)	1.502(7)
C(79)-C(80)	1.355(7)
C(79)-H(79)	0.9300
C(80)-C(81)	1.372(6)
C(80)-H(80)	0.9300
C(81)-N(5)	1.336(5)
C(81)-H(81)	0.9300
C(82)-H(82A)	0.9600
C(82)-H(82B)	0.9600
C(82)-H(82C)	0.9600
C(83)-N(6)	1.335(4)

C(83)-C(84)	1.375(5)
C(83)-H(83)	0.9300
C(84)-C(85)	1.377(6)
C(84)-C(88)	1.501(6)
C(85)-C(86)	1.370(6)
C(85)-H(85)	0.9300
C(86)-C(87)	1.371(6)
C(86)-H(86)	0.9300
C(87)-N(6)	1.342(5)
C(87)-H(87)	0.9300
C(88)-H(88A)	0.9600
C(88)-H(88B)	0.9600
C(88)-H(88C)	0.9600
N(5)-Zn(1)	2.027(3)
N(6)-Zn(2)	2.031(3)
O(1)-Zn(1)	1.995(3)
O(2)-Zn(1)	2.403(3)
O(5)-Zn(2)	2.025(2)
O(5)-Zn(1)	2.081(2)
O(6)-Zn(1)	2.381(3)
O(9)-Zn(2)	1.979(3)
O(10)-Zn(2)	2.386(3)
O(13)-Zn(1)	2.035(2)
O(14)-Zn(2)	1.974(2)

O(2)-C(1)-O(1)	120.6(4)
O(2)-C(1)-C(2)	123.0(4)
O(1)-C(1)-C(2)	116.3(4)
C(3)-C(2)-C(1)	116.3(3)
C(3)-C(2)-H(2A)	108.2
C(1)-C(2)-H(2A)	108.2
C(3)-C(2)-H(2B)	108.2
C(1)-C(2)-H(2B)	108.2
H(2A)-C(2)-H(2B)	107.4
C(10)-C(3)-C(4)	108.0(3)
C(10)-C(3)-C(2)	126.2(3)
C(4)-C(3)-C(2)	125.6(3)

C(9)-C(4)-C(5)	120.2(3)
C(9)-C(4)-C(3)	107.8(3)
C(5)-C(4)-C(3)	131.8(3)
C(6)-C(5)-C(4)	118.6(3)
C(6)-C(5)-H(5)	120.7
C(4)-C(5)-H(5)	120.7
O(3)-C(6)-C(5)	124.9(3)
O(3)-C(6)-C(7)	114.4(4)
C(5)-C(6)-C(7)	120.6(3)
C(8)-C(7)-C(6)	121.6(4)
C(8)-C(7)-H(7)	119.2
C(6)-C(7)-H(7)	119.2
C(7)-C(8)-C(9)	117.9(3)
C(7)-C(8)-H(8)	121.1
C(9)-C(8)-H(8)	121.1
C(8)-C(9)-C(4)	121.1(3)
C(8)-C(9)-N(1)	131.4(3)
C(4)-C(9)-N(1)	107.2(3)
C(3)-C(10)-N(1)	109.0(3)
C(3)-C(10)-C(12)	128.7(3)
N(1)-C(10)-C(12)	122.3(3)
O(3)-C(11)-H(11A)	109.5
O(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(4)-C(13)-N(1)	122.2(3)
O(4)-C(13)-C(14)	120.3(3)
N(1)-C(13)-C(14)	117.4(3)
C(19)-C(14)-C(15)	119.3(3)

C(19)-C(14)-C(13)	118.2(3)
C(15)-C(14)-C(13)	122.3(3)
C(16)-C(15)-C(14)	121.0(3)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(17)	118.8(3)
C(15)-C(16)-H(16)	120.6
C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	121.6(3)
C(18)-C(17)-Cl(1)	119.1(3)
C(16)-C(17)-Cl(1)	119.3(3)
C(17)-C(18)-C(19)	119.4(3)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(14)-C(19)-C(18)	120.0(3)
C(14)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
O(6)-C(20)-O(5)	118.2(3)
O(6)-C(20)-C(21)	122.4(3)
O(5)-C(20)-C(21)	119.4(3)
C(22)-C(21)-C(20)	113.8(3)
C(22)-C(21)-H(21A)	108.8
C(20)-C(21)-H(21A)	108.8
C(22)-C(21)-H(21B)	108.8
C(20)-C(21)-H(21B)	108.8
H(21A)-C(21)-H(21B)	107.7
C(29)-C(22)-C(23)	108.3(3)
C(29)-C(22)-C(21)	126.6(3)
C(23)-C(22)-C(21)	125.1(3)
C(24)-C(23)-C(28)	119.7(3)
C(24)-C(23)-C(22)	132.9(3)
C(28)-C(23)-C(22)	107.4(3)
C(25)-C(24)-C(23)	119.1(3)
C(25)-C(24)-H(24)	120.4
C(23)-C(24)-H(24)	120.4
O(7)-C(25)-C(24)	115.8(3)
O(7)-C(25)-C(26)	123.5(3)

C(24)-C(25)-C(26)	120.6(3)
C(27)-C(26)-C(25)	121.0(3)
C(27)-C(26)-H(26)	119.5
C(25)-C(26)-H(26)	119.5
C(28)-C(27)-C(26)	118.1(3)
C(28)-C(27)-H(27)	121.0
C(26)-C(27)-H(27)	121.0
C(27)-C(28)-C(23)	121.5(3)
C(27)-C(28)-N(2)	131.5(3)
C(23)-C(28)-N(2)	106.9(3)
C(22)-C(29)-N(2)	109.1(3)
C(22)-C(29)-C(31)	129.5(4)
N(2)-C(29)-C(31)	121.2(3)
O(7)-C(30)-H(30A)	109.5
O(7)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
O(7)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
O(8)-C(32)-N(2)	121.2(4)
O(8)-C(32)-C(33)	123.5(3)
N(2)-C(32)-C(33)	115.3(3)
C(34)-C(33)-C(38)	118.9(4)
C(34)-C(33)-C(32)	120.2(4)
C(38)-C(33)-C(32)	120.8(3)
C(33)-C(34)-C(35)	120.4(4)
C(33)-C(34)-H(34)	119.8
C(35)-C(34)-H(34)	119.8
C(36)-C(35)-C(34)	119.2(4)
C(36)-C(35)-H(35)	120.4
C(34)-C(35)-H(35)	120.4

C(35)-C(36)-C(37)	121.5(4)
C(35)-C(36)-Cl(2)	119.8(3)
C(37)-C(36)-Cl(2)	118.7(3)
C(38)-C(37)-C(36)	118.7(4)
C(38)-C(37)-H(37)	120.7
C(36)-C(37)-H(37)	120.7
C(37)-C(38)-C(33)	121.3(4)
C(37)-C(38)-H(38)	119.3
C(33)-C(38)-H(38)	119.3
O(10)-C(39)-O(9)	120.1(3)
O(10)-C(39)-C(40)	123.3(3)
O(9)-C(39)-C(40)	116.5(3)
C(41)-C(40)-C(39)	117.2(3)
C(41)-C(40)-H(40A)	108.0
C(39)-C(40)-H(40A)	108.0
C(41)-C(40)-H(40B)	108.0
C(39)-C(40)-H(40B)	108.0
H(40A)-C(40)-H(40B)	107.2
C(48)-C(41)-C(42)	107.8(3)
C(48)-C(41)-C(40)	125.9(3)
C(42)-C(41)-C(40)	126.2(3)
C(43)-C(42)-C(47)	120.5(3)
C(43)-C(42)-C(41)	131.7(3)
C(47)-C(42)-C(41)	107.7(3)
C(44)-C(43)-C(42)	118.7(3)
C(44)-C(43)-H(43)	120.6
C(42)-C(43)-H(43)	120.6
C(43)-C(44)-O(11)	124.9(3)
C(43)-C(44)-C(45)	120.7(3)
O(11)-C(44)-C(45)	114.4(3)
C(46)-C(45)-C(44)	121.5(3)
C(46)-C(45)-H(45)	119.3
C(44)-C(45)-H(45)	119.3
C(45)-C(46)-C(47)	118.3(3)
C(45)-C(46)-H(46)	120.9
C(47)-C(46)-H(46)	120.9
C(46)-C(47)-C(42)	120.3(3)

C(46)-C(47)-N(3)	131.9(3)
C(42)-C(47)-N(3)	107.4(3)
C(41)-C(48)-N(3)	109.1(3)
C(41)-C(48)-C(50)	127.9(3)
N(3)-C(48)-C(50)	122.8(3)
O(11)-C(49)-H(49A)	109.5
O(11)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
O(11)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(48)-C(50)-H(50A)	109.5
C(48)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(48)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
O(12)-C(51)-N(3)	120.4(3)
O(12)-C(51)-C(52)	121.3(3)
N(3)-C(51)-C(52)	118.2(3)
C(53)-C(52)-C(57)	118.7(3)
C(53)-C(52)-C(51)	122.9(3)
C(57)-C(52)-C(51)	118.2(3)
C(54)-C(53)-C(52)	121.3(3)
C(54)-C(53)-H(53)	119.3
C(52)-C(53)-H(53)	119.3
C(55)-C(54)-C(53)	118.7(3)
C(55)-C(54)-H(54)	120.7
C(53)-C(54)-H(54)	120.7
C(56)-C(55)-C(54)	121.3(3)
C(56)-C(55)-Cl(3)	119.7(3)
C(54)-C(55)-Cl(3)	119.0(3)
C(55)-C(56)-C(57)	119.3(3)
C(55)-C(56)-H(56)	120.4
C(57)-C(56)-H(56)	120.4
C(56)-C(57)-C(52)	120.7(3)
C(56)-C(57)-H(57)	119.7

C(52)-C(57)-H(57)	119.7
O(13)-C(58)-O(14)	125.3(3)
O(13)-C(58)-C(59)	116.6(3)
O(14)-C(58)-C(59)	118.2(3)
C(60)-C(59)-C(58)	111.3(3)
C(60)-C(59)-H(59A)	109.4
C(58)-C(59)-H(59A)	109.4
C(60)-C(59)-H(59B)	109.4
C(58)-C(59)-H(59B)	109.4
H(59A)-C(59)-H(59B)	108.0
C(67)-C(60)-C(61)	108.0(3)
C(67)-C(60)-C(59)	127.6(3)
C(61)-C(60)-C(59)	124.4(3)
C(62)-C(61)-C(66)	120.4(3)
C(62)-C(61)-C(60)	131.7(3)
C(66)-C(61)-C(60)	107.9(3)
C(63)-C(62)-C(61)	118.3(3)
C(63)-C(62)-H(62)	120.9
C(61)-C(62)-H(62)	120.9
C(62)-C(63)-O(15)	124.6(4)
C(62)-C(63)-C(64)	120.6(3)
O(15)-C(63)-C(64)	114.8(4)
C(65)-C(64)-C(63)	121.9(4)
C(65)-C(64)-H(64)	119.0
C(63)-C(64)-H(64)	119.0
C(64)-C(65)-C(66)	117.7(4)
C(64)-C(65)-H(65)	121.1
C(66)-C(65)-H(65)	121.1
C(65)-C(66)-C(61)	121.0(3)
C(65)-C(66)-N(4)	131.6(3)
C(61)-C(66)-N(4)	107.2(3)
C(60)-C(67)-N(4)	109.3(3)
C(60)-C(67)-C(69)	128.3(4)
N(4)-C(67)-C(69)	122.3(3)
O(15)-C(68)-H(68A)	109.5
O(15)-C(68)-H(68B)	109.5
H(68A)-C(68)-H(68B)	109.5

O(15)-C(68)-H(68C)	109.5
H(68A)-C(68)-H(68C)	109.5
H(68B)-C(68)-H(68C)	109.5
C(67)-C(69)-H(69A)	109.5
C(67)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69B)	109.5
C(67)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5
O(16)-C(70)-N(4)	121.1(4)
O(16)-C(70)-C(71)	123.3(4)
N(4)-C(70)-C(71)	115.5(3)
C(72)-C(71)-C(76)	119.0(4)
C(72)-C(71)-C(70)	119.6(3)
C(76)-C(71)-C(70)	121.3(3)
C(73)-C(72)-C(71)	120.8(3)
C(73)-C(72)-H(72)	119.6
C(71)-C(72)-H(72)	119.6
C(72)-C(73)-C(74)	118.8(4)
C(72)-C(73)-H(73)	120.6
C(74)-C(73)-H(73)	120.6
C(75)-C(74)-C(73)	122.0(4)
C(75)-C(74)-Cl(4)	119.7(3)
C(73)-C(74)-Cl(4)	118.4(3)
C(76)-C(75)-C(74)	118.7(3)
C(76)-C(75)-H(75)	120.7
C(74)-C(75)-H(75)	120.7
C(75)-C(76)-C(71)	120.7(4)
C(75)-C(76)-H(76)	119.6
C(71)-C(76)-H(76)	119.6
N(5)-C(77)-C(78)	123.8(4)
N(5)-C(77)-H(77)	118.1
C(78)-C(77)-H(77)	118.1
C(79)-C(78)-C(77)	116.0(4)
C(79)-C(78)-C(82)	123.1(5)
C(77)-C(78)-C(82)	120.9(5)
C(80)-C(79)-C(78)	121.0(4)

C(80)-C(79)-H(79)	119.5
C(78)-C(79)-H(79)	119.5
C(79)-C(80)-C(81)	119.4(5)
C(79)-C(80)-H(80)	120.3
C(81)-C(80)-H(80)	120.3
N(5)-C(81)-C(80)	121.4(4)
N(5)-C(81)-H(81)	119.3
C(80)-C(81)-H(81)	119.3
C(78)-C(82)-H(82A)	109.5
C(78)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5
C(78)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5
N(6)-C(83)-C(84)	123.6(4)
N(6)-C(83)-H(83)	118.2
C(84)-C(83)-H(83)	118.2
C(83)-C(84)-C(85)	116.9(4)
C(83)-C(84)-C(88)	119.7(4)
C(85)-C(84)-C(88)	123.5(4)
C(86)-C(85)-C(84)	120.7(4)
C(86)-C(85)-H(85)	119.6
C(84)-C(85)-H(85)	119.6
C(85)-C(86)-C(87)	118.6(4)
C(85)-C(86)-H(86)	120.7
C(87)-C(86)-H(86)	120.7
N(6)-C(87)-C(86)	122.1(4)
N(6)-C(87)-H(87)	119.0
C(86)-C(87)-H(87)	119.0
C(84)-C(88)-H(88A)	109.5
C(84)-C(88)-H(88B)	109.5
H(88A)-C(88)-H(88B)	109.5
C(84)-C(88)-H(88C)	109.5
H(88A)-C(88)-H(88C)	109.5
H(88B)-C(88)-H(88C)	109.5
C(13)-N(1)-C(10)	125.3(3)
C(13)-N(1)-C(9)	126.7(3)

C(10)-N(1)-C(9)	107.8(3)
C(29)-N(2)-C(28)	108.3(3)
C(29)-N(2)-C(32)	125.4(3)
C(28)-N(2)-C(32)	126.1(3)
C(51)-N(3)-C(47)	126.8(3)
C(51)-N(3)-C(48)	123.7(3)
C(47)-N(3)-C(48)	107.9(3)
C(70)-N(4)-C(67)	126.2(3)
C(70)-N(4)-C(66)	126.0(3)
C(67)-N(4)-C(66)	107.6(3)
C(77)-N(5)-C(81)	118.5(3)
C(77)-N(5)-Zn(1)	119.9(3)
C(81)-N(5)-Zn(1)	121.6(3)
C(83)-N(6)-C(87)	118.1(3)
C(83)-N(6)-Zn(2)	119.1(2)
C(87)-N(6)-Zn(2)	122.8(3)
C(1)-O(1)-Zn(1)	100.4(3)
C(1)-O(2)-Zn(1)	81.9(3)
C(6)-O(3)-C(11)	117.2(3)
C(20)-O(5)-Zn(2)	137.7(2)
C(20)-O(5)-Zn(1)	98.29(19)
Zn(2)-O(5)-Zn(1)	123.26(10)
C(20)-O(6)-Zn(1)	86.2(2)
C(25)-O(7)-C(30)	118.7(3)
C(39)-O(9)-Zn(2)	100.2(2)
C(39)-O(10)-Zn(2)	81.7(2)
C(44)-O(11)-C(49)	117.7(3)
C(58)-O(13)-Zn(1)	137.2(2)
C(58)-O(14)-Zn(2)	125.6(2)
C(63)-O(15)-C(68)	118.2(4)
O(1)-Zn(1)-N(5)	149.36(13)
O(1)-Zn(1)-O(13)	94.05(12)
N(5)-Zn(1)-O(13)	96.47(11)
O(1)-Zn(1)-O(5)	100.97(11)
N(5)-Zn(1)-O(5)	107.90(11)
O(13)-Zn(1)-O(5)	88.98(9)
O(1)-Zn(1)-O(6)	96.39(13)

N(5)-Zn(1)-O(6)	90.81(11)
O(13)-Zn(1)-O(6)	145.91(9)
O(5)-Zn(1)-O(6)	57.20(8)
O(1)-Zn(1)-O(2)	56.97(12)
N(5)-Zn(1)-O(2)	92.68(12)
O(13)-Zn(1)-O(2)	116.22(14)
O(5)-Zn(1)-O(2)	145.74(12)
O(6)-Zn(1)-O(2)	96.54(13)
O(14)-Zn(2)-O(9)	109.73(12)
O(14)-Zn(2)-O(5)	102.11(10)
O(9)-Zn(2)-O(5)	95.56(10)
O(14)-Zn(2)-N(6)	109.15(11)
O(9)-Zn(2)-N(6)	134.79(13)
O(5)-Zn(2)-N(6)	98.02(10)
O(14)-Zn(2)-O(10)	98.26(11)
O(9)-Zn(2)-O(10)	57.89(10)
O(5)-Zn(2)-O(10)	151.02(10)
N(6)-Zn(2)-O(10)	94.49(11)

Symmetry transformations used to generate equivalent atoms:

Table 4: 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)	51(2)	56(2)	49(2)	23(2)	15(2)	27(2)
C(2)	56(2)	40(2)	43(2)	12(2)	1(2)	17(2)
C(3)	48(2)	38(2)	32(2)	13(1)	4(2)	17(2)
C(4)	42(2)	42(2)	30(2)	11(1)	7(1)	21(2)
C(5)	49(2)	53(2)	46(2)	18(2)	10(2)	30(2)
C(6)	40(2)	72(3)	50(2)	27(2)	13(2)	29(2)
C(7)	46(2)	59(2)	58(2)	30(2)	13(2)	17(2)
C(8)	45(2)	44(2)	49(2)	21(2)	10(2)	21(2)
C(9)	39(2)	40(2)	31(2)	13(1)	7(1)	17(2)
C(10)	41(2)	39(2)	43(2)	14(2)	3(2)	11(2)
C(11)	57(3)	126(5)	125(5)	64(4)	31(3)	59(3)
C(12)	43(2)	66(3)	112(4)	47(3)	16(2)	11(2)
C(13)	36(2)	49(2)	48(2)	11(2)	4(2)	20(2)
C(14)	32(2)	46(2)	37(2)	12(2)	2(1)	17(2)
C(15)	57(2)	48(2)	38(2)	7(2)	1(2)	30(2)
C(16)	61(2)	63(3)	32(2)	8(2)	6(2)	31(2)
C(17)	41(2)	46(2)	38(2)	14(2)	2(2)	11(2)
C(18)	52(2)	38(2)	52(2)	9(2)	9(2)	18(2)
C(19)	43(2)	46(2)	44(2)	8(2)	12(2)	21(2)
C(20)	29(2)	30(2)	43(2)	4(1)	3(1)	6(1)
C(21)	36(2)	41(2)	45(2)	2(2)	12(2)	14(2)
C(22)	30(2)	37(2)	44(2)	9(2)	17(1)	14(1)
C(23)	27(2)	36(2)	45(2)	8(1)	14(1)	12(1)
C(24)	28(2)	34(2)	53(2)	14(2)	11(2)	7(1)
C(25)	38(2)	45(2)	54(2)	21(2)	13(2)	12(2)
C(26)	39(2)	48(2)	44(2)	12(2)	7(2)	10(2)
C(27)	36(2)	37(2)	53(2)	9(2)	10(2)	3(2)
C(28)	33(2)	36(2)	49(2)	14(2)	14(2)	10(2)
C(29)	34(2)	45(2)	48(2)	13(2)	11(2)	10(2)
C(30)	89(4)	85(4)	74(3)	46(3)	-12(3)	-1(3)
C(31)	60(3)	71(3)	57(3)	30(2)	15(2)	13(2)
C(32)	53(2)	42(2)	62(2)	23(2)	19(2)	10(2)

C(33)	46(2)	34(2)	53(2)	20(2)	20(2)	8(2)
C(34)	55(2)	45(2)	54(2)	16(2)	22(2)	18(2)
C(35)	61(3)	40(2)	44(2)	9(2)	12(2)	7(2)
C(36)	49(2)	55(2)	36(2)	19(2)	13(2)	11(2)
C(37)	55(2)	51(2)	53(2)	23(2)	22(2)	20(2)
C(38)	54(2)	31(2)	58(2)	16(2)	20(2)	5(2)
C(39)	47(2)	37(2)	43(2)	14(2)	13(2)	18(2)
C(40)	69(3)	33(2)	36(2)	6(2)	12(2)	19(2)
C(41)	55(2)	35(2)	24(2)	5(1)	8(2)	14(2)
C(42)	46(2)	36(2)	26(2)	5(1)	4(1)	17(2)
C(43)	54(2)	43(2)	35(2)	6(2)	4(2)	26(2)
C(44)	43(2)	50(2)	35(2)	1(2)	4(2)	20(2)
C(45)	43(2)	42(2)	45(2)	9(2)	11(2)	9(2)
C(46)	47(2)	38(2)	40(2)	12(2)	5(2)	16(2)
C(47)	40(2)	36(2)	28(2)	4(1)	4(1)	16(2)
C(48)	46(2)	34(2)	31(2)	5(1)	8(2)	8(2)
C(49)	50(3)	98(4)	105(4)	26(3)	15(3)	41(3)
C(50)	57(3)	44(2)	58(2)	4(2)	15(2)	5(2)
C(51)	38(2)	45(2)	45(2)	3(2)	5(2)	17(2)
C(52)	38(2)	41(2)	39(2)	9(2)	8(2)	17(2)
C(53)	45(2)	46(2)	34(2)	10(2)	6(2)	19(2)
C(54)	45(2)	43(2)	38(2)	5(2)	2(2)	16(2)
C(55)	48(2)	38(2)	48(2)	10(2)	10(2)	18(2)
C(56)	64(3)	54(2)	52(2)	14(2)	-2(2)	32(2)
C(57)	51(2)	55(2)	43(2)	2(2)	-6(2)	25(2)
C(58)	32(2)	35(2)	34(2)	-4(1)	3(1)	9(1)
C(59)	34(2)	39(2)	52(2)	4(2)	11(2)	14(2)
C(60)	29(2)	40(2)	44(2)	8(2)	9(1)	14(1)
C(61)	23(2)	41(2)	48(2)	13(2)	10(1)	14(1)
C(62)	31(2)	46(2)	57(2)	24(2)	13(2)	10(2)
C(63)	40(2)	71(3)	50(2)	31(2)	9(2)	15(2)
C(64)	36(2)	74(3)	45(2)	15(2)	-1(2)	8(2)
C(65)	39(2)	46(2)	52(2)	13(2)	5(2)	7(2)
C(66)	32(2)	43(2)	45(2)	18(2)	8(2)	14(2)
C(67)	35(2)	50(2)	41(2)	9(2)	5(2)	14(2)
C(68)	90(4)	110(5)	87(4)	69(4)	17(3)	2(3)
C(69)	66(3)	70(3)	49(2)	19(2)	2(2)	14(2)

C(70)	51(2)	48(2)	58(2)	22(2)	12(2)	20(2)
C(71)	51(2)	34(2)	51(2)	21(2)	17(2)	15(2)
C(72)	54(2)	28(2)	57(2)	10(2)	12(2)	10(2)
C(73)	48(2)	36(2)	55(2)	13(2)	15(2)	14(2)
C(74)	48(2)	41(2)	35(2)	13(2)	13(2)	4(2)
C(75)	66(3)	27(2)	45(2)	6(2)	15(2)	7(2)
C(76)	68(3)	38(2)	54(2)	18(2)	24(2)	24(2)
C(77)	38(2)	57(2)	56(2)	6(2)	9(2)	15(2)
C(78)	42(2)	84(3)	58(3)	-7(2)	2(2)	31(2)
C(79)	61(3)	57(3)	96(4)	-21(3)	-16(3)	10(2)
C(80)	67(3)	43(3)	111(4)	2(3)	-6(3)	-3(2)
C(81)	55(3)	37(2)	77(3)	10(2)	2(2)	5(2)
C(82)	66(3)	136(5)	63(3)	2(3)	-9(3)	45(3)
C(83)	50(2)	42(2)	47(2)	7(2)	16(2)	20(2)
C(84)	53(2)	65(3)	47(2)	4(2)	14(2)	33(2)
C(85)	52(3)	64(3)	62(3)	-13(2)	2(2)	17(2)
C(86)	62(3)	39(2)	80(3)	1(2)	9(2)	4(2)
C(87)	60(3)	37(2)	59(2)	13(2)	15(2)	15(2)
C(88)	98(4)	101(4)	54(3)	12(3)	15(3)	57(3)
Cl(1)	92(1)	64(1)	54(1)	30(1)	16(1)	22(1)
Cl(2)	52(1)	97(1)	53(1)	9(1)	2(1)	15(1)
Cl(3)	75(1)	41(1)	78(1)	12(1)	10(1)	25(1)
Cl(4)	55(1)	66(1)	53(1)	10(1)	10(1)	-5(1)
N(1)	36(2)	40(2)	44(2)	17(1)	8(1)	15(1)
N(2)	40(2)	38(2)	53(2)	17(1)	13(1)	7(1)
N(3)	41(2)	35(2)	40(2)	9(1)	6(1)	12(1)
N(4)	39(2)	40(2)	51(2)	20(1)	5(1)	8(1)
N(5)	37(2)	40(2)	49(2)	4(1)	8(1)	10(1)
N(6)	43(2)	36(2)	43(2)	6(1)	10(1)	14(1)
O(1)	94(2)	69(2)	65(2)	43(2)	4(2)	32(2)
O(2)	103(3)	92(3)	64(2)	32(2)	-28(2)	-8(2)
O(3)	49(2)	114(3)	101(3)	66(2)	33(2)	44(2)
O(4)	53(2)	84(2)	95(2)	47(2)	35(2)	40(2)
O(5)	37(1)	33(1)	48(1)	12(1)	17(1)	18(1)
O(6)	54(2)	31(1)	100(2)	21(1)	25(2)	17(1)
O(7)	57(2)	60(2)	63(2)	33(2)	-2(1)	1(1)
O(8)	63(2)	53(2)	112(3)	43(2)	6(2)	14(2)

O(9)	105(2)	48(2)	46(2)	22(1)	27(2)	40(2)
O(10)	128(3)	48(2)	37(2)	7(1)	15(2)	31(2)
O(11)	43(2)	71(2)	64(2)	13(2)	10(1)	24(1)
O(12)	48(2)	51(2)	87(2)	-1(2)	-16(2)	14(1)
O(13)	44(1)	55(2)	41(1)	12(1)	11(1)	28(1)
O(14)	45(1)	53(2)	55(2)	23(1)	20(1)	19(1)
O(15)	63(2)	107(3)	62(2)	52(2)	0(2)	1(2)
O(16)	71(2)	63(2)	93(2)	38(2)	-3(2)	23(2)
Zn(1)	33(1)	31(1)	42(1)	10(1)	6(1)	7(1)
Zn(2)	44(1)	30(1)	38(1)	9(1)	14(1)	13(1)

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

	x	y	z	U(eq)
H(2A)	4464	8885	5568	56
H(2B)	3243	8807	5785	56
H(5)	6821	10475	5754	54
H(7)	7778	13231	5424	63
H(8)	5715	13162	5340	53
H(11A)	8993	11268	6180	136
H(11B)	10083	11510	5866	136
H(11C)	8779	10662	5620	136
H(12A)	1819	9455	5788	109
H(12B)	1374	10040	5389	109
H(12C)	1792	10517	5980	109
H(15)	3723	11832	4466	55
H(16)	4113	12867	3870	60
H(18)	3476	14961	4808	56
H(19)	3070	13912	5406	52
H(21A)	3205	7697	8363	48
H(21B)	2437	8302	8119	48
H(24)	1919	8002	6927	47
H(26)	-880	5809	5916	54
H(27)	-1088	4763	6520	53
H(30A)	20	6716	5356	137
H(30B)	257	7835	5316	137
H(30C)	-880	7232	5551	137
H(31A)	2290	6360	8662	95
H(31B)	2073	5264	8403	95
H(31C)	946	5529	8568	95
H(34)	-1746	2561	7004	60
H(35)	-3894	1939	6659	62
H(37)	-4123	4551	7240	60
H(38)	-1981	5179	7557	58
H(40A)	5784	6351	9339	55

H(40B)	4316	5980	9274	55
H(43)	2374	4473	9230	51
H(45)	1693	1851	9705	53
H(46)	3763	1978	9741	50
H(49A)	502	4324	9515	120
H(49B)	-809	3458	9309	120
H(49C)	179	3718	8948	120
H(50A)	7341	5681	9144	85
H(50B)	7611	4683	9110	85
H(50C)	7872	5376	9649	85
H(53)	4878	1808	8919	49
H(54)	4541	131	8701	51
H(56)	6839	324	10028	66
H(57)	7226	2015	10228	60
H(59A)	8544	6867	7347	49
H(59B)	8263	7189	6813	49
H(62)	9427	7548	8304	53
H(64)	12169	10012	9144	67
H(65)	12204	10829	8455	57
H(68A)	9104	7444	9150	149
H(68B)	10019	7276	9599	149
H(68C)	10016	6887	9020	149
H(69A)	8647	8540	6411	97
H(69B)	9822	9507	6442	97
H(69C)	8590	9594	6599	97
H(72)	13041	10273	7392	57
H(73)	15175	11074	7716	55
H(75)	14569	13570	8229	58
H(76)	12449	12786	7869	60
H(77)	6949	8973	8262	62
H(79)	9737	11607	8691	97
H(80)	9189	11972	7899	100
H(81)	7512	10829	7303	73
H(82A)	9566	9973	9141	134
H(82B)	8143	9310	9094	134
H(82C)	8645	10438	9360	134
H(83)	3766	6513	6655	54

H(85)	1135	3890	5992	77
H(86)	1458	3311	6751	79
H(87)	2960	4357	7442	62
H(88A)	2309	6368	5845	118
H(88B)	1487	5295	5532	118
H(88C)	2957	5696	5578	118

Appendix D: Crystal structure data of $[Zn(diclo)_2(apy)_2]$ **(5)**

Table 1: Crystal data and structure refinement for complex **(5)**.

Empirical formula	C39.50 H35 Cl4 N6 O4.50 Zn	
Formula weight	872.91	
Temperature	295(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3725(6) Å	α= 93.720(1)°.
	b = 11.0190(8) Å	β= 98.353(1)°.
	c = 23.477(2) Å	γ = 94.552(1)°.
Volume	2129.7(3) $Å^3$	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.874 mm^{-1}	
F(000)	896	
Crystal size	0.22 x 0.15 x 0.11 mm^3	
Theta range for data collection	1.86 to 27.00°.	
Index ranges	-10<=h<=10, -14<=k<=14, -29<=l<=29	
Reflections collected	23393	
Independent reflections	9161 [R(int) = 0.0332]	
Completeness to theta = 27.00°	98.6 %	
Absorption correction	None	
Max. and min. transmission	0.9099 and 0.8309	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9161 / 8 / 535	
Goodness-of-fit on F^2	1.242	
Final R indices [I>2sigma(I)]	R1 = 0.0976, wR2 = 0.2436	
R indices (all data)	R1 = 0.1089, wR2 = 0.2506	
Largest diff. peak and hole	1.305 and -0.698 $e.Å^{-3}$	

Table 2: 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)
C(1)	4809(6)	3994(5)	1213(2)	43(1)
C(2)	5280(7)	2708(5)	1291(3)	50(1)
C(3)	3964(6)	1740(5)	1027(2)	42(1)
C(4)	3964(8)	1194(6)	479(3)	55(2)
C(5)	2816(9)	272(6)	241(3)	63(2)
C(6)	1636(9)	-132(6)	547(3)	60(2)
C(7)	1589(7)	416(5)	1090(2)	51(1)
C(8)	2713(6)	1366(5)	1329(2)	39(1)
C(9)	1530(8)	1562(5)	2226(2)	53(2)
C(10)	1751(12)	515(7)	2529(3)	79(2)
C(11)	709(17)	127(9)	2893(4)	104(4)
C(12)	-568(18)	770(13)	2962(4)	129(5)
C(13)	-862(12)	1800(10)	2680(4)	102(3)
C(14)	188(8)	2166(7)	2308(3)	65(2)
C(15)	2277(8)	5941(6)	2614(2)	50(1)
C(16)	1152(8)	6060(7)	3065(2)	60(2)
C(17)	1904(7)	6139(6)	3688(2)	52(1)
C(18)	1914(10)	7210(7)	4030(3)	69(2)
C(19)	2504(11)	7286(7)	4618(3)	77(2)
C(20)	3086(10)	6289(7)	4863(3)	74(2)
C(21)	3109(8)	5228(6)	4535(3)	58(2)
C(22)	2537(7)	5135(6)	3945(2)	49(1)
C(23)	2900(10)	2954(7)	3824(3)	69(2)
C(24)	1901(14)	2363(9)	4155(4)	96(3)
C(25)	2290(20)	1244(12)	4386(6)	134(5)
C(26)	3650(30)	753(13)	4264(7)	150(7)
C(27)	4640(19)	1270(11)	3932(6)	128(5)
C(28)	4290(12)	2380(7)	3711(4)	86(3)
C(29)	1957(7)	6334(5)	270(2)	41(1)
C(30)	805(8)	6560(5)	-198(2)	53(1)
C(31)	-710(8)	6763(6)	-119(3)	60(2)
C(32)	-1124(8)	6765(6)	435(3)	61(2)

C(33)	41(7)	6540(5)	872(3)	49(1)
C(34)	6498(7)	7006(6)	1955(2)	47(1)
C(35)	7858(8)	7830(7)	1969(3)	68(2)
C(36)	7715(9)	8862(8)	1684(3)	77(2)
C(37)	6257(9)	9035(6)	1358(3)	67(2)
C(38)	4985(7)	8199(5)	1352(3)	50(1)
C(39)	7384(13)	7530(16)	3782(6)	70(4)
C(40)	5900(20)	8110(20)	3719(16)	220(20)
C(41)	7420(20)	6410(20)	4006(9)	108(7)
Cl(1)	3400(5)	-280(2)	2450(1)	118(1)
Cl(2)	-196(3)	3447(2)	1934(1)	85(1)
Cl(3)	146(4)	2956(3)	4275(1)	129(1)
Cl(4)	5540(3)	3049(3)	3284(1)	115(1)
N(1)	2642(6)	1970(4)	1872(2)	48(1)
N(2)	2563(7)	4045(5)	3594(2)	57(1)
N(3)	1577(5)	6331(4)	803(2)	39(1)
N(4)	3490(7)	6145(5)	189(2)	55(1)
N(5)	5066(5)	7185(4)	1637(2)	38(1)
N(6)	6559(7)	5987(6)	2248(3)	69(2)
O(1)	3643(5)	4298(3)	1477(2)	47(1)
O(2)	5495(5)	4653(4)	902(2)	52(1)
O(3)	1721(5)	6282(4)	2119(2)	50(1)
O(4)	3580(6)	5523(6)	2721(2)	77(2)
O(5)	8252(13)	7770(12)	3447(5)	94(4)
Zn(1)	3084(1)	5981(1)	1524(1)	35(1)

Table 3: Bond lengths [Å] and angles [°] for complex **(5)**.

C(1)-O(2)	1.230(6)
C(1)-O(1)	1.284(6)
C(1)-C(2)	1.516(8)
C(2)-C(3)	1.506(8)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.384(8)
C(3)-C(8)	1.398(7)
C(4)-C(5)	1.372(10)
C(4)-H(4)	0.9300
C(5)-C(6)	1.367(10)
C(5)-H(5)	0.9300
C(6)-C(7)	1.381(8)
C(6)-H(6)	0.9300
C(7)-C(8)	1.382(8)
C(7)-H(7)	0.9300
C(8)-N(1)	1.410(7)
C(9)-C(14)	1.381(10)
C(9)-N(1)	1.403(7)
C(9)-C(10)	1.404(9)
C(10)-C(11)	1.370(13)
C(10)-Cl(1)	1.718(10)
C(11)-C(12)	1.352(17)
C(11)-H(11)	0.9300
C(12)-C(13)	1.372(18)
C(12)-H(12)	0.9300
C(13)-C(14)	1.382(10)
C(13)-H(13)	0.9300
C(14)-Cl(2)	1.738(8)
C(15)-O(4)	1.216(7)
C(15)-O(3)	1.279(6)
C(15)-C(16)	1.522(8)
C(16)-C(17)	1.500(8)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700

C(17)-C(18)	1.382(9)
C(17)-C(22)	1.398(8)
C(18)-C(19)	1.391(10)
C(18)-H(18)	0.9300
C(19)-C(20)	1.365(11)
C(19)-H(19)	0.9300
C(20)-C(21)	1.360(10)
C(20)-H(20)	0.9300
C(21)-C(22)	1.394(8)
C(21)-H(21)	0.9300
C(22)-N(2)	1.415(8)
C(23)-C(24)	1.375(12)
C(23)-N(2)	1.383(9)
C(23)-C(28)	1.418(12)
C(24)-C(25)	1.421(16)
C(24)-Cl(3)	1.707(12)
C(25)-C(26)	1.36(2)
C(25)-H(25)	0.9300
C(26)-C(27)	1.34(2)
C(26)-H(26)	0.9300
C(27)-C(28)	1.396(14)
C(27)-H(27)	0.9300
C(28)-Cl(4)	1.708(11)
C(29)-N(3)	1.334(6)
C(29)-N(4)	1.355(7)
C(29)-C(30)	1.402(8)
C(30)-C(31)	1.342(10)
C(30)-H(30)	0.9300
C(31)-C(32)	1.394(10)
C(31)-H(31)	0.9300
C(32)-C(33)	1.358(8)
C(32)-H(32)	0.9300
C(33)-N(3)	1.356(7)
C(33)-H(33)	0.9300
C(34)-N(5)	1.353(7)
C(34)-N(6)	1.354(8)
C(34)-C(35)	1.395(9)

C(35)-C(36)	1.362(11)
C(35)-H(35)	0.9300
C(36)-C(37)	1.377(11)
C(36)-H(36)	0.9300
C(37)-C(38)	1.349(9)
C(37)-H(37)	0.9300
C(38)-N(5)	1.341(7)
C(38)-H(38)	0.9300
C(39)-O(5)	1.176(15)
C(39)-C(41)	1.38(2)
C(39)-C(40)	1.436(10)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
Cl(4)-H(1N2)	2.52(5)
N(1)-H(1N1)	0.850(10)
N(2)-H(1N2)	0.851(10)
N(3)-Zn(1)	2.037(4)
N(4)-H(1N4)	0.851(10)
N(4)-H(2N4)	0.850(10)
N(5)-Zn(1)	2.016(4)
N(6)-H(1N6)	0.851(10)
N(6)-H(2N6)	0.849(10)
O(1)-Zn(1)	1.949(4)
O(1)-H(1N1)	2.16(4)
O(2)-H(1N4)	2.05(2)
O(3)-Zn(1)	1.956(4)
O(4)-H(1N6)	2.06(2)
O(4)-H(1N2)	2.21(4)

O(2)-C(1)-O(1)	124.6(5)
O(2)-C(1)-C(2)	120.3(5)
O(1)-C(1)-C(2)	115.0(5)
C(3)-C(2)-C(1)	113.0(4)

C(3)-C(2)-H(2A)	109.0
C(1)-C(2)-H(2A)	109.0
C(3)-C(2)-H(2B)	109.0
C(1)-C(2)-H(2B)	109.0
H(2A)-C(2)-H(2B)	107.8
C(4)-C(3)-C(8)	118.3(5)
C(4)-C(3)-C(2)	120.8(5)
C(8)-C(3)-C(2)	120.9(5)
C(5)-C(4)-C(3)	121.6(6)
C(5)-C(4)-H(4)	119.2
C(3)-C(4)-H(4)	119.2
C(6)-C(5)-C(4)	120.0(6)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	119.4(6)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-H(6)	120.3
C(6)-C(7)-C(8)	121.2(6)
C(6)-C(7)-H(7)	119.4
C(8)-C(7)-H(7)	119.4
C(7)-C(8)-C(3)	119.3(5)
C(7)-C(8)-N(1)	121.9(5)
C(3)-C(8)-N(1)	118.8(5)
C(14)-C(9)-N(1)	122.7(6)
C(14)-C(9)-C(10)	116.2(6)
N(1)-C(9)-C(10)	121.1(7)
C(11)-C(10)-C(9)	121.9(9)
C(11)-C(10)-Cl(1)	119.3(8)
C(9)-C(10)-Cl(1)	118.8(6)
C(12)-C(11)-C(10)	119.1(9)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	122.3(9)
C(11)-C(12)-H(12)	118.9
C(13)-C(12)-H(12)	118.9
C(12)-C(13)-C(14)	117.8(10)
C(12)-C(13)-H(13)	121.1

C(14)-C(13)-H(13)	121.1
C(13)-C(14)-C(9)	122.8(8)
C(13)-C(14)-Cl(2)	118.3(8)
C(9)-C(14)-Cl(2)	118.9(5)
O(4)-C(15)-O(3)	123.7(5)
O(4)-C(15)-C(16)	121.6(5)
O(3)-C(15)-C(16)	114.7(5)
C(17)-C(16)-C(15)	117.5(5)
C(17)-C(16)-H(16A)	107.9
C(15)-C(16)-H(16A)	107.9
C(17)-C(16)-H(16B)	107.9
C(15)-C(16)-H(16B)	107.9
H(16A)-C(16)-H(16B)	107.2
C(18)-C(17)-C(22)	118.4(6)
C(18)-C(17)-C(16)	119.8(6)
C(22)-C(17)-C(16)	121.8(6)
C(17)-C(18)-C(19)	121.2(7)
C(17)-C(18)-H(18)	119.4
C(19)-C(18)-H(18)	119.4
C(20)-C(19)-C(18)	119.6(7)
C(20)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2
C(21)-C(20)-C(19)	120.4(6)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	120.9(6)
C(20)-C(21)-H(21)	119.5
C(22)-C(21)-H(21)	119.5
C(21)-C(22)-C(17)	119.5(6)
C(21)-C(22)-N(2)	121.9(6)
C(17)-C(22)-N(2)	118.6(5)
C(24)-C(23)-N(2)	122.3(8)
C(24)-C(23)-C(28)	117.3(8)
N(2)-C(23)-C(28)	120.3(7)
C(23)-C(24)-C(25)	120.9(12)
C(23)-C(24)-Cl(3)	119.8(7)
C(25)-C(24)-Cl(3)	119.3(10)

C(26)-C(25)-C(24)	118.7(14)
C(26)-C(25)-H(25)	120.7
C(24)-C(25)-H(25)	120.7
C(27)-C(26)-C(25)	123.1(14)
C(27)-C(26)-H(26)	118.5
C(25)-C(26)-H(26)	118.5
C(26)-C(27)-C(28)	118.8(14)
C(26)-C(27)-H(27)	120.6
C(28)-C(27)-H(27)	120.6
C(27)-C(28)-C(23)	121.3(11)
C(27)-C(28)-Cl(4)	119.4(10)
C(23)-C(28)-Cl(4)	119.3(6)
N(3)-C(29)-N(4)	119.0(5)
N(3)-C(29)-C(30)	120.8(5)
N(4)-C(29)-C(30)	120.2(5)
C(31)-C(30)-C(29)	120.4(6)
C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	119.8
C(30)-C(31)-C(32)	119.4(6)
C(30)-C(31)-H(31)	120.3
C(32)-C(31)-H(31)	120.3
C(33)-C(32)-C(31)	117.6(6)
C(33)-C(32)-H(32)	121.2
C(31)-C(32)-H(32)	121.2
N(3)-C(33)-C(32)	124.0(6)
N(3)-C(33)-H(33)	118.0
C(32)-C(33)-H(33)	118.0
N(5)-C(34)-N(6)	117.4(5)
N(5)-C(34)-C(35)	120.9(6)
N(6)-C(34)-C(35)	121.7(6)
C(36)-C(35)-C(34)	119.3(6)
C(36)-C(35)-H(35)	120.4
C(34)-C(35)-H(35)	120.4
C(35)-C(36)-C(37)	119.4(6)
C(35)-C(36)-H(36)	120.3
C(37)-C(36)-H(36)	120.3
C(38)-C(37)-C(36)	118.8(6)

C(38)-C(37)-H(37)	120.6
C(36)-C(37)-H(37)	120.6
N(5)-C(38)-C(37)	123.6(6)
N(5)-C(38)-H(38)	118.2
C(37)-C(38)-H(38)	118.2
O(5)-C(39)-C(41)	118.6(16)
O(5)-C(39)-C(40)	115.2(13)
C(41)-C(39)-C(40)	119.4(15)
C(39)-C(40)-H(40A)	109.4
C(39)-C(40)-H(40B)	109.2
H(40A)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40C)	109.8
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(39)-C(41)-H(41A)	109.5
C(39)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(39)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(28)-Cl(4)-H(1N2)	67.8(9)
C(9)-N(1)-C(8)	121.9(4)
C(9)-N(1)-H(1N1)	114(4)
C(8)-N(1)-H(1N1)	118(4)
C(23)-N(2)-C(22)	122.3(5)
C(23)-N(2)-H(1N2)	109(4)
C(22)-N(2)-H(1N2)	119(4)
C(29)-N(3)-C(33)	117.7(5)
C(29)-N(3)-Zn(1)	125.8(4)
C(33)-N(3)-Zn(1)	116.5(4)
C(29)-N(4)-H(1N4)	118(5)
C(29)-N(4)-H(2N4)	115(6)
H(1N4)-N(4)-H(2N4)	121(8)
C(38)-N(5)-C(34)	117.9(5)
C(38)-N(5)-Zn(1)	117.7(4)
C(34)-N(5)-Zn(1)	124.3(4)
C(34)-N(6)-H(1N6)	116(7)

C(34)-N(6)-H(2N6)	122(7)
H(1N6)-N(6)-H(2N6)	109(9)
C(1)-O(1)-Zn(1)	120.8(3)
C(1)-O(1)-H(1N1)	106.8(16)
Zn(1)-O(1)-H(1N1)	131.6(15)
C(1)-O(2)-H(1N4)	116(2)
C(15)-O(3)-Zn(1)	114.3(4)
C(15)-O(4)-H(1N6)	132(3)
C(15)-O(4)-H(1N2)	100.5(15)
H(1N6)-O(4)-H(1N2)	126(3)
O(1)-Zn(1)-O(3)	112.00(16)
O(1)-Zn(1)-N(5)	111.96(16)
O(3)-Zn(1)-N(5)	111.17(17)
O(1)-Zn(1)-N(3)	111.03(17)
O(3)-Zn(1)-N(3)	100.92(17)
N(5)-Zn(1)-N(3)	109.23(17)

Symmetry transformations used to generate equivalent atoms:

Table 4: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **(5)**. 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)	38(3)	44(3)	44(3)	4(2)	3(2)	0(2)
C(2)	36(3)	51(3)	66(4)	10(3)	11(3)	6(2)
C(3)	39(3)	43(3)	46(3)	8(2)	9(2)	14(2)
C(4)	62(4)	55(4)	56(4)	10(3)	25(3)	24(3)
C(5)	89(5)	56(4)	45(3)	-8(3)	14(3)	22(3)
C(6)	69(4)	55(4)	49(3)	-3(3)	-5(3)	7(3)
C(7)	53(3)	52(3)	45(3)	-2(2)	10(3)	-4(3)
C(8)	43(3)	38(3)	36(3)	6(2)	3(2)	2(2)
C(9)	68(4)	53(3)	33(3)	-4(2)	11(3)	-18(3)
C(10)	132(7)	54(4)	46(4)	2(3)	18(4)	-19(4)
C(11)	176(11)	73(6)	61(5)	11(4)	35(6)	-40(7)
C(12)	179(13)	131(10)	72(6)	-10(6)	65(7)	-80(9)
C(13)	94(6)	127(8)	83(6)	-28(6)	51(5)	-38(6)
C(14)	59(4)	74(4)	58(4)	-14(3)	21(3)	-23(3)
C(15)	59(4)	68(4)	28(3)	11(2)	12(2)	11(3)
C(16)	55(4)	95(5)	37(3)	16(3)	16(3)	30(3)
C(17)	57(3)	72(4)	31(3)	8(3)	17(2)	19(3)
C(18)	95(5)	63(4)	56(4)	8(3)	23(4)	26(4)
C(19)	117(7)	67(4)	50(4)	-9(3)	21(4)	19(4)
C(20)	96(6)	87(5)	34(3)	-1(3)	1(3)	9(4)
C(21)	71(4)	64(4)	40(3)	8(3)	8(3)	12(3)
C(22)	49(3)	61(4)	39(3)	2(2)	10(2)	7(3)
C(23)	88(5)	61(4)	52(4)	-9(3)	-5(4)	6(4)
C(24)	134(8)	82(6)	68(5)	17(4)	14(5)	-22(5)
C(25)	206(16)	89(8)	100(8)	14(7)	14(9)	-26(9)
C(26)	240(20)	81(8)	119(11)	16(7)	-11(12)	1(10)
C(27)	176(13)	83(7)	114(9)	-23(7)	-26(9)	52(8)
C(28)	115(7)	58(4)	76(5)	-17(4)	-17(5)	18(4)
C(29)	46(3)	38(3)	36(3)	4(2)	3(2)	1(2)
C(30)	73(4)	49(3)	32(3)	3(2)	-3(3)	1(3)
C(31)	64(4)	55(4)	55(4)	6(3)	-17(3)	10(3)
C(32)	46(3)	68(4)	66(4)	0(3)	-6(3)	14(3)

C(33)	44(3)	57(3)	46(3)	0(3)	4(2)	5(3)
C(34)	43(3)	58(3)	40(3)	3(2)	2(2)	7(3)
C(35)	39(3)	100(6)	60(4)	8(4)	3(3)	-7(3)
C(36)	64(5)	89(5)	73(5)	11(4)	12(4)	-27(4)
C(37)	73(5)	50(4)	82(5)	20(3)	24(4)	-1(3)
C(38)	47(3)	45(3)	57(3)	7(3)	6(3)	8(2)
C(39)	24(5)	137(14)	50(7)	28(8)	10(5)	-12(7)
C(40)	200(30)	59(13)	410(60)	-20(20)	100(40)	30(17)
C(41)	78(12)	153(19)	98(13)	62(13)	25(10)	-11(12)
Cl(1)	200(3)	80(2)	79(1)	16(1)	17(2)	50(2)
Cl(2)	69(1)	93(1)	92(1)	-1(1)	11(1)	12(1)
Cl(3)	125(2)	148(3)	120(2)	5(2)	61(2)	-29(2)
Cl(4)	95(2)	122(2)	134(2)	-23(2)	36(2)	37(2)
N(1)	60(3)	43(3)	39(2)	-2(2)	15(2)	-11(2)
N(2)	70(3)	63(3)	41(3)	3(2)	14(2)	16(3)
N(3)	36(2)	46(2)	32(2)	1(2)	1(2)	0(2)
N(4)	58(3)	77(4)	32(2)	10(2)	12(2)	10(3)
N(5)	39(2)	35(2)	40(2)	-1(2)	5(2)	4(2)
N(6)	54(3)	83(4)	68(4)	28(3)	-10(3)	7(3)
O(1)	47(2)	37(2)	62(2)	6(2)	23(2)	4(2)
O(2)	60(2)	53(2)	49(2)	12(2)	22(2)	5(2)
O(3)	59(2)	65(3)	31(2)	10(2)	14(2)	13(2)
O(4)	60(3)	131(5)	51(3)	32(3)	21(2)	40(3)
O(5)	69(7)	122(10)	103(9)	54(8)	24(6)	30(7)
Zn(1)	37(1)	40(1)	28(1)	4(1)	4(1)	4(1)

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

	x	y	z	U(eq)
H(2A)	6246	2597	1117	60
H(2B)	5542	2607	1700	60
H(4)	4762	1459	266	66
H(5)	2841	-78	-128	75
H(6)	871	-770	391	71
H(7)	787	140	1298	61
H(11)	879	-568	3089	125
H(12)	-1273	504	3210	154
H(13)	-1737	2239	2738	122
H(16A)	585	6785	3000	72
H(16B)	345	5365	2998	72
H(18)	1520	7892	3864	83
H(19)	2502	8013	4842	93
H(20)	3470	6335	5257	88
H(21)	3511	4556	4708	69
H(25)	1622	856	4616	161
H(26)	3898	23	4418	180
H(27)	5547	896	3851	154
H(30)	1093	6570	-566	63
H(31)	-1477	6900	-431	72
H(32)	-2160	6914	503	73
H(33)	-233	6529	1242	59
H(35)	8853	7676	2171	81
H(36)	8593	9445	1709	92
H(37)	6151	9715	1145	80
H(38)	3999	8334	1138	60
H(40A)	6077	8898	3932	325
H(40B)	5085	7616	3867	325
H(40C)	5549	8215	3319	325
H(41A)	7818	5842	3744	161
H(41B)	6340	6114	4058	161

H(41C)	8113	6482	4372	161
H(1N1)	2910(80)	2734(14)	1920(30)	57(19)
H(1N2)	2960(70)	4080(50)	3281(14)	45(16)
H(1N4)	4070(80)	5790(60)	440(30)	82
H(2N4)	3640(100)	6090(70)	-162(11)	82
H(1N6)	5690(60)	5750(80)	2370(40)	104
H(2N6)	7360(70)	5880(80)	2500(30)	104

Table 6: Hydrogen bonds for complex **(5)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(1N6)...O(4)	0.851(10)	2.06(2)	2.896(8)	169(9)
N(4)-H(2N4)...O(2)#1	0.850(10)	2.12(3)	2.918(6)	156(7)
N(4)-H(1N4)...O(2)	0.851(10)	2.05(2)	2.882(7)	167(8)
N(2)-H(1N2)...Cl(4)	0.851(10)	2.52(5)	2.968(6)	114(5)
N(2)-H(1N2)...O(4)	0.851(10)	2.21(4)	2.881(7)	136(5)
N(1)-H(1N1)...O(1)	0.850(10)	2.16(4)	2.887(6)	143(6)

Symmetry transformations used to generate equivalent atoms:

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

Appendix E: Crystal structure data of $[Zn(diclo)_2(dmph)]$ **(11)**

Table 1: Crystal data and structure refinement for complex **(11)**.

Empirical formula	C84 H66 Cl8 N8 O9 Zn2	
Formula weight	1745.79	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.213(1) Å	α= 71.108(2)°.
	b = 15.515(1) Å	β= 75.432(2)°.
	c = 22.987(2) Å	γ = 70.367(1)°.
Volume	3831.5(6) $Å^3$	
Z	2	
Density (calculated)	1.513 Mg/m^3	
Absorption coefficient	0.971 mm^{-1}	
F(000)	1788	
Crystal size	0.29 x 0.26 x 0.12 mm^3	
Theta range for data collection	1.44 to 27.00°.	
Index ranges	-15<=h<=15, -19<=k<=19, -29<=l<=29	
Reflections collected	42526	
Independent reflections	16545 [R(int) = 0.0421]	
Completeness to theta = 27.00°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8924 and 0.7660	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16545 / 1 / 1011	
Goodness-of-fit on F^2	1.281	
Final R indices [I>2sigma(I)]	R1 = 0.0807, wR2 = 0.1791	
R indices (all data)	R1 = 0.0926, wR2 = 0.1848	
Largest diff. peak and hole	1.490 and -0.540 $e.Å^{-3}$	

Table 2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **(11)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1323(4)	7456(3)	3382(2)	25(1)
C(2)	196(4)	8186(3)	3184(2)	28(1)
C(3)	354(4)	9137(3)	2801(2)	23(1)
C(4)	303(4)	9404(4)	2163(2)	30(1)
C(5)	451(4)	10265(4)	1787(2)	33(1)
C(6)	669(5)	10878(4)	2036(3)	37(1)
C(7)	732(5)	10631(4)	2663(2)	32(1)
C(8)	574(4)	9761(3)	3049(2)	24(1)
C(9)	662(4)	10107(3)	4010(2)	29(1)
C(10)	-267(5)	10912(4)	4063(3)	35(1)
C(11)	-270(5)	11527(4)	4383(3)	40(1)
C(12)	661(5)	11328(4)	4688(3)	40(1)
C(13)	1578(5)	10520(4)	4678(2)	36(1)
C(14)	1565(5)	9922(4)	4343(2)	31(1)
C(15)	2204(4)	4248(3)	4119(2)	30(1)
C(16)	2042(4)	3292(3)	4196(2)	28(1)
C(17)	2972(4)	2507(3)	4535(2)	25(1)
C(18)	2730(5)	2078(4)	5170(2)	33(1)
C(19)	3583(6)	1336(4)	5474(2)	39(1)
C(20)	4679(5)	1035(4)	5153(2)	37(1)
C(21)	4953(5)	1457(4)	4527(2)	32(1)
C(22)	4099(4)	2185(3)	4216(2)	23(1)
C(23)	5303(4)	2137(3)	3191(2)	23(1)
C(24)	6234(4)	2512(3)	2869(2)	27(1)
C(25)	7187(5)	2053(4)	2502(2)	33(1)
C(26)	7219(5)	1180(4)	2455(2)	37(1)
C(27)	6320(5)	789(4)	2750(2)	35(1)
C(28)	5351(5)	1267(3)	3111(2)	29(1)
C(29)	2891(5)	6185(3)	4980(2)	27(1)
C(30)	3465(5)	6334(4)	5385(2)	37(1)
C(31)	4617(5)	6332(4)	5224(2)	37(1)
C(32)	5241(5)	6200(3)	4636(2)	31(1)

C(33)	6450(5)	6189(3)	4422(3)	36(1)
C(34)	6990(5)	6078(4)	3850(3)	36(1)
C(35)	6350(4)	5991(3)	3442(2)	27(1)
C(36)	6837(4)	5954(3)	2822(3)	34(1)
C(37)	6153(5)	5933(3)	2444(2)	33(1)
C(38)	4981(4)	5926(3)	2671(2)	25(1)
C(39)	5178(4)	5987(3)	3634(2)	21(1)
C(40)	4616(4)	6067(3)	4253(2)	22(1)
C(41)	1617(5)	6212(4)	5140(3)	37(1)
C(42)	4208(5)	5909(4)	2265(2)	38(1)
C(43)	8286(4)	10154(3)	881(2)	27(1)
C(44)	8527(4)	11117(3)	613(2)	24(1)
C(45)	7623(4)	11846(3)	223(2)	21(1)
C(46)	7920(5)	12117(4)	-418(2)	30(1)
C(47)	7161(5)	12822(4)	-789(2)	34(1)
C(48)	6073(5)	13275(4)	-520(2)	34(1)
C(49)	5728(5)	13006(3)	119(2)	29(1)
C(50)	6490(4)	12285(3)	500(2)	24(1)
C(51)	5080(4)	12435(3)	1461(2)	25(1)
C(52)	4204(4)	11966(3)	1764(2)	25(1)
C(53)	3161(5)	12378(4)	2089(3)	36(1)
C(54)	2922(5)	13306(4)	2113(3)	44(1)
C(55)	3735(5)	13795(4)	1825(3)	39(1)
C(56)	4808(4)	13366(3)	1515(2)	28(1)
C(57)	9618(4)	7119(3)	1532(2)	29(1)
C(58)	10562(4)	6181(4)	1693(2)	30(1)
C(59)	10065(4)	5362(3)	2095(2)	27(1)
C(60)	10162(4)	5023(4)	2725(2)	38(1)
C(61)	9793(5)	4238(5)	3088(2)	46(2)
C(62)	9302(5)	3798(4)	2831(3)	45(2)
C(63)	9166(5)	4140(4)	2210(2)	35(1)
C(64)	9542(4)	4921(3)	1833(2)	24(1)
C(65)	9143(4)	4816(3)	865(2)	25(1)
C(66)	8164(4)	5238(3)	546(2)	27(1)
C(67)	7894(5)	4815(4)	181(2)	38(1)
C(68)	8573(6)	3923(4)	131(3)	43(1)
C(69)	9539(6)	3480(4)	430(3)	41(1)

C(70)	9826(5)	3929(3)	781(2)	32(1)
C(71)	6457(4)	8335(3)	2628(2)	23(1)
C(72)	5403(4)	8364(3)	3050(2)	26(1)
C(73)	4388(4)	8452(3)	2862(2)	27(1)
C(74)	4407(4)	8537(3)	2230(2)	22(1)
C(75)	3387(4)	8657(3)	1987(3)	30(1)
C(76)	3431(4)	8748(3)	1377(2)	30(1)
C(77)	4524(4)	8732(3)	954(2)	26(1)
C(78)	4622(5)	8806(4)	322(2)	35(1)
C(79)	5679(5)	8804(4)	-55(2)	37(1)
C(80)	6662(5)	8743(3)	187(2)	30(1)
C(81)	5540(4)	8642(3)	1173(2)	22(1)
C(82)	5493(4)	8523(3)	1829(2)	19(1)
C(83)	7580(4)	8219(4)	2834(2)	30(1)
C(84)	7820(5)	8768(4)	-225(2)	42(1)
Cl(1)	-1509(1)	11153(1)	3734(1)	45(1)
Cl(2)	2707(1)	8878(1)	4365(1)	42(1)
Cl(3)	6219(1)	3599(1)	2942(1)	41(1)
Cl(4)	4180(1)	778(1)	3454(1)	39(1)
Cl(5)	4477(1)	10805(1)	1740(1)	37(1)
Cl(6)	5859(1)	13985(1)	1191(1)	41(1)
Cl(7)	7270(1)	6356(1)	614(1)	40(1)
Cl(8)	11120(1)	3382(1)	1099(1)	41(1)
N(1)	660(4)	9480(3)	3693(2)	26(1)
N(2)	4344(3)	2597(3)	3568(2)	27(1)
N(3)	3468(3)	6041(2)	4430(2)	21(1)
N(4)	4509(3)	5937(2)	3259(2)	19(1)
N(5)	6153(3)	11998(3)	1150(2)	25(1)
N(6)	9431(4)	5276(3)	1207(2)	27(1)
N(7)	6501(3)	8415(2)	2029(2)	20(1)
N(8)	6589(3)	8664(3)	790(2)	23(1)
O(1)	1464(3)	6611(2)	3382(2)	37(1)
O(2)	2060(3)	7678(3)	3546(2)	43(1)
O(3)	3054(3)	4492(2)	3713(2)	39(1)
O(4)	1563(4)	4763(3)	4457(2)	50(1)
O(5)	8809(4)	9503(3)	621(2)	45(1)
O(6)	7541(3)	10026(2)	1360(2)	40(1)

O(7)	8917(4)	7203(2)	1192(2)	44(1)
O(8)	9522(4)	7775(3)	1750(2)	49(1)
O(1W)	724(4)	3758(4)	5751(3)	69(2)
Zn(1)	2868(1)	5814(1)	3743(1)	22(1)
Zn(2)	7898(1)	8564(1)	1278(1)	24(1)

Table 3: Bond lengths [Å] and angles [°] for complex **(11)**.

C(1)-O(2)	1.239(6)
C(1)-O(1)	1.263(6)
C(1)-C(2)	1.523(6)
C(2)-C(3)	1.502(6)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(8)	1.396(7)
C(3)-C(4)	1.399(7)
C(4)-C(5)	1.378(7)
C(4)-H(4)	0.9500
C(5)-C(6)	1.379(8)
C(5)-H(5)	0.9500
C(6)-C(7)	1.382(7)
C(6)-H(6)	0.9500
C(7)-C(8)	1.400(7)
C(7)-H(7)	0.9500
C(8)-N(1)	1.422(6)
C(9)-C(10)	1.392(7)
C(9)-N(1)	1.393(6)
C(9)-C(14)	1.399(7)
C(10)-C(11)	1.379(8)
C(10)-Cl(1)	1.739(5)
C(11)-C(12)	1.379(8)
C(11)-H(11)	0.9500
C(12)-C(13)	1.374(8)
C(12)-H(12)	0.9500
C(13)-C(14)	1.391(7)
C(13)-H(13)	0.9500
C(14)-Cl(2)	1.742(5)
C(15)-O(4)	1.238(6)
C(15)-O(3)	1.280(6)
C(15)-C(16)	1.510(7)
C(16)-C(17)	1.510(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(17)-C(22)	1.396(7)
C(17)-C(18)	1.396(7)
C(18)-C(19)	1.391(8)
C(18)-H(18)	0.9500
C(19)-C(20)	1.364(8)
C(19)-H(19)	0.9500
C(20)-C(21)	1.381(7)
C(20)-H(20)	0.9500
C(21)-C(22)	1.392(7)
C(21)-H(21)	0.9500
C(22)-N(2)	1.415(6)
C(23)-C(24)	1.387(7)
C(23)-C(28)	1.400(6)
C(23)-N(2)	1.400(6)
C(24)-C(25)	1.383(7)
C(24)-Cl(3)	1.742(5)
C(25)-C(26)	1.380(8)
C(25)-H(25)	0.9500
C(26)-C(27)	1.357(8)
C(26)-H(26)	0.9500
C(27)-C(28)	1.398(7)
C(27)-H(27)	0.9500
C(28)-Cl(4)	1.737(5)
C(29)-N(3)	1.332(6)
C(29)-C(30)	1.410(7)
C(29)-C(41)	1.495(7)
C(30)-C(31)	1.361(8)
C(30)-H(30)	0.9500
C(31)-C(32)	1.417(8)
C(31)-H(31)	0.9500
C(32)-C(40)	1.400(7)
C(32)-C(33)	1.431(8)
C(33)-C(34)	1.352(8)
C(33)-H(33)	0.9500
C(34)-C(35)	1.426(7)
C(34)-H(34)	0.9500
C(35)-C(39)	1.389(7)

C(35)-C(36)	1.410(7)
C(36)-C(37)	1.362(8)
C(36)-H(36)	0.9500
C(37)-C(38)	1.398(7)
C(37)-H(37)	0.9500
C(38)-N(4)	1.331(6)
C(38)-C(42)	1.498(7)
C(39)-N(4)	1.363(6)
C(39)-C(40)	1.440(6)
C(40)-N(3)	1.368(6)
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-O(5)	1.246(6)
C(43)-O(6)	1.247(6)
C(43)-C(44)	1.520(6)
C(44)-C(45)	1.518(6)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900
C(45)-C(46)	1.382(6)
C(45)-C(50)	1.409(7)
C(46)-C(47)	1.377(7)
C(46)-H(46)	0.9500
C(47)-C(48)	1.373(8)
C(47)-H(47)	0.9500
C(48)-C(49)	1.385(7)
C(48)-H(48)	0.9500
C(49)-C(50)	1.400(7)
C(49)-H(49)	0.9500
C(50)-N(5)	1.408(6)
C(51)-N(5)	1.390(6)
C(51)-C(52)	1.407(7)
C(51)-C(56)	1.409(6)
C(52)-C(53)	1.368(7)

C(52)-Cl(5)	1.736(5)
C(53)-C(54)	1.386(8)
C(53)-H(53)	0.9500
C(54)-C(55)	1.361(8)
C(54)-H(54)	0.9500
C(55)-C(56)	1.385(7)
C(55)-H(55)	0.9500
C(56)-Cl(6)	1.735(5)
C(57)-O(8)	1.232(6)
C(57)-O(7)	1.249(6)
C(57)-C(58)	1.524(7)
C(58)-C(59)	1.521(7)
C(58)-H(58A)	0.9900
C(58)-H(58B)	0.9900
C(59)-C(60)	1.392(7)
C(59)-C(64)	1.411(7)
C(60)-C(61)	1.381(9)
C(60)-H(60)	0.9500
C(61)-C(62)	1.375(9)
C(61)-H(61)	0.9500
C(62)-C(63)	1.385(8)
C(62)-H(62)	0.9500
C(63)-C(64)	1.387(7)
C(63)-H(63)	0.9500
C(64)-N(6)	1.389(6)
C(65)-N(6)	1.386(6)
C(65)-C(70)	1.395(7)
C(65)-C(66)	1.415(7)
C(66)-C(67)	1.373(7)
C(66)-Cl(7)	1.744(5)
C(67)-C(68)	1.378(8)
C(67)-H(67)	0.9500
C(68)-C(69)	1.375(9)
C(68)-H(68)	0.9500
C(69)-C(70)	1.389(8)
C(69)-H(69)	0.9500
C(70)-Cl(8)	1.740(6)

C(71)-N(7)	1.332(6)
C(71)-C(72)	1.400(6)
C(71)-C(83)	1.498(6)
C(72)-C(73)	1.365(7)
C(72)-H(72)	0.9500
C(73)-C(74)	1.410(7)
C(73)-H(73)	0.9500
C(74)-C(82)	1.411(6)
C(74)-C(75)	1.423(7)
C(75)-C(76)	1.352(7)
C(75)-H(75)	0.9500
C(76)-C(77)	1.438(7)
C(76)-H(76)	0.9500
C(77)-C(78)	1.398(7)
C(77)-C(81)	1.402(7)
C(78)-C(79)	1.362(8)
C(78)-H(78)	0.9500
C(79)-C(80)	1.408(8)
C(79)-H(79)	0.9500
C(80)-N(8)	1.335(6)
C(80)-C(84)	1.496(7)
C(81)-N(8)	1.364(6)
C(81)-C(82)	1.446(6)
C(82)-N(7)	1.361(6)
C(83)-H(83A)	0.9800
C(83)-H(83B)	0.9800
C(83)-H(83C)	0.9800
C(84)-H(84A)	0.9800
C(84)-H(84B)	0.9800
C(84)-H(84C)	0.9800
N(1)-H(1N)	0.8947
N(2)-H(2N)	0.7500
N(3)-Zn(1)	2.066(4)
N(4)-Zn(1)	2.072(4)
N(5)-H(5N)	0.7442
N(6)-H(6N)	0.7367
N(7)-Zn(2)	2.113(4)

N(8)-Zn(2)	2.112(4)
O(1)-Zn(1)	1.946(3)
O(3)-Zn(1)	2.010(3)
O(5)-Zn(2)	2.113(4)
O(6)-Zn(2)	2.222(4)
O(7)-Zn(2)	2.104(4)
O(8)-Zn(2)	2.281(5)
O(1W)-H(1W)	0.90(7)
O(1W)-H(2W)	0.91(2)

O(2)-C(1)-O(1)	121.5(4)
O(2)-C(1)-C(2)	121.4(4)
O(1)-C(1)-C(2)	117.1(4)
C(3)-C(2)-C(1)	114.3(4)
C(3)-C(2)-H(2A)	108.7
C(1)-C(2)-H(2A)	108.7
C(3)-C(2)-H(2B)	108.7
C(1)-C(2)-H(2B)	108.7
H(2A)-C(2)-H(2B)	107.6
C(8)-C(3)-C(4)	118.4(4)
C(8)-C(3)-C(2)	122.9(4)
C(4)-C(3)-C(2)	118.7(4)
C(5)-C(4)-C(3)	121.3(5)
C(5)-C(4)-H(4)	119.3
C(3)-C(4)-H(4)	119.3
C(4)-C(5)-C(6)	120.1(5)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	119.9(5)
C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	120.5(5)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(3)-C(8)-C(7)	119.9(4)
C(3)-C(8)-N(1)	118.5(4)
C(7)-C(8)-N(1)	121.6(4)

C(10)-C(9)-N(1)	123.1(5)
C(10)-C(9)-C(14)	115.3(5)
N(1)-C(9)-C(14)	121.4(5)
C(11)-C(10)-C(9)	123.0(5)
C(11)-C(10)-Cl(1)	117.5(4)
C(9)-C(10)-Cl(1)	119.5(4)
C(10)-C(11)-C(12)	119.4(5)
C(10)-C(11)-H(11)	120.3
C(12)-C(11)-H(11)	120.3
C(13)-C(12)-C(11)	120.4(5)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	118.9(5)
C(12)-C(13)-H(13)	120.6
C(14)-C(13)-H(13)	120.6
C(13)-C(14)-C(9)	122.9(5)
C(13)-C(14)-Cl(2)	118.0(4)
C(9)-C(14)-Cl(2)	119.1(4)
O(4)-C(15)-O(3)	121.1(5)
O(4)-C(15)-C(16)	120.8(5)
O(3)-C(15)-C(16)	118.1(4)
C(15)-C(16)-C(17)	110.6(4)
C(15)-C(16)-H(16A)	109.5
C(17)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
C(17)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	108.1
C(22)-C(17)-C(18)	118.2(4)
C(22)-C(17)-C(16)	120.5(4)
C(18)-C(17)-C(16)	121.3(5)
C(19)-C(18)-C(17)	120.8(5)
C(19)-C(18)-H(18)	119.6
C(17)-C(18)-H(18)	119.6
C(20)-C(19)-C(18)	120.0(5)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	120.6(5)

C(19)-C(20)-H(20)	119.7
C(21)-C(20)-H(20)	119.7
C(20)-C(21)-C(22)	119.8(5)
C(20)-C(21)-H(21)	120.1
C(22)-C(21)-H(21)	120.1
C(21)-C(22)-C(17)	120.5(4)
C(21)-C(22)-N(2)	120.8(4)
C(17)-C(22)-N(2)	118.7(4)
C(24)-C(23)-C(28)	116.3(4)
C(24)-C(23)-N(2)	122.9(4)
C(28)-C(23)-N(2)	120.8(4)
C(25)-C(24)-C(23)	122.9(5)
C(25)-C(24)-Cl(3)	118.4(4)
C(23)-C(24)-Cl(3)	118.6(4)
C(26)-C(25)-C(24)	118.7(5)
C(26)-C(25)-H(25)	120.6
C(24)-C(25)-H(25)	120.6
C(27)-C(26)-C(25)	120.8(5)
C(27)-C(26)-H(26)	119.6
C(25)-C(26)-H(26)	119.6
C(26)-C(27)-C(28)	119.9(5)
C(26)-C(27)-H(27)	120.0
C(28)-C(27)-H(27)	120.0
C(27)-C(28)-C(23)	121.2(5)
C(27)-C(28)-Cl(4)	119.1(4)
C(23)-C(28)-Cl(4)	119.7(4)
N(3)-C(29)-C(30)	120.5(5)
N(3)-C(29)-C(41)	117.8(4)
C(30)-C(29)-C(41)	121.7(5)
C(31)-C(30)-C(29)	120.9(5)
C(31)-C(30)-H(30)	119.5
C(29)-C(30)-H(30)	119.5
C(30)-C(31)-C(32)	119.5(5)
C(30)-C(31)-H(31)	120.2
C(32)-C(31)-H(31)	120.2
C(40)-C(32)-C(31)	116.7(5)
C(40)-C(32)-C(33)	119.4(5)

C(31)-C(32)-C(33)	123.9(5)
C(34)-C(33)-C(32)	121.1(5)
C(34)-C(33)-H(33)	119.4
C(32)-C(33)-H(33)	119.4
C(33)-C(34)-C(35)	120.2(5)
C(33)-C(34)-H(34)	119.9
C(35)-C(34)-H(34)	119.9
C(39)-C(35)-C(36)	116.8(4)
C(39)-C(35)-C(34)	120.5(5)
C(36)-C(35)-C(34)	122.7(5)
C(37)-C(36)-C(35)	119.7(5)
C(37)-C(36)-H(36)	120.1
C(35)-C(36)-H(36)	120.1
C(36)-C(37)-C(38)	120.3(5)
C(36)-C(37)-H(37)	119.8
C(38)-C(37)-H(37)	119.8
N(4)-C(38)-C(37)	121.1(4)
N(4)-C(38)-C(42)	117.5(4)
C(37)-C(38)-C(42)	121.5(4)
N(4)-C(39)-C(35)	123.1(4)
N(4)-C(39)-C(40)	117.5(4)
C(35)-C(39)-C(40)	119.3(4)
N(3)-C(40)-C(32)	123.0(4)
N(3)-C(40)-C(39)	117.6(4)
C(32)-C(40)-C(39)	119.4(4)
C(29)-C(41)-H(41A)	109.5
C(29)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(29)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(38)-C(42)-H(42A)	109.5
C(38)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(38)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5

O(5)-C(43)-O(6)	120.3(5)
O(5)-C(43)-C(44)	120.5(5)
O(6)-C(43)-C(44)	119.2(4)
C(45)-C(44)-C(43)	113.5(4)
C(45)-C(44)-H(44A)	108.9
C(43)-C(44)-H(44A)	108.9
C(45)-C(44)-H(44B)	108.9
C(43)-C(44)-H(44B)	108.9
H(44A)-C(44)-H(44B)	107.7
C(46)-C(45)-C(50)	118.6(4)
C(46)-C(45)-C(44)	119.8(4)
C(50)-C(45)-C(44)	121.5(4)
C(47)-C(46)-C(45)	122.1(5)
C(47)-C(46)-H(46)	119.0
C(45)-C(46)-H(46)	119.0
C(48)-C(47)-C(46)	119.5(5)
C(48)-C(47)-H(47)	120.3
C(46)-C(47)-H(47)	120.3
C(47)-C(48)-C(49)	120.2(5)
C(47)-C(48)-H(48)	119.9
C(49)-C(48)-H(48)	119.9
C(48)-C(49)-C(50)	120.6(5)
C(48)-C(49)-H(49)	119.7
C(50)-C(49)-H(49)	119.7
C(49)-C(50)-N(5)	121.4(4)
C(49)-C(50)-C(45)	118.9(4)
N(5)-C(50)-C(45)	119.7(4)
N(5)-C(51)-C(52)	122.3(4)
N(5)-C(51)-C(56)	122.6(4)
C(52)-C(51)-C(56)	115.0(4)
C(53)-C(52)-C(51)	122.9(4)
C(53)-C(52)-Cl(5)	118.7(4)
C(51)-C(52)-Cl(5)	118.4(4)
C(52)-C(53)-C(54)	119.7(5)
C(52)-C(53)-H(53)	120.1
C(54)-C(53)-H(53)	120.1
C(55)-C(54)-C(53)	119.9(5)

C(55)-C(54)-H(54)	120.0
C(53)-C(54)-H(54)	120.0
C(54)-C(55)-C(56)	120.3(5)
C(54)-C(55)-H(55)	119.9
C(56)-C(55)-H(55)	119.9
C(55)-C(56)-C(51)	122.1(5)
C(55)-C(56)-Cl(6)	119.2(4)
C(51)-C(56)-Cl(6)	118.7(4)
O(8)-C(57)-O(7)	120.3(5)
O(8)-C(57)-C(58)	120.8(5)
O(7)-C(57)-C(58)	118.9(4)
C(59)-C(58)-C(57)	113.4(4)
C(59)-C(58)-H(58A)	108.9
C(57)-C(58)-H(58A)	108.9
C(59)-C(58)-H(58B)	108.9
C(57)-C(58)-H(58B)	108.9
H(58A)-C(58)-H(58B)	107.7
C(60)-C(59)-C(64)	119.6(5)
C(60)-C(59)-C(58)	119.6(5)
C(64)-C(59)-C(58)	120.8(4)
C(61)-C(60)-C(59)	120.4(5)
C(61)-C(60)-H(60)	119.8
C(59)-C(60)-H(60)	119.8
C(62)-C(61)-C(60)	119.9(5)
C(62)-C(61)-H(61)	120.0
C(60)-C(61)-H(61)	120.0
C(61)-C(62)-C(63)	120.5(5)
C(61)-C(62)-H(62)	119.7
C(63)-C(62)-H(62)	119.7
C(62)-C(63)-C(64)	120.6(5)
C(62)-C(63)-H(63)	119.7
C(64)-C(63)-H(63)	119.7
C(63)-C(64)-N(6)	122.1(5)
C(63)-C(64)-C(59)	118.8(4)
N(6)-C(64)-C(59)	119.1(4)
N(6)-C(65)-C(70)	122.9(4)
N(6)-C(65)-C(66)	122.1(4)

C(70)-C(65)-C(66)	114.9(4)
C(67)-C(66)-C(65)	123.2(5)
C(67)-C(66)-Cl(7)	118.6(4)
C(65)-C(66)-Cl(7)	118.2(4)
C(66)-C(67)-C(68)	119.6(5)
C(66)-C(67)-H(67)	120.2
C(68)-C(67)-H(67)	120.2
C(69)-C(68)-C(67)	119.7(5)
C(69)-C(68)-H(68)	120.2
C(67)-C(68)-H(68)	120.2
C(68)-C(69)-C(70)	120.2(5)
C(68)-C(69)-H(69)	119.9
C(70)-C(69)-H(69)	119.9
C(69)-C(70)-C(65)	122.4(5)
C(69)-C(70)-Cl(8)	118.4(4)
C(65)-C(70)-Cl(8)	119.1(4)
N(7)-C(71)-C(72)	121.5(4)
N(7)-C(71)-C(83)	117.3(4)
C(72)-C(71)-C(83)	121.1(4)
C(73)-C(72)-C(71)	120.8(4)
C(73)-C(72)-H(72)	119.6
C(71)-C(72)-H(72)	119.6
C(72)-C(73)-C(74)	119.0(4)
C(72)-C(73)-H(73)	120.5
C(74)-C(73)-H(73)	120.5
C(73)-C(74)-C(82)	117.1(4)
C(73)-C(74)-C(75)	123.0(4)
C(82)-C(74)-C(75)	119.8(4)
C(76)-C(75)-C(74)	121.6(4)
C(76)-C(75)-H(75)	119.2
C(74)-C(75)-H(75)	119.2
C(75)-C(76)-C(77)	120.2(4)
C(75)-C(76)-H(76)	119.9
C(77)-C(76)-H(76)	119.9
C(78)-C(77)-C(81)	117.7(5)
C(78)-C(77)-C(76)	122.5(5)
C(81)-C(77)-C(76)	119.8(4)

C(79)-C(78)-C(77)	119.4(5)
C(79)-C(78)-H(78)	120.3
C(77)-C(78)-H(78)	120.3
C(78)-C(79)-C(80)	120.5(5)
C(78)-C(79)-H(79)	119.7
C(80)-C(79)-H(79)	119.7
N(8)-C(80)-C(79)	121.0(5)
N(8)-C(80)-C(84)	117.9(5)
C(79)-C(80)-C(84)	121.1(5)
N(8)-C(81)-C(77)	122.6(4)
N(8)-C(81)-C(82)	117.7(4)
C(77)-C(81)-C(82)	119.7(4)
N(7)-C(82)-C(74)	122.9(4)
N(7)-C(82)-C(81)	118.3(4)
C(74)-C(82)-C(81)	118.8(4)
C(71)-C(83)-H(83A)	109.5
C(71)-C(83)-H(83B)	109.5
H(83A)-C(83)-H(83B)	109.5
C(71)-C(83)-H(83C)	109.5
H(83A)-C(83)-H(83C)	109.5
H(83B)-C(83)-H(83C)	109.5
C(80)-C(84)-H(84A)	109.5
C(80)-C(84)-H(84B)	109.5
H(84A)-C(84)-H(84B)	109.5
C(80)-C(84)-H(84C)	109.5
H(84A)-C(84)-H(84C)	109.5
H(84B)-C(84)-H(84C)	109.5
C(9)-N(1)-C(8)	122.7(4)
C(9)-N(1)-H(1N)	117.3
C(8)-N(1)-H(1N)	103.0
C(23)-N(2)-C(22)	121.1(4)
C(23)-N(2)-H(2N)	122.6
C(22)-N(2)-H(2N)	107.5
C(29)-N(3)-C(40)	119.4(4)
C(29)-N(3)-Zn(1)	129.2(3)
C(40)-N(3)-Zn(1)	111.4(3)
C(38)-N(4)-C(39)	118.9(4)

C(38)-N(4)-Zn(1)	129.7(3)
C(39)-N(4)-Zn(1)	111.3(3)
C(51)-N(5)-C(50)	123.0(4)
C(51)-N(5)-H(5N)	123.4
C(50)-N(5)-H(5N)	104.8
C(65)-N(6)-C(64)	124.9(4)
C(65)-N(6)-H(6N)	118.6
C(64)-N(6)-H(6N)	106.9
C(71)-N(7)-C(82)	118.6(4)
C(71)-N(7)-Zn(2)	129.4(3)
C(82)-N(7)-Zn(2)	111.6(3)
C(80)-N(8)-C(81)	118.8(4)
C(80)-N(8)-Zn(2)	129.4(3)
C(81)-N(8)-Zn(2)	111.8(3)
C(1)-O(1)-Zn(1)	108.3(3)
C(15)-O(3)-Zn(1)	104.0(3)
C(43)-O(5)-Zn(2)	92.5(3)
C(43)-O(6)-Zn(2)	87.5(3)
C(57)-O(7)-Zn(2)	94.4(3)
C(57)-O(8)-Zn(2)	86.6(3)
H(1W)-O(1W)-H(2W)	115(6)
O(1)-Zn(1)-O(3)	106.06(15)
O(1)-Zn(1)-N(3)	125.41(15)
O(3)-Zn(1)-N(3)	120.81(15)
O(1)-Zn(1)-N(4)	119.55(15)
O(3)-Zn(1)-N(4)	98.16(15)
N(3)-Zn(1)-N(4)	81.63(15)
O(7)-Zn(2)-N(8)	95.27(14)
O(7)-Zn(2)-O(5)	105.13(16)
N(8)-Zn(2)-O(5)	101.58(16)
O(7)-Zn(2)-N(7)	108.38(16)
N(8)-Zn(2)-N(7)	80.34(14)
O(5)-Zn(2)-N(7)	146.12(14)
O(7)-Zn(2)-O(6)	156.99(15)
N(8)-Zn(2)-O(6)	104.47(15)
O(5)-Zn(2)-O(6)	59.74(14)
N(7)-Zn(2)-O(6)	86.82(13)

O(7)-Zn(2)-O(8)	58.61(14)
N(8)-Zn(2)-O(8)	153.52(14)
O(5)-Zn(2)-O(8)	90.47(17)
N(7)-Zn(2)-O(8)	102.62(15)
O(6)-Zn(2)-O(8)	101.97(15)

Symmetry transformations used to generate equivalent atoms:

Table 4: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **(11)**. 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)	19(2)	18(2)	29(2)	4(2)	-2(2)	-5(2)
C(2)	20(2)	23(2)	41(3)	-6(2)	-10(2)	-5(2)
C(3)	12(2)	20(2)	34(3)	-4(2)	-6(2)	-1(2)
C(4)	18(2)	31(3)	39(3)	-10(2)	-13(2)	2(2)
C(5)	24(2)	43(3)	22(2)	-2(2)	-7(2)	-2(2)
C(6)	34(3)	31(3)	37(3)	2(2)	-5(2)	-9(2)
C(7)	35(3)	33(3)	32(3)	-3(2)	-7(2)	-18(2)
C(8)	20(2)	23(2)	26(2)	-3(2)	-3(2)	-4(2)
C(9)	30(3)	27(2)	28(3)	-2(2)	-5(2)	-12(2)
C(10)	37(3)	32(3)	36(3)	-5(2)	-15(2)	-9(2)
C(11)	46(3)	26(3)	42(3)	-8(2)	-4(3)	-7(2)
C(12)	55(4)	39(3)	35(3)	-14(2)	0(3)	-26(3)
C(13)	42(3)	45(3)	29(3)	-7(2)	-6(2)	-23(3)
C(14)	32(3)	35(3)	25(2)	-4(2)	-2(2)	-14(2)
C(15)	24(2)	26(2)	37(3)	-6(2)	-16(2)	0(2)
C(16)	21(2)	36(3)	31(3)	-11(2)	0(2)	-12(2)
C(17)	31(3)	25(2)	23(2)	-6(2)	-7(2)	-14(2)
C(18)	40(3)	40(3)	26(3)	-13(2)	0(2)	-20(2)
C(19)	67(4)	34(3)	20(2)	-1(2)	-13(3)	-20(3)
C(20)	55(4)	29(3)	30(3)	-7(2)	-21(3)	-8(2)
C(21)	39(3)	30(3)	27(3)	-7(2)	-8(2)	-8(2)
C(22)	32(3)	21(2)	22(2)	-6(2)	-10(2)	-10(2)
C(23)	28(2)	17(2)	18(2)	0(2)	-9(2)	-1(2)
C(24)	31(3)	19(2)	28(2)	-2(2)	-13(2)	-2(2)
C(25)	27(3)	42(3)	25(3)	-6(2)	-7(2)	-5(2)
C(26)	36(3)	41(3)	28(3)	-16(2)	-8(2)	8(2)
C(27)	48(3)	26(3)	29(3)	-8(2)	-14(2)	-1(2)
C(28)	41(3)	25(2)	21(2)	0(2)	-12(2)	-9(2)
C(29)	38(3)	15(2)	22(2)	-4(2)	-9(2)	3(2)
C(30)	58(4)	27(3)	21(2)	-8(2)	-9(2)	0(2)
C(31)	60(4)	25(3)	32(3)	-7(2)	-26(3)	-7(2)
C(32)	42(3)	20(2)	35(3)	-3(2)	-19(2)	-7(2)

C(33)	43(3)	26(3)	47(3)	-1(2)	-30(3)	-11(2)
C(34)	29(3)	29(3)	52(3)	-1(2)	-18(2)	-11(2)
C(35)	26(2)	20(2)	34(3)	-3(2)	-10(2)	-4(2)
C(36)	20(2)	25(2)	46(3)	-4(2)	4(2)	-7(2)
C(37)	37(3)	28(3)	26(3)	-7(2)	6(2)	-9(2)
C(38)	35(3)	21(2)	19(2)	-3(2)	-5(2)	-7(2)
C(39)	25(2)	11(2)	26(2)	-1(2)	-11(2)	-2(2)
C(40)	28(2)	12(2)	22(2)	0(2)	-10(2)	-2(2)
C(41)	36(3)	36(3)	33(3)	-14(2)	9(2)	-6(2)
C(42)	51(3)	41(3)	25(3)	-10(2)	-9(2)	-13(3)
C(43)	26(2)	25(2)	33(3)	-6(2)	-10(2)	-6(2)
C(44)	22(2)	24(2)	27(2)	-6(2)	-7(2)	-7(2)
C(45)	26(2)	20(2)	22(2)	-4(2)	-5(2)	-13(2)
C(46)	34(3)	34(3)	28(3)	-9(2)	-1(2)	-20(2)
C(47)	44(3)	41(3)	19(2)	1(2)	-6(2)	-24(3)
C(48)	43(3)	29(3)	28(3)	3(2)	-18(2)	-11(2)
C(49)	32(3)	25(2)	30(3)	-4(2)	-10(2)	-6(2)
C(50)	33(3)	22(2)	21(2)	-3(2)	-7(2)	-15(2)
C(51)	29(2)	21(2)	22(2)	-5(2)	-8(2)	-3(2)
C(52)	30(3)	22(2)	24(2)	-4(2)	-9(2)	-6(2)
C(53)	29(3)	38(3)	36(3)	0(2)	-9(2)	-11(2)
C(54)	30(3)	45(3)	48(3)	-17(3)	-4(3)	3(3)
C(55)	38(3)	26(3)	50(3)	-15(2)	-5(3)	1(2)
C(56)	34(3)	25(2)	26(2)	-6(2)	-6(2)	-10(2)
C(57)	26(2)	28(3)	32(3)	-8(2)	5(2)	-12(2)
C(58)	21(2)	37(3)	36(3)	-16(2)	-2(2)	-8(2)
C(59)	14(2)	32(3)	26(2)	-8(2)	0(2)	1(2)
C(60)	22(3)	60(4)	26(3)	-15(3)	-6(2)	-1(2)
C(61)	31(3)	71(4)	18(2)	3(3)	-3(2)	-4(3)
C(62)	33(3)	50(4)	33(3)	9(3)	5(2)	-14(3)
C(63)	33(3)	34(3)	34(3)	-5(2)	1(2)	-12(2)
C(64)	20(2)	27(2)	19(2)	-3(2)	-1(2)	-4(2)
C(65)	27(2)	26(2)	20(2)	0(2)	2(2)	-15(2)
C(66)	36(3)	23(2)	22(2)	-7(2)	2(2)	-11(2)
C(67)	47(3)	44(3)	30(3)	-4(2)	-5(2)	-27(3)
C(68)	65(4)	41(3)	35(3)	-15(3)	-1(3)	-32(3)
C(69)	55(4)	28(3)	43(3)	-16(2)	4(3)	-18(3)

C(70)	38(3)	25(2)	30(3)	-4(2)	-2(2)	-12(2)
C(71)	23(2)	18(2)	27(2)	-6(2)	-5(2)	-6(2)
C(72)	30(3)	26(2)	20(2)	-4(2)	-2(2)	-10(2)
C(73)	23(2)	27(2)	28(2)	-10(2)	5(2)	-7(2)
C(74)	18(2)	18(2)	29(2)	-5(2)	-2(2)	-6(2)
C(75)	17(2)	31(3)	44(3)	-14(2)	-2(2)	-6(2)
C(76)	22(2)	30(3)	44(3)	-11(2)	-13(2)	-6(2)
C(77)	30(3)	21(2)	32(3)	-10(2)	-9(2)	-5(2)
C(78)	47(3)	29(3)	36(3)	-10(2)	-21(3)	-8(2)
C(79)	63(4)	26(3)	22(2)	-7(2)	-11(3)	-9(3)
C(80)	39(3)	21(2)	27(3)	-11(2)	-1(2)	-4(2)
C(81)	27(2)	13(2)	24(2)	-5(2)	-5(2)	-2(2)
C(82)	23(2)	12(2)	22(2)	-3(2)	-5(2)	-5(2)
C(83)	26(2)	34(3)	30(3)	-6(2)	-8(2)	-9(2)
C(84)	51(4)	45(3)	18(2)	-9(2)	5(2)	-5(3)
Cl(1)	37(1)	44(1)	51(1)	-16(1)	-19(1)	5(1)
Cl(2)	31(1)	51(1)	43(1)	-15(1)	-14(1)	-2(1)
Cl(3)	44(1)	32(1)	51(1)	-12(1)	-5(1)	-17(1)
Cl(4)	58(1)	34(1)	30(1)	-1(1)	-10(1)	-24(1)
Cl(5)	51(1)	28(1)	35(1)	-4(1)	-12(1)	-17(1)
Cl(6)	47(1)	30(1)	48(1)	-10(1)	0(1)	-19(1)
Cl(7)	37(1)	33(1)	44(1)	-9(1)	-12(1)	-2(1)
Cl(8)	41(1)	27(1)	46(1)	-6(1)	-5(1)	-1(1)
N(1)	29(2)	24(2)	23(2)	-1(2)	-7(2)	-7(2)
N(2)	27(2)	20(2)	25(2)	-3(2)	-1(2)	-1(2)
N(3)	26(2)	16(2)	19(2)	-5(1)	-8(2)	0(2)
N(4)	22(2)	17(2)	17(2)	-2(1)	-5(2)	-3(1)
N(5)	30(2)	21(2)	18(2)	-3(2)	-5(2)	-2(2)
N(6)	39(2)	16(2)	25(2)	-3(2)	-6(2)	-8(2)
N(7)	17(2)	17(2)	27(2)	-7(2)	-3(2)	-4(1)
N(8)	26(2)	18(2)	22(2)	-7(2)	-1(2)	-5(2)
O(1)	28(2)	23(2)	62(3)	-7(2)	-21(2)	-3(1)
O(2)	30(2)	29(2)	75(3)	-12(2)	-31(2)	0(2)
O(3)	38(2)	18(2)	56(2)	-10(2)	-3(2)	-7(2)
O(4)	55(3)	38(2)	54(3)	-23(2)	-3(2)	-2(2)
O(5)	44(2)	28(2)	60(3)	-19(2)	11(2)	-13(2)
O(6)	45(2)	28(2)	37(2)	-3(2)	8(2)	-15(2)

O(7)	45(2)	23(2)	69(3)	-15(2)	-30(2)	2(2)
O(8)	68(3)	34(2)	49(2)	-24(2)	-3(2)	-10(2)
O(1W)	27(2)	82(4)	74(4)	-3(3)	5(2)	-12(2)
Zn(1)	19(1)	23(1)	23(1)	-7(1)	-6(1)	-3(1)
Zn(2)	20(1)	23(1)	26(1)	-5(1)	2(1)	-7(1)

Table 5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **(11)**.

	x	y	z	U(eq)
H(2A)	-131	7935	2940	33
H(2B)	-389	8270	3562	33
H(4)	164	8983	1986	36
H(5)	403	10436	1357	39
H(6)	776	11470	1776	44
H(7)	883	11054	2833	39
H(11)	-907	12083	4393	47
H(12)	668	11752	4905	48
H(13)	2210	10373	4897	44
H(16A)	2094	3203	3781	34
H(16B)	1251	3264	4434	34
H(18)	1974	2295	5398	39
H(19)	3401	1039	5904	47
H(20)	5260	531	5363	44
H(21)	5723	1250	4309	39
H(25)	7807	2334	2285	40
H(26)	7879	849	2214	45
H(27)	6349	190	2711	42
H(30)	3042	6437	5775	45
H(31)	5000	6419	5504	44
H(33)	6881	6260	4686	43
H(34)	7799	6058	3720	43
H(36)	7639	5942	2670	40
H(37)	6475	5924	2024	39
H(41A)	1166	6775	4864	56
H(41B)	1327	6239	5574	56
H(41C)	1523	5641	5087	56
H(42A)	3599	5604	2523	57
H(42B)	4684	5552	1962	57
H(42C)	3834	6559	2044	57
H(44A)	8542	11359	959	29
H(44B)	9315	11040	352	29

H(46)	8672	11808	-608	36
H(47)	7388	12993	-1229	40
H(48)	5554	13774	-772	40
H(49)	4967	13315	301	35
H(53)	2602	12030	2298	43
H(54)	2191	13600	2329	53
H(55)	3567	14434	1837	47
H(58A)	11022	6023	1301	36
H(58B)	11108	6256	1914	36
H(60)	10485	5335	2906	45
H(61)	9879	4001	3515	55
H(62)	9053	3255	3081	54
H(63)	8813	3836	2039	42
H(67)	7243	5135	-36	46
H(68)	8376	3616	-108	51
H(69)	10010	2866	396	49
H(72)	5395	8321	3473	31
H(73)	3679	8456	3152	32
H(75)	2657	8674	2260	36
H(76)	2738	8824	1227	37
H(78)	3957	8858	156	42
H(79)	5755	8844	-483	44
H(83A)	8166	7642	2751	44
H(83B)	7433	8168	3282	44
H(83C)	7878	8769	2605	44
H(84A)	7861	9425	-390	63
H(84B)	7899	8502	-571	63
H(84C)	8460	8392	16	63
H(1W)	790(60)	4170(50)	5370(30)	49
H(2W)	-20(30)	3830(40)	5970(30)	49
H(1N)	1236	8935	3732	31
H(2N)	4152	3125	3517	32
H(5N)	6436	11478	1238	30
H(6N)	9184	5794	1150	20(14)

Table 6: Hydrogen bonds for complex **(11)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(2W)...O(1)#1	0.91(2)	2.15(3)	3.009(6)	157(6)
O(1W)-H(1W)...O(4)	0.90(7)	2.12(7)	2.977(7)	158(6)
N(2)-H(2N)...O(3)	0.75	2.21	2.914(5)	155.8
N(1)-H(1N)...O(2)	0.89	2.00	2.821(5)	152.0
N(6)-H(6N)...O(7)	0.74	2.13	2.833(5)	159.3
N(5)-H(5N)...O(6)	0.74	2.17	2.905(5)	169.1

Symmetry transformations used to generate equivalent atoms:

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

Appendix F: Crystal structure data of $[Zn(diclo)_2(DMSO)_2]$

Table 1: Crystal data and structure refinement for $[Zn(diclo)_2(DMSO)_2]$.

Empirical formula	C32 H32 Cl4 N2 O6 S2 Zn	
Formula weight	811.89	
Temperature	293(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 12.147(1) Å	α= 90°.
	b = 11.472(1) Å	β= 90°.
	c = 25.121(3) Å	γ = 90°.
Volume	3500.6(6) $Å^3$	
Z	4	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	1.172 mm^{-1}	
F(000)	1664	
Crystal size	0.40 x 0.24 x 0.08 mm^3	
Theta range for data collection	2.93 to 28.00°.	
Index ranges	-15<=h<=16, -15<=k<=15, -32<=l<=33	
Reflections collected	28629	
Independent reflections	4205 [R(int) = 0.0360]	
Completeness to theta = 28.00°	99.5 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9121 and 0.6514	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4205 / 0 / 215	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.0936	
R indices (all data)	R1 = 0.0508, wR2 = 0.0976	
Largest diff. peak and hole	0.631 and -0.254 $e.Å^{-3}$	

Table 2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Zn(diclo)_2(DMSO)_2]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9558(2)	3520(2)	4773(1)	22(1)
C(2)	8580(2)	4150(2)	4834(1)	25(1)
C(3)	8139(2)	4411(2)	5330(1)	32(1)
C(4)	8676(2)	4034(2)	5782(1)	34(1)
C(5)	9665(2)	3444(2)	5742(1)	31(1)
C(6)	10097(2)	3210(2)	5244(1)	24(1)
C(7)	10247(2)	2142(2)	4096(1)	22(1)
C(8)	10985(2)	2030(2)	3670(1)	23(1)
C(9)	11213(2)	921(2)	3478(1)	29(1)
C(10)	10747(2)	-59(2)	3709(1)	34(1)
C(11)	10045(2)	58(2)	4137(1)	34(1)
C(12)	9785(2)	1159(2)	4329(1)	29(1)
C(13)	11571(2)	3085(2)	3454(1)	26(1)
C(14)	10869(2)	3932(2)	3136(1)	29(1)
C(17)	8371(3)	8647(2)	2918(2)	62(1)
C(18)	7204(3)	6871(3)	3300(1)	64(1)
Cl(1)	7915(1)	4641(1)	4263(1)	33(1)
Cl(2)	11384(1)	2561(1)	5201(1)	34(1)
N(1)	9998(1)	3281(2)	4272(1)	26(1)
O(1)	11366(1)	4722(1)	2873(1)	37(1)
O(2)	9849(1)	3867(2)	3139(1)	36(1)
O(3)	9237(2)	6560(2)	2971(1)	45(1)
S(1)	8179(1)	7145(1)	2791(1)	38(1)
Zn(1)	10000	5350(1)	2500	28(1)

Table 3: Bond lengths [Å] and angles [°] for $[Zn(diclo)_2(DMSO)_2]$.

C(1)-N(1)	1.395(2)
C(1)-C(6)	1.398(3)
C(1)-C(2)	1.399(3)
C(2)-C(3)	1.388(3)
C(2)-Cl(1)	1.738(2)
C(3)-C(4)	1.379(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.383(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.382(3)
C(5)-H(5)	0.9300
C(6)-Cl(2)	1.735(2)
C(7)-C(12)	1.389(3)
C(7)-C(8)	1.404(3)
C(7)-N(1)	1.412(3)
C(8)-C(9)	1.388(3)
C(8)-C(13)	1.504(3)
C(9)-C(10)	1.386(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.379(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.389(3)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(14)	1.520(3)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-O(2)	1.242(3)
C(14)-O(1)	1.273(3)
C(17)-S(1)	1.768(3)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-S(1)	1.771(3)
C(18)-H(18A)	0.9600

C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
N(1)-H(1N)	0.8243
O(1)-Zn(1)	2.0376(17)
O(2)-Zn(1)	2.3459(17)
O(3)-S(1)	1.5196(17)
O(3)-Zn(1)	2.0457(16)
Zn(1)-O(1)#1	2.0376(17)
Zn(1)-O(3)#1	2.0457(16)
Zn(1)-O(2)#1	2.3459(17)
Zn(1)-C(14)#1	2.513(2)

N(1)-C(1)-C(6)	122.22(18)
N(1)-C(1)-C(2)	121.69(18)
C(6)-C(1)-C(2)	115.98(18)
C(3)-C(2)-C(1)	122.41(19)
C(3)-C(2)-Cl(1)	119.39(17)
C(1)-C(2)-Cl(1)	118.19(16)
C(4)-C(3)-C(2)	119.3(2)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	120.3(2)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	119.4(2)
C(6)-C(5)-H(5)	120.3
C(4)-C(5)-H(5)	120.3
C(5)-C(6)-C(1)	122.51(19)
C(5)-C(6)-Cl(2)	118.78(17)
C(1)-C(6)-Cl(2)	118.65(16)
C(12)-C(7)-C(8)	120.34(19)
C(12)-C(7)-N(1)	122.22(19)
C(8)-C(7)-N(1)	117.44(18)
C(9)-C(8)-C(7)	118.45(19)
C(9)-C(8)-C(13)	121.23(19)
C(7)-C(8)-C(13)	120.18(18)
C(10)-C(9)-C(8)	121.2(2)

C(10)-C(9)-H(9)	119.4
C(8)-C(9)-H(9)	119.4
C(11)-C(10)-C(9)	119.9(2)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(10)-C(11)-C(12)	120.1(2)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(7)-C(12)-C(11)	120.0(2)
C(7)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(8)-C(13)-C(14)	116.00(18)
C(8)-C(13)-H(13A)	108.3
C(14)-C(13)-H(13A)	108.3
C(8)-C(13)-H(13B)	108.3
C(14)-C(13)-H(13B)	108.3
H(13A)-C(13)-H(13B)	107.4
O(2)-C(14)-O(1)	121.2(2)
O(2)-C(14)-C(13)	121.2(2)
O(1)-C(14)-C(13)	117.5(2)
S(1)-C(17)-H(17A)	109.5
S(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
S(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
S(1)-C(18)-H(18A)	109.5
S(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
S(1)-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(7)	123.13(17)
C(1)-N(1)-H(1N)	114.5
C(7)-N(1)-H(1N)	115.0
C(14)-O(1)-Zn(1)	96.01(14)
C(14)-O(2)-Zn(1)	82.79(13)

S(1)-O(3)-Zn(1)	120.73(9)
O(3)-S(1)-C(17)	105.40(13)
O(3)-S(1)-C(18)	105.79(14)
C(17)-S(1)-C(18)	97.54(17)
O(1)#1-Zn(1)-O(1)	138.54(9)
O(1)#1-Zn(1)-O(3)	97.91(7)
O(1)-Zn(1)-O(3)	110.03(7)
O(1)#1-Zn(1)-O(3)#1	110.03(7)
O(1)-Zn(1)-O(3)#1	97.91(7)
O(3)-Zn(1)-O(3)#1	94.60(11)
O(1)#1-Zn(1)-O(2)#1	59.48(6)
O(1)-Zn(1)-O(2)#1	89.67(6)
O(3)-Zn(1)-O(2)#1	157.40(6)
O(3)#1-Zn(1)-O(2)#1	93.46(7)
O(1)#1-Zn(1)-O(2)	89.67(6)
O(1)-Zn(1)-O(2)	59.49(6)
O(3)-Zn(1)-O(2)	93.46(7)
O(3)#1-Zn(1)-O(2)	157.40(6)
O(2)#1-Zn(1)-O(2)	87.03(9)
O(1)#1-Zn(1)-C(14)#1	30.24(7)
O(1)-Zn(1)-C(14)#1	113.92(7)
O(3)-Zn(1)-C(14)#1	128.08(7)
O(3)#1-Zn(1)-C(14)#1	105.16(7)
O(2)#1-Zn(1)-C(14)#1	29.36(6)
O(2)-Zn(1)-C(14)#1	86.12(6)

Symmetry transformations used to generate equivalent atoms:

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

Table 4: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Zn(diclo)_2(DMSO)_2]$. 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)	22(1)	18(1)	25(1)	0(1)	3(1)	-3(1)
C(2)	21(1)	24(1)	29(1)	-2(1)	-3(1)	-3(1)
C(3)	23(1)	31(1)	42(1)	-12(1)	7(1)	-2(1)
C(4)	37(1)	36(1)	29(1)	-10(1)	11(1)	-10(1)
C(5)	37(1)	32(1)	24(1)	0(1)	-1(1)	-6(1)
C(6)	23(1)	20(1)	30(1)	1(1)	0(1)	0(1)
C(7)	20(1)	23(1)	24(1)	-1(1)	-2(1)	1(1)
C(8)	21(1)	27(1)	22(1)	-1(1)	-4(1)	3(1)
C(9)	27(1)	34(1)	26(1)	-6(1)	-2(1)	6(1)
C(10)	34(1)	25(1)	42(1)	-12(1)	-7(1)	4(1)
C(11)	33(1)	24(1)	45(1)	2(1)	-5(1)	-5(1)
C(12)	26(1)	29(1)	32(1)	1(1)	3(1)	-2(1)
C(13)	26(1)	32(1)	22(1)	0(1)	3(1)	1(1)
C(14)	44(1)	27(1)	16(1)	-3(1)	-2(1)	1(1)
C(17)	69(2)	37(2)	81(2)	1(2)	-17(2)	4(1)
C(18)	51(2)	58(2)	83(2)	4(2)	5(2)	3(2)
Cl(1)	26(1)	32(1)	41(1)	2(1)	-8(1)	3(1)
Cl(2)	29(1)	32(1)	40(1)	1(1)	-7(1)	8(1)
N(1)	29(1)	23(1)	25(1)	2(1)	4(1)	4(1)
O(1)	47(1)	35(1)	28(1)	8(1)	-7(1)	-9(1)
O(2)	33(1)	46(1)	29(1)	8(1)	-2(1)	9(1)
O(3)	48(1)	52(1)	33(1)	-15(1)	-14(1)	22(1)
S(1)	47(1)	37(1)	30(1)	-8(1)	-16(1)	12(1)
Zn(1)	29(1)	34(1)	21(1)	0	-1(1)	0

Table 5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Zn(diclo)_2(DMSO)_2]$.

	x	y	z	U(eq)
H(3)	7489	4835	5356	38
H(4)	8372	4178	6115	41
H(5)	10036	3206	6047	38
H(9)	11686	834	3189	35
H(10)	10909	-796	3575	40
H(11)	9745	-601	4296	41
H(12)	9302	1238	4614	35
H(13A)	12171	2821	3229	32
H(13B)	11894	3504	3751	32
H(17A)	8615	8752	3279	93
H(17B)	7687	9052	2867	93
H(17C)	8914	8953	2678	93
H(18A)	6559	7336	3240	96
H(18B)	7518	7067	3639	96
H(18C)	7007	6060	3297	96
H(1N)	9805	3737	4036	38

Table 6: Hydrogen bonds for [$Zn(diclo)_2(DMSO)_2$] [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(2)	0.82	2.26	2.932(2)	138.8
N(1)-H(1N)...Cl(1)	0.82	2.58	2.9727(18)	110.4

Symmetry transformations used to generate equivalent atoms:

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