Faculty of Graduate Studies

New mixed ligand cobalt (II/III) complexes based on the drug sodium valproate and bioactive nitrogen-donor ligands. Synthesis, structure and biological properties.

معقدات جديدة تشمل ايون الكوبالت (+2/+3) مع حمض الفالبرويت والقواعد النيتروجينية النشطة بيولوجيا. التحضير، التركيب الهيكلي والخصائص البيولوجية.

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New mixed ligand cobalt complexes based on the drug sodium valproate and bioactive nitrogen-donor ligands. Synthesis, structure and biological properties.

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Contents:

List of Figures:

List of Tables:

List of Schemes:

Abbreviations:

Valp	Valporate
Na_{valp}	Sodium valporate
2-ampy	2-aminopyridine
Quin	Quinoline
2,9-dmp	2,9-dimethyl-1,10-phenanthroline
1,10-phen	1,0-phenathroline
BNPP	Bis(4-nitrophenyl) phosphate
DMSO	Dimethyl sulfoxide
MeOH	Methanol
H	Hour
m.p	Melting point
RT	Room temperature
Temp	Temperature
V_o	Initial rate
IZD	Inhibition zone diameter
IR	Infrared
UV-Vis	Ultraviolet-Visible

Abstract:

New cobalt valproate complexes with different nitrogen based ligands were synthesized and characterized using various techniques such as IR, UV-Vis, single crystal X-ray diffraction as well as other physical properties. The general formula of the prepared complexes is $[Co_n(valp)_m(L)_z]$, (n = 1,2…; m = 1,2,…; Z = 1,2…). The complexes $[Co_2(valp)_4]$ **(1)**, $[Co(valp)_2(2\text{-}ampy)_2]$ **(2)**, $[Co_2(valp)_4(quin)_2]$ **(3)**, $[Co(valp)_2(2,9\text{-}dmp)]$ **(4)** and $[Co(valp)_2(H_2O)(1,10\text{-}phen)]$ **(5)** showed different carboxylate coordination modes. The crystal structure of the complexes **2**, **3**, **4** and **5** were solved by using single crystal X-ray diffraction.

In-vitro, anti-bacterial activities for the desired cobalt complexes were investigated against five gram-positive (*Staphylococcus aureus, Micrococcus luteus, Bacillus subtilis, Enterococcus faecalis* and *Staphylococcus epidermidis*) and four gram-negative bacteria (*Escherichia coli, Klebsiella pneumonia, Proteus mirabilis* and *Pseudomonas aeruginosa*) by using Agar diffusion method. All cobalt valporate complexes didn't show anti-bacterial activity against all gram-negative bacteria. In addition, complex **3** didn't exhibit any anti-bacterial activity against gram-positive bacteria.

Complex **2** only showed anti-bacterial activity against *S. aureus* with IZD equal 17.5 mm. Complex **4** showed good anti-bacterial activity against all gram-positive bacteria with IZD ranging between 15-28 mm. Complex **5** showed low inhibition activity against all gram-positive bacteria except *E. faecalis* with IZD ranging between 11.3-13.7 mm. Also, the rate of BNPP hydrolysis was studied at different temperatures, pH and concentrations and found to be in the following order: **3** > **4** > **5** > **2**.

ملخص:

تم تحضير وتشخيص مركبات الكوبالت فالبرويت الجديدة مع القواعد النيتروجينية المختلفة باستخدام أجهزة متنوعة مثل طيف الأشعة تحت الحمراء وجهاز طيف الأشعة فوق البنفسجية والمرئية وجهاز حيود الأشعة السينية البلورية (X-ray). والصيغة الشكلية العامة لهذه المركبات هي

($[Co_n(valp)_m(L)_z]$, ($n = 1, 2,\dots$; $m = 1, 2,\dots$; $Z = 1, 2,\dots$))

والمركبات المعقدة التالية: $[Co_2(valp)_4]$ **(1)**, $[Co(valp)_2(2\text{-}ampy)_2]$ **(2)**, $[Co_2(valp)_4(quin)_2]$ **(3)**, $[Co(valp)_2(2,9\text{-}dmp)]$ **(4)** and $[Co(valp)_2(H_2O)(1,10\text{-}phen)]$ **(5)** أظهرت أشكال مختلفة لطرق ارتباط حمض الكاربوكسيل. وتم تحديد البنية البلورية للمركبات **2, 3, 4, 5**.

في *vitro* تم دراسة تأثير مركبات الكوبالت ضد خمس أنواع من البكتيريا موجبة غرام (*Staphylococcus aureus, Micrococcus luteus, Bacillus subtilis, Enterococcus feacalis* and *Staphylococcus epidermidis*) و ضد أربعة أنواع من البكتيريا سالبة غرام (*Escherichia coli, Klebsiella pneumonia, Proteus mirabilis* and *Proteus aeruginosa*) باستخدام طريقة الانتشار في الآجار. حيث تبين أن كافة مركبات الكوبالت فالبرويت لم تظهر أي نشاط ضد جميع أنواع البكتيريا سالبة غرام غير أن المركب **3** لم يظهر نشاطا ضد كلا نوعي البكتيريا (سالبة وموجبة غرام)

وكما أظهرت النتائج أن المركب **2** أظهر نشاطا ضد نوع من أنواع البكتيريا موجبة غرام يطلق عليه *S. aureus* حيث أن قطر نطاق التثبيط لهذه البكتيريا يساوي 17.5 ملم في حين أن المركب **4** أظهر نشاطا فعالا ضد جميع أنواع البكتيريا موجبة غرام التي أقطارها تنحصر بين 15-28 ملم ، بينما المركب **5** أظهر نشاط قليل ضد جميع أنواع البكتيريا موجبة غرام ما عدا *E. ferabis* حيث أقطارها تتراوح بين 11.3-13.7 ملم. وأيضا تم دراسة سرعة تحلل BNPP مع اختلاف الظروف المستخدمة (درجة الحرارة، درجة الحموضة والتركيز). أظهرت النتائج أن تحلل BNPP مع هذه المركبات يكون بالترتيب التالي **3** > **4** > **2** > **5**.

1. Introduction:

1.1 General information about the chemical elements:

The chemical elements which are essential to continue the life in plants, human and animals are about 25 elements.[1,2] In general, the chemical elements can be classified into four categories. Firstly, bulk elements like H, O, C, P and S.[1,3] These elements appear in major cellular components such as nucleic acids, proteins, metabolites and lipids–membranes.[1,3] The second category is macro minerals and ions such as Ca, Mg, K, Na, Cl, SO_4^{-2} and PO_4^{-3}. Charge carrier is the biological function of potassium and sodium ions so that it helps the biological system in many ways for instance, maintain the osmotic pressure and nerve impulse. Nevertheless, magnesium ions act as trigger of reactions and structures in isomerases, hydrolases and phosphate transfer but calcium ions act as trigger, charge carrier and structural role.[1] Thirdly, trace elements which are involved in enzymatic activities like Cu, Fe and Zn.[1,4] Finally, ultra-trace elements which consist of metals like Li, Cd, Ni, Cr, Mo and Mn and nonmetals such as B, As, I, F, Si and Se.[1]

In biological systems, 23 elements have physiological activities in human body as shown in Figure 1.[5] Among these elements, 11 elements can be classified as TE (trace elements) and UTE (ultra-trace elements) and they include transition metals such as molybdenum, zinc, copper, cobalt, iron, manganese, chromium and vanadium and nonmetals like iodine, fluorine and selenium. In addition, some elements like Li, Cd, Ni, B and Si were recently added to the TE and UTE list.[5,6]

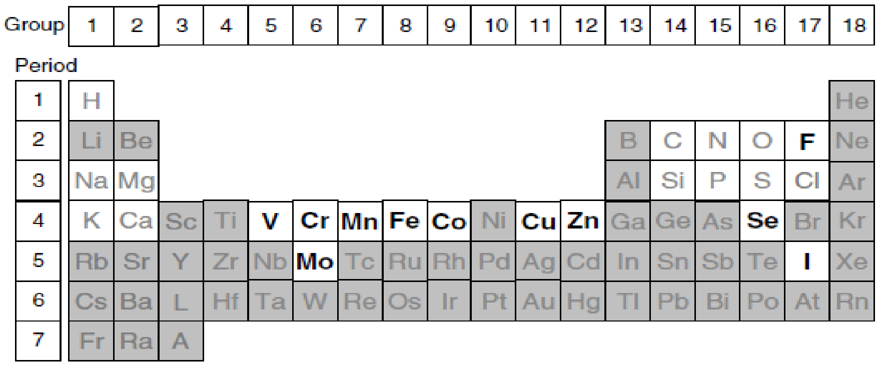


Figure 1: The Periodic Table with white background indicating the essential elements for human body and black characters indicating the trace and ultra trace elements.

Although the chemical elements are essential in human body but they are required in varied concentration.[5,6] Table 1 shows the concentration range of TE and UTE which are needed in less than 100 mg/day while the macro minerals are needed in concentration larger than 100 mg/day.[2,5–8] In addition, these elements can be toxic or produces adverse effects when their concentrations become larger/ lower than the optimum amount that the human body needs.[5,6]

Table 1: The daily amount of essential TE and UTE required for adults.

Element	Intake (mg/day)
Iron (males)	10
Iron (females)	18
Zinc	15
Manganese	2.5 to 5.0
Fluorine	1.5 to 4.0
Copper	2.0 to 3.0
Molybdenum	0.15 to 0.5
Chromium	0.05 to 0.2
Selenium	0.5 to 0.2
Iodine	0.5

1.2 Metals in biological systems:

Transition metals are both stored and transported in living organisms in appropriate concentrations and can be used as cofactors or metalloproteins which are found in microorganisms, animals and plants.[7,8]

There are many examples for transition metals found in the living organisms such as chromium, nickel, iron, copper and zinc and the oxidation state of these elements depend on the position of the element in the biological system.[7,8] Table 2 shows examples of enzymes containing transition metal in biological system.[9]

Table 2: Examples of enzymes containing transition metal in biological system.

Ion	**Examples of enzymes containing this ion**
Cupric	Cytochrome oxidase
Ferrous or Ferric	Catalase, Cytochrome (via Heme), Nitrogenase, Hydrogenase
Magnesium	Glucose 6-phosphatase, Hexokinase, DNA polymerase
Manganese	Arginase
Molybdenum	Nitrate reductase, Nitrogenase
Nickel	Urease
Zinc	Alcohol dehydrogenase, Carbonic anhydrase, DNA polymerase

Transition metals which exhibit different oxidation states can be coordinated with negatively charged ligands and enhance their use in pharmacological applications.[10] Metal ion complexes such as iron, bismuth, calcium, copper, cobalt and zinc are playing a crucial role in the development of antimicrobial agents.[11,12] Cobalt based ligand complexes have an important antiviral and antibacterial effects.[11,12]

1.2.1 Cobalt in biological systems:

Co^{3+} ion can be found in different biological systems such as vitamin B12 (cobalamin) which is a cofactor for many enzymes like methyl transferases, dehalogenases and isomerases (Figure 2) and it's a key important in biological system in the formation of blood and the normal functioning of the nervous system and brain.[11–15]

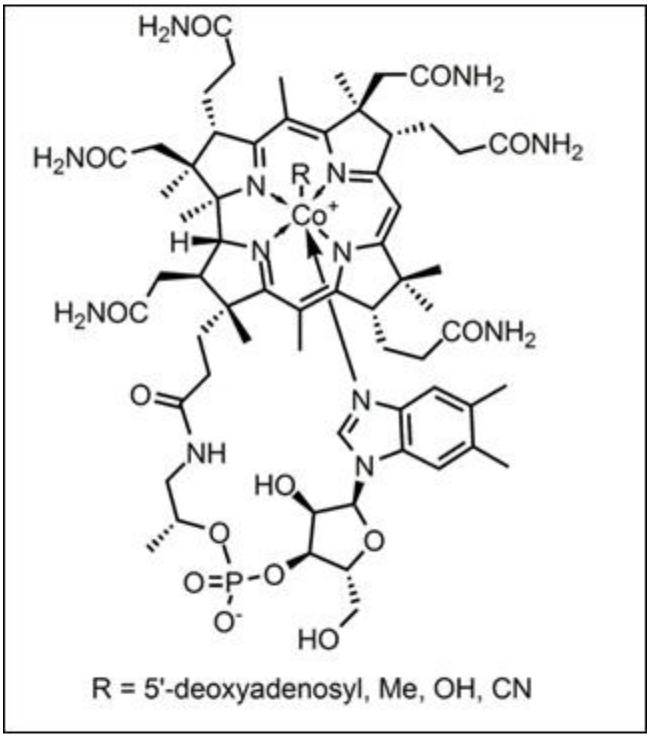


Figure 2 : Vitamin B12 structure.

Vitamin B12 is stabilized by a chelating tetra dentate macrocycle known as a corrin which contains four nitrogen atoms located in equatorial positions in the octahedral geometry.[11,12,16] The axial positions consist of dimethylbenzimidazole ligand and R group which may be hydroxyl or cyano or deoxyadenosyl or methyl.[12,14] Cyanocobalamin found in food and it is used as a supplements. The other forms of cobalamin like 5-deoxyadenosyl and methyl are used as a co-factors for methionine synthase which is essential for the synthesis of pyrimidines and purines.[14]

In addition to its uses in bioinorganic chemistry, cobalt can be used in biotechnology as a catalyst in industrial applications such as nitrile hydratase, glucose isomerase, methylmalonyl-CoA carboxytransferase and methionine aminopeptidase.[12,17,18] The oxidation state of cobalt in these enzymes is +2 except +3 in nitrile hydratase.[12,17]

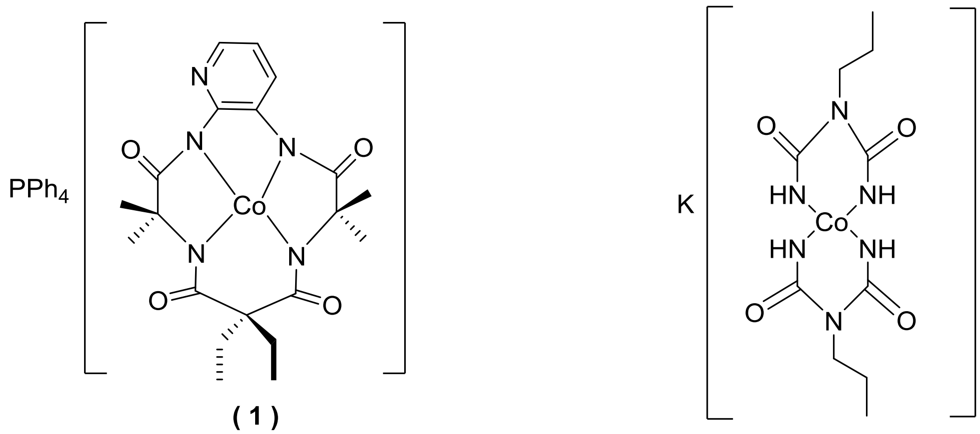
1.3 Cobalt as an element:

Cobalt which is the 33rd most abundant element, is a silvery grey solid at RT, it has been found in different media such as surface water, air, groundwater, sediment and soil.[19] The oxidation state of cobalt is +2 or +3 but cobalt(III) ion is unstable in aqueous solution so it can be reduced to Co(II) or chelating with oxygen or nitrogen donor ligand to increase its stability.[12,19]

Co(II) ion with a d^7electron configuration is a borderline Lewis acid having the ability to form complexes with hard and soft bases.[20,21] This ion can easily react with other molecules to form complexes with coordination numbers four or six.[21,22] The geometry of Co(II) complexes are generally octahedral, tetrahedral and square planar with high spin configuration but low spin Co(II) complexes with strong field ligands such as $[Co(CN)_5]^{-3}$ are also found.[21,23]

Tetrahedral Co(II) complexes are more familiar than in other transition metals because of the small energy difference between the high spin tetrahedral and octahedral geometries.[21]

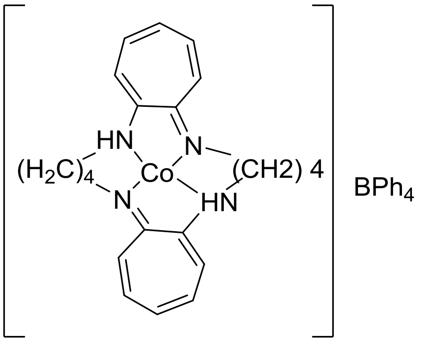
The geometry of Co(III) complexes are almost octahedral or distorted with d^6 low spin electronic configuration. However, high spin Co(III) octahedral complexes with weak field ligands such as $[CoF_3(H_2O)_3]$ and $[CoF_6]^{-3}$ are found. Although square planar complexes are uncommon, but stable complexes with special ligands were successfully prepared such as complex **1** and **2** which are shown in Figure 3. In addition, Co(III) tetrahedral complexes like complex **3** is shown in Figure 4.[21]



(1)

(2)

Figure 3: Examples of Co(III) square planar complexes.



(3)

Figure 4: Example of Co(III) tetrahedral complexes.

There are many cobalt compounds which were produced by the International Program on Chemical Safety (IPCS) and found in the market such as cobalt(II) chloride, cobalt(II) sulfide, cobalt(II) nitrate, cobalt naphthenate, cobalt(II) acetate tetrahydrate, cobalt(II) nitrate hexahydrate and cobalt(II) chloride hexahydrate[19,24] which was used in the present work.

1.4 Nitrogen chelate ligands:

In organic chemistry, structures can be classified into two types, carbocyclic or heterocyclic. Carbocyclic structures contain only carbon atoms but heterocyclic contains carbon atoms with one or more other atoms such as nitrogen, sulfur and oxygen which is the most common heteroatom. The chemistry of heterocyclic compounds is very important and can be used in agriculture, medicine and many other applications. Moreover, they can be found in human body as main building blocks in nucleic acids and vitamins.[25]

Pyridine has three charged and two uncharged resonances (Figure 5).[25] 2-aminopyridine and quinoline are examples of the pyridine derivatives that often act as a monodentate ligands.[25,26]

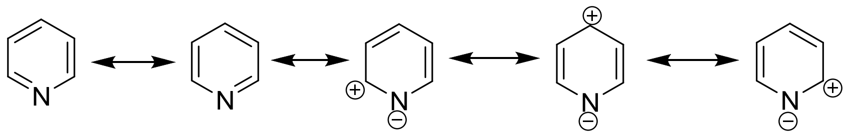


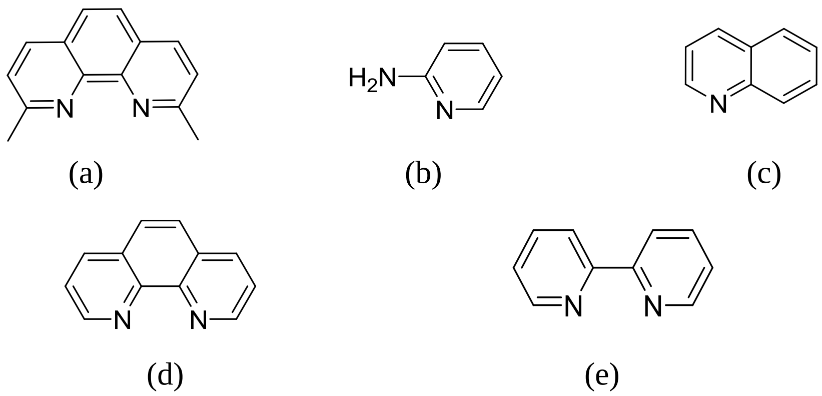
Figure 5: The resonance structures of pyridine.

Nitrogen based ligands can be used in the synthesis and design of compounds in biological, chemotherapy and pharmacological applications such as anti-rheumatics, anti-septics and anti-histamines.[26,27]

1,10-Phenanthroline is an efficient chelating nitrogen donor ligand which produces stable complexes in a solution with transition and post transition metal ions. 1,10-Phenanthroline complexes possess additional properties because it contains heteroaromatic and aromatic groups; i.e. 1,10-phenanthroline copper complex has an antitumor activity and inhibition for RNA and DNA polymerase activities.[27,28] In addition, $[Ag_2(phen)_2(mal)]\cdot 2H_2O$ and $[Cu(phen)_2mal)]\cdot 2H_2O$ complexes have effective inhibition against the growth of microorganisms such as inhibiting the growth of Candida albicans (phen = 1,10-phenanthroline and $malH_2$ = malonic acid).[29]

2-aminopyridine (2-ampy) has a great importance in pharmacological applications and synthesis of pharmaceuticals such as anti-inflammatory and anti-histamines. This ligand can react with different metal ions in various binding modes; monodentate coordination through pyridine nitrogen atom or it can act as bidentate ligand through pyridine nitrogen atom and exocyclic amine nitrogen.[26] 2,2-bipyridine (2,2-bipy) exhibits anti-microbial properties.[30,31] This ligand almost reacts with first row transition metals in a bidentate coordination mode to form very stable chelating complexes.[31]

The ligands 2-amino pyridine, quinoline, 2,9-dimethyl-1,10-phenanthroline and 1,10-phenanthroline exhibit anti-tumor, anti-bacterial, anti-viral, anti-malarial and anti-fungal activities. [32–34] In the present and previous studies these ligands were used as bioactive nitrogen bases.[33,35] The chemical structure of 2,9-dimethyl-1,10-phenanthroline, 2-aminopyridine, quinoline, 1-10-phenanthroline and 2,2-bipyridine ligands were shown in Figure 6.



(a) (b) (c)

(d) (e)

Figure 6: Nitrogen donor-ligands used in the present work research: a) 2,9-dimethyl-1,10-phenanthroline, b) 2-aminopyridine, c) quinoline, d) 1,10-phenanthroline, e) 2,2-bipyridine.

1.5 Cobalt ion nitrogen-base ligand complexes:

Metal complexes with organic chelating ligands are important in biological systems including anti-viral, anti-inflammatory, anti-fungal, anti-bacterial, anti-tumor and cytotoxicity activities.[27,36] The biological activities of these metal complexes depend on the type of the metal ion (M^{+n}) and the nature of the used ligand.[37,38]

In recent studies, researchers prepared mixed ligands with transition metal complexes containing 2,2'-bipyridine or 1,10-phenanthroline and other ligands such as halides (I, Cl and Br), diethylenetetramine, oxydiacetate, oxalate and schiff bases to produce compounds with enhanced various biological activities in human body.[31]

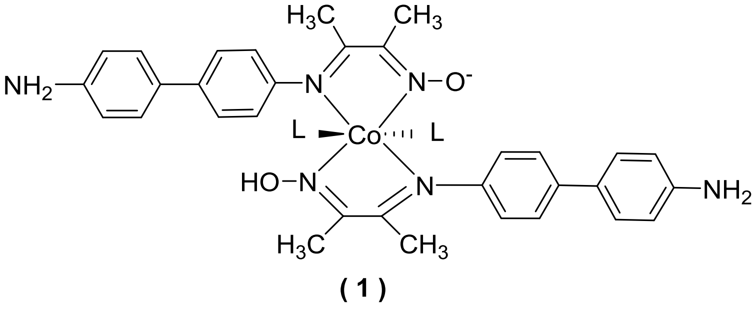
Cobalt(II) complexes with N- and O- donor ligands have been studied in a wide range of biological applications because it has diverse properties in anti-microbial activities such as anti-tumor properties. The activity of transition metal complexes can be improved by using different N-heterocyclic ligands such as 1,10-phenanthroline, 2-aminopyridine and 2-methylamino pyridine.[26]

There are many examples of Co complexes with N-donor ligands which can be used in anti-microbial activity such as $Co(2\text{-}ampy)_2(dca)_2$, this complex was tested in eight microorganisms, 4 yeasts (Cryptococcus neoformans, Candida albicans ATCC P37039, Candida glabrata and Candida albicans 194B) and 4 types of bacteria (Gram-positive, *Staphylococcus aureus* and Gram-negatives, *Pseudomonas aeruginosa, Escherichia coli and Salmonella typhi*). This complex showed moderate activity compared to the free ligands (2-ampy and dca) but it has higher activity than the reference drug nystatin against C. albicans 194B and C. glabrata yeasts. This indicates that the interaction between metal ions and N-donor ligands plays an important role to enhance the antimicrobial activity.[26]

1.5.1 Cobalt ion complexes with anti-bacterial activity:

The anti-bacterial activity of the transition metal complexes with bidentate N-donor ligands like o-phenyldiamine, bipyridine and phenanthroline is higher than monodentate ligands like pyridine.[39,40]. Generally, mononuclear M^{+n} complexes are less active than dinuclear complexes and the nature of the nitrogen donor ligands will also affect the anti-bacterial activity.[39,41]

There are many cobalt complexes which have been studied and showed an anti-bacterial activity using simple zone inhibition techniques such as complex **1** (Figure 7).[12,15] Complex **1** which contains amine-imine-oxime ligand, showed the activity against *Bacillius subtilis* but the effectiveness of the control antibiotics kanamycin and tetracycline were found to be higher than that of complex **1** which showed no activity against *Staphylococcus aureus*, *Enterobacter fecalis* and *Escherichia coli*.[12]



(1)

L = acetate

Figure 7: Structure of oxime cobalt(III) complex.

Cobalt complexes of 1,10-phenanthroline and 2,2-bipyridine such as $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$ (Figure 8) showed anti-bacterial activity against nine types of bacteria as listed in Table 3.[29,31] 1,10-Phenanthroline ligand showed the highest anti-bacterial activity against all tested bacteria with high IZD (inhibition zone diameter) from 28-32 mm while 2,2-bipyridine exhibits the selective anti-bacterial activities with lower IZD values from 7-14 mm.[31]

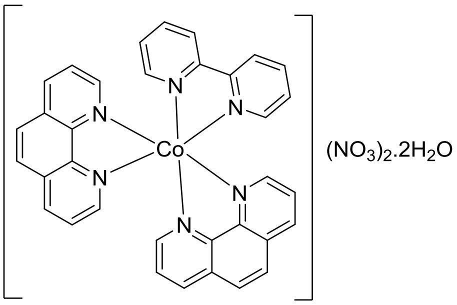


Figure 8: Structure of $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$.

Table 3: Anti-bacterial activities of $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$

Bacteria	Inhibition zone growth diameter (mm)				
	phen	bpy	$Co(NO_3)_3.6H_2O$	complex	RA
Enterobacter choacae	32	-	11	22	28
Staphylococcus aureus	31	9	10	24	30
Escherichia coli	31	14	13	22	22
Morganella morganii	30	-	11	23	27
Salmonella thyphi	32	9	12	25	30
Klebsiella pneumoniae	28	-	11	20	29
Shigella flexineri	31	13	13	22	22
Citrobacter freundi	30	10	-	16	21
Pseudomonas aeruginosa	31	7	11	23	25

Phen = 1,10-phenanthroline, bpy = 2,2’-bipyridine, complex = $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$, RA = gentamycin which is a reference antibiotics.

1.5.2 Cobalt ion complexes with anti-tumor activity:

Cisplatin (Figure 9) is the most effective and potent chemotherapeutic drug used to treat various tumor tissues such as ovarian carcinomas, bladder, head and neck tumors.[15,42,43] At the same time, many types of cancer developed resistance to this drug and different side effects like nephrotoxicity, neurotoxicity and gastrointestinal reactions in human body were recorded. In attempt to overcome the toxicity and side effects, researchers prepared many transition metal derivatives in anti-cancer drugs to produce modified metal based anti-cancer agents with high efficiency and low toxicity.[15,43]

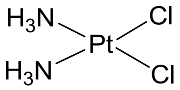


Figure 9: Structure of cisplatin.

Metals in biological systems gain their importance due to the ability of the positive M^{+n} ion to interact with the negative charge in biological molecules.[42,44] The primary pharmacological target of anticancer agents is DNA, the interaction between the metal complex and DNA is very important to understand the relationship between biological and pharmaceutical activities. Various spectroscopic techniques such as fluorescence, CD and electronic absorption spectroscopy are used to study this interaction.[15]

Cobalt ion has been widely used in therapeutic drugs because it has a variety of geometries, coordination numbers and oxidation states.[45] Moreover, it is less toxic than other metals like platinum.[15] Among the most common ligands which were used to prepare Co complexes as anticancer agents are phenanthroline and tridentate N,O-donor ligands.[46]

There are many anticancer Cobalt complexes and derivatives such as $[Co(QCT)_2]\cdot Cl\cdot 1.5H_2O$ (Figure 10) and $[Co(QCMT)(CH_3OH)Cl_2]$ (Figure 11) where QCT is quinoline-2-carboxaldehyde thiosemicarbazones and QCMT is quinoline-2-carboxaldehydeN^4-methyl-thiosemicarbazone.[15]

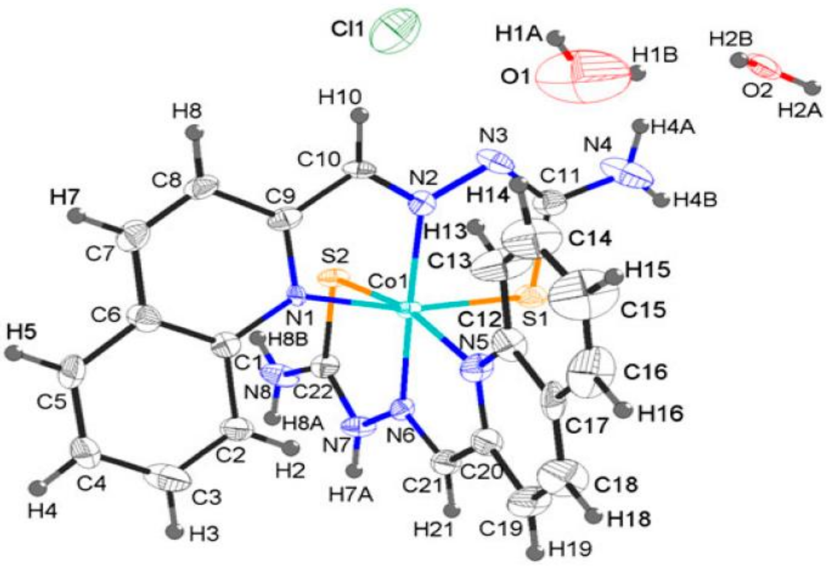


Figure 10: Structure of [Co(QCT)$_2$]·Cl·1.5H$_2$O complex (**4**).

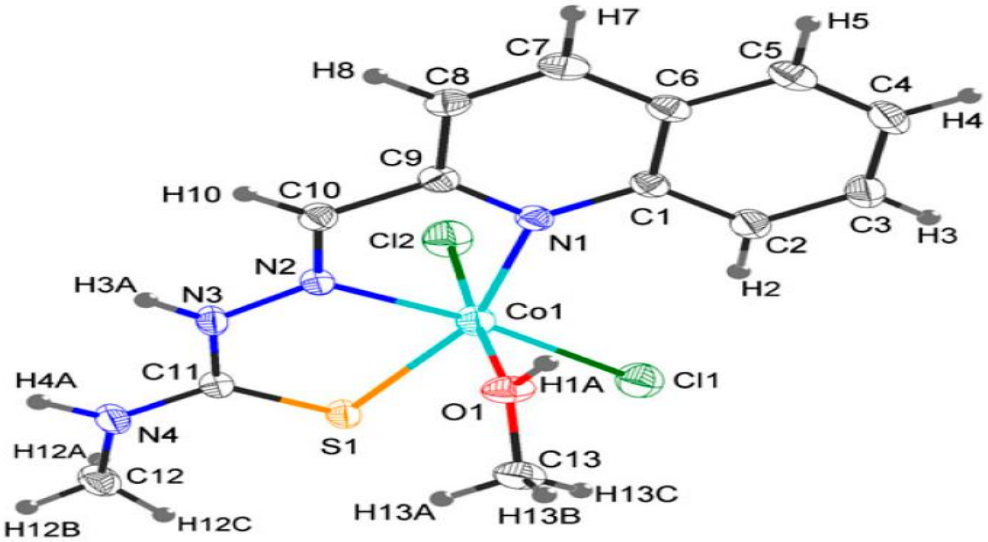


Figure 11: Structure of [Co(QCMT)(CH$_3$OH)Cl$_2$] complex (**5**).

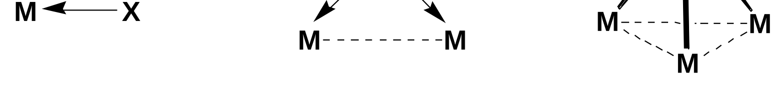
Cytotoxicity tests for complexes **4** and **5** were carried by using different types of cells which are human breast adenocarcinoma MCF-7, cisplatin-resistant A-549/CDDP and human lung adenocarcinoma A-549 cell lines and the results from this experiment were compared with cisplatin as a positive control.[15]

The results showed that the inhibition rate of cisplatin against A-549 cell line is higher than the inhibition rate of complexes **4** and **5** while cisplatin is less active than the two Co(II) complexes against A-549/CDDP and MCF-7 cell lines. When the inhibition rate of complexes **4** and **5** and their free ligands (QCMT and QCT) were studied against A-549 and A-549/CDDP, the results showed that both complexes were more active than their parent ligands.[15]

1.6 Carboxylic acids:

Carboxylic acids are important precursors used in the synthesis of many in inorganic organometallic complexes.[47] Different carboxylic acids and their derivatives such as cinnamic acid, valproic acid and ibuprofen were used in various medicinal and pharmaceutical applications.[48,49] In recent studies, researchers prepared carboxylate groups with transition metals such as Zn, Co and Cu to increase the biological efficiency of these carboxylates in the biological and pharmaceutical applications.[50]

The carboxylate group can bind with metal ions in various modes as shown in Figure 12.[50–53] These carboxylate groups can act as neutral molecular ligands or as anionic monodentate, bidentate or bridging bidentate ligands.[27,50]



2e-terminal 4e-μ-bridging 6e-μ_3-bridging

Figure 12: Different binding modes between the carboxylate groups and metals.

Figure 13 shows the bonding geometries for metal carboxylate complexes, free anion in aqueous solution, monodentate bonding, chelating bidentate and bridging bidentate. For the same metal ion, the distance between the carbon atom and the two oxygen atoms (n_1 and n_2) in free anion, chelating bidentate and bridging bidentate are approximately equal while in monodentate bonding, the C-O$_{\text{(bounded)}}$ bond is longer than the C-O$_{\text{(unbounded)}}$ bond.[54]

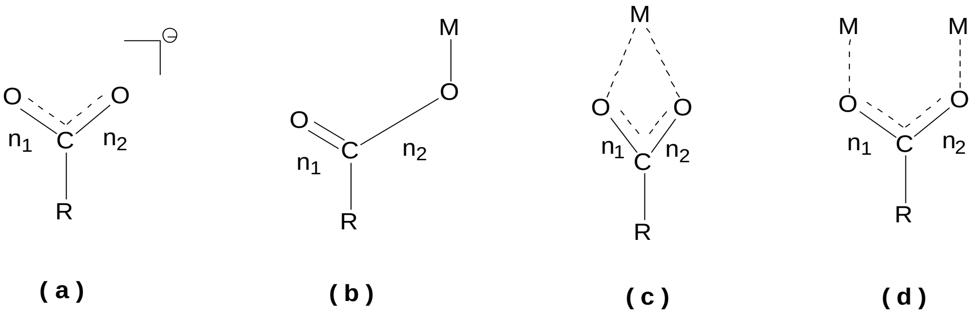


Figure 13: Bonding geometries for metal carboxylate complexes. a) free anion in aqueous solution, b) monodentate bonding, c) chelating bidentate, d) bridging bidentate.

1.7 IR spectroscopy for carboxylic acid and heterocyclic compounds:

The absorption band of the carbonyl group in free carboxylic acids is found between 1690 cm^{-1} and 1760 cm^{-1}. The IR spectra for metal carboxylates show two bands, symmetric and asymmetric stretching which are typically absorbed in the 1,400-1,530 cm^{-1} region for $\nu_{as}(COO^-)$ and 1,390-1410 cm^{-1} region for $\nu_s(COO^-)$.[54–56] In addition, bending ($\nu_\delta(COO^-)$~ 745 cm^{-1}), out of plane twisting

($\nu_\tau(COO^-)$~ 580 cm^{-1}) and rocking ($\nu_p(COO^-)$~ 550 cm^{-1}) are also characteristic modes of the carboxylate group.[56]

The difference between asymmetric and symmetric stretching bands ($\Delta\nu = \nu_{as} - \nu_s$) was used to predict the carboxylate coordination mode in the metal complexes and this value is commonly compared to the free carboxylate ion.[54,55,56]
In general, the Δν value of the free anion is less than in monodentate bonding mode (Δν (free anion) << Δν (monodentate complexes)) but it is larger than in the chelating bidentate metal complexes (Δν (free anion) >> Δν (chelating complexes)). On the other hand, Δν bridging bidentate is smaller or similar to the Δν in free anion (Δν (bridging complexes) ≤ Δν (free anion)).[54,56,57] Change the angle and bond distances in metal carboxylates, will also change the Δν value.[54]

The C-H stretching band in heterocyclic compounds such as pyrrole and pyridine is absorbed in the 3000–3080 cm^{-1} range and the N-H stretching band is observed in the 3200–3500 cm^{-1}range, however, its position depends on the degree of association and hydrogen bonding. The ring stretching band is observed in the 1300–1600 cm^{-1} whereas the out-of-plane C–H bending band is shown in the 600–800 cm^{-1} range.[58]

1.8 Valporic acid:

Valporic acid (2-propylvaleric or n-dipropylacetic or 2-propylpentanoic acid) is a short chain fatty acid which is a carboxylic acid and it was discovered accidentally in 1882 by Pierre Eymard (Figure 14) who used it as solvent in many biological systems such as anti-epileptic drugs.[59–63]

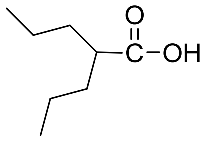


Figure 14 : The chemical structure of valporic acid.

Valporic acid which is a pharmacologically active compound is rapidly metabolized in the liver. In addition, it gained its high bioavailability from the unique short chain fatty acid structure that leading to easier delivery to cells and organisms.[60,63] Valproic acid is stable at r.t, highly soluble in organic solvents and slightly soluble in water, but it dissociates in alkaline water solution.[63]

Recently, valproic acid has a wide range clinical uses such as antibiotic drugs for treatment of many diseases such as migraines, epilepsy, and bipolar disorder.[59,61,63] But it causes many side effects in human organisms such as gastrointestinal disturbances, headache, hair loss and weight gain. Valproate complexation with metal may reduce these side effects and enhance the biological activity.[61,63,64]

In 2012, Mahto et al. prepared modified valproic acid structures by replacing one of the CH_3 group by $-NH_2$ or $-CH_2CH_3$ or -OH or –H. The modified derivatives showed better drug activity than valproic acid as a result of external and internal hydrogen bonds and Vander Waals interactions between the drug complexes and specific proteins.[65]

1.9 Metal valporate complexes:

Metal based drugs have been extensively found in inorganic, pharmaceutical and medicinal chemistry to produce new drugs which depend on metal ions and organic ligands.[28] The transition metal with carboxylate complexes are used in biological systems and industrial applications such as dirhenium(III) dichlorotetraisobutyrate which inhibits cancer cells while dirhodium(II) tetraacetate which is used as catalyst.[66]

There are many examples of metal valporate complexes such as copper, cadmium(II), cobalt(II), zinc(II) and manganese(II).[67–70] Tabrizi and McArdle have studied cadmium(II), cobalt(II) and manganese(II) valproate with 1,10-phenanthroline and imidazole. These complexes were synthesized and characterized by using various techniques like single crystal X-ray diffraction. The crystal structure of $[Cd(valp)_2(imidazole)_2]$ is shown in Figure 15. The complexes were tested for their biological activities such as anti-bacterial activity by using agar diffusion method and anti-cancer cells.[70]

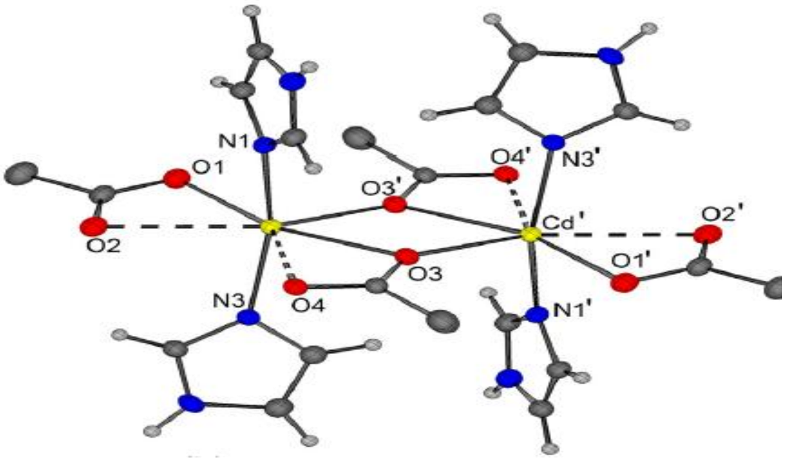


Figure 15: Crystal structure of [Cd(valp)$_2$(imidazole)$_2$].

1.10 BNPP hydrolysis:

The hydrolytic cleavage of phosphatediester bond is very difficult to occur, but the hydrolysis may be enhanced by using an artificial catalyst which may be organic or inorganic compound. The temperature, structure of the catalyst and the pH value are factors affecting the hydrolysis of phosphatediester bond.[71,72] The hydrolysis of BNPP is very important in environmental, industrial and biological applications.[73,74]

One possible mechanism of the BNPP catalytic cleavage is shown in Figure 16. In the first step, water molecule coordinate with metal complex to produce complex **A**. Secondly, the metal complex in aqueous solution is coordinated to oxygen atom on the P=O of BNPP, forming complex **B**. Thirdly, intramolecular metal hydroxide in complex **B** attacks the P atom in BNPP molecule to release p-nitrophenol and this step is the key step of hydrolysis. Fourthly, water molecule quickly coordinates again with complex to produce **D** then p-nitrophenol and phosphoric acid are quickly released. Finally, water molecule is bonded again to the metal complex and thus the catalytic cycle is completed.[71–73,75]

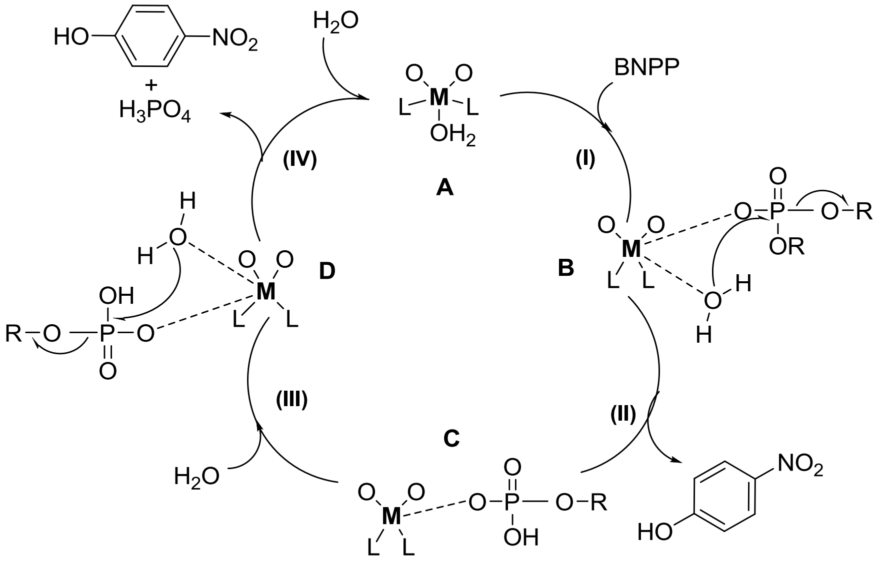
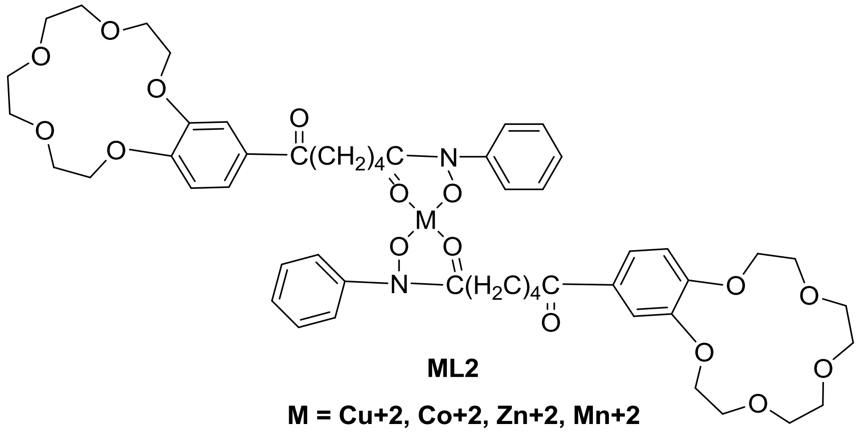


Figure 16: The possible mechanism of the BNPP catalytic cleavage.

There are many examples of transition metals which can be used as catalysts in the hydrolysis of BNPP (bis(4-nitrophenyl)phosphate) such as Cu(II), Mn(II), Mn(III), Zn(II), Ln(III) and Co(II) complexes to provide high effectiveness and selectivity.[73,74,76] These complexes have strong affinities as catalysts because they have high oxidation state, strong Lewis acidity and charge density.[74]

The K_{obs} constants (pseudo first order rate) for the hydrolysis of BNPP were calculated depending on the initial rate method using the following equations, $(rate)_0 = (dc/dt)_0 = (dA/dt)_0/\varepsilon$ and $(rate)_0 = k_{obs} [ML]_0$ where $(rate)_0$ is initial rate, A is absorbance, c is a concentration and $[ML]_0$ is the initial concentration of the complex. The rate of release of p-nitrophenol from BNPP hydrolysis was determined at 400 nm by using UV-Vis spectrophotometer.[71,73]

There are many Mn(II), Zn(II), Cu(II) and Co(II) complexes which have been used as catalysts for the hydrolysis of BNPP under different concentration, temp and pH values, Co(II) benzo-15-crown-5 is shown in Figure 17 as an example.[73,74]



ML2

M = Cu+2, Co+2, Zn+2, Mn+2

Figure 17: Structure of metal benzo-15-crown-5.

The K_{obs} of BNPP hydrolysis without catalyst is 1.12×10^{-11} s^{-1} while it is increase by a factor of 3.24×10^{5}, 3.06×10^{5}, 2.34×10^{5}, 2.24×10^{5} for CoL_2, CuL_2, ZnL_2 and MnL_2 catalyst, respectively at pH = 7.50. The catalytic activity of Co^{+2} is the largest one compared to Cu^{+2}, Zn^{+2} and Mn^{+2}.[73]

Jan Qing and Ci Li studied the interaction of $Ce(NO_3)$ with nitrogen heterocyclic ligand as a catalyst and this reaction showed first order behavior. The rate constant (K_{obs}) of the BNPP catalytic cleavage was 4.18×10^{-1} s^{-1} and the K_{obs} of the non-catalyzed BNPP hydrolysis was 10^{-11} s^{-1}.[74]

1.11 Aim of the research:

The present work focuses on the synthesis and characterization of cobalt valproate complexes with various nitrogen base ligands such as 1,10-phenanthroline, 2-amino pyridine…, the general formula of these complexes is $[Co_n(valp)_m(L)_z]$, (n = 1, 2…; m = 1, 2,…; Z = 1, 2…; L = nitrogen base ligand).

The complexes will be characterized by using various techniques such as IR, magnetic moment, UV-Vis, single crystal X-ray diffraction. The complexes will be tested for their biological activity. In addition, the application of their phosphate hydrolysis enzymes will be conducted.

2. Experimental:

2.1 Materials:

All reagents, chemicals and solvents which were purchased from commercial sources, were used without further purification. *Escherichia coli, Staphylococcus aureus, Micrococcus luteus, Bacillus subtilis, Klebsiella pneumonia, Proteus mirabilis, Enterococcus faecalis, Pseudomonas aeruginosa* and *Staphylococcus epidermidis* were obtained from Biology Department in Birzeit University.

2.2 Apparatus:

Melting points were measured by using Electrothermal melting point apparatus. IR spectra of cobalt complexes were taken on a Bruker Tensor II as KBr pellets in the region 200-4000 cm^{-1}. UV-Vis spectra in MeOH solvent in the region 200-800 nm were determined by using Agilent 8453 photodiode array (PDA) spectrophotometer. The magnetic susceptibility measurements of powdered complexes were determined by magnetic susceptibility, $HgCo(NSC)_4$ complex (mercury cobalt-thiocyanate) was used as standard complex.

2.3 Synthesis and characterization of cobalt valporate complexes:

All cobalt valporate complexes were prepared at room temperature (RT).

2.3.1 Synthesis of cobalt valporate $[Co_2(valp)_4]$ (1):

Sodium valproate (2.00 g, 12.1 mmol) in water was slowly added to a stirred aqueous solution of $CoCl_2.6H_2O$ (1.42 g, 6.0 mmol), then the formed purple solid was filtered from aqueous solution, washed with cold water and air dried. The complex was characterized by using IR-spectroscopy, UV-spectroscopy.

Yield = 86.50%; m.p = 58 ^{o}C; IR (KBr, cm^{-1}): 2959, 2872, 1556, 1450, 1419, 1330, 753, 469; UV-Vis (MeOH, λ (nm) (ϵ/$Lmol^{-1}cm^{-1}$)): 270 (7576.5), 492 (43.6).

2.3.2 Synthesis of cobalt valporate 2-aminopyridine complex $[Co(valp)_2(2\text{-}ampy)_2]$ (2):

2-ampy (0.96 g, 10.2 mmol) in MeOH was slowly added to a stirred MeOH solution of complex **1** (0.93 g, 2.6 mmol), the solution was then stirred for 3.5 h, the solvent was evaporated and a pink precipitate was obtained. The complex was characterized by using IR-spectroscopy, UV-spectroscopy, magnetic moment and single crystal X-ray diffraction. Recrystallization from methanol produced suitable crystals for X-ray structure determination.

Yield = 79.85%; m.p = 121-125 ^{o}C; IR (KBr, cm^{-1}): 3413, 3331, 3080, 3070, 2959, 2930, 2870, 1651, 1565, 1495, 1448, 1329, 1270, 1226, 1156, 1113, 1066, 1003, 864, 769, 740, 657, 518, 451; UV-Vis (MeOH, λ (nm) (ϵ/Lmol^{-1}cm^{-1})): 235 (20072), 295 (8022.1), 520 (20.2); μ_{eff} = 4.83 BM.

2.3.3 Synthesis of cobalt valporate quinoline $[Co_2(valp)_4(quin)_2]$ (3):

Quin (0.91 ml, 0.98 g, 7.6 mmol) was slowly added to a stirred MeOH solution of complex **1** (1.36 g, 3.8 mmol), then the solution was stirred for 5 h, the solvent was evaporated and a green precipitate was obtained. The complex was characterized by using IR-spectroscopy, UV-spectroscopy, magnetic moment and single crystal X-ray diffraction. Recrystallization from methanol produced suitable crystals for X-ray structure determination.

Yield = 26.23%; m.p = 110-111 ^{o}C; IR (KBr, cm^{-1}): 3100, 3050, 2956, 2930, 2870, 1613, 1560, 1510, 1450, 1417, 1241, 1145, 1110, 1050, 803, 782, 735, 520, 467; UV-Vis (MeOH, λ (nm) (ϵ/Lmol^{-1}cm^{-1})): 213 (49030), 276 (9119), 366 (3.6), 520 (2.6).

2.3.4 Synthesis of cobalt valporate 2,9-dimethyl-1,10-phenanthroline complex [Co(valp)$_2$(2,9-dmp)] (4):

2,9-dmp (0.14 g, 0.66 mmol) was dissolved in 10 ml MeOH, then the solution was added to a stirred MeOH solution of complex **1** (0.12 g, 0.33 mmol), then the solution was stirred for 3 h, the solvent was evaporated and a purple precipitate was obtained. The complex was characterized by using IR-spectroscopy, UV-spectroscopy, magnetic moment and single crystal X-ray diffraction. Recrystallization from methanol produced suitable crystals for X-ray structure determination.

Yield = 87.81%; m.p = 134-139 ^{o}C; IR (KBr, cm^{-1}): 3090, 3050, 2954, 2930, 2850, 1544, 1495, 1480, 1410, 1400, 1220, 1111, 1033, 864, 762, 760, 654, 549, 474;UV-Vis (MeOH, λ (nm) (ϵ/Lmol^{-1}cm^{-1})): 230 (33601), 270 (27432), 329 (1183.9), 502 (12.8), 521 (12.5); μ_{eff} = 4.33 BM.

2.3.5 Synthesis of cobalt valporate 1,10-phenanthroline complex [Co(valp)$_2$(H$_2$O)(1,10-phen)] (5):

1,10-phen (0.44 g, 2.2 mmol) was dissolved in 10 ml MeOH, then the solution was added to a stirred MeOH solution of complex **1** (0.78 g, 2.2 mmol), then the solution was stirred for 5.5 h, the solvent was evaporated and a brown precipitate was obtained. The complex was characterized by using IR-spectroscopy, UV-spectroscopy, magnetic moment and single crystal X-ray diffraction. Recrystallization from methanol produced suitable crystals for X-ray structure determination.

Yield = 82.57%; m.p = 125-126 ^{o}C; IR (KBr, cm^{-1}): 3100, 2958, 2930, 2869, 1587, 1514, 1445, 1422, 1420, 1400, 1219, 1160, 1141, 848, 758, 727, 645, 552, 490; UV-Vis (MeOH, λ (nm) (ϵ/Lmol^{-1}cm^{-1})): 270 (61829), 228 (36510), 525 (33.9); μ_{eff} = 4.50 BM.

2.4 X-ray single crystal diffraction:

Single crystal X-ray analysis of complexes **2**, **3**, **4** and **5** were carried out by attaching single crystal to a glass fibber with epoxy glue, and then it transferred to X-ray diffractometer system (Bruker SMART APEX CCD) which is controlled by using Pentium-based PC running the SMART software package. The three-circle goniometer of a single crystal which was mounted with χ fixed at +54.76°, was rapidly cooled to -150 ^{o}C.[77–79] The diffracted graphite-monochromated (Kα radiation λ = 0.71073 Å) was detected on a phosphor screen at -44 ^{o}C and it held at 6.0 cm from the crystal. A detector array of 512 X 512 pixels (a pixel size ~120 µm) was used to collect data. The calibration of detector centroid and crystal to detector distance were applied by using a least-squares analysis of the unit cell parameters, YLID was used as a reference crystal.[77]

After the crystal of the compound was put in the cantered of the X-ray beam, a series of 30 data frames which measured at 0.3° increments of ω, were collected with three different values (2θ and φ) to calculate a preliminary unit cell and to assess the overall crystal quality of the compound. The intensity data was measured by put the detector at -28 ^{o}C but the intensity images were collected at 0.3° intervals of ω through 20 sec.[77]

After that, the raw data frames were transferred to another computer to integrate by using SAINT program package ((SAINT-NT V5.0, BRUKER AXS GMBH, D-76181 Karlsruhe). To update the background frame information was used this 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 through the current frame. The structure was refined and solved by using SHELXTL software package (SHELXTL-NT V6.1, BRUKER AXS GMBH, Karlsruhe).[77] Crystal data and structure refinements are summarized in Tables 4 and 5.

Table 4 : Crystallographic data and structure refinements for complexes **2** and **3**.

	Complex **2**	Complex **3**
Empirical formula	$C_{26} H_{42} Co N_4 O_4$	$C_{50} H_{74} Co_2 N_2 O_8$
Formula weight	533.57	948.97
Temperature	293(1) K	295(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pbca
Unit cell dimensions	a = 9.810(2) Å α = 74.032(3)° b = 14.660(2) Å β = 89.287(3)° c = 21.820(4) Å γ = 84.123(3)°	a = 20.541(3) Å α = 90° b = 11.247(1) Å β = 90° c = 22.443(3) Å γ = 90°
Volume	3000.5(8) Å^3	5184.7(1) Å^3
Z	4	4
Density (calculated)	1.181 Mg/m^3	1.216 Mg/m^3
Absorption coefficient	0.606 mm^{-1}	0.690 mm^{-1}
F(000)	1140	2024
Crystal size	0.50 x 0.08 x 0.08 mm^3	0.55 x 0.21 x 0.11 mm^3
Theta range for data collection	2.29 to 26.00°.	2.26 to 26.00°.
Index ranges	-12<=h<=12, -18<=k<=17, -26<=l<=26	-25<=h<=25, -13<=k<=13, -27<=l<=27
Reflections collected	25036	48124
Independent reflections	11567 [R(int) = 0.0835]	5070 [R(int) = 0.0882]
Completeness to theta = 26.00°	98.3 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9531 and 0.7516	0.9280 and 0.7029
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11567 / 4 / 568	5070 / 4 / 214
Goodness-of-fit on F^2	1.132	1.397
Final R indices[a] [I>2sigma(I)]	R1 = 0.1519, wR2 = 0.3215	R1 = 0.2198, wR2 = 0.4492
R indices (all data)	R1 = 0.2611, wR2 = 0.3809	R1 = 0.2352, wR2 = 0.4579
Largest diff. peak and hole	0.718 and -0.636 e.Å^{-3}	1.097 and -0.684 e.Å^{-3}

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ and $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

Table 5 : Crystallographic data and structure refinements for complexes **4** and **5**.

	Complex **4**	Complex **5**
Empirical formula	$C_{30} H_{42} Co N_2 O_4$	$C_{28} H_{40} Co N_2 O_5$
Formula weight	553.59	543.55
Temperature	295(1) K	295(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/c
Unit cell dimensions	a = 14.138(2) Å α = 90°. b = 22.216(3) Å β = 94.974(2)° c = 9.865(1) Å γ = 90°	a = 19.561(4) Å α = 90° b = 18.810(4) Å β = 106.223(4)° c = 16.177(4) Å γ = 90°
Volume	3086.7(7) $Å^3$	5715(2) $Å^3$
Z	4	8
Density (calculated)	1.191 Mg/m^3	1.263 Mg/m^3
Absorption coefficient	0.590 mm^{-1}	0.638 mm^{-1}
F(000)	1180	2312
Crystal size	0.51 x 0.15 x 0.14 mm^3	0.26 x 0.18 x 0.13 mm^3
Theta range for data collection	2.59 to 27.00°.	2.17 to 27.00°.
Index ranges	-18<=h<=18, -28<=k<=28, -12<=l<=12	-24<=h<=24, -24<=k<=24, -20<=l<=20
Reflections collected	32838	30976
Independent reflections	6698 [R(int) = 0.0805]	6224 [R(int) = 0.0689]
Completeness to theta = 26.00°	99.5 %	99.7 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9220 and 0.7530	0.9216 and 0.8516
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints /parameters	6698 / 10 / 276	6224 / 0 / 329
Goodness-of-fit on F^2	1.334	1.438
Final R indices [I>2sigma(I)]	R1 = 0.1972, wR2 = 0.3880	R1 = 0.1605, wR2 = 0.2873
R indices[a] (all data)	R1 = 0.2363, wR2 = 0.4106	R1 = 0.1695, wR2 = 0.2913
Largest diff. peak and hole	0.817 and -0.784 $e.Å^{-3}$	0.685 and -1.329 $e.Å^{-3}$

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o$ and $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

2.5 Anti-bacterial activity:

The anti-bacterial activities for cobalt complexes were investigated against five gram-positive (*Staphylococcus aureus, Micrococcus luteus, Bacillus subtilis, Enterococcus faecalis* and *Staphylococcus epidermidis*) and four gram-negative bacteria (*Escherichia coli, Klebsiella pneumonia, Proteus mirabilis* and *Pseudomonas aeruginosa*).

In-vitro, anti-bacterial test was carried out by using Agar diffusion method. The sterile saline was prepared by dissolving 0.5 g of NaCl in 500 ml of water (0.9% of NaCl) then this solution was autoclaved. The single bacterial colonies was dissolved in the sterile saline until the turbidity of the suspended cells reached to the McFarland 0.5 Standard then the bacterial inoculate were spread on the surface of the Muller Hinton nutrient agar by using a sterile cotton swab. After that, the wells (6 mm in diameter) in the agar plate were made by using Sterile glassy borer.[29,80]

Cobalt complexes were dissolved in DMSO in concentration 6 mg/ml after that 25 µL of the test samples were added into the respective wells in plates then these plates were incubated at 37 °C for 12-24 h. Gentamycin (G) and Erythromycin (E) were used as positive control while DMSO was used as negative control. The activities of the complexes were determined by measuring IZD (inhibition zone diameter) in mm (millimetre). The results from this part were determined by calculating the average of three trials and that are stated as average ± standard error.[67,69,81]

2.6 Kinetic measurements of BNPP hydrolysis:

The kinetic experiments were performed at different temperatures (25 ^{o}C, 37 ^{o}C and 40 ^{o}C), different pH values (7.04, 7.48 and 7.91) and different catalytic concentrations from 1×10^{-3} to 1×10^{-6} M.

HEPES buffer, (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) was used to maintain a constant pH value. The buffer solutions were prepared by dissolving 50 μM of HEPES buffer in minimum amount of deionized water then the pH of the solution was adjusted with HCl or NaOH after that BNPP was dissolved in buffer solution and the volume of the solution was adjusted to 100 ml in the volumetric flask.[82,83]

Different concentrations of the cobalt complexes were prepared in MeOH solution in order to use them as catalysis in the BNPP hydrolysis process. The rate of p-nitrophenol formation was measured using UV-Vis spectrophotometer at $\lambda = 400$ nm ($\varepsilon = 13400$ Lmol^{-1}cm^{-1}).[83–85]

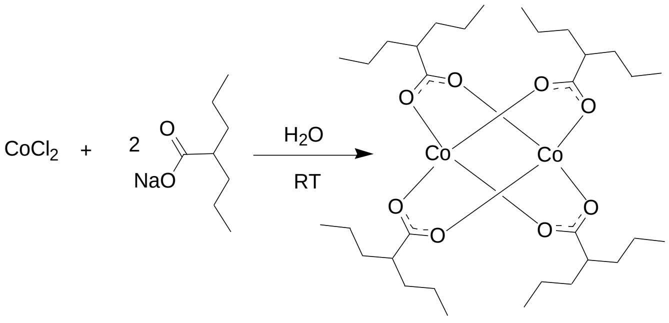
The kinetic experiments were carried in triplicates by adding 1.5 ml of the cobalt complex into 1.5 ml of BNPP solution in a quartz cell at constant temp, then the solution was immediately mixed and the kinetic measurement was performed.[83,84] The initial rate (V_o) was calculated from the slope of the linear plot of p-nitrophenol concentration against time; $[(\text{rate})_0 = (dc/dt)_0 = (dA/dt)_0/\varepsilon]$.[73]

3. Results and discussion:

3.1 Synthesis of cobalt complexes:

Cobalt valporate complex [Co_2(valp)$_4$] (**1**) was prepared at RT by adding 2 equivalent of sodium valporate to 1 equivalent of $CoCl_2$ as shown in Scheme 1. The purple solid product was formed in 86.50% yield.

Scheme 1: Synthesis of [Co_2(valp)$_4$] (**1**).



1

Cobalt valporate complexes **2-5** with different molar ratios of the N-donor ligands were synthesized as shown in Scheme 2. The physical properties of complexes **1-5** are listed in Table 6.

Scheme 2: Synthesis of complexes **2**, **3**, **4** and **5**.

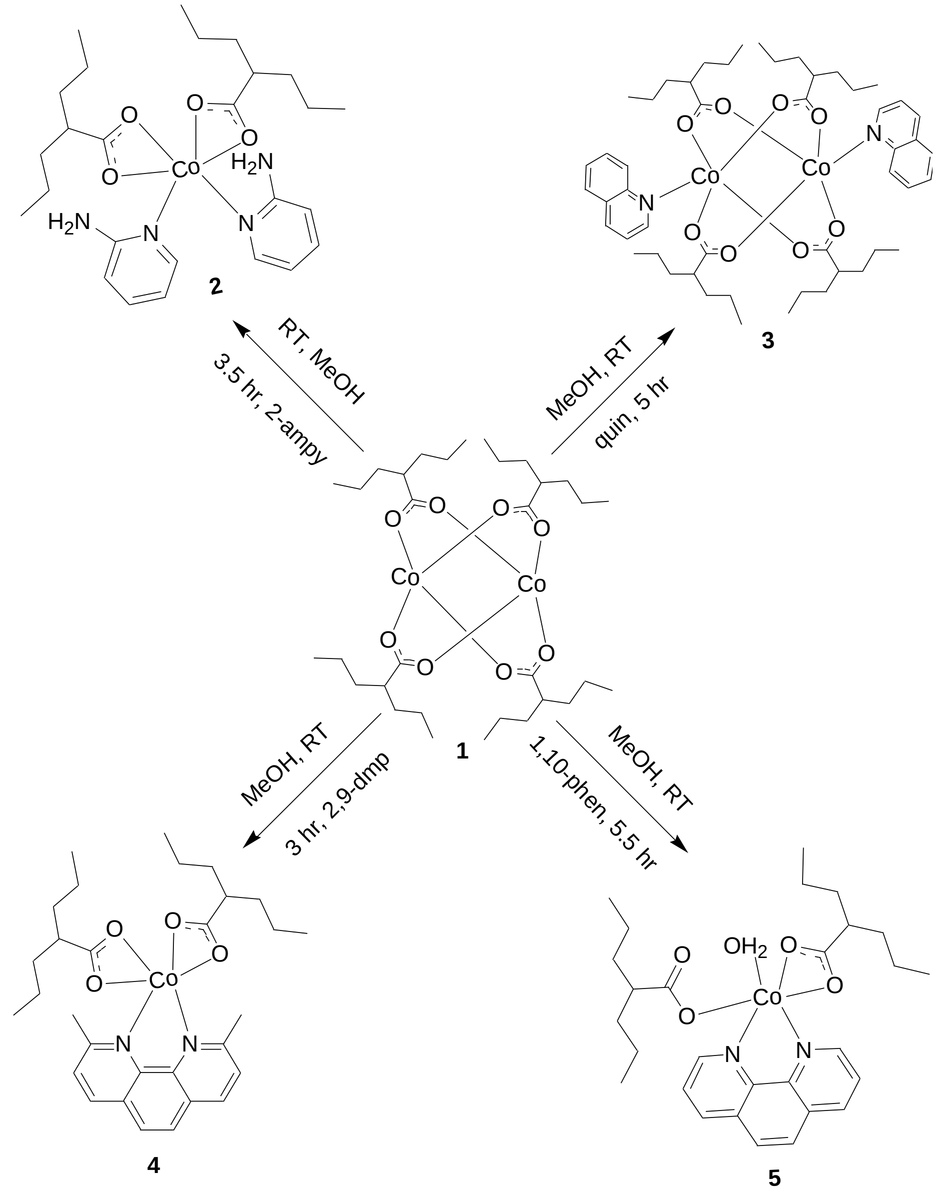


Table 6 : Physical properties and %yields of complexes **1**-**5**.

Complex	**m.p (^{o}C)**	**% Yield**	**Solubility**
$Co_2(valp)_4$ (**1**)	58	86.50	CH_3OH, ether, petroleum ether
$Co(valp)_2(2\text{-}ampy)_2$ (**2**)	121-125	79.85	CH_3OH, ether, CH_2Cl_2, CH_3CN, $(CH_3)_2CO$, C_2H_5OH, $CHCl_3$
$Co_2(valp)_4(quin)_2$ (**3**)	110-111	26.23	CH_3OH, ether, CH_2Cl_2, CH_3CN, $(CH_3)_2CO$, C_2H_5OH, $CHCl_3$
$Co(valp)_2(2,9\text{-}dmp)$ (**4**)	134-139	87.81	CH_3OH, C_2H_5OH, $(CH_3)_2CO$, CH_3CN, CH_2Cl_2, $CHCl_3$
$Co(valp)_2(H_2O)(1,10\text{-}phen)$ (**5**)	125-126	82.57	CH_3OH, CH_2Cl_2, $CHCl_3$, C_2H_5OH, $(CH_3)_2CO$

3.2 IR spectroscopy:

The prepared cobalt complexes were characterized by measuring their IR spectra in the range of 200-4000 cm^{-1} as KBr disk. The bands assignment and their corresponding wave numbers for Na_{valp}[67,86–88] and complex **1** are summarized in Table 7. The IR spectra for complex **1** shows two carboxylate stretching bands asymmetric, $\nu_{as}(COO^-)$ at 1556 cm^{-1} and symmetric, $\nu_s(COO^-)$ at 1419 cm^{-1}. The difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is $\Delta\nu(COO^-)$ and its value (137 cm^{-1}) for complex **1** is the same as in Na_{valp} which may indicate bridging bidentate coordination mode between cobalt and the valporate carboxylic group.[54,56]

Table 7 : Assignment of IR bands and wave numbers for Na_{valp} and complex **1**.

Assignments	Na_{valp} (cm^{-1})	Complex **1** (cm^{-1})
$\nu(C\text{-}H)_{aliph}$	2960, 2930, 2870	2959, 2872
$\nu_{as}(COO^-)$	1548	1556
$\nu_s(COO^-)$	1411	1419
$\delta(C\text{-}H)$	1465, 1420, 1380	1450
$\rho(CH3)$	1350, 780	1330, 753
$\Delta\nu(COO^-)$	137	137
$\nu(Co\text{-}O)$	-	469

The IR spectral data for complexes **2-5** are listed in Table 8. For complexes **2** and **4** the $\nu_{as}(COO^-)$ at 1565 cm^{-1} and 1544 cm^{-1} and $\nu_s(COO^-)$ at 1448 cm^{-1} and 1410 cm^{-1}, respectively have been observed. The $\Delta\nu$ values for complexes **2** and **4** (117, 134 cm^{-1}, respectively) are less than $\Delta\nu$ of Na_{valp} (137 cm^{-1}) which indicate bidentate chelating coordination mode.

However, in complex **3** the $\nu_{as}(COO^-)$ was observed at 1560 cm^{-1} and $\nu_s(COO^-)$ at 1450 cm^{-1}, $\Delta\nu$ (COO^-) = 110 cm^{-1} which is smaller than $\Delta\nu$ of Na_{valp} supporting a bidentate bridging coordination mode. Two primary amine NH absorption frequencies at $\nu_{as}(NH_2)$ = 3413 cm^{-1} and $\nu_{as}(NH_2)$ = 3331 cm^{-1} were also observed and suggest that the coordination mode with metal to be through the pyridine nitrogen atom as supported by its X-ray structure analysis.

Complex **5** showed two $\nu_{as}(COO^-)$ bands at 1587 cm^{-1} and 1514 cm^{-1} and two $\nu_s(COO^-)$ bands at 1445 cm^{-1} and 1422 cm^{-1}, respectively. The $\Delta\nu$ values of complex **5** are 142 cm^{-1} and 92 cm^{-1}. 92 cm^{-1} is smaller than $\Delta\nu$ of Na_{valp}, at the same time 142 cm^{-1} is larger than $\Delta\nu$ of the free salt, and these results indicate that this complex contains monodentate and bidentate chelating coordination modes.

In general, the ν(M-O) and ν(M-N) for metal complexes appear as weak bands at (430-474) cm^{-1} and (524-576) cm^{-1}, respectively.[89] These bands for complexes **1-5** were shown in Table 7 and Table 8.

Table 8 : Assignment of IR bands and wave numbers for complexes **2-5**.

Assignments	Complex **2** (cm^{-1})	Complex **3** (cm^{-1})	Complex **4** (cm^{-1})	Complex **5** (cm^{-1})
$\nu(C\text{-}H)_{ar}$	3080, 3070	3100, 3050	3090, 3050	3100
$\nu(C\text{-}H)_{aliph}$	2959, 2930, 2870	2956, 2930, 2870	2954, 2930, 2850	2958, 2930, 2869
$\nu_{as}(N\text{-}H)$ $\nu_{s}(N\text{-}H)$	3413 3331	-	-	-
$\delta(NH_2)$	1651	-	-	-
NH wagging	657	-	-	-
$\nu_{as}(COO^-)$	1565	1560	1544	1587, 1514
$\nu_{s}(COO^-)$	1448	1450	1410	1445, 1422
$\Delta\nu(COO^-)$	117	110	134	142, 92
$\nu(C\text{-}NH_2)$	1329	-	-	-
$\nu(C\text{-}C)_{ring}$	1651	1613	-	-
$\nu(C\text{-}C)_{ring} + \delta(C\text{-}H)$	1495	1510, 1417	1495, 1480, 1400	1400, 1420
$\delta(C\text{-}H)_{ring}$ (In plane)	1270, 1226, 1156, 1113, 1066, 1003	1241, 1145, 1110, 1050	1220, 1111, 1033	1219, 1160, 1141
$\delta(C\text{-}H)_{ring}$ (Out of plane)	-	-	654	645
$\gamma(C\text{-}H)$	864, 769	803, 782	864, 762	848, 727
$\delta(COO^-)$	740	735	760	758
$\nu(Co\text{-}O)$	451	467	474	490
$\nu(Co\text{-}N)$	518	520	549	552

3.3 Magnetic moments and UV-Vis spectral data for cobalt complexes:

In general, the electronic transition of transition metal complexes can be classified into three types, d-d transition, intra-ligand transition bands and metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT).[90]

The electronic spectra of cobalt complexes were recorded in MeOH solution. The electronic transition data for complexes **1-5** and their parent ligands are summarized in Table 9.

Table 9 : The electronic data for complexes **1-5** and their parent ligands.

Complex	**λ_{max} (nm)**	**€ (Lmol^{-1}cm^{-1})**	**Pure ligands**	**λ_{max} (nm)**	**€ (Lmol^{-1}cm^{-1})**
$Co_2(valp)_4$ (**1**)	270 492	7576.5 43.55	-	-	-
$Co(valp)_2(2\text{-}ampy)_2$ (**2**)	235 295 520	20072 8022.1 20.2	2-ampy	234 291	11479 5569.5
$Co_2(valp)_4(quin)_2$ (**3**)	213 276 366 520	49030 9119 3.6 2.6	Quin	204 225 276	44107 41442 3605.9
$Co(valp)_2(2,9\text{-}dmp)$ (**4**)	230 270 329 502 521	33601 27432 1183.9 12.8 12.5	2,9-dmp	231 272	58280 184090
$Co(valp)_2(H_2O)(1,10\text{-}phen)$ (**5**)	270 228 525	61829 36510 33.9	1,10-phen	266 225	45919 45488

The magnetic moment of the prepared Co-complexes have been determined by the number of unpaired electrons which are calculated by using the spin only formula. Table 10 shows the magnetic properties for complexes **2**, **4** and **5**. On the other hand, the magnetic moments for complexes **1** and **3** couldn't be measured due to unsuccessful packing process.

Table 10**:** Magnetic properties for complexes **2**, **4** and **5**.

Complex	**Magnetic moments (μ_{eff}) (BM)**	**# of unpaired electrons (n)**
$Co(valp)_2$ $(2\text{-}ampy)_2$ (**2**)	4.83	4
$Co(valp)_2$ $(2,9\text{-}dmp)$ (**4**)	4.33	3
$Co(valp)_2(H_2O)(1,10\text{-}phen)$ (**5**)	4.50	4

The electronic spectra of complex **1** exhibits two bands. The band at 270 nm (7576.5 $Lmol^{-1}cm^{-1}$) is assigned to the charge transfer band with extinction coefficients larger than 1000 $Lmol^{-1}cm^{-1}$ whereas the band at 492 nm (43.55 $Lmol^{-1}cm^{-1}$) was assigned to the cobalt d-d transition.[90]

The bands between 213-295 nm for complexes **2**, **3**, **4** and **5** are assigned to the intra-ligand transition bands in addition to charge transfer bands. The results also showed similarities between the cobalt complexes and their parent ligands and complex **1** with very small shifts caused by Co coordination. Complex **4** showed an additional band at 329 nm which may be assigned as charge transfer band.

The magnetic moments for complexes **2** and **5** are 4.50 and 4.83 BM, respectively. These values indicate the presence of four unpaired electrons supporting a high spin d^6 octahedral geometry. The electronic spectra of these complexes exhibit one d-d transition band for each complex; 520 nm for complex **2** and 525 nm for complex **5**. Moreover, high spin Co(III) octahedral complexes **2** and **5** were obtained because 2-ampy, water and 1,10-phen ligands in the present case behaved as weak field ligands.[21]

The magnetic moment of complex **4** is 4.33 BM. This value is consistent with the presence of three unpaired electrons which indicates a high spin d^7 octahedral geometry. The electronic spectra for complex **3** and **4** exhibit two d-d transition bands at 366 nm (3.6 $Lmol^{-1}cm^{-1}$) and 520 nm (2.6 $Lmol^{-1}cm^{-1}$) for complex **3** and at 502 nm (12.8 $Lmol^{-1}cm^{-1}$) and 521 nm (12.5 $Lmol^{-1}cm^{-1}$) for complex **4** as a result of $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ electronic transition bands. The third band ($^4T_{1g} \rightarrow {}^4A_{2g}(F)$) is embedded in the charge transfer bands and intra-ligand transition bands. The UV-Vis spectral data for complexes **3** and **4** are similar to those observed for [Co(2-ampy)$_2$(dca)$_2$].[26,91]

3.4 X-ray spectroscopy:

The crystal structure of complexes **2**, **3**, **4** and **5** had been determined by using single crystal X-ray diffraction. Recrystallization of the complexes by slow evaporation of methanol solution gave suitable single crystals used for their structure determination. The crystal data and parameters of these complexes are shown in Table 4 and 5 detailed crystallographic data are presented in Appendices.

3.4.1 Crystal structure of complex 2 [Co(valp)$_2$(2-ampy)$_2$]:

The crystal structure of complex **2** was shown in Figure 18. The mononuclear [Co(valp)$_2$(2-ampy)$_2$] complex crystallizes in triclinic crystal system and P-1 space group. For the four molecules per unit cell, the asymmetric unit (one molecule) consists of one Co(III) cation, two bidentate chelating valp groups and two monodentate 2-ampy ligands forming distorted octahedral geometry; (O(2)-Co(1)-O(1) = 59.5(2)°, O(1)-Co(1)-O(3) = 95.6(3)°, O(4)-Co(1)-O(3) = 103.5(3)°, O(4)-Co(1)-N(3) = 103.5(3)°, N(1)-Co(1)-N(3) = 96.5(3)°, O(2)-Co(1)-N(1) =

106.3(3)^{o}). Selected bond distances (Å) and bond angles (^{o}) for complex **2** are reported in Table 11.

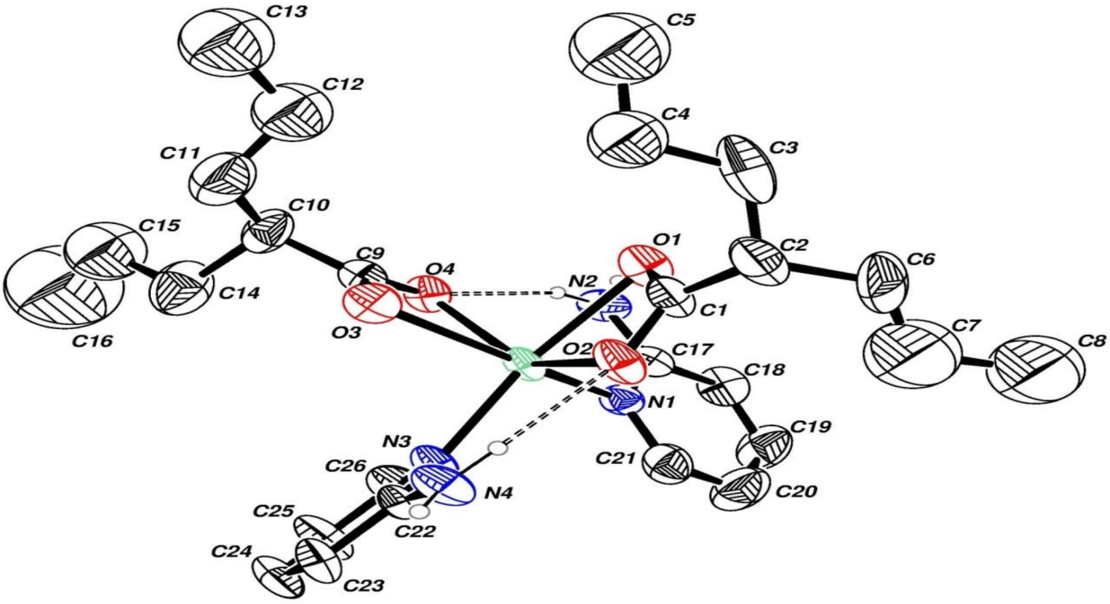


Figure 18: X-ray structure of Co(valp)$_2$(2-ampy)$_2$ (**2**).

Table 11**:** Selected bond distances (Å) and bond angles (^{o}) for complex **2**.

Bond	**Distance (Å)**	**Bonds**	**Angle (^{o})**
Co(1)-N(1)	2.072(9)	O(2)-Co(1)-O(1)	59.5(2)
Co(1)-N(3)	2.081(8)	O(1)-Co(1)-O(3)	95.6(3)
Co(1)-O(1)	2.292(7)	O(2)-Co(1)-N(1)	106.3(3)
Co(1)-O(2)	2.053(7)	N(1)-Co(1)-N(3)	96.5(3)
Co(1)-O(3)	2.367(8)	O(4)-Co(1)-N(3)	103.5(3)
Co(1)-O(4)	2.042(7)	O(4)-Co(1)-O(3)	58.3(2)
C(9)-O(3)	1.233(11)	C(17)-N(1)-Co(1)	126.9(7)
C(9)-O(4)	1.264(10)	C(26)-N(3)-Co(1)	115.7(7)
C(22)-N(3)	1.353(11)	C(9)-O(4)-Co(1)	97.8(6)
C(26)-N(3)	1.341(14)	C(9)-O(3)-Co(1)	83.5(6)
C(17)-N(1)	1.362(11)	C(1)-O(1)-Co(1)	85.8(7)

The bond distances of Co-N and Co-O are ligand dependent, the average bond distances of Co-N (2.077 Ǻ) and Co-O (2.189 Ǻ) in complex **2** are longer than those found in [*cis*-Co(en)$_2$(C$_8$H$_7$O$_2$)$_2$](C$_8$H$_7$O$_2$.2H$_2$O) (1.945 Å) and (1.910 Å) respectively, where C$_8$H$_7$O$_2$ is *p*-methyl benzoate and en is ethylene diamine.[92]

The N(1)-Co(1)-N(3) (96.5^o) and O(1)-Co(1)-O(3) (95.6^o) bond angles in complex **2** are shorter than the same angles found in [Zn(valp)$_2$(2-ampy)$_2$] complex (102.84^o, 124.92^o, respectively).[67]

Intramolecular hydrogen bonding within a molecule and intermolecular hydrogen bonding between molecules play a key role in the complex geometry and in stabilizing the complex in the solid state.[27,81, 93]

The hydrogen bonding in complex **2** are summarized in Table 12. The data show four intermolecular hydrogen bonding; (N(2)-H(2N2)...O(7)#2 = 2.22 Å, N(4)-H(2N4)...O(6) = 2.18 Å, N(6)-H(2N6)...O(3) = 2.19 Å and N(8)-H(2N8)...O(1)#1 = 2.12 Å) and two intramolecular hydrogen bonds (N(2)-H(1N2)...O(4) = 2.12 Å and N(4)-H(1N4)...O(2) = 2.10 Å).

Table 12**:** Hydrogen bonds in complex **2**.

D-H...A **(Å)**	d(D-H) **(Å)**	d(H...A) **(Å)**	d(D...A) **(Å)**	<(DHA) **(°)**
N(8)-H(2N8)...O(1)#1	0.86	2.12	2.921(9)	154.6
N(8)-H(1N8)...O(5)	0.86	2.10	2.925(10)	159.7
N(6)-H(2N6)...O(3)	0.86	2.19	2.984(10)	152.8
N(6)-H(1N6)...O(8)	0.86	2.15	2.980(11)	160.7
N(4)-H(2N4)...O(6)	0.86	2.18	3.009(10)	160.8
N(4)-H(1N4)...O(2)	0.86	2.10	2.931(11)	161.8
N(2)-H(1N2)...O(4)	0.86	2.12	2.947(11)	162.5
N(2)-H(2N2)...O(7)#2	0.86	2.22	3.019(10)	155.0

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z #2 x,y-1,z

3.4.2 Crystal structure of complex 3 [$Co_2(valp)_4(quin)_2$]:

The crystal structure of complex **3** was shown in Figure 19. The dinuclear [$Co_2(valp)_4(quin)_2$] complex crystallizes in orthorhombic crystal system and Pbca space group. For the four molecules per unit cell, the asymmetric unit (one molecule) consists of two Co cations, four valp and two quin molecules. Selected bond distances and bond angles for complex **3** are listed in Table 13.

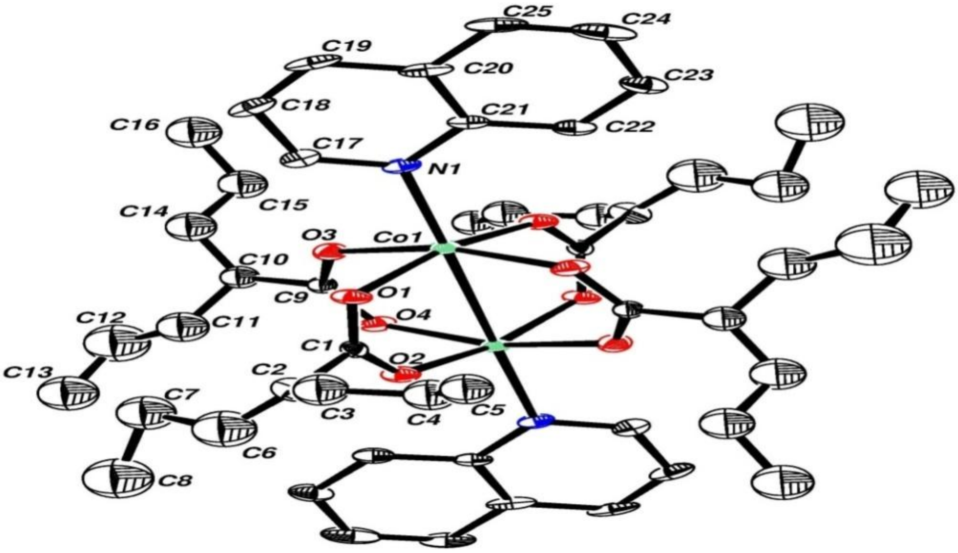


Figure 19: X-ray structure of $Co_2(valp)_4(quin)_2$ (**3**).

Table 13**:** Selected bond distances (Å) and bond angles (^{o}) for complex **3**.

Bond	**Distance (Å)**	**Bonds**	**Angle (^{o})**
Co(1)-Co(1)#1	2.791(3)	O(1)-Co(1)-O(3)	86.7(4)
Co(1)-N(1)	2.106(9)	O(3)-Co(1)-N(1)	94.5(4)
Co(1)-O(3)	2.055(9)	O(2)#1-Co(1)-N(1)	97.9(4)
Co(1)-O(2)#1	2.037(9)	O(4)#1-Co(1)-N(1)	102.2(4)
Co(1)-O(1)	2.046(9)	O(3)-Co(1)-Co(1)#1	79.2(2)
O(2)-Co(1)#1	2.037(9)	O(1)-Co(1)-Co(1)#1	87.4(2)
O(4)-Co(1)#1	2.034(8)	C(17)-N(1)-Co(1)	114.1(9)
C(17)-N(1)	1.300(17)	C(1)-O(1)-Co(1)	117.4(8)
C(21)-N(1)	1.371(16)	C(9)-O(3)-Co(1)	127.8(8)
C(9)-O(3)	1.242(14)	N(1)-Co(1)-Co(1)#1	171.4(3)
C(9)-O(4)	1.245(13)	C(9)-O(4)-Co(1)#1	122.0(8)
C(1)-O(1)	1.225(13)	C(1)-O(2)-Co(1)#1	131.4(8)
C(1)-O(2)	1.249(13)	C(22)-C(21)-N(1)	120.7(11)

The distorted octahedral geometry around each Co center consists of four oxygen atoms from four valporate bidentate chelating ligands, one nitrogen atom from quinoline monodentate ligand; O(1)-Co(1)-O(3) = 86.7(4)^o, O(3)-Co(1)-N(1) = 94.5(4)^o, O(2)#1-Co(1)-N(1) = 97.9(4)^o, O(4)#1-Co(1)-N(1) = 102.2(4)^o, O(3)-Co(1)-Co(1)#1 = 79.2(2)^o and O(1)-Co(1)-Co(1)#1 = 87.4(2)^o.

The (Co-Co) bounding distance is 2.791(3) Å which is shorter than Zn-Zn bond in [$Zn_2(valp)_4(quin)_2$] (2.948(3) Å).[67] The average bond distances of Co-O (2.043

Å) and Co-N (2.106 Å) are similar to previously reported values (2.07 Å and 2.090 Å, receptivity).[94]

3.4.3 Crystal structure of complex 4 [Co(valp)$_2$(2,9-dmp)]:

The crystal structure of complex **4** was shown in Figure 20. The mononuclear [Co(valp)$_2$(2,9-dmp)] complex crystallizes in monoclinic crystal system and P2(1)/c space group. For the four molecules per unit cell, the asymmetric unit (one molecule) consists of one Co(II), two bidentate chelating valp groups and one bidentate 2,9-dmp molecule forming distorted octahedral geometry; N(2)-Co(1)-N(1) = 78.5(3)^o, O(3)-Co(1)-N(1) = 110.7(3)^o, O(3)-Co(1)-O(4) = 58.5(4)^o, O(2)-Co(1)-O(4) = 94.4(5)^o, O(2)-Co(1)-O(1) = 59.6(3)^o and N(2)-Co(1)-O(1) = 101.1(3)^o. Selected bond distances and bond angles for complex **4** are listed in Table 14.

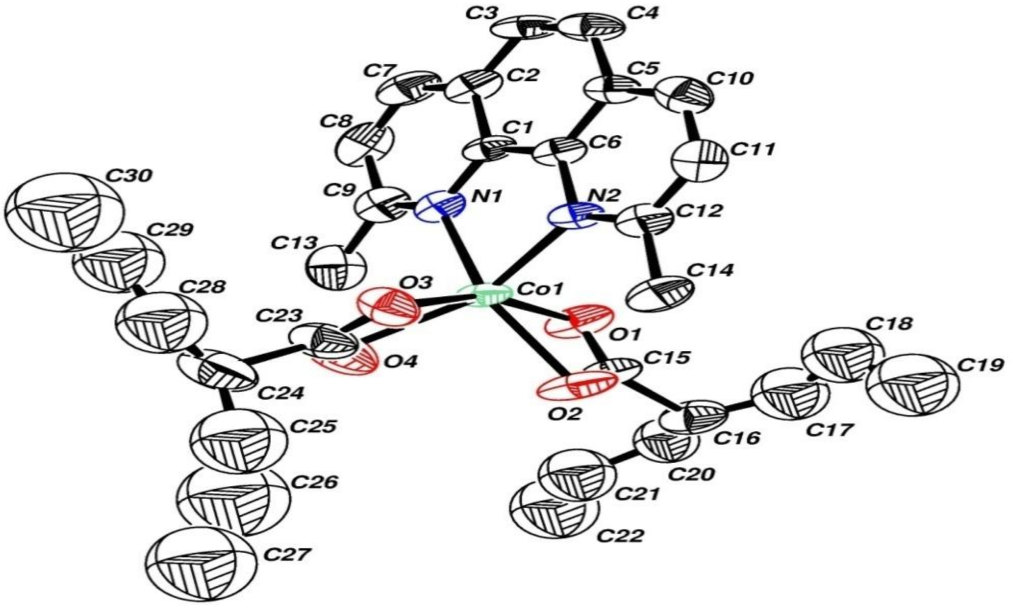


Figure 20: X-ray structure of Co(valp)$_2$(2,9-dmp) (**4**).

Table 14**:** Selected bond distances (Å) and bond angles (^{o}) for complex **4**.

Bond	**Distance (Å)**	**Bonds**	**Angle (^{o})**
Co(1)-N(1)	2.137(8)	N(2)-Co(1)-N(1)	78.5(3)
Co(1)-N(2)	2.119(8)	O(3)-Co(1)-N(1)	110.7(3)
Co(1)-O(1)	2.126(7)	O(3)-Co(1)-O(4)	58.5(4)
Co(1)-O(2)	2.125(7)	O(2)-Co(1)-O(4)	94.4(5)
Co(1)-O(3)	2.124(8)	O(2)-Co(1)-O(1)	59.6(3)
Co(1)-O(4)	2.161(11)	N(2)-Co(1)-O(1)	101.1(3)
C(1)-N(1)	1.366(12)	C(1)-N(1)-Co(1)	111.8(6)
C(9)-N(1)	1.295(15)	C(6)-N(2)-Co(1)	113.1(6)
C(6)-N(2)	1.366(10)	C(15)-O(1)-Co(1)	90.5(6)
C(12)-N(2)	1.304(13)	C(15)-O(2)-Co(1)	91.2(6)
C(15)-O(1)	1.240(12)	C(23)-O(3)-Co(1)	92.6(8)
C(15)-O(2)	1.217(12)	C(23)-O(4)-Co(1)	90.2(10)
C(23)-O(3)	1.207(16)	O(3)-C(23)-O(4)	118.7(13)
C(23)-O(4)	1.229(15)	O(2)-C(15)-O(1)	118.6(10)

The average bond distances of Co-O (2.134 Å) and Co-N (2.128 Å) are similar to the reported values in cobalt-2,9-dimethyl-1,10-phenanthroline complexes (2.135 Å and 2.136 Å, receptivity).[95] In addition, the bond distances of Co-O in complex **4** are in agreement with related Co-O bonds in cobalt carboxylate complexes which are in the 2.0406 (12) to 2.2460 (12) Å range.[96]

3.4.4 Crystal structure of complex 5 [Co(valp)$_2$(H$_2$O)(1,10-phen)]:

The crystal structure of complex **5** was shown in Figure 21. The mononuclear [Co(valp)$_2$(H$_2$O)(1,10-phen)] complex was crystallized in monoclinic crystal system and C2/c space group. For the eight molecules per unit cell, the asymmetric unit (one molecule) consists of one Co(III), one monodentate valp, one bidentate valp, one 1,10-phen and one water molecule revealing distorted octahedral arrangement; O(3)-Co(1)-N(2) = 89.6(2)^o, O(1)-Co(1)-O(2) = 59.9(2)^o, O(3)-Co(1)-O(2) = 92.2(3)^o, O(1)-Co(1)-N(1) = 86.8(2)^o, O(1W)-Co(1)-N(1) = 88.7(2)^o and O(1W)-Co(1)-N(2) = 109.0(2)^o. The two asymmetric units are bounded to each other by two water molecules through hydrogen bonding which further stabilized the structure. Selected bond distances and bond angles for complex **5** are listed in Table 15.

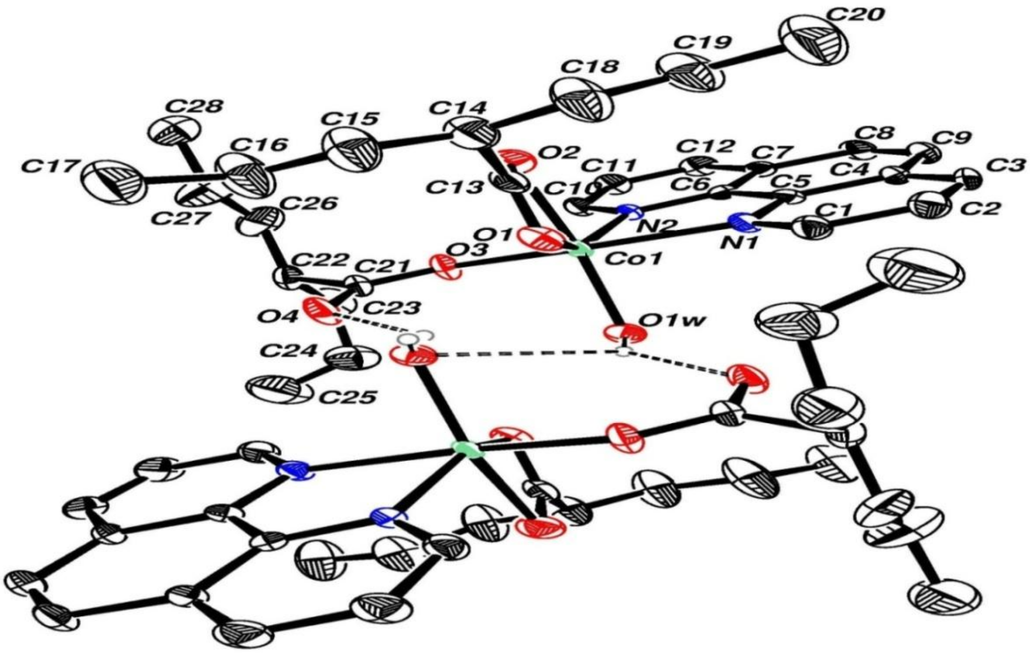


Figure 21: X-ray structure of Co(valp)$_2$(H$_2$O) (1,10-phen) (**5**).

Table 15: Selected bond distances (Å) and bond angles (°) for complex **5**.

Bond	**Distance (Å)**	**Bonds**	**Angle (°)**
Co(1)-O(1)	2.158(6)	O(3)-Co(1)-N(2)	89.6(2)
Co(1)-O(2)	2.214(7)	O(1)-Co(1)-O(2)	59.9(2)
Co(1)-O(3)	2.017(5)	O(3)-Co(1)-O(2)	92.2(3)
Co(1)-N(1)	2.177(6)	O(1)-Co(1)-N(1)	86.8(2)
Co(1)-N(2)	2.141(6)	O(1W)-Co(1)-N(1)	88.7(2)
Co(1)-O(1W)	2.067(5)	O(1W)-Co(1)-N(2)	109.0(2)
C(13)-O(1)	1.264(11)	C(21)-O(3)-Co(1)	137.7(6)
C(13)-O(2)	1.243(11)	C(5)-N(1)-Co(1)	113.4(5)
C(21)-O(3)	1.246(9)	C(6)-N(2)-Co(1)	115.3(5)
C(21)-O(4)	1.231(10)	C(13)-O(1)-Co(1)	90.5(5)
C(21)-C(22)	1.540(12)	C(13)-O(2)-Co(1)	88.5(5)
O(1W)-H(1W1)	0.8741	Co(1)-O(1W)-H(1W1)	111.3
O(1W)-H(2W1)	0.8234	H(1W1)-O(1W)-H(2W1)	128.5
C(1)-N(1)	1.319(10)	O(2)-C(13)-O(1)	121.1(8)
C(5)-N(1)	1.354(10)	O(4)-C(21)-O(3)	127.3(8)
C(6)-N(2)	1.351(9)	N(2)-C(6)-C(5)	116.9(7)
C(10)-N(2)	1.312(9)	N(1)-C(5)-C(6)	117.9(6)

The average bond distance of Co-N in complex **5** (2.159 Å) is longer than those found in [Co(1,10-phen)(4-OMe-3,6-DBSQ)$_2$ (1.956 Å) where 4-OMe-3,6-DBSQ is 4-methoxy-3,6- di-tert-butyl-benzoquinone-1,2.[97]

The values of C-O bond distance in carboxylate group depend on the bonding geometry for metal carboxylate group. In monodentate carboxylate group, the bond distances are 1.235 (2) Å and 1.305 (2) Å while in bidentate carboxylate groups it is 1.267 (2) Å.[96] The covalent and non-covalent bonds of C-O in monodentate valporate in complex **5** are 1.246(9) Å and 1.231(10) Å, respectively which are close to bond distances in monodentate carboxylate groups. On the other hand, the average values of C-O bidentate bonds in complex **5** is 1.254 Å which is close to bond distance found in bidentate carboxylate groups.[96]

The hydrogen bonds for complex **5** are summarized in Table 16 which shows only one intermolecular hydrogen bonding O(1W)-H(1W1)...O(4)#1 (1.94 Å). This bond affects the geometry and stability of the complex.[81] The structure of the desired complex was stabilized by a site of H-Bonds, as seen in Figure 21. One water molecule or more were cited in the crystal lattice several ---O…..H bonds also were detected with less than 3 Å length which reveled 3D-network H-bonds.

Table 16: Hydrogen bond for complex **5**.

D-H...A (Å)	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (^{o})
O(1W)-H(1W1)...O(4)#1	0.87	1.94	2.611(8)	132.0

3.5 Biological activity (*In-vitro*):

3.5.1 Anti-bacterial activity:

The *In-vitro* anti-bacterial activity for complexes **1-5** were tested against gram-positive and gram-negative bacteria by using agar diffusion method. The results are summarized in Table 17 and 18 for gram-negative and gram-positive bacteria, respectively.

Table 17: *In-vitro* anti-bacterial activity data for complexes **1-5** against gram-negative bacteria.

Compounds	*E. coli*	*K. pneumoniae*	*p. mirabilis*	*p. aeruginosa*
G	25.3 ± 0.9	34.7 ± 3.4	27.0 ± 1.0	20.0 ± 1.8
E	24.0 ± 1.6	21.5 ± 0.5	17.3 ± 0.9	21.7 ± 3.3
$CoCl_2$	-	-	-	-
Valp	-	-	-	-
DMSO	-	-	-	-
Complex **1**	-	-	-	-
Complex **2**	-	-	-	-
2-ampy	-	-	-	-
Complex **3**	-	-	-	-
Quin	-	-	-	-
Complex **4**	-	-	-	-
2,9-dmp	-	-	-	-
Complex **5**	-	-	-	-
1,10-phen	31.0 ± 0.6	32.0 ± 1.0	33.0 ± 0.6	-

Table 18: *In-vitro* anti-bacterial activity data for complexes **1**-**5** against gram positive bacteria.

Compounds	*S. aureus*	*M. Luteus*	*B. subtilis*	*E. faecalis*	*S. epidemidis*
G	29.3 ± 3.2	34.7 ± 3.4	29.3 ± 4.4	16.3 ± 0.9	34.7 ± 1.4
E	41.3 ± 1.4	40.0 ± 0.1	36.0 ± 2.1	-	45.0 ± 0.7
$CoCl_2$	12.0 ± 3.0	-	-	-	-
Valp	-	-	-	-	-
DMSO	-	-	-	-	-
Complex **1**	-	-	-	-	-
Complex **2**	17.5 ± 1.5	-	-	-	-
2-ampy	-	-	-	-	-
Complex **3**	-	-	-	-	-
Quin	-	-	-	-	-
Complex **4**	20.0 ± 0.6	19.5 ± 0.5	16.5 ± 2.5	15.5 ± 2.5	28.0 ± 2.0
2,9-dmp	23.3 ± 0.9	19.3 ± 0.4	16.3 ± 0.7	-	31.0 ± 0.6
Complex **5**	13.0 ± 1.9	11.3 ± 0.3	11.5 ± 1.5	-	13.7 ± 1.9
1,10-phen	16.8 ± 0.3	35.7 ± 0.3	32.7 ± 1.2	19.0 ± 0.8	16.3 ± 0.8

All cobalt valporate complexes didn’t show anti-bacterial activity against all gram-negative bacteria because the gram-negative bacteria contains more layers than gram-positive bacteria in their cell wall which called outer membrane. The outer membrane which consists lipopolysaccharides, resists the antibiotic and it contains porin proteins which is permeable only small molecules such as glucose.[98] In addition, complex **3** didn’t exhibit any anti-bacterial activity against gram-positive bacteria.

Complex **2** only showed anti-bacterial activity against *S. aureus* with IZD equal 17.5 mm. Complex **4** showed good anti-bacterial activity against all tested microorganisms with IZD ranging between 15-28 mm but the parent ligand 2,9-dmp showed higher anti-bacterial activity compared to complex **4** except *M. luteus* and *M. subtili*s were it showed slightly higher anti-bacterial activity than its parent ligand. On the other hand, complex **4** showed anti-bacterial activity against *E. faecalis* whereas its parent ligand didn’t show any anti-bacterial activity.

Complex **5** showed low inhibition activity against all gram-positive bacteria except *E. faecalis* with IZD between 11.3-13.7 mm, these values are lower than those for its parent ligand 1,10-phen.

Complex **1**, valp and $CoCl_2$ didn’t show any anti-bacterial activity against gram-positive and gram-negative bacteria except $CoCl_2$ which showed low inhibition activity against S. *aureus* with IZD equal 12 mm. The complexation of cobalt valporate with nitrogen donor ligands showed low inhibition activity against gram-positive bacteria compared to the positive controls (E and G).

3.6 BNPP catalytic hydrolysis:

The rate of BNPP hydrolysis was studied at different temperatures, pH and concentrations. The optimum condition for BNPP hydrolysis was obtained by changing one of the above factors while maintaining the other two constant. All cobalt valporate complexes were used as catalyst.

3.6.1 Effect of pH on BNPP catalytic hydrolysis:

Figure 22 and Figure 23 show the Abs versus time relationship for complex **3** and complex **4**, respectively at different pH values and constant temp and concentration of both BNPP and complexes. The initial rate (V_o) of BNPP hydrolysis was calculated by measuring the absorbance of p-nitrophenol against time at 400 nm.[83,84] The V_o values (mol/L.S) are 1×10^{-8}, 3×10^{-9} and 5×10^{-9} at pH = 7.91, 7.46 and 7.02, respectively for complex **3** and 3×10^{-8}, 4×10^{-9} and 2×10^{-8} at pH = 7.91, 7.48 and 7.02, respectively for complex **4**. The maximum V_o was obtained at pH = 7.91 for complexes **3** and **4**.

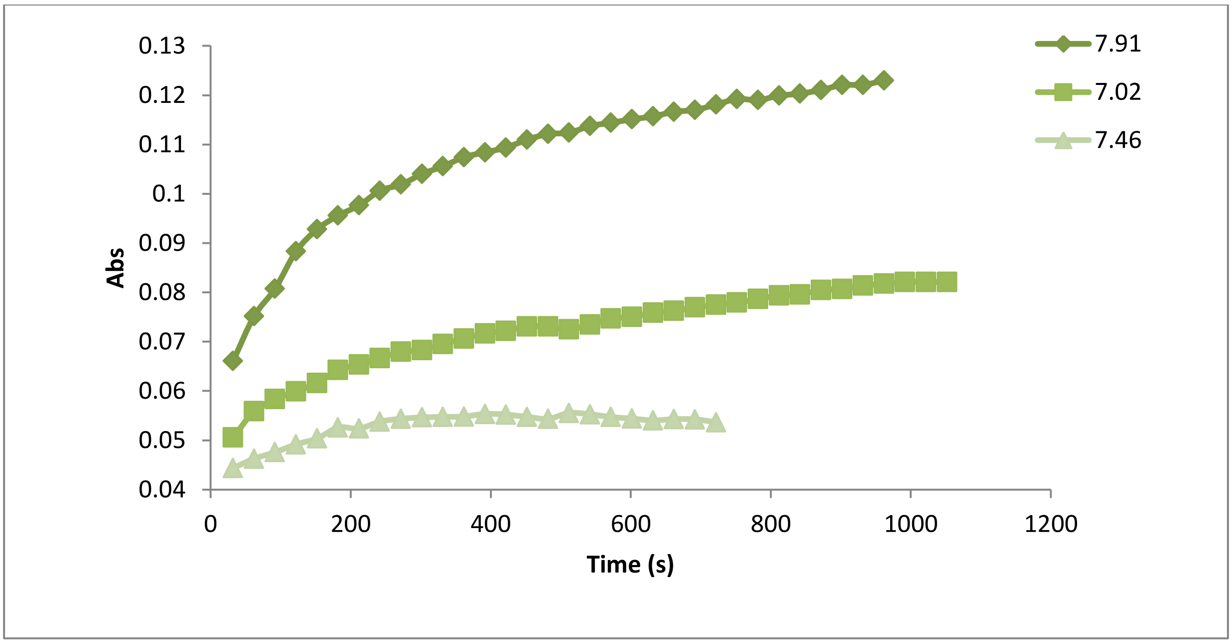


Figure 22: BNPP hydrolysis by complex **3** in MeOH /HEPEs buffer solution with different pH values under the selected conditions (T = 37 °C, [complex **3**] = 2×10^{-3} M and [BNPP] = 1×10^{-4} M).

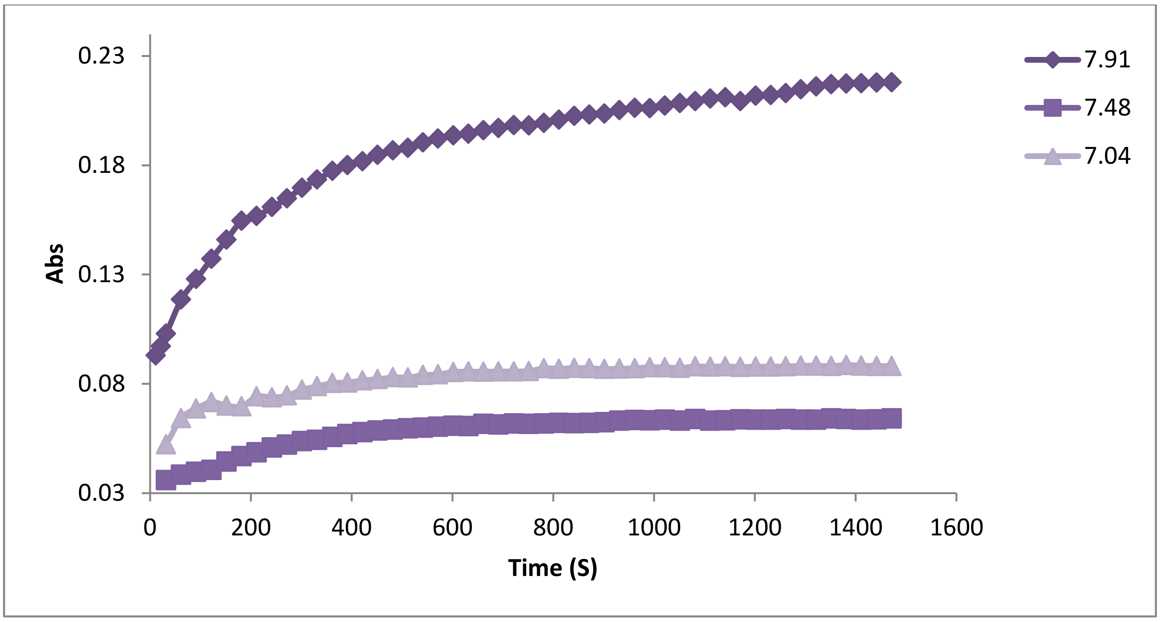


Figure 23: BNPP hydrolysis by complex **4** in MeOH /HEPEs buffer solution with different pH values under the selected conditions (T = 25 ^{o}C, [complex **4**] = 2×10^{-3} M and [BNPP] = 1×10^{-4} M).

3.6.2 Effect of temperature on the BNPP catalytic hydrolysis:

Figure 24 and Figure 25 show the Abs versus time relationship for complex **3** and complex **4**, respectively at different temp values and constant pH and concentration of both BNPP and complexes. The V_o values (mol/L.S) are 1.8×10^{-8} and 1.7×10^{-8} at 25 ^{o}C and 37 ^{o}C for complex **3** and 2×10^{-8}, 1×10^{-8} and 3×10^{-9} at 25 ^{o}C, 37 ^{o}C and 40 ^{o}C for complex **4**. The maximum V_o was obtained at 25 ^{o}C for complexes **3** and **4**.

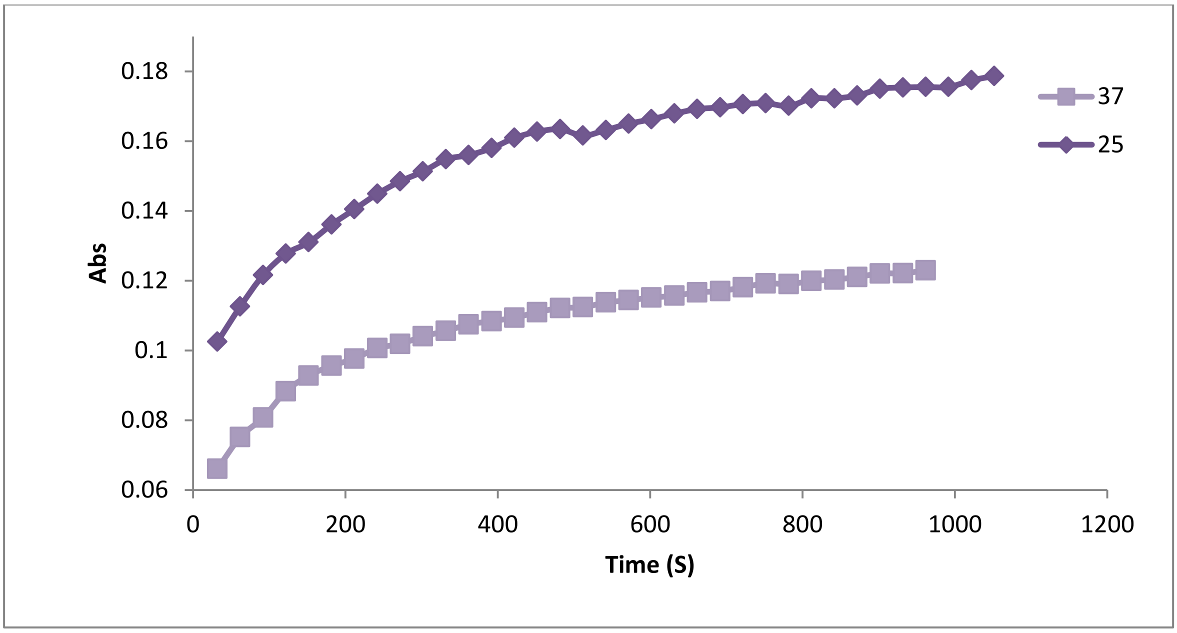


Figure 24: BNPP hydrolysis by complex **3** in MeOH /HEPEs buffer solution with different temp values under the selected conditions (pH = 7.91, [complex **3**] = 2×10^{-3} M and [BNPP] = 1×10^{-4} M).

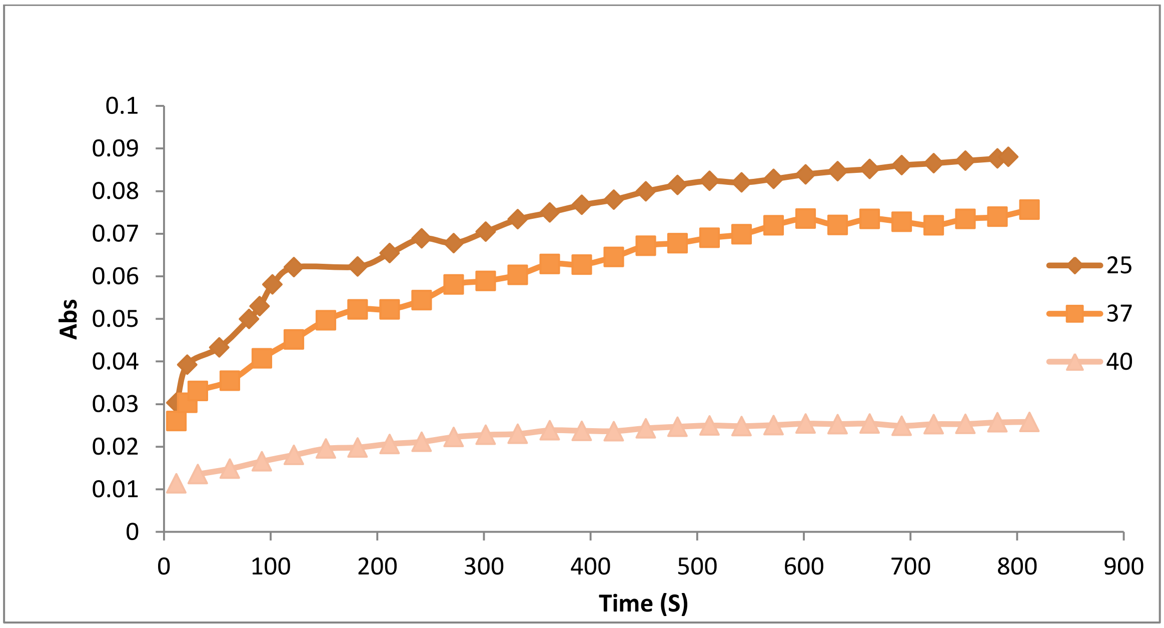


Figure 25: BNPP hydrolysis by complex **4** in MeOH /HEPEs buffer solution with different temp values under the selected conditions (pH = 7.04, [complex **4**] = 2×10^{-4} M and [BNPP] = 1×10^{-4} M).

All complexes **2**, **3**, **4** and **5** showed similar trend in the hydrolysis of BNPP. The hydrolysis of BNPP has been analyzed by using Michaelis–Menten equation[76] ($1/V_o = 1/V_{max} + K_m/V_{max}[BNPP]$ (Figure 26).

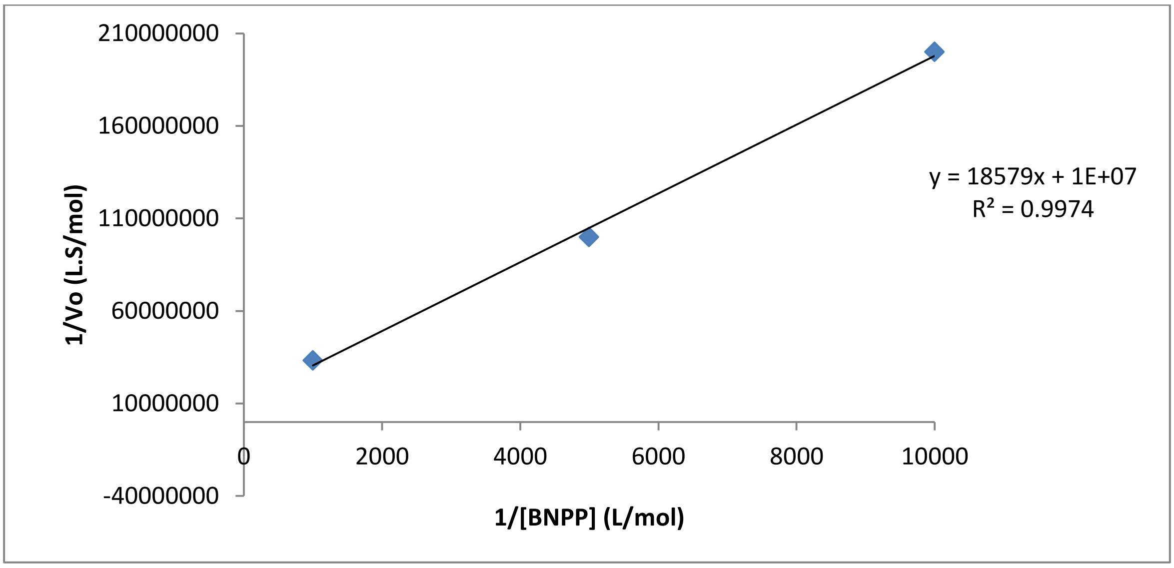


Figure 26: Second order rate for complex **2** with different [BNPP] under the selected conditions (pH = 7.91, temp = 25 °C and [complex **2**] = 2×10^{-4} M).

The Kinetic parameters of BNPP hydrolysis were shown in Table 19. The results from this study showed that the rate of BNPP hydrolysis by the prepared complexes was in the following order: **3** > **4** > **5** > **2** and their values are higher than other synthetic chemical models ($K_{cat}/K_m = 1.3 - 43 \times 10^{-5}$ M^{-1} s^{-1} at 35 °C and pH 7.3-10.5 for Zn complexes).[76] Complex **3** shows the highest activity due to it's dimer complex.

Table 19: Kinetic parameters of the phosphate diester group hydrolysis for complexes **2**, **3**, **4** and **5** at different BNPP concentrations.

Concentration (M)		V_o (mol/L.S)	V_{max} (mol/L.S)	K_m (mol/L)	$K_{cat}{}^a$ (S^{-1})	2-order rate $K_{BNPP}{}^b$ ($L.mol^{-1}.S^{-1}$)
Complexes	BNPP					
2 (2×10^{-4})	1×10^{-3}	3.0×10^{-8}	1×10^{-7}	1.9×10^{-3}	5×10^{-4}	0.026×10^{1}
2 (2×10^{-4})	2×10^{-4}	1.0×10^{-8}				
2 (2×10^{-4})	1×10^{-4}	5.0×10^{-9}				
3 (2×10^{-6})	1×10^{-3}	1.0×10^{-8}	1.0×10^{-8}	6.5×10^{-6}	5×10^{-3}	7.70×10^{2}
3 (2×10^{-6})	1×10^{-4}	9.0×10^{-9}				
3 (2×10^{-6})	1×10^{-5}	6.0×10^{-9}				
4 (2×10^{-4})	1×10^{-3}	5.5×10^{-8}	1×10^{-7}	3.5×10^{-4}	5×10^{-4}	0.143×10^{1}
4 (2×10^{-4})	2×10^{-4}	3.1×10^{-8}				
4 (2×10^{-4})	1×10^{-4}	2.0×10^{-8}				
5 (2×10^{-4})	1×10^{-3}	6.0×10^{-8}	1×10^{-7}	3.7×10^{-4}	5×10^{-4}	0.135×10^{1}
5 (2×10^{-4})	2×10^{-4}	3.2×10^{-8}				
5 (2×10^{-4})	1×10^{-4}	2.0×10^{-8}				

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

4. Conclusion:

The new cobalt complexes with valporate in the presence of N-donor ligands were fully characterize by IR, UV-Vis and X-ray crystallography spectrophotometric techniques. The synthesized complexes were $[Co_2(valp)_4]$ **(1)**, $[Co(valp)_2(2\text{-}ampy)_2]$ **(2)**, $[Co_2(valp)_4(quin)_2]$ **(3)**, $[Co(valp)_2(2,9\text{-}dmp)]$ **(4)** and $[Co(valp)_2(H_2O)(1,10\text{-}phen)]$ **(5)**.

The crystal structure of **2**, **3**, **4** and **5** had been determined by using single crystal X-ray diffraction. Structure **2** and **4** revealed distorted octahedral geometries with two bidentate valp groups and two monodentate 2-ampy ligands in complex **2** and with two valp groups and one bidentate 2,9-dmp in complex **4**, and in, the asymmetric unit (one molecule) of complex **5** consists of one Co(III) cation, one monodentate valp, one bidentate valp, one 1,10-phen and water molecules revealing distorted octahedral arrangement. In complex **3**, the distorted octahedral geometry around each Co center of the binuclear complex consists of four oxygen atoms from four valporate bidentate chelating ligands, one nitrogen atom from quinoline monodentate ligand.

All cobalt valporate complexes showed anti-bacterial activity against all gram-positive bacteria except complex **3** but these complexes didn't exhibit any anti-bacterial activity against gram-negative bacteria. In general, the complexation of cobalt valporate with nitrogen donor ligands showed low inhibition activity against gram-positive bacteria compared to the positive controls (E and G).

The rate of BNPP hydrolysis was studied in order to determine the effect of cobalt complexes on the phosphatase hydrolysis. The results showed that the hydrolysis rate of BNPP was decreased in the following order: **3** > **4** > **5** > **2** and their values are higher than other synthetic chemical models.

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Appendices:

Appendix A: Crystal structure data of [Co(valp)$_2$(2-ampy)$_2$] (2):

Table 1: Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7501(13)	1098(8)	7881(6)	83(3)
C(2)	9043(16)	906(11)	8016(8)	119(6)
C(3)	9828(14)	790(10)	7452(9)	138(7)
C(4)	9680(20)	1631(14)	6883(9)	163(7)
C(5)	10330(30)	1403(19)	6354(12)	254(12)
C(6)	9350(20)	22(19)	8582(10)	230(13)
C(7)	8730(30)	-100(20)	9115(15)	263(14)
C(8)	9120(30)	-1000(20)	9676(13)	263(12)
C(9)	4714(10)	2512(7)	6512(5)	64(3)
C(10)	4235(19)	2885(9)	5818(6)	109(5)
C(11)	5240(20)	3389(13)	5420(8)	158(7)
C(12)	6480(20)	2822(17)	5321(10)	195(9)
C(13)	7390(30)	3390(19)	4785(12)	247(11)
C(14)	2803(18)	3529(15)	5792(8)	166(7)
C(15)	2010(30)	3700(20)	5164(10)	238(11)
C(16)	540(30)	3830(40)	5120(20)	530(30)
C(17)	3950(9)	-267(7)	8174(5)	60(3)
C(18)	3654(11)	-1056(9)	8661(7)	91(4)
C(19)	3563(18)	-1002(13)	9258(8)	138(6)
C(20)	3820(20)	-178(14)	9403(8)	144(7)
C(21)	4087(14)	553(9)	8915(7)	99(4)
C(22)	4156(12)	3556(6)	8075(5)	64(3)
C(23)	3183(16)	4270(8)	8124(6)	99(4)
C(24)	1810(17)	4235(9)	8060(7)	113(5)
C(25)	1386(13)	3383(9)	7978(7)	110(5)
C(26)	2387(14)	2700(9)	7931(6)	93(4)
C(27)	6709(11)	6054(8)	8361(6)	73(3)
C(28)	7167(15)	5714(9)	9045(6)	96(4)
C(29)	6180(20)	6306(15)	9397(7)	193(10)

C(30)	6680(30)	6310(20)	9991(15)	287(15)
C(31)	6410(40)	7150(30)	10174(15)	331(18)
C(32)	7264(16)	4648(10)	9309(6)	113(5)
C(33)	8401(16)	4125(11)	9043(7)	124(5)
C(34)	8440(20)	3027(10)	9318(9)	203(10)
C(35)	3461(14)	7327(8)	7168(6)	82(3)
C(36)	1961(14)	7580(10)	7044(8)	112(5)
C(37)	1860(20)	8527(17)	6381(11)	205(9)
C(38)	560(30)	8320(30)	6133(16)	370(20)
C(39)	550(40)	8940(30)	5492(16)	360(20)
C(40)	1258(14)	7719(11)	7597(9)	124(6)
C(41)	1391(18)	6856(12)	8179(10)	146(7)
C(42)	770(20)	7009(15)	8759(9)	192(8)
C(43)	6930(13)	5114(6)	6714(5)	67(3)
C(44)	7956(15)	4408(7)	6632(6)	91(4)
C(45)	9260(15)	4570(9)	6632(7)	106(4)
C(46)	9630(14)	5391(10)	6731(7)	112(5)
C(47)	8606(13)	6033(7)	6826(6)	84(4)
C(48)	6796(10)	8891(7)	6741(6)	66(3)
C(49)	6793(13)	9767(7)	6270(8)	94(4)
C(50)	6586(17)	9828(9)	5656(8)	117(5)
C(51)	6351(17)	9019(10)	5487(7)	121(5)
C(52)	6332(13)	8204(8)	5950(6)	86(4)
Co(1)	5009(1)	1716(1)	7701(1)	58(1)
Co(2)	6015(1)	6847(1)	7214(1)	62(1)
N(1)	4203(8)	554(6)	8309(4)	66(2)
N(2)	3993(10)	-222(6)	7583(5)	86(3)
N(3)	3736(9)	2759(5)	7972(4)	68(2)
N(4)	5461(9)	3603(6)	8152(4)	81(3)
N(5)	7285(9)	5906(5)	6841(4)	62(2)
N(6)	5603(10)	5000(6)	6688(4)	86(3)
N(7)	6512(9)	8112(5)	6576(4)	67(2)
N(8)	7127(8)	8814(5)	7350(5)	74(3)
O(1)	6857(7)	695(5)	7579(4)	83(2)
O(2)	6893(7)	1782(5)	8077(4)	84(2)
O(3)	5410(8)	2949(5)	6778(4)	84(2)
O(4)	4241(7)	1755(4)	6828(3)	71(2)
O(5)	7107(8)	6793(5)	8023(3)	80(2)

O(6)	5901(8)	5605(5)	8150(3)	81(2)
O(7)	4140(8)	7765(5)	7466(4)	84(2)
O(8)	4076(8)	6740(5)	6913(4)	83(2)

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

C(1)-O(1)	1.217(12)
C(1)-O(2)	1.285(12)
C(1)-C(2)	1.528(17)
C(2)-C(3)	1.48(2)
C(2)-C(6)	1.53(2)
C(2)-H(2)	0.9800
C(3)-C(4)	1.49(2)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.41(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-C(7)	1.28(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.54(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-O(3)	1.233(11)
C(9)-O(4)	1.264(10)
C(9)-C(10)	1.524(16)
C(10)-C(11)	1.43(2)
C(10)-C(14)	1.60(2)
C(10)-H(10)	0.9800
C(11)-C(12)	1.45(2)
C(11)-H(11A)	0.9700

C(11)-H(11B)	0.9700
C(12)-C(13)	1.57(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.529(16)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.443(19)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-N(2)	1.274(12)
C(17)-N(1)	1.362(11)
C(17)-C(18)	1.391(14)
C(18)-C(19)	1.327(18)
C(18)-H(18)	0.9300
C(19)-C(20)	1.38(2)
C(19)-H(19)	0.9300
C(20)-C(21)	1.334(19)
C(20)-H(20)	0.9300
C(21)-N(1)	1.324(14)
C(21)-H(21)	0.9300
C(22)-N(4)	1.304(12)
C(22)-N(3)	1.353(11)
C(22)-C(23)	1.368(15)
C(23)-C(24)	1.364(18)
C(23)-H(23)	0.9300
C(24)-C(25)	1.412(17)
C(24)-H(24)	0.9300
C(25)-C(26)	1.353(16)
C(25)-H(25)	0.9300
C(26)-N(3)	1.341(14)
C(26)-H(26)	0.9300

C(27)-O(5)	1.228(12)
C(27)-O(6)	1.249(11)
C(27)-C(28)	1.497(15)
C(28)-C(32)	1.503(16)
C(28)-C(29)	1.57(2)
C(28)-H(28)	0.9800
C(29)-C(30)	1.39(3)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.40(4)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31A)	0.9600
C(31)-H(31B)	0.9600
C(31)-H(31C)	0.9600
C(32)-C(33)	1.492(17)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-C(34)	1.554(19)
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(35)-O(8)	1.250(13)
C(35)-O(7)	1.267(12)
C(35)-C(36)	1.490(17)
C(36)-C(40)	1.435(19)
C(36)-C(37)	1.70(2)
C(36)-H(36)	0.9800
C(37)-C(38)	1.480(18)
C(37)-H(37A)	0.9700
C(37)-H(37B)	0.9700
C(38)-C(39)	1.445(18)
C(38)-H(38A)	0.9700
C(38)-H(38B)	0.9700
C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600

C(39)-H(39C)	0.9600
C(40)-C(41)	1.52(2)
C(40)-H(40A)	0.9700
C(40)-H(40B)	0.9700
C(41)-C(42)	1.46(2)
C(41)-H(41A)	0.9700
C(41)-H(41B)	0.9700
C(42)-H(42A)	0.9600
C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(43)-N(6)	1.334(13)
C(43)-N(5)	1.345(11)
C(43)-C(44)	1.415(14)
C(44)-C(45)	1.325(16)
C(44)-H(44)	0.9300
C(45)-C(46)	1.364(16)
C(45)-H(45)	0.9300
C(46)-C(47)	1.358(16)
C(46)-H(46)	0.9300
C(47)-N(5)	1.327(13)
C(47)-H(47)	0.9300
C(48)-N(7)	1.343(11)
C(48)-N(8)	1.343(12)
C(48)-C(49)	1.407(15)
C(49)-C(50)	1.333(17)
C(49)-H(49)	0.9300
C(50)-C(51)	1.376(17)
C(50)-H(50)	0.9300
C(51)-C(52)	1.338(16)
C(51)-H(51)	0.9300
C(52)-N(7)	1.347(12)
C(52)-H(52)	0.9300
Co(1)-O(4)	2.042(7)
Co(1)-O(2)	2.053(7)
Co(1)-N(1)	2.072(9)
Co(1)-N(3)	2.081(8)
Co(1)-O(1)	2.292(7)
Co(1)-O(3)	2.367(8)

Co(2)-O(5)	2.054(7)
Co(2)-O(8)	2.056(7)
Co(2)-N(7)	2.088(8)
Co(2)-N(5)	2.088(8)
Co(2)-O(7)	2.318(7)
Co(2)-O(6)	2.342(7)
N(2)-H(1N2)	0.8600
N(2)-H(2N2)	0.8600
N(4)-H(1N4)	0.8600
N(4)-H(2N4)	0.8600
N(6)-H(1N6)	0.8600
N(6)-H(2N6)	0.8600
N(8)-H(1N8)	0.8600
N(8)-H(2N8)	0.8600

O(1)-C(1)-O(2)	119.8(11)
O(1)-C(1)-C(2)	125.1(11)
O(2)-C(1)-C(2)	115.0(11)
C(3)-C(2)-C(1)	112.4(12)
C(3)-C(2)-C(6)	110.3(13)
C(1)-C(2)-C(6)	109.8(15)
C(3)-C(2)-H(2)	108.1
C(1)-C(2)-H(2)	108.1
C(6)-C(2)-H(2)	108.1
C(2)-C(3)-C(4)	115.1(14)
C(2)-C(3)-H(3A)	108.5
C(4)-C(3)-H(3A)	108.5
C(2)-C(3)-H(3B)	108.5
C(4)-C(3)-H(3B)	108.5
H(3A)-C(3)-H(3B)	107.5
C(5)-C(4)-C(3)	110(2)
C(5)-C(4)-H(4A)	109.6
C(3)-C(4)-H(4A)	109.6
C(5)-C(4)-H(4B)	109.6
C(3)-C(4)-H(4B)	109.6
H(4A)-C(4)-H(4B)	108.1
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5

H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-C(2)	124(2)
C(7)-C(6)-H(6A)	106.4
C(2)-C(6)-H(6A)	106.4
C(7)-C(6)-H(6B)	106.4
C(2)-C(6)-H(6B)	106.4
H(6A)-C(6)-H(6B)	106.5
C(6)-C(7)-C(8)	121(3)
C(6)-C(7)-H(7A)	107.0
C(8)-C(7)-H(7A)	107.0
C(6)-C(7)-H(7B)	107.0
C(8)-C(7)-H(7B)	107.0
H(7A)-C(7)-H(7B)	106.7
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(3)-C(9)-O(4)	120.4(11)
O(3)-C(9)-C(10)	123.5(10)
O(4)-C(9)-C(10)	115.7(10)
C(11)-C(10)-C(9)	112.2(14)
C(11)-C(10)-C(14)	112.4(14)
C(9)-C(10)-C(14)	108.2(12)
C(11)-C(10)-H(10)	108.0
C(9)-C(10)-H(10)	108.0
C(14)-C(10)-H(10)	108.0
C(10)-C(11)-C(12)	116.4(18)
C(10)-C(11)-H(11A)	108.2
C(12)-C(11)-H(11A)	108.2
C(10)-C(11)-H(11B)	108.2
C(12)-C(11)-H(11B)	108.2
H(11A)-C(11)-H(11B)	107.3
C(11)-C(12)-C(13)	113(2)

C(11)-C(12)-H(12A)	109.0
C(13)-C(12)-H(12A)	109.0
C(11)-C(12)-H(12B)	109.0
C(13)-C(12)-H(12B)	109.0
H(12A)-C(12)-H(12B)	107.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(10)	113.1(18)
C(15)-C(14)-H(14A)	109.0
C(10)-C(14)-H(14A)	109.0
C(15)-C(14)-H(14B)	108.9
C(10)-C(14)-H(14B)	109.0
H(14A)-C(14)-H(14B)	107.8
C(16)-C(15)-C(14)	123(3)
C(16)-C(15)-H(15A)	106.6
C(14)-C(15)-H(15A)	106.6
C(16)-C(15)-H(15B)	106.5
C(14)-C(15)-H(15B)	106.6
H(15A)-C(15)-H(15B)	106.5
C(15)-C(16)-H(16A)	110.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	108.4
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(2)-C(17)-N(1)	114.2(10)
N(2)-C(17)-C(18)	125.5(11)
N(1)-C(17)-C(18)	120.3(11)
C(19)-C(18)-C(17)	120.2(13)
C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(18)-C(19)-C(20)	120.2(15)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9

C(21)-C(20)-C(19)	116.5(15)
C(21)-C(20)-H(20)	121.8
C(19)-C(20)-H(20)	121.8
N(1)-C(21)-C(20)	126.8(13)
N(1)-C(21)-H(21)	116.6
C(20)-C(21)-H(21)	116.6
N(4)-C(22)-N(3)	119.3(9)
N(4)-C(22)-C(23)	122.3(11)
N(3)-C(22)-C(23)	118.4(11)
C(24)-C(23)-C(22)	123.7(13)
C(24)-C(23)-H(23)	118.1
C(22)-C(23)-H(23)	118.1
C(23)-C(24)-C(25)	117.1(12)
C(23)-C(24)-H(24)	121.4
C(25)-C(24)-H(24)	121.4
C(26)-C(25)-C(24)	116.8(12)
C(26)-C(25)-H(25)	121.6
C(24)-C(25)-H(25)	121.6
N(3)-C(26)-C(25)	125.3(11)
N(3)-C(26)-H(26)	117.3
C(25)-C(26)-H(26)	117.3
O(5)-C(27)-O(6)	121.2(12)
O(5)-C(27)-C(28)	118.8(10)
O(6)-C(27)-C(28)	119.9(11)
C(27)-C(28)-C(32)	113.3(11)
C(27)-C(28)-C(29)	104.9(11)
C(32)-C(28)-C(29)	116.2(13)
C(27)-C(28)-H(28)	107.3
C(32)-C(28)-H(28)	107.3
C(29)-C(28)-H(28)	107.3
C(30)-C(29)-C(28)	113(2)
C(30)-C(29)-H(29A)	108.9
C(28)-C(29)-H(29A)	108.9
C(30)-C(29)-H(29B)	108.9
C(28)-C(29)-H(29B)	108.9
H(29A)-C(29)-H(29B)	107.7
C(29)-C(30)-C(31)	117(3)
C(29)-C(30)-H(30A)	108.0

C(31)-C(30)-H(30A)	108.0
C(29)-C(30)-H(30B)	108.0
C(31)-C(30)-H(30B)	108.0
H(30A)-C(30)-H(30B)	107.2
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(33)-C(32)-C(28)	114.2(12)
C(33)-C(32)-H(32A)	108.7
C(28)-C(32)-H(32A)	108.7
C(33)-C(32)-H(32B)	108.7
C(28)-C(32)-H(32B)	108.7
H(32A)-C(32)-H(32B)	107.6
C(32)-C(33)-C(34)	112.2(14)
C(32)-C(33)-H(33A)	109.2
C(34)-C(33)-H(33A)	109.2
C(32)-C(33)-H(33B)	109.2
C(34)-C(33)-H(33B)	109.2
H(33A)-C(33)-H(33B)	107.9
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
O(8)-C(35)-O(7)	119.7(12)
O(8)-C(35)-C(36)	118.5(12)
O(7)-C(35)-C(36)	121.4(11)
C(40)-C(36)-C(35)	111.8(13)
C(40)-C(36)-C(37)	116.8(14)
C(35)-C(36)-C(37)	104.2(13)
C(40)-C(36)-H(36)	107.9
C(35)-C(36)-H(36)	107.9
C(37)-C(36)-H(36)	107.9
C(38)-C(37)-C(36)	96(2)

C(38)-C(37)-H(37A)	112.6
C(36)-C(37)-H(37A)	112.6
C(38)-C(37)-H(37B)	112.6
C(36)-C(37)-H(37B)	112.6
H(37A)-C(37)-H(37B)	110.1
C(39)-C(38)-C(37)	100(3)
C(39)-C(38)-H(38A)	111.7
C(37)-C(38)-H(38A)	111.7
C(39)-C(38)-H(38B)	111.8
C(37)-C(38)-H(38B)	111.8
H(38A)-C(38)-H(38B)	109.5
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(36)-C(40)-C(41)	114.8(13)
C(36)-C(40)-H(40A)	108.6
C(41)-C(40)-H(40A)	108.6
C(36)-C(40)-H(40B)	108.6
C(41)-C(40)-H(40B)	108.6
H(40A)-C(40)-H(40B)	107.5
C(42)-C(41)-C(40)	115.4(16)
C(42)-C(41)-H(41A)	108.4
C(40)-C(41)-H(41A)	108.4
C(42)-C(41)-H(41B)	108.4
C(40)-C(41)-H(41B)	108.4
H(41A)-C(41)-H(41B)	107.5
C(41)-C(42)-H(42A)	109.5
C(41)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(41)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
N(6)-C(43)-N(5)	118.7(9)
N(6)-C(43)-C(44)	121.3(9)
N(5)-C(43)-C(44)	120.0(11)

C(45)-C(44)-C(43)	119.2(10)
C(45)-C(44)-H(44)	120.4
C(43)-C(44)-H(44)	120.4
C(44)-C(45)-C(46)	121.1(12)
C(44)-C(45)-H(45)	119.4
C(46)-C(45)-H(45)	119.4
C(47)-C(46)-C(45)	117.2(13)
C(47)-C(46)-H(46)	121.4
C(45)-C(46)-H(46)	121.4
N(5)-C(47)-C(46)	124.5(10)
N(5)-C(47)-H(47)	117.7
C(46)-C(47)-H(47)	117.7
N(7)-C(48)-N(8)	119.4(9)
N(7)-C(48)-C(49)	119.6(11)
N(8)-C(48)-C(49)	121.0(10)
C(50)-C(49)-C(48)	121.1(11)
C(50)-C(49)-H(49)	119.4
C(48)-C(49)-H(49)	119.4
C(49)-C(50)-C(51)	119.0(12)
C(49)-C(50)-H(50)	120.5
C(51)-C(50)-H(50)	120.5
C(52)-C(51)-C(50)	118.2(13)
C(52)-C(51)-H(51)	120.9
C(50)-C(51)-H(51)	120.9
C(51)-C(52)-N(7)	124.9(11)
C(51)-C(52)-H(52)	117.5
N(7)-C(52)-H(52)	117.5
O(4)-Co(1)-O(2)	136.4(3)
O(4)-Co(1)-N(1)	103.4(3)
O(2)-Co(1)-N(1)	106.3(3)
O(4)-Co(1)-N(3)	103.5(3)
O(2)-Co(1)-N(3)	104.1(3)
N(1)-Co(1)-N(3)	96.5(3)
O(4)-Co(1)-O(1)	90.9(3)
O(2)-Co(1)-O(1)	59.5(2)
N(1)-Co(1)-O(1)	87.8(3)
N(3)-Co(1)-O(1)	163.5(3)
O(4)-Co(1)-O(3)	58.3(2)

O(2)-Co(1)-O(3)	91.1(3)
N(1)-Co(1)-O(3)	161.4(3)
N(3)-Co(1)-O(3)	85.4(3)
O(1)-Co(1)-O(3)	95.6(3)
O(5)-Co(2)-O(8)	141.4(3)
O(5)-Co(2)-N(7)	103.0(3)
O(8)-Co(2)-N(7)	102.3(3)
O(5)-Co(2)-N(5)	100.6(3)
O(8)-Co(2)-N(5)	104.5(3)
N(7)-Co(2)-N(5)	97.4(3)
O(5)-Co(2)-O(7)	94.1(3)
O(8)-Co(2)-O(7)	59.3(3)
N(7)-Co(2)-O(7)	85.8(3)
N(5)-Co(2)-O(7)	163.8(3)
O(5)-Co(2)-O(6)	58.4(3)
O(8)-Co(2)-O(6)	93.5(3)
N(7)-Co(2)-O(6)	161.3(3)
N(5)-Co(2)-O(6)	88.1(3)
O(7)-Co(2)-O(6)	93.8(3)
C(21)-N(1)-C(17)	115.8(10)
C(21)-N(1)-Co(1)	116.7(8)
C(17)-N(1)-Co(1)	126.9(7)
C(17)-N(2)-H(1N2)	120.0
C(17)-N(2)-H(2N2)	120.0
H(1N2)-N(2)-H(2N2)	120.0
C(26)-N(3)-C(22)	118.6(9)
C(26)-N(3)-Co(1)	115.7(7)
C(22)-N(3)-Co(1)	124.7(7)
C(22)-N(4)-H(1N4)	120.0
C(22)-N(4)-H(2N4)	120.0
H(1N4)-N(4)-H(2N4)	120.0
C(47)-N(5)-C(43)	117.6(9)
C(47)-N(5)-Co(2)	115.3(6)
C(43)-N(5)-Co(2)	126.2(7)
C(43)-N(6)-H(1N6)	120.0
C(43)-N(6)-H(2N6)	120.0
H(1N6)-N(6)-H(2N6)	120.0
C(48)-N(7)-C(52)	117.0(9)

C(48)-N(7)-Co(2)	124.9(7)
C(52)-N(7)-Co(2)	117.2(7)
C(48)-N(8)-H(1N8)	120.0
C(48)-N(8)-H(2N8)	120.0
H(1N8)-N(8)-H(2N8)	120.0
C(1)-O(1)-Co(1)	85.8(7)
C(1)-O(2)-Co(1)	95.0(7)
C(9)-O(3)-Co(1)	83.5(6)
C(9)-O(4)-Co(1)	97.8(6)
C(27)-O(5)-Co(2)	97.2(7)
C(27)-O(6)-Co(2)	83.2(7)
C(35)-O(7)-Co(2)	84.2(7)
C(35)-O(8)-Co(2)	96.7(7)

Table 3: Anisotropic displacement parameters ($Å^2 x 10^3$) for complex **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)	74(8)	68(8)	110(10)	-35(7)	-21(7)	16(7)
C(2)	103(12)	118(13)	150(14)	-75(11)	-47(10)	39(9)
C(3)	82(11)	85(11)	240(20)	-30(13)	-60(13)	5(9)
C(6)	126(16)	340(30)	146(17)	10(20)	-42(14)	110(20)
C(9)	56(6)	44(6)	96(8)	-17(6)	21(6)	-26(5)
C(10)	169(16)	72(9)	82(10)	-4(7)	3(10)	-36(10)
C(11)	210(20)	146(16)	112(13)	-26(12)	-18(13)	-25(16)
C(14)	115(14)	210(20)	143(16)	1(14)	-21(12)	-9(14)
C(17)	30(5)	69(7)	90(8)	-30(6)	7(5)	-18(5)
C(18)	63(8)	81(9)	125(11)	-9(8)	23(8)	-40(7)
C(19)	171(17)	121(14)	96(12)	20(11)	23(11)	-33(12)
C(20)	220(20)	120(14)	93(12)	-35(11)	-29(12)	-26(14)
C(21)	124(12)	61(8)	111(11)	-19(8)	-3(9)	-8(8)
C(22)	78(8)	34(5)	76(7)	-14(5)	0(6)	6(5)
C(23)	111(12)	52(7)	123(11)	-14(7)	-8(9)	20(8)
C(24)	108(12)	74(10)	150(13)	-35(9)	0(10)	37(9)
C(25)	71(9)	70(9)	201(15)	-63(9)	-7(9)	6(7)
C(26)	89(10)	78(8)	133(11)	-59(8)	-10(8)	-19(7)
C(27)	55(7)	65(7)	113(10)	-43(7)	2(6)	-21(6)
C(28)	119(11)	86(9)	83(9)	-18(7)	-15(8)	-27(8)

C(29)	280(30)	220(20)	80(11)	-63(13)	-37(14)	10(20)
C(32)	133(13)	113(12)	85(9)	-12(8)	9(9)	-26(10)
C(33)	113(12)	118(13)	125(12)	-21(10)	5(10)	21(10)
C(34)	320(30)	59(10)	198(19)	2(11)	-36(18)	30(13)
C(35)	99(10)	44(6)	102(9)	-14(6)	-11(8)	-9(7)
C(36)	68(9)	103(11)	179(15)	-62(11)	-1(10)	-16(8)
C(40)	61(9)	105(12)	219(19)	-64(13)	-1(11)	-15(8)
C(41)	140(15)	112(14)	220(20)	-92(14)	64(14)	-35(11)
C(43)	101(9)	32(5)	72(7)	-17(5)	12(6)	-22(6)
C(44)	131(12)	31(6)	126(10)	-52(6)	13(9)	-1(7)
C(45)	91(11)	68(9)	164(14)	-43(9)	12(10)	0(8)
C(46)	84(10)	78(9)	172(14)	-34(9)	-16(9)	-6(8)
C(47)	87(9)	36(6)	134(11)	-30(6)	8(8)	-4(6)
C(48)	61(7)	36(6)	102(9)	-20(6)	0(6)	-5(5)
C(49)	93(9)	34(6)	160(13)	-34(8)	9(9)	-10(6)
C(50)	166(15)	50(8)	117(12)	6(8)	-20(11)	-4(8)
C(51)	186(16)	74(10)	100(11)	-22(8)	-26(10)	3(10)
C(52)	131(11)	51(7)	76(8)	-18(6)	-1(8)	-12(7)
Co(1)	61(1)	35(1)	87(1)	-33(1)	-12(1)	-5(1)
Co(2)	74(1)	29(1)	91(1)	-27(1)	-10(1)	-11(1)
N(1)	71(6)	60(5)	73(6)	-29(5)	-2(5)	-4(4)
N(2)	114(8)	63(6)	103(8)	-57(6)	2(6)	-17(5)
N(3)	69(6)	36(4)	109(7)	-35(4)	-11(5)	-10(4)
N(4)	65(6)	67(6)	132(8)	-59(6)	-3(6)	-14(5)
N(5)	62(6)	37(4)	89(6)	-21(4)	-4(5)	-9(4)
N(6)	106(8)	51(5)	122(8)	-54(5)	3(6)	-21(5)
N(7)	87(6)	30(4)	85(6)	-19(4)	2(5)	-8(4)
N(8)	77(6)	24(4)	130(8)	-31(5)	-8(6)	-15(4)
O(1)	71(5)	71(5)	124(6)	-53(5)	-28(4)	-10(4)
O(2)	76(5)	57(4)	131(6)	-47(4)	-31(5)	4(4)
O(3)	97(6)	65(5)	104(6)	-41(4)	-3(4)	-28(4)
O(4)	82(5)	48(4)	91(5)	-25(4)	-4(4)	-22(4)
O(5)	102(6)	49(4)	92(5)	-19(4)	-7(4)	-25(4)
O(6)	86(6)	55(4)	102(6)	-20(4)	-12(4)	-8(4)
O(7)	72(5)	68(5)	126(6)	-48(5)	4(5)	-10(4)
O(8)	84(6)	47(4)	125(6)	-34(4)	-20(5)	-3(4)

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

	x	y	z	U(eq)
H(2)	9345	1453	8133	143
H(3A)	9540	245	7336	166
H(3B)	10791	646	7572	166
H(4A)	8710	1827	6784	195
H(4B)	10080	2158	6973	195
H(5A)	11301	1314	6424	380
H(5B)	10100	1913	5976	380
H(5C)	10019	826	6304	380
H(6A)	9210	-523	8427	276
H(6B)	10317	-24	8678	276
H(7A)	7762	-89	9026	316
H(7B)	8840	447	9268	316
H(8A)	8808	-1545	9582	394
H(8B)	8686	-909	10056	394
H(8C)	10093	-1090	9738	394
H(10)	4073	2336	5664	131
H(11A)	5497	3879	5605	190
H(11B)	4818	3709	5007	190
H(12A)	6237	2264	5208	233
H(12B)	7011	2604	5716	233
H(13A)	6958	3488	4377	370
H(13B)	8274	3033	4793	370
H(13C)	7509	3996	4855	370
H(14A)	2240	3218	6140	200
H(14B)	2974	4139	5852	200
H(15A)	2332	4267	4874	286
H(15B)	2308	3173	4993	286
H(16A)	174	3225	5199	792
H(16B)	254	4217	4700	792
H(16C)	194	4146	5429	792
H(18)	3518	-1622	8568	109
H(19)	3328	-1523	9579	166
H(20)	3798	-134	9820	172
H(21)	4206	1121	9009	119

H(23)	3475	4810	8205	119
H(24)	1180	4749	8071	136
H(25)	463	3297	7956	132
H(26)	2117	2144	7864	112
H(28)	8088	5907	9069	115
H(29A)	6028	6958	9131	232
H(29B)	5305	6044	9452	232
H(30A)	7668	6155	9998	345
H(30B)	6307	5803	10311	345
H(31A)	6679	7680	9840	497
H(31B)	6921	7102	10557	497
H(31C)	5449	7257	10250	497
H(32A)	7387	4488	9768	135
H(32B)	6404	4430	9224	135
H(33A)	9268	4325	9139	148
H(33B)	8293	4290	8583	148
H(34A)	8401	2868	9775	305
H(34B)	9266	2723	9194	305
H(34C)	7661	2809	9156	305
H(36)	1595	7048	6933	134
H(37A)	1768	9134	6482	246
H(37B)	2616	8497	6096	246
H(38A)	589	7653	6135	440
H(38B)	-224	8481	6371	440
H(39A)	1125	9439	5476	543
H(39B)	-371	9218	5369	543
H(39C)	886	8582	5204	543
H(40A)	293	7897	7489	149
H(40B)	1608	8248	7709	149
H(41A)	975	6343	8076	175
H(41B)	2358	6646	8265	175
H(42A)	1170	7519	8865	287
H(42B)	938	6436	9102	287
H(42C)	-197	7173	8691	287
H(44)	7718	3836	6578	109
H(45)	9935	4116	6564	127
H(46)	10544	5506	6733	134
H(47)	8849	6600	6885	101

H(49)	6937	10313	6388	113
H(50)	6601	10408	5347	141
H(51)	6209	9039	5063	146
H(52)	6185	7659	5831	103
H(1N2)	4171	296	7310	103
H(2N2)	3845	-711	7458	103
H(1N4)	6044	3130	8136	97
H(2N4)	5738	4106	8218	97
H(1N6)	4994	5428	6752	103
H(2N6)	5356	4498	6607	103
H(1N8)	7156	8269	7630	89
H(2N8)	7310	9309	7459	89

Appendix B: Crystal structure data of [$Co_2(valp)_4(quin)_2$] (3):

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

	x	y	z	U(eq)
C(1)	8964(6)	444(10)	4401(5)	60(3)
C(2)	8295(9)	573(14)	4113(9)	111(6)
C(3)	7865(15)	1360(30)	4346(12)	191(11)
C(4)	7727(15)	1390(30)	4947(11)	177(11)
C(5)	7304(12)	2330(20)	5218(11)	165(9)
C(6)	8120(20)	-180(40)	3670(20)	278(19)
C(7)	8561(19)	-490(30)	3160(17)	245(15)
C(8)	8110(20)	-1570(40)	2940(20)	350(30)
C(9)	10624(6)	-585(11)	4043(5)	65(3)
C(10)	10983(10)	-885(18)	3491(9)	122(6)
C(11)	10563(17)	-1620(30)	3109(14)	217(13)
C(12)	10730(30)	-2360(40)	2617(19)	360(30)
C(13)	10090(20)	-2730(40)	2337(16)	300(20)
C(14)	11402(14)	-20(30)	3229(14)	205(12)
C(15)	12003(14)	220(30)	3524(13)	195(11)
C(16)	12466(17)	1080(30)	3255(16)	247(16)
C(17)	10493(7)	3250(13)	4211(8)	93(4)
C(18)	10651(8)	4417(16)	4017(10)	117(6)

C(19)	10835(7)	5225(14)	4411(12)	118(7)
C(20)	10851(6)	4902(11)	5020(9)	95(6)
C(21)	10699(6)	3732(10)	5191(7)	72(3)
C(22)	10746(7)	3410(11)	5772(8)	86(4)
C(23)	10928(8)	4200(14)	6200(9)	111(6)
C(24)	11076(10)	5365(18)	6030(14)	150(10)
C(25)	11037(9)	5705(12)	5457(13)	124(8)
Co(1)	10146(1)	1202(1)	4922(1)	65(1)
N(1)	10507(5)	2926(7)	4767(5)	69(3)
O(1)	9310(4)	1329(6)	4431(4)	80(3)
O(2)	9089(4)	-572(7)	4593(4)	78(2)
O(3)	10569(5)	483(8)	4175(4)	83(3)
O(4)	10403(4)	-1438(7)	4333(4)	80(3)

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

C(1)-O(1)	1.225(13)
C(1)-O(2)	1.249(13)
C(1)-C(2)	1.525(19)
C(2)-C(3)	1.36(3)
C(2)-C(6)	1.36(4)
C(2)-H(2)	0.9800
C(3)-C(4)	1.379(17)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.49(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-C(7)	1.50(5)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.61(5)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-H(8A)	0.9601

C(8)-H(8B)	0.9601
C(8)-H(8C)	0.9601
C(9)-O(3)	1.242(14)
C(9)-O(4)	1.245(13)
C(9)-C(10)	1.48(2)
C(10)-C(14)	1.42(3)
C(10)-C(11)	1.47(3)
C(10)-H(10)	0.9800
C(11)-C(12)	1.421(19)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.50(6)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.426(18)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.48(4)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-N(1)	1.300(17)
C(17)-C(18)	1.42(2)
C(17)-H(17)	0.9300
C(18)-C(19)	1.32(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.41(3)
C(19)-H(19)	0.9300
C(20)-C(25)	1.39(3)
C(20)-C(21)	1.406(18)
C(21)-C(22)	1.357(19)
C(21)-N(1)	1.371(16)
C(22)-C(23)	1.36(2)

C(22)-H(22)	0.9300
C(23)-C(24)	1.40(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.34(3)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
Co(1)-O(4)#1	2.034(8)
Co(1)-O(2)#1	2.037(9)
Co(1)-O(1)	2.046(9)
Co(1)-O(3)	2.055(9)
Co(1)-N(1)	2.106(9)
Co(1)-Co(1)#1	2.791(3)
O(2)-Co(1)#1	2.037(9)
O(4)-Co(1)#1	2.034(8)

O(1)-C(1)-O(2)	127.2(11)
O(1)-C(1)-C(2)	118.0(11)
O(2)-C(1)-C(2)	114.8(11)
C(3)-C(2)-C(6)	121(3)
C(3)-C(2)-C(1)	119.1(19)
C(6)-C(2)-C(1)	120(2)
C(3)-C(2)-H(2)	91.9
C(6)-C(2)-H(2)	91.9
C(1)-C(2)-H(2)	91.9
C(2)-C(3)-C(4)	122(3)
C(2)-C(3)-H(3A)	106.9
C(4)-C(3)-H(3A)	106.9
C(2)-C(3)-H(3B)	106.9
C(4)-C(3)-H(3B)	106.9
H(3A)-C(3)-H(3B)	106.7
C(3)-C(4)-C(5)	122(3)
C(3)-C(4)-H(4A)	106.8
C(5)-C(4)-H(4A)	106.8
C(3)-C(4)-H(4B)	106.8
C(5)-C(4)-H(4B)	106.8
H(4A)-C(4)-H(4B)	106.6
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5

H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(2)-C(6)-C(7)	123(4)
C(2)-C(6)-H(6A)	106.7
C(7)-C(6)-H(6A)	106.7
C(2)-C(6)-H(6B)	106.7
C(7)-C(6)-H(6B)	106.7
H(6A)-C(6)-H(6B)	106.6
C(6)-C(7)-C(8)	93(3)
C(6)-C(7)-H(7A)	113.1
C(8)-C(7)-H(7A)	113.0
C(6)-C(7)-H(7B)	113.0
C(8)-C(7)-H(7B)	113.0
H(7A)-C(7)-H(7B)	110.4
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(3)-C(9)-O(4)	126.0(11)
O(3)-C(9)-C(10)	117.7(13)
O(4)-C(9)-C(10)	116.3(13)
C(14)-C(10)-C(11)	120(2)
C(14)-C(10)-C(9)	119(2)
C(11)-C(10)-C(9)	108.9(19)
C(14)-C(10)-H(10)	101.5
C(11)-C(10)-H(10)	101.5
C(9)-C(10)-H(10)	101.5
C(12)-C(11)-C(10)	130(4)
C(12)-C(11)-H(11A)	104.8
C(10)-C(11)-H(11A)	104.8
C(12)-C(11)-H(11B)	104.8
C(10)-C(11)-H(11B)	104.8
H(11A)-C(11)-H(11B)	105.8
C(11)-C(12)-C(13)	106(4)

C(11)-C(12)-H(12A)	110.5
C(13)-C(12)-H(12A)	110.5
C(11)-C(12)-H(12B)	110.5
C(13)-C(12)-H(12B)	110.5
H(12A)-C(12)-H(12B)	108.7
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-C(15)	118(3)
C(10)-C(14)-H(14A)	107.9
C(15)-C(14)-H(14A)	107.9
C(10)-C(14)-H(14B)	107.9
C(15)-C(14)-H(14B)	107.9
H(14A)-C(14)-H(14B)	107.2
C(14)-C(15)-C(16)	119(3)
C(14)-C(15)-H(15A)	107.5
C(16)-C(15)-H(15A)	107.5
C(14)-C(15)-H(15B)	107.5
C(16)-C(15)-H(15B)	107.5
H(15A)-C(15)-H(15B)	107.0
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(1)-C(17)-C(18)	123.2(16)
N(1)-C(17)-H(17)	118.4
C(18)-C(17)-H(17)	118.4
C(19)-C(18)-C(17)	119.7(18)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(18)-C(19)-C(20)	118.4(13)
C(18)-C(19)-H(19)	120.8
C(20)-C(19)-H(19)	120.8

C(25)-C(20)-C(21)	118.5(18)
C(25)-C(20)-C(19)	121.5(16)
C(21)-C(20)-C(19)	120.0(15)
C(22)-C(21)-N(1)	120.7(11)
C(22)-C(21)-C(20)	119.8(14)
N(1)-C(21)-C(20)	119.5(15)
C(21)-C(22)-C(23)	121.6(14)
C(21)-C(22)-H(22)	119.2
C(23)-C(22)-H(22)	119.2
C(22)-C(23)-C(24)	119(2)
C(22)-C(23)-H(23)	120.7
C(24)-C(23)-H(23)	120.7
C(25)-C(24)-C(23)	121.0(19)
C(25)-C(24)-H(24)	119.5
C(23)-C(24)-H(24)	119.5
C(24)-C(25)-C(20)	120.5(16)
C(24)-C(25)-H(25)	119.7
C(20)-C(25)-H(25)	119.7
O(4)#1-Co(1)-O(2)#1	92.0(4)
O(4)#1-Co(1)-O(1)	88.2(4)
O(2)#1-Co(1)-O(1)	163.6(3)
O(4)#1-Co(1)-O(3)	163.1(3)
O(2)#1-Co(1)-O(3)	88.5(4)
O(1)-Co(1)-O(3)	86.7(4)
O(4)#1-Co(1)-N(1)	102.2(4)
O(2)#1-Co(1)-N(1)	97.9(4)
O(1)-Co(1)-N(1)	98.2(4)
O(3)-Co(1)-N(1)	94.5(4)
O(4)#1-Co(1)-Co(1)#1	84.5(2)
O(2)#1-Co(1)-Co(1)#1	76.3(2)
O(1)-Co(1)-Co(1)#1	87.4(2)
O(3)-Co(1)-Co(1)#1	79.2(2)
N(1)-Co(1)-Co(1)#1	171.4(3)
C(17)-N(1)-C(21)	119.2(11)
C(17)-N(1)-Co(1)	114.1(9)
C(21)-N(1)-Co(1)	126.5(9)
C(1)-O(1)-Co(1)	117.4(8)
C(1)-O(2)-Co(1)#1	131.4(8)

C(9)-O(3)-Co(1)	127.8(8)
C(9)-O(4)-Co(1)#1	122.0(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table 3: Anisotropic displacement parameters (Å^{2}x 10^3) for complex **3**. 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)	77(8)	53(6)	52(6)	-6(5)	-4(5)	-3(6)
C(2)	119(13)	66(9)	147(15)	-14(9)	-24(12)	29(9)
C(17)	90(10)	76(9)	111(12)	13(9)	14(9)	-10(8)
C(18)	91(11)	93(12)	168(18)	65(13)	13(11)	-18(10)
C(19)	64(9)	56(9)	230(20)	57(12)	12(12)	-14(7)
C(20)	44(7)	43(7)	198(19)	-3(9)	23(9)	-6(5)
C(21)	53(7)	42(6)	120(11)	-5(7)	1(7)	-9(5)
C(22)	80(9)	47(7)	132(13)	-10(8)	1(9)	-8(6)
C(23)	103(12)	84(10)	145(15)	-47(10)	9(10)	-18(9)
C(24)	105(14)	79(13)	270(30)	-86(17)	14(19)	-19(11)
C(25)	87(11)	25(6)	260(30)	-3(12)	-3(16)	-6(6)
Co(1)	78(1)	36(1)	81(1)	1(1)	3(1)	-12(1)
N(1)	67(6)	35(5)	105(8)	12(5)	7(6)	-3(4)
O(1)	80(6)	43(4)	117(7)	2(4)	-18(5)	-12(4)
O(2)	76(6)	46(4)	113(7)	6(4)	-8(5)	-6(4)
O(3)	99(7)	69(5)	83(6)	-10(4)	16(5)	-13(5)
O(4)	85(6)	56(5)	98(6)	-8(4)	25(5)	-17(4)

Table 4: Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for complex **3**.

	x	y	z	U(eq)
H(2)	8458	1162	3828	133
H(3A)	7455	1240	4141	229
H(3B)	8016	2149	4237	229
H(4A)	8142	1426	5154	213
H(4B)	7533	630	5047	213
H(5A)	7490	3095	5143	247

H(5B)	7273	2197	5640	247
H(5C)	6878	2286	5044	247
H(6A)	7723	140	3493	334
H(6B)	7998	-927	3855	334
H(7A)	8990	-736	3289	294
H(7B)	8596	146	2867	294
H(8A)	7665	-1397	3024	526
H(8B)	8238	-2284	3148	526
H(8C)	8169	-1685	2520	526
H(10)	11297	-1472	3637	147
H(11A)	10334	-2143	3383	260
H(11B)	10237	-1080	2955	260
H(12A)	10964	-3058	2751	435
H(12B)	10992	-1932	2334	435
H(13A)	10002	-3544	2429	449
H(13B)	10119	-2631	1912	449
H(13C)	9746	-2236	2489	449
H(14A)	11162	717	3197	246
H(14B)	11501	-281	2827	246
H(15A)	12231	-527	3570	234
H(15B)	11899	505	3921	234
H(16A)	12903	861	3358	371
H(16B)	12376	1865	3403	371
H(16C)	12418	1074	2829	371
H(17)	10373	2690	3927	111
H(18)	10625	4613	3615	141
H(19)	10952	5987	4291	142
H(22)	10652	2631	5881	104
H(23)	10954	3970	6597	133
H(24)	11203	5913	6318	180
H(25)	11136	6485	5353	149

Appendix C: Crystal structure data of [Co(valp)$_2$(2,9-dmp)] (4):

Table 1: 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)	3222(8)	4239(3)	4417(9)	70(3)
C(2)	3139(9)	4194(4)	2983(10)	84(3)
C(3)	3966(12)	4166(5)	2292(10)	99(4)
C(4)	4816(11)	4187(5)	2945(12)	99(4)
C(5)	4938(9)	4222(4)	4376(10)	77(3)
C(6)	4125(8)	4249(3)	5120(8)	69(2)
C(7)	2234(14)	4178(6)	2355(13)	116(5)
C(8)	1466(12)	4191(6)	3065(17)	121(5)
C(9)	1600(10)	4234(5)	4516(13)	100(3)
C(10)	5798(10)	4246(5)	5140(14)	99(4)
C(11)	5833(9)	4283(5)	6522(14)	97(3)
C(12)	5014(9)	4294(4)	7172(11)	83(3)
C(13)	750(10)	4235(7)	5343(17)	137(5)
C(14)	5076(10)	4363(6)	8711(11)	108(4)
C(15)	2738(9)	3389(5)	8645(10)	96(4)
C(16)	2764(12)	2803(6)	9493(14)	125(5)
C(17)	3590(20)	2481(12)	9420(30)	218(10)
C(18)	4500(20)	2581(13)	9170(30)	235(11)
C(19)	5160(20)	2537(14)	10180(30)	288(15)
C(20)	1908(14)	2520(9)	9450(20)	164(6)
C(21)	1090(20)	2834(13)	9790(30)	231(11)
C(22)	250(20)	2576(15)	10020(30)	316(17)
C(23)	2251(13)	5298(6)	8110(14)	117(5)
C(24)	1868(15)	5907(9)	8600(20)	173(8)
C(25)	1920(20)	5884(16)	10030(30)	292(16)
C(26)	1220(30)	5638(19)	10740(40)	410(30)
C(27)	1170(30)	5931(17)	12010(40)	380(20)
C(28)	2200(20)	6409(12)	7970(30)	255(13)
C(29)	1900(20)	6475(13)	6590(30)	263(13)
C(30)	2310(30)	6988(17)	6020(40)	420(30)
Co(1)	2825(1)	4317(1)	7281(1)	74(1)
N(1)	2443(7)	4275(3)	5139(8)	75(2)
N(2)	4176(6)	4278(3)	6507(6)	65(2)

O(1)	2492(7)	3387(3)	7407(7)	114(3)
O(2)	3006(8)	3860(4)	9178(7)	127(4)
O(3)	3073(7)	5222(3)	7913(9)	110(3)
O(4)	1687(8)	4883(5)	7871(13)	168(5)

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

C(1)-N(1)	1.366(12)
C(1)-C(6)	1.399(14)
C(1)-C(2)	1.412(12)
C(2)-C(7)	1.372(19)
C(2)-C(3)	1.406(16)
C(3)-C(4)	1.314(18)
C(3)-H(3)	0.9300
C(4)-C(5)	1.409(15)
C(4)-H(4)	0.9300
C(5)-C(10)	1.375(16)
C(5)-C(6)	1.417(13)
C(6)-N(2)	1.366(10)
C(7)-C(8)	1.34(2)
C(7)-H(7)	0.9300
C(8)-C(9)	1.431(19)
C(8)-H(8)	0.9300
C(9)-N(1)	1.295(15)
C(9)-C(13)	1.509(19)
C(10)-C(11)	1.362(16)
C(10)-H(10)	0.9300
C(11)-C(12)	1.371(16)
C(11)-H(11)	0.9300
C(12)-N(2)	1.304(13)
C(12)-C(14)	1.520(14)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-O(2)	1.217(12)

C(15)-O(1)	1.240(12)
C(15)-C(16)	1.547(16)
C(16)-C(20)	1.36(2)
C(16)-C(17)	1.37(3)
C(16)-H(16)	0.9800
C(17)-C(18)	1.35(3)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-C(19)	1.31(3)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-C(21)	1.41(3)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.36(3)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-O(3)	1.207(16)
C(23)-O(4)	1.229(15)
C(23)-C(24)	1.55(2)
C(24)-C(28)	1.379(16)
C(24)-C(25)	1.406(17)
C(24)-H(24)	0.9800
C(25)-C(26)	1.371(18)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-C(27)	1.418(19)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600

C(28)-C(29)	1.404(17)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-C(30)	1.419(18)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600
Co(1)-N(2)	2.119(8)
Co(1)-O(3)	2.124(8)
Co(1)-O(2)	2.125(7)
Co(1)-O(1)	2.126(7)
Co(1)-N(1)	2.137(8)
Co(1)-O(4)	2.161(11)

N(1)-C(1)-C(6)	118.9(8)
N(1)-C(1)-C(2)	121.7(10)
C(6)-C(1)-C(2)	119.4(10)
C(7)-C(2)-C(3)	124.2(11)
C(7)-C(2)-C(1)	116.6(12)
C(3)-C(2)-C(1)	119.2(11)
C(4)-C(3)-C(2)	121.6(10)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	121.4(11)
C(3)-C(4)-H(4)	119.3
C(5)-C(4)-H(4)	119.3
C(10)-C(5)-C(4)	125.2(11)
C(10)-C(5)-C(6)	115.6(9)
C(4)-C(5)-C(6)	119.1(11)
N(2)-C(6)-C(1)	117.6(9)
N(2)-C(6)-C(5)	123.1(9)
C(1)-C(6)-C(5)	119.3(8)
C(8)-C(7)-C(2)	121.9(12)
C(8)-C(7)-H(7)	119.1
C(2)-C(7)-H(7)	119.1
C(7)-C(8)-C(9)	118.7(13)

C(7)-C(8)-H(8)	120.6
C(9)-C(8)-H(8)	120.6
N(1)-C(9)-C(8)	121.1(13)
N(1)-C(9)-C(13)	119.1(12)
C(8)-C(9)-C(13)	119.8(14)
C(11)-C(10)-C(5)	120.3(11)
C(11)-C(10)-H(10)	119.9
C(5)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	120.7(11)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-H(11)	119.6
N(2)-C(12)-C(11)	122.1(10)
N(2)-C(12)-C(14)	118.4(10)
C(11)-C(12)-C(14)	119.4(11)
C(9)-C(13)-H(13A)	109.5
C(9)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(9)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(2)-C(15)-O(1)	118.6(10)
O(2)-C(15)-C(16)	119.9(10)
O(1)-C(15)-C(16)	121.4(11)
C(20)-C(16)-C(17)	120.9(19)
C(20)-C(16)-C(15)	113.1(15)
C(17)-C(16)-C(15)	112.9(15)
C(20)-C(16)-H(16)	102.6
C(17)-C(16)-H(16)	102.5
C(15)-C(16)-H(16)	101.5
C(18)-C(17)-C(16)	139(3)
C(18)-C(17)-H(17A)	101.2
C(16)-C(17)-H(17A)	100.7

C(18)-C(17)-H(17B)	103.1
C(16)-C(17)-H(17B)	104.5
H(17A)-C(17)-H(17B)	105.0
C(19)-C(18)-C(17)	119(3)
C(19)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18A)	107.2
C(19)-C(18)-H(18B)	107.4
C(17)-C(18)-H(18B)	106.5
H(18A)-C(18)-H(18B)	107.1
C(18)-C(19)-H(19A)	107.9
C(18)-C(19)-H(19B)	109.2
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	111.3
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(16)-C(20)-C(21)	121(2)
C(16)-C(20)-H(20A)	105.8
C(21)-C(20)-H(20A)	104.2
C(16)-C(20)-H(20B)	108.9
C(21)-C(20)-H(20B)	109.8
H(20A)-C(20)-H(20B)	106.5
C(22)-C(21)-C(20)	125(3)
C(22)-C(21)-H(21A)	111.4
C(20)-C(21)-H(21A)	108.9
C(22)-C(21)-H(21B)	99.4
C(20)-C(21)-H(21B)	103.1
H(21A)-C(21)-H(21B)	106.3
C(21)-C(22)-H(22A)	103.8
C(21)-C(22)-H(22B)	116.4
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	107.9
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(3)-C(23)-O(4)	118.7(13)
O(3)-C(23)-C(24)	122.7(14)
O(4)-C(23)-C(24)	118.5(16)
C(28)-C(24)-C(25)	119(2)
C(28)-C(24)-C(23)	115.1(18)

C(25)-C(24)-C(23)	107(2)
C(28)-C(24)-H(24)	104.3
C(25)-C(24)-H(24)	105.0
C(23)-C(24)-H(24)	104.4
C(26)-C(25)-C(24)	124(3)
C(26)-C(25)-H(25A)	105.3
C(24)-C(25)-H(25A)	106.6
C(26)-C(25)-H(25B)	106.5
C(24)-C(25)-H(25B)	107.4
H(25A)-C(25)-H(25B)	106.4
C(25)-C(26)-C(27)	111(3)
C(25)-C(26)-H(26A)	110.2
C(27)-C(26)-H(26A)	110.7
C(25)-C(26)-H(26B)	108.6
C(27)-C(26)-H(26B)	107.8
H(26A)-C(26)-H(26B)	108.1
C(26)-C(27)-H(27A)	107.8
C(26)-C(27)-H(27B)	110.7
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.9
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(24)-C(28)-C(29)	116(2)
C(24)-C(28)-H(28A)	108.9
C(29)-C(28)-H(28A)	109.0
C(24)-C(28)-H(28B)	108.0
C(29)-C(28)-H(28B)	107.4
H(28A)-C(28)-H(28B)	107.5
C(28)-C(29)-C(30)	112(2)
C(28)-C(29)-H(29A)	109.7
C(30)-C(29)-H(29A)	108.7
C(28)-C(29)-H(29B)	108.0
C(30)-C(29)-H(29B)	110.9
H(29A)-C(29)-H(29B)	107.9
C(29)-C(30)-H(30A)	109.8
C(29)-C(30)-H(30B)	110.9
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	107.7

H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
N(2)-Co(1)-O(3)	90.8(3)
N(2)-Co(1)-O(2)	104.7(4)
O(3)-Co(1)-O(2)	100.9(3)
N(2)-Co(1)-O(1)	101.1(3)
O(3)-Co(1)-O(1)	159.1(3)
O(2)-Co(1)-O(1)	59.6(3)
N(2)-Co(1)-N(1)	78.5(3)
O(3)-Co(1)-N(1)	110.7(3)
O(2)-Co(1)-N(1)	148.2(3)
O(1)-Co(1)-N(1)	88.7(3)
N(2)-Co(1)-O(4)	146.8(4)
O(3)-Co(1)-O(4)	58.5(4)
O(2)-Co(1)-O(4)	94.4(5)
O(1)-Co(1)-O(4)	112.1(4)
N(1)-Co(1)-O(4)	99.3(5)
C(9)-N(1)-C(1)	119.9(9)
C(9)-N(1)-Co(1)	128.0(8)
C(1)-N(1)-Co(1)	111.8(6)
C(12)-N(2)-C(6)	118.2(9)
C(12)-N(2)-Co(1)	128.7(6)
C(6)-N(2)-Co(1)	113.1(6)
C(15)-O(1)-Co(1)	90.5(6)
C(15)-O(2)-Co(1)	91.2(6)
C(23)-O(3)-Co(1)	92.6(8)
C(23)-O(4)-Co(1)	90.2(10)

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	115(8)	46(5)	50(5)	1(4)	13(5)	-26(5)
C(2)	136(10)	60(6)	53(5)	-10(4)	-15(6)	-33(6)
C(3)	169(12)	88(8)	47(5)	-19(5)	39(7)	-48(8)
C(4)	156(12)	71(7)	78(7)	-22(5)	52(8)	-35(7)
C(5)	115(8)	52(5)	67(6)	-15(4)	30(6)	-22(5)
C(6)	111(8)	45(4)	50(4)	-11(3)	8(5)	-24(4)

C(7)	184(15)	93(9)	67(7)	3(6)	-7(9)	-33(9)
C(8)	122(11)	113(11)	117(12)	6(8)	-52(9)	-25(8)
C(9)	120(10)	83(8)	93(8)	-4(6)	-2(8)	-20(7)
C(10)	108(9)	76(7)	115(10)	-17(6)	31(8)	-11(6)
C(11)	95(8)	84(7)	108(9)	-13(7)	-11(7)	-9(6)
C(12)	107(8)	65(6)	76(6)	-3(5)	7(6)	-24(6)
C(13)	98(10)	142(14)	168(15)	-5(10)	-6(10)	-13(9)
C(14)	139(10)	117(9)	64(6)	8(6)	-14(6)	-23(8)
C(15)	148(11)	85(7)	55(6)	9(5)	9(6)	-31(7)
C(16)	170(14)	102(9)	107(10)	24(8)	34(9)	-39(10)
C(23)	151(14)	97(10)	108(10)	-36(7)	46(10)	-25(9)
C(24)	204(18)	158(16)	170(17)	-50(14)	92(15)	-9(14)
Co(1)	117(1)	62(1)	45(1)	-6(1)	22(1)	-23(1)
N(1)	98(6)	59(4)	66(5)	1(4)	-6(5)	-21(4)
N(2)	95(6)	60(4)	39(3)	-13(3)	3(3)	-28(4)
O(1)	195(9)	79(5)	65(5)	-2(4)	0(5)	-45(5)
O(2)	240(11)	95(6)	47(4)	-1(4)	18(5)	-63(6)
O(3)	127(7)	78(5)	131(7)	-17(5)	46(6)	-15(5)
O(4)	159(9)	139(9)	217(13)	-82(9)	72(9)	-35(7)

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

	x	y	z	U(eq)
H(3)	3911	4130	1349	119
H(4)	5348	4180	2453	119
H(7)	2151	4158	1410	139
H(8)	859	4173	2623	145
H(10)	6359	4238	4711	118
H(11)	6418	4302	7029	116
H(13A)	765	3883	5906	205
H(13B)	179	4236	4742	205
H(13C)	767	4588	5906	205
H(14A)	4617	4654	8952	162
H(14B)	5701	4496	9033	162
H(14C)	4948	3983	9119	162
H(16)	2839	2961	10423	150

H(17A)	3666	2308	10321	261
H(17B)	3403	2146	8818	261
H(18A)	4644	2310	8444	282
H(18B)	4525	2987	8812	282
H(19A)	5762	2613	9833	432
H(19B)	5157	2137	10551	432
H(19C)	5062	2823	10886	432
H(20A)	1983	2200	10120	197
H(20B)	1782	2328	8572	197
H(21A)	1278	3135	10475	277
H(21B)	896	3053	8962	277
H(22A)	421	2261	10660	474
H(22B)	-115	2409	9241	474
H(22C)	-128	2871	10440	474
H(24)	1189	5898	8302	208
H(25A)	2489	5663	10324	350
H(25B)	2011	6292	10360	350
H(26A)	1325	5210	10866	488
H(26B)	612	5692	10213	488
H(27A)	1603	5731	12663	568
H(27B)	537	5907	12294	568
H(27C)	1348	6345	11937	568
H(28A)	2891	6406	8080	306
H(28B)	1991	6762	8440	306
H(29A)	1215	6515	6474	315
H(29B)	2069	6111	6118	315
H(30A)	2954	7037	6406	624
H(30B)	1955	7345	6182	624
H(30C)	2311	6924	5055	624

Appendix D: Crystal structure data of [Co(valp)$_2$(H$_2$O)(1,10-phen)] (5):

Table 1: 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)	303(5)	2468(5)	-1126(6)	54(2)
C(2)	-365(5)	2570(6)	-1702(7)	67(3)

C(3)	-769(4)	1996(6)	-2027(6)	60(3)
C(4)	-524(4)	1310(5)	-1777(5)	46(2)
C(5)	159(4)	1257(5)	-1174(5)	41(2)
C(6)	438(4)	574(4)	-872(4)	36(2)
C(7)	36(4)	-42(4)	-1172(5)	41(2)
C(8)	-651(4)	32(6)	-1786(6)	59(3)
C(9)	-901(4)	666(6)	-2075(6)	58(2)
C(10)	1344(4)	-68(4)	-10(5)	44(2)
C(11)	983(5)	-710(5)	-251(6)	54(2)
C(12)	329(5)	-693(5)	-826(6)	54(2)
C(13)	1206(4)	2330(5)	1150(6)	53(2)
C(14)	938(6)	2819(7)	1737(8)	79(3)
C(15)	1478(7)	3158(8)	2384(9)	109(5)
C(16)	2130(7)	2869(9)	2878(10)	127(7)
C(17)	2595(8)	3211(10)	3598(10)	134(7)
C(18)	270(6)	3144(8)	1312(9)	106(5)
C(19)	-337(7)	2800(8)	762(10)	103(5)
C(20)	-979(8)	3160(9)	313(11)	134(6)
C(21)	3007(4)	1258(5)	1362(5)	47(2)
C(22)	3423(5)	637(5)	1891(6)	57(2)
C(23)	3629(7)	96(7)	1315(10)	102(4)
C(24)	4071(7)	357(8)	736(10)	103(4)
C(25)	4801(9)	415(11)	1099(14)	169(9)
C(26)	3045(8)	354(7)	2491(8)	95(4)
C(27)	2860(11)	816(10)	3086(10)	139(7)
C(28)	2505(9)	541(11)	3715(9)	148(8)
Co(1)	1572(1)	1574(1)	67(1)	33(1)
N(1)	565(3)	1834(3)	-866(4)	39(1)
N(2)	1092(3)	557(3)	-304(4)	31(1)
O(1)	1508(3)	2603(3)	630(4)	54(2)
O(2)	1099(3)	1679(3)	1156(4)	61(2)
O(3)	2447(3)	1087(3)	811(4)	52(2)
O(4)	3255(3)	1860(3)	1523(4)	63(2)
O(1W)	2091(3)	1893(3)	-821(3)	46(1)

Table 2: Bond lengths [Å] and angles [°] for complex **5**:

C(1)-N(1)	1.319(10)
C(1)-C(2)	1.389(12)
C(1)-H(1)	0.9300
C(2)-C(3)	1.355(14)
C(2)-H(2)	0.9300
C(3)-C(4)	1.396(13)
C(3)-H(3)	0.9300
C(4)-C(5)	1.421(10)
C(4)-C(9)	1.430(12)
C(5)-N(1)	1.354(10)
C(5)-C(6)	1.428(11)
C(6)-N(2)	1.351(9)
C(6)-C(7)	1.408(10)
C(7)-C(12)	1.401(12)
C(7)-C(8)	1.437(11)
C(8)-C(9)	1.323(13)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-N(2)	1.312(9)
C(10)-C(11)	1.398(11)
C(10)-H(10)	0.9300
C(11)-C(12)	1.356(12)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-O(2)	1.243(11)
C(13)-O(1)	1.264(11)
C(13)-C(14)	1.517(13)
C(14)-C(15)	1.415(15)
C(14)-C(18)	1.433(15)
C(14)-H(14)	0.9800
C(15)-C(16)	1.411(18)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.416(17)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600

C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(19)	1.423(16)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(20)	1.434(17)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-O(4)	1.231(10)
C(21)-O(3)	1.246(9)
C(21)-C(22)	1.540(12)
C(22)-C(26)	1.474(15)
C(22)-C(23)	1.508(17)
C(22)-H(22)	0.9800
C(23)-C(24)	1.523(18)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.39(2)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(27)	1.418(19)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-C(28)	1.476(19)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
Co(1)-O(3)	2.017(5)
Co(1)-O(1W)	2.067(5)
Co(1)-N(2)	2.141(6)

Co(1)-O(1)	2.158(6)
Co(1)-N(1)	2.177(6)
Co(1)-O(2)	2.214(7)
O(1W)-H(1W1)	0.8741
O(1W)-H(2W1)	0.8234

N(1)-C(1)-C(2)	123.2(9)
N(1)-C(1)-H(1)	118.4
C(2)-C(1)-H(1)	118.4
C(3)-C(2)-C(1)	119.2(9)
C(3)-C(2)-H(2)	120.4
C(1)-C(2)-H(2)	120.4
C(2)-C(3)-C(4)	120.5(7)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	116.4(8)
C(3)-C(4)-C(9)	125.6(7)
C(5)-C(4)-C(9)	118.0(8)
N(1)-C(5)-C(4)	122.5(8)
N(1)-C(5)-C(6)	117.9(6)
C(4)-C(5)-C(6)	119.6(7)
N(2)-C(6)-C(7)	123.2(7)
N(2)-C(6)-C(5)	116.9(7)
C(7)-C(6)-C(5)	119.9(7)
C(12)-C(7)-C(6)	117.0(7)
C(12)-C(7)-C(8)	124.0(8)
C(6)-C(7)-C(8)	118.9(8)
C(9)-C(8)-C(7)	120.9(8)
C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(4)	122.6(8)
C(8)-C(9)-H(9)	118.7
C(4)-C(9)-H(9)	118.7
N(2)-C(10)-C(11)	124.3(7)
N(2)-C(10)-H(10)	117.9
C(11)-C(10)-H(10)	117.9
C(12)-C(11)-C(10)	118.5(8)
C(12)-C(11)-H(11)	120.7

C(10)-C(11)-H(11)	120.7
C(11)-C(12)-C(7)	119.8(8)
C(11)-C(12)-H(12)	120.1
C(7)-C(12)-H(12)	120.1
O(2)-C(13)-O(1)	121.1(8)
O(2)-C(13)-C(14)	120.3(9)
O(1)-C(13)-C(14)	118.6(9)
C(15)-C(14)-C(18)	123.7(11)
C(15)-C(14)-C(13)	114.7(9)
C(18)-C(14)-C(13)	112.8(9)
C(15)-C(14)-H(14)	99.9
C(18)-C(14)-H(14)	99.9
C(13)-C(14)-H(14)	99.9
C(16)-C(15)-C(14)	128.0(12)
C(16)-C(15)-H(15A)	105.3
C(14)-C(15)-H(15A)	105.3
C(16)-C(15)-H(15B)	105.3
C(14)-C(15)-H(15B)	105.3
H(15A)-C(15)-H(15B)	106.0
C(15)-C(16)-C(17)	124.2(13)
C(15)-C(16)-H(16A)	106.3
C(17)-C(16)-H(16A)	106.3
C(15)-C(16)-H(16B)	106.3
C(17)-C(16)-H(16B)	106.3
H(16A)-C(16)-H(16B)	106.4
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(14)	126.4(12)
C(19)-C(18)-H(18A)	105.7
C(14)-C(18)-H(18A)	105.7
C(19)-C(18)-H(18B)	105.7
C(14)-C(18)-H(18B)	105.7
H(18A)-C(18)-H(18B)	106.2
C(18)-C(19)-C(20)	124.2(13)

C(18)-C(19)-H(19A)	106.3
C(20)-C(19)-H(19A)	106.3
C(18)-C(19)-H(19B)	106.3
C(20)-C(19)-H(19B)	106.3
H(19A)-C(19)-H(19B)	106.4
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(4)-C(21)-O(3)	127.3(8)
O(4)-C(21)-C(22)	117.7(7)
O(3)-C(21)-C(22)	115.0(8)
C(26)-C(22)-C(23)	115.6(10)
C(26)-C(22)-C(21)	110.8(9)
C(23)-C(22)-C(21)	111.1(8)
C(26)-C(22)-H(22)	106.2
C(23)-C(22)-H(22)	106.2
C(21)-C(22)-H(22)	106.2
C(22)-C(23)-C(24)	117.2(11)
C(22)-C(23)-H(23A)	108.0
C(24)-C(23)-H(23A)	108.0
C(22)-C(23)-H(23B)	108.0
C(24)-C(23)-H(23B)	108.0
H(23A)-C(23)-H(23B)	107.2
C(25)-C(24)-C(23)	117.2(15)
C(25)-C(24)-H(24A)	108.0
C(23)-C(24)-H(24A)	108.0
C(25)-C(24)-H(24B)	108.0
C(23)-C(24)-H(24B)	108.0
H(24A)-C(24)-H(24B)	107.2
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

C(27)-C(26)-C(22)	119.8(12)
C(27)-C(26)-H(26A)	107.4
C(22)-C(26)-H(26A)	107.4
C(27)-C(26)-H(26B)	107.4
C(22)-C(26)-H(26B)	107.4
H(26A)-C(26)-H(26B)	106.9
C(26)-C(27)-C(28)	120.8(16)
C(26)-C(27)-H(27A)	107.1
C(28)-C(27)-H(27A)	107.1
C(26)-C(27)-H(27B)	107.1
C(28)-C(27)-H(27B)	107.1
H(27A)-C(27)-H(27B)	106.8
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
O(3)-Co(1)-O(1W)	92.7(2)
O(3)-Co(1)-N(2)	89.6(2)
O(1W)-Co(1)-N(2)	109.0(2)
O(3)-Co(1)-O(1)	107.1(2)
O(1W)-Co(1)-O(1)	97.5(2)
N(2)-Co(1)-O(1)	148.0(2)
O(3)-Co(1)-N(1)	165.7(2)
O(1W)-Co(1)-N(1)	88.7(2)
N(2)-Co(1)-N(1)	76.5(2)
O(1)-Co(1)-N(1)	86.8(2)
O(3)-Co(1)-O(2)	92.2(3)
O(1W)-Co(1)-O(2)	157.2(2)
N(2)-Co(1)-O(2)	93.2(2)
O(1)-Co(1)-O(2)	59.9(2)
N(1)-Co(1)-O(2)	91.9(2)
C(1)-N(1)-C(5)	118.2(7)
C(1)-N(1)-Co(1)	128.3(6)
C(5)-N(1)-Co(1)	113.4(5)
C(10)-N(2)-C(6)	117.2(6)
C(10)-N(2)-Co(1)	127.5(5)

C(6)-N(2)-Co(1)	115.3(5)
C(13)-O(1)-Co(1)	90.5(5)
C(13)-O(2)-Co(1)	88.5(5)
C(21)-O(3)-Co(1)	137.7(6)
Co(1)-O(1W)-H(1W1)	111.3
Co(1)-O(1W)-H(2W1)	116.4
H(1W1)-O(1W)-H(2W1)	128.5

Table 3: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	43(5)	54(5)	61(6)	15(4)	8(4)	0(4)
C(2)	53(5)	66(6)	78(7)	33(6)	13(5)	16(5)
C(3)	29(4)	92(7)	53(5)	39(5)	1(4)	12(4)
C(4)	25(3)	72(6)	36(4)	6(4)	1(3)	-11(4)
C(5)	28(4)	59(5)	39(4)	1(4)	13(3)	-12(3)
C(6)	34(4)	50(5)	27(3)	5(3)	11(3)	-8(3)
C(7)	38(4)	52(5)	35(4)	-5(3)	12(3)	-18(4)
C(8)	37(4)	81(7)	55(5)	-15(5)	6(4)	-28(5)
C(9)	33(4)	82(7)	50(5)	1(5)	-3(4)	-18(4)
C(10)	31(4)	45(5)	52(5)	7(4)	5(3)	0(3)
C(11)	54(5)	37(4)	70(6)	4(4)	14(5)	-4(4)
C(12)	64(6)	39(5)	60(5)	-7(4)	19(5)	-19(4)
C(13)	31(4)	73(6)	51(5)	-20(5)	6(4)	-9(4)
C(14)	63(6)	93(9)	78(8)	-33(6)	15(6)	1(6)
C(15)	83(9)	127(12)	100(10)	-65(9)	0(7)	19(8)
C(16)	76(9)	161(15)	127(12)	-94(11)	-1(8)	9(9)
C(17)	79(9)	193(18)	117(12)	-52(12)	8(8)	13(10)
C(18)	71(8)	118(11)	113(11)	-43(9)	0(7)	35(8)
C(19)	70(8)	108(11)	124(12)	-32(9)	19(8)	26(7)
C(20)	94(11)	154(16)	135(14)	-23(12)	-1(10)	49(10)
C(21)	35(4)	59(5)	40(4)	-1(4)	-3(3)	-6(4)
C(22)	55(5)	53(5)	49(5)	9(4)	-10(4)	-5(4)
C(23)	91(9)	70(8)	133(12)	31(8)	14(9)	9(7)
C(24)	90(10)	101(10)	131(12)	16(9)	50(9)	23(8)
C(25)	106(14)	180(20)	220(20)	53(17)	44(15)	-9(13)
C(26)	127(11)	82(9)	69(8)	35(7)	19(8)	13(8)

C(27)	210(20)	138(15)	89(11)	29(10)	70(12)	15(14)
C(28)	125(13)	240(20)	76(10)	13(12)	28(9)	-53(14)
Co(1)	25(1)	34(1)	36(1)	-2(1)	1(1)	-8(1)
N(1)	28(3)	38(3)	47(4)	8(3)	6(3)	-1(3)
N(2)	26(3)	35(3)	31(3)	-1(2)	6(2)	-5(2)
O(1)	39(3)	50(4)	70(4)	-9(3)	13(3)	-7(3)
O(2)	63(4)	55(4)	67(4)	-6(3)	21(3)	-19(3)
O(3)	37(3)	46(3)	58(4)	3(3)	-12(3)	1(2)
O(4)	46(3)	50(4)	75(4)	5(3)	-13(3)	-16(3)
O(1W)	45(3)	40(3)	55(3)	-6(3)	19(3)	-5(2)

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

	x	y	z	U(eq)
H(1)	578	2866	-913	65
H(2)	-532	3027	-1862	80
H(3)	-1213	2059	-2420	72
H(8)	-923	-371	-1984	71
H(9)	-1339	693	-2488	70
H(10)	1793	-86	384	53
H(11)	1186	-1139	-22	65
H(12)	75	-1112	-990	65
H(14)	778	2465	2087	95
H(15A)	1606	3577	2110	130
H(15B)	1244	3332	2799	130
H(16A)	2408	2773	2480	153
H(16B)	2017	2410	3082	153
H(17A)	2818	3608	3406	200
H(17B)	2953	2881	3899	200
H(17C)	2329	3376	3977	200
H(18A)	105	3365	1763	127
H(18B)	382	3531	975	127
H(19A)	-475	2435	1107	123
H(19B)	-171	2554	328	123
H(20A)	-1138	3454	708	201
H(20B)	-1340	2816	62	201
H(20C)	-890	3451	-134	201

H(22)	3869	839	2249	69
H(23A)	3196	-114	953	122
H(23B)	3894	-280	1677	122
H(24A)	3989	38	247	124
H(24B)	3892	821	514	124
H(25A)	4895	692	1617	253
H(25B)	5012	643	699	253
H(25C)	5003	-51	1233	253
H(26A)	2609	135	2148	114
H(26B)	3337	-23	2820	114
H(27A)	2555	1183	2755	166
H(27B)	3294	1050	3412	166
H(28A)	2006	482	3438	222
H(28B)	2568	871	4182	222
H(28C)	2709	91	3932	222
H(1W1)	2177	2350	-787	69
H(2W1)	2295	1580	-1018	69