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Transition metal complexes of aromatic hydrazide ligand.

Research Project

Submitted to the department of (chemistry) in partial fulfillment of the requirements for the degree of B.A or BSc. in (chemistry)

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Supervisor recommendation

I am the student's supervisor, Sumaya Sangar Sabir. I support that the student has completed all the requirements for submitting the research drawn entitled ‘Transition metal complexes of aromatic hydrazide ligand’’ according to the numbered administrative order / / on oct. in accordance with the instructions of Salahaddin university quality assurance and it is ready for discussion.

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Research project lecturer

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Transition metal complexes of aromatic hydrazide ligand

Sumaya Sangar Sabir & Lec. Rezan A. Saleh

Abstract

My research is about complexes of transition metals with the derivatives of aromatic hydrazide ligand. Hydrazides ligand is five-membered ring compound containing carbonyl oxygen and amino nitrogen as donor atoms with chemical formula [R-CO-NH-NH_2]. Hydrazides and their metallic complexes show fungicide and antibacterial activity. They also act as a good potential for oral drugs used for the treatment of genetic disorders like thalassemia. Transition metal complexes of hydrazides and also find application in chemotherapy as well as their hydrazone derivatives. Aromatic hydrazide ligand can form complexes with transition metals such as Mn(II), Co(II), Rh(II), Ni(II), Pd(II), Pt(II), Cu(II) and Cd(II) in which the hydrazide ligand can either acts as a neutral monodentate ligand that bound to the metal ions through amino nitrogen atom or it functions as a bidentate chelating ligand that coordinated to the metal ions through amino nitrogen and carbonyl oxygen atoms.

Also my research consists of some parts which include: Introduction and metal complexes of (Mn(II), Co(II), Rh(II), Ni(II), Pd(II), Pt(II), Cu(II), Cd(II)) with derivatives of aromatic hydrazide ligand.

Keywords: *Transition Metal complexes, aromatic, hydrazide ligand, review.*

Part One

1. Introduction

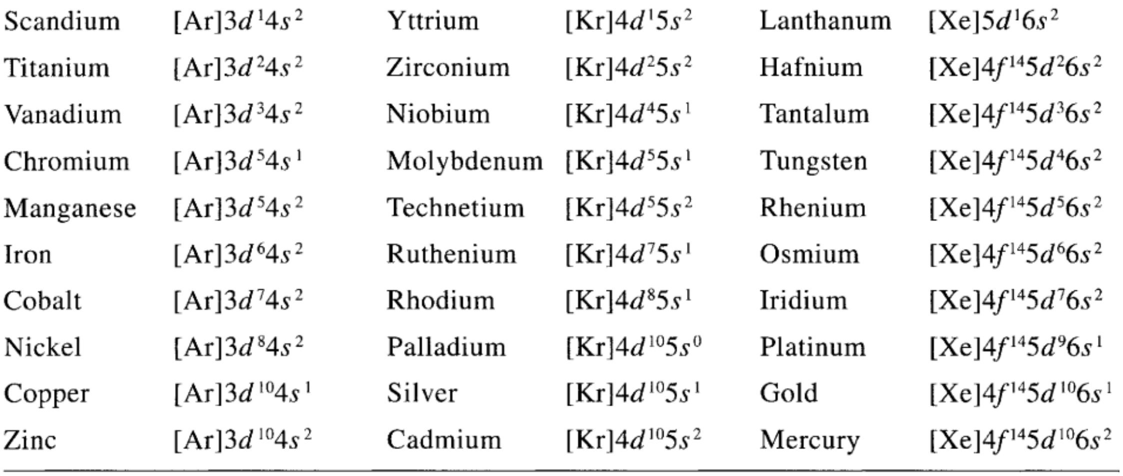
1.1 Coordination compound

Coordination compounds contain complex ions, in which ligands form coordinate bonds to the metal. Thus, the ligand must have a lone pair of electrons, and the metal must have an empty orbital of suitable energy available for bonding (b1). The central atom is an acceptor, with the surrounding species each bringing (at least) one lone pair of electrons to donate to an empty orbital on the central atom, and each of these electron-pair donors is called a ligand when attached. The central atom is a metal or metalloid, and the compound that results from bond formation is called a coordination compound, coordination complex or often simply a complex. The simple yet distinctive concept of the coordinate bond (also sometimes called a dative bond) $M + :L \rightarrow M : L$. The product alternatively may be written as $M \leftarrow :L$ or $M \leftarrow L$, where M = transition metal and L = ligand, where the arrow denotes the direction of electron donation, or, where the nature of the bonding is understood, simply as ML (b2). Ligands can be group into different classes based on the number of donor atoms (sites) they possess. A ligand with one donor site is called monodentate (e.g. H_2O, NH_3, CN^-, Cl^-). Bidentate ligands are those with two binding sites e.g. ethylenediamine ($H_2NCH_2CH_2NH_2$), oxalate (C_2O_4). These ligands are capable of forming ring structure (Chelate) with central metal. Tridentate ligands possess three donor atoms e.g. diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$). They have capacity to form two ring structure around the central metal. Ligands with four donor sites are said to be quadridentate e.g. triethylenetetraamine ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$), they are capable of forming complexes with four ring structures. Polydentate ligands have many donor sites e.g. EDTA (ethylenediaminetetraacetate). Another category of ligands are called ambidentate ligands because they have two heteroatoms and any can be used to coordinate to metal depending on the reaction conditions e.g. SCN^- (it can either coordinate through S or N), NO_2^- (it can coordinate through O or N) (b4).

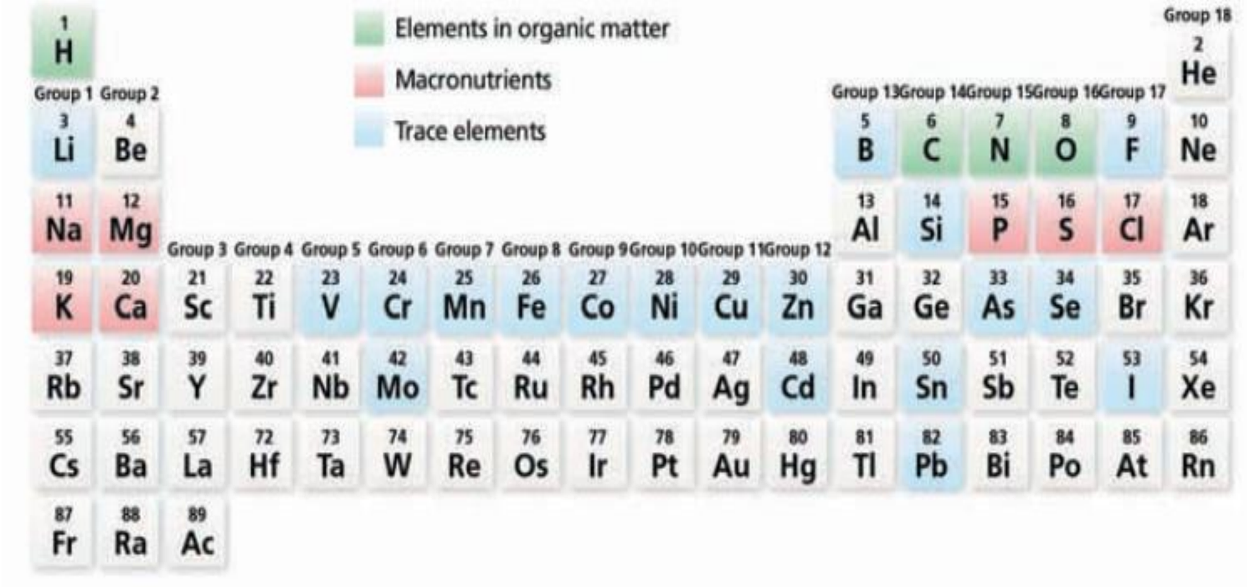
1.2 Transition metals

The transition elements comprise groups 3 to 12 and are found in the central region of the standard periodic table (**Fig. 1.1**). This group is further subdivided into those of the first row (the elements scandium to zinc), the second row (the elements yttrium to cadmium) and the third row (the elements lanthanum to mercury). The term 'transition' arises from the elements' supposed transitional positions between the metallic elements of groups 1 and 2 and the predominantly non-metallic elements of groups 13 to 18. Nevertheless, the transition elements are also, and interchangeably, known as the transition metals in view of their typical metallic properties (b3). Inorganic chemists generally restrict the term transition metal to an element that has at least one simple ion with an incomplete outer set d-electrons (b5). Generally, the ground-state electronic configurations of the first, second and third-row d-block metals follows the progressive filling of the 3d, 4d and 5d atomic orbitals, respectively. Nevertheless, there are exceptions, such as the ground state of chromium, which is $[Ar]4s^1 3d^5$ rather than $[Ar]4s^2 3d^4$ (**Table 1**). d-Block metals can show several oxidation states as their valence electrons can be present in more than one atomic orbital. M^{2+} and M^{3+} ions of the first-row d-block metals follow the general formula $[Ar]3d^n$.

Table 1 Electronic configuration of transition elements



Scandium	$[Ar]3d^1 4s^2$	Yttrium	$[Kr]4d^1 5s^2$	Lanthanum	$[Xe]5d^1 6s^2$
Titanium	$[Ar]3d^2 4s^2$	Zirconium	$[Kr]4d^2 5s^2$	Hafnium	$[Xe]4f^{14} 5d^2 6s^2$
Vanadium	$[Ar]3d^3 4s^2$	Niobium	$[Kr]4d^4 5s^1$	Tantalum	$[Xe]4f^{14} 5d^3 6s^2$
Chromium	$[Ar]3d^5 4s^1$	Molybdenum	$[Kr]4d^5 5s^1$	Tungsten	$[Xe]4f^{14} 5d^4 6s^2$
Manganese	$[Ar]3d^5 4s^2$	Technetium	$[Kr]4d^5 5s^2$	Rhenium	$[Xe]4f^{14} 5d^5 6s^2$
Iron	$[Ar]3d^6 4s^2$	Ruthenium	$[Kr]4d^7 5s^1$	Osmium	$[Xe]4f^{14} 5d^6 6s^2$
Cobalt	$[Ar]3d^7 4s^2$	Rhodium	$[Kr]4d^8 5s^1$	Iridium	$[Xe]4f^{14} 5d^7 6s^2$
Nickel	$[Ar]3d^8 4s^2$	Palladium	$[Kr]4d^{10} 5s^0$	Platinum	$[Xe]4f^{14} 5d^9 6s^1$
Copper	$[Ar]3d^{10} 4s^1$	Silver	$[Kr]4d^{10} 5s^1$	Gold	$[Xe]4f^{14} 5d^{10} 6s^1$
Zinc	$[Ar]3d^{10} 4s^2$	Cadmium	$[Kr]4d^{10} 5s^2$	Mercury	$[Xe]4f^{14} 5d^{10} 6s^2$



🟩 Elements in organic matter
🟥 Macronutrients
🟦 Trace elements

Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1 H 🟩																	2 He
3 Li 🟦	4 Be											5 B 🟦	6 C 🟩	7 N 🟩	8 O 🟩	9 F 🟦	10 Ne
11 Na 🟥	12 Mg 🟥											13 Al	14 Si 🟦	15 P 🟥	16 S 🟥	17 Cl 🟥	18 Ar
19 K 🟥	20 Ca 🟥	21 Sc	22 Ti	23 V 🟦	24 Cr 🟦	25 Mn 🟦	26 Fe 🟦	27 Co 🟦	28 Ni 🟦	29 Cu 🟦	30 Zn 🟦	31 Ga	32 Ge	33 As 🟦	34 Se 🟦	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo 🟦	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd 🟦	49 In	50 Sn 🟦	51 Sb	52 Te	53 I 🟦	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb 🟦	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

Figure 1.1 Periodic table of elements

1.4 Hydrazide ligand

In the last two decades, much interest has been focused on compounds containing hydrazide and hydrazone moieties and their complexes with first row transition metals. Such interest has been growing due to their use in medicine (for treatment of tuberculosis), biological systems and analytical chemistry (r20). The coordination chemistry of transition metals with ligands from the hydrazide family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metal (46). Hydrazides [R-CO-NH-NH_2] and their analogues have continued to attract interest in the literature because of their ability to readily coordinate (chelate) to a variety of transition metals using carbonyl oxygen and amino nitrogen as donor atoms forming five-membered ring (51). There are strong and documented evidences that a large number of hydrazides and their complexes exhibit diverse biological activities including antitumour, antiinflammatory, trypanocidal, leishmanicidal, anti-HIV, antidiabetic, antimalarial, anticonvulsant, antifungal (44,10). Hydrazides and their metallic complexes also show fungicide and antibacterial activity (2). Hydrazide derivatives have been reported to possess a broad spectrum of antibacterial activities. They also act as a good potential for oral drugs used for the treatment of genetic disorders like thalassemia (6). Transition metal complexes of hydrazides and also find application in chemotherapy as well as their hydrazone derivatives (13). Introduction of -C=O group in the hydrazide moiety is known as acyl hydrazone. Benzohydrazide derivative complexes are coordination compounds that coordinate benzohydrazide derivative ligands to a central metal ion or atom. Benzohydrazide derivative ligands contain both a hydrazine group (-NH-NH_2) and a benzoyl group (-$C_6H_5C(O)$-). The coordination of these ligands with a metal center results in a complex with unique properties and potential applications. The -NH-NH-hydrazide fragment plays an important role in medicinal chemistry. Earlier work has demonstrated that some drugs show increased activity when administered as metal chelates rather in the form of original organic compounds (45). Carboxylic acid hydrazides have equally been used in polymer stabilization, metal extractants and in solving ion-exchange problems. N-substituted hydrazides are of wide interest because of their diverse biological (3-5) and clinical applications. This created interest in researchers who have synthesized variety of hydrazide derivatives and screened them for their various biological activities (38). Hydrazides themselves or mixed in more complex drugs have been used in medicine and veterinary medicine as antibacterial agents (r31). This class of compounds and their analogues have the ability to readily coordinate to a variety of transition metals. In addition, it is known that one way to improve the biological activity of organic compounds is complexing them to a transition metal, therefore, many hydrazides complexes have been synthesized and characterized (r27). Is well know that hydrazides compounds containing one amide moiety which have a strong ability to form metal complexes (**Fig. 1.2**). This ligand system shows the keto-enol tautomerism and can acts as mononegative bidentate or mononegative tridentate (r18).

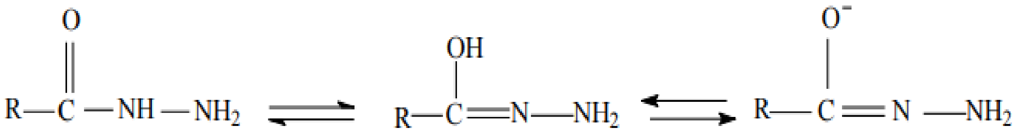


Figure 1.2 keto-enol tautomerism of hydrazide

Part Two

2. Literature Review

2.1 Complexes of aromatic hydrazide ligand

In 1995, Dodoff and coworkers, synthesized complexes $[Pt(NH_3)(pmbah)Cl_2]$ **(Fig. 2.1)** , and $[Pt(pcbah)_2X_2]$ **(Fig. 2.2)** (**pmbah** = 4-methoxybenzoic acid hydrazide, **pcbah** = 4-chlorobenzoic acid hydrazide; X = Cl, Br, I). The synthesized complexes are characterized by elemental analysis, electric conductivity, ^{1}H NMR, IR, and electronic spectra. According to the characterization data, all complexes were formed as *cis*-square planar structure with hydrazide ligands coordinated to the platinum metal via the nitrogen atom of NH_2 group (5).

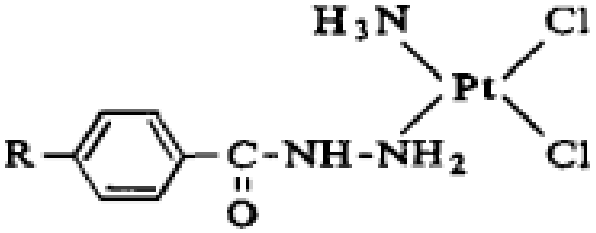


Figure 2.1 Structure of $[Pt(NH_3)(pmbah)Cl_2]$

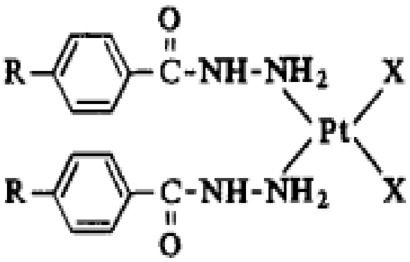


Figure 2.2 Structure of $[Pt(pcbah)_2X_2]$, where X = Cl, Br, I

In 2003, Odunola and coworkers, synthesized [Ni(bah)$_3$]Cl$_2$.3CH$_3$OH **(Fig. 2.3)** complex, where **bah** = benzoic acid hydrazide. The x-ray structure of the synthesized complex reveals that the hydrazide ligand behaves as a neutral bidentate chelating ligand coordinated to nickel metal through carbonyl oxygen and the amino nitrogen atoms of the hydrazide moiety in a six-coordinate pseudo-octahedral arrangement (41).

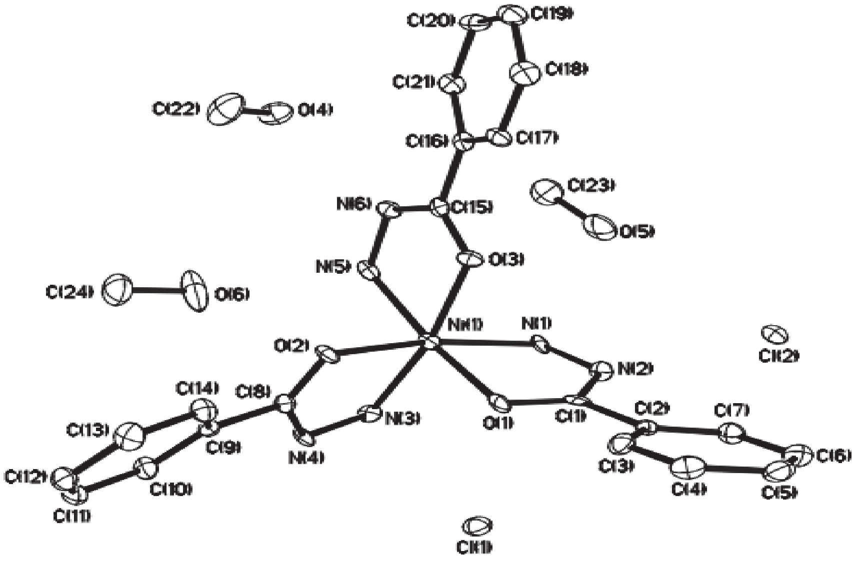


Figure 2.3 Structure of [Ni(bah)$_3$]Cl$_2$.3CH$_3$OH

In 2008, Jimenez and coworkers, synthesized two new complexes of the type [Co(bzlmh)(H$_2$O)(CH$_3$CN)$_2$](ClO$_4$)CH$_3$CN (**Fig.2.4**) and [RhCl$_2$(bzlm)(CH$_3$CN)]CH$_3$CN **(Fig 2.5)** (where **bzlmh** derived from 6-acetyl-1,3,7-trimethyllumazine (lumazine = pteridine-2,4(1H,3H)-dione) and benzohydrazide. Both complexes have been characterized by single crystal X-ray. In cobalt complex the **bzlm** ligand coordinated to the metal in a tetradentate fashion through (O4, N5, N61 and O63), while in rhodium complex it coordinated to the metal ion a tridentate fashion at (N5, N61 and O63) donor atoms (21).

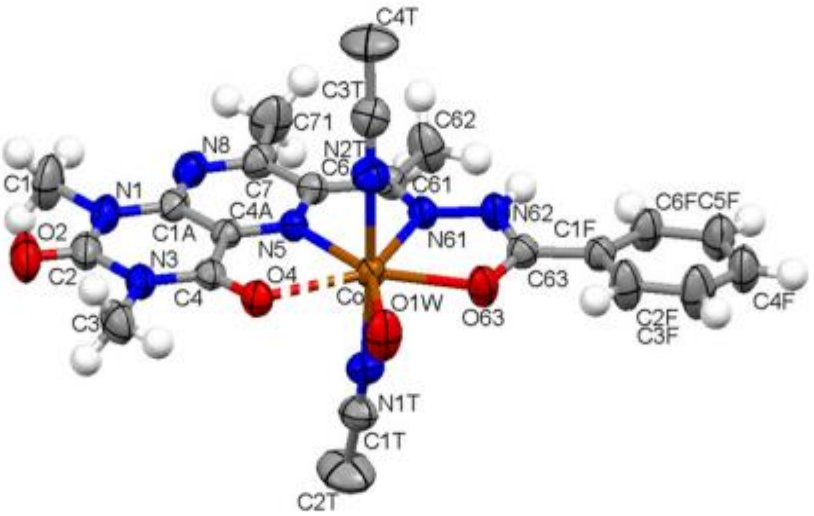


Figure 2.4 Structure of [Co(bzlmh)(H_2O)(CH_3CN)$_2$]$^{+2}$

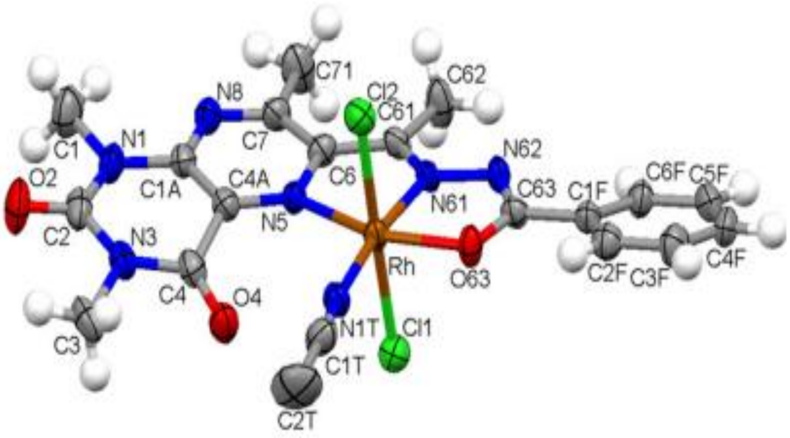


Figure 2.5 Structure of [RhCl_2(bzlm)(CH_3CN)]CH_3CN

In 2013, Ain and coworkers, synthesized a series of mixed ligand palladium(II) complexes containing the derivatives of hydrazide ligand. The chemical formula of the synthesized complex are [Pd$Cl_2$$L_2$] (**1-4a L** = substituted and unsubstituted benzohydrazide) and [PdCl_2L] (**5,6a** L = pyridine carbohydrazides) (**Fig. 2.6**). Magnetic susceptibility and conductivity measurements represented a square planar structure for all of the complexes. In complexes (**1–4a**) the L-ligands have shown monodentate behavior that coordinated to the palladium metal through N-atom. However, in complexes **5a** and

6a the L-ligands were coordinated in a bidentate fashion through both N and O atoms producing stable five-membered chelate ring (44).

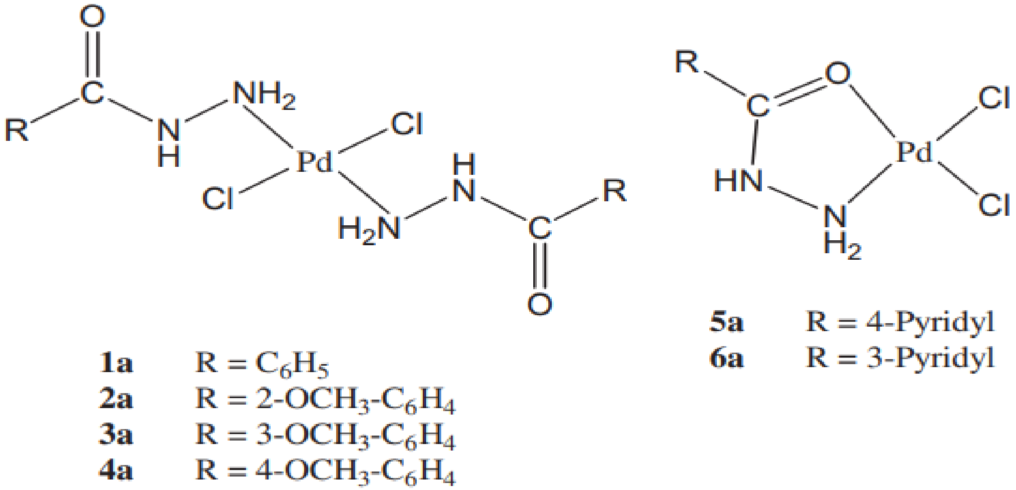


Figure 2.6 Structure of palladium (II) complexes

In 2014, Gudasi and coworkers, synthesize [Ni(aheb)$_2$]Cl$_2$.4H$_2$O (**Fig. 2.7**) (where **aheb** =(*E*)-2-amino-N’-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide. During complexation the Ni(II) ion has got oxidized to Ni(IV). The X-ray single crystal analysis of the synthesized complex has confirmed an octahedral geometry around the nickel metal ion. The **aheb** ligand behaved as a tridentate ligand that coordinated to the nickel atom through N,O,O-atoms (22).

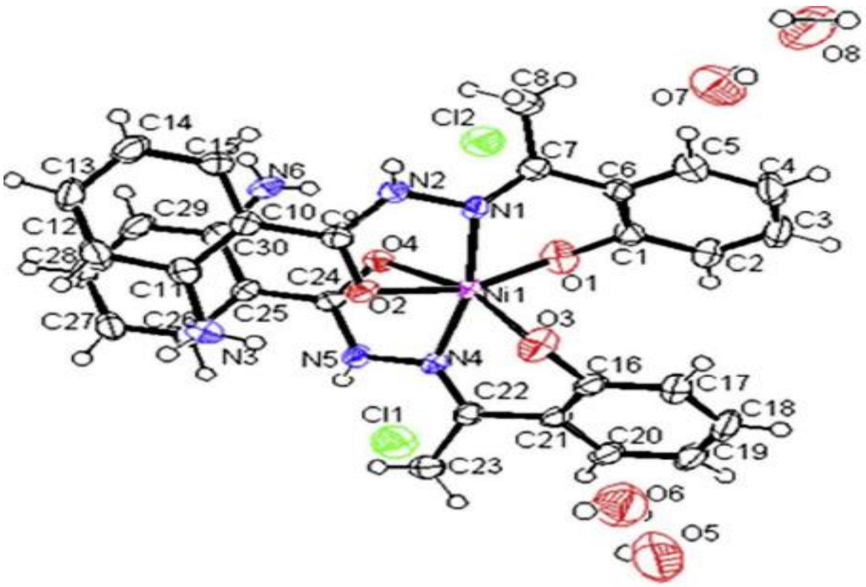


Figure 2.7 Structure of [Ni(aheb)$_2$]Cl$_2$.4H$_2$O

In 2015, Rodrigues and coworkers, synthesized mixed ligand Pt(II) complex of the type *cis*-[PtCl$_2$(bcz)$_2$] (**Fig. 2.8**) where **bcz** = benzyl carbazate. Characterization data such as FT-IR, ^{1}H-nmr and mass spectra of the synthesized complex revealed that the hydrazide ligand coordinated to the platinum metal through nitrogen atom of NH$_2$ group and the complex was formed as a square planar geometry (7).

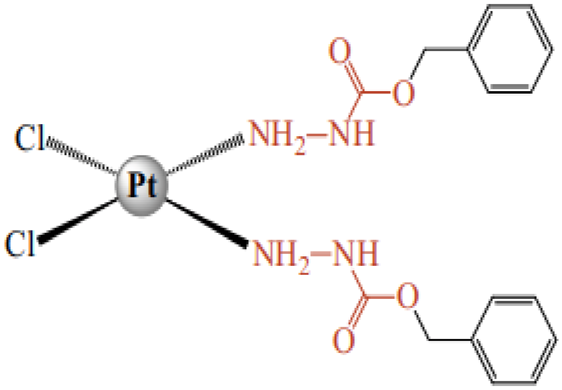


Figure 2.8 Structure of *cis*-[PtCl$_2$(bzc)$_2$]

In 2016, Qadir and coworkers, synthesized a new nickel (II) complex of formula $[Ni(L)_2(tmed)]$ **(Fig 2.9)** (**LH** = 4-acetylpyridine benzoyl hydrazone, **tmed** = tetramethylethylenediamine). The complex was characterized by single crystal X-ray diffraction analysis which shows that Ni(II) has an octahedral geometry with two oxygen and two nitrogen atoms from two hydrazone ligands and two nitrogen atoms from tetramethylethylenediamine (32).

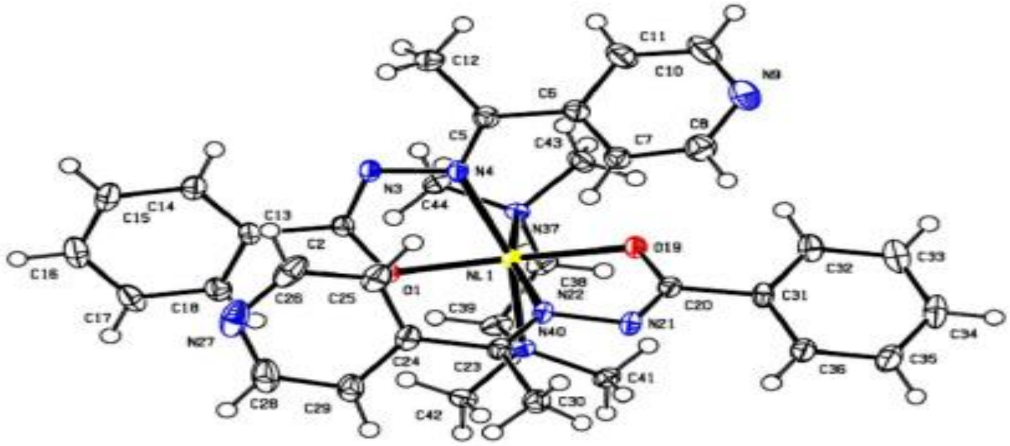


Figure 2.9 Structure of $[Ni(L)_2(tmed)]$

In 2016, Abdel and coworkers, synthesized a series of complexes containing the derivative of hydrazide ligand of the type $[Mn_2(HL)_3Cl_2(H_2O)_2].Cl_2.2H_2O$ **(Fig. 2.10)** and $[Co_2(HL)_3Cl_2(H_2O)].Cl_2.3H_2O.0.25EtOH$ **(Fig. 2.11)**, $[Ni(HL)Cl(H_2O)_3]Cl.0.5H_2O$ **(Fig. 2.12)**, $[Cu(HL)Cl(H_2O)]Cl.0.5EtOH$ **(Fig. 2.13)**, $[Cd(HL)_2(NO_3)_2].0.25EtOH$ **(Fig. 2.14).** The structures were confirmed by analytical and different spectral techniques. All complexes have an octahedral geometry, except Cu(II) complex has square planar structure. IR spectra established that ligand coordinates with metal ions through nitrogen and oxygen atoms of amino and carbonyl groups of hydrazide moiety in neutral form. The antioxidant activity of compounds was proved, where Cu(II) complex displays higher antioxidant activity than that of other complexes (51).

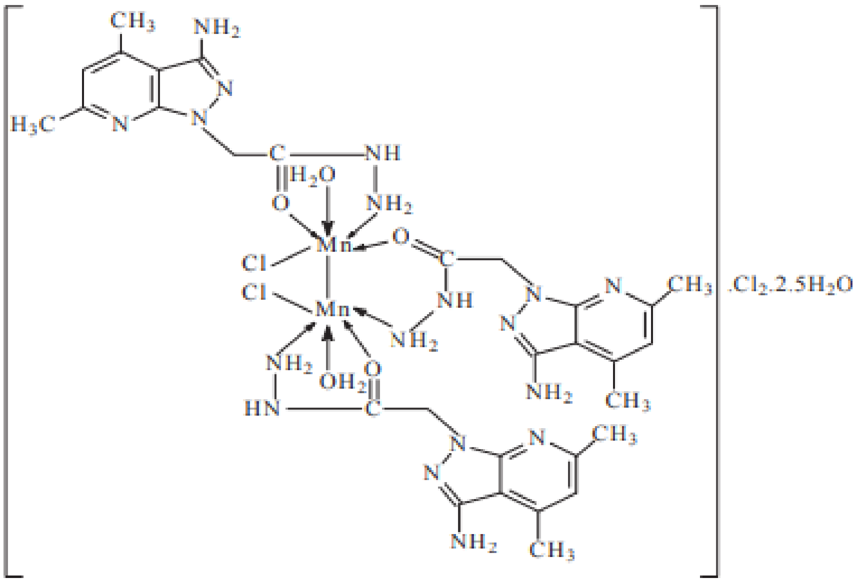


Figure 2.10 Structure of $[Mn_2(HL)_3Cl_2(H_2O)_2]Cl_2.2H_2O$

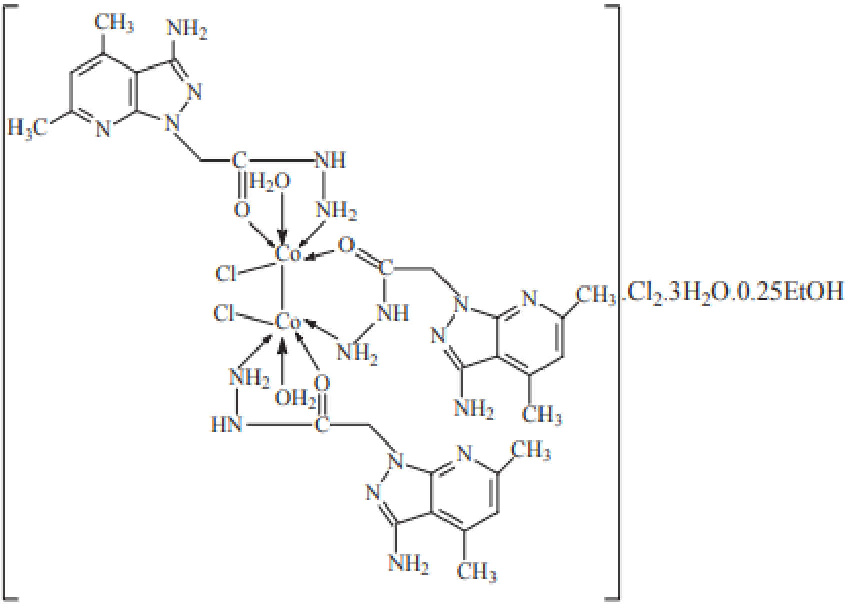


Figure 2.11 Structure of $[Co_2(HL)_3Cl_2(H_2O)]Cl_2.3H_2O.0.25EtOH$

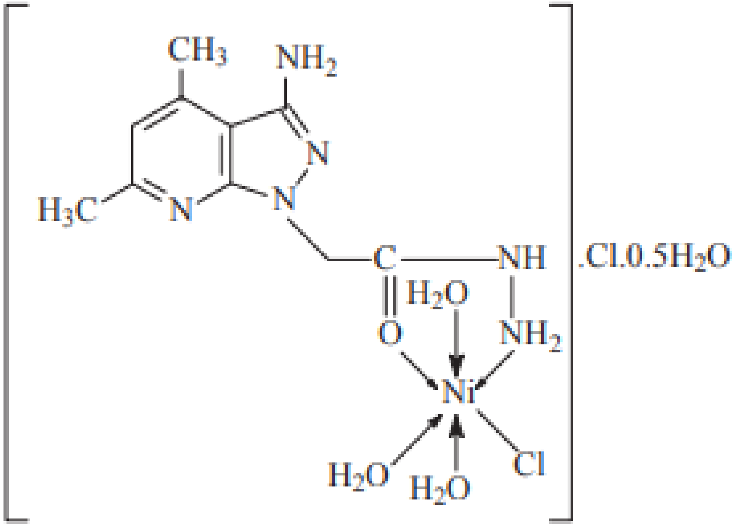


Figure 2.12 Structure of [Ni(HL)Cl(H_2O)$_3$]Cl.0.5H_2O

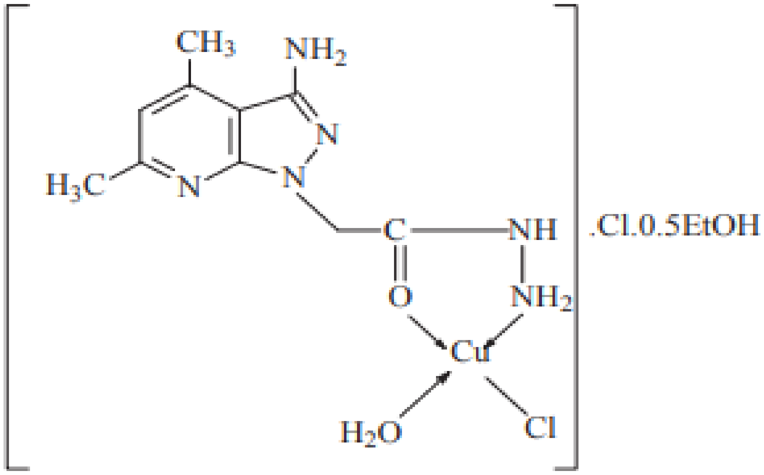


Figure 2.13 Structure of [Cu(HL)Cl(H_2O)]Cl.0.5EtOH

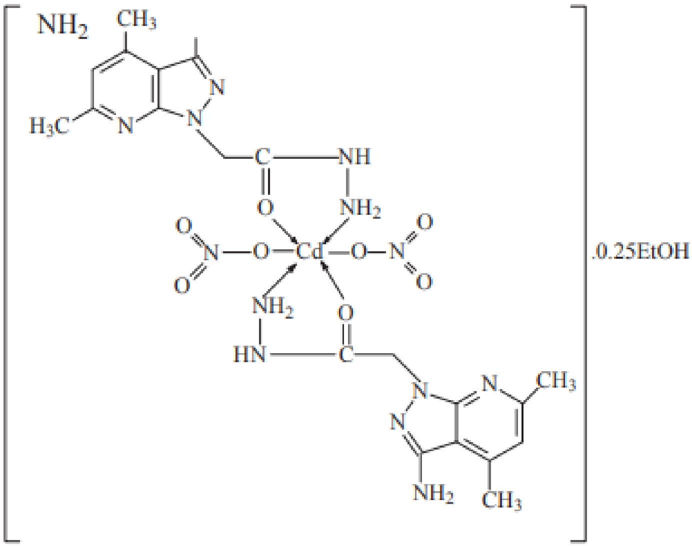


Figure 2.14 Structure of [Cd(HL)$_2$(NO$_3$)$_2$].0.25EtOH

In 2019, Tan and coworkers, synthesized [CoL$_2$]NO$_3$.2H$_2$O **(Fig. 2.15)** and [MnL$_2$] **(Fig. 2.16)** complexes, where HL = 4-bromo-N'-(pyridin-2-ylmethylene)benzohydrazide. Molecular structures of both complexes were confirmed by single crystal X-ray crystallography. The coordination geometry around the cobalt atom and the manganese atom in both complexes are octahedral, with two pyridine N atoms, two imino N atoms, and two enolate O atoms from the ligands. The compounds were evaluated for their antibacterial and antifungal activities by MTT assay (33).

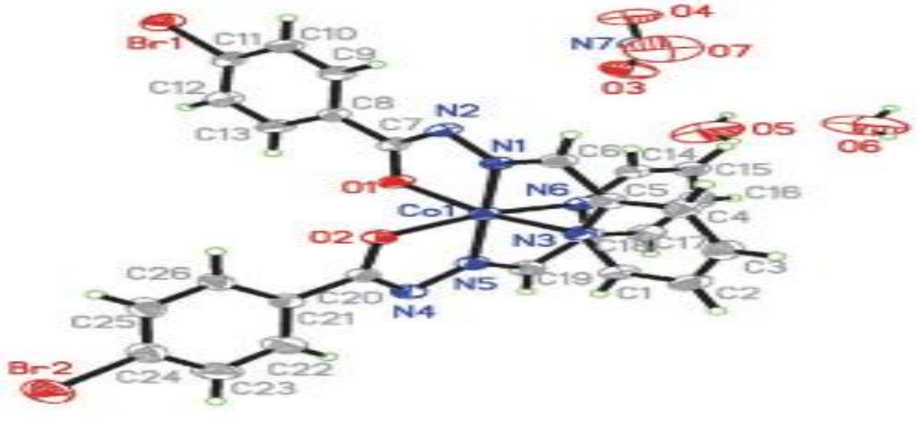


Figure 2.15 Molecular structure of [CoL$_2$]NO$_3$.2H$_2$O

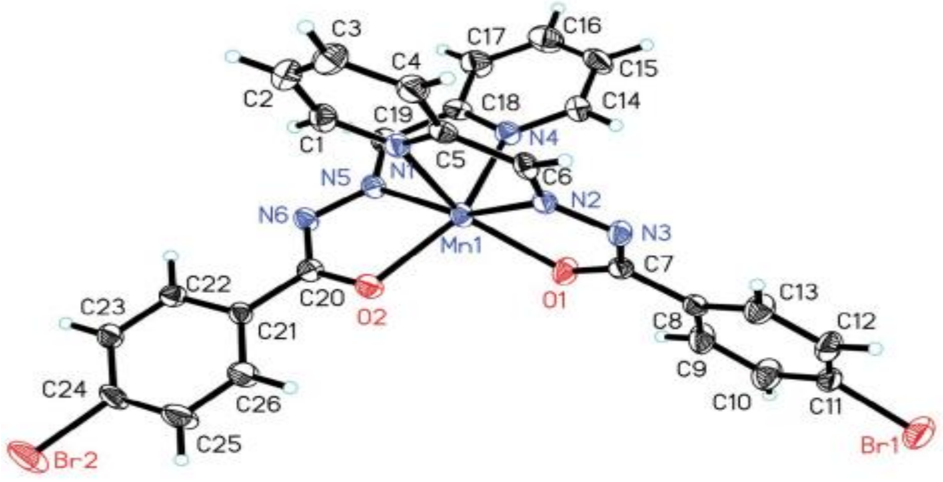


Figure 2.16 Molecular structure of [MnL_2]

In 2021, Tan and lei, synthesized a new mononuclear copper(II) complexes of the type [Cu(HL1)Br_2] (**1**) **(Fig. 2.17)** and [$CuL_2(HL_2)]ClO_4.0.5H_2O$ (**2**) **(Fig. 2.18)**, where HL1 = 4-tert-butyl-N'-(1-(pyridin-2-yl)ethylidene)benzohydrazide and HL2 = 4-bromo-N'-(pyridin-2-ylmethylene)benzohydrazide. Single crystal X-ray analysis indicate that the Cu atom in complex **1** is in distorted square pyramidal coordination, while in complex **2** is in octahedral coordination geometry (34).

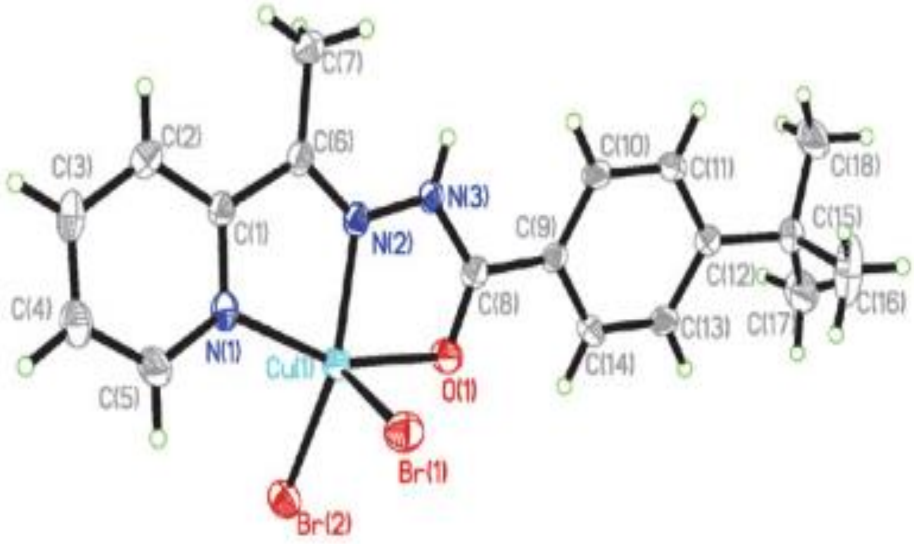


Figure 2.17 Molecular structure of [Cu(HL1)Br_2] (1)

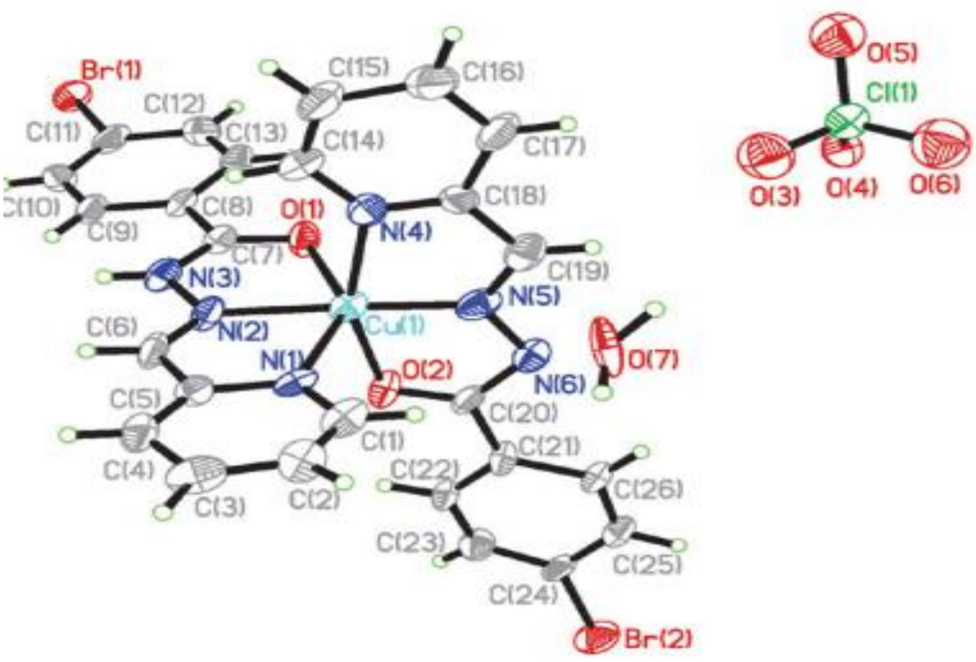


Figure 2.18 Molecular structure of [CuL_2(HL_2)]ClO_4.0.5H_2O (2)

In 2023, Al-Jibori and Al-Janabi, synthesized five bivalent metal complexes of Co(II), Ni(II) and Cu(II) with N-(4-dimethylamino)benzylidene)benzohydrazide **(Hdmby)** ligand with the general formula [M$(dmby)_2(H_2O)_2$] (**Fig. 2.19**) where M(II) = Co (**1**), Ni (**2**) and Cu (**3**) .The prepared complexes were characterized by ^{1}H NMR, IR spectrometry, UV-Vis spectra, conductivity measurements and magnetic susceptibility. All complexes were found to have an octahedral geometry. The antimicrobial activity of the synthesized complexes were investigated against three pathogenic bacteria and the order of activity of the complexes was determined to be [Cu$(dmby)_2(H_2O)_2$] > [Ni$(dmby)_2(H_2O)_2$] > [Co$(dmby)_2(H_2O)_2$] (25).

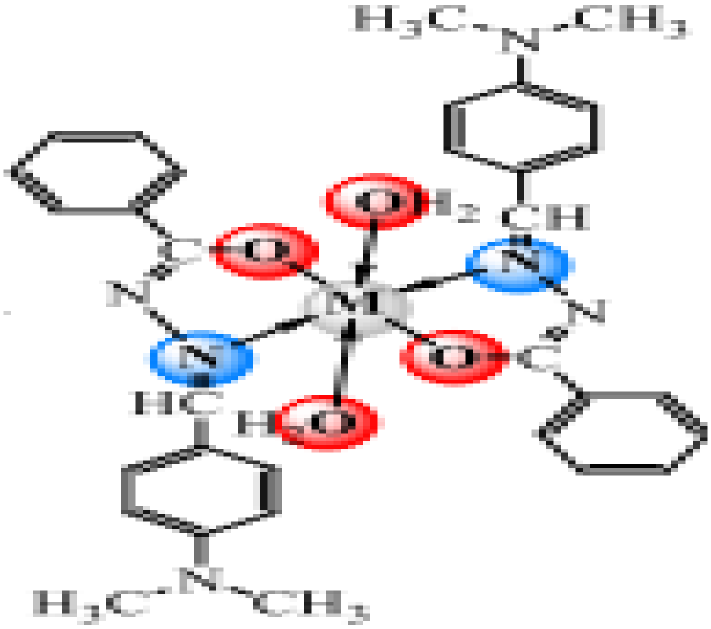


Figure 2.19 Structure of [M(dmby)$_2$(H$_2$O)$_2$] where M(II) = Co (1), Ni (2), Cu (3)

Conclusion

This study is a review project, aims to collect some of the transition metal complexes of aromatic hydrazide ligand. According to the reported literature, hydrazide ligand can form complexes with transition metals like Mn(II), Co(II), Rh(II), Ni(II), Pd(II), Pt(II), Cu(II) and Cd(II) in a square planar, distorted square pyramidal or an octahedral coordination geometry. Characterization data as well as X-ray structure of the synthesized complexes reveal that the hydrazide ligand behaves either as a neutral monodentate ligand that coordinates to the metal ions through amino nitrogen atom or as a neutral bidentate chelating ligand that form five-membered ring structure with the metal ions through amino nitrogen and carbonyl oxygen donor atoms. The reported literature displayed that some complexes of hydrazide ligand exhibited significant antibacterial, antioxidant and antifungal activities.

References