The Role of Ligand Denticity on the Synthesis of Mixed-Ligand Complexes: A Short Review

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Abstract:

Mixed-ligand complexes of different metal ions were studied and presented in a variety of ligand types and geometries. It is important to show the role of primary and secondary ligands in the synthesis process, considering the chelation effect of di- and tri-dentate ligands. Meanwhile, the steric effect and ligand size are significant. But the most important point is the sequence of addition of interacting ligands to decide who is coming first to be primary and who is coming next to be considered secondary, therefore, mixed-ligand complex can't be prepared if the sequence of addition is reversed. This paper reviews the definition, importance and the illustration of important molecules like 8-hydroxyquinoline (HQ) and 1,10- phenanthroline (Phen), ...et cetera which are strong bidentate ligands, beside the designed and synthesized large ligands like Schiff-bases which are multidentate ligands, to figure out their role in the synthesis of mixed-ligand complexes.

Keywords: Mixed Ligand Complexes, Multidentate Ligands, 8-Hydroxyquinoline, 1, 10- Phenanthroline.

1. Introduction

Mixed-ligand complexes have gained significant importunacy due to their stability and reactivity when compared with one type ligand complexes. They have at least two different-type ligands associated with the same metal cation in a complex compound. Possessing of different kind ligands can lead to resemble the bio-available molecules, therefore, improving biological activity in addition to catalytic efficiency, and material properties in a synergistic effect. Moreover, mixed-ligand complexes have gained significant importunacy due to their rigidity, solubility in organic solvents, when the complex overall charge is electrically neutral, and in water, when an overall charge, reactivity, coloured and stability constant, which is a quantitative measure of the thermodynamic stability of coordination complexes in solution, when compared with one type-ligand complex.

The study of mixed-ligand complexes provides insights into metal-ligand interactions, effect of chelating ligands and role of ligand denticity in the synthesis under controlled conditions. This article is organized to focus on: First deeply insights into metal-ligand interactions. Then, has a look on the effect of chelating ligands. After that, is studying the role of ligand denticity in the synthesis of mixed-ligand complexes under controlled conditions. Finally, summary and outlooks.

2. Ligand Denticity and Coordination Geometry

Simply, Kindeel et al., (2013) reported preparation of several mixed ligand complexes from 8-hydroxyquinoline (HQ) as

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bidentate ligand and from any monodentate ligand like 2-Picoline (2-Pic), figure 1. The mole ratio was [1:2:2] [M: Q:2-Pic] of six coordination number. Hence that the suggested octahedral shape was of trans not cis considering the steric effect, therefore, priority of addition is important that HQ is the primary ligand and 2-Pic is the secondary ligand.

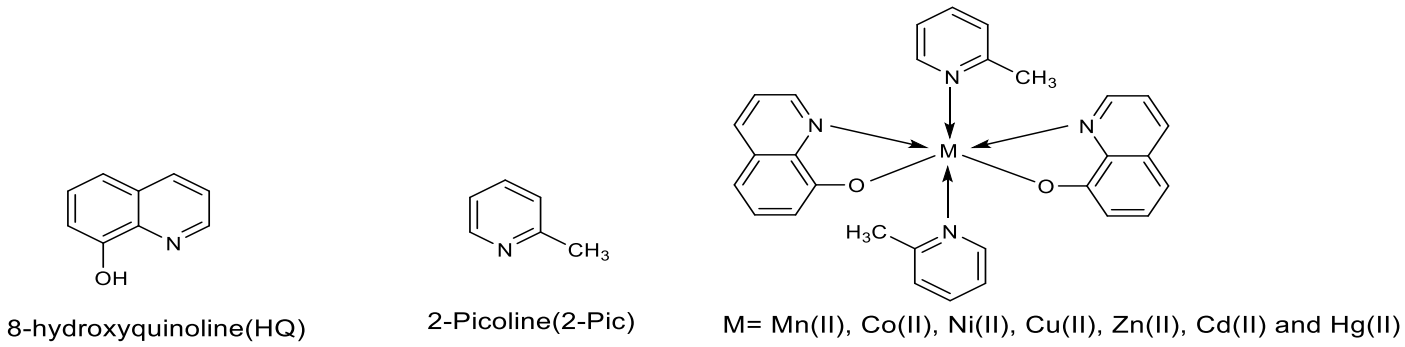


Figure 1. Divalent metal ion mixed-ligand complexes derived from 8-hydroxyquinoline and 2- Picolinate.

Simply, Abebe et al., (Abebe et al. 2017) reported mixed-ligand complexes of copper (II) chloride have been synthesized from 1, 10-phenanthroline (Phen) as primary ligand and thymine (Thy) or adenine (Ad) as secondary ligand, figure 2. The hot solution of thymine or adenine (1 mmol) was added to the mixture of Cu (II) and Phen of [1:2] molar ratio respectively, a square pyramidal geometry has been proposed for [Cu (Phen)2(Thy)] Cl2 and [Cu (Phen)2(Ad)] Cl2 complexes. Hence, copper (II) cation initially satisfied with two Phen ligands, thus, additional ligand like Thy and Ad can coordinates resulting mixed ligand complexes.

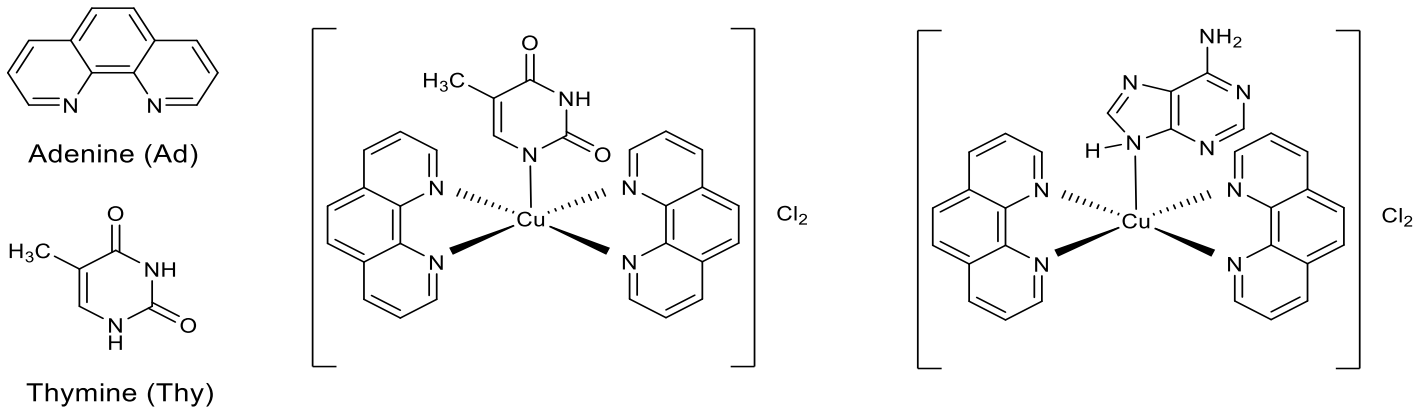


Figure 2. Copper (II) mixed-ligand complexes containing thymine or adenine and 1, 10-phenanthroline.

3. Steric Effects and Ligand Competition

Al Naimi, (2016) reported that Schiff base N1-benzylidenebenezene-1,2-diamine (L) and 8-hydroxyquinoline (HQ) are participate in the synthesis of neutral mixed ligand complexes derived from Zn (II), Cd (II) and Hg (II) metal ions in [M: L: Q] [1:1:2] ratio, figure 3. The predicted octahedral shape of six coordination numbers formed from three bidentate ligands, hence that L is a large molecule (size maters) and considered as primary ligand. Therefore, the smaller and strong Q ligands considered as secondary ligands. The addition sequence and ligand strength played role in the synthesis of these complexes.

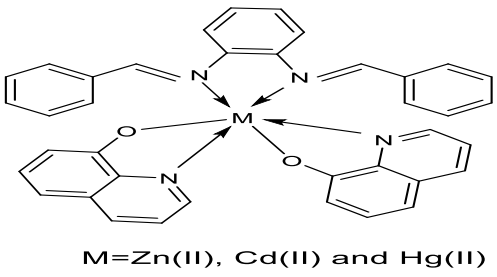


Figure 3. Mixed-ligand complexes derived from diamine and 8-hydroxyquinoline

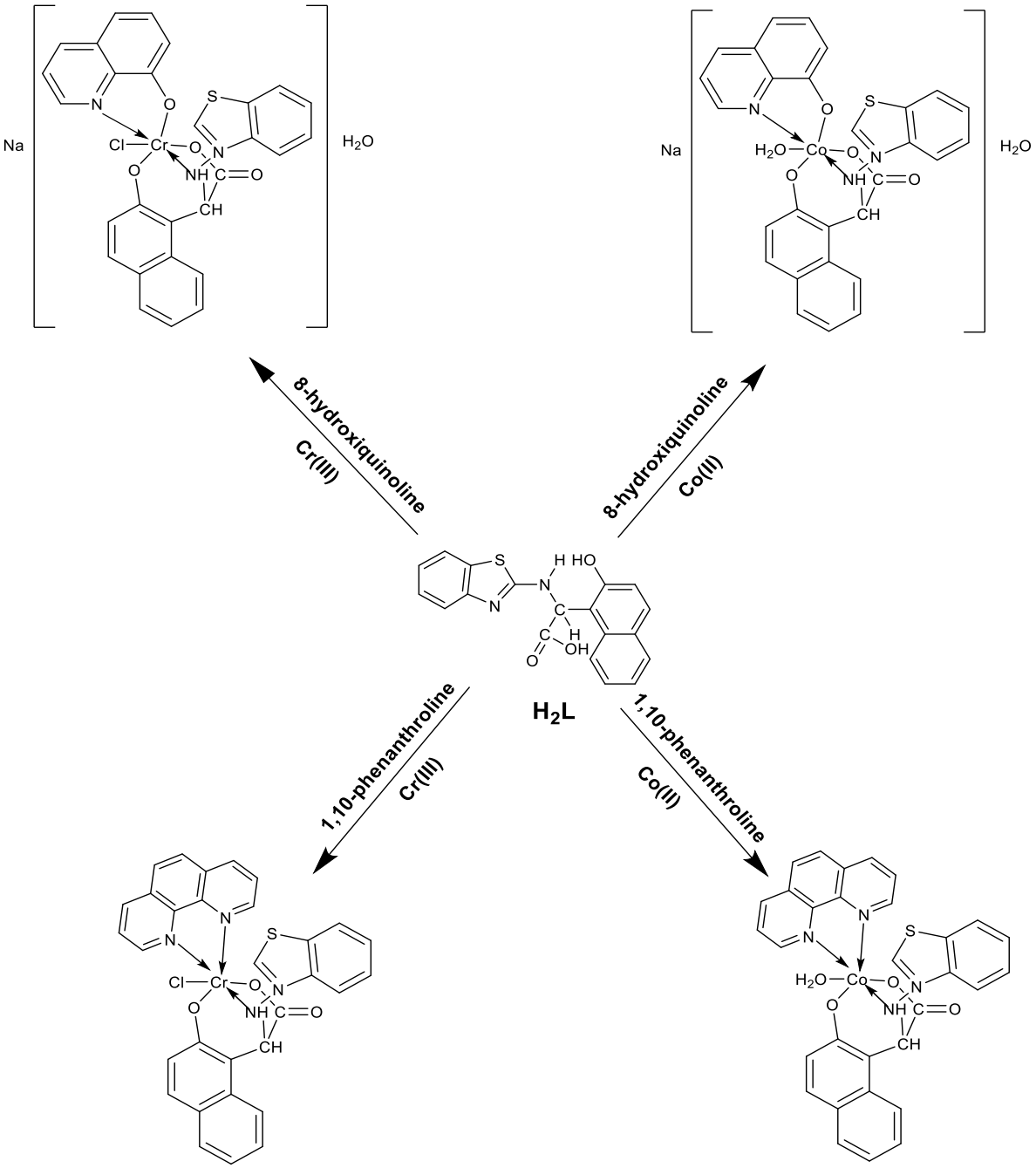
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Mahdi and Alabdali, (Mahdi & Alabdali 2023) reported cobalt (II) and chromium (III) mixed-ligand complexes have been synthesized under strong basic media from alpha-amino acid (H2L) as primary ligand and 8-hydroxyquinoline (HQ) or 1,10-phenanthroline (Phen) as secondary ligand, scheme 1. Hence those in an octahedral environment, H2L coordinated first in tridentate denticity allowing HQ or Phen to coordinate as bidentate.

Therefore, the suggested formula is:

Na [Co(L)(Q) H2O]. H2O, [Co(L)(Phen)H2O], Na [Cr(L)(Q) Cl]. H2O, [Cr(L)(Phen)Cl].

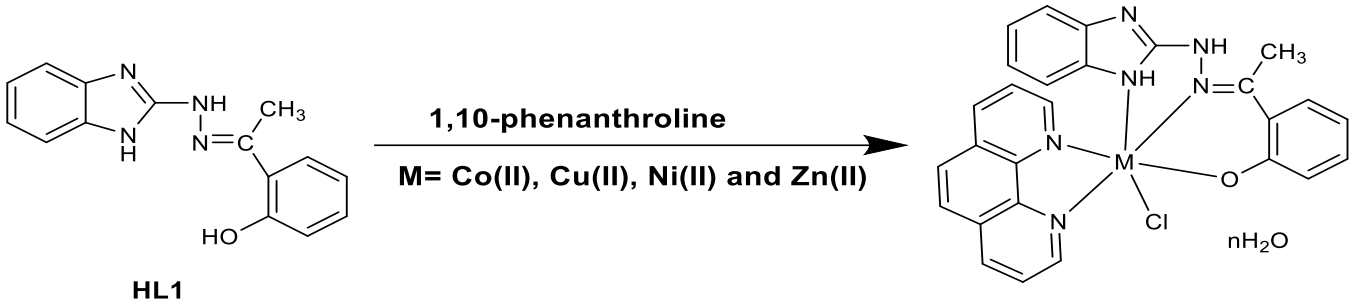
The bulky H2L comes first then the strong HQ or Phen, the order of addition is important to prevent strong ligands overcome and dominate in the synthesis of the complexes.



Scheme 1. Octahedral cobalt (II) and chromium (III) mixed-ligand complexes derived from H2L, HQ and Phen

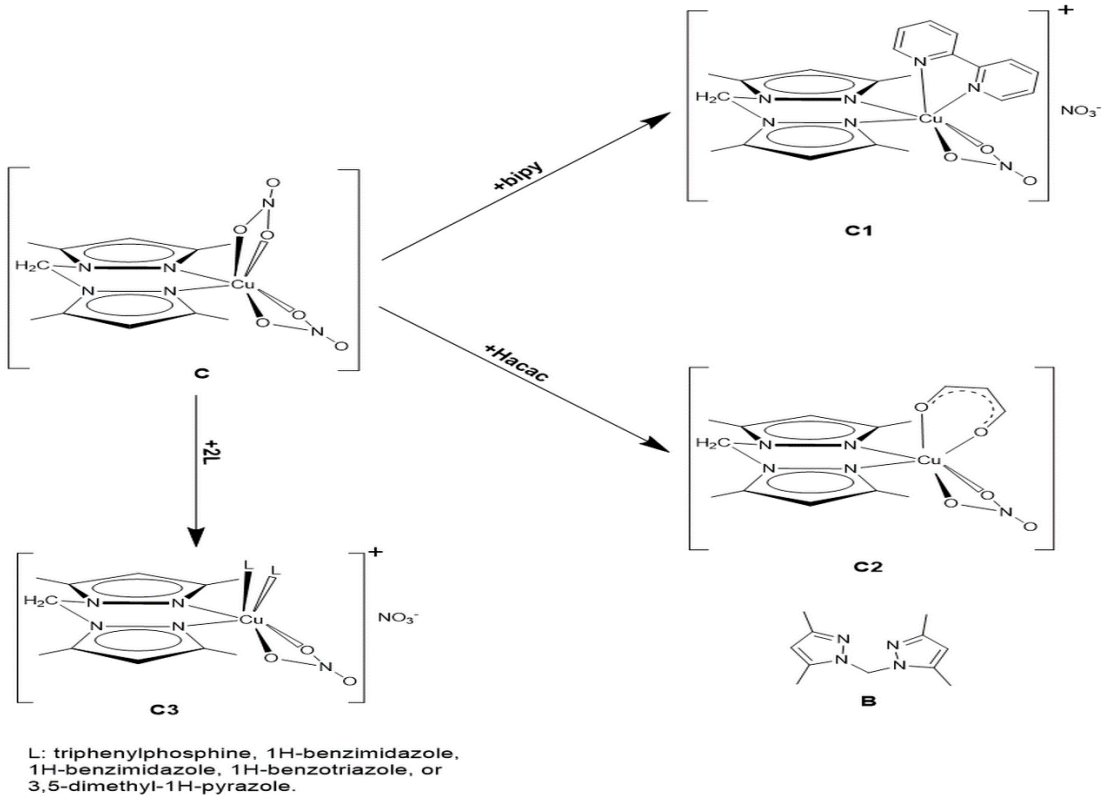
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Saikishore et al., (Saikishore et al 2021) reported mixed-ligand complexes of Co (II), Cu (II), Ni (II) and Zn (II) have been synthesized and investigated, scheme 2. They derived from synthesized Schiff base (HL1) which acts as primary ligand and 1, 10-phenanthroline (Phen) as secondary ligand. Hence, HL1 is a bulky tridentate ligand and existed in an octahedral shape after coordination from three sites, therefore, addition of Phen secondly will achieve production of mixed-ligand complex. Hence, that Phen is bidentate ligand and chloride ion is a part of the coordination sphere.



Scheme 2. Co (II), Cu (II), Ni (II) and Zn (II) mixed-ligand complexes derived from HL1 and Phen

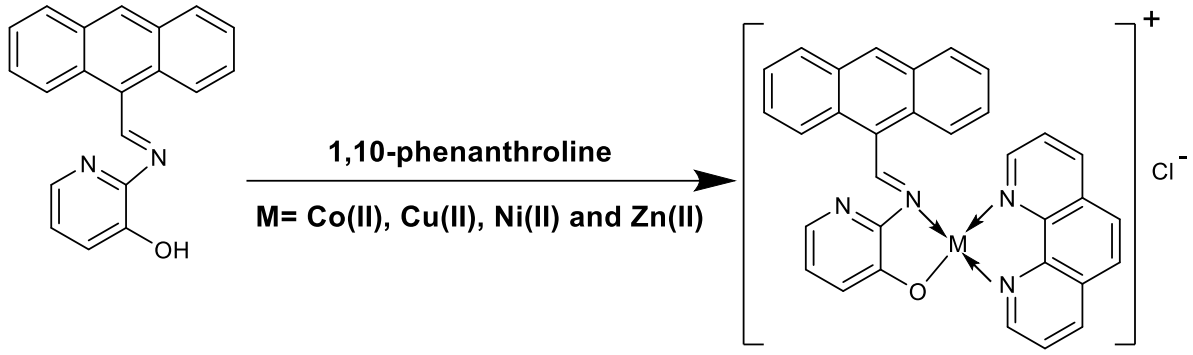
Potapov and Khlebnikov, (Potapov & Khlebnikov 2006) reported the synthesized bis(pyrazol-1-yl) methane (B) as primary ligands have been interacted with copper (II) nitrate in the beginning forming C complex, then, bidentate (2,2-bipyridyl bipy and acetylacetone Hacac) or monodentate L (triphenylphosphine, 1H-benzimidazole, 1H-benzotriazole, and 3,5-dimethyl-1H-pyrazole) as secondary ligands were added to produce C1, C2 and C3 mixed-ligand complexes respectively, scheme 3. Hence, the bulky B ligand in C complex restricts bidentate and monodentate ligands ligation in the form of octahedral geometry. Therefore, the six-coordination number was satisfied by the small nitrate ions in all complexes.



Scheme 3. Copper (II) mixed-ligand complexes C1, C2 and C3 derived from bis(pyrazol-1-yl) methane

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Fathima et al., (Fathima et al 2019) reported the primary ligand Schiff base (9-anthraldehyde, 2- amino-3-hydroxy pyridine) and Co (II), Cu (II), Ni (II) or Zn (II) metal chloride salt were mixed, then secondary ligand 1,10- phenanthroline (Phen) was added to the mixture, scheme 4. The mixture underwent four hours of sonication, followed by reflux stirring for twenty hours. In spite of the primary ligand is bidentate, anthracene group stand and prevent interacting of two ligands with the metal ion, therefore, the presence of strong Phen ligand allows the possibility to produce mixed-ligand complexes of tetrahedral shape. Hence, tetrahedral geometry also played an important part in the formation of mixed-ligand complexes, that suggestion octahedral geometry could takes us to another bend of the synthesis path.



Scheme 4. Mixed-ligand complexes of Co (II), Cu (II), Ni (II) and Zn (II) derived from Schiff base and Phen.

Agwara et al., (Agwara et al 2010) reported an example of complicated case in the synthesis of octahedral mixed-ligand complexes is mixing two bidentate strong ligands in a competition when interacting with metal ion figure 4. 1, 10-phenanthroline (Phen) and 2,2'-bipyridine (Bpy) participated in preparing variable ratios of metal to ligands [M:BPy:Phen]. Cobalt complex [Co (Bpy)(Phen)2] (NO3)2 .2H2O was prepared by adding dropwise a solution of Phen (2mmol) to Co (NO3)2 . 6H2O (1mmol) followed by addition of Bpy (1mmol) while still stirring, mole ratio was [1:1:2] [M:BPy:Phen] and the yield percent was 20%. Copper complex [Cu (Bpy)(Phen) (H2O)2] Cl2 .2H2O was obtained in the same procedure by adding 1mmol of both Phen and Bpy to produce mixed-ligand complex of mole ratio [1:1:1] [M:BPy:Phen] and yield percent 28%. Zinc complex [Zn (BPy)2(Phen)] Cl2 .6H2O was obtained in the same procedure by adding 1mmol of Phen and 2mmol of BPy to produce mixed-ligand complex of mole ratio [1:2:1] [M:BPy:Phen] and yield percent 47%. Hence, the metal to ligands ratios and yield percentages (low) are variable. Herein, the metal type could play role in the synthesis of these complexes.

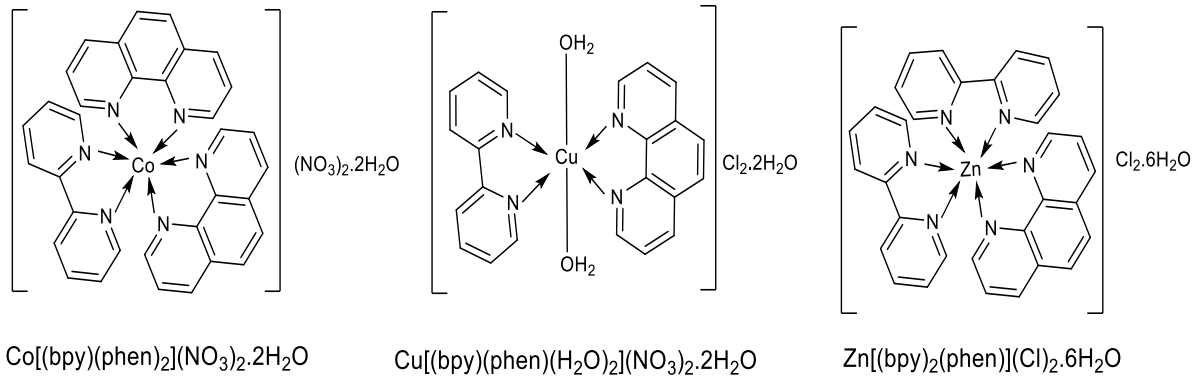


Figure 4. Mixed-ligand complexes of Co (II), Cu (II) and Zn (II) derived from BPy and Phen.

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Fayad et al., (Fayad et al 2013) reported the presence of weak ligand in facing strong one, the sequence of addition is important in addition to concentration. 2 mmol of L-valine in aqueous ethanol containing sodium hydroxide (2mmol) were added to a solution of MCl2.nH2O (1 mmol). 1mmol of 1,10-phenanthroline (Phen) was added to the mixture to obtain mixed-ligand complexes of mole ratio [2Val:M: Phen] as shown in figure 5. Hence, only one Phen can coordinate to the metal due to steric hindrance of two L-valine ligands in the coordination sphere.

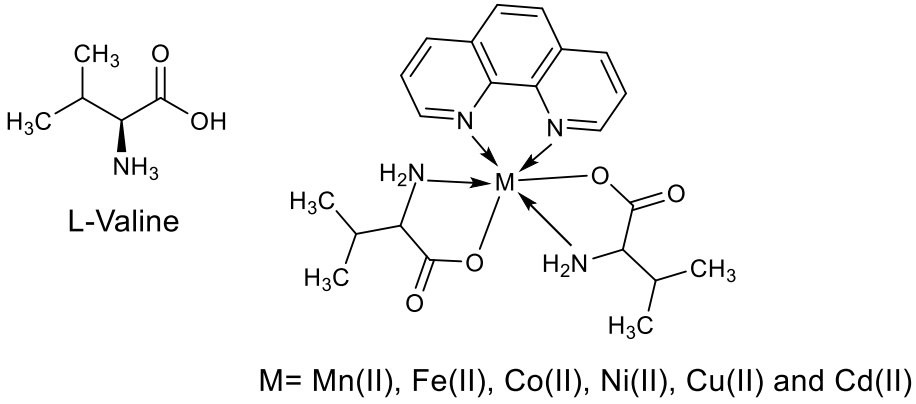


Figure 5. Metal mixed-ligand complexes containing L-valine and Phen.

Barve et al., (2009) reported mixed-ligand copper (II) complexes derived from maltolate ligand and series of diimine ligands like bpy, phen, phendione, dppz and bpg co-ligands, figure 6. Aqueous solution of copper (II) nitrate triaqua was added to an alcoholic solution of maltolate ligands then diimine added.

Square-pyramidal geometry was suggested in which the axial site has been occupied by a coordinated nitrate or water molecule for [Cu(bpy)(maltol)(NO3)], [Cu(phen)(maltol)(H2O)] + and [Cu(bpg)(maltol)(NO3)] complexes, and square-based geometry for [Cu(phendione)(maltol)] + and [Cu(dppz)(maltol)] +. Figure 7 shows the suggested shapes of the synthesized mixed-ligand complexes. Hence that all ligands are bidentate, therefore, succession of addition is significant considering the strength of the ligands.

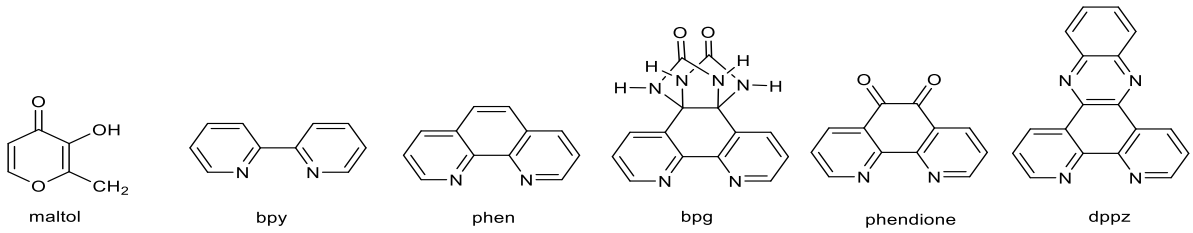


Figure 6. Structures of maltolate and diimine ligands.

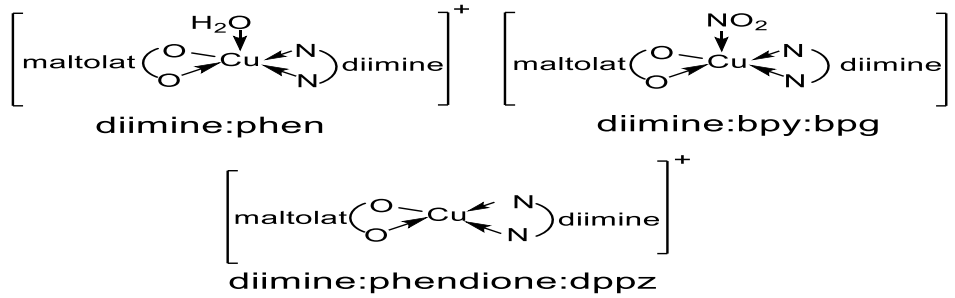


Figure 7. Suggested geometries of copper (II) complexes containing maltolate and diimine ligands

Quyoom et al., (2013) reported dicarboxylic acids of amino acid for example aspartic and glutamic were good candidate ligands in the synthesis of mixed ligand complexes. They coordinated to the central metal ion as tridentate ligands through the amino nitrogen and the two oxygen atoms of the terminal two carboxylate groups. Cu (II) and Ni (II) cations interacted with aspartic or glutamic as primary ligand then with benzimidazole or 2-methyl benzimidazole compounds as secondary ligand, figure 8. Both metal complexes are octahedral shaped. Hence, benzimidazole and 2-methyl benzimidazole are monodentate ligands. Therefore, aqua ligands completed the coordination number due to disability of the complex to possess more large ligands because of the steric factor.

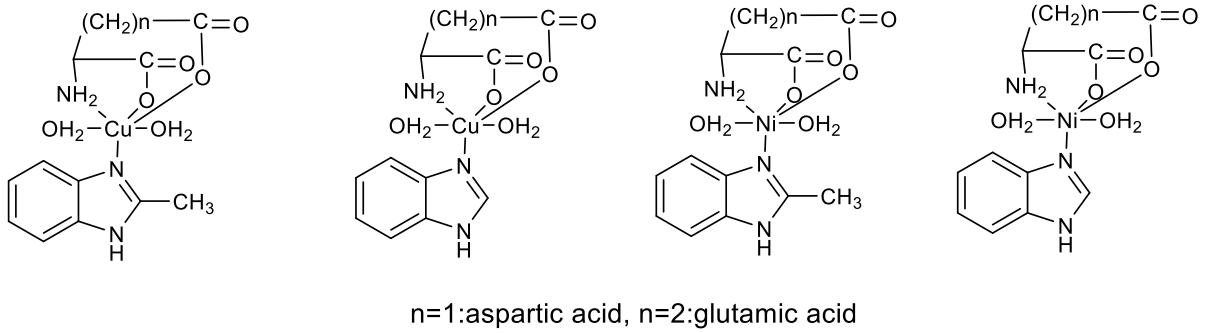


Figure 8. Cu (II) and Ni (II) mixed-ligand complexes derived from Dicarboxylic amino acid and benzimidazoles.

Alabdali and Al-Amery, (2019) reported mixed-ligand complexes of Co (II) and Cu (II) derived from histidine (HL1) as primary ligand and (N-4-methoxy phenyl) amino phenyl acetonitrile (L2) as secondary ligand. Chelating behavior of HL1 is tridentating while L2 is bidentating in an octahedral geometry, figure 9. The suggested formula of cobalt and copper complexes are [CoL1L2Cl]. H2O and [CuL1L2Cl] respectively. Hence, order of addition is important that the tridentate ligand HL1 must considered as primary ligand

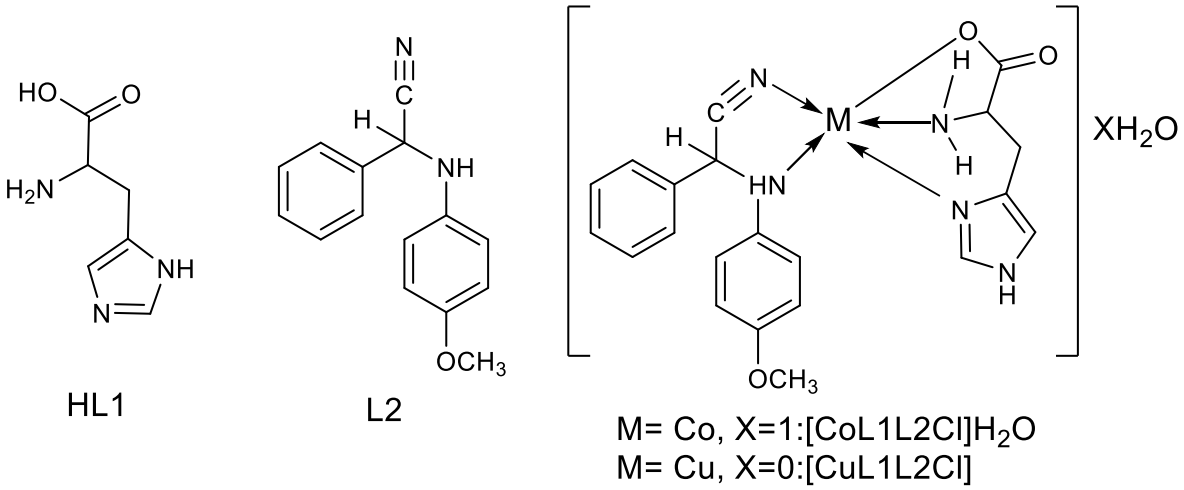


Figure 9. Co (II) and Cu (II) mixed-ligand complexes derived from histidine amino acid and amino acetonitrile.

Kumar, (Kumar 2009) reported mixed-ligand complex of Co (II) obtained from two carboxylic acids, figure 10. Histidine (HL1) acts as a tridentate ligand and hippuric acid (HL2) behaves as a bidentate ligand. Hence HL1 interacted first in a coordination mode N2O, while HL2 interaction was NO-mode in octahedral shape. The sixth coordination position is satisfied by a water molecule. Hence, order of addition is important that the tridentate ligand HL1 must considered as primary ligand.

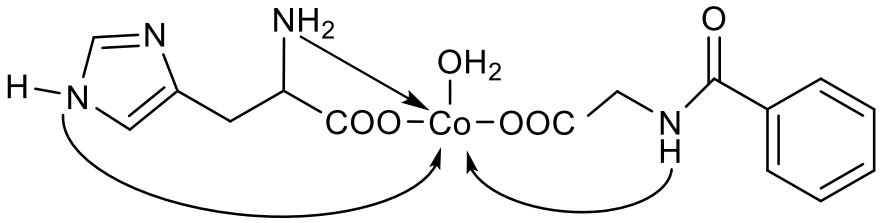


Figure 10. Co (II) mixed-ligand complex derived from histidine amino acid and hippuric acid.

4. Conclusion

According to previous literatures there are diversity of ligand types, denticity of the ligand played an important role especially the tridentate in an octahedral field, mainly it considered as primary ligand to ensure occupation of three coordination sites, then secondary fulfill the coordination number. Bidentate bulky ligand also could be primary ligand due to steric effect (size matters) when compared with strong bidentate ligand. Deciding primary and secondary bidentate ligands depend on strength of ligands, strong ligand cannot be added fist, weaker one must have the opportunity to interact first. Moreover, complex geometry is fundamental in the synthesis of mixed ligand complexes, bidentae ligand cannot be used in the preparation of tetrahedral or square based mixed ligand complexes, tridentate could be used as primary ligand in those geometries.

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