

Spectral and Redox Studies of Mixed Ligand Complexes with Transition Metal Ions: Synthesis, Characterization and Antimicrobial Activities

Jitendra Kumar

Research Scholar,

Dept. of Chemistry,

Radha Govind University, Ramgrah, Jharkhand

Abstract

Cu (II), Co (II), Mn (II), and Ni (II) mixed ligand chelates were synthesised and studied using various physicochemical approaches from L1 (4-chloroaniline & salicylaldehyde), L2 (benzaldehyde & 2-aminophenol), and L3 (4-nitroaniline & 2-hydroxyacetophenone). The edifices were depicted utilizing components investigation, molar conductance, infrared spectra, electronic spectra, and a cyclic voltammogram. As a bidentate monobasic ligand, deprotonated phenolic oxygen and azomethine nitrogen atoms coordinate the Schiff base. The low electrical conductance values of the complexes indicate that they are non-electrolytes. The electrochemical behavior, anodic and cathodic potentials, and number of electron transfers were estimated using a cyclic voltammogram. Using the paper disc technique and laying the chelates on the surface of nutritional agar, the antibacterial activity of the produced chelates against harmful bacteria such as *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumoniae*, and *Bacillus subtilis* was tested. Chelation results in Schiff base complexes with greater antibacterial activity than free Schiff base.

Condensation of 4-dimethylaminobenzaldehyde with 2-aminophenol as the primary ligand and 2-nitroaniline (L2) as the secondary ligand in a molar ratio of $M:L^1:L^2$ [1:1:1] brought about the development of new mixed ligand chelates from divalent and trivalent metal particles (Cr, Co, Ni, and Cu ions) and Schiff base (L1). The mixed Schiff base and chelates were portrayed utilizing different instruments, including essential examination, molar conductivity, attractive second estimations, infrared and electronic spectra.

Keywords: *Ligand chelates, Staphylococcus, 2-aminophenol, 4-nitroaniline, salicylaldehyde, antibacterial.*

1. Introduction

Metal complexes with mixed ligands have been shown to play critical roles in biological systems such as galactoseoxidase (GO), chlorophyll, vitamin B12, laccases, and haemoglobin. Pyrimidine, a component of

DNA and RNA, has numerous pharmacological properties, including being a potent bactericide and fungicide. Analgesic, antihypertensive, antitumor, antimalarial, antioxidant, antimitotic, and anti-HIV properties are found in many pyrimidine derivatives. The growing number of studies on Schiff bases mixed ligands, as well as the various properties investigated in these studies (anticancer, antimicrobial, and so on), prompted us to conduct research in this area. Mixed ligand buildings are more organically dynamic than the constituent ligands of homoligated bis-edifices. Changes in the compound design of Schiff bases can likewise extraordinarily regulate their electronic and attractive properties, which can be achieved by involving different progress metals that structure different mathematical designs in the hole of the large scale cycle, like mixed ligand metal buildings.

Schiff base ligands assume a significant part in coordination science because of their simplicity of creating stable buildings with a high level of progress metal particles. Chelating ligands containing N, S, and O donor atoms are particularly important due to the wide range of applications in which they are linked to metal ions. Potential analgesic, antipyretic, anti-inflammatory, and anti - rheumatic medications include some pyrimidine compounds. Among heterocyclic counterparts, 4-aminoantipyrine is believed to be a superior reagent in biological, physiological, clinical, and quantitative application. It produces a wide range of Schiff base complexes with schiff bases derived.

Benzylidene-4-iminoantipyrine and dimethyl glyoxime had been used to create Schiff base ligand Cu (II), Co (II), Ni (II), VO(II), and Zn (II) compounds, which also are discussed in this paper. Nutrient broth has been used as a substrate to investigate the physiological effects of a copper chelation towards microorganisms such Staphylococcus, S. pneumoniae, Bacillus treated carefully, Escherichia, and Staphylococcus epidermidis.

2. Transition Metal Ions

Most transition metals are distinguished from metals in Groups 1, 2, and 13 by their ability to form multiple cations with varying ionic charges. Iron, for example, frequently forms two distinct ions. Now and again, it can lose two electrons to shape the Fe^{2+} particle and three electrons to frame the Fe^{3+} particle. Tin and lead, which are p-block elements rather than d-block elements, can also combine to form multiple ions.

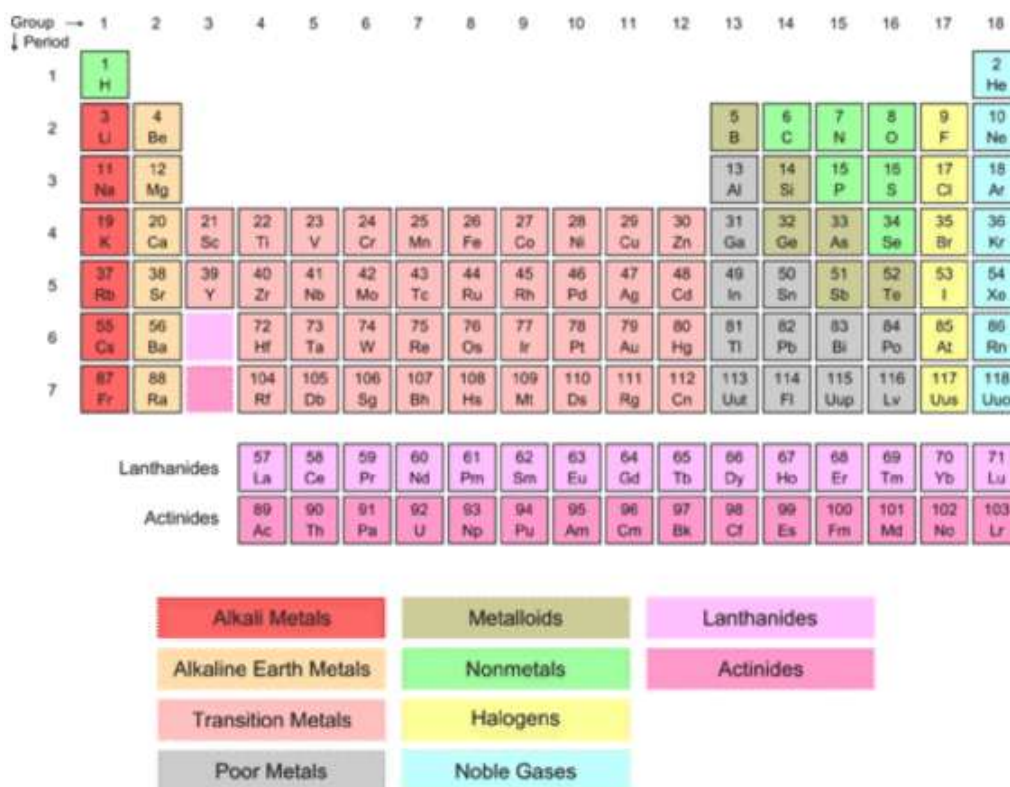


Figure: 1. Transition metal ions

The fact that transition metals have unfilled inner d shells complicates ionic formation. Although the energy level of the next higher s orbitals is lower than the d level, it is these s electrons that are removed during ionisation.

2.1. Uses for Transition Metals

Since this gathering contains such countless metals, they have a large number of uses. Numerous metals are utilized in electronic parts, while others (like gold and silver) are utilized in money related frameworks. Iron is a tough and versatile underlying material. Cobalt, nickel, platinum, and different metals are utilized as impetuses in various substance responses. Zinc is a significant part of batteries.

Table: 1. Common Transition Metal Ions

| 1+ | 2+ | 3+ | 4+ |
|--|----------------------------------|----------------------------------|-----------------------------|
| copper (I), Cu ⁺ | cadmium, Cd ²⁺ | chromium (III), Cr ³⁺ | lead (IV), Pb ⁴⁺ |
| gold (I), Au ⁺ | chromium (II), Cr ²⁺ | cobalt (III), Co ³⁺ | tin (IV), Sn ⁴⁺ |
| mercury (I), Hg ₂ ²⁺ | cobalt (II), Co ²⁺ | gold (III), Au ³⁺ | |
| silver, Ag ⁺ | copper (II), Cu ²⁺ | iron (III), Fe ³⁺ | |
| | iron (II), Fe ²⁺ | | |
| | lead (II), Pb ²⁺ | | |
| | manganese (II), Mn ²⁺ | | |
| | mercury (II), Hg ²⁺ | | |
| | nickel (II), Ni ²⁺ | | |
| | platinum (II), Pt ²⁺ | | |
| | tin (II), Sn ²⁺ | | |
| | zinc, Zn ²⁺ | | |

3. Experimental

Cobalt (II) chloride hexahydrate and nickel (II) salts hexahydrate of analytical grade were utilized straight out of the package. From E. Merck, chiral saccharides were obtained. S. D. Fine Chemicals in Bombay, India provided the saccharide. Standard practices were employed to purify and dry the solvents used, which also included ethanol, methanol, and chloroform. 10. E. Monsanto provided the N, N-dimethyl found at higher, which was employed directly without additional purification. We bought the bacterial and fungi subcultures from the Enzyme decreases Institute in Bombay.

2.1. Synthesis of Schiff Base

One for about 30 minutes, 1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one (4-aminoantipyrine) and benzaldehyde were swirled in an alcohol solution (20 mL) of the substances. After freezing, benzylidene-4-iminoantipyrine (B4AAP), a yellow solid, was purified and condensed again after methanol.

2.2. Synthesis of Cu (II), Co (II), Ni (II) and Zn (II) Complexes

In a 250 mL RB flask, an ethanolic solution of dimethyl glyoxime (10 mmol), 4-aminoantipyrine (2.03 g, 10 mmol), and Cu (II)/Co (II)/Ni (II)/Zn (II) chloride salt (10 mmol) was prepared. 1 g of sodium hydroxide was added to this solution, furthermore, the subsequent arrangement was bubbled under reflux on a water shower for 12 hours with steady blending. The arrangement was then separated and cooled for 12 hours at 0 degrees Celsius. The solidified strong item was gathered by filtration and washed with ethanol. The preparation for the Cu (II), Ni (II), Zn (II) and Co (II) complexes was given by the Scheme 1. Oxovanadium (II) complex was synthesized by utilizing the same procedure using vanadyl sulphate as a metal salt and the reaction is carried out in presence of 5% aqueous sodium acetate solution (instead of 1 g NaOH). The preparation for the vanadyl complex was given by Scheme 2.

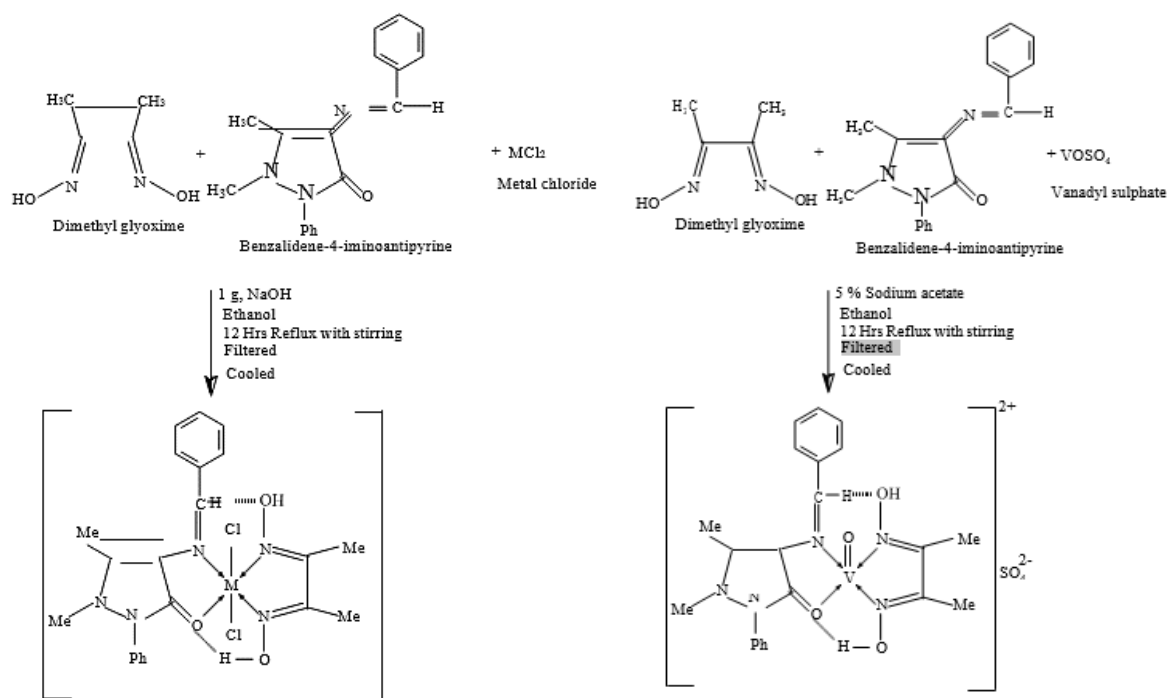


Figure: 2. M = Cu (II), Co (II), Zn (II) and Ni (II)

Table: 2. Physiological and scientific relevant data on metal cations.

| Mixture | Melt. / Decomp Point (°C) | Colour | Found (Calcd) (%) | | | | | M x 10- 2 (mho cm2 mol-1) | eff... (B. M.) |
|--------------------------------|------------------------------------|--------|----------------------|------------------|----------------|------------------|------------------|---------------------------------------|----------------------|
| | | | M | C | H | N | Cl | | |
| [CuB4AAP(DMG)Cl ₂] | 196 | Green | 11.98 (11.73) | 48.65 (48.75) | 4.18 (4.62) | 12.14 (12.93) | 13.32 (13.11) | 1.2 | 1.81 |
| [NiB4AAP(DMG)Cl ₂] | 216 | Green | 50.12 (10.94) | 48.17 (49.19) | 4.68 (4.66) | 13.18 (13.04) | 12.86 (13.23) | 3.6 | 2.37 |
| [CoB4AAP(DMG)Cl ₂] | 214 | Pink | 10.81 (10.58) | 48.67 (49.16) | 4.58 (4.66) | 13.12 (13.04) | 13.26 (13.22) | 3.9 | 3.96 |
| [VOB4AAP(DMG)]SO ₄ | 198 | Green | 8.52 (8.94) | 26.48 (46.32) | 4.32 (4.39) | 12.47 (12.28) | -- -- | 96.4 | 1.35 |
| [ZnB4AAP(DMG)Cl ₂] | 187 | Yellow | 12.06 (12.12) | 46.34 (48.54) | 4.51 (4.60) | 12.16 (12.87) | 12.43 (23.05) | 2.3 | - |

2.3. General Preparing of the Mixed Ligands Metal Complexes

Metal edifices were made utilizing the overall strategy, metal chlorides, and the Schiff base. The edifices were blended involving a comparable strategy and reagents in the molar proportion of M: L:2. (Q). An ethanolic solution (10mL, 1mmol) of the appropriate ZnCl₂ [0.136gm, 1mmol], CdCl₂.2H₂O [0.201gm, 1mmol], and HgCl₂ [0.271gm, 1mmol] was added to an ethanolic solution (10mL) of the Schiff base, primary ligand (L) [0.2843g/mol, 1mmol] (0.145gm) The precipitated complexes were filtered and washed with distilled water.

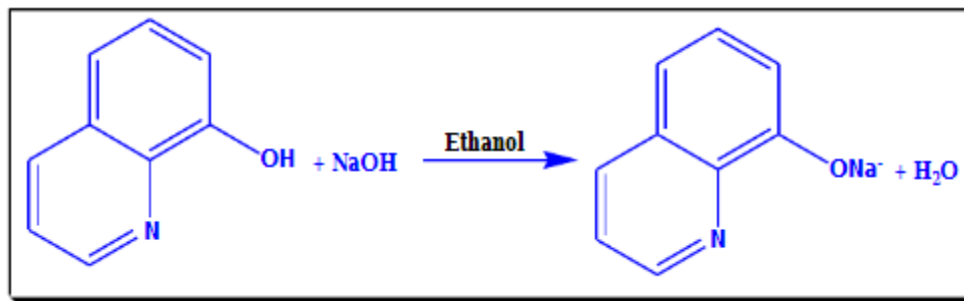


Figure: 3. Sodiumoxyquinolate.

2.4. Synthesis of Mixed Ligand Chelates

An overall method was utilized for the combination of chelates in gentle fundamental media. To 25 ml of Schiff base and 2-nitroaniline solution, 0.01 moles of the salts [CrCl₃6H₂O; 2.67 g, CoCl₂6H₂O; 2.38 g, NiCl₂6H₂O; 2.37 g, or CuCl₂2H₂O; 1.71 g] were added. A couple of drops of smelling salts arrangement (10%) were added to the blend to bring it up to the pH of 6 - 7 where the encourage will frame. The blends were refluxed for 3 hours. The chelates with particular tones were separated, washed with hot ethanol a few times, and dried. The yields are displayed in Table 3.

3. Results and Discussion

Table 2 summarises the ligands' and complexes' analytical data, as well as some physical properties. The analytical data from the complexes are consistent with the general formula [MB₄AAP(DMG)Cl₂], whereas the vanadyl complex has the general formula [VOB₄AAP(DMG)] SO₄, where M = Cu(II), Co(II), Zn(II), and Ni(II), B₄AAP = C₁₈H₁₇N₃O, and DMG = C₄H₈N₂O₂. Their attractive susceptibilities at room temperature are steady with octahedral calculation around the focal metal particle, except for the vanadyl complex, which exists in square pyramidal math. The low conductance information of the chelates upholds their non-electrolytic nature, while the higher conductance information of the vanadium chelate backings its electrolytic nature.

The responses of the ligands (L¹, L²) with the metal particles being scrutinized produce chelates of the sort [M(L¹ L²)(OH)_x(H₂O)_y]nH₂O, where n addresses the quantity of hydrated water atoms (as displayed in Table 3). The responses can be addressed utilizing the conditions underneath.

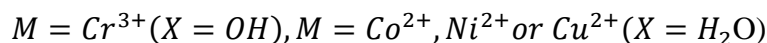
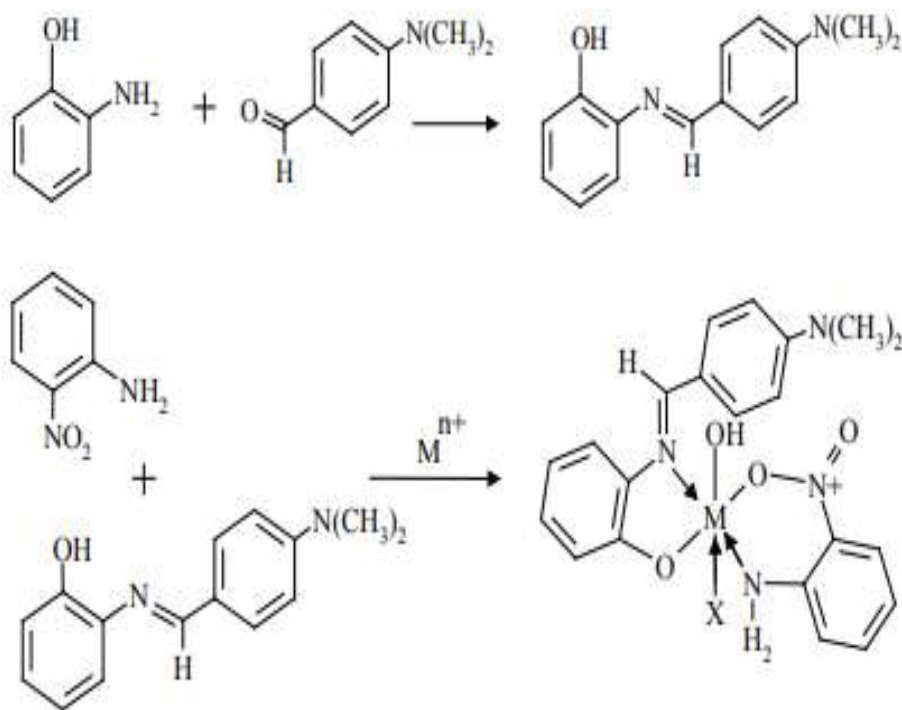


Figure: 4. Chemical equations of synthesis

3.1. Microanalyses and Molar Conductance Measurements

The CHN elemental analysis data of the synthesised mixed ligand chelates form a 1:1:1 [M:L¹:L²] ratio, as shown in (Table 3). Theoretical values were found to be consistent with observed data. The virtue of the Schiff base and mixed ligand chelates was resolved utilizing TLC and CHN essential investigations. The chelates studied in this study have molar conductance values ranging from 4.25 to 15.64 ohm⁻¹ cm² mole⁻¹, confirming their non-electrolytic nature.

Table: 3. Essential investigations and related properties of the Schiff base and the chelates.

| Ligand/ Chelate | M. wt | colour | Yield (%) | C% Calc. | C% Exp. | %H Cal c. | %H Exp. | %N Calc. | %N Exp. | μ BM | Λ^* |
|---------------------------------------|-------|---------------|-----------|----------|---------|-----------|---------|----------|---------|----------|-------------|
| Schiff base (L^1) | 329 | Bright yellow | 87.00 | 85.00 | 71.78 | 6.78 | 5.82 | 21.54 | 14.68 | - | - |
| $[Cr(L^1 L^2)(OH)_2] \cdot 6H_2O$ | 540 | Burnt sienna | 72.12 | 41.65 | 48.21 | 4.28 | 4.19 | 8.49 | 8.99 | 4.01 | 8.73 |
| $[Co(L^1 L^2)(OH)(H_2O)] \cdot 6H_2O$ | 468 | Burnt umber | 75.48 | 39.90 | 41.26 | 4.72 | 4.12 | 9.10 | 8.29 | 4.68 | 15.64 |
| $[Ni(L^1 L^2)(OH)(H_2O)] \cdot 6H_2O$ | 594 | Deep verdant | 70.53 | 42.50 | 44.20 | 4.77 | 4.14 | 8.97 | 9.56 | 3.69 | 5.23 |
| $[Cu(L^1 L^2)(OH)(H_2O)] \cdot 3H_2O$ | 473 | Red umber | 77.79 | 39.79 | 48.10 | 3.78 | 4.17 | 9.98 | 9.87 | 2.12 | 4.25 |

3.2. Infrared Spectral Studies

Appointing the groups is all very troublesome because of the chelate idea of the IR spectra of the mixed ligand chelates with differing powers. Nonetheless, in view of reports in the writing, endeavors have been made to appoint a portion of the significant vibrational extending groups. The infrared phantom consequences of the ligands, as well as their Cr(III), Co(II), Ni(II), and Cu(II) mixed ligand chelates, were recorded in (Table 4). The presence of hydrated and coordinated water molecules is indicated by bands in the 4120-4010 cm^{-1} range in the spectra of mixed ligand chelates. Meanwhile, the same spectra show bands in the 1759-1620 cm^{-1} range assigned to (HC=N) vibration, with the shift to low frequency compared to the Schiff base (L^1) confirming this group's participation in chelation via nitrogen atom. The NH_2 and NO_2 groups can also participate in coordination, as evidenced by the positions of the bands in the 2-nitroaniline spectrum at 2269 and 1804 cm^{-1} , respectively (L^2). The shifting of the NH_2 group band in the spectra of mixed ligand chelates suggests that the nitrogen atom is involved in chelation. The shifting of the 2-nitroaniline - NO_2 group band in the spectra of mixed ligand chelates suggests that this group is involved in metal ion bonding. (M-O) and (M-N) vibrations produce new bands in the 540-348 and 508-452 cm^{-1} ranges that do not exist in free ligands,

what's more, the presence of these groups upholds the support of oxygen and nitrogen molecules of the azomethine, NO₂ and OH bunches in the chelation cycle.

Table: 4. Infrared and electronic spectral data of ligands and chelates.

| Ligand/ Chelate | ν NO ₂ | ν OH(H ₂ O) | ν NH ₂ | ν C=N | ν M-O | ν M-N | nm (cm ⁻¹) |
|---|-----------------------|----------------------------|-----------------------|-----------|-----------|-----------|-------------------------------|
| Schiff Base (L ¹) | - | 4447 | - | 1388 | - | - | 358(42,452) |
| 2-nitroaniline (L ²) | 1804 | - | 2269 | - | - | - | 352(48,985), 289(29,448) |
| [Cr(L ¹ L ²) (OH) ₂].6H ₂ O | 1804 | 4341 | 2210 | 1452 | 720 | 652 | 653(28,446) |
| [Co(L ¹ L ²) (OH)(H ₂ O)].6H ₂ O | 1468 | 4239 | 2209 | 1501 | 540 | 452 | 396(18,254), 689(12,315) |
| [Ni([L ¹ L ²) (OH)(H ₂ O)].6H ₂ O | 1527 | 4120 | 2208 | 1620 | 438 | 508 | 324(27,064), 378(24,319) |
| [Cu(L ¹ L ²) (OH)(H ₂ O)].3H ₂ O | 1608 | 4010 | 2207 | 1759 | 441 | 612 | 369 (24,789), 783 (13,463) |

4. Conclusion

The mixed ligand chelates were ready and described utilizing notable physiochemical methods, yielding data about how Schiff bases as essential ligands can chelate with bidentate ligands as auxiliary ligands while likewise affirming the presence of an octahedral math for all mixed ligand chelates. The numerical plans of the chelates are proposed in the as of late referred to intensify conditions.

The ligand and its edifices have been broadly read up for their antimicrobial movement against microorganisms, for example, Staphylococcus aureus, Klebsiela pneumoniae, Bacillus subtilis, Escherichia coli, and Salmonella typhi. Most of the edifices have higher action than the free ligands. For Ni(II), Cu(II), Co(II), and Mn, new heterocyclic mixed ligand edifices containing a pyrimidine ring were blended and portrayed (II).

5. References

1. A. Kulkarni, P.G. Avaji, G.B. Bagihalli, S.A.Patil, *J.Coord. Chem.*, 2009, 62(3), 481.
2. A.D.Kulkarni, S.A. Patil, P.S. Badami, *J.Sulf.Chem.* 2009.
3. Al Zoubi, W. (2013) *Biological Activities of Schiff Bases and Their Complexes: A Review of Recent Works. International Journal of Organic Chemistry*, 3, 73-95.
<http://dx.doi.org/10.4236/ijoc.2013.33A008>.
4. Al-Noor, T. H., & Abdul Karim, L. K. (2016). *Synthetic, Spectroscopic And Antibacterial Studies of Metal (II) Mixed Ligand Complexes of Trimethoprim Antibiotic and Anthranilic Acid. TOFIQ Journal of Medical Sciences*, 3(2), 64-75.
5. El-Zweay, R.S., El-Ajaily, M.M., Ben-Gweirif, S.F. and Maihub, A.A. (2013) *Preparation, Characterization and Antibacterial Activity of some Mixed Ligand Chelates. Journal of the Chemical Society of Pakistan*, 35, 67-71.
6. Enquist, P. A. (2012). *Derivatives of 8-hydroxyquinoline - antibacterial agents that target intra- and extracellular Gram-negative pathogens. Bioorg Med Chem Lett.*, 22, 3550-3553.
7. G.G. Mohamed, Z.H.A. El-Wahab, *Mixed ligand complexes of bis(phenylimine) Schiff base ligands incorporating pyridinium moiety - Synthesis, characterization and antibacterial activity, Spectrochimica Acta 61A (2005) 1059-1068.*
8. Glcan, M.; Sonmez, M. *Phosphorus Sulfur and Silicon* 2011,186, 1962–1971.
9. Halli, M.B. and Ravindra. S. Malipatil. (2011) *Synthesis, Characterization and Spectral Studies of Metal (II) Complexes Derived from Benzofuran-2-Carbohydrazide and 2-Acetylthiophene Schiff's Base. Der Pharma Chemica*, 3, 146-157.
10. I. Mohanram, J. Meshram, A. Shaikh, B. Kandpal, *Microwave-assisted one-pot synthesis of bioactive Ugi-4CR using fluorite as benign and heterogeneous catalyst, Synth. Commun.* 43(24) (2013) 3322-3328.
11. Jadhav, S.S., Kolhe, N.H. and Athare, A.E. (2013) *Synthesis, and Characterization of Mixed Ligands Complexes of Salicyladoxime, Dimethylglyoxime and Benzoin with Mn(II) and Their Biological Activity. International Journal of Pharmacy and Biological Sciences*, 4, 45-54.
12. M. Ramana, C.Nagda, M.Himaja, *Design and evaluation of mucoadhesive buccal drug delivery systems containing metoprolol tartrate, Ind. Jour. Pharm. Sci.* 69(4) (2012) 515-518.
13. M.Ravanasiddappa ., T.Sureshg ., Syed K., S.C Radhavendray., C.Basavaraja and S.D Angadi., *E-j.chem.*, 2008, 5(2), 395-403.

14. M.S. Suresh, V. Prakash, *Preparation characterization and antibacterial studies of chelates of Schiff's base derived from 4-aminoantipyrine vanillin and ophenylene diamine, Int.J. Curr. Res. 3(2) (2011) 68-75.*
15. Maihub, A.A., El-Ajaily, M.M. and El-Hassy, N.A. (2012) *Titanium(IV), Chromium(III) and Iron(III) Complexes of Schiff Base Derived from Aldehyde and Primary Amine. International Journal of ChemTech Research, 4, 631-633.*
16. Melnick, A., & Delbrgs, A. (2007). *Medical Microbiology, McGraw Hil-USA.*
17. N. Raman, T.Baskaran, A. Selvan, and R.Jeyamurugan, *J.Iran.chem., 2008, 1, 129-139.*
18. Sönmez, M.; C, elebi, M.; Berber, I. *Eur. J. Med. Chem. 2010,45, 1935–1940.*
19. Tümer, M.; Deligönül, N.; Gölçü, A.; Akgün, E.; Dolaz, M.; Demirelli, H.; Dıgrak, M. *Trans. Met. Chem. 2006,*
20. V.Reddy, N. Patil and S.D.Angadi, *E-J chem., 2008,5(3), 577-583.*