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2. Complexes of Transition Metals with Schiff's Base

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Abstract:

Significant contributions to the development of coordination or inorganic chemistry have been made by schiff bases. In addition to being widely used in industry, schiff bases and their complexes are adaptable substances with a wide range of biological activities, such as antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic qualities. They are created by condensation of an amino compound with carbonyl compounds. Schiff bases were important for the development of inorganic, bioinorganic, and optical materials as well as for the advancement of coordination chemistry. Most of the more often used classes of organic molecules are made up of schiff bases, which are frequently used in organic, inorganic, and analytical chemistry. Schiff base ligands are very helpful because they can form stable metal complexes with a variety of transition and other metal ions. A Schiff base is produced when a primary amine condenses with an aldehyde or ketone. We will talk about in this essay. Transition Metal Complexes with Schiff's Base.

Keywords:

Schiff Bases, Inorganic, Antimalarial, Antiproliferative, Antiviral, Antipyretic, Spectroscopic, Metal–Ligand Complexation, Transition Metal Complexes, Synthesis, Metal Ions, Dyes, Polymers, Photodetectors.

2.1 Introduction:

Inorganic chemists are particularly interested in transition metal Schiff base complexes because of their distinctive spectroscopic, chemical, and structural characteristics, which are frequently significantly impacted by the ligand structure. Coordination complexes comprising substituted ketones have been observed to display a broad spectrum of stereochemistry and bonding interactions due to their varied structural and physical characteristics. In recent years, there has been a growing interest in the synthesis of unsymmetrical coordination complexes by the interaction of transition metal ions with tetradentate. This comprehension encompasses an enhanced comprehension of metal–ligand complexation, location of metal binding sites, and molecular self-assembly.

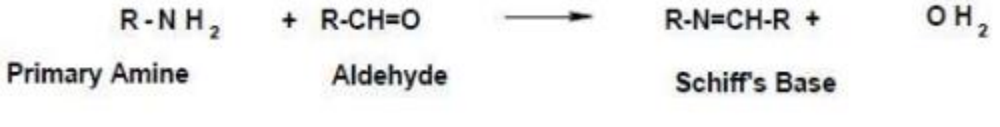
Improving understanding in these domains will enable the development of new and enhanced supramolecular chemistry, bioengineering, and catalytic systems through the utilization of coordination complexes.

It seems that less research has been done on the unsymmetrical Schiff base complexes made from acetophenone than on the symmetrical tetradentate Schiff base complexes, which have been synthesized and characterized in great detail. The transition metal complexes of the unsymmetrical Schiff base formed from acetophenones and carbohydrazide have not been documented in any literature. Thus, our work covers the synthesis and characterization of Schiff base ligand and its complexes, thereby extending our interest in Schiff base ligands and their metal chelates. Using infrared, molar conductance, magnetic moment, solid reflectance, and thermal analysis, the coordination behavior of the ligand with transition metal ions (Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II), Cd (II), Zn (II), UO2(II), and Th (IV)) is first studied.

The azomethine or imine (–C=N) unit is sustained by schiff bases. Hugo Schiff first reported on the main condensation of amines with carbonyl compounds. Schiff bases are widely used in many fields of chemistry, including organic and inorganic chemistry and biology. The clinical and commercial significance of Schiff bases and their metal complexes for medical purposes is growing. Because of their wide spectrum of biological actions, including their ability to be anti-inflammatory, analgesic, antibacterial, antispasmodic, tuberculosis, anti-cancer, antioxidant, and anthelmintic, schiff bases have gained importance in the medical and pharmaceutical fields.

Additionally, schiff bases are used as corrosion inhibitors, pigments, dyes, catalysts, polymeric stabilizers, and intermediates in chemical synthesis. After a literature review, it is established that metal complexes have higher biological activity than free organic molecules. Biological activity has increased since the transition metals of Schiff bases were implemented. Schiff bases have been identified as a pivotal point in the creation of inorganic biochemistry and optical materials, and they have played a major part in the evolution of coordination chemistry. The alteration of an existing medicine by combining it with a metal core has garnered attention in recent years as a novel therapy against resistant organism. Thus, we created and studied transition metal complexes from 2-carboxybenzaldehyde and sulphadiazine.

In the realm of coordination chemistry, the Schiff base ligands and their metal complexes are particularly significant. A brief general review of the chemistry of Schiff bases and their metal complexes is required because the current work focuses on the complexes of Schiff base ligands. The first condensed result of amines with carbonyl compounds was obtained by German scientist Hugo Schiff (Schiff, 1864) and was named Schiff base because it included an Azomethine group (-CH=N-).



Where an aromatic or aliphatic group may be represented by "R." Aliphatic aldehydes' Schiff's bases are easily polymerized and relatively unstable. On the other hand, aromatic aldehydes with an efficient conjugation system have comparatively higher stability. Schiff bases are often bi- or tridentate ligands that can combine with numerous transition metals to generate extremely stable complexes. Schiff's base offers a wide range of applications in medicinal chemistry.

Prior to now, a lot of attention has been paid to the complexing properties of bi, tri, and tetradentate Schiff base ligands with possible donor sites that include oxygen-nitrogen, oxygen-sulfur, nitrogen-sulfur, and oxygen-nitrogen-sulfur. When the Schiff bases are sufficiently proximal to the azomethine 2 group to form five or six membered chelating rings upon reaction with the metal ion, then these functional groups, such as -OH, -SH, or -NO, etc., are regarded useful chelating agents. The majority of cases regarding the stability of the complexes have focused on the characteristics of the ligand rather than the metal ion.

This work uses a Schiff base that has been produced and its complexes formed from salicylaldehyde and urea.

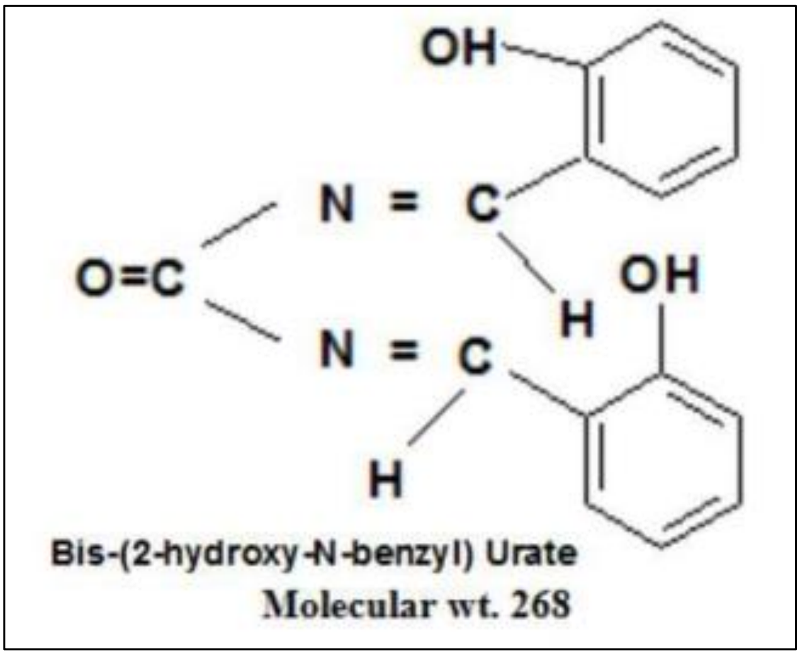


Figure 2.1: Structure of ligand (Schiff base)

Schiff bases are helpful in medicine as antibiotics and anti-inflammatory drugs, in catalysis, as chelating ligands in coordination chemistry, and in industry for their anticorrosion qualities. The metal complexes of amino acid-based Schiff bases serve as models for several significant biological systems and are highly efficient metal chelators.

We have decided to do research in this area since there is a large range of potential Schiff-base metal complexes with ligand and coordination environment choices. In order to learn more about associated structural and spectral features as well as their antibacterial capabilities, we report the synthesis and characterization of a Schiff base formed from 2-hydroxy-5-methyl acetophenone and glycine in the current study. We also discuss the metal complexes of this Schiff base.

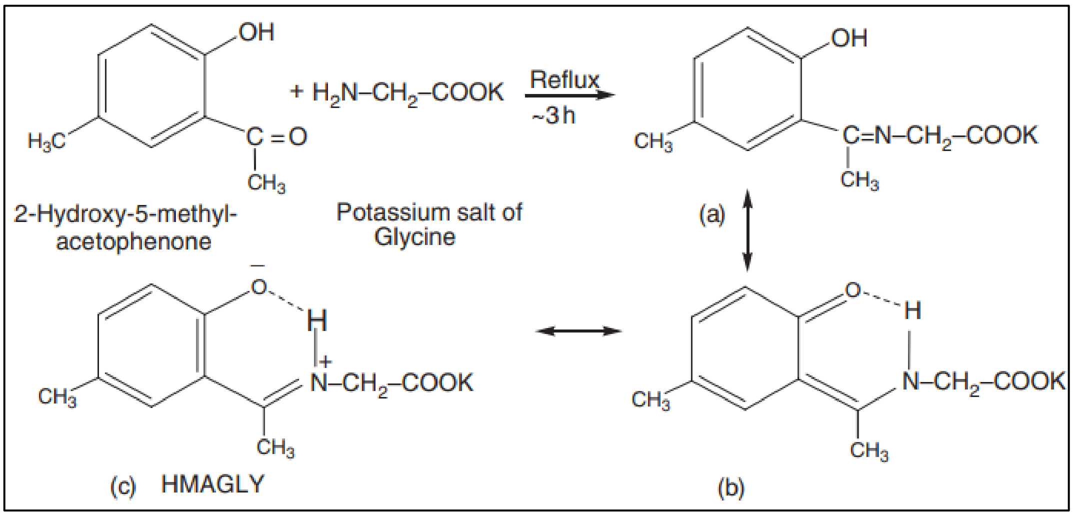


Figure 2.2: The schematic representation of synthesis of HMAGLY.

2.2 Applications:

A great deal of research has been done on schiff bases, semi carbazones, thiosemicarbazones, and their metal complexes because of their numerous biological activities, including antifungal, antitumor, antibacterial, and anticancer properties; they are also used as catalysts and in medicines. They are also employed in pyrotechnic mixtures, dyes, polymers, nanotechnology, lasers, transistors, and defense as gas-generating agents. Imine derivatives are utilized in biological systems as photodetectors, in optical computers for radiation measurement and control, in molecular memory storage, imaging systems, and as organic material in reversible optical memories (Figure 3).

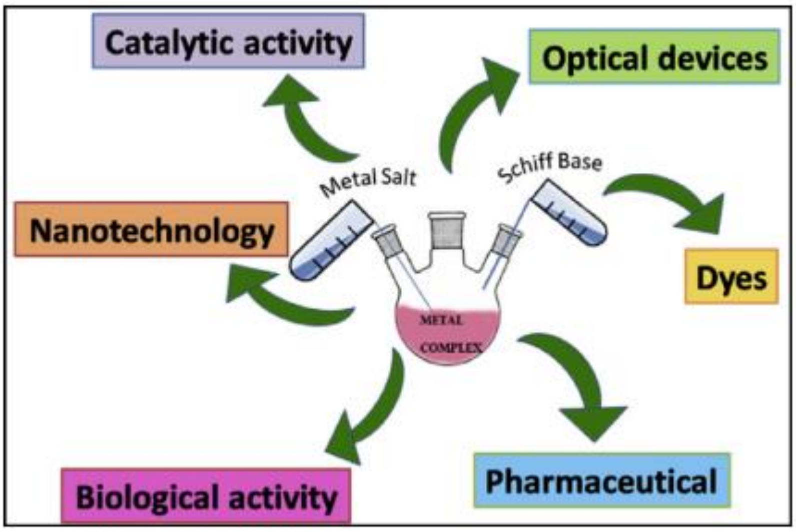


Figure 2.3: Schematic presentation of application of complexes of imine derivatives

2.3 Biological Activities of Schiff Bases:

Typically, schiff bases are bi- or tridentate ligands that have the ability to combine with transition metals to produce extremely stable complexes. Schiff base reactions are helpful in organic synthesis for the production of carbon-nitrogen bonds. New Schiff bases (Figure 4) generated from 4-amino-5-sulfanyl-1.2.4-triazoles and glyoxal, biacetyl, or benzil have been used to produce complexes of Co (II) and Ni (II). Each has an overall octahedral shape and the stoichiometry ML (H2O)2, with L coordination provided by the two thiolato sulfurs and two imimine nitrogens. A sample Co (II) complex was assessed for oxytocic properties, and several of the complexes were investigated for antibacterial and antifungal properties. Moreover, it was discovered that complex(c) (R; Me, R1; H) inhibited the oxytocic activity of oxytocin on a rat uterus that was isolated (Table 1)

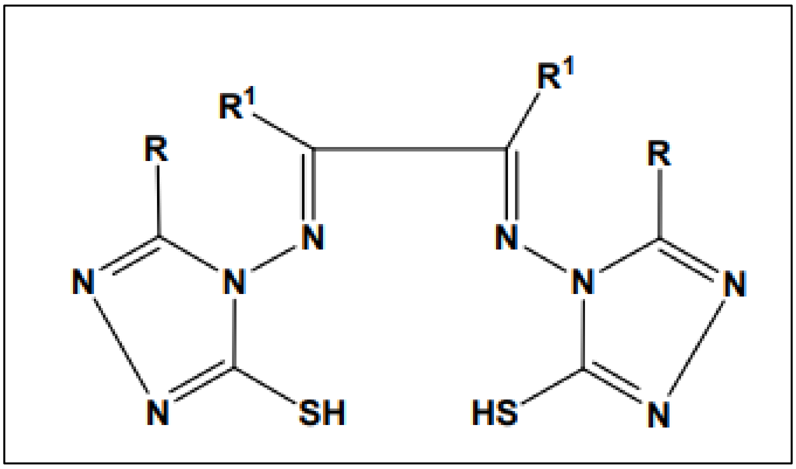
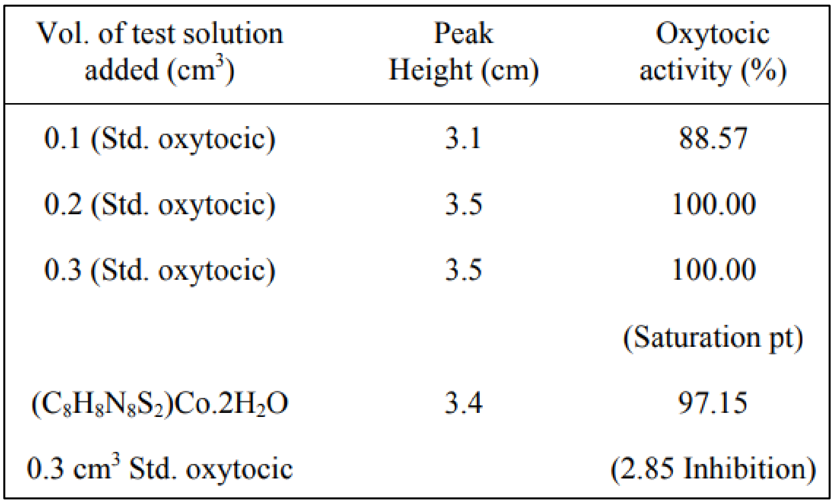


Figure 2.4: Complexes of Co (II) and Ni (II) with new Schiff base.

Table 2.1. Data showing the oxytocic activity of cobalt (II) complex(c).



Vol. of test solution added (cm^3)	Peak Height (cm)	Oxytocic activity (%)
0.1 (Std. oxytocic)	3.1	88.57
0.2 (Std. oxytocic)	3.5	100.00
0.3 (Std. oxytocic)	3.5	100.00 (Saturation pt)
$(C_8H_8N_8S_2)Co.2H_2O$ 0.3 cm^3 Std. oxytocic	3.4	97.15 (2.85 Inhibition)

Schiff bases find extensive use in the food, dye, analytical, catalytic, fungicidal, agrochemical, and biological industries. Deep mycosis is becoming more common, thus there is a greater focus on finding new, low-toxicity antimicrobial medications that are more effective.

Because of their structural diversity and ease of preparation, schiff-base complexes are regarded as some of the most significant stereochemical models in main group and transition metal coordination chemistry.

With many of them being employed as somewhat successful models of biological compounds, Schiff-base complexes have a great deal of biological potential. They have contributed significantly to the advancement of modern coordination chemistry and are also essential to the creation of optical materials, inorganic biology, and catalysis.

2.3.1 Antimicrobial Activities:

- **Antibacterial Activities:**

The antibacterial activity of a schiff base produced from indoline-2, 3-dione, and 2-aminobenzoic acid against Staphylococcus aureus was demonstrated via its tin complex. When the compounds were compared to the usual medication, imipenem, the results showed that while the compounds were active, their activity was not as high. One possible explanation for this activity is the presence of hydroxyl and phenyl groups. The coordination and polarity of a tin (IV) atom with the oxygen of the ligand may be the cause of the higher activity in the organotin complexes. The results mirrored the previously published data about the biological activity of organotin complexes, with ligand < MeSnL < PhSnL < BZ3SnL being the order of increasing activities. Co (II), Cu (II), Ni (II), Mn (II), and Cr (III) complexes with Schiff bases derived from 2,6-diacetylpyridine and 2-pyridine carboxaldehyde with 4-amino-2,3-dimethyl-1-phenyl3-pyrozolin-5-one exhibit antibacterial and antifungal activities against the following microorganisms: Micrococcus leteus, Bacillus megaterium, Escherichia coli, Klebsiella aureus, Mycobacterium Smegmatis, Pseudomonas aeruginosa, Enterococcus cloacae, Bacillus aureus, and Escherichia coli. It was observed from the data that the L1 ligand had little effect against S. aureus, while it was more effective against E. coli. In almost all cases, metal complexes are more effective against bacteria than L2.

Using the MTT method, the antibacterial activity of the Schiff base 4-chloro-2-(2-morphiolinoethylimino) methylphenolato methanolchloro and its Zn (II) complex was assessed against two strains of Gram-positive bacteria (B. subtilis and S. aureus) and two strains of Gram negative bacteria (E. coli and P. fluorescence). With a minimum inhibitory concentration (MIC) of 12.5µgmL-1, the Schiff base exhibited noteworthy efficacy against a pair of Gram-negative bacterial strains, while remaining inert against the other two strains. With regard to both Gram-positive and Gram-negative bacteria, the zinc complex exhibited a broad spectrum of bactericidal activities that were either comparable to or more effective than those of commercial antibiotics (Kanamycin and penicillin). The benzofuran-2-carbohydrazide and benzaldehyde [BPMC] or 3,4-dimethoxybenzaldehyde [BDMePMC] benzofuran complexes of Co (II), Ni (II), Cu (II), Zn (II), Cd (II), and Hg (II) exhibited biological activity. When compared to free ligands, the Cu (II), Zn (II), and Ni (II) complexes of [BPMC] and the Cu (II) and Zn (II) complexes of [BDMeOPMC] are more active against S. aurious than the Co (II) and Cd (II) complexes of [BPMC] are toward E. coli. The Cu (II), Co (II), Ni (II), and Cd (II) complexes of [BDMeOPMC] are more active than the parent ligands in the case of A. fumigatus, however none of the complexes are active against A. niger.

- **Antifungal Activities:**

Investigations were conducted on the microbiological activity of N-(2-hydroxy-1-naphthalidene) phenylglycine and its transition metal complexes. It can be inferred from the antifungal screening data that the ligand's activity has enhanced as a result of complexation. In comparison to the ligand and the equivalent metal salts, Cu (II), Ni (II), and Co (II) complexes have demonstrated superior antifungal activity. A yeast-like fungus called Candida albicans was used to investigate two bidentate Schiff base ligands: 2- (2-hydroxy-3, 5-dichloro/dibromo) benzaldehyde- [4- (3-methyl-3-mesitylcyclobutyl)-1, 3-thiazol-2-yl] hydrazone, L1H, and L2H, as well as their metal complexes. Salicylaldimine, which contains formaldehyde and piperazine moity, together with its metal polychelates, was found to have fungicidal properties against two yeast species, Aspergillus and Candida albicans.

Against Candida albicans, the Cu (II)-polychelate shown strong activity, whereas the other showed little activity. Since enzymes that depend on free hydroxyl groups for their activity seem to be particularly vulnerable to deactivation by the metal ion of polychelates, the presence of N and O donor groups in the ligand and its metal polychelates hindered the synthesis of enzymes. In comparison to the ligand, all metal polychelates are more hazardous. Neutral compounds containing aniline (L1) /p-nitroaniline (L2) /p-methoxyaniline (L3) and Schiff bases generated from 3-nitrobenzylidene-4-aminoanttipyrine and Co (II), Ni (II), Cu (II), and Zn (II) exhibited antifungal action. When the MIC values of the ligands and their complexes are compared, it can be seen that the complexes have more antimicrobial properties. Tweedy's chelation theory and the overtone notion can both be used to explain the complexes' increased activity.

2.4 Synthesis Procedure of Transition Metal Complexes:

Typically, the ligand and metal salts (metal nitrates hexahydrate) are combined in a 2:1 ratio in methanol solvent, and the mixture is agitated for two hours at a temperature of 70–80 °C. Here, we dissolve a 2 mmol (2 equ.) ligand in 10 ml of methanol in a beaker, and then we take 1 mmol (1 equ.) of metal salt nitrates in a different beaker of methanol. Add the metal salt solution dropwise using a dropper after stirring the ligand solution in a round-bottom flask for 10 minutes. observed and documented the reaction's progress using the TLC method. While it sometimes took some time, the formation process in many complexes discovered color and precipitate production immediately. Run these reactions for a duration of two to three hours. The synthesized product was first cleaned with an ethanol solution and then extracted once more at room temperature using the remaining solvent. Additional pure form of the compounds were obtained; weight was taken; yield was assessed; melting point was measured; and characterization was carried out. (Scheme-1).

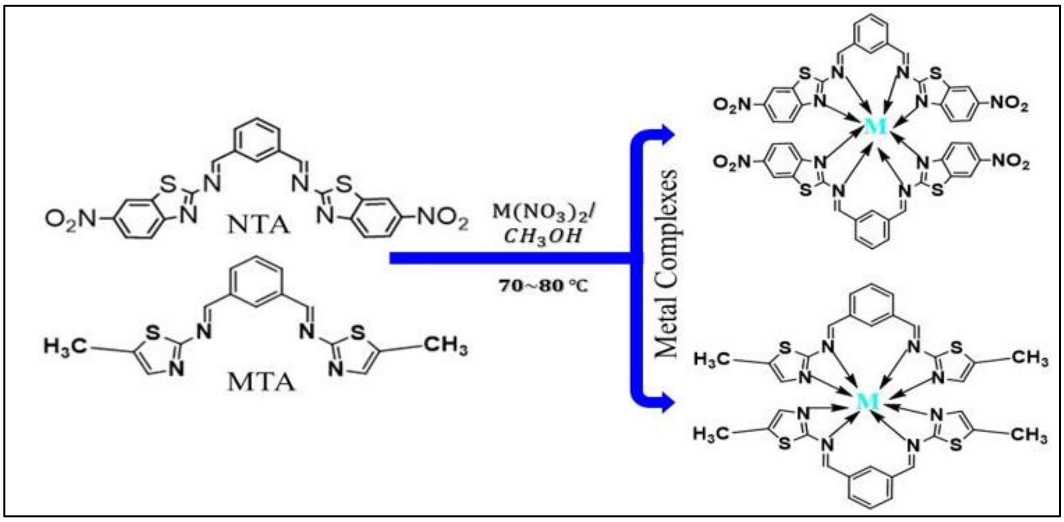


Figure 2.5: Schematic diagram of synthesis process of the complexes M-NTA and M-MTA Metal Complexes formation.

Co (II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (cobalt nitrate) 0.182 g in methanol. Solid honey gold powder; yield- 70% (0.355g), MP-287℃; FT-IR (cm-1): 3860.86, 2361.42, 1649.37, 1291.58, 747.50, (SI-1), UV-Vis. Absorption at 367 nm (λmax); ESI-MS(e/z): 547.43 (calculated); Elemental estimation: C 48.27; H 2.21; Co 10.77; N 15.35; O 11.69; S 11.71 (approx.), C 48.22; H 2.15; Co 10.82; N 15.45; O 11.63; S 11.75 (observed).

Ni (II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (nickel nitrate) 0.182 g in methanol; solid wine red powder; yield- 78% (0.396g), MP-256℃ ; FT-IR(cm-1): 3843.92, 3743.73, 3648.55, 2361.84, 1692.72, 1330.68; (SI-2), UV-Vis absorption at 363 nm(λmax); ESI-MS (e/z): 545.19 (calculated), 545.97 (observed) SI-11; Elemental estimation: C 48.29; H 2.21; N 15.36; Ni 10.73; O 11.70; S 11.72 (approx.), C 48.31; H 2.24; N 15.30; Ni 10.68; O 11.71; S 11.65 (observed).

Cu (II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (copper nitrate) 0.187 g in methanol; solid golden brown powder; yield- 63% (0.323g), MP-254℃ ; FT-IR (cm-1): 3843.70, 3678.18, 2361.88, 1692.91, 1293.63, 748.54; (SI-3), UV-Vis absorption at 365nm (λmax); ESI-MS (e/z): 550.97 (calculated), 550.92(observed) SI-12; Elemental estimation: C 47.86; H 2.19; Cu 11.51; N 15.22; O 11.59; S 11.62 (approx.), C 47.81; H 2.29; Cu 11.47; N 15.14; O 11.62; S 11.53 (observed).

Zn (II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1mmol metal salt (zinc nitrate) 0.189 g in methanol; solid lemon yellow powder; yield- 75% (0.387g), MP-271℃ ; FT-IR (cm-1): 3860.85, 3744.05, 3678.18, 2361.56, 1741.83, 1693.02, 1291.95, 747.36; (SI-4), UV-Vis absorbance at 372nm (λmax); ESI-MS (e/z): 553.88 (calculated); Elemental estimation: C 47.71; H 2.18; N 15.17; O 11.55; S 11.58; Zn 11.80 (approx.), C 47.74; H 2.23; N 15.20; O 11.50; S 11.53; Zn 11.87 (observed).

Cd (II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (cadmium nitrate) 0.236 g in methanol; solid orange powder; yield- 71% (0.470g), MP-289℃; FT-IR (cm-1): 3843.90, 3743.79, 3648.38, 2361.82, 1741.81, 1692.65, 1292.07, 1120.19, 745.78; (SI-5),UV-Vis absorbance at 382 nm (λmax); ESI-MS (e/z): 601.94 (calculated); Elemental estimation: C 43.97; H 2.01; Cd 18.71; N 13.99; O 10.65; S 10.67 (approx.), C 44.03; H 2.11; Cd 18.63; N 14.09; O 10.55; S 10.71 (observed)

Co (II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol (cobalt nitrate) 0.182 g in methanol; solid yellow powder; yield-64% (0.403g), MP-234℃ ; FT-IR (cm-1): 3860.90, 3743.64, 3678.16, 3648.52, 3619.40, 2361.73, 1741.68, 1693.20, 1646.38, 1515.72, 1464.35, 1425.79; (SI-6), UV-Vis absorption at 371nm (λmax); ESI-MS (e/z): 385.37(calculated) ; Elemental estimation: C 49.84; H 3.69; Co 15.25; N 14.58; S 16.60 (approx.), C 49.87; H 3.66; Co 15.29; N 14.54; S 16.64 (observed)

Ni (II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (nickel nitrate) 0.182 g in methanol; solid duty green powder; yield- 77% (0.485g), MP-252℃ ; FT-IR (cm-1): 3843.77, 3743.74, 3678.15, 3648.65, 3619.41, 2361.63, 1741.67, 1693.12, 1646.38, 1516.03, 1463.92, 1396.44, 827.82; (SI-7), UV-Vis absorbance at 363 nm (λmax); ESI-MS (e/z): 385.13(calculated) ; Elemental estimation: C 49.90; H 3.66; N 14.55; Ni 15.24; S 16.65 (approx.), C 49.95; H 3.61; N 14.50; Ni 15.19; S 16.67 (observed).

Cu (II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (copper nitrate) 0.187 g in methanol; solid dandelion powder; yield- 73% (0.492g), MP-241℃ ; FT-IR (cm-1): 3843.89, 3743.75, 3619.30, 2361.91, 1693.21, 1646.28, 1516.35, 1461.99, 1329.98, 1297.32, 1127.26, 822.56, 750.38; (SI-8), UV-Vis absorbance at 273-328nm (λmax); ESI-MS (e/z): 389 (calculated) ; Elemental estimation: C 49.28; H 3.62; Cu 16.29; N 14.37; S 16.44 (approx.), C 49.23; H 3.59; Cu 16.32; N 14.34; S 16.47 (observed).

Zn (II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (zinc nitrate) 0.189 g in methanol; solid yellow powder; yield- 75% (0.507g), MP- 238℃; FT-IR (cm-1): 3844.06, 3743.66, 3678.39, 3648.44, 3619.38, 2361.85, 1741.68, 1693.33, 1646.35, 1515.73, 1425.97 cm-1; (SI-9), UV-Vis absorbance at 368nm (λmax); ESI-MS (e/z): 391.00 (observed) SI-13 ; Elemental estimation: C 49.05; H 3.60; N 14.30; S 16.37; Zn 16.69 (approx.), C 49.12; H 3.64; N 14.10; S 16.34; Zn, 16.73 (observed).

Cd (II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (cadmium nitrate) 0.236 g in methanol; solid tiger yellow powder; Yield 67% (0.485g), MP-247℃; FT-IR (cm-1): 3860.8 3743.68, 3678.16, 3648.49, 3619.44, 2361.97, 1741.78, 1693.11, 1646.58, 1515.69, 1425.85, 1330.44; (SI-10), UV-Vis absorbance at 360nm (λmax); ESI-MS (e/z): 440.91 (observed) SI-14; Elemental estimation: C 43.79; H 3.22; Cd 25.61; N 12.77; S 14.61 (approx.); C 43.76; H 3.20; Cd 25.66; N 12.79; S 14.59 (observed).

2.5 Conclusion:

Schiff bases are highly significant compounds due to their diverse range of characteristics and their capacity to form complexes with other metal ions, including transition metal ions. The numerous uses of schiff bases and their metal complexes in biological processes, as nonlinear optical devices, as catalytic agents, as therapeutic agents, in the identification of metal ions, in the extraction of metal ions from aqueous solutions, in dyes, and in other industrial and biological domains have generated a great deal of interest over the years.

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