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BIOLOGICAL EVALUATION OF TRANSITION METAL COMPLEXES DERIVED FROM N, S BIDENTATE LIGANDS: SYNTHESIS AND CHARACTERIZATION



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Abstract

Metals are essential cellular components that have been hand-picked by nature to perform a range of activities in biochemical processes that are absolutely necessary for living creatures. Metals are required in order for biochemical processes to take place, hence live organisms cannot exist without them. The existence of transition metal complexes is essential to a variety of chemical and biological processes, including catalysis, the synthesis of materials, photochemistry, and the operation of biological systems. Medicinal inorganic chemistry offers the ability to make advantage of the specific properties of metal ions throughout the process of producing new drugs. For medicinal purposes, a wide variety of metals and salts derived from those metals have been used throughout the whole of human history. As the field of inorganic chemistry continues to make progress toward development, the relevance of transition metal complexes as therapeutic molecules is becoming more crucial. Because of recent advancements in inorganic chemistry, it is now possible to create a wide range of transition metal complexes with organic ligands of interest. These complexes have the potential to be used as therapeutic agents. It was previously believed that it was impossible to construct complexes like this. The purpose of this study is to offer an overview of the function of metals as well as recent developments in the field of medical bioinorganic chemistry. The study focuses on unique tactics for the production of revolutionary metal-based drugs and their prospective applications.

Keywords: Metals, Medicinal bioinorganic, Photochemistry.

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INTRODUCTION:

Human biology relies heavily on the involvement of metal ions in a broad range of functions. Certain metal ions have been linked to the development of diseases like Iron deficiency diseases including pernicious anemia and vitamin[1][2] A deficiency diseases like stunted development not getting enough zinc in one's diet), and congenital heart disease (caused by a copper deficiency). Lack of copper in the diet has been linked to baby heart disease. in their diet, which is only one example of a condition that may be brought on by a shortage of particular metal ions.

Alzheimer's disease is only one of several disorders that may be exacerbated by a deficiency of certain metal ions. The ability to cure problems caused by inadequate metal-ion function is a crucial part of medical bioinorganic chemistry. Medical bioinorganic chemistry also relies heavily on the ability to conduct molecular-level analyses of diseases. Metal ions are an essential part of life, and without them, the science couldn't possibly serve its original diagnostic and therapeutic purposes. Redox activity, a variety of coordination modes, and reactivity toward organic substrates are just a few of the characteristics that set metals apart from other substances. The density of metals is greater than that of most other materials.

These features are responsible for the metallic luster seen on metal surfaces. Due to their inherent reactivity, metals are often put to very limited uses in everyday life. In addition, several clinical problems, including cancer, have been related to exposure to very high levels of metal ions. As a result of these considerations, coordination complexes have gained a favorable reputation as appealing probes in the area of [3]medicinal chemistry. This is true whether the complexes are in the form of actual medicines or of "pro-drugs." Metal ions, which are present in a wide variety of minerals and may be sourced

from elements like zinc and copper, are required for all organisms to operate normally. Many different types of biological processes across the natural world rely heavily on metal ions that might be isolated.

Copper, iron, and manganese are all examples of transition metals that play important roles in many biological processes. [4] Transition metals are often found near the active regions of proteins and enzymes, where they perform a wide range of actions, including electron transport, catalysis, and structural roles. These functions may have a catalytic role, facilitate electron transport, or contribute to the structure [5] of a molecule. However, many clinical illnesses, including cancer, have been related to improper metabolic processing of these essential metals. Among these possible clinical illnesses is cancer.

Although "trace metals" are only required in very low concentrations for a wide range of biological functions, even these low levels need careful monitoring and management. Recent studies have paved the way for the investigation of transition metal complexes with the hope that they might serve as therapy of a wide range of human illnesses and ailments. All transition metals have a similar property: they can interact only with certain negatively charged molecules, regardless of their oxidation state.[6][7] Metal-based pharmaceuticals with varied pharmacological uses and therapeutic potential have been discovered as a direct consequence of the properties of transition metals. These pharmaceuticals have also been created. Thanks to recent advances in inorganic chemistry, it is now possible to explore further possible medical uses of metal complexes. The greater accessibility of such centers has made this a reality.

Transition metal complexes are increasingly being used as therapeutic agents in the field of clinical medicine. Beneficial compounds, such as those with

anti-inflammatory, anti-infectious, and anti-diabetic properties, may be produced with the usage of these complexes. Transition metal complexes are now the subject of intensive research and development with the hope that they may one day be used as medications. Despite their many limitations and bad effects, Even today, transition metal complexes are the backbone of the chemotherapeutic drug industry. the area of medical treatment. This is the case despite the fact that their services come with a number of downsides[8].

Due to the advent of organic ligands that include a variety of donor groups, a growing number of people are showing an interest in the scientific discipline of coordination chemistry. The introduction of a wide variety of donor groups into organic ligands has made this feasible.1-2, and if the ligand in issue is of any biological relevance, this impact is much amplified. Antibiotic⁵, anti-coagulant⁶⁻⁷, anticancer⁸, and antiinflammatory⁹ qualities are only a few of the reasons why coumarins have attracted so much attention from scientists in the domains of biology, organic chemistry, and medicine. The coumarin family of organic compounds has emerged as a modern-day powerhouse, with several applications in the pharmaceutical, chemical, and food sectors.[9][10] The coumarins are an important part of this class of compounds. The seeds, roots, and leaves of many different plant species contain coumarin derivatives, a kind of secondary metabolite. Multiple biological impacts of these secondary metabolites have been shown. Transition metal chemistry is intriguing because of the wide variety of applications it has. Coordination compounds are useful because of the many functions they serve in both chemical and biological systems. Coordination compounds are therefore recognized as important classes of molecules. Using N-aminoquinolone as a starting material, Al-Amery synthesized complexes with Schiff bases and reported their antibacterial

activity. The results of the antimicrobial evaluation were released first.

This investigation details the construction of several recently constructed complexes and an examination of their features. These complexes had previously been synthesized in a laboratory setting. To create these complexes, the metalions worked together with four different donor atoms.[11]

REVIEW LITERATURE

Anju Malik and the other researchers working under her leadership deserve credit for the success of this study. Each of the tellurium(IV) complexes is a crystalline solid that exhibits a unique range of hues. To assert that these solids absorb no moisture is a safe assumption since they neither take in nor give out any moisture. In addition, it retains its original shape even when subjected to a steady temperature. They can be dissolved in polar donor solvents like dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), but not in non-polar organic solvents or less polar organic solvents. They are insoluble in all other organic solvents, even less polar organic solvents.[13] These polar liquids serve as electron donors in a chemical process. They are insoluble in all organic solvents, including certain organic solvents, and even in less polar organic solvents. In a series of assays employing the "Broth Dilution Method" and standard drugs like ampicillin and chloramphenicol for antibacterial activity and nystatin and greseofulvin for antifungal activity, it was found that organyltellurium(IV) complexes displayed greater antibacterial activity than antifungal activity as compared to free ligand. In contrast, unbound ligand showed much stronger antifungal activity than bound ligand.

Srivastava and Shailendra Pande (2). There was evidence that these bases mitigated the effects of epileptic attacks. A wide range of aldehydes, ketones, and cyclic ketones were used to generate these schiff bases.

Abdullahio. Sobola et al. (3) detailed the synthesis of the Schiff bases of salicylaldehyde and o-vanillin with 2- and 3-aminoand (aminomethyl)pyridine, respectively, and their Copper metal complexes that were studied using various spectroscopic techniques. Results from experiments conducted on *Candida albicans* revealed that ligands built from o-vanillin were very effective in combating the fungus. The antifungal drug ketoconazole is widely available. However, this chemical has far more antifungal action than ketoconazole. The antibacterial activity of the Cu(II) complexes was also found to be comparable to or even greater to that of the free ligands. This was determined by assessing the Cu(II) complexes' performance in relation to that of the free ligands. This truth was learned via experimental testing.

Rafiu Shaibu and Gareth M. Watkins (4) published a study describing the synthesis of substituted hydroxy ben Zaldy mines. We were able to do this by mixing the right amounts of salicylaldehyde, o-vanillin, p-vanillin, or vanillin with 2-aminomethyl pyridine. In place of the desired ingredient, you might [14][15] use salicylaldehyde, p-vanillin, or vanillin. In addition, they discussed the many spectroscopic approaches that had been used to provide an explanation for the compounds. It was found that the intramolecular hydrogen bonding was affected by the electronic effects of the substituents and solvents in one of two ways: either via the conjugation of the heterocyclic ring, or by a change in the nitrogen atom's ability to enter into hydrogen bonding. Both of these processes were shown to be accountable for the shift. These two phenomena occurred at the same time. Methanol and dimethylformamide were used as solvents in the experiments performed to investigate the electrical effects of different substituted hydroxybenzaldehyde's.

Condensation of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one with 2-

aminopyridine, p-phenylenediamine, and o-phenylenediamine led to the formation of Schiff bases. Several spectroscopic analyses of their compounds with metals including lanthanum (III), neodymium (III), and erbium (III) indicated three unique chelation pathways. Mononegative (OO) bidentate ligands, monobasic (NO) bidentate ligands, and dinegative (N2O2) tetradentate ligands are the terms used to describe these pathways. The excitation studies showed that the erbium complexes and the neodymium complexes both fluoresced in their own distinctive ways.

The OBJECTIVE OF THE STUDY:

1. To study on investigate the biological assessment of transition metal complexes.
2. To study on analytical data of Schiff bases and the metal complexes they produce.

METHOD

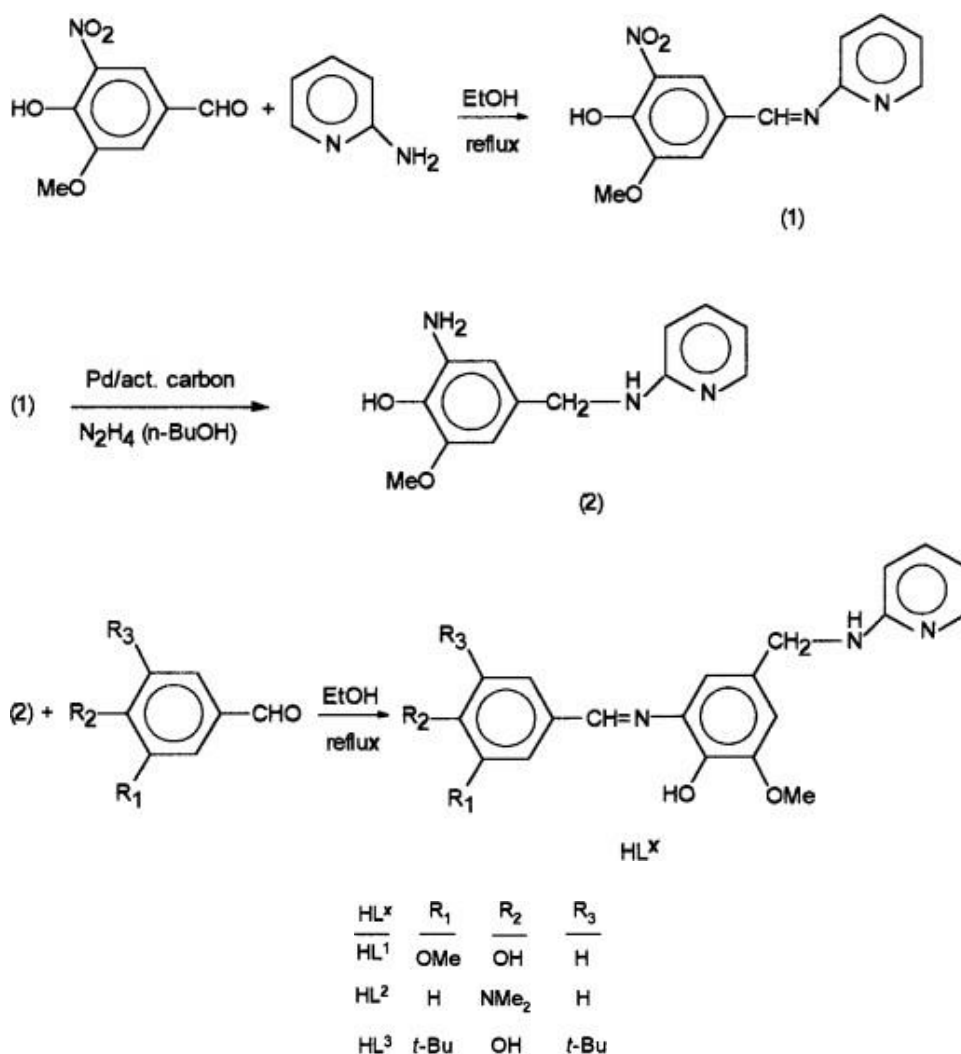
Metal salts were purchased from E. Merck and put to use in the same form in which they were purchased by the company. Fluka was used to collect 5-nitrovanillin, vanillin, 3,5-di-t-butyl4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde, and Pd/C (10%). Vanillin was also acquired. In order to arrive at the prices for the solvents, standard operating processes were utilized, and the solvents themselves were of an analytical quality..

Physical measurements

Carbon, hydrogen, and nitrogen all went through the process of being elementally analysed on a Carlo Erba 1106 elemental analyzer. Infrared spectra were acquired by employing KBr discs measuring 4000 cm on a side and 400 cm in thickness in order to collect data on a Shimadzu 8300 FT-IR spectrophotometer. Electronic spectra were gathered across the whole 200 to 900 nm wavelength range using a Shimadzu UV160A spectrophotometer. For the purpose of carrying out magnetic measurements, the Gouy method was applied, and Hg[Co(SCN)₄] was employed

in its capacity as the calibrant. The molar conductances of Schiff base ligands and the conductances of their transition metal complexes in DMSO (approximately 103 M) were measured with a Toa CM 405 conductivity metre at room temperature. These measurements were taken to determine the conductances of the complexes. Titration with EDTA was the technique that was utilised throughout the metal analysis that was carried out [13]. The ^1H and ^{13}C nuclear magnetic resonance spectra were collected using an instrument with a Varian XL-200 that was designed for nuclear magnetic resonance (NMR). Mass spectra of the ligands were

acquired and recorded using a VG ZabSpec GC-MS spectrometer that was outfitted with fast atom bombardment. TMS was used throughout the experiment as the internal standard, while deuterated DMSO was used throughout as the solvent. Thermal studies were performed on samples that ranged from 10 mg to 100 mg in size using Shimadzu DTA 50 and TG 50 H models respectively. In a dry N_2 atmosphere with temperatures ranging from 25 to 750 degrees Celsius, the d.t.a. and t.g. curves were generated by heating the sample at a rate of 10 degrees Celsius per minute⁻¹.



for 3±4 h. After that, it was brought down to room temperature, and the solvent was evaporated in a vacuum. The orange product that had been precipitated was

filtered out and then washed with C_6H_{14} . Yield: (87%), m.p.: 128 °C. Electronic spectra (EtOH, λ_{max} / nm): 402, 288, 231. I.r. values (in KBr pellets, cm^{-1}) are as

follows: 3344 for OAH, 1635 for C@N, 1596, 1560, and 1463 for the pyridine ring. After dissolving N-(pyridyl)-3-methoxy-4-hydroxy-5-aminobenzylamine (2) in pure EtOH (100 cm³), the resulting solution was heated to 80 degrees Celsius. Ligand (1) weighed 0.556 grammes and had a concentration of 2 millimoles. After adding Pd/C (10%) (0.70 g) to this solution at the same temperature, N₂H₄ · H₂O (20 cm³) (100%) was dropwise added; the mixture was then agitated and heated under reux for 50 minutes. Following the process of bringing the mixture down to room temperature, it was filtered, and the trate was evaporated until no trace of EtOH remained. The CHCl₃ solvent was used to remove the soiled yellow residue. The extract was concentrated in a vacuum before being chilled to 10 degrees Celsius in a refrigerator. After being filtered out and rinsed with cold C₆H₁₄, the crystals that had formed had a pale yellow colour. Yield: (85.4%), m.p.: 145 °C (dec.). Electronic spectra (EtOH, kmax/nm): 380, 294, 235, 225.

Molecular spectra (KBr pellets, cm⁻¹): 3388 (OAH), 3309 (NH₂), 3095 (NH), 2910 (CH₂), 1600, 1515, 1461 and 1450 (pyridine ring). Schiff Base ligands The Schiff base ligands HL1, HL2, and HL3 were all produced using processes that were quite similar to one another. The derivative of the benzaldehyde (5 mmol) (vanillin for HL₁, 4-dimethylaminobenzaldehyde for HL₂ and 3,5-di-t-butyl-4-hydroxybenzaldehyde for HL₃) in absolute EtOH (20 cm³) was carefully added, with stirring, to a solution of freshly prepared N-(pyridyl)-3-methoxy-4-hydroxy-5- amino benzylamine (5 mmol, 1.125 g) in absolute EtOH (30 cm³). The resultant mixture was cooked under redux for two to three hours, after which it was allowed to sit at room temperature for two to three hours. Following the extraction of the solvent, the resultant solid was subjected to a modification, after which it was recrystallized from EtOH and then dried in a vacuum desiccator. Copper(II) complexes

A solution of Cu(AcO)₂ · H₂O (0.5 mmol, 0.100 g) in MeOH (10 cm³) was added to a solution of each ligand (1 mmol) [HL1 (0.379 g), HL2 (0.376 g), or HL3 (0.461 g)] in pure EtOH (40 cm³). The mixture was then stirred. After being heated to 80 degrees Celsius with constant stirring, the liquid eventually became brown. After the complexes had been precipitated, they were filtered out, washed with cold EtOH, and then dried in a vacuum over P₄O₁₀.

To a solution of the ligand (1 mmol) [HL1 (0.379 g), HL2 (0.376 g), or HL3 (0.449 g)] in absolute EtOH (40 cm³), a solution of Co(AcO)₂ · 4H₂O (0.5 mmol, 0.125 g) in absolute EtOH was added. The mixture was heated to 80 degrees Celsius and decreased for two to four hours. After separating out the precipitated product, it was washed with cold EtOH and then dried in a vacuum over P₄O₁₀. Nickel(II) complexes To generate nickel(II) complexes of the ligands HL₁, HL₂, and HL₃, a technique was followed that was similar to the procedure used to prepare the other complexes. The metal salt used was Ni(AcO)₂ · 4H₂O, and pure EtOH was used as the solvent. Oxovanadium(IV) complexes Oxovanadium(IV) complexes of the ligands HL₁, HL₂, and HL₃ were created by using a technique that was similar to the one used to prepare the other complexes. The metal salt used in this process was VO(SO₄) · 5H₂O, and pure EtOH was used as the solvent.

Zinc (II) complexes

Zinc (II) complexes of the ligands HL1, HL2, and HL3 were generated by using a process that was similar to the procedure that was used to prepare the other complexes. Zn(AcO)₂ · 2H₂O was used as the metal salt, and pure EtOH was used as the solvent for the reaction. Establishment of cultures of microorganisms Test organisms for an antibacterial investigation included Bacillus subtilis IMG 22 (a bacterium), Saccharomyces cerevisiae WET 136 (a yeast), Escherichia coli DM (a bacterium), Klebsiella pneumoniae DIG 1319 (a bacterium), and Micrococcus luteus

LA 2971 (a bacterium). Both the bacterial strain and the yeast strain were seeded into nutritional broth (Difco) and malt extract broth (Difco), respectively, before being placed in an incubator for 24 and 48 hours. The test microorganisms were injected in a separate manner into the sterile Mueller Hinton Agar (Oxoid) for bacteria and the Sabouraud Dextrose Agar for yeast before the Disc Diffusion technique was carried out. The compounds were dissolved in DMF as 100 µg/disc solutions and absorbed on the sterile paper antibiotic discs. The antibiotic discs were then placed in wells (6 mm diameter) cut in the agar media, and the plates were incubated at 32 °C for bacteria (18–24 hours), and at 25 °C for yeast (72 hours). After forty-eight hours, the inhibitory zones that had formed on the plates were evaluated (Table 6). DMF was the sole solvent used to absorb the control samples. The results of three separate tests are averaged together and shown in Table 6.

The ¹H-NMR and ¹³C-NMR spectra

The spectra of compounds 1 and 2 are listed in Table 2, which is organized by ¹³C-NMR and ¹H-NMR. An unshielded -HN-C(=S)S resonance was seen at 196.62 and 196.08 ppm in the ¹³C-NMR spectra of compounds 1 and 2, respectively. Based on the locations of the chemical shifts observed, it has been shown that tautomer 1 or tautomer 2 of thione predominates in DMSO-d₆ solution. Because electronegative residues are so near to the CH₂ group, it is protected from the environment. The -CH₂ group is located between the CSS group and the benzene ring and is allocated between 36.84 and 38.04 ppm.[26]

As a consequence, the -CH₂ subgroup was allotted between 36.84 and 38.04 parts per million. In both 1 and 2, the signal was measured to be between 19.40 and 19.41 ppm, and it was found that the aromatic group protected the free CH₃ connected to the benzene ring. Aromatic rings of Schiff bases exhibited resonances in the range of

112.53-147.13 ppm, which were ascribed to carbon nuclei. These results are consistent with those found by Dilovi and coworkers in their earlier study [27]. All of the signals were consistent with the supplied structure, and DEPT NMR was able to verify the assignment of resonance peaks to the carbon atoms that make up the aromatic rings. The presence of the methoxy carbon atom was shown by a signal with a value between 55.74 and 55.88 ppm, which seemed to be the signal closest to the septet splitting of the solvent. Due to its near proximity to the electronegative oxygen atom, the methylene molecule's carbon is less well shielded than other portions of the molecule. The Schiff bases also showed a -CH resonance between 158.85 and 161.98 ppm, which is quite similar to the CSS group. Because of the electronegative process done on the carbon atom, this resonance is now more visible and accessible.

There seemed to be a proton immediately linked to the N atom next to the -C=S and -N=C, as shown by the ¹H-NMR spectra of compounds 1 and 2, which revealed chemical shifts at 13.29 and 13.22 ppm. These chemical shifts were associated with a singlet in the spectra corresponding to a sp²-type proton. A chemical shift at 13.29 ppm confirmed the presence of this proton. These physicochemical changes indicated the presence of a proton bound to the N atom next to the -N=C.

This proton signal seemed to be unprotected while being quite near to the electronegative nitrogen atom. Because of their close closeness, it appeared. The methylene (-CH₂) proton, located in the space between the sulfur atom and [28]the benzene ring, was easily distinguished at a concentration of 4.38 ppb. The reason for this is because the methylene proton occupies this gap. The singlet that results from a -CH proton losing its protective shell may be seen between 7.70 and 8.30 ppm. When an electronegative sulfur atom was placed in close proximity to the proton,

the resulting electron repulsion caused the -CH proton to develop at the site where shielding had been removed. The proximity of the proton was a contributing factor. At 2.29 and 2.30 ppm, a singlet was detected, which corresponded to a proton of the sp³ type (represented by the notation -CH₃). This proton is found in the dithiocarbazate backbone, at the ortho position of the ring that connects to the benzene ring. The benzene ring also acted as a barrier, protecting this proton from harm. Singlet was first seen at 2.29 and 2.30 ppm. At 3.80 ppm (1) and 3.74 ppm (2), the methyl proton of the methoxy group (O-CH₃) was also present at a detectable level. Chemical shifts between 6.92 and 7.70 ppm were discovered to have the resonant frequencies corresponding to aromatic proton nuclei. Compounds 1 and 2 have the predicted number of hydrogens based on their structures, as measured by their ¹H-NMR spectra's integration values.

The infrared spectrum

The infrared spectra of the molecules may provide information regarding the presence or absence of functional groups. These functional groups are necessary for the formation of Schiff bases and metal complexes. The results of a study comparing the infrared spectra of Schiff bases (1 and 2) and metal complexes (3 through 8) are shown in Table 3. A Fourier transform was used for the study. The infrared spectra of compounds 1 and 2 showed that the strong bands corresponding to aldehydic $\nu(\text{C}=\text{O})$ had vanished,[29] suggesting that the condensation reaction had been effective.

The spectra of compounds 1 and 2 demonstrate this. For some reason, in the metal complexes (3-8), the stretching vibrations of $\nu(\text{N}-\text{H})$ at 3085 and 3099 cm⁻¹ could not be isolated. This occurs because complexation leads to deprotonation of the nitrogen atom. The strong peaks at 1598 and 1609 cm⁻¹ in compounds 1 and 2 were caused by the azomethine group. As was indicated before, these peaks were

consistent with $\nu(\text{C}=\text{N})$. After being complexed with the metal ions, this stretching band moved to lower wavenumbers [30]. Since the value of $\nu(\text{C}=\text{N})$ declined throughout complexation, this study provides further support for the idea that the azomethine nitrogen was responsible for the coordination of compounds 1 and 2 to the metal ions. Shifts in the hydrazinic $\nu(\text{N}-\text{N})$ band to higher and lower wavenumbers in the infrared spectra of complexes 3–6 are indicative of metal coordination.

This occurrence was linked to the reduction in repulsion between lone pairs of electrons on the nitrogen atoms that occurred as a consequence of complexation, indicating that the metal was coordinated through the nitrogen atom in the azomethine. The nitrogen atom in the azomethine molecule was implicated as the point of metal coordination based on the available data. The thione tautomer is the sole known form of compounds 1 and 2. Why? Because at 736 and 775 cm⁻¹, there are significant $\nu(\text{C}=\text{S})$ bands.[31] This conclusion was compatible with others since NMR data confirmed the fact that these bands were absent from the spectra of compounds 3-8. For both compounds 1 and 2, the $\nu(\text{CSS})$ splitting was located between 729 and 770 cm⁻¹. This provided substantial proof that the proton loss during coordination of chemicals 1 and 2 to the metal ions occurred at the sulfur thiolate.

IR Spectra

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This was linked to the fact that complexation reduced the repulsion between lone pairs of electrons on nitrogen atoms. The nitrogen atom in the azomethine molecule was implicated as the point of metal coordination based on the available data. The thione tautomer is the sole known form of compounds 1 and 2. Why? Because at 736 and 775 cm^{-1} , there are significant $\nu(\text{C=S})$ bands. This conclusion was compatible with others since NMR data confirmed the fact that these bands were absent from the spectra of compounds 3-8. For both compounds 1 and 2, the $\nu(\text{CSS})$ splitting was located between 729 and 770 cm^{-1} . This provided substantial proof that the proton loss during coordination of chemicals 1 and 2 to the metal ions occurred at the sulfur thiolate. $\pi \rightarrow \pi^*$ transition, which is analogous to the electron pairs of the azomethine bond that do not participate in bonding. The bands

that could be seen between 324 and 352 nm related to an intraligand. $\pi \rightarrow \pi^*$ transition, while bands at 422[33] nm belonged to an LMCT transition and bands at 601–624 nm corresponded to d-d band transitions, which is a transition that occurs at a longer wavelength. transitions that occur at shorter wavelengths are not as common. $2 E_g \rightarrow 4 A_{2g}$. The extreme degree of pressure $\pi \rightarrow \pi^*$ transition overlapping with the LMCT transitions, which resulted in the absence of the LMCT bands in certain instances. The happening of a certain event $S \rightarrow \text{Cu}$ In square planar dithiocarbazate Cu(II) complexes, the LMCT band that centers about 422 nm is often seen. Because the d-d transition is a spin-forbidden transition, all of the Cu(II) complexes demonstrated a weak d-d transition. This is the reason for the relative weakness of the d-d band attributed to the tetrahedral and square planar complexes.

Because of the presence of, the Ni(II) complexes exhibited absorption bands in the range of 342–354, 444, and 609 nm. $\pi \rightarrow \pi^*$ transitions, LMCT transitions, and d-d transitions, respectively. Specifically, the three d-d bands that correspond to $1 A_{1g} \rightarrow 1 A_{2g}$, $1 A_{1g} \rightarrow 1 B_{1g}$, and $1 A_{1g} \rightarrow 1 E_{1g}$ Transitions with the E_{1g} mode are characteristic of square-planar Ni(II) complexes. The magnetic moments for each of the Ni(II) complexes provided further evidence that the postulated square planar arrangement was correct. Because of the occurrence of the LMCT transition, the electronic spectra of the yellow Zn(II) complexes only displayed a band in the area 341–354 nm. An electron moves from an orbital that is characterized by ligands the majority of the time to an orbital that is characterized by zinc the majority of the time. The great intensity of the LMCT transition of Zn(II) complexes and the sensitivity of their energies to the polarity of the solvent were the two characteristics that were used to identify this transition.

Details on both crystal and molecular structures

Structures of Molecules

Both the form 1 and form 2 isomeric crystal structures have been successfully solved. The molecular structure of 1 is shown in Figure 1, and its key geometric properties are tabulated in Table 4. You might look for both of them in the same study.[34] With a root mean square distance of 0.014 angstroms, the CN2S2 atoms in the center pack closely together to form a coplanar structure. Given the size of the dihedral angle, we may deduce that the next tolyl ring is twisted perpendicular to this plane. $82.70(4)^\circ$ When compared to the methoxy-substituted ring, which is practically coplanar, the dihedral angle produced by the central residue is 6.14 degrees. $(5)^\circ$. [35]

This suggests that the outer rings are almost perpendicular to one another. In reality, the dihedral angle between the rings is $87.05(5)^\circ$ because the letter L is a universally recognized symbol for the shape of molecules. Given its value, it is clear that the methoxy group has a coplanar structure with the ring it is attached to. C11'O1C11C12 represents the torsional angle of $4.4(2)^\circ$. Since the ipso- and para-carbon atoms of the tolyl group lie on the hypothesized plane, the molecule possesses mirror symmetry apart from the tolyl-

methyl group. The reason for this is because the tolyl group contains no methyl groups. This is a ballpark figure based on current information about the circumstance. The syn arrangement of the thione-S1 and amino-H atoms poses a significant problem for the crystal packing, as detailed in section 2.5.

C1-S1 bond distance is substantially less compared to C1-S2 bond distance and C2-S2 bond distance is smaller compared to C2-S1 bond distance (Table 1). As a result, it seems that the throne C1S1 bond has many features with double bonds. The planarity of the central residue does not provide strong evidence for extensive delocalization. This is because both N1N2 and C9N2 have bond lengths that are consistent with single bonds and double bonds π -The E conformation is characterized by the distribution of electrons among these atoms, with the double bond between C9 and N2 serving as the structural anchor.[36] Furthermore, the angles subtended by the thione-S1 atom at the C1 atom are always larger than those subtended by the bond between S2C1N1, which is consistent with the dual nature of the thione C1S1 bond.

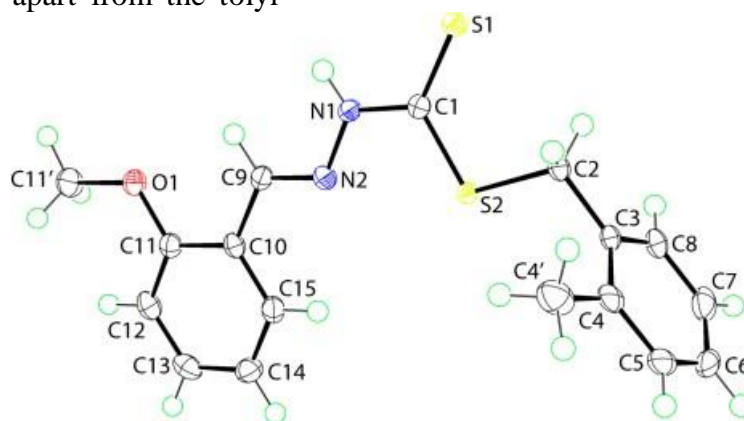


Figure 1. The molecular structure of 1 displaying a 70% displacement ellipsoid and an atom labeling scheme..

Table 2. Specific angular and rotational parameters (Å, °) for 1 and 2.

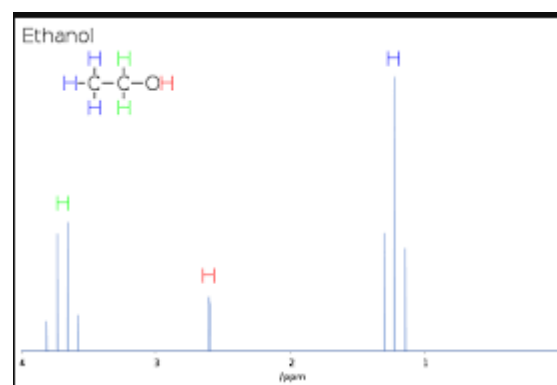
Parameter	1	2
C1-S1	1.6611(11)	1.6721(13)
C1-S2	1.7588(12)	1.7532(12)
C2-S2	1.8247(12)	1.8233(14)
C1-N1	1.3473(17)	1.3370 (19)
N1-N2	1.3693(14)	1.3759 (18)
C9-N2	1.2821(18)	1.2792 (18)
S1-C1-S2	123.77(1)	121.61(8)
S1-C1-N1	121.02(16)	114.69(10)
S2-C1-N1	114.21(11)	111.62(10)
C1-N1-N2	114.76(10)	113.66(11)
N1-N2-C9	115.56(11)	112.60(11)

The molecular structure of the element 2 in its entirety by clicking on the link provided in figure 2. The structure of the 3-methoxy isomer in 1 is very nearly identical to that of the 2-methoxy isomer in 1. As a result, the dihedral angles are calculated to be 80.01(3) degrees, and the central CN2S2 atoms have a relative standard deviation of 0.010 angstroms. 1.58(7)° by using the tolyl and methoxyphenyl rings.[37] The dihedral angle between the rings is 81.19 degrees. (4)° The methoxy group and the ring it is attached to form a plane, or L, which is called coplanarity.(C12'-O1-C12-C11 = 179.28(13)°) In addition, apart from the tolyl-methyl group, the symmetry of the whole molecule is quite close to that of compound 1. All of the essential geometric features, as well as the anti-disposition of the thione-S1 and amine-H atoms, are consistent with what was pre.

NMR

The method known as nuclear magnetic resonance spectroscopy, which is more commonly abbreviated as nmr, has emerged as the method of choice for examining the molecular structure of organic compounds. This may be accomplished by a number of

different approaches. Because it is the only one of the spectroscopic processes that normally requires a full examination and interpretation of the entire spectrum, it is the only one of those approaches that can be said to be unique. Nuclear magnetic resonance (NMR) is a non-destructive method, and with today's modern instruments, precise data may be obtained from samples that weigh less than one milligram. Despite the fact that bigger amounts of material are required than for mass spectroscopy, NMR is a technique that uses nuclear magnetic resonance.

**Figure:2 NMR synthesis**

MASS

Mass Spectrometry Settings

MS detection was done in ESI-MS data were acquired by switching between full-spectrum mode and selected-ion monitoring (SIM), detecting a number of specific m/z -values related to the reporter-ligand, the metal-reporter-ligand complex, the ligand of interest, and/or complexes of

the metal-ion and the ligand of interest. This was done in order to determine the stability of the reporter-ligand complex. During the direct injection, in addition to the ligand and complex m/z -values, a system monitoring chemical known as SMC was continually detected in SIM in order to monitor the overall stability of the system as well as any possible ion suppression effects..

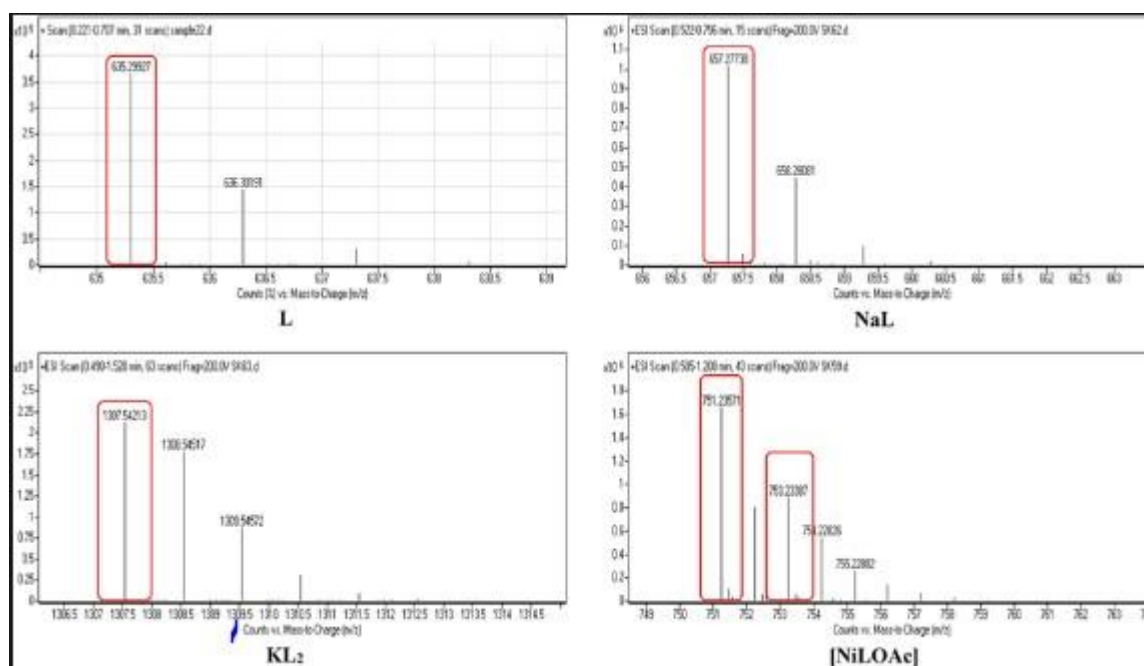


Figure 3: Mass

LC

The preparation and characterization of metal complexes and metal–ligand interactions have historically played a foundational role in many branches of chemistry and beyond 3, and continue to play a key role in a variety of research areas ranging from bioinorganic chemistry⁴ to molecular framework materials⁵ to small molecule catalysis..

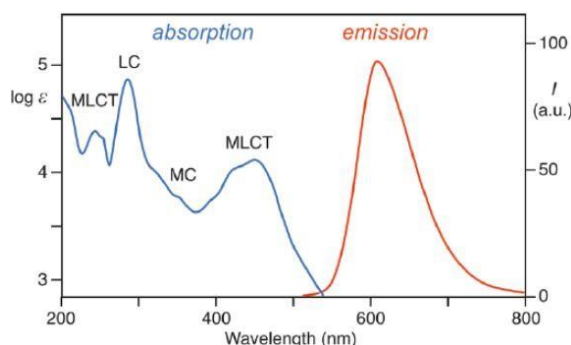
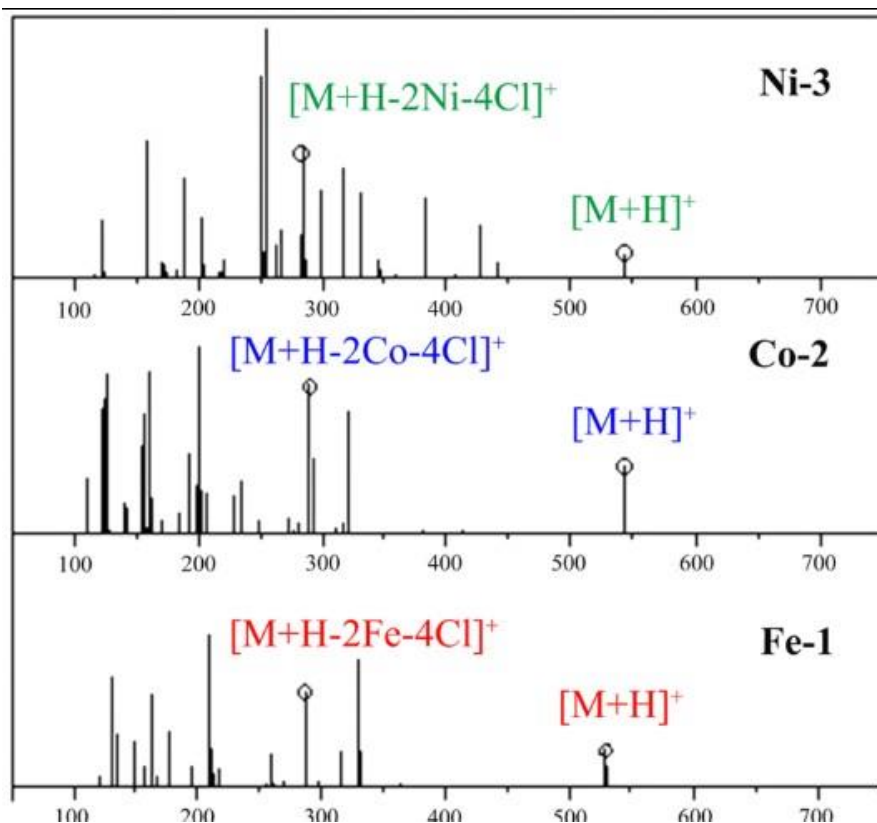


Figure 4 LC And Metal–Ligand

MS

MS/MS Settings

A Micromass Q-TOF2 mass spectrometer (Wythenshawe, Manchester, UK) outfitted with a Z-spray ESI source was utilized for the purposes of structural elucidation and the identification of complexes..



Figur 5 MS COMPLEX

IR

A comparison is made between the infrared spectra of a free ligand and that of the complex. Confirmation that a complex has formed can be obtained by observing a shift in the location of the characteristic bands, an increase or reduction in the total number of bands, or the development of a new link between atoms of the same metal. This chapter delves into each of these aspects in further detail. The free ligand has a certain

symmetry, but when it complexes with another molecule, that symmetry is broken, which results in the formation of extra bands. Also included are metal carbonyls, all of their many varieties, as well as their unique bands and other features. Isotopic substitution is yet another crucial factor to consider. Isotopic substitution is employed in situations when there is uncertainty regarding the identification of critical bands..

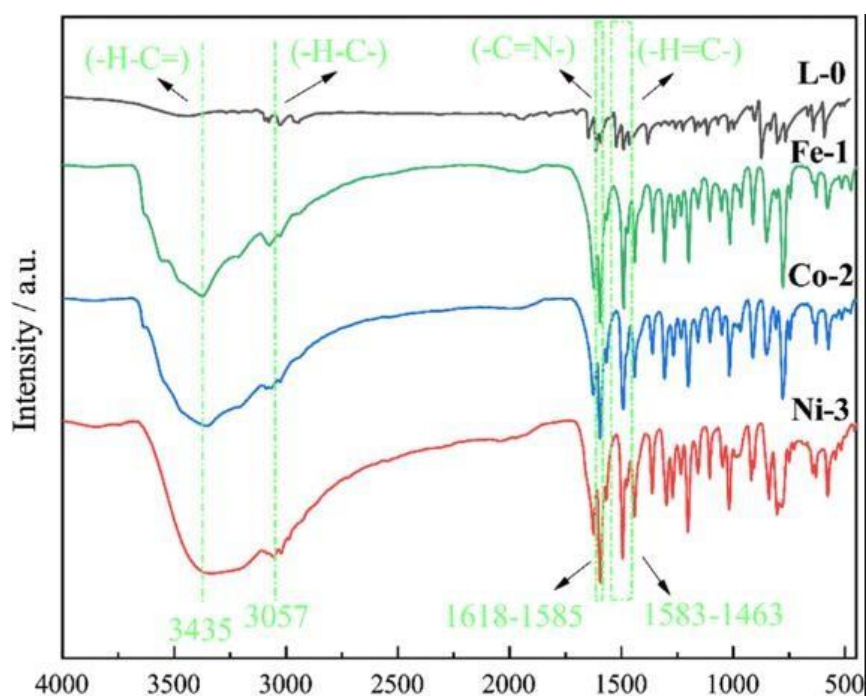


Figure 6 The IR Spectrum

RESULT

Table 1 is a listing of the analytical results obtained from the HL1, HL2, and HL3 ligands in conjunction with their respective metal complexes. As a microcrystalline solid, the Schiff base ligands *N*-(pyridyl)-3-methoxy-4-hydroxy-5-nitrobenzaldimine (1) were produced after being synthesised from 5-nitrovanillin and 2-aminopyridine in an absolute solution of ethyl alcohol. The yield was very close to quantifiable. The substance is not affected by changes in temperature and is soluble in common organic solvents such EtOH, CHCl₃, and MeOH. C₆H₁₄, PhMe, and C₇H₁₆ are only slightly soluble in the compound. EtOH is used as a solvent, Pd/C (10%) is used as a catalyst, and N₂H₄ · H₂O (100%) is used as a reducing reagent in this Schiff base reaction, which results in the azomethine and nitro groups being reduced to amines. The chemical *N*-(pyridyl)-3-methoxy-4-hydroxy-5-aminobenzylamine (2), which was produced in a low yield, is unstable at room temperature and decomposes after being left to stand for some time. The newly discovered amine compound may be dissolved in CHCl₃, EtOH, and MeOH, but it cannot be dissolved in typical apolar

organic solvents like C₆H₁₄, PhMe, or C₇H₁₆. In order to successfully synthesise the bidentate Schiff base ligands, three different benzaldehyde derivatives needed to be used.

The most water-soluble Schiff base ligand is HL3, which is produced from 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. However, while all ligands are soluble in typical polar organic solvents like EtOH, CHCl₃, MeOH, Me₂CO, DMF, and DMSO, nonpolar organic solvents like C₆H₁₄, PhMe, and C₇H₁₆ and C₆H₆ only have a limited degree of solubility.

None of the ligands are affected by changes in temperature or humidity at room temperature. When compared to the yield of the HL3 ligand, the yields of the HL1 and HL2 ligands are significantly greater. In a similar fashion, the yields of the various complexes are similarly distinct from one another. The fact that the yield of the complexes containing the HL3 ligand is lower than that of the complexes containing the HL1 and HL2 ligands suggests that the steric impact of the *t*-Bu groups on the benzeneoid ring is responsible for lowering the yield of the complexes. All complexes are stable at room temperature. The ligands

HL1 and HL3, which are complexes of copper(II) and cobalt(II), are most soluble in ethyl alcohol.

But none of the complexes are insoluble in solvents such as DMF, DMSO, THF, or dioxane. Molar conductivities of HL1, HL2, and HL3 ligands, as well as their coordination compounds in DMSO, were found to be in the range of $2.5 \pm 10.4 \text{ W} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, and this information is shown in Table 2. These findings point to the fact that the ligand coordinates to the metal ions to produce neutral coordination molecules, which is accompanied by the release of the anion. Because their molar conductances are far lower than those of 1:1 electrolytes [15], it is generally agreed that none of these substances can be classified as electrolytes. Table 3 contains the information on the infrared spectrum data of the ligands and their metal complexes.

Strong bands may be seen in the spectrum of the HL1 and HL3 ligands at 3580 and 3602 cm^{-1} . These bands have been attributed to the vibration of the free OH group. This band does not change to the lower or higher wave numbers when it is present in the complexes, which is suggestive of the fact that this free OH group is not coordinated to the metal ions. The vibrations of the NH and CH₂ groups may be attributed, respectively, to the bands detected in the range 3138 ± 3010 and $2925 \pm 2912 \text{ cm}^{-1}$ in the spectra of the HL1, HL2, and HL3 ligands. These bands can be found in the ranges 3138 ± 3010 and $2925 \pm 2912 \text{ cm}^{-1}$. The fact that these bands appear in the complexes at about the same frequency ranges demonstrates that the nitrogen atom that makes up the NH group is not coordinated to the metal ions. The ligands HL1 and HL3, respectively

Table 1. Analytical and physical data of compounds

Compound	Colour	M.p. (°C)	Yield (%)	Found (Calcd.) (%)			
				C	H	N	M
HL ¹	light yellow	194	75.4	66.1 (66.5)	5.3 (5.5)	10.9 (11.1)	–
[Cu(L ¹) ₂]·H ₂ O	light brown	249	57.9	60.2 (60.2)	5.0 (5.0)	10.1 (10.0)	7.7 (7.6)
Co(L ¹) ₂	red brown	> 250	63.5	61.9 (61.8)	4.9 (4.9)	10.3 (10.3)	7.2 (7.2)
[Ni(L ¹) ₂]·2H ₂ O	green yellow	> 250	57.6	59.3 (59.2)	5.1 (5.2)	9.9 (9.9)	6.9 (6.8)
[VO(L ¹) ₂]·H ₂ O	brown	240 ^d	78.7	59.9 (59.9)	5.1 (5.4)	10.0 (10.8)	8.1 (8.0)
Zn(L ¹) ₂ ·2H ₂ O	yellow	> 250	57.6	58.8 (58.8)	5.1 (5.1)	9.7 (9.8)	7.7 (7.6)
HL ²	yellow	192	80.1	70.0 (70.2)	6.0 (6.4)	14.7 (14.9)	–
[Cu(L ²) ₂]·2H ₂ O	dark red	> 250	62.3	62.2 (62.1)	6.0 (5.9)	13.2 (13.2)	7.7 (7.5)
[Co(L ²) ₂]·H ₂ O	dark red	> 250	59.6	63.8 (63.9)	5.8 (5.8)	13.6 (13.5)	7.2 (7.1)
[Ni(L ²) ₂]·H ₂ O	orange	> 250	55.4	63.6 (63.6)	5.7 (5.8)	13.6 (13.5)	7.2 (7.1)
[VO(L ²) ₂]·2H ₂ O	orange	> 250	66.3	61.9 (61.9)	5.9 (5.9)	13.1 (13.1)	7.9 (7.8)
[Zn(L ²) ₂]·H ₂ O	yellow	> 250	59.7	63.3 (63.4)	5.7 (5.8)	13.5 (13.4)	7.9 (7.8)
HL ³	yellow	187	68.7	68.0 (68.1)	5.6 (5.7)	15.8 (15.9)	–
[Cu(L ³) ₂]·H ₂ O	red	> 250	50.3	67.1 (67.1)	7.0 (7.0)	8.4 (8.4)	6.4 (6.3)
[Co(L ³) ₂]·2H ₂ O	light brown	> 250	53.1	66.2 (66.2)	7.1 (7.1)	8.3 (8.3)	5.9 (5.8)
[Ni(L ³) ₂]·H ₂ O	light brown	> 250	50.2	67.7 (67.6)	7.1 (7.0)	9.9 (9.9)	5.8 (5.9)
[VO(L ³) ₂]·2H ₂ O	dark orange	> 250	59.4	65.7 (65.7)	7.1 (7.1)	8.2 (8.2)	6.6 (6.5)
[Zn(L ³) ₂]·2H ₂ O	light yellow	> 250	48.2	65.7 (65.8)	7.1 (7.0)	8.3 (8.2)	6.4 (6.4)

reveal large bands in the ranges of 2640 ± 2550 and $2650 \pm 2500 \text{ cm}^{-1}$, respectively. These broad bands can be attributable to the stretching vibration of the OAH group coupled intramolecularly with the nitrogen atom of the CH@N group (OAH14N), as seen in Figure 1. As a consequence of the proton being replaced

by cations that are coordinated to oxygen, these wide bands are no longer visible in the complexes. Additionally, bands in the range of $1625 \pm 1593 \text{ cm}^{-1}$ can be seen in the spectra of the ligands. These bands are the result of the vibration of the azomethine group. As a consequence of the coordination of the nitrogen atom of the

azomethine to the metal ion, these are altered in the complexes towards values that are either lower or higher. When compared to the identical group in the complex, the stretching vibration of the Schiff base phenolic (CAOH) group exhibits a comparable effect, which indicates that oxygen is coordinated to the metal ion [16]. Strong bands can be seen in the ligands at 1517 ± 1425 and 1050 ± 1015 cm^{-1} ranges. These bands can be linked to the pyridine ring vibration, which can be found in [17]. These bands are not moved while considering the complexes. Based on these findings, we are led to believe that the nitrogen atom that is part of the pyridine ring is not coordinated to the metal ion. It

should come as no surprise that the presence of hydrated water molecules is responsible for the diffused nature and broadness of the bands in the 3427 ± 3320 cm^{-1} region in the spectra of the complexes that include hydrated water molecules [18]. Strong bands are seen in the region of 998 ± 976 cm^{-1} in the oxovanadium(IV) complexes, which can be attributed to the stretching vibration of the (V@O) group [19]. These bands can be found in the oxovanadium(IV) complexes. The m(MAN) and m(MAO) stretching is responsible for the bands in the complexes that may be found in the ranges of 617 ± 461 and 459 ± 410 cm^{-1} respectively..

Table 2. Magnetic moment, molar conductance and electronic spectra of the Schiff base ligands and their complexes

Compound	μ_{eff} (B.M.) ^a	Λ_{M} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	$\lambda_{\text{max}}/\text{nm}$ (EtOH)
HL ¹	–	2.8	356(sh), 308, 282, 217
[Cu(L ¹) ₂]·H ₂ O	1.83	8.3	621, 354(sh), 347, 238(sh), 219(sh), 209
Co(L ¹) ₂	4.13	9.2	608(sh), 348, 283(sh), 219(sh), 210
[Ni(L ¹) ₂]·2H ₂ O	diamag.	10.4	381(sh), 339, 280(sh), 233(sh), 211
[VO(L ¹) ₂]·H ₂ O	1.66	9.5	713, 480(sh), 346, 233(sh), 212
Zn(L ¹) ₂ ·2H ₂ O	diamag.	7.3	376(sh), 348, 307, 284, 226(sh), 215
HL ²	–	2.5	390, 307, 236, 211
[Cu(L ²) ₂]·2H ₂ O	1.90	5.7	625(sh), 393, 316(sh), 244, 205(sh)
[Co(L ²) ₂]·H ₂ O	4.23	5.4	638(sh), 393, 316(sh), 244, 205
[Ni(L ²) ₂]·H ₂ O	diamag.	4.7	474(sh), 387, 322(sh), 238, 207
[VO(L ²) ₂]·2H ₂ O	1.68	4.2	710(sh), 456(sh), 346, 236, 209
[Zn(L ²) ₂]·H ₂ O	diamag.	3.9	392, 325, 240, 206
HL ³	–	2.7	454(sh), 335, 308(sh), 235, 213
[Cu(L ³) ₂]·H ₂ O	1.97	8.0	630(sh), 354(sh), 344, 211
[Co(L ³) ₂]·2H ₂ O	4.50	8.7	613(sh), 354, 344, 235, 207
[Ni(L ³) ₂]·H ₂ O	diamag.	9.1	580(sh), 489, 458, 341(sh), 291, 225
[VO(L ³) ₂]·2H ₂ O	1.73	9.8	741(sh), 502(sh), 326(sh), 240, 206
[Zn(L ³) ₂]·2H ₂ O	diamag.	5.8	452(sh), 344, 289(sh), 232(sh), 210

A Magnetic moment per metal atom.

Table 3. I.r. spectral data of the ligands and their complexes

Compound	$\nu(\text{H}_2\text{O}/\text{OH})$	$\nu(\text{NH})$	$\nu(\text{CH}_2)$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})^a$	$\nu(\text{Py})$	$\nu(\text{V}=\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
HL ¹	–	3010	2925	1593	1344	1512, 1461	–	–	–
[Cu(L ¹) ₂]·H ₂ O	3380	3010	2904	1600	1285	1555, 1440	–	520	418
Co(L ¹) ₂	–	3010	2937	1601	1283	1512, 1427	–	574	457
[Ni(L ¹) ₂]·2H ₂ O	3400	3010	2937	1601	1278	1514, 1427	–	510	459
[VO(L ¹) ₂]·H ₂ O	3320	3010	2939	1597	1284	1518, 1427	988	492	455
Zn(L ¹) ₂ ·2H ₂ O	3350	3010	2937	1596	1282	1510, 1458	–	518	443
HL ²	–	3130	2916	1625	1364	1510, 1425	–	–	–
[Cu(L ²) ₂]·2H ₂ O	3427	3168	2925	1599	1320	1529, 1434	–	534	455
[Co(L ²) ₂]·H ₂ O	3427	3136	2956	1625	1315	1564, 1423	–	540	440
[Ni(L ²) ₂]·H ₂ O	3425	3140	2825	1604	1350	1523, 1429	–	538	425
[VO(L ²) ₂]·2H ₂ O	3420	3142	2958	1625	1319	1596, 1425	976	461	410
[Zn(L ²) ₂]·H ₂ O	3423	3135	2918	1605	1305	1558, 1431	–	495	420
HL ³	–	3138	2912	1601	1344	1517, 1431	–	–	–
[Cu(L ³) ₂]·H ₂ O	3400	3145	2935	1615	1319	1507, 1470	–	461	434
[Co(L ³) ₂]·2H ₂ O	3423	3120	2956	1650	1316	1552, 1427	–	605	426
[Ni(L ³) ₂]·H ₂ O	3400	3120	2924	1666	1305	1530, 1460	–	589	426
[VO(L ³) ₂]·2H ₂ O	3370	3125	2914	1602	1313	1521, 1431	998	617	420
[Zn(L ³) ₂]·2H ₂ O	3425	3110	2922	1606	1312	1517, 1431	–	610	424

The electronic spectra were recorded using EtOH, CHCl₃, C₆H₁₄, PhMe, and C₇H₁₆ as the solvent. This was done so that the ketoimine-enoximone tautomeric forms (Figure 2) of the Schiff base ligands HL₁, HL₂, and HL₃ could be investigated. As can be shown in Table 4, the n → p* and p → p* transitions of the ligands in polar solvents such as C₆H₁₄, PhMe, and C₇H₁₆ may be detected in the ranges of 408± 302 and 289± 214 nm, respectively. These transitions can be seen in the ligands. In polar solvents such as CHCl₃ and EtOH, the same transitions may be seen in the wavelength ranges of 492 to 303 and 283 to 211 nm. In a polar solvent, the tautomeric form of ketoimine is the one that the ligands

prefer. To phrase it another way, the enoximone is the tautomeric form that predominates in polar solvents. In the EtOH solvent, the electronic spectra of the ligands and their complexes were measured and recorded (Table 4). Because of the presence of the azomethine group in the complexes, certain n → p* transitions have a lower energy state as a result. According to these findings, the nitrogen atom that is part of the imine group seems to be coordinated to the metal ion. In addition, the charge transfer bands may be seen as new bands in the spectra of certain of the complexes made up of the HL₁ ligand, the HL₂ ligand, and the HL₃ ligand. These bands can be seen in the range of 489 to 381 nanometers.

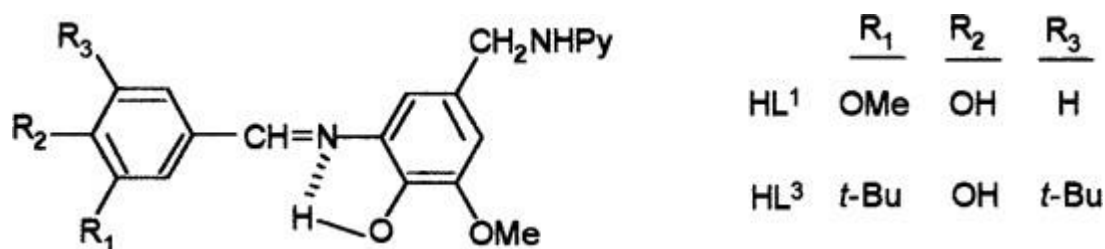


Fig. 1. Intramolecular H-bonding for the ligands HL1 and HL3 .

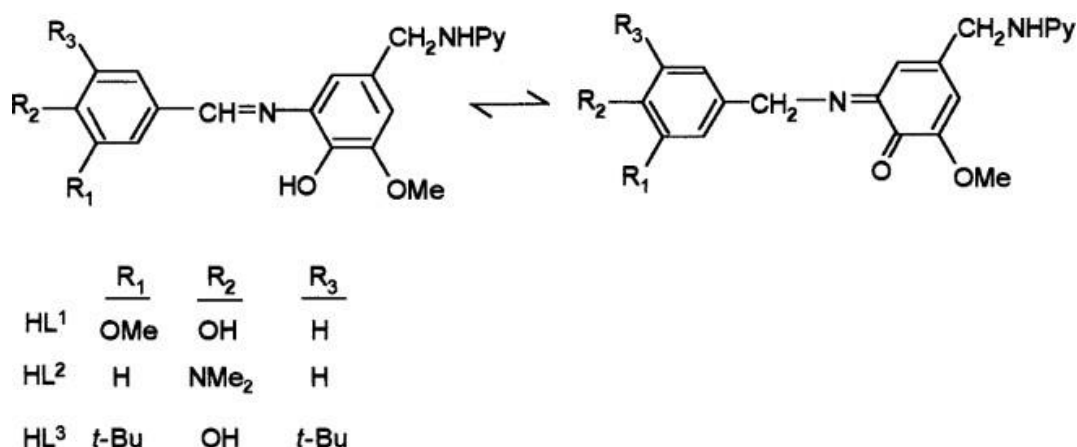


Fig. 7. versions of the Schiff base ligands that are keto-enol tautomeric..

Table 4. Spectroscopic information on the ligands' electronic states in organic solvents (λ_{max} /nm)

Ligands	EtOH	CHCl ₃	C ₆ H ₁₄	C ₇ H ₁₆	PhMe
HL ¹	356 ^a , 308, 282, 217	357 ^a , 319 ^a , 304, 283	358 ^a , 339 ^a , 318 ^a , 302, 263, 224	357 ^a , 339, 317 ^a , 304, 277	363 ^a , 319 ^a , 305, 286
HL ²	390, 307, 236 211	492 ^a , 389, 317 ^a , 236 ^a	388 ^a , 349, 312 ^a , 247 ^a , 233, 219	390 ^a , 372, 349, 308 ^a , 235 ^a , 214 ^a	408 ^a , 388, 367 ^a , 312 ^a
HL ³	454 ^a , 335, 308 ^a , 235, 213	365 ^a , 346 ^a , 329, 303 ^a	355 ^a , 334, 322, 230	354 ^a , 334, 323, 230	363 ^a , 342 ^a , 289 ^a

(ligand centre to metal or metal centre to ligand) [22]. The d-d transitions of the cobalt(II) ion are the source of the bands that may be found in the cobalt(II) complexes in the range of 638–608 nm. In the case of the other compounds, the d-to-d transition may be seen in the range from 741 to 580 nm. At room temperature, the magnetic susceptibilities of all compounds were determined (Figure 3). The B.M. values of 1.83, 1.90, and 1.97 that are displayed by the copper(II) complexes provide evidence that the copper(II) ion has a square-planar shape [23]. The nickel(II) complexes exhibit diamagnetism and have a square-planar shape centred on the metal. The values of 4.13, 4.23, and 4.50 B.M., respectively, for the Co(L1)₂, [Co(L2)₂] $\dot{\text{a}}$ H₂O, and [Co(L3)₂] $\dot{\text{a}}$ 2H₂O complexes are compatible with tetrahedral structures. The magnetic moments of the oxovanadium(IV) complexes are 1.66, 1.68, and 1.73 B.M., which confirms that the squarepyramidal shape of the oxovanadium(IV) ions [24]. All zinc(II) complexes exhibit diamagnetism and are of the tetrahedral crystal structure. Table 5 presents the ¹H

and ¹³C nuclear magnetic resonance spectrum data at room temperature for the ligands HL₁, HL₂, and HL₃, which were dissolved in DMSO-d₆. These results show all of the predicted signals. Singlet signals in the range of 10.8–12.0 ppm may be seen in the ¹H n.m.r. spectra of the ligands; these signals are thought to be caused by the protonation of the OH group. Because NH and OH protons vanish when D₂O is exchanged for them, it is simple to identify them as NH and OH protons. In a similar fashion, all of the ligands exhibit peaks that are caused by the pyridine and benzenoid rings, as well as the azomethine, methoxy, methylene, and secondary amine groups [25–27]. The protons of the ANMe₂ group may be attributed to the presence of a strong singlet in the ¹H n.m.r. spectrum of the HL₂ ligand. This singlet can be seen at 3.41 ppm. Additionally, the singlet that was detected at 1.4 ppm in the HL₃ ligand can be attributed to the protons that are present in the *t*-Bu groups. Signals in the 162.7±164.5 ppm range that appear in the ¹³C nuclear magnetic resonance spectra of the ligands may be ascribed to the carbon atoms that

make up the azomethine group (Table 5). In the region of 104 to 158.3 ppm, one may notice the signals that are caused by the carbon atoms that make up the benzenoid and pyridine rings. The carbon atoms that make up the methoxy and methylene groups are located between the ranges of 55.2 and 56.1 and 58.5 and 60.7 ppm, respectively. The carbon atoms that make up the ANMe₂ and t-Bu groups are the cause of the signals that may be found at 30.4 and 32.0 ppm. At a concentration of 36.0 ppm, the quaternary carbon atom of the t-Bu group may be found. The molecular ion peaks of the ligands could be seen in the mass spectra, and they were located at m/z 377 [M+1]⁺ and 380 [M+1]⁺.

CONCLUSION:

It also looked at the coordination chemistry of certain monomeric complexes that we synthesized throughout our inquiry. This was done so that we might learn more about the topic at hand. The formation of these complexes is the result of the interaction between the didentate azo ligand PANR and various metal ions. Physicochemical and spectroscopic techniques were used to determine not only the kind of bonding between the complexes but also their overall architectures. The complexes' capacity to maintain stability and non-ionicity over time was aided by their octahedral shape around the central metal atom.

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