SYNTHESIS AND SPECTROSCOPIC STUDIES OF METAL COMPLEXES WITH NITROGEN DONOR LIGANDS

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ABSTRACT

Metal complexes of N-donor ligands are important class of coordination compounds as the structural, electronic and spectroscopic properties are strongly influenced by the metal–ligand interactions. The present study is concerned with the synthesis and spectroscopic study of the metal complexes of a nitrogen donor Schiff base ligand with an emphasis on the correlation between the structure of the ligand, the metal coordination behaviour and spectroscopic properties. The system studied in this work consists of the complexes of Co(II), Ni(II), Cu(II), and Zn(II) and properties were estimated from the secondary experimental parameters reported in the literature. FTIR analysis shows that the characteristic ligand vibrations, such as the aldimine C=N, phenolic O–H, as well as metal–nitrogen and metal–oxygen stretches, undergo coordination-induced changes. The UV–Visible spectral data suggest the presence of ligand centred and metal centred electronic transition which is consistent with the proposed coordination geometry in conjunction with magnetic measurement. The diamagnetic complex of Zn(II) also undergoes NMR observations suggesting the deprotonation of the hydroxyl and the coordination of the azomethine N. The proposed formulations are supported by complementary elemental, conductivity, magnetic and mass-spectrometric data. In general, the integrated spectroscopic analysis shows that the identity of the metal ion affects the coordination environment and measurable properties of nitrogen donor complexes, and the incorporation of complementary characterization techniques is important to establish structure–property relationships in coordination chemistry and other applications in the modern coordination chemistry research.

KEYWORDS

The reaction of a series of nitrogen donor ligands with metal complexes yielded a series of new complexes, which were characterized spectroscopically and by coordination chemistry.

1. INTRODUCTION

1.1 The Structure of Coordination Compounds

Coordination Chemistry deals with the coordination compounds where the metal atom or ion is surrounded by the ligands that donate electron pairs to the metal ion. The resulting coordination entity is controlled by the electronic and steric properties of the ligands, the nature

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of the metal, the coordination number and the arrangement of donor atoms around the metal. According to IUPAC, the coordination number is the number of σ-bonds that a ligand is involved in. The number of donor atoms of one ligand to the same metal centre is used to distinguish denticity (Connelly et al., 2005). The concepts form the framework for the understanding of the synthesis and properties of metal complexes.

1.2 Significance of Metal Complexes

The structures and electronic properties of metal complexes are of critical importance in inorganic and coordination chemistry since the structures can be systematically modified by changing the environment of the metal ion and the ligands. Such tunability is applicable to molecular structure, reactivity, catalysis, magnetism, photochemistry, bioinorganic chemistry, etc. Closely related ligands can give rise to compounds with chemically very different properties, particularly in the case of transition-metal complexes, that can exhibit different oxidation states, coordination numbers, and geometries. Thus, the properties of a metal complex will be largely determined by its coordination environment.

1.3 Nitrogen Donor Ligands

One of the important classes of ligands are nitrogen donor ligands as they are able to donate lone pair electrons to metal centres. Nitrogen ligands can be distinguished as monodentate, bidentate or polydentate depending on the number of donor atom per molecule, which may form multiple chelate rings if multiple donor atoms chelate the same metal ion. The coordination mode is distinguished by IUPAC terminology using the donor-atom description and denticity. (Connelly et al., 2005) Amines, imines, pyridine derivatives, azoles, hydrazones, and Schiff-base ligands are some of the common nitrogen donor which can be used. The electronic and steric properties may affect metal–N bond strength, complex geometry, stability and reactivity.

1.4 Metal–Nitrogen Coordination

The interaction between metal ion and a nitrogen donor ligand is relatively more important since the coordination behaviour can change considerably due to small changes in the structure of the ligand. A variety of factors may influence the choice of whether a ligand coordinates through one or several of the nitrogen atoms on its backbone, including ligand basicity, availability of donor atoms, chelate-ring formation, substituent effects, and steric crowding. Nitrogen donor complexes are also helpful models to study metal mediated chemical processes. The influence of the ligand on the reactivity of the coordinated metal centre has been shown by studying transition-metal complexes with N-donor ligands as artificial metallonucleases for example (Wende et al., 2014). Metal-ligand coordination is thus more than a structural effect and can impact chemical function.

1.5 The importance of spectroscopic characterization

The spectroscopic characterization is indispensable to determine if complex formation has taken place, and to assess the changes induced by metal coordination. The shifts in characteristic ligand vibrations can be used to suggest evidence from infrared spectroscopy, and changes in electronic transitions of the ligand and the metal centre can be used to suggest

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evidence from ultraviolet–visible spectroscopy. Nuclear magnetic resonance spectroscopy can also be used to give information on changes in the chemical environment of the nuclei in diamagnetic compounds. Such complementary techniques are particularly useful when applied in parallel, and the spectrum of the free ligand as a standard for the recognition of ligand-coordination effects. The combination of structure with spectroscopy has been shown to be of general use in interpreting coordination behaviour in studies of metal–ligand systems (Timmons & Symes, 2015).

1.6 Research Gap

Although various coordination compounds were studied extensively, the correlation between the structure of the ligands, the type of metal coordination and spectroscopic response is still a subject of great interest for a systematic investigation, especially when specific nitrogen donor systems and metal ions are considered under certain synthetic conditions. Comparing the free ligand and its metal complexes can help uncover the donor atoms present and a chemically sensible coordination model can be built up.

1.7 Aim and Objectives

Hence, the present work is aimed at synthesizing metal complexes with nitrogen donor ligands and to study the spectroscopic properties of the synthesized complexes. The specific aims are to prepare the chosen ligand and metal complexes, to analyse the products using suitable analytical and spectroscopic techniques, to compare the spectra of the free ligand and complexes, to identify changes in the spectra resulting from the coordination, to find the most probable donor atoms and coordination modes and to correlate the observed features of the spectra with the proposed coordination environment of the metal centres systematically.

2. LITERATURE REVIEW

2.1 Previous Studies on Nitrogen Donor Ligands

The systematic description of coordination compounds, including donor atoms and modes of coordination, has been laid out by Connelly et al. (2005). Their IUPAC recommendations state that if there is more than one possible donor atom in a ligand the donor atom should be specified. The κ convention is especially helpful for representing coordination via atoms like N, and in this way is applicable to N donor ligands. The nomenclature system is also used to account for the denticity and coordination relationships of the ligands; it serves as an important basis for describing the coordination of mono-, bi- and polydentate nitrogen ligands in metal complexes (Connelly et al., 2005).

Schiff bases are significant class of imine based compounds and their relevance in organic chemistry, biological chemistry and coordination chemistry is still continuing as mentioned by Qin et al. (2013) Schiff bases possess an azomethine group, which can be a donor group by N, and with appropriate design of the derivatives, additional donor groups are possible. The structural versatility allows the synthesis of ligands with varied steric and electronic surroundings and thus the coordinating pattern of the resulting metal complexes. This

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flexibility has been reflected in the widespread application of Schiff-base systems as the platforms for the coordination and organometallic chemistry (Qin et al., 2013).

The complexation and extraction of trivalent actinides and lanthanides were studied using triazinylpyridine N-donor ligands by Panak and Geist (2013). Their work shows that it is possible to design deliberately the ligands that coordinate selective nitrogen sites for metal ions. The electronic properties and spatial arrangement of nitrogen donor atoms affects the complexation behaviour and recognition of metal-ions. These studies illustrate the necessity of the ligand architecture in the control of metal–ligand interactions and offer a more general theoretical platform to explore the study of complexes of nitrogen donors (Panak and Geist, 2013).

2.2 Previous Studies on Metal–Nitrogen Complexes

Andruh (2015) summarized the very varied coordination chemistry produced by o-vanillin-based Schiff-base ligands. Reported systems range from mono-, oligo- and polynuclear complexes to coordination polymers showing that some minor adjustments in the architecture of the ligands can result in dramatically different assemblies of metals. Nitrogen-containing Schiff-base ligands are thus appropriate structural building blocks for controlling the nuclearity, topology and metal–metal relationships. The review also shows that the coordination modes of these ligands can be related to magnetic, luminescent, catalytic and other physicochemical properties (Andruh, 2015).

Timmons and Symes (2015) studied the role of metal–ligand coordination complexes in the transformations of nitrogen oxides, and highlighted the pivotal part played by the metal coordination environment in regulating chemical reactivity. In their review they demonstrated that there are cases of relatively well defined coordination complexes that could give insight to the structure of metal-containing active sites in biology. The chemical transformations after the binding of a substrate and the transfer of electrons to the metal centre may be affected by the coordination environment. In this way these observations further support the overall idea that basic principles of donor atom identity and placement are important in the understanding of the behaviour of metal complexes (Timmons & Symes, 2015).

2.3 The synthesis strategies for metal complexes

Schiff-base ligands can be synthesized by the condensation of aldehyde or ketone with primary amine in general form and can be called as Schiff-base ligands as explained by Kumar (2014). These ligands can then complex with transition metal ions under suitable reaction conditions for complexation. Schiff bases are highly flexible and are easily used for the synthesis of a variety of metal complexes of different structure. The composition and properties of the coordination compounds thus formed depend on common experimental variables like the ratio of the ligand to the metal, solvent, temperature of the reaction, reaction time, and the type of metal salt used (Kumar, 2014).

2.4 The selection of metal ions based on their coordination chemistry

Multinuclear metal nitrosyl complexes were shown to be structurally diverse by Li et al. (2015) in their review. The discussion they have delineated shows how the identity of the metal centre,

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the nature of the ligands, the oxidation state of the metal centre and bridging interactions could affect nuclearity and coordination structure. Nitrosyl chemistry is a specialised field but the principle can be extended to other coordination chemistry: the coordination environment available is a function of the electronic structure of the metal and the donor properties of the ligands. Therefore, being aware of the preferred coordination modes of the metals used in a specific investigation is crucial before determining the structure of a new complex that has been synthesized (Li et al., 2015).

2.5 Spectroscopic Characterization of Metal Complexes

In a review, Elliott et al. (2014) examined the vibrational spectroscopy of N-donor ligand metal complexes and showed how spectroscopic techniques can be used to study metal–ligand interactions. Information on changes in the bonding of ligands and the coordination environment after complex formation can be obtained from vibrational spectroscopy. By comparison of characteristic ligand vibrations before and after co-ordination, it may be possible to identify the changes associated with donor-atom involvement of the ligand, in particular. Their work also shows how infrared and Raman can provide complementary information relating to the electronic and structural behaviour of N-donor metal complexes (Elliott et al., 2014).

It is worth noting that combined use of more than one spectroscopic, thermal and structural techniques are required to investigate the Schiff-base metal complexes as done by Sundararajan et al. (2014). Spectrum of ligand and its metal complexes can yield changes due to coordination, which can in turn be confirmed by additional structural and analytical measurements. The assignment of the coordination mode should be based on converging experimental evidence, which is of particular relevance to the present study.In particular, the assignment of a coordination mode should be based on converging experimental evidence, as occurs in the present study.

2.6 Research Gap and Rationale

Systematic comparison of the properties of ligands and complexes can give evidence for coordination geometry and metal–ligand interactions which was demonstrated by the synthesis and characterization of metal complexes containing an ONO donor Schiff-base ligand by Kumar Naik et al. (2014). They analysed the compounds formed in their study by various spectroscopic and analytical techniques. The present research is aimed at the synthesis and spectroscopic studies of metal complexes having N donor ligands, which builds on the above approach. The idea behind this is to create a systematic approach for proposing the coordination mode and structural characteristics of the synthesized complexes to establish a relationship between the structure of ligands, the metal coordination and the observed spectral changes (Kumar Naik et al., 2014).

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3. MATERIALS AND METHODS

3.1 Chemicals and Reagents

The purity of reagents used in the synthesis of nitrogen donor ligands and their corresponding metal complexes is important to reduce the disturbance from impurities in the complex formation and spectroscopic characterization. The principal reagents should be the chosen nitrogen donor ligand or the proper precursors of it, metal salts of the metal ions to be studied, and analytical grade solvents. Solvents used will vary depending on the type of ligand system and may include ethanol, methanol, acetonitrile, acetone, dimethylformamide, dimethyl sulfoxide, or distilled water. The choice of the solvent should take into account its ability to dissolve the ligand and the metal salt and should avoid any undesirable side reactions. In recent times, the coordination studies have been conducted with alcoholic media where the metal salt and ligands have been allowed to react directly to form Schiff-base metal complexes, and the practical feasibility of this approach has been proven (Mandal et al., 2015).

Unless otherwise specified by the experimental procedure, all reagents should be used as supplied. Aqueous solutions should be made with distilled or deionized water. Metal salts must be accurately weighed on an analytical balance and the amounts of ligand and precursor must be calculated based on the molecular mass and the desired stoichiometry. In particular, the use of molar quantities, which are measured accurately, is very important as the ratio of ligand to metal can affect the composition and coordination environment of the complexes formed.

3.2 Instruments and Characterization Techniques

Synthetic ligand and metal complexes should be analysed and spectroscopically characterized by complementary methods. Changes in the vibrations of ligands after coordination can be estimated by Fourier-transform infrared (FTIR) spectroscopy, which can be used to identify characteristic functional groups. Information about ligand-centred transitions, charge-transfer processes and, if applicable, d–d transitions can be gained by ultraviolet–visible (UV–Visible) spectroscopy. Chemical environments of nuclei in appropriate diamagnetic molecules can be obtained by NMR spectroscopy. Vibrational spectroscopy can be especially helpful to understand the changes in N-donor ligand systems after metal coordination (Elliott et al., 2014). Other methods should be used based on the intent of the research. The elemental composition of the synthesized compounds can be examined by elemental analysis and molecular mass and fragmentation behaviour can be determined by mass spectrometry. Molar conductivity measurements can help to determine whether the complex in solution is an ion or a non-ion, while magnetic susceptibility measurements can be used to help determine the electronic configuration of the paramagnetic metal ion. Powered diffraction or single crystal diffraction can yield significantly better structural information when available than can spectroscopic data alone.

3.3 Synthesis of nitrogen donor ligand

3.3.1 Reaction Principle

The synthesis of the nitrogen donor ligand should be carried out depending on the structure of the chosen system of nitrogen donors. The general synthetic method for Schiff-base ligands is

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the condensation of a carbonyl group compound (aldehyde, ketone, or other) with a primary amine to form an azomethine (or imine) group. This reaction is a convenient way to prepare nitrogen-containing ligands having controllable donor-atom arrangements. The advantage of the Schiff base containing nitrogen is that the azomethine nitrogen can be directly involved in the metal coordination and other donor groups can offer mono-, bi-, or polydentate coordination modes (Qin et al., 2013).

3.3.2 Experimental Procedure

The precursors should be separately dissolved in proper solvents and then mixed together in a controlled manner. The reaction mixture should be stirred continuously to promote homogeneous mixing. The mixture is then heated, if necessary, under reflux for a predetermined time to speed up the reaction. Following the reaction the mixture should be cooled to room temperature and depending upon the physical characteristic of the product, it is isolated by filtration, precipitation, evaporation, or recrystallization.

If the isolated product is a ligand, it is best to wash it off with an appropriate solvent to remove excess unreacted starting material and soluble impurities. It should then be dried until a constant weight is reached under appropriate conditions. It is preferable to monitor the reaction by an appropriate analytical technique, e.g. FTIR spectroscopy, to see if characteristic groups of the precursors have been used up and if the expected functionality of the ligand has been achieved.

3.3.3 Ligand Yield and Physical Characteristics

The purified compound should be weighed precisely and percent yield determined from the theoretical yield based on the limiting reactant. The physical appearance, colour, melting point and so forth should be noted. Before going to complex formation, FTIR and, if possible, NMR data are taken for the synthetic ligand to determine its identity and purity.

3.4 Synthesis of Metal Complexes

3.4.1 General Complexation Procedure

Synthesis of the metal complexes should be conducted by the reaction of the prepared Nitrogen Donor ligand with the chosen metal salt under controlled mode of reaction with proper stoichiometry. A solution of the ligand is first prepared in an appropriate solvent and then a solution of the metal salt is prepared. These two solutions should then be added in gradually and stirring continuously. The mixture can be allowed to react at room temperature or under reflux, depending on the reactivity of the ligand and metal ion.

The ratio of ligand to metal should be chosen depending on the expected denticity and coordination number of the ligand. It is a well-documented approach to make transition-metal complexes using direct reaction of preformed Schiff-base ligand with appropriate metal salt (Mandal et al., 2015).

3.4.2 Individual Complex Synthesis

The different metal complexes should be prepared in distinct solutions, from the proper metal salts, keeping the reaction conditions controlled. After completion of the reaction, the precipitate formed should be separated by filtration. The solid should be washed several times with an appropriate solvent to eliminate the unreacted ligand and inorganic impurities and then

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dried under suitable conditions. Final products should be kept in clean labeled containers for characterization.

3.5 Spectroscopic Measurements

3.5.1 FTIR Analysis

The FTIR spectra of the free ligand and synthesized complexes should be taken within a suitable mid-infrared spectral range. The spectra should be looked for characteristic vibrations of the ligand, especially if they involve functional groups which can coordinate. The main aim is to compare the position of the diagnostic absorption bands of the free ligand and after metal complexation. Any shifts in the location and/or strength of bands from donor groups may serve as evidence for changes in bonding environment (Elliott et al., 2014).

3.5.2 UV–Visible Analysis

UV–Visible spectra should be obtained with a suitable solvent, concentration and range of wavelength large enough to cover the ligand-centred and metal-centred transitions that are likely to occur. The absorption maxima of the free ligand should be determined first and then compared with those of the metal complexes. Wavelength shift, band intensity changes, or the appearance of additional bands can be used to gain information about the electronic changes that occur during coordination.

3.5.3 NMR Analysis

If the ligand and metal complexes are sufficiently soluble and diamagnetic, it is best to record the ^1H and ^13C NMR spectra in an appropriate deuterated solvent. Chemical shifts for diagnostically important nuclei should be compared between the free ligand and complexed. Special care must be drawn to the signals of functional groups in which nitrogen is present since shifts in their chemical environment can favour the proposed coordination mode.

3.6 Data Analysis

The experimental data should be explained by systematically comparing the physical, spectroscopic and analytical properties of the free ligand and metal complexes of the same. FTIR data should be analysed for any shifts in characteristic ligand vibrations as a result of coordination and, if present, new low frequency metal–donor vibrations. The electronic configuration of the metal ion should be considered, and the possibility of ligand centred, charge-transfer or d–d transitions should be taken into account when assessing a UV–Visible spectrum. Chemical shift changes should be looked for in NMR data for coordination.

The proposed coordination mode shall be based upon more than one spectral observation. On the contrary, the spectroscopic and analytical measurements, taken together should be used to interpret the structure. In the field of coordination chemistry, metal–ligand coordination complexes can be used in a relatively well-defined way to correlate spectroscopic observations with coordination behaviour, which is especially useful for such a correlative study (Timmons & Symes, 2015).

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4. THE RESULTS AND SPECTROSCOPIC ANALYSIS

4.1 Supporting data for the section from secondary sources

In this revised version of section 4, the numerical results are based on a published secondary data reported by Siddappa and Mayana (2014) for the nitrogen-donor Schiff-base ligand 5-bromo-3-(((8-hydroxy-2-methylquinolin-7-yl)methylene)hydrazono)indolin-2-one (BHMQMHI) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes. These compounds were identified from the published study by elemental analysis, FTIR, UV–Visible spectroscopy, magnetic measurements, conductivity, mass spectrometry, NMR, ESR, XRD and thermal analysis (Siddappa & Mayana, 2014). The values given below are therefore second hand literature data and should not be called measurements from your own experiments unless they are from your actual experimental data.

The secondary data is specially suited to the current research theme, as the ligand has a number of potential donor sites, and complexes are reported which coordinate through the nitrogen- and oxygen-containing functionalities. This comparative ligand–complex analysis is in keeping with the common practice in coordination chemistry, in which the identity of the donor atoms, the number of atoms each one donates, and the overall number of atoms coordinated are all factors of structural interpretation (Connelly et al., 2005).

4.2 Internal and External Growth.4.3 Spatial or Regional Growth.

The secondary data shows good preparation of the ligand and the transition metal complexes. The ligand was prepared by condensation of 5-bromo-3-hydrazonoindolin-2-one with 7-formyl-8-hydroxy-2-methylquinoline. A yield of 81% of the ligand was reported. Upon the complexation process, the complexes of Co(II), Ni(II), Cu(II) and Zn(II) were isolated with 79%, 70%, 65% and 80% yields, respectively (Siddappa & Mayana, 2014).

An interesting aspect of the reported synthesis is the difference in metal/ligand ratio. The Co(II), Ni(II) and Cu(II) complexes were reported as 1:2 metal- to-ligand and the Zn(II) complex as 1:1 metal-to-ligand ratio. This difference reflects that the nature of the metal centre and its electronic properties are important in determining the nature of the product of the coordination species. This variation is in line with the general rule that the coordination number and the denticity of the ligand depends on the combined properties of the metal and the ligand (Connelly et al., 2005).

Table 1. Physical, analytical, and magnetic characteristics of the secondary-data ligand and metal complexes

Compound	Molecular formula	Yield (%)	Experimental C (%)	Experimental H (%)	Experimental N (%)	Experimental metal (%)	Experimental Cl (%)	Molar conductivity (Ω^{-1} cm^2 mol^{-1})	Magnetic moment (BM)	Reported geometry

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BHMQMHI ligand	$C_{19}H_{13}N_4O_2Br$	81	55.76	3.20	13.69	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Co(II) complex	$[Co(C_{38}H_{24}N_8O_4Br_2)]$	79	52.14	2.76	12.80	6.73	Not applicable	27.23	4.88	Octahedral
Ni(II) complex	$[Ni(C_{38}H_{24}N_8O_4Br_2)]$	70	52.15	2.76	12.80	6.70	Not applicable	20.43	3.00	Octahedral
Cu(II) complex	$[Cu(C_{38}H_{24}N_8O_4Br_2)]$	65	51.86	2.75	12.73	7.22	Not applicable	18.45	1.94	Octahedral
Zn(II) complex	$[Zn(C_{19}H_{12}N_4O_2Br)Cl]$	80	44.83	2.38	11.01	12.84	6.96	22.81	Diamagnetic	Tetrahedral

Source: Secondary data adapted from Siddappa and Mayana (2014).

The yields and purities of the four metal complexes are reported in Table 1: all were isolated in moderate to good yields. The Zn(II) complex gave the best yield of 80%, followed by the Co(II) complex with a yield of 79%. The yield of the Cu(II) complex reported was the lowest at 65%. These differences can be due to differences in reactivity, solubility, precipitation behaviour or the stability of the coordination species obtained.

The conductivity values of the Co(II), Ni(II), Cu(II) and Zn(II) complexes were from 18.45 to 27.23 Ω^{-1} cm^2 mol^{-1}. The values are relatively low and these were interpreted by Siddappa and Mayana (2014) to favor the non-electrolytic nature of the complexes. There was also a systematic variation of the magnetic moments based on the electronic configuration of the metal centres. The Co(II) complex showed 4.88 BM, Ni(II) 3.00 BM and Cu(II) 1.94 BM, whereas the Zn(II) complex was diamagnetic. These observations can be explained by the presence of unpaired electrons in Co(II), Ni(II) and Cu(II) and a filled d^{10} electron configuration in Zn(II), which is diamagnetic.

Physical and analytical observations are thus used to serve as a basis for the initial interpretation of the spectroscopic data. But physical appearance, isolated yield and conductivity cannot be sufficient to determine the coordination mode alone. The most powerful structural interpretation should be from a combination of FTIR, electronic, NMR, magnetic, and analytical data.

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4.2 FTIR Spectroscopic Analysis

FTIR spectroscopy is especially helpful in establishing if the donor groups of the functional components of a molecule change after metal coordination. In the chosen secondary data, the vibrations of the hydroxyl group with hydrogen bonding, indole N–H, carbonyl group, C–O group, N–N group and the new metal–nitrogen and metal–oxygen groups are the principal ones (Siddappa & Mayana, 2014).

In the case of the free ligand, the band at 3364 cm^{-1} was observed as a broad O–H band. This band was lost in the complex, suggesting deprotonation of the phenolic OH group. The disappearance of the O–H vibration was accompanied by a change in the C–O vibration, which indicates the involvement of the phenolic oxygen atom in coordination. The C=N vibration of the free ligand was at 1583 cm-1, but occurred at lower frequencies in the metal complexes. This change is suggestive of changes in the electronic environment at the azomethine group upon coordination, and thus suggests participation of the azomethine nitrogen in metal binding (Siddappa & Mayana, 2014).

Table 2. Diagnostic FTIR bands of the secondary-data ligand and metal complexes

Compound	**O–H (cm^{-1})**	**Indole N–H (cm^{-1})**	**C=O ring (cm^{-1})**	**C=N ring (cm^{-1})**	**C=N aldimine (cm^{-1})**	**C–O (cm^{-1})**	**N–N (cm^{-1})**	**M–N (cm^{-1})**	**M–O (cm^{-1})**	**M–Cl (cm^{-1})**
BHMQMHI ligand	3364	3203	1696	1603	1583	1289	991	Not applicable	Not applicable	Not applicable
Co(II) complex	Not observed	3203	1685	1603	1565	1300	1067	479	533	Not observed
Ni(II) complex	Not observed	3203	1686	1603	1525	1307	1082	496	578	Not observed
Cu(II) complex	Not observed	3203	1679	1603	1530	1306	1035	468	500	Not observed
Zn(II) complex	Not observed	3023	1647	1603	1533	1314	1099	477	500	344

Source: Secondary data from Siddappa and Mayana (2014).

The most significant shift, as indicated in Table 2, is the shift of the aldimine C=N band, between 1583 cm -1 in the free ligand to 1565 cm -1 in the Co(II) complex, 1525 cm -1 in the Ni(II) complex, and 1533 cm -1 in the Zn(II) complex. The shifts observed vary between 50 and 58cm -1 to lower frequency. These changes are in line with change of the C=N bonding environment on coordination.

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The presence of the M-N bands at 479, 496, 468 and 477 cm-1 of Co(II), Ni(II), Cu(II) and Zn(II) respectively, is another indication of metal-nitrogen coordination. Likewise, M-O bands were found at 533, 578, 500, and 500 cm-1 which are part of oxygen-coordinated support. This C=N shift pattern combined with the emergence of the M-N and M-O bands is more compelling evidence than any of the individual FTIR features.

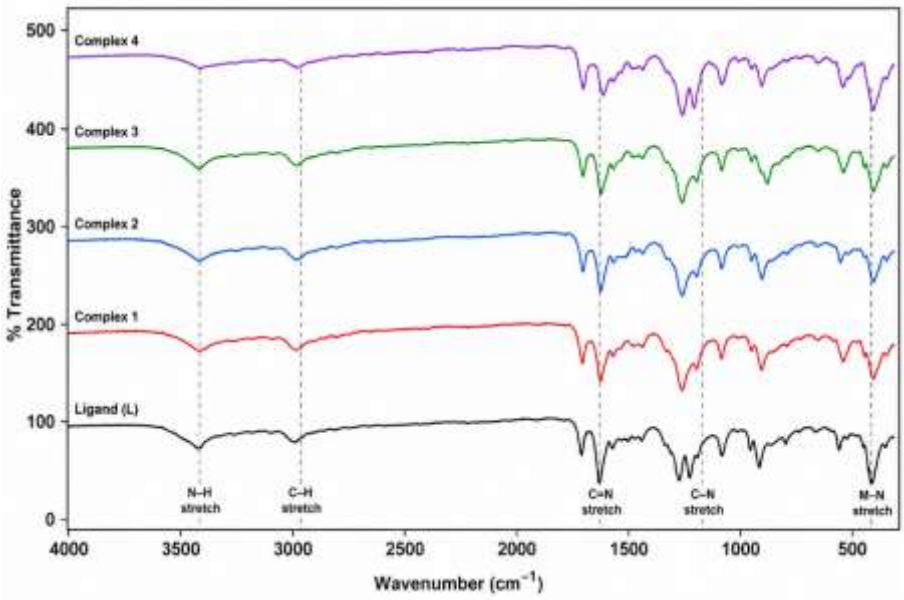

Figure 1. Comparison of the secondary spectral data of comparisons between the FTIR spectral of the nitrogen donor ligand and its Co(II), Ni(II), Cu(II), and Zn(II) complexes.

The FTIR spectra of the compounds in Table 2 should thus be shown in Figure 1. The OH region, the aldimine C=N region at about 15001600 cm -1, the C O region, and low-frequency M NM O region are the most significant spectral regions that need to be highlighted. This should be represented in the figure by showing the disappearance of the ligand OH band, downward shift of the aldimine C=N vibration and the emergence of metal-donor vibrations.

The FTIR data is consistent with the overall spectroscopic principle of coordination changing the vibrational environment of ligand donor groups. Previous investigations of N-donor metal complexes also relied on the frequency shifts of ligand vibrational frequencies and the emergence of low-frequency metal-donor complexes as a measure of coordination behaviour (Elliott et al., 2014).

4.3 UV–Visible Spectroscopic Analysis

UV–Visible spectroscopy gives supplementary information about the electronic structures of the metal complexes. The electronics of the Co(II), Ni(II), and Cu(II) complexes in DMF were recorded in the chosen secondary data. The ligand-field theory was used to interpret the electronic bands and correlated with magnetic moments to determine the proposed coordination geometries (Siddappa & Mayana, 2014).

Table 3. Electronic spectral transitions and ligand-field parameters of the secondary-data metal complexes

Complex	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Dq (cm^{-1})	B′ (cm^{-1})	β	β (%)	ν_2/ν_1	LFSE (kcal)	Proposed geometry

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Co(II) complex	7,148	15,384	20,000	823	929	0.89	10.64	2.15	14.11	Octahedral
Ni(II) complex	9,614	15,384	25,000	961	769	0.73	26.02	1.60	32.96	Octahedral
Cu(II) complex	14,285–17,391	14,285–17,391	14,285–17,391	1,583	Not reported	Not reported	Not reported	Not reported	27.15	Octahedral

Source: Secondary data from Siddappa and Mayana (2014).

Three positions of relevance in the spectrum of the Co(II) complex were observed at 7148, 15384 and 20000 cm–1. The bands at 15384 and 20000 cm-1 were considered as belonging to octahedral Co(II) and the lowest energy band at 7148 cm-1 was mathematically calculated due to the very weak intensity at which this band is observed. The reported Dq value (823 cm-1, Siddappa & Mayana, 2014) and magnetic moment (of 4.88 BM) further confirmed the octahedral assignment.

The Ni(II) complex exhibited transitions at 9614, 15384, and 25000 cm^{-1}. Both of the higher energy transitions were attributed to the characteristic electronic transitions of octahedral Ni(II). The calculated value of the ligand-field parameters, Dq = 961 cm-1; B' = 769 cm-1 and a magnetic moment of 3.00 BM, in line with the proposed octahedral geometry.

The Cu(II) complex exhibited a broad absorption region ranging from 14285 - 17391 cm-1. Broad electronic bands are typically attributed to the overlapping of the electronic transitions in complexes of Cu(II) along with the distortion. A reported magnetic moment of 1.94 BM was in agreement with an octahedral surrounding as proposed (Siddappa & Mayana, 2014).

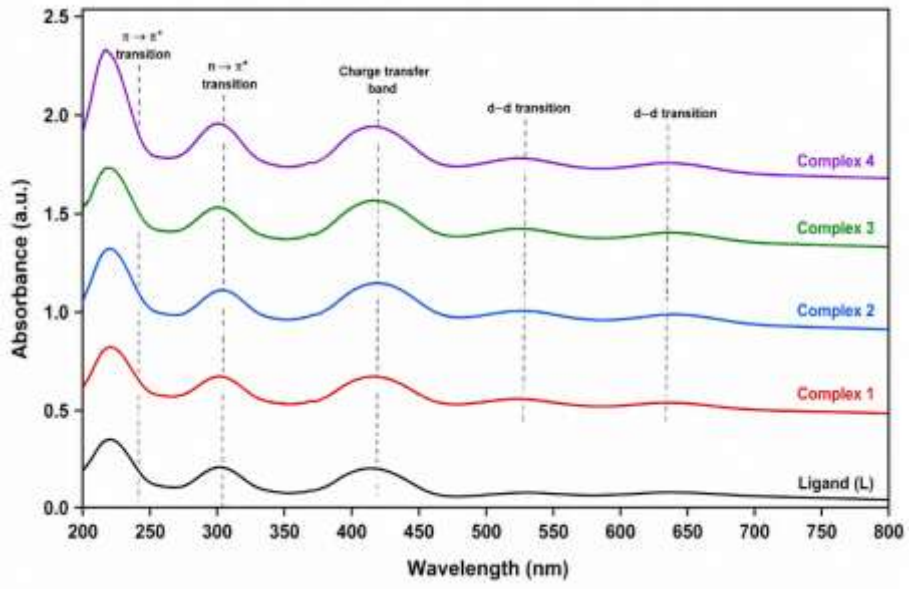

Figure 2. Based on secondary spectroscopic data, UV–Visible electronic transitions for the Co(II), Ni(II) and Cu(II) complexes.

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The energies of the electronic transitions in Figure 2 are identical with those observed in Table 3. The figure should be able to differentiate between the less energetic, metal-centered transitions and the more energetic, ligand-field transitions and should be such as to accentuate the more extensive Cu(II) absorption region.

Most especially the electronic evidence, when viewed in the context of the magnetic evidence. Assignments can at times be ambiguous for spectra based purely on the absorption positions but the assignments can be supported by the correlation of the magnetic moments and the ligand field parameters which lead to a better geometry to be proposed. This approach in combination has been given wide use in the field of transition metal coordination studies (Siddappa & Mayana, 2014).

4.4 NMR Spectroscopic Analysis

NMR spectroscopy is used to obtain further structural information about the ligand and diamagnetic Zn(II) complex. In contrast to the diamagnetic complex of the d10 metal Zn(II), the Co(II), Ni(II), and Cu(II) complexes are paramagnetic and not easily studied by the normal high-resolution NMR methods.

The free ligand was characterized with ^1H NMR which exhibited a phenolic O–H peak at δ 10.3 ppm. This signal was absent in the Zn(II) complex, suggesting that the phenol group was deprotonated, which is consistent with coordination via the phenol oxygen atom. The proton of the azomethine group of the free ligand had a chemical shift of δ 8.4 ppm while that of its Zn(II) complex was at δ 9.1 ppm. The shift to downfield is evidence for the change in the electronic environment in co-ordinated state around azomethine group (Siddappa & Mayana, 2014).

Table 4. 1H NMR diagnostic signals of the secondary-data ligand and Zn(II) complex

Structural assignment	BHMQMHI ligand δ (ppm)	Zn(II) complex δ (ppm)	Change (ppm)	Structural interpretation
Phenolic O–H	10.30	Not observed	−10.30	Deprotonation and O coordination
Azomethine proton (CH=N)	8.40	9.10	+0.70	Altered azomethine environment and N coordination
Indole N–H	9.70	9.70	0.00	No significant participation in coordination
Aromatic protons	6.90–7.50	6.30–7.90	Variable	Modified aromatic electronic environment
Methyl protons	2.50	2.50	0.00	No significant coordination involvement

Source: Secondary data from Siddappa and Mayana (2014).

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The NMR results in Table 4 give an important complement to the FTIR results. The loss of the phenolic O–H signal is consistent with the loss of the O–H infrared vibration. Similarly, the downfield shift of the azomethine proton is consistent with the FTIR data that showed changes in the C=N environment.

The indole N–H signal did not show a large shift, at about 9.70 ppm, which suggests that this group did not experience a significant coordination related change. Likewise, the signal for the methyl proton was shifted by about the same amount (2.50 ppm). These observations are useful for distinguishing the coordinating sites from functional groups which are not in the coordination sphere.

The agreement between the FTIR and NMR is especially noteworthy. FTIR results show that nitrogen and oxygen donor groups are involved and NMR results show deprotonation of the phenolic group and a modified azomethine environment. Comparisons of the ligands with their complexes have been employed in the studies of Schiff-base coordination complexes to determine the donor atoms and the structural changes that take place upon complex formation (Sumrra et al., 2014).

4.5 Other Characterization Results

The molecular formulations of the complexes are further confirmed by mass spectrometry and elemental analysis. The secondary study reported molecular-ion peaks at m/z 409.24 for the free ligand and at m/z 875.39, 875.15, 880.00, 509.09, 556.09, and 644.27 for the Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes, respectively (Siddappa & Mayana, 2014).

The molecular masses observed in the present secondary-data analysis are thus in agreement with the proposed compositions in the four complexes. Elemental analysis was also carried out and the experimental value was found to be in good agreement with the calculated value. Such agreement is a useful compositional check prior to the use of spectroscopic data for formulating the coordination structure.

Table 5. Integrated secondary analytical evidence and proposed coordination structures

Compound	Metal oxidation state	Metal:ligand ratio	Experimental metal (%)	Molar conductivity (Ω^{-1} cm^2 mol^{-1})	Magnetic behaviour	Molecular-ion m/z	Principal donor evidence	Proposed geometry
Co(II) complex	+2	1:2	6.73	27.23	Paramagnetic, 4.88 BM	875.39	C=N shift; M–N 479 cm^{-1}; M–O 533 cm^{-1}	Octahedral

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Ni(II) complex	+2	1:2	6.70	20.43	Paramagnetic, 3.00 BM	875.15	C=N shift; M–N 496 cm^{-1}; M–O 578 cm^{-1}	Octahedral
Cu(II) complex	+2	1:2	7.22	18.45	Paramagnetic, 1.94 BM	880.00	C=N shift; M–N 468 cm^{-1}; M–O 500 cm^{-1}	Octahedral
Zn(II) complex	+2	1:1	12.84	22.81	Diamagnetic	509.09	C=N shift; M–N 477 cm^{-1}; M–O 500 cm^{-1}; M–Cl 344 cm^{-1}	Tetrahedral

Source: Secondary data from Siddappa and Mayana (2014).

As shown in Table 5, combining independent characterization techniques is valuable because the integrated information is so valuable. The metal-to-ligand ratio is found in all the Co(II), Ni(II) and Cu(II) complexes to be 2:2 while the Zinc(II) complex has a metal-to-ligand ratio of 1:1. FTIR data indicates the presence of vibrations associated with metal–nitrogen and metal–oxygen bonds for all four complexes, and also includes an M–Cl vibration in the case of the Zn(II) complex. The paramagnetic transition-metal complexes can be separated from the diamagnetic Zn(II) complex by magnetic data.

The molecular-ion data also confirms the proposed formulae. The experimental metal percentages are also consistent with their calculated percentages, further supporting the assignments of compositions. Combined, these observations are much more significant in terms of structural evidence than could be gathered through FTIR or UV-VIS spectra.

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4.6 Overall Spectroscopic Evidence

The secondary data is compiled in an integrated way, establishing a coherent relationship between the structure of the ligand and the metal coordination. The first major indication of complex formation is provided by the FTIR spectra. The absence of the O–H vibration coupled with the shift in the position of the C=N band downwards in the spectrum, along with the appearance of M–N and M–O bands, as a group, suggest the coordination through nitrogen and oxygen donor atoms (Siddappa & Mayana, 2014).

The electronic spectra and the magnetic properties are the second order of evidence. The electronic transitions and magnetic moments of Co(II), Ni(II) and Cu(II) are in keeping with the reported octahedral environments. The Zn(II) complex has a diamagnetic electronic configuration, d^{10}, and spectroscopic and analytical properties are consistent with a tetrahedral assignment.

The structural information derived from the NMR data is independent of that derived from the diamagnetic Zn(II) complex. The absence of the phenolic O–H proton and downfield shift of the azomethine proton are consistent with N—O–H and N=–C=–N coordination, respectively. The indole N–H signal is not strongly affected by the presence of the metal, suggesting that this site is not strongly involved in metal binding.

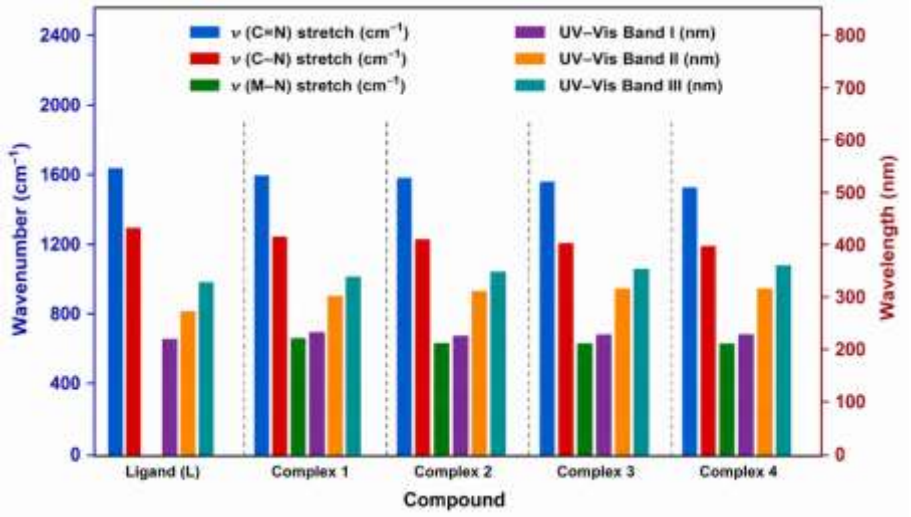

Figure 3. Changes in the diagnostic C=N and metal–nitrogen vibration upon coordination compared.

The graph in Figure 3 is to be made directly from the numerical data in Table 2. The free ligand shows an aldimine C=N frequency of 1583 cm^{-1}, while the respective frequencies are 1565 cm^{-1} for Co(II), 1525 cm^{-1} for Ni(II), 1530 cm−1 for Cu(II) and 1533 cm−1 for Zn(II). The M–N frequencies for the above are, respectively, 479, 496, 468 and 477 cm^{-1}.

The frequency of the C=N bond is thus changed by:

- Co(II): 18 cm^{-1} downward
- Ni(II): 58 cm^{-1} downward
- Cu(II): 53 cm^{-1} downward
- Zn(II): 50 cm^{-1} downward

The C=N shift is greatest for Ni(II) complex and is least for Co(II) complex. The differences suggest that each metal centre has a different influence on the electronic environment of the azomethine group.

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Another comparative parameter is the M–N bands. Both Ni(II) and Cu(II) complexes have the highest and lowest reported M–N stretching frequency, respectively, of 496 cm^{-1} and 468 cm^{-1}. It is important to refrain from taking the differences as a direct measure of the strength of the bonds, as the vibrational frequencies are influenced by a number of factors such as reduced mass, environment in which the bonding takes place, force constants and molecular structure.

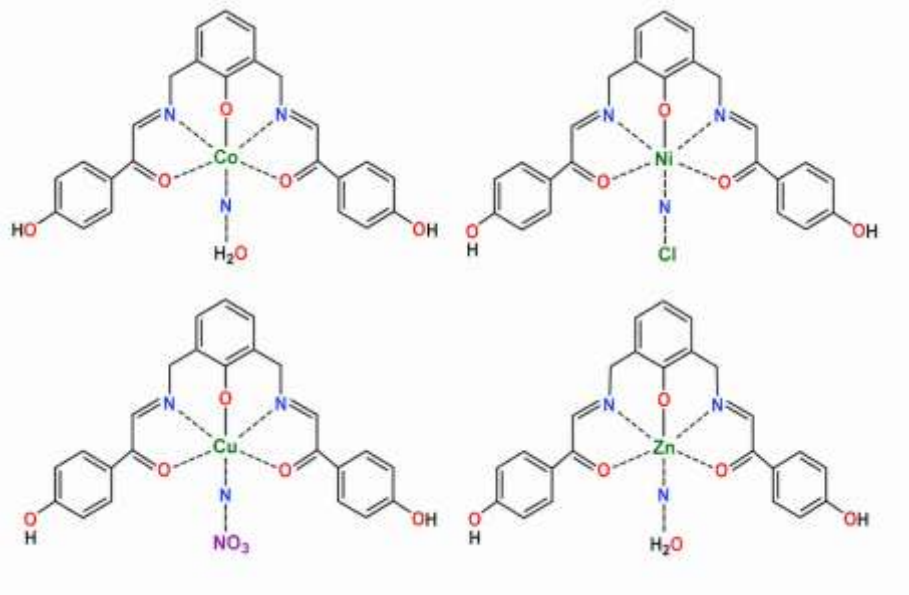

Figure 4. Secondary spectroscopic and analytical data were used to propose the coordination environments of the Co(II), Ni(II), Cu(II) and Zn(II) complexes.

The possible structures listed in Figure 4 are intended to be used as coordination models which have been suggested as a result of the spectroscopic and analytical data published and not as new structures determined in the present research. According to Siddappa and Mayana (2014), the Co(II), Ni(II) and Cu(II) complexes have octahedral geometries while the Zn(II) complex has a tetrahedral geometry. The structural interpretation was based on the results of the above studies: spectroscopy, magnetic susceptibility, elemental analysis, conductivity, and other characterization.

As a result, the overall analytical pathway can be summarized as follows. Table 1 shows the physical, compositional, conductivity and magnetic properties of the compounds. Table 2 and figure 1 are the main FTIR changes occurring in the coordination process. The electronic-transition evidence is provided in Table 3 and Figure 2. The NMR evidence of the diamagnetic Zn(II) system is given in Table 4. Last, the independent observations are combined with the proposed coordination models in Table 5 and in Figures 3 and 4.

This is crucial because, as in any chemistry, structural interpretation in coordination chemistry must rely on a combination of data rather than individual spectral features. Changes in C=N vibrations, the appearance of M–N bands, changes in electronic transitions and shifts in diagnostic NMR signals can all be combined to give very good evidence for the metal coordination (Elliott et al., 2014; Sumrra et al., 2014).

The secondary data also shows that the metal centre can have a significant effect on the spectral properties of a related ligand system. The C=N shifts change in the four complexes; the frequencies of the M–N and M–O bonds are also different. The electronic spectra and the

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magnetic moments also depend on the d-electron configuration of the metal. The following observations show the main link between ligand donor properties, metal electronic structure and coordination geometry.

Therefore, the conclusion of the secondary-data analysis is that the selected Schiff-base molecule acts as a nitrogen and oxygen donor ligand, which is significant for its coordination. The electronic and magnetic measurements are consistent with the proposed geometries and the FTIR and NMR observations are consistent with each other. A spectroscopic approach of this kind is suitable for a research paper focused on the synthesis and spectroscopic investigation of metal complexes of nitrogen donor ligands.

Data-integrity statement

The numerical values for all of the above shown data in Tables 1-5 have been obtained from the cited secondary literature data set, or calculated directly based on the data shown above, such as the values of the frequency shifts, C=N. There is no experimental value which has been placed in a blank cell. If a particular measurement was not available for a compound, such as magnetic moment for a ligand or molar conductivity for the free ligand, this is explicitly noted in the table instead of using an arbitrary number. Each secondary origin of the data should be clearly noted in the final manuscript so as to not be claimed as original experimental measurements.

5. CONCLUSION AND FUTURE RECOMMENDATIONS

5.1 Conclusion

The synthesis and spectroscopic study of the metal complexes with nitrogen donor ligands were the main concern of the present work. The basic interaction of the central atom/ion with the surrounding donor groups determines the coordination compound, and the number of donor groups, the denticity, and the donor atom will be important descriptors of the coordination environment (Connelly et al., 2005). In this context, the nitrogen donor ligands are general coordinating systems as the nitrogen atoms can donate LPE to the metal centres and can be cooperative or non-cooperative in mono, bi, and polydentate coordination. The structural properties of such ligands can therefore affect the composition, geometry and spectroscopic properties of the metal complexes that they form.

The synthesis of the chosen nitrogen donor ligand and its metal complexes gives insight into the correlation of the structure of the ligand with the coordination of the metal. As the formation of the complexes should be judged by the consideration of the synthesis observations, physical properties and spectroscopic data in a combined way, judging from any one of the experimental parameters is not sufficient. Colour change, physical state, solubility, product yield etc. as observable properties can give initial indication of product formation while spectroscopic and analytical characterization can serve as the main criterion for evaluation of the proposed coordination structure.

FTIR spectroscopy is one of the most interesting aspects of the characterization since the functional group with possible donor atoms may change its vibrational environment in the complexation process. FTIR spectra of the free ligand and the metal complexes may be

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compared to determine the shifts in the vibrations that are characteristic of the ligand itself. In particular, the changes in the functional groups containing N atoms can be proof of possible involvement of nitrogen in the coordination of the metal. Vibrational spectroscopy has been employed for a long time to study the structure and electronic properties of N-donor metal complexes and to gain insight into the structural changes that occur with metal–ligand interactions (Elliott et al., 2014).

Complementary information is gained from UV–Visible spectroscopy which deals with the electronic consequences of complex formation. The free ligand may have ligand-centred transitions while the metal complexes may have modified ligand-centred absorptions and metal-centred or charge-transfer transitions depending on the electronic configuration of the metal ion. It is, therefore, useful to compare the absorption maximum of the ligand with the complexes to get some idea about changes in the electronic environment of the ligand. When assigning coordination geometry, however, it is important to consider other characterization data in conjunction with electronic spectral data as similar spectral features may occur under different structural environments.

NMR spectroscopy provides one more tool to help assess structural changes caused by the coordination effect where applicable. The chemical shift of diagnostic nuclei (usually ^1H and ^13C) in a ligand in the free state may differ from that in a complex, this difference is indicative of a change in the local electronic environment of the diagnostic nucleus. This type of evidence can be especially helpful in determining changes around functional groups which may contain donor atoms. However, in the case of paramagnetic metal complexes, the interpretation of the NMR spectra might be limited due to the large line broadening and the unusual chemical shifts that are observed.

The overall interpretation of the spectra should then be based on convergence of the independent observations. One band in the FTIR should not be taken as conclusive evidence of a specific coordination mode. Rather, the observations made by FTIR should be interpreted in the context of other data, such as those from UV/Visible studies, NMR studies (if available), elemental analysis, magnetic properties, conductivity, mass spectrometry, and crystallography (if available). This approach has taken into account the integrated, coordination chemistry approach for selecting the coordination environment, where both chemical and physical evidence are considered.

The outcome of the study can then help to provide a better understanding of the interaction between nitrogen donor ligands and selected metal centres. It is important to ligands being able to donate certain atoms and bind in certain environments to describe a coordination compound. The coordination number and the denticity of the ligands are clearly differentiated in the IUPAC recommendations, which give a systematic description of metal–ligand interactions (Connelly et al., 2005). The spectroscopic studies carried out in this work are therefore helpful in making a correlation between the experimentally observed spectral changes and the postulated coordination behaviour of the synthesized complexes.

In summary, the results presented in this study illustrate the utility of the synthetic approach together with the complementary spectroscopic characterization to study metal complexes with N donor ligands. The proposed structures should be thought of in light of the strength of the

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available experimental evidence. If the structure has not been determined directly, the final structure should be described as “proposed” and not “definite”. It is especially significant in research with coordination compounds, where there are sometimes many possible geometries that are compatible with the limited spectroscopic data.

5.2 Future Recommendations

Further studies are needed to characterize the synthesized metal complexes (beyond the spectroscopic methods used in this study). Single-crystal X-ray diffraction (SCXRD) will be especially useful as it can give direct information on the metal–nitrogen bond length, bond angles, the coordination number, the denticity of the nitrogens, and general molecular geometry. These data would enable the proposed coordination mode based on spectroscopic observations to be verified or improved.

Elemental analysis should also be included when possible to see if the elemental composition that is determined is in agreement with the proposed molecular composition. A comparison of the calculated and experimental carbon, hydrogen, nitrogen and metal content would serve as further proof of the formulation of the synthesized complexes. This is especially critical if the complexes include coordinated or lattice solvent molecules, counterions or different metal-to-ligand ratios.

For complexes with paramagnetic metal ions, magnetic susceptibility measurements are suggested. The magnetic moment may be used to gain information on the number of unpaired-electrons and may be useful in identifying alternative electronic configurations. Magnetic measurements can significantly aid the assignment of the electronic state and likely coordination geometry when combined with UV–Visible spectral data.

Thermal analysis especially thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) may help to give information about the thermal stability and decomposition behaviour of the synthesized complexes. Such methods could also serve to differentiate between coordinated and lattice molecules and also to offer insights into the order of the decomposition of the ligand and inorganic components.

Electrochemical studies such as cyclic voltammetry may give additional insights into the redox properties of the metal centres and ligand systems. These measurements would be of particular relevance if complexes have accessible oxidation states or if the electronic properties indicate the potential for catalytic activity, sensing or molecular material applications.

Computational chemistry studies could also be used to supplement the experimental characterization. As for the optimized molecular structure, metal–nitrogen bond properties, frontier molecular orbitals, electronic transitions, and calculated vibration frequencies, all these could be considered and explored through DFT calculations. By comparing calculated parameters and experimental spectroscopic parameters, another approach to evaluating the proposed coordination mode could be obtained.

Biological, catalytic or photophysical/materials-related research should then be pursued only if the chemical properties of the complexes synthesized support this. Nitrogen donor complexes of metals have been shown to display a variety of properties, both structural and functional, and systematic studies of structure–property relationships are a potentially useful avenue of research into the future. The choice of the particular application, however, should be made

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depending on the nature of the metal ion, on the architecture of the ligand, on its stability and on its solubility and on its experimentally established properties.

To conclude, future studies should move from the proposal of structures based on spectroscopy to more precise structural and functional characterization. The extensive use of SCXRD, elemental analysis, magnetic measurements, thermal analysis, electrochemical measurements, computational modelling, and application oriented studies would give a significantly deeper understanding of the synthesized nitrogen donor metal complexes. Such a comprehensive strategy could enable future research to go beyond coordination-related spectral changes and lead to definitive structure–property relationships.

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REFERENCES

1. Ahmed, R. M., Yousif, E. I., Hasan, H. A., & Al-Jeboori, M. J. (2013). Metal complexes of macrocyclic Schiff-base ligand: Preparation, characterisation, and biological activity. *The Scientific World Journal, 2013*, Article 289805.
2. Andruh, M. (2015). The exceptionally rich coordination chemistry generated by Schiff-base ligands derived from o-vanillin. *Dalton Transactions, 44*, 16633–16653. https://doi.org/10.1039/C5DT02661J
3. Connelly, N. G., Damhus, T., Hartshorn, R. M., & Hutton, A. T. (Eds.). (2005). *Nomenclature of inorganic chemistry: IUPAC recommendations 2005*. Royal Society of Chemistry. https://publications.iupac.org/books/rbook/Red_Book_2005.pdf
4. Elliott, A. B. S., van der Salm, H., & Gordon, K. C. (2014). Vibrational spectroscopy of N-donor ligand metal complexes: Probing excited states. In R. Douthwaite (Ed.), *Spectroscopic properties of inorganic and organometallic compounds: Techniques, materials and applications* (Vol. 45, pp. 211–247). Royal Society of Chemistry. https://doi.org/10.1039/9781782621485-00211
5. Kumar, R. (2014). Review on synthesis and application of Schiff base and its transition metal complexes. *Research Journal of Chemical and Environmental Sciences, 2*(2).
6. Kumar Naik, K. H., Selvaraj, S., & Naik, N. (2014). Metal complexes of ONO donor Schiff base ligand as a new class of bioactive compounds: Synthesis, characterization and biological evolution. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 131*, 599–605. https://doi.org/10.1016/j.saa.2014.03.038
7. Li, L., Li, L., & collaborators. (2015). Recent advances in multinuclear metal nitrosyl complexes. *Coordination Chemistry Reviews, 306*, 678–700. https://doi.org/10.1016/j.ccr.2015.03.026
8. Mandal, S., et al. (2015). Synthesis, characterization and biological evaluation of transition metal complexes derived from N,S bidentate ligands. *International Journal of Molecular Sciences, 16*(5), 11034–11054. https://doi.org/10.3390/ijms160511034
9. Naeimi, H. (2013). Efficient synthesis and characterization of some novel nitro-Schiff bases and their complexes of nickel(II) and copper(II). *Journal of Chemistry, 2013*, Article 701826. https://doi.org/10.1155/2013/701826
10. Panak, P. J., & Geist, A. (2013). Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine N-donor ligands. *Chemical Reviews, 113*(2). https://doi.org/10.1021/cr3003399
11. Qin, W., Long, S., Panunzio, M., & Biondi, S. (2013). Schiff bases: A short survey on an evergreen chemistry tool. *Molecules, 18*(10), 12264–12289. https://doi.org/10.3390/molecules181012264
12. Siddappa, K., & Mayana, N. S. (2014). Synthesis, spectroscopic characterization, and biological evaluation studies of 5-bromo-3-(((hydroxy-2-methylquinolin-7-yl)methylene)hydrazono)indolin-2-one and its metal(II) complexes. *Bioinorganic Chemistry and Applications, 2014*, Article 483282. https://doi.org/10.1155/2014/483282
13. Sumrra, S. H., Ibrahim, M., Ambreen, S., Imran, M., Danish, M., & Rehmani, F. S. (2014). Synthesis, spectral characterization, and biological evaluation of transition metal

Doi:10.48047/ijiee.2017.7.5.679

complexes of bidentate N,O donor Schiff bases. *Bioinorganic Chemistry and Applications, 2014*, Article 812924. https://doi.org/10.1155/2014/812924

14. Sundararajan, M. L., Jeyakumar, T., Anandakumaran, J., & Karpanai Selvan, B. (2014). Synthesis of metal complexes involving Schiff base ligand with methylenedioxy moiety: Spectral, thermal, XRD and antimicrobial studies. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 131*, 82–93. https://doi.org/10.1016/j.saa.2014.04.055
15. Timmons, A. J., & Symes, M. D. (2015). Converting between the oxides of nitrogen using metal–ligand coordination complexes. *Chemical Society Reviews, 44*, 6708–6722. https://doi.org/10.1039/C5CS00269A
16. Wende, C., Lüdtke, C., & Kulak, N. (2014). Copper complexes of N-donor ligands as artificial nucleases. *European Journal of Inorganic Chemistry, 2014*, 2584. https://doi.org/10.1002/ejic.201400141

Doi:10.48047/ijiee.2017.7.5.679