"Exploring Metal–Ligand Interactions in Schiff Base Complexes of Fe (III), Ru (III), Co (II) and Related Metals"

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Abstract: Schiff base ligands are widely used in coordination chemistry due to their strong chelating ability and structural flexibility. In the present study, Schiff base complexes of Fe (III), Ru (III), Co (II), and related transition metals have been synthesized and investigated. The metal–ligand interactions were analyzed using electronic spectral data to understand their coordination behavior and geometry. The results indicate that Schiff bases form stable complexes through coordination via azomethine nitrogen and other donor groups. Fe (III) complexes exhibit octahedral geometry with high-spin configuration, while Ru (III) complexes show low-spin behavior with significant charge transfer transitions. Co (II) complexes predominantly display tetrahedral geometry, supported by characteristic spectral bands. The study highlights the importance of ligand structure in influencing bonding, geometry, and stability of the complexes, making them useful for applications in catalysis and material science.

Keywords: Schiff base, metal–ligand interaction, transition metals, Fe (III), Ru (III), Co (II), chelation

Introduction:

Schiff bases are an important group of organic compounds that contain a characteristic azomethine group (>C=N–). These compounds are usually formed when a primary amine reacts with an aldehyde or ketone through a condensation reaction. Because of this functional group, Schiff bases have a strong ability to bind with metal ions, which makes them very useful as ligands in coordination chemistry. Over time, they have become one of the most widely studied ligands due to their stability and versatility.

For a Schiff base to act as an effective chelating ligand, it should contain not only the azomethine nitrogen but also another donor atom such as oxygen, nitrogen, or sulfur. Functional groups like –OH, –SH, $–NO_2$, and $–NH_2$ enhance the binding ability of the ligand.

These groups help in forming stable five- or six-membered rings when the ligand binds to a metal ion. This process, known as chelation, increases the stability of the metal complex and also changes its electronic properties, which is important for many chemical and biological uses.

Schiff base metal complexes have attracted a lot of attention because of their wide range of structures and applications. Transition metals such as Fe(III), Ru(III), and Co(II) easily form complexes with these ligands. These complexes show different shapes or geometries like octahedral, square planar, and tetrahedral, depending on factors such as the type of metal ion, its oxidation state, and the structure of the ligand. In some cases, more complex geometries like square pyramidal or trigonal bipyramidal are also observed.

Fe(III) complexes with Schiff bases are especially important because they are often found in biological systems and are useful in catalytic reactions. These complexes usually have octahedral geometry and are mostly high-spin due to the moderate strength of the ligand field. However, when strong ligands are present, low-spin complexes can also form. Their electronic spectra are mainly dominated by charge transfer transitions, which makes d–d transitions difficult to observe.

Ru (III) Schiff base complexes are known for their good stability and ability to take part in redox reactions. These complexes generally show low-spin configurations and strong bonding between the metal and ligand. Because of this, they often have some covalent character. Their spectra are usually complex due to overlapping of d–d transitions and charge transfer bands, making them useful in catalytic and electron transfer processes.

Co (II) Schiff base complexes are also widely studied because they can exist in different geometries, mainly tetrahedral or octahedral. The geometry depends on the type of ligand attached to the metal. The electronic spectra of Co (II) complexes are well understood and provide useful information about their structure. In particular, tetrahedral Co (II) complexes show characteristic absorption bands in the visible region, which helps in identifying their geometry.

Apart from Fe (III), Ru (III), and Co (II), other metals like Ni (II), Cu (II), and Pd (II) also form stable complexes with Schiff bases. These metals show different coordination behaviors, which increases the variety and importance of Schiff base chemistry. By changing the structure of the ligand, it is possible to control the properties of the metal complexes.

Schiff base metal complexes are not only important in theoretical chemistry but also have practical applications. They are used in catalysis, medicine, material science, and environmental studies. Many of these complexes show biological activities such as antimicrobial, antifungal, and anticancer effects. Their ability to act as catalysts in chemical reactions also makes them valuable in industrial processes.

Therefore, studying metal–ligand interactions in Schiff base complexes is very important for understanding their structure, bonding, and properties. In this work, special attention is given to the complexes of Fe (III), Ru (III), Co (II), and related metals, with a focus on their electronic spectral behavior and coordination characteristics.

Literature Review:

An enormous number of Co (II) edifices with tetradentate ligands have been readied, the fundamental impetus for their readiness being the bizarre oxygen-conveying property showed by a few. The oxygen-conveying properties of these substances have been reviewed24,25.

Pd (II) and Pt (II) buildings of bis-bidentate salicylaldimine edifices, for example, M(R-sal)2 where M=Pd or Pt and R=ethyl, n-pentyl, isopropyl or t-butyl have been accounted for which are all diamagnetic26.

The Zn (II)- salicylaldimine buildings have been minimal contemplated attributable to the shut shell setup of Zn (II). The bis bidentate buildings of the metal are typically tetrahedral27. In any case, the structure of Zn(sal)2en.H2O has been demonstrated to be square pyramidal28 due to the steric requirements forced by the natural ligand. Lindoy29 has evaluated the job of metal particles in the amalgamation of different Schiff base buildings.

Pujar and Bharamgoudar30 have revealed the union and portrayal of Fe (III), Co (II), Ni (II) and Cu (II) edifices with a Schiff base got from 5-phenylazosalicylaldehyde and aniline. The edifices have been recommended to have either dimeric or straight structures.

Schiff bases acquired by gathering chloroanilines and toluidines with salicylaldehyde have been cooperated with dioxouranium (VI) and the subsequent species described by natural examination, ghostly and conductance data31. The ligands attach to the metal through hydroxyl oxygen and imine nitrogen. The buildings with coordination number eight have been allocated a hexagonal bipyramid structure.

Rai et al.32 have done the union and portrayal of the divalent Co, Ni and Cu edifices of Schiff bases got from 3-hydroxyiminobutane-2-one and aniline and toludines. The edifices are related with octahedral geometry with some measure of tetragonal twisting.

Buildings of divalent Co, Ni, Cu, Fe, Mn, Cd and Hg particles with Schiff bases got from benzoin and 2-amino-5-phenyl-1,3,4-oxadiazole and 2-amino-5-(p-anisil)- 1,3,4-oxadiazole have been readied and characterized33. The ligands are tridentate with ONN grouping. Co, Ni, Cu, Fe and Mn buildings are octahedral while Cd and Hg edifices are tetrahedral.

Patel and Patel34 have cooperated divalent Cu, Ni, Co, Zn and Mn particles with a polymeric Schiff base got from 5,5-methylenebis(3-bromosalicylaldehyde) and hexane-1,6-diamine. The ligand shows tetradentate conduct planning with the metal particles through its azomethine and deprotonated phenolic gatherings. The geometry and the warm steadiness of the edifices have been shown up at.

The complexation conduct of acetophenone glycine and acetophenone alanine towards divalent Fe, Co, Ni, Cu, Zn and Hg has been studied35. The ligands show dibasic, tridentate conduct with ONO benefactor set. Fe, Co, Ni and Cu buildings are dimeric while Zn and Hg edifices are monomeric.

Cu (II), Ni (II), Co (II) and Mn (II) buildings of Schiff bases got from dehydroacetic corrosive and aniline, p-chloroaniline, p-iodoaniline and p-phenetidine and portrayed by different physicochemical data37. All the buildings have been accounted for to have an octahedral geometry, the Mn (II) edifices being with dimeric nature.

Raman and Thangarajan38 have detailed a novel 14-membered macrocyclic Schiff base got from 3-cinnamalideneacetanalide and o-phenylenediamine - a tetradentate and emphatically conjugated ligand to frame a cationic strong building with Cu (II), Ni (II), Co (II) and Zn (II). The edifices have been basically and naturally assessed indicating higher movement than the ligand. molar conductance and mass, IR, UV-Vis, 1H NMR and ESR spectraldata39. The information show that the edifices have a piece of ML type. Square plannar geometry has been recommended for all the buildings except for VO(IV) complex which has square pyramidal geometry.

Objectives of the Study:

1. To synthesize Schiff base ligands and their complexes with Fe (III), Ru (III), Co (II), and related metals.
2. To investigate the coordination behavior and bonding nature of metal–ligand interactions.
3. To characterize the synthesized complexes using spectroscopic and analytical techniques.

Research Methodology:

The Fe (III), Ru (III), Co (II), buildings with all the ligands were readied utilizing particular metal chlorides edifices utilizing metal acetic acid derivations.

Fe (III) buildings:

To an answer of anhydrous ferric chloride (BDH) in methanol, a hot methanolic arrangement of the ligand was included gradually with mixing. The blend was refluxed on a high temp water shower. It was concentrated constrained to two-third the first volume and cooled. The strong that isolated out was sifted, washed with water, hot methnol and ether and was vacuum dried over intertwined CaCl2.

Ru (III) edifices:

Ruthenium trichloride trihydrate (SRL) (1.0g) was broken down in concentrated hydrochloric corrosive and weakened with water to 100 ml to give 0.1N arrangement concerning hydrochloric corrosive. An aliquot of this arrangement was treated with an equivalent volume of methanol and was included drop-wise, with a hot methanolic arrangement of the ligand with mixing. The blend was refluxed on a high temp water shower. It was concentrated constrained to two-third the first volume and cooled. The strong that isolated out was separated, washed with water, hot methanol and ether and was vacuum dried over combined CaCl2.

Co (II) buildings:

To a methanolic arrangement of cobaltous chloride (CoCl2.6H2O), a hot methanolic arrangement of the ligand was included gradually with mixing. The blend was refluxed on a high temp water shower. It was concentrated constrained to two-third the first volume and cooled. The strong that isolated out was separated, washed with water, hot methanol and ether and was vacuum dried over melded CaCl2.

Analysis of the study:

Table-: Electronic spectral data of the metal complexes of HBABS

S. No.	Metal Complex	Frequencies (cm^{-1})		
		V_1	V_2	V_1
1	Ru-HBABS	16650	18410	22600
2	Co-HBABS	11900	–	20000
3	Ni-HBABS	17700	–	24100
4	Cu-HBABS	15625	20830	–
5	Pd-HBABS	15150	19610	25640
6	Ru-FMABS	10610	15110	2230
7	Co-FMABS	10080	18250	26310
8	Ni-FMABS	15230	21690	–
9	Cu-FMABS	15110	21600	–
10	Pd-FMABS	15800	18650	23640
11	Ru-TMABS	12050	14290	21280
12	Co-TMABS	12080	15680	19650
13	Ni-TMABS	15150	21800	–
14	Cu-TMABS	–	15000	21500
15	Pd-TMABS	16100	18200	23800

The subtleties of Fe (III) spectra are very little known in view of the more noteworthy inclination of the particle to have charge move groups in UV-V is locale that dark the turn

taboo and consequently powerless d-d groups. In so far as they are known, be that as it may, the ghastly highlights of Fe (III) particle in octahedral condition are as per the hypothetical desires.

Fe (III) is high turn in about all its octahedral buildings, aside from those with the most grounded ligands, exemplified by [Fe (CN)6]3-, [Fe (Phen)3]3+, and so on. In high-turn edifices, the ground condition of iron is 6A1g and four feeble groups are relied upon comparing to the transitons36.

$^6A_{1g} \longrightarrow {}^4T_{2g}(G)$

$^6A_{1g} \longrightarrow {}^4T_{2g}(G)$

$^6A_{1g} \longrightarrow {}^4A_{1g}, {}^4E_g(G)$ and

$^6A_{1g} \longrightarrow {}^4T_{2g}(D)$

However, all these transitions are not generally observed.

The low-spin complexes, with t_{2g}^5 configuration, possess $^2T_{2g}$ ground state and the following four transitions are expected[37].

$^2T_{2g} \longrightarrow {}^4T_{1g}$

$^2T_{2g} \longrightarrow {}^4T_{2g}$

$^2T_{2g} \longrightarrow {}^2T_{1g}, {}^2A_{2g}$ and

$^2T_{2g} \longrightarrow {}^2Eg$

There is a proof of high request of electron delocalization and covalence in low-turn edifices.

Tetrahedral edifices of Fe (III) are fundamentally high-turn though five facilitate buildings might be high-turn or low-turn contingent upon the quality of the ligands.

The present Fe (III) edifices show no d-d groups, inferable from changes in them being turn – taboo. In any case, in view of different information acquired, they have been doled out octahedral geometry.

Ru (III) edifices:

The ground state design of low-turn Ru (III) buildings is t2g5 with one unpaired electron and the relating ground term as 2T2g. The electronic spectra of low-turn Ru (III) edifices are commonly confounded with numerous d-d advances conceivable from 2T2g ground state and furthermore the charge move groups.

The present Ru(III) complexes reveal three peaks in the region 10610 – 22600 cm^{-1} which may be assigned in the increasing order of frequency to the transitions $^2T_{2g} \longrightarrow {}^4T_{1g}$, $^2T_{2g} \longrightarrow {}^4T_{2g}$ and $^2T_{2g} \longrightarrow {}^2A_{2g}$, $^2T_{1g}$ of octahedral geometry[37].

Co (II) buildings:

The Co (II) particle having the electronic design [Ar] 3d7 is most popular for the development of octahedral and tetrahedral buildings. In octahedral geometry, the ground state can be either 4T1g relating to the high-turn design t2g5 eg2 or 2Eg comparing to the low-turn setup t2g6 eg1, the last being conceivable just with the solid documented ligands. In a tetrahedral geometry, the main conceivable ground term is 4A2 relating to the arrangement e4 t2g3.

The electronic spectra of Co (II) in its various geometries are notable. The noticeable assimilation range of [Co (H2O)6]2+ was first clarified by Abragam and Pryce38. As per them, the mind-boggling gives three tops at 8350, 17850 and 20000cm-1 which are allotted individually to the advances

$$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$$

$$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$$

$$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$$

of octahedral geometry. Comparative outcomes have been accounted for by Ballhausen and Jorgenson for another Co (II) complexes39.

Tetrahedral edifices are shaped for the most part with halides for example [CoCl4]2-. These edifices, with the ground term 4A2, likewise show three groups in the areas 3000-5000, 6000-10000 and 15000-20000cm-1 assignable individually to the transitions 40,41.

$$^4A_2(F) \longrightarrow {}^4T_2(F)$$

$$^4A_2(F) \longrightarrow {}^4T_1(F) \text{ and}$$

$$^4A_2(F) \longrightarrow {}^4T_1(P)$$

Be that as it may, in the greater part of the edifices, the primary band – the one of most reduced vitality has been minimal watched.

Square planar Co (II) edifices are scant. A couple edifices of this geometry have been accounted for with bis(salicylal) ehtylenediamine, phthalocyanins, porphyrins and so forth

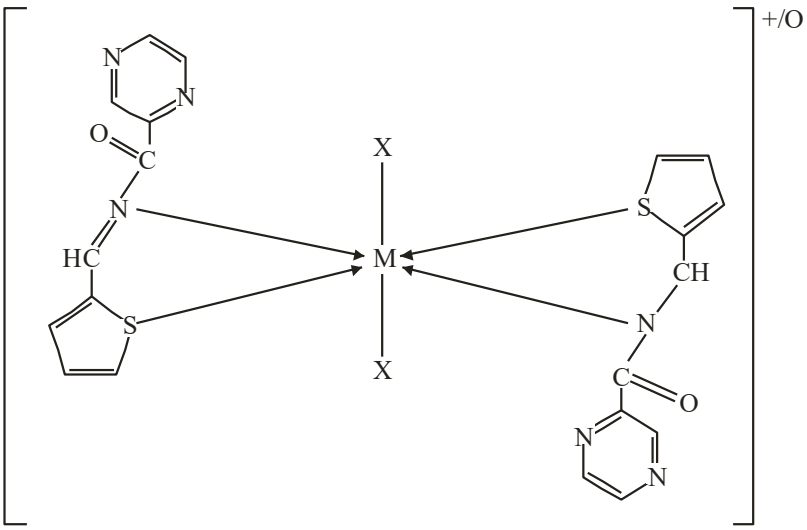
The present Co (II) edifices show two (or) three tops around 12000, 15500 and 20000cm-1 that might be doled out separately to the advances.

$$^4A_2(F) \longrightarrow {}^4T_2(F)$$

$$^4A_2(F) \longrightarrow {}^4T_1(F) \text{ and}$$

$$^4A_2(F) \longrightarrow {}^4T_1(P)$$

of tetrahedral geometry[45].



M = Fe, Ru, Co, Ni and Cu; X = Cl, OAc
Fig. 75. : Structure of Fe(III), Ru(III) and Co(II), Ni(II), Cu(II) complexes of TMPCA

Final conclusion:

In this study, the metal–ligand interactions in Schiff base complexes of Fe (III), Ru (III), Co (II), and other related metals were carefully examined using electronic spectral data. The results clearly show that Schiff base ligands have a strong ability to coordinate with different transition metal ions, forming stable and well-defined complexes.

The Fe (III) complexes did not show clear d–d transition bands, mainly because these transitions are spin-forbidden and are often hidden by strong charge transfer bands. However, based on the overall spectral behavior and supporting data, these complexes are best described as having octahedral geometry. The high-spin nature of Fe (III) in these complexes also suggests that the ligand field strength is moderate.

The Ru (III) complexes displayed more complicated spectra due to the presence of both d–d transitions and charge transfer bands. These observations indicate a low-spin configuration and suggest strong interaction between the metal ion and the ligand. This also points to some degree of covalent character in bonding and electron delocalization within the complex.

The Co (II) complexes showed absorption bands in the range of about 12000 to 20000 cm^{-1}. These bands match well with known transitions for tetrahedral Co (II) complexes. Therefore, most of the Co (II) complexes prepared in this work are likely to have tetrahedral geometry. The spectral results are consistent with previously reported data, which supports the accuracy of these findings.

Overall, the study confirms that Schiff base ligands are very effective in forming stable complexes with transition metals. The electronic spectral analysis helped in understanding the geometry, bonding nature, and electronic properties of these complexes. It also shows that by modifying the ligand structure, it is possible to control the properties of the metal complexes.

The edifices of Fe (III), Ru (III), Co (II), Ni (II), Cu (II), Pd (II), Zn (II), Cd (II) and Hg (II) with TMPCA has been portrayed by different physico-synthetic information. The metal: natural ligand stoichiometry has been seen as 1: 2 with Fe (III), Ru (III), Co (II), Ni (II) and Cu (II) buildings and 1:1 in rest of the edifices.

All the metal complexes are non-electrolytes in DMF except for Fe (III) and Ru (III) buildings which show 1:1 conduct.

The ligand shows neutral, bidentate behaviour towards the metal particles planning through azomethine nitrogen and thiophene sulfur. Fe (III), Ru (III), Co (II), Ni (II) and Cu (II) buildings are paramagnetic relating individually to five, one, three, two and one unpaired

electrons while the others are diamagnetic. As showed by their electronic spectra, the Ru (III), Co (II),

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