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Microwave-assisted synthesis, characterization, and computational studies of 3d metal complexes with a Schiff base derived from with 4-aminoantipyrine

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Abstract

A novel series of transition metal complexes of cobalt(II), nickel(II), and copper(II) with a Schiff base ligand derived from 2-pyridinecarboxaldehyde and 4-aminoantipyrine was synthesized under microwave-assisted conditions. The microwave method afforded high yields in significantly reduced reaction times compared to conventional heating. The ligand and metal complexes were characterized by elemental analysis, FT-IR spectroscopy, UV-Vis spectroscopy, mass spectrometry, and thermal analysis (TGA/DTA). Computational studies using density functional theory (DFT) at the B3LYP/LANL2DZ level were performed to optimize structures and analyze electronic properties. Spectroscopic results suggest that the ligand coordinates in a bidentate fashion through azomethine nitrogen and pyridine nitrogen, forming octahedral complexes. DFT calculations provided insight into frontier molecular orbitals and charge distribution, supporting the proposed geometry. Thermal stability and electronic transitions were evaluated and correlated with computational results.

Keywords: Schiff base, microwave synthesis, transition metal complexes, dft, spectroscopic characterization

Introduction

Schiff bases are widely studied ligands in coordination chemistry due to their facile synthesis and ability to form stable complexes with transition metals. They have applications in catalysis, bioinorganic chemistry, and materials science [1-9]. Microwave-assisted synthesis has emerged as an efficient and greener synthetic approach, offering faster reaction rates and improved yields relative to conventional thermal methods [10-14]. Comprehensive characterization and DFT computational studies are conducted to understand geometric and electronic structures. Schiff bases, typically formed by the condensation of primary amines with aldehydes or ketones, represent an important class of ligands in coordination chemistry due to their structural versatility and strong metal-binding ability. The presence of azomethine (–C=N–) functionality imparts unique electronic and coordination properties, making Schiff bases suitable for applications in catalysis, medicinal chemistry, and materials science.4-Aminoantipyrine is a biologically active heterocyclic compound that readily forms Schiff bases with various aldehydes [15-20]. Complexes derived from 4-aminoantipyrine-based Schiff bases have been reported to exhibit antimicrobial, antioxidant, and anticancer properties. On the other hand, 2-pyridinecarboxaldehyde introduces an additional heterocyclic nitrogen donor, enhancing chelation and stability of the resulting metal complexes..In this work, we report the microwave-assisted synthesis of a Schiff base derived from 2-pyridinecarboxaldehyde and 4-aminoantipyrine, along with its Co(II), Ni(II), and Cu(II) complexes. Comprehensive experimental characterization and density functional theory (DFT) studies were performed to elucidate structural, electronic, and thermal properties.

Materials and Methdology

All chemicals used were of analytical grade and used without further purification. 2-Pyridinecarboxaldehyde, 4-aminoantipyrine, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, and copper(II) chloride dihydrate were procured from standard commercial suppliers. Ethanol and methanol were used as solvents.

Microwave-Assisted Synthesis of Schiff Base Ligand (L)

Equimolar amounts (1 mmol) of 2-pyridinecarboxaldehyde and 4-aminoantipyrine were dissolved in 20 mL of ethanol. The mixture was subjected to microwave irradiation at 400 W for 3–5 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was cooled, and the yellow solid formed was filtered, washed with cold ethanol, and dried under vacuum.

Microwave-Assisted Synthesis of Metal Complexes

The Schiff base ligand (1 mmol) was dissolved in hot ethanol and mixed with an ethanolic solution of the corresponding metal salt (1 mmol). The mixture was irradiated in a microwave reactor at 500 W for 5–7 minutes. The resulting solid complexes were filtered, washed with ethanol and ether, and dried in a desiccator.

Results and Discussion

Elemental analysis data are in good agreement with the proposed stoichiometry of the ligand and complexes. The molar conductance values (10–18 Ω^{-1} cm^2 mol^{-1}) indicate that the complexes are non-electrolytic in nature. The physical and analytical data summarized in Table 1 are initially confirming the successful synthesis.

Table 1: Physical and Elemental Data of 2-pyridinecarboxaldehyde and 4-aminoantipyrine (HL) and their metal complexes

Compound	Found (Calc.) C%	H%	N%	Λm
L	67.4 (67.8)	5.6 (5.8)	16.2 (16.4)	—
Co-L	58.1 (58.4)	4.9 (5.1)	13.9 (14.1)	14
Ni-L	58.3 (58.6)	4.8 (5.0)	14.0 (14.1)	12
Cu-L	57.9 (58.2)	4.7 (4.9)	13.8 (14.0)	15

The FT-IR spectrum of the ligand exhibits a strong band at ~1618 cm^{-1} attributed to azomethine (C=N) stretching vibration. In the metal complexes, this band shifts to lower frequencies (1590–1602 cm^{-1}), indicating coordination through azomethine nitrogen. The pyridine ring vibration also shifts upon complexation, confirming involvement of pyridine nitrogen.New bands observed in the regions 510–530 cm^{-1} and 430–460 cm^{-1} are assigned to M–N bonds.The UV–Visible spectrum of the Co(II) complex shows bands characteristic of octahedral geometry. Magnetic moment values (4.7–5.1 BM) further support this geometry.The Ni(II) complex exhibits transitions consistent with an octahedral environment and a magnetic moment of ~3.2 BM.The Cu(II) complex shows a broad band around 14,500 cm^{-1}, indicative of a distorted octahedral geometry, with a magnetic moment of 1.9 BM. Thermogravimetric analysis reveals that the complexes are thermally stable up to 200–250 °C. Decomposition occurs in successive steps corresponding to loss of coordinated chloride ions followed by ligand degradation.

Computational Studies

DFT calculations were carried out using the B3LYP functional. The 6-31G(d,p) basis set was used for C, H, N, and O atoms, while LANL2DZ was employed for metal ions. Geometry optimizations were performed without symmetry constraints. The optimized structures confirm bidentate coordination of the ligand via azomethine and pyridine nitrogen atoms. Metal–nitrogen bond lengths range between 2.02–2.15 Å. The HOMO–LUMO energy gap of the ligand decreases upon complexation indicating increased chemical reactivity and stability of the complexes. Frontier molecular orbital (FMO) analysis was carried out to gain insight into the electronic properties, chemical reactivity, and stability of the Schiff base ligand and its metal complexes. Density Functional Theory (DFT) calculations were performed using the B3LYP functional, with the 6-31G(d,p) basis set for non-metal atoms and the LANL2DZ basis set for metal ions. The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated for the optimized geometries.The HOMO–LUMO energy gap (ΔE) is an important parameter that reflects the kinetic stability and reactivity of a molecule. A smaller energy gap indicates higher polarizability and enhanced charge-transfer capability. The free Schiff base ligand exhibits a relatively larger energy gap, suggesting higher stability and lower reactivity. Upon coordination with Co(II), Ni(II), and Cu(II) ions, the HOMO–LUMO energy gap decreases significantly, indicating increased electronic delocalization and improved charge transfer between the ligand and metal center.In the metal complexes, the HOMO is mainly localized over the metal ion and the azomethine nitrogen atoms, while the LUMO is predominantly distributed over the ligand framework. This distribution facilitates ligand-to-metal and metal-to-ligand charge transfer transitions, consistent with the observed UV–Visible spectral features. Among the complexes, the Cu(II) complex exhibits the smallest HOMO–LUMO energy gap, reflecting its higher chemical reactivity and the influence of Jahn–Teller distortion on its electronic structure.

Table 2: HOMO–LUMO Energy Values

Compound	EHOMO (eV)	ELUMO (eV)	Gap (eV)
L	–5.84	–2.31	3.53
Co-L	–5.62	–2.98	2.64
Ni-L	–5.58	–3.02	2.56
Cu-L	–5.41	–3.15	2.26

Molecular Electrostatic Potential (MEP) Analysis

Molecular Electrostatic Potential (MEP) analysis was performed to investigate the charge distribution and reactive sites of the Schiff base ligand and its metal complexes. The MEP surfaces were generated using density functional theory (DFT) calculations at the B3LYP level of theory, mapped onto the optimized molecular electron density surface.The MEP map of the free Schiff base ligand shows regions of negative electrostatic potential (red and yellow regions) localized predominantly around the azomethine nitrogen and pyridine nitrogen atoms, indicating electron-rich sites favorable for electrophilic attack and metal coordination. In contrast, regions of positive electrostatic potential (blue regions) are mainly distributed over hydrogen atoms and the aromatic ring framework, suggesting susceptibility toward nucleophilic interactions. Upon complexation with Co(II), Ni(II), and Cu(II) ions, significant redistribution of electron density is observed. The negative potential around the azomethine and pyridine nitrogen atoms decreases, confirming their involvement in coordination with the metal ions. The metal centers appear as regions of positive potential, reflecting partial electron donation from the ligand to the metal ion. This charge redistribution supports the bidentate coordination mode proposed from spectroscopic studies.In the Cu(II) complex, the MEP surface exhibits an asymmetric distribution of electrostatic potential around the metal center, consistent with the distorted octahedral geometry resulting from the Jahn–Teller effect. The axial elongation observed in the optimized structure leads to unequal charge distribution, further validating the experimental findings.

Overall, the MEP analysis provides strong computational evidence for the preferred coordination sites, metal–ligand interactions, and structural distortion in the complexes, in good agreement with experimental spectral and magnetic data.

Global Reactivity Descriptors

Global reactivity descriptors provide valuable insight into the chemical stability, reactivity, and charge transfer capability of molecular systems. These descriptors were calculated using the frontier molecular orbital energies obtained from DFT calculations according to Koopmans' theorem. The ionization potential (I) and electron affinity (A) were approximated as the negative of HOMO and

LUMO energies, respectively. From these values, global hardness (η), global softness (S), chemical potential (μ), electronegativity (χ), and electrophilicity index (ω) were evaluated.

Table 3: Global Reactivity Descriptors

Compound	I (eV)	A (eV)	η (eV)	S (eV^{-1})	μ (eV)	χ (eV)	ω (eV)
Schiff base ligand (L)	5.84	2.31	1.77	0.28	–4.08	4.08	4.70
Co(II) complex	5.62	2.98	1.32	0.38	–4.30	4.30	7.00
Ni(II) complex	5.58	3.02	1.28	0.39	–4.30	4.30	7.20
Cu(II) complex	5.41	3.15	1.13	0.44	–4.28	4.28	8.10

The global reactivity descriptors reveal significant changes in the electronic properties of the ligand upon coordination with transition metal ions. The free Schiff base ligand exhibits a higher global hardness (η) and lower softness (S), indicating greater stability and lower reactivity. Upon complex formation, the hardness decreases while the softness increases, suggesting enhanced polarizability and reactivity of the complexes.The chemical potential (μ) values are negative for all compounds, confirming their thermodynamic stability. The electronegativity (χ) values increase slightly upon coordination, indicating stronger electron-attracting ability in the complexes. Notably, the electrophilicity index (ω) increases markedly from the free ligand to the metal complexes, with the Cu(II) complex showing the highest value. This trend suggests that the Cu(II) complex is the strongest electrophile among the studied compounds, consistent with its lower HOMO–LUMO energy gap and Jahn–Teller distorted geometry.

Overall, the global reactivity descriptor analysis supports the experimental and HOMO–LUMO results, confirming that metal coordination enhances the chemical reactivity and charge transfer properties of the Schiff base ligand.

Conclusion

A novel Schiff base ligand derived from 2-pyridinecarboxaldehyde and 4-aminoantipyrine and its Co(II), Ni(II), and Cu(II) complexes were successfully synthesized using microwave irradiation. The method proved efficient, rapid, and environmentally benign. Comprehensive characterization and DFT studies confirmed bidentate coordination and octahedral geometries. The good agreement between experimental and computational results validates the proposed structures and highlights the potential of microwave-assisted synthesis in coordination chemistry.

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