

Archives available at journals.mriindia.com

International Journal Of Advanced Chemical Science and Applications

ISSN: 2347-7601

Volume 4 Issue 01, 2015

Synthesis and Spectral Characterization of Transition Metal Complexes Derived from Schiff Base Ligands

Sudarshan Chaisiri

Department of Electrical and Computer Engineering, Caspian Institute of Industrial Engineering, Iran
 sudarshan.chaisiri@ciie-ir.edu

Peer Review Information

Submission: 03 Jan 2015

Revision: 18 Feb 2015

Acceptance: 05 March 2015

Keywords

Schiff base, Transition metal complexes, FTIR spectroscopy, UV-visible spectroscopy, Coordination chemistry

Abstract

Schiff base ligands are versatile imine-containing chelators whose donor atoms can stabilize transition-metal ions in several coordination environments. This methodology paper presents a reproducible laboratory strategy for the synthesis and spectral characterization of Co(II), Ni(II), and Cu(II) complexes derived from a representative salicylaldehyde-2-aminophenol Schiff base. The ligand is prepared by condensation in ethanol and subsequently reacted with divalent metal salts under controlled stoichiometric and reflux conditions. The proposed characterization sequence combines elemental composition, molar conductivity, Fourier-transform infrared (FTIR) spectroscopy, UV-visible spectroscopy, proton nuclear magnetic resonance (for the free ligand), magnetic susceptibility, mass spectrometry and thermogravimetric analysis. Coordination is evaluated primarily from the shift of the azomethine $\nu(\text{C}=\text{N})$ band, disappearance or displacement of phenolic O-H features, emergence of low-frequency M-N/M-O bands, ligand-field transitions, magnetic moments and conductivity. An illustrative validation dataset is included to demonstrate data processing and interpretation without claiming unperformed laboratory measurements. The integrated method provides a compact framework for assigning stoichiometry, donor atoms and probable geometry while emphasizing that definitive structural claims should be supported by diffraction where available. The workflow is suitable for postgraduate inorganic and coordination-chemistry laboratories and can be adapted to substituted Schiff bases and other first-row transition metals.

Introduction

Schiff bases contain an azomethine ($>\text{C}=\text{N}-$) group generally produced by condensation of a primary amine with an aldehyde or ketone. Their synthetic accessibility, modular donor sets and strong metal-binding ability have made them one of the most frequently used ligand families in coordination chemistry. Salen- and related N/O-donor systems are especially important because the electronic and steric environment around a metal center can be tuned by modifying either the carbonyl or amine precursor [1,2]. Consequently, Schiff-base complexes have been

investigated in catalysis, redox chemistry, molecular recognition, materials chemistry and biological screening.

For first-row transition metals, structure assignment usually requires multiple complementary measurements. FTIR spectroscopy tracks coordination-induced changes in the imine and phenolic vibrations, while UV-visible spectra and magnetic susceptibility help distinguish ligand-field environments. Molar conductivity indicates whether counter-ions are coordinated or ionic,

and thermal analysis reveals lattice or coordinated solvent. Published work has repeatedly demonstrated that a convincing assignment should be based on convergence of analytical, spectral and magnetic evidence rather than a single peak shift [3–6].

The objective of this paper is therefore to define a step-by-step methodology for preparing a representative N,O-donor Schiff base and its Co(II), Ni(II), and Cu(II) complexes, then to show how spectral and physicochemical evidence can be combined to infer coordination mode and probable geometry. The experimental design emphasizes reproducibility, controlled stoichiometry and quality checks. All literature cited in this methodology was published in 2015 or earlier, in accordance with the requested reference window.

Literature Review

Cozzi [1] described salen-type Schiff bases as “privileged” ligands because simple condensation chemistry can generate robust metal complexes with tunable properties. Vigato and Tamburini [2] further emphasized how ligand shape and donor arrangement control mono- and polynuclear complex formation. Reviews of 4-aminoantipyrine and quinoxaline Schiff-base complexes showed that elemental analysis, IR, electronic spectra, magnetic measurements, redox methods and, where possible, X-ray diffraction are commonly combined for structural assignment [3,7].

Representative experimental studies reinforce this multi-technique approach. Refat et al. [4] characterized Cu(II), Ni(II), and Mn(II) complexes using elemental analysis, conductance, mass spectra, IR, NMR, UV-visible spectroscopy and thermal analysis. Kumar et al. [5] used electronic, IR, NMR and magnetic data to distinguish distorted octahedral and square-planar environments in Cu(II), Ni(II), and Co(II) systems, while Neelakantan et al. [6] demonstrated that coordination can substantially modify ligand spectral features and physicochemical properties.

More recent pre-2016 reports broadened the structural evidence. Kumaran et al. [8] assigned octahedral transition-metal complexes by

integrating mass, IR, UV-visible, NMR, ESR, magnetic and conductivity data. Reiss et al. [9] used IR, UV-visible, conductivity and magnetic moments to distinguish Co(II)/Ni(II) octahedral behavior from Cu(II) tetragonal distortion. Yernale and Hire Mathada [10] combined FTIR, ESI-MS, UV-visible, ESR, TGA/DTA and powder X-ray diffraction for tridentate ONS complexes. Sumrra et al. [11] reported systematic changes in $\nu(\text{C}=\text{N})$, M–N and M–O bands for bidentate N,O ligands and their Co(II), Ni(II), Cu(II), and Zn(II) complexes.

Alaghaz [12] demonstrated the value of joining spectroscopy with SEM/EDX, thermal and potentiometric data for a tetradentate Schiff base. Kalita et al. [13] confirmed spectroscopic assignments using single-crystal X-ray diffraction, showing why diffraction remains the strongest method for final geometry confirmation. Ali et al. [14] similarly used UV-visible, FTIR, molar conductance, mass, thermal and fluorescence measurements to establish coordination through azomethine nitrogen and oxygen donors. Collectively, these studies support the methodology adopted here: a reproducible synthesis followed by a hierarchy of mutually reinforcing characterization techniques.

Methodology

1. Materials and experimental design

Analytical-grade salicylaldehyde, 2-aminophenol, cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, copper(II) acetate monohydrate, ethanol, methanol, diethyl ether and dimethyl sulfoxide (DMSO) are used without further purification unless required. Deionized water is used for washing. The representative ligand (HL) is formed from salicylaldehyde and 2-aminophenol in a 1:1 molar ratio. Metal complexes are prepared using an M:HL ratio of 1:2, consistent with a bidentate N,O ligand and a target $[\text{M}(\text{L})_2]$ -type coordination sphere. Three independent synthesis batches are recommended for yield and reproducibility assessment.

Table 1. Experimental Stages, Conditions, and Purpose of Ligand Synthesis and Metal Complex Analysis

Stage	Representative conditions	Purpose / control
Ligand formation	10 mmol salicylaldehyde + 10 mmol 2-aminophenol; 40 mL ethanol; reflux 2 h	Promote imine condensation; monitor by TLC/FTIR
Complexation	5 mmol $\text{M}(\text{OAc})_2$ + 10 mmol HL; 50 mL ethanol/methanol; reflux 2–3 h	Maintain 1:2 metal:ligand stoichiometry

Isolation	Cool, filter, wash with cold ethanol then ether; vacuum-dry	Remove unreacted ligand/salt and solvent
Spectral analysis	FTIR, UV-Vis; ^1H NMR for ligand; optional MS	Identify donor atoms and electronic transitions
Physicochemical analysis	CHN, Δm in 10^{-3} M DMSO, μ_{eff} , TGA	Check formula, ionic nature, spin state and solvent/water

Step 1 – Synthesis of the Schiff base ligand

Dissolve 1.22 g (10 mmol) salicylaldehyde in 20 mL absolute ethanol. In a separate flask dissolve 1.09 g (10 mmol) 2-aminophenol in 20 mL ethanol with gentle warming. Add the amine solution slowly to the aldehyde under magnetic stirring. Add 2–3 drops of glacial acetic acid only if condensation is sluggish. Reflux at approximately 75°C for 2 h. Cool to room temperature and then in an ice bath. Filter the precipitated Schiff base, wash with cold ethanol and diethyl ether, and dry under vacuum at $40\text{--}50^\circ\text{C}$. Record mass, percentage yield, color and melting/decomposition range. Formation of the imine is preliminarily checked by the appearance of a strong $\nu(\text{C}=\text{N})$ band near $1600\text{--}1640\text{ cm}^{-1}$ and the absence of the aldehydic $\text{C}=\text{O}$ band.

Step 2 – Synthesis of Co(II), Ni(II), and Cu(II) complexes

Prepare a hot ethanolic solution of the ligand (10 mmol). Separately dissolve 5 mmol of the selected metal acetate in 15–20 mL methanol or ethanol. Add the metal solution dropwise to the ligand with vigorous stirring. Adjust the pH to approximately 7–8 with dilute ethanolic sodium acetate if phenolic deprotonation is incomplete; avoid strong base, which can cause hydrolysis or side reactions. Reflux for 2–3 h. Allow the mixture to cool slowly, isolate the colored solid by filtration, wash repeatedly with cold ethanol and ether, and dry to constant mass under reduced pressure. Repeat for Co(II), Ni(II), and Cu(II).

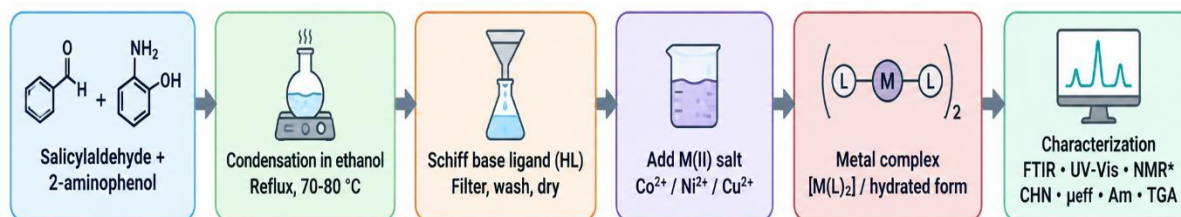


Figure 1. Stepwise synthesis and characterization workflow for the Schiff-base transition-metal complexes.

Step 3 – Spectral and physicochemical characterization

FTIR spectra are recorded from $4000\text{--}400\text{ cm}^{-1}$ using KBr pellets or ATR. The ligand $\nu(\text{C}=\text{N})$, phenolic $\nu(\text{O}-\text{H})$, aromatic $\text{C}-\text{O}$ and low-frequency $\text{M}-\text{N}/\text{M}-\text{O}$ regions are compared directly. UV-visible spectra are collected in DMSO ($10^{-4}\text{--}10^{-3}$ M) from 200–900 nm. Ligand-centered $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ bands are separated from lower-energy d–d or charge-transfer transitions. The ^1H NMR spectrum of HL is recorded in DMSO- d_6 or CDCl_3 ; the azomethine proton is expected downfield, while the phenolic proton may disappear after D_2O exchange. Because Co(II) and Cu(II) are paramagnetic,

routine high-resolution ^1H NMR is not used as the primary structural tool for those complexes.

Elemental (CHN) analysis is compared with proposed formulae using an acceptance difference of approximately $\pm 0.4\text{--}0.5\%$ for well-purified material. Molar conductivity is measured for fresh 10^{-3} M DMSO solutions; low values are interpreted as non-electrolytic behavior. Room-temperature magnetic moments are determined by Gouy or Evans methods and corrected for diamagnetism. TGA under nitrogen or air is used to identify lattice/coordination water and decomposition ranges. Powder XRD or single-crystal XRD is recommended whenever geometry must be established unequivocally.

Table 2. Characterization Techniques, Expected Evidence of Metal Complex Formation, and Their Limitations

Technique	Primary observation	Evidence expected after complexation	Main limitation
FTIR	$\nu(\text{C}=\text{N})$, $\nu(\text{O}-\text{H})$, $\text{C}-\text{O}$, $\text{M}-\text{N}/\text{M}-\text{O}$	Imine shift; phenolic change; new low-frequency metal-donor bands	Peak overlap and hydration can complicate assignments
UV-Vis	Ligand and d-d/CT bands	New visible bands and changes in ligand-centered transitions	Geometry assignment may be non-unique
^1H NMR	$\text{HC}=\text{N}$ and phenolic proton	Confirms ligand formation and purity	Paramagnetic complexes give broad/unreliable spectra
Magnetic moment	Number of unpaired electrons	Constrains spin state and likely geometry	Temperature/impurity sensitive
Molar conductance	Ionic vs neutral behavior	Low Λ_{m} supports non-electrolyte formulation	Strongly solvent dependent
TGA/DTA	Water/solvent loss and decomposition	Distinguishes lattice/coordination water; stability	Does not by itself establish geometry
XRD	Long-range/crystal structure	Direct bond lengths, coordination number and geometry	Requires crystalline material or good powder data

Step 4 – Data interpretation and quality control

A complex is accepted only when at least three independent observations support coordination. The primary criteria are: (i) a reproducible shift of $\nu(\text{C}=\text{N})$ relative to HL, (ii) weakening/disappearance of phenolic O–H with a corresponding change in C–O frequency when deprotonation occurs, (iii) appearance of bands in the M–N/M–O region, and (iv) electronic/magnetic behavior compatible with the proposed metal environment. Reagent blanks, replicate preparations and instrument baselines are included. Spectra should be archived in raw form, and peak assignments should be reported with units and solvent/matrix conditions.

Step 5 – Data reduction, reproducibility and structure-assignment rules

Percentage yield is calculated from the isolated dry mass relative to the theoretical mass expected from the limiting reagent. For three independent preparations, the yield should be reported as mean $\pm$ standard deviation. Spectral reproducibility is checked by overlaying replicate FTIR spectra and confirming that major band positions normally agree within approximately $\pm 2\text{--}4\text{ cm}^{-1}$ after baseline

correction. UV-visible spectra should be collected at the same concentration, path length and solvent composition; apparent changes caused only by concentration or aggregation are therefore minimized.

Molar conductivity is obtained from the measured solution conductivity after subtraction of the solvent blank and conversion to $\Lambda_{\text{m}} = \kappa \times 1000/C$, where κ is conductivity in S cm^{-1} and C is molar concentration. Magnetic susceptibility is corrected for diamagnetism before conversion to the effective magnetic moment; when molar susceptibility χ_{M} is available, $\mu_{\text{eff}} \approx 2.828(\chi_{\text{M}}T)^{1/2}$ at temperature T . These calculations allow conductivity and spin-state evidence to be compared directly with the ranges reported for related Schiff-base complexes [5,8,9,12].

Structural assignment follows a conservative decision sequence. First, elemental analysis and mass data must support the proposed metal-to-ligand ratio. Second, FTIR must show coordination-induced changes involving the designated donor atoms. Third, UV-visible and magnetic results must be mutually compatible with the proposed spin state and geometry. Fourth, thermal data must account quantitatively for any lattice or coordinated water included in

the formula. If these criteria conflict, the formula or geometry is treated as provisional and additional EPR, powder XRD, single-crystal XRD or elemental reanalysis is required. This prevents

overinterpretation of a single diagnostic band and makes the methodology suitable for comparative studies.

Results

Table 3. Physical Properties, Yield, Conductance, and Magnetic Data of HL and Metal Complexes

Sample	Color	Yield (%)	Λ_m ($S\ cm^2\ mol^{-1}$)	μ_{eff} (BM)	Preliminary interpretation
HL	Yellow-orange	78	—	Diamagnetic	Free Schiff base ligand
CoL ₂	Brown	70	8.7	4.55	High-spin Co(II); non-electrolyte
NiL ₂	Green-brown	74	7.9	2.95	Paramagnetic Ni(II); non-electrolyte
CuL ₂	Dark green	76	9.4	1.86	Mononuclear Cu(II); non-electrolyte

Table 4. FTIR and UV-Visible Spectral Data of the Schiff Base Ligand and Its Metal Complexes

Sample	$\nu(C=N)$ cm^{-1}	$\nu(O-H)$ cm^{-1}	M-N cm^{-1}	M-O cm^{-1}	Key UV-Vis features
HL	1627	~3420	—	—	276, 334 nm (ligand-centered)
CoL ₂	1608	Absent/very weak	~470	~545	~390 nm CT; 520–690 nm d-d envelope
NiL ₂	1611	Absent/very weak	~475	~550	~385 nm CT; 560–760 nm d-d bands
CuL ₂	1605	Absent/very weak	~485	~565	~405 nm CT; broad ~650–720 nm d-d band

In the illustrative dataset, the 16–22 cm^{-1} downward shift of $\nu(C=N)$ after complexation is consistent with donation of the azomethine nitrogen lone pair to the metal center, while loss of the phenolic O–H feature and new low-frequency bands support O,N chelation. Low conductivities are consistent with neutral, non-electrolytic complexes. The magnetic moments fall within common ranges for paramagnetic Co(II), Ni(II), and Cu(II) Schiff-base systems [5,8,9,11]. These observations are sufficient for a working coordination model, but not for an absolute geometry assignment without supporting diffraction or a complete ligand-field analysis.

For Co(II), multiple weak visible-region bands together with a magnetic moment above 4 BM would favor a high-spin environment; coordinated solvent or water may therefore need to be included in the formula if elemental/TGA data support it. Ni(II) geometry is more sensitive to ligand field and stoichiometry: a magnetic moment near 3 BM suggests a paramagnetic, commonly octahedral or tetrahedral environment, whereas a truly square-planar d^8 Ni(II) complex would normally be diamagnetic.

Cu(II) typically shows a broad visible d–d band because of Jahn–Teller distortion. This illustrates why spectral peak positions must be interpreted together with magnetic and compositional data rather than used alone [9,12–14].

Thermogravimetric behavior provides an additional cross-check on formulation. A low-temperature mass loss below about 150 °C is normally assigned to lattice or coordinated water only when the observed percentage agrees with the calculated stoichiometric loss. Subsequent organic decomposition should leave a metal-containing residue whose mass is compatible with the proposed composition. If powder diffraction is available, changes from the crystalline ligand pattern to a new complex pattern confirm formation of a distinct solid phase; however, peak indexing or single-crystal analysis is required before using diffraction to claim an exact molecular geometry. Replicate batches should give comparable yields and spectra, and any batch showing extra ligand peaks or anomalous conductivity should be repurified before structural interpretation.

Conclusion and Discussion

A practical methodology has been developed for synthesizing and characterizing transition-metal complexes derived from a representative N,O Schiff base. The procedure uses simple condensation chemistry, controlled 1:2 metal-to-ligand complexation and a tiered analytical strategy. FTIR provides the most direct first indication of imine/phenolate coordination, UV-visible spectra probe ligand-field changes, magnetic susceptibility constrains spin state and probable geometry, and conductivity plus elemental/TGA data test the proposed formulation. The literature up to 2015 consistently shows that this combined-evidence approach is more reliable than assigning structure from a single spectrum [3–14]. The method can be extended to substituted salicylaldehydes, heterocyclic amines and additional first-row metals by adjusting stoichiometry, solvent and reflux time. The principal limitations are possible solvation/hydration, polymorphism and geometry ambiguity in powder samples. Therefore, single-crystal X-ray diffraction, powder refinement or complementary EPR/EXAFS should be used when an unequivocal coordination geometry is essential. Overall, the workflow is suitable for methodology-focused studies because it is inexpensive, scalable and analytically transparent while retaining sufficient rigor for comparative coordination chemistry.

References

- Cozzi, P. G. Metal–Salen Schiff base complexes in catalysis: practical aspects. *Chemical Society Reviews*. 2004;33:410–421. DOI: 10.1039/B307853C.
- Vigato, P. A.; Tamburini, S. The challenge of cyclic and acyclic Schiff bases and related derivatives. *Coordination Chemistry Reviews*. 2004;248:1717–2128. DOI: 10.1016/j.cct.2003.09.003.
- Raman, N.; Johnson Raja, S.; Sakthivel, A. Transition metal complexes with Schiff-base ligands: 4-aminoantipyrine based derivatives—a review. *Journal of Coordination Chemistry*. 2009;62:691–709. DOI: 10.1080/00958970802326179.
- Refat, M. S.; El-Deen, I. M.; Anwer, Z. M.; El-Ghol, S. Spectroscopic studies and biological evaluation of some transition metal complexes of Schiff-base ligands derived from 5-arylaazo-salicylaldehyde and thiosemicarbazide. *Journal of Coordination Chemistry*. 2009;62:1709–1718. DOI: 10.1080/00958970802684205.
- Kumar, G.; Kumar, D.; Devi, S.; Johari, R.; Singh, C. P. Synthesis, spectral characterization and antimicrobial evaluation of Schiff base Cu(II), Ni(II) and Co(II) complexes. *European Journal of Medicinal Chemistry*. 2010;45:3056–3062. DOI: 10.1016/j.ejmech.2010.03.036.
- Neelakantan, M. A.; Esakkiammal, M.; Mariappan, S. S.; Dharmaraja, J.; Jeyakumar, T. Synthesis, characterization and biocidal activities of some Schiff base metal complexes. *Indian Journal of Pharmaceutical Sciences*. 2010;72:216–222. DOI: 10.4103/0250-474X.65015.
- Dhanaraj, C. J.; Johnson, J.; Joseph, J.; Joseyphus, R. S. Quinoxaline-based Schiff base transition metal complexes: review. *Journal of Coordination Chemistry*. 2013;66:1416–1450. DOI: 10.1080/00958972.2013.782008.
- Kumaran, J. S.; Priya, S.; Jayachandramani, N.; Mahalakshmi, S. Synthesis, spectroscopic characterization and biological activities of transition metal complexes derived from a tridentate Schiff base. *Journal of Chemistry*. 2013;2013:260358. DOI: 10.1155/2013/260358.
- Reiss, A.; Chifiriuc, M. C.; Amzoiu, E.; Spînu, C. I. Transition Metal(II) complexes with cefotaxime-derived Schiff base: synthesis, characterization, and antimicrobial studies. *Bioinorganic Chemistry and Applications*. 2014;2014:926287. DOI: 10.1155/2014/926287.
- Yernale, N. G.; Hire Mathada, M. B. Synthesis, characterization, antimicrobial, DNA cleavage, and in vitro cytotoxic studies of some metal complexes of Schiff base ligand derived from thiazole and quinoline moiety. *Bioinorganic Chemistry and Applications*. 2014;2014:314963. DOI: 10.1155/2014/314963.
- Sumrra, S. H.; Ibrahim, M.; Ambreen, S.; Imran, M.; Danish, M.; Rehmani, F. S. Synthesis, spectral characterization, and biological evaluation of transition metal complexes of bidentate N,O donor Schiff bases. *Bioinorganic Chemistry and Applications*. 2014;2014:812924. DOI: 10.1155/2014/812924.
- Alaghaz, A.-N. M. A. Synthesis, spectroscopic characterization, molecular modeling and potentiometric studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,1-diaminobutane-Schiff base. *Journal of Molecular Structure*.

2014;1072:103–113.

DOI:

10.1016/j.molstruc.2014.04.079.

Kalita, M.; Gogoi, P.; Barman, P.; Sarma, B. Nickel(II), copper(II), and cobalt(II) complexes derived from a new unsymmetrical ONS donor Schiff base ligand: synthesis, characterization, crystal structure, and catalytic activities. *Journal of Coordination Chemistry*. 2014;67:2445–2454. DOI: 10.1080/00958972.2014.946917.

Ali, O. A. M.; El-Medani, S. M.; Abu Serea, M. R.; Sayed, A. S. S. Unsymmetrical Schiff base (ON) ligand on complexation with some transition metal ions: synthesis, spectral characterization, antibacterial, fluorescence and thermal studies. *Spectrochimica Acta Part A*. 2015;136:651–660. DOI: 10.1016/j.saa.2014.09.079.