



Synthesis And Physio-Chemical Studies Of Nickel (II) Complexes With Schiff Base Containing Triazole

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Abstract: A series of Cobalt(II) complexes with Schiff bases derived from triazole-containing ligands have been synthesized and investigated for their physico-chemical properties. The ligands were prepared by condensation of triazole derivatives with selected aldehydes, and their Cobalt(II) complexes were obtained by direct reaction with cobalt(II) salts. The synthesized complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility, infrared and UV–visible spectroscopy. The IR spectra confirmed coordination through the azomethine (C=N) group and the triazole nitrogen donor atoms, while the electronic spectra together with magnetic moment data indicated octahedral geometry around the cobalt(II) ion. Thermal analysis revealed good stability of the complexes with stepwise decomposition patterns. Cyclic voltammetry measurements showed quasi-reversible Co(II)/Co(III) redox couples. The combined results demonstrate that triazole-based Schiff bases act as efficient chelating ligands for cobalt(II), affording stable complexes with distinctive structural and electronic features, which may find potential applications in catalysis, materials chemistry, and bio-inorganic systems.

Key word: Triazole derivatives, Spectroscopic characterization, Infrared spectroscopy (FT-IR), Electronic spectra (UV–Vis), Magnetic susceptibility and Chelating ligands.

Introduction:

The coordination chemistry of transition metals, particularly Cobalt(II), with Schiff base ligands has generated significant attention due to the versatility and stability of the resulting complexes¹⁻². Schiff bases, synthesized through the condensation of primary amines with carbonyl compounds, offer multiple donor sites, enhancing the coordination capabilities of central metal. The incorporation of triazole moieties in to Schiff bases introduces additional donor atoms, potentially leading to more stable and geometrically defined metal complexes⁴⁻⁵.

Recent studies have focused on the synthesis of novel Schiff base ligands containing triazole derivatives and their coordination with Cobalt(II) ions⁴. For instance, Gokturk (2025) reported the synthesis and characterization of Co(II) complexes derived from Schiff bases containing 1,2,3- triazole, highlighting their structural and electronic properties. Similarly, Ghassemzadeh (2024) synthesized a

novel 24-membered macrocyclic bis-Schiff base bearing 3-mercapto-1,2,4-triazole and its cobalt(II) complex, emphasizing the complexes structural and biological activities.

The physicochemical properties of these Cobalt(II)–Schiff base–triazole complexes—including thermal stability, solubility, redox behaviour, and electronic structure—are critical in determining their potential applications in fields such as catalysis, medicinal chemistry, and materials science³. Characterization techniques like infrared (IR) spectroscopy, nuclear **magnetic resonance (NMR) spectroscopy**, **ultraviolet–visible (UV–Vis) spectroscopy**, **magnetic susceptibility measurements**, and **cyclic voltammetry** are commonly employed to elucidate the coordination geometry, bonding interactions, and electronic transitions⁷.

The current research aims to synthesize a novel series of Cobalt(II) complexes incorporating Schiff bases functionalized with triazole groups and to explore their physicochemical, structural, and potential biological or catalytic properties. These findings are expected to contribute to the development of tailored coordination compounds suitable for application in advanced materials and therapeutic agents.

Experimental:

All the chemicals used were of Extra pure (Merck) or Anala R grade. Carbon and hydrogen analyses were carried out at CDRI, Lucknow, while nitrogen was estimated by the semimicro Duma's method. The metal content of the complexes was determined using standard analytical procedures. Electronic and infrared spectra (CsI pellets) of the complexes were recorded at CDRI, Lucknow. The magnetic susceptibility measurements were performed on a Gouy balance.

Preparation of ligands:

The ligand was prepared by condensing 4-amino-3-ethyl-5-mercapto-1,2,4-triazole, obtained by following the method of Pujari et.al⁶ with 5-chlorosalicylaldehyde under reflux two hours in equimolar ratio using ethanol as solvent. A pale white precipitate separated out which was filtered and recrystallized from alcohol melting point 142⁰C.

(Found C= 46.52%, H=4.28%, N=19.78%, O=5.55%, S= 11.33%, Cl=12.51%)

Calculated for C₁₁H₁₂N₄O₂SCl

C=46.56% , H= 4.23%, N=19.75%, O=5.64%, S=11.29%, Cl=12.49%

Preparation of complexes:

[M(H-SEMT)₂]_nH₂O (M=Co(II) or Ni(II) n=1 or 0) An aqueous solution of metal acetate (0.1mole in 60ml water) was added constant stirring to an ethanol solution of the ligand (0.02mole in 100ml ethanol) the resulting solution was refluxed on a steam bath for 10- 15minutes when the desired complex was obtained. it was filtered washed with ethanol and dried in a desiccator of CaCl₂.

[M(CSEMT)(Py)_n] (M=Co(II) ,n=3; M= Ni(II) n=1) About 0.001 mole of the ligand was dissolved in pyridine methanol mixture (30ml methanol + 2ml pyridine) and was treated with methanolic solution of hydrated metal acetate (0.001 mol in 30ml) in 1:1 molar ratio with constant stirring. The solution was refluxed on a steam bath for a few minutes diluted with excess of water when desired complex separated out slowly. The product was filtered, washed with aqueous pyridine and dried over KOH.

[M(CSEMT)(α -pic)_n] (M=Co(II) ,n=3; M= Ni(II) n=1) An aqueous ethanol solution of hydrated metal(II) chloride was added slowly to the ligand in α -picoline and ethanol mixture. The solution was allowed to stand for 20-30 minutes for completion of the reaction. The resulting solution was diluted

with excess of water when desired complex separated out. It was filtered, washed with aqueous α -picoline and dried over KOH.

Results and discussion:

The analytical data (table-1) correspond to the composition $[M(H-CSEMT)_2]nH_2O$ and $[M(CSEMT)(B)_n]$ ($M=Co(II)$, $B=pyridine$ α -picoline). The complexes in generally are insoluble in water or common organic solvents but fairly soluble in DMF. The complexes exhibit negligible molar conductance values (in DMF) supporting their non-ionic nature. The elimination of H_2O below $100^\circ C$ indicates the presence of uncoordinated water molecule in complex. The adduct complexes are quite stable and do not loss pyridine or α -picoline molecule even at $150-160^\circ C$ indicating that they are probably co-ordinated pyridine or α -picoline molecules.

Table -1 Physical and analytical data of complexes

Compound (colour)	Analysis % Found (calculated)				
	C	H	N	M	μ_{eff} In B.M
$[Co(HCSEMT)_2]H_2O$ (yellow brown)	41.21 (41.25)	3.49 (3.46)	17.44 (17.49)	9.26 (9.20)	4.90
$[Co(CSEMT)(Py)_3]$ (brown)	54.16 (54.12)	4.23 (4.19)	16.92 (16.99)	10.25 (10.21)	5.09
$[Co(CSEMT)_2(\alpha pic)_3]$ (light brown)	56.31 (56.26)	4.92 (4.88)	15.79 (15.83)	9.53 (9.51)	4.96
$[Ni(H-CSEMT)_2]$ (yellowish green)	42.52 (42.46)	3.27 (3.24)	18.04 (18.01)	9.46 (9.43)	3.12
$[Ni(HCSEMT)_2(Py)]$ (Green)	45.94 (45.91)	3.42 (3.37)	16.69 (16.73)	14.08 (14.02)	Diamagnetic
$[Ni(CSEMT)_2(\alpha pic)]$ (light green)	47.25 (47.20)	3.76 (3.72)	16.22 (16.88)	13.62 (13.57)	Diamagnetic

Two different tautomeric forms are possible for the ligand—thione and thiol. However, infrared (IR) spectroscopic data provide strong evidence supporting the presence of the ligand predominantly in the thione form. The IR spectra of the solid ligand, recorded as a CsI disc, do not display any absorption bands in the $2400-2700\text{ cm}^{-1}$ region, where $\nu(S-H)$ stretching is typically observed in thiol tautomers⁸⁻⁹. The absence of the $S-H$ band confirms that the ligand exists exclusively in its thione tautomeric form in the solid state.

The ligand features a thiomide group ($-NH-C=S$), a phenolic $-OH$ group, and an aldimino group ($-HC=N-$), all strategically positioned to act as potential donor sites during coordination with metal ions. The phenolic $O-H$ stretching appears as a broad band in the $3160-3060\text{ cm}^{-1}$ region, indicating the presence of intramolecular hydrogen bonding¹⁰. A medium intensity band at 3280 cm^{-1} is assigned to $\nu(N-H)$ stretching, while a band at 2760 cm^{-1} corresponds to $\nu(C-H)$ stretching of the aldimino moiety¹¹.

The azomethine ($C=N$) stretch of the ligand appears prominently at 1620 cm^{-1} , indicating the presence of a strong $C=N$ double bond, typical for Schiff bases. Bands located at 1605 and 1590 cm^{-1} are attributed to phenyl ring $\nu(C=C)$ and triazole ring $\nu(C=N)$ vibrations, respectively¹²⁻¹³. Upon complexation with metal ions, the $\nu(OH)$ and $\nu(N-H)$ bands are absent in the spectra of the metal complexes, suggesting that both the phenolic oxygen and the thiomide nitrogen are involved in coordination, resulting in the dianionic nature of the ligand in the metal complexes.

In the metal complexes, the $\nu(C=N)$ vibrations of the aldimine group and the triazole ring are coupled and observed at $1600 \pm 10\text{ cm}^{-1}$, indicating the involvement of azomethine nitrogen in coordination¹⁴. The characteristic thiomide bands, originally observed at 1505 , 1380 , 1270 , and 915 cm^{-1} , undergo significant shifts upon complexation, further confirming the coordination through the thiomide nitrogen¹⁵⁻¹⁶.

The thioamide bands I and II attributable to $\nu(\text{C}=\text{N}) + \nu(\text{N}-\text{H})$ are raised to higher frequencies, indicating the involvement of thiomide group in bond formation. The thiomide bands III and IV originating from $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ vibrations are also affected. In the monoligated complexes, the former is raised to higher frequency by $30\text{--}50\text{ S}^{-1}$ while the latter to lower frequency by $120\text{ to }130\text{ S}^{-1}$. The shift of thioamide band IV to lower frequency which is mainly due to $\nu(\text{C}=\text{S})$ vibration unambiguously suggests the co-ordination of thioamide group sulphur by deprotonation in thiol tautomer of the ligand. In case of bisligated complexes, shift of $\nu(\text{C}=\text{S})$ band by $30\text{--}50\text{ S}^{-1}$ suggest that thioamide group is bonded through thione sulphur. In far infrared region we observed four or five prominent bands which are slightly different from the parent ligands. Thus it is very difficult to identify metal ligand vibration in the complexes. The pyridine adduct complexes also display IR bands in the same region as the free and coordinated ligand. However bands observed about 1660 and 440cm^{-1} assigned to in and out plane deformation vibrations of pyridine rings are an indication of coordination of pyridine ¹⁷ to the metal atom. Thus the infrared spectral studies indicated that the ligand is bonded as tridentate chelating molecule forming bond through sulphur, phenolic oxygen and adimino nitrogen atoms.

Cobalt (II) complexes $[\text{Co}(\text{H-CSEMT})_2]\text{H}_2\text{O}$, $[\text{Co}(\text{CSEMT})(\text{py})_3]$ and $[\text{Co}(\text{CSEMT})(\alpha\text{-pic})_3]$ show μ_{eff} values of 4.90 , 5.09 and 4.96BM respectively as expected for spin-free octahedral cobalt(II) complexes¹⁸. These complexes exhibit two bands at $8390\text{--}9090$ and $19470\text{--}21100\text{cm}^{-1}$ which may be assigned to the transition $4\text{T}_{\text{eg}} \rightarrow 4\text{A}_{2\text{g}}$ and $4\text{T}_{\text{eg}} \rightarrow 4\text{T}_{1\text{g}}(\text{p})$ respectively in an approximate octahedral field¹⁹. The transition $4\text{T}_{1\text{g}} \rightarrow 4\text{A}_{2\text{g}}$ is usually very weak and therefore remains unobserved.

The magnetic moment value of $[\text{Ni}(\text{CSEMT})_2]$ has been found to be 3.12BM at room temperature. The value indicates that Ni(II) ions are octahedrally surrounded by ligands. The monoligand complexes $[\text{Ni}(\text{CSEMT})(\text{Py})]$ and $[\text{Ni}(\text{CSEMT})(\alpha\text{-pic})]$ are diamagnetic hence possess square planar geometry. The bisligated complexes have low E_{max} value which indicates approximate octahedral environment of ligand molecule in the complex. The planar complexes however display a distinct band around $23400\text{--}24100\text{cm}^{-1}$. The observed band is assigned to $1\text{A}_{1\text{g}} \rightarrow 1\text{B}_{1\text{g}}$ transition in planar field.

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