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SYNTHESIS AND SPECTRAL STUDIES OF HETEROBIMETALLIC SCHIFF BASE COMPLEXES

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ABSTRACT

This paper describes the synthesis of six novel Schiff base heterobimetallic complexes of nickel(II) and silver(I) and their spectral characteristics. The Schiff base was synthesized *via* condensation of *o*-Hydroxyacetophenone and 1,2-Diaminopropane in molar ratio 2:1. The characterization of the synthesized complexes was done with the aid of molar conductance, elemental analysis, FTIR, electronic spectral analysis and magnetic moment studies. The complexes obtained are non-electrolytes, colored and stable. Spectral analyses of the hetero bimetallic complexes suggest square planar geometry with coordination number four for all the complexes.

Keywords: Electronic Spectra, FTIR Spectra, Nickel(II), Schiff Base, Hetero Bimetallic Complex

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INTRODUCTION

Schiff bases have azomethine and azo groups and possess a strong ability to form complexes with transition elements.[1-3] Schiff base serves as a framework for various natural and synthetic complexes. Schiff frameworks with varying coordination geometries can be constructed with the involvement of different elements *viz.* alkali and alkaline earth metals, p-block elements, transition elements, lanthanides and actinides.[4,5] From the past several years, stress on the development of Schiff base complexes has been laid due to its various applications as antifungal, antibacterial, antitubecular, antimalarial, anticancer and antitumor drugs.[6-11] Sinn *et al* had prepared several bidentate metal complexes and tetradentate homo binuclear complexes of Schiff base.[12,13] These complexes act as a simple bidentate chelating ligand that coordinates through their cis-oxygen atoms to form binuclear metal complexes. Lashanizadegar *et al* had synthesized Ni(II) complexes of unsymmetrical Schiff base ligand condensed from Salicylaldehyde and *N*-(2-Hydroxyacetophenone)-1-amino-2-phenylenediamine.[14] Studies on Cu(II)-Hg(II) heterobimetallic Schiff base complexes *viz.* $[(CuL\text{-}CH_3)_2.HgCl_2]$, $[CuL\text{-}CH_2\text{-}HgCl_2]$ and $[(CuL\text{-}CH_3).HgCl_2]$ have been reported.[15]Literature survey reveals no reported work on heterobimetallic complexes of Schiff base with a silver(I). We, herein, in this communication, describe the synthesis and spectral characterization of nickel(II) heterobimetallic Schiff base complexes of *o*-Hydroxyacetophenone and silver(I) chelates of 1-Nitroso-2-naphthol, 2,4,6-Trinitrophenol, 8-Hydroxyquinoline, *o*-Nitrophenol, 2,4-Dinitrophenol, or *o*-Aminobenzoic acid.

EXPERIMENTAL

Material and Methods

For the experiments, chemicals of A.R. grade were used. For recording ultraviolet-visible spectra, Systronics Double Beam Spectrophotometer 2202 was used. Infrared spectral studies were recorded in the KBr phase on Shimadzu 8201 FTIR spectrophotometer. Systronics conductivity meter (model-306) was employed for measuring the molar conductance of the samples. Melting point measurements were performed on the Electrical T-1150 m.p. apparatus. The magnetic behavior of the complexes was analyzed by the Faraday method. Elemental analysis of carbon, hydrogen and nitrogen were done with CHN B6450 elemental analyzer.

Synthesis of the Schiff Base

o-Hydroxyacetophenone and 1,2-Diaminopropane were very slowly mixed in a molar ratio of 2:1 in boiling ethanol with constant stirring. The solution obtained was further refluxed with the help of a magnetic stirrer for 5 minutes. When the solution attained room temperature, it was cooled in an ice bath. Yellow-colored solid of *N,N′*-1,2-Propylenebis(2-hydroxyacetophenonimine) was obtained. The solid was washed twice with a little volume of ice-cold ethanol and then dried. It was further recrystallized from ethanol. The melting point of the prepared Schiff base is 91°C.

Synthesis of Nickel(II) Schiff Base Complex

A solution of nickel acetate in ethanol was added slowly with continuous stirring to the prepared solution of Schiff base in 1:1 molar ratio under hot conditions. The mixture was further refluxed for 85 min at 80 °C. Orange colored solid complex (yield=76%) was obtained. The solid complex was separated by filtration, washed twice with absolute ethanol and dried.

Synthesis of Heterobimetallic Complexes

An equimolar mixture of *N,N′*-1,2-Propylenebis(2-hydroxyacetophenoniminato)nickel(II) and silver(I) chelate of 1-Nitroso-2-naphthol, 2,4,6-Trinitrophenol, 8-Hydroxyquinoline, *o*-Nitrophenol, 2,4-Dinitrophenol or *o*-Aminobenzoic acid were added in hot ethanolic medium with constant stirring and then refluxed at 80 °C for 15 minutes on a magnetic stirrer. On cooling, the colored precipitate was obtained. It was filtered, washed with absolute ethanol and then dried.

RESULTS AND DISCUSSION

The physical properties of the heterobimetallic Schiff base complexes are shown in Table-1. The complexes are colored and crystalline in nature. They are stable under ordinary conditions. The complexes are highly soluble in acetone, methanol, benzene, chloroform, DMSO and DMF but partially soluble in water. The heterobimetallic complexes decompose at a higher temperature between 195-258 °C. This reflects the higher stability of the complexes. The elemental analysis data for heterobimetallic complexes shown in Table-2 are in fair accord with the calculated values.

Molar Conductance

Conductivity studies of the heterobimetallic complexes were carried out in ethanol at a concentration of 10^{-3} M at 30(±5) °C. The conductivity values of complexes were found to be very low in the range 0.5-1.6 $\Omega^{-1}cm^2mol^{-1}$ (Table-1). These values correspond that the heterobimetallic complexes are of non-electrolytic behaviour.[16]

Magnetic Moment

Low magnetic moment values (approaching zero) are observed for *N,N′*-1,2-Propylenebis(2-hydroxy acetophenoniminato)nickel(II) and its heterobimetallic complexes *viz.* $C_{25}H_{24}N_3O_5NiAg$, $C_{25}H_{23}N_4O_7NiAg$, $C_{25}H_{22}N_5O_9NiAg$, $C_{28}H_{26}N_3O_3NiAg$, $C_{26}H_{26}N_3O_4NiAg$ and $C_{29}H_{26}N_3O_4NiAg$ [Table-4]. This reflects square planar geometry around nickel(II) in the complexes.[17]

Table-1: Physical Properties of the Hetero BimetallicComplexes

Complex	Colour	Decomposition Temp. (°C)	Conductivity (ohm^{-1} cm^2 mol^{-1})
$C_{25}H_{24}N_3O_5NiAg$	Light brown	258	1.6
$C_{25}H_{23}N_4O_7NiAg$	Brown	234	0.5
$C_{25}H_{22}N_5O_9NiAg$	Deep orange	250	0.8
$C_{28}H_{26}N_3O_3NiAg$	Brown	248	1.0
$C_{26}H_{26}N_3O_4NiAg$	Grey	195	1.1
$C_{29}H_{26}N_3O_4NiAg$	Brownish green	252	1.4

Infrared Spectra

The infrared spectra for the metal complex ligand $C_{19}H_{20}N_2O_2Ni$ were recorded. A spectral band at 1529 cm^{-1} originated which is attributed to phenolic C–O str. band.[18] When the ligand $C_{19}H_{20}N_2O_2Ni$ formed heterobimetallic complexes with the silver(I) metal chelates of 1-Nitroso-2-naphthol, 2,4,6-Trinitro

phenol, 8-Hydroxyquinoline, *o*-Nitrophenol, 2,4-Dinitrophenol or *o*-Aminobenzoic acid, shifting and splitting of the phenolic C–O str. band was observed and therefore in $C_{25}H_{22}N_5O_9NiAg$, spectral bands emerge at 1531 and 1560 cm^{-1} whereas, in $C_{28}H_{26}N_3O_3NiAg$, bands arise at 1518 and 1571 cm^{-1}. Similar shifting and splitting effects are also observed in $C_{26}H_{26}N_3O_4NiAg$ and $C_{29}H_{26}N_3O_4NiAg$ [Table-3]. The consequent shifting and splitting of phenolic C–O str. bands in the heterobimetallic complexes justifies the coordination through phenolic oxygen.[19]

Table-2: Elemental Analyses of the Hetero Bimetallic Complexes

Complex	Analysis (%), Found(Calculated)					% Yield
	C	H	N	Ni	Ag	
$C_{25}H_{24}N_3O_5NiAg$	55.67 (56.91)	3.78 (4.12)	6.81 (6.87)	9.38 (9.59)	16.51 (17.62)	78
$C_{25}H_{23}N_4O_7NiAg$	45.21 (45.70)	3.28 (3.37)	8.51 (8.53)	7.31 (8.93)	15.11 (16.42)	82
$C_{25}H_{22}N_5O_9NiAg$	41.86 (42.77)	2.98 (3.16)	9.75 (9.98)	7.25 (8.36)	13.92 (15.37)	76
$C_{28}H_{26}N_3O_3NiAg$	53.91 (54.41)	3.99 (4.08)	6.77 (6.80)	8.81 (9.50)	16.69 (17.45)	72
$C_{26}H_{26}N_3O_4NiAg$	51.08 (51.19)	4.11 (4.13)	6.88 (6.89)	8.71 (9.62)	16.42 (17.68)	88
$C_{29}H_{26}N_3O_4NiAg$	52.86 (53.91)	3.68 (3.90)	6.11 (6.50)	8.34 (9.08)	15.67 (16.70)	90

Far-infrared spectra for the metal complex ligand $C_{19}H_{20}N_2O_2Ni$ arise at 475, 527 and 569 cm^{-1} due to M─N(str) and M─O(str) modes respectively.[20-24] There is a shift in the position of these bands towards higher energy side[25] after the formation of heterobimetallic complexes and are observed in the range 447-611 cm^{-1} (Table-3).

Table-3: Infrared Spectral Bands around 1530 cm^{-1} and Far-Infrared bands of Metal Complex and Hetero Bimetallic Complexes

Complexes	υ_{C-O} str (in cm^{-1})	Far-Infrared Spectra $\upsilon_{M-O/M-N}$ str (in cm^{-1})
$C_{19}H_{20}N_2O_2Ni$	1529	475, 527, 569
$C_{25}H_{22}N_5O_9NiAg$	1531, 1560	501, 531, 575, 611
$C_{28}H_{26}N_3O_3NiAg$	1518, 1571	484, 503, 545, 584, 609
$C_{26}H_{26}N_3O_4NiAg$	1532, 1597	484, 527, 593
$C_{29}H_{26}N_3O_4NiAg$	1530, 1551	447, 496, 549, 573

Electronic Spectra

The electronic spectra were recorded in the wavelength region 200-800 nm at room temperature. Electronic bands were observed in the region 242-392 nm for the metal complex ligand $C_{19}H_{20}N_2O_2Ni$. The strong and high energy bands in this region correspond to $\pi \rightarrow \pi^*$ transitions in the aromatic ring and >C=N chromophore.[26-28] The intense absorption band at 392 nm originates due to charge transfer transitions in this nickel(II) complex which suggests square planar geometry with coordination number 4.[29,30] Similar electronic bands appear in the wavelength range 333-396 nm for the heterobimetallic complexes (Table-4). This indicates that the square planar geometry of Ni(II) is maintained even after the formation of heterobimetallic complexes (Fig.-1).

Table-4: Magnetic Behavior and Electronic Spectral Data of the Metal Complex and Hetero Bimetallic Complexes

Complexes	Magnetic Behavior	Electronic Transitions (in nm)
$C_{19}H_{20}N_2O_2Ni$	Diamagnetic	242, 321, 392
$C_{25}H_{24}N_3O_5NiAg$	Diamagnetic	336, 396
$C_{25}H_{23}N_4O_7NiAg$	Diamagnetic	351, 394
$C_{25}H_{22}N_5O_9NiAg$	Diamagnetic	340, 391

$C_{28}H_{26}N_3O_3NiAg$	Diamagnetic	348, 394
$C_{26}H_{26}N_3O_4NiAg$	Diamagnetic	333, 394
$C_{29}H_{26}N_3O_4NiAg$	Diamagnetic	338, 392

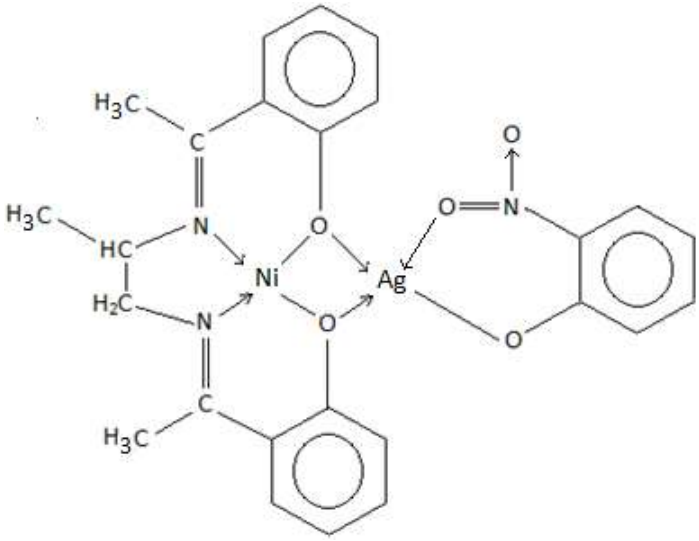

Fig.-1:Schiff Base Heterobimetallic Complex, $C_{25}H_{24}N_3O_5NiAg$

CONCLUSION

The research paper describes the synthesis of a Schiff base and its six novel heterobimetallic complexes. The synthesized complexes are colored, crystalline and non-electrolytic in nature. The analytical techniques and spectral characterization of the heterobimetallic complexes suggest the formation of stable complexes and propose square planar geometry around nickel(II).

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