



Studies on Heterobinuclear Complexes Derived from Rubidium and Caesium Salts of Acetyl Salicylic Acid (ASPIRIN) with N, N'-1,2-ethylenebis(5-nitrosalicylaldiminato) Nickel(II)

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ABSTRACT

Hetero binuclear complexes, [NiE5NSRbAp] and [NiE5NSCsAp], have been synthesized from Rubidium(I) and Caesium(I) salt of Acetyl salicylic acid (ASPIRIN) and N,N'-1,2-ethylenebis(5-nitrosalicylaldiminato) nickel(II) as ligand, respectively. This ligand [NiE5NS] has been prepared from Nickel(II) acetate and salen type dibasic Schiff base derived from 5-nitrosalicylaldehyde and Ethylenediamine. These novel hetero binuclear complexes obtained in pure solid state and their structures have been characterized with the help of Elemental analysis, Solubility, Magnetic property, Molar conductance measurement, FT-IR and Electronic absorption spectra. The results suggested molecular formula [NiLRbL⁺].3H₂O and [NiL(H₂O)₂CsL⁺] with Square planar and Distorted octahedral geometry about Ni²⁺, respectively for the two hetero binuclear complexes [NiE5NSRbAp] and [NiE5NSCsAp] where L = Deprotonated Schiff base ligand N,N'-1,2-ethylenebis(5-nitrosalicylaldiminato) nickel(II), L' = Acetyl salicylate.

Keywords: Hetero, Binuclear, Complex, N,N'-1,2-ethylenebis(5-nitrosalicylaldiminato)nickel(II), Aspirin, Rubidium, Caesium, Square planar, Distorted octahedral.

INTRODUCTION

Deprotonated salen type Schiff bases act as tetradentate N₂O₂ type ligand and form complexes with transition metals. It is well investigated that donor oxygen atoms of these N₂O₂ type ligands have ability to co-ordinate with two metal ions.¹⁻³ This ability of the phenolic donor oxygen atoms of such ligands, has been used to synthesize hetero binuclear complexes holding two metal ions in close proximity-one of transition metal and other alkali metal.^{4,5} Schiff base transition metal complexes have

a great medicinal values and industrial applications⁶, and metal ions play an important role in biological systems⁷. Greater permeability of metal complexes than metal ions further augments their importance. Numerous hetero binuclear complexes have been reported in past several years but a very little work on hetero binuclear complex with alkali metal as one of the metal centres has been published. Acetyl salicylic acid (ASPIRIN) is a common drug and Rubidium or Caesium ions are handled by living organisms similar to Potassium. In the present paper synthesis and characterisation of hetero binuclear



complexes derived from Rubidium(I) and Caesium(I) salt of Acetyl salicylic acid (aspirin) and N,N'-1,2-ethylenebis(5-nitrosalicylaldiminato) nickel(II) as ligand, have been discussed. These studies may be useful for carrying out further research to design and develop drug from these synthesized complexes or their modified forms for therapeutic use in order to minimize side effects of Aspirin.

MATERIALS AND METHODS

Chemicals used in the synthesis of metal Schiff base and hetero binuclear complexes were of A. R. Grade. Melting point of the synthesized complexes was determined using ESICO International Auto Melting Point Apparatus 1934. Elemental Analyser EUROVECTOR EA3000 was used to estimate Carbon, Hydrogen, Nitrogen and Oxygen. Rubidium, Caesium and Nickel was estimated by ICP-MS of Agilent Technologies model no.7800. Magnetic moment of the synthesized complexes was measured by the Vibrating Sample Magnetometer (VSM). FT-IR Spectrum of synthesized complexes was recorded on Thermo Nicolet Avatar 370 in the range 4000-400 cm^{-1} by KBr beam splitter. Electronic absorption spectrum of 10^{-4}M solution of the complexes was recorded between 200-900nm by Shimadzu UV-Visible Spectrometer Model UV-2450 using UV Probe 2.32 software.

Synthesis of N,N'-1,2-ethylenebis(5-nitrosalicylal-diminato) nickel(II)

5-nitrosalicylaldehyde and 1,2-ethylenediamine in 2:1 molar ratio were allowed to react in ethanolic medium, and by crystallisation process solid Schiff base N,N'-1,2-bis(5-nitrosalicylidine) ethylenediamine crystals were obtained. Ethanolic solutions of Schiff base and Nickel acetate tetrahydrate were mixed in 1:1 molar ratio, refluxed below 40°C for 20 min, filtered, washed with little

ethanol, dried and obtained the bright maroon coloured crystalline solid of Nickel(II) Schiff base⁸.

Synthesis of Hetero binuclear complexes from Rubidium and Caesium salt of Acetyl salicylic acid and Nickel(II) Schiff base

Ethanolic solutions of Rubidium or Caesium acetyl salicylate and Nickel(II) Schiff base in 1:1 stoichiometric proportion were mixed together, and the resulting solution was refluxed for 25 min at about 40°C and cooled to ice temperature when coloured hetero binuclear complexes [NiE5NSRbAp] and [NiE5NSCsAp] were separated out. The complexes were filtered, washed with little ethanol and dried.

RESULTS AND DISCUSSION

Physical properties

The synthesized hetero binuclear complexes are crystalline solid, coloured and non-hygroscopic. The complex [NiE5NSRbAp] is soluble in Petroleum ether, DMF and DMSO whereas [NiE5NSCsAp] is soluble in Acetone, DMF and DMSO. However, both the complexes are insoluble in water. Both the complexes do not decompose up to 250°C Table 1.

Elemental Analysis

The estimated elemental data of the complexes are in good agreement with calculated value Table 1.

Molar Conductance Measurement

Molar conductance of 10^{-3}M solution of the synthesized complexes in DMF was measured at $20(\pm 0.5)^\circ\text{C}$, and is found between 7.6-7.90 $\text{S.cm}^2.\text{mole}^{-1}$ Table 1. The low molar conductance value (up to 10.1 $\text{S.cm}^2.\text{mole}^{-1}$) of the synthesized complexes suggests their non-electrolytic nature⁹⁻¹³.

Table 1: Physical and Analytical Data of the Synthesized Complexes

Synthesized Complex	Colour	Yield	m.p. ($^\circ\text{C}$)	Molar Conductance ($\text{S.cm}^2.\text{mol}^{-1}$)	Elemental Analysis Data In % Est. (cal)						
					C	H	N	O	Ni	Rb	Cs
[NiE5NSRbAp]	Harvest Gold	76	238	7.9	40.8 (40.89)	3.49 (3.41)	7.73 (7.63)	28.33 (28.35)	7.89 (8.00)	11.66 (11.65)	--
[NiE5NSCsAp]	Chinese Gold	75.26	247	7.6	39.10 (39.31)	3.09 (3.01)	7.35 (7.34)	25.03 (25.16)	7.65 (7.69)	--	17.66 (17.42)

Magnetic Moment Measurement

Effective magnetic moment (μ_{eff}) of the synthesized complexes [NiE5NSRbAp] and

[NiE5NSCsAp] at 301K are 0 B.M. and 2.97 B.M., respectively Table 2. The result suggests hetero binuclear complex [NiE5NSRbAp] to be Diamagnetic

whereas hetero binuclear complex [NiE5NSCsAp] to be Paramagnetic.

Table 2: Magnetic moment and UV-Vis spectral data of the complexes

Synthesized complex	μ_{eff} in B.M. at 301 K	Electronic Transitions
[NiE5NSRbAp]	0	Broad band ranging 225–511nm with a peak at $\lambda_{\text{max}}=431\text{nm}$ and a shoulder at 355nm
[NiE5NSCsAp]	2.97	Broad band ranging 222–502nm with a peak at $\lambda_{\text{max}}=454\text{nm}$ and a shoulder at 353nm

FT-IR Spectra

Absorption band position of certain chemical bonds of interest in FT-IR Spectrum of Aspirin, [NiE5NS], [NiE5NSRbAp] and [NiE5NSCsAp] have been summarized in Table 3.

A very strong band at 1649 cm^{-1} in [NiE5NS] spectrum is for $\nu_{\text{C=N}}$ stretching¹⁴. The shift of the absorption band of $\nu_{\text{C=N}}$ stretching towards lower wave number indicates coordination of the

imine nitrogen to the Ni^{2+} ion during [NiE5NS] complex formation¹⁵⁻¹⁷. Presence of new band at 663 cm^{-1} is for $\nu_{\text{M-N}}$ stretching vibrations and sharp, medium to weak bands in the range $500\text{--}700\text{ cm}^{-1}$ is for nitrogen-metal ($\nu_{\text{N-M}}$) stretching vibrations^{18,19}. The absence of sharp characteristic absorption band in the region $3600\text{--}3700\text{ cm}^{-1}$ due to phenolic O–H stretching vibrations and also the absence of broad band in the region $3200\text{--}3300\text{ cm}^{-1}$ due to intermolecular hydrogen bond, indicates deprotonation during formation of nickel complex of Schiff base [NiE5NS]. Phenolic C–O stretching vibrations absorption band appears at 1242 cm^{-1} in [NiE5NS], at 1317 cm^{-1} in [NiE5NSRbAp] and at 1244 cm^{-1} in [NiE5NSCsAp]. Shifting of phenolic C–O stretching vibration towards higher wave number indicates coordination of phenolic oxygen atom to $\text{Ni}^{2+}/\text{Rb}^+/\text{Cs}^+$ ion during complex formation. This fact is further substantiated by the presence of oxygen-metal bond stretching vibration ($\nu_{\text{O-M}}$) bands in the region $416\text{--}505\text{ cm}^{-1}$.

Table 3: Absorption Band Positions in FT-IR Spectra

Chemical Bond	Mode of Vibration	Absorption Band Position (in cm^{-1})			
		Aspirin	[NiE5NS]	[NiE5NSRbAp]	[NiE5NSCsAp]
O–H	Stretching	2649 br, 2821 br	NA	NP	NP
Carboxylic C–O	Stretching	1313 s	NA	1470 s	1439 s
Carboxylic C=O	Stretching	1591 s	NA	1600 s	1596 s
Carboxylic C=O	Stretching	1684 s	NA	1635 s	1651 s
Ester C–O	Stretching	1265 s	NA	1317 br & vs	1307 vs
Ester C–O	Stretching	NA	1242 s	1317 br & vs	1244 s
Phenolic C=N	Stretching	NA	1649 vs	1635 vs	1651 vs
Azomethine					

NA=Not Applicable, NP=Not Present, br=broad, vs=very strong, s=strong

Further, absence of absorption band of carboxylic O–H bond (Str) in synthesized hetero binuclear complexes indicates deprotonation of carboxylic O–H bond during rubidium/caesium salt formation, and shift of absorption band of carboxylic C–O (Str) towards higher wave number in synthesized hetero binuclear complexes as compared to aspirin further substantiates the fact of deprotonation of carboxylic O–H and conversion of it into O–Rb/Cs. Comparison of absorption band

position of carboxylic C=O (Str) in FT-IR spectra of Aspirin and hetero binuclear complexes, we find no major shift in wave number which indicates non-involvement of oxygen atom lone pair of carboxylic C=O in coordination during complex formation. However, slight shift of absorption band of ester C=O (Str) towards lower wave number from aspirin to hetero binuclear complexes indicates presence of hydrogen bonding between ester C=O group and H_2O (water of crystallisation). On comparison of FT-IR spectrum of

Aspirin and hetero binuclear complexes, we find major shift in absorption band of ester C–O (Str) towards higher wave number which indicates coordination of oxygen atom of ester C–O with Rubidium or Caesium during complex formation. This fact is supported by the presence of oxygen-metal bond stretching vibration (ν_{O-M}) bands in the region 416–505 cm^{-1} . A broad band at 3448 cm^{-1} indicates presence of H_2O as water of crystallisation in $[\text{NiE5NSRbAp}]$ molecule. A broad absorption band centred at 3433 cm^{-1} in FT-IR spectrum of $[\text{NiE5NSCsAp}]$ is assigned for O–H stretching vibrations in coordinated water molecules which can be interpreted as presence of coordinated water molecules in the complex²⁰⁻²² because there is appearance of non-ligand absorption bands at 734 cm^{-1} and 643 cm^{-1} assignable to the rocking and wagging modes of coordinated water, respectively²⁰⁻²⁴. Thus, there is presence of H_2O molecule in coordination sphere of the complex $[\text{NiE5NSCsAp}]$.

Electronic Absorption Spectra

Band positions in UV-Visible spectra of the hetero binuclear complexes are summarised in Table 2. Study of complex $[\text{NiE5NSRbAp}]$ spectrum excludes possibility of square pyramidal and octahedral geometry around Ni^{2+} ion as no bands are present between 500–1000nm. Further appearance of no band above 1000nm excludes possibility of tetrahedral geometry around Ni^{2+} ion. For a square planar geometry around Ni^{2+} ion there must be appearance of two bands in region 420–500 nm assignable to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions²⁵. In this case these two bands have been obscured by the CT band at that region. Hence, in the complex $[\text{NiE5NSRbAp}]$ there is square planar geometry around Ni^{2+} ion. This is further supported by zero magnetic moment of complex $[\text{NiE5NSRbAp}]$ which indicates its diamagnetic nature and low spin complex.

In the $[\text{NiE5NSCsAp}]$ spectrum, appearance of a band at 824nm excludes possibility of square pyramidal and square planar geometry around Ni^{2+} ion. Further appearance of no band above 1000nm excludes possibility of tetrahedral geometry around Ni^{2+} ion. Presence of an absorption band in the region 700–1000nm confirms that the coordination number of Ni^{2+} in the adduct $[\text{NiE5NSCsAp}]$ is 6 with octahedral geometry. For an octahedral geometry around Ni^{2+} ion there must be appearance of three bands in region 300–450nm, 450–700nm and 700–1000nm assignable to ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$, ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ transitions,

respectively. Shoulder at 353nm is due to ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ d–d transition and band at 824nm is due to ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ d–d transition^{26,27}. In this case one absorption band corresponding to ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ d-d transition has been obscured by the CT band at that region²⁸. Hence, in the complex $[\text{NiE5NSCsAp}]$ there is octahedral geometry around Ni^{2+} ion. This is further supported by magnetic moment of complex $[\text{NiE5NSCsAp}]$ which indicates its paramagnetic and high spin nature and corresponds to the presence of two unpaired electrons^{14,29-30}. However, presence of H_2O molecules in coordination sphere put geometry of $\text{Ni}(\text{II})$ ion in complex under John-Teller distortion resulting Ni^{2+} ion in distorted octahedral geometry. Many researchers in their investigations have reported octahedral geometry around Ni^{2+} in various complexes which supports present findings about geometry for synthesized complex $[\text{NiE5NSCsAp}]$.^{31,32}

From the above results and discussion, it may be summarised that geometry about Ni^{2+} ion is square planar and distorted octahedral with coordination number 4 and 6 and general formula $[\text{NiLRbL}'] \cdot 3\text{H}_2\text{O}$ and $[\text{NiL}(\text{H}_2\text{O})_2\text{CsL}']$ for the complexes $[\text{NiE5NSRbAp}]$ and $[\text{NiE5NSCsAp}]$, respectively. The suggested structure of these hetero binuclear complexes is shown in Fig.1 and Fig. 2, respectively.

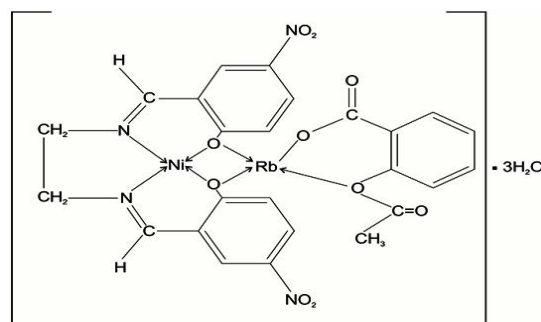


Fig. 1. Hetero binuclear complex $[\text{NiLRbL}'] \cdot 3\text{H}_2\text{O}$, $\text{NiRbC}_{25}\text{H}_{25}\text{N}_4\text{O}_{13}$

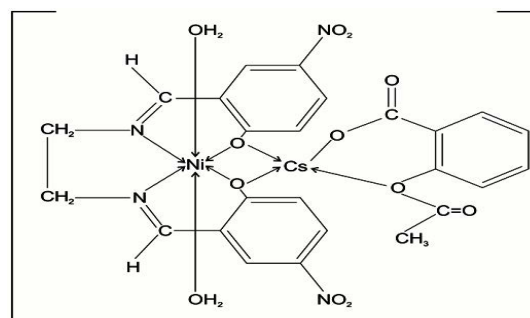


Fig. 2. Hetero binuclear complex $[\text{NiL}(\text{H}_2\text{O})_2\text{CsL}']$, $\text{NiCsC}_{25}\text{H}_{25}\text{N}_4\text{O}_{12}$

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Conflict of Interest

The author declares that there is no conflict of interest.

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