

Heterobinuclear Complexes Derived from Rubidium and Caesium Salts of Acetyl Salicylic Acid (ASPIRIN) with N,N'-1,2-Ethylenebis(o-hydroxyacetophenoniminato) Copper(II): Synthesis and Characterization

Dr. Sanjay Kumar

Associate Professor, Department of Chemistry, Patna Science College,
Patna University, Patna, India
kumarsanjay.psc@gmail.com
<https://orcid.org/0000-0003-0617-1743>

Abstract: Copper Schiff base has been developed from N₂O₂ type ligand N,N'-ethylenebis(ortho-hydroxyacetophenonimine) (Eohacp) derived from ethylenediamine and ortho-hydroxyacetophenone, and copper (II) salt. Novel Heterobinuclear complexes have been synthesized from Rubidium and Caesium Salts of Acetyl Salicylic Acid (RbAp and CsAp) and the Copper Schiff base, N,N'-1,2-Ethylenebis(o-hydroxyacetophenoniminato) Copper(II) (CuEohacp) as ligand. Structure elucidation of these synthesized hetero-binuclear complexes [CuEohacpRbAp] and [CuEohacpCsAp] have been done with the help of Elemental analysis, Solubility, Magnetic moment and Molar conductance measurements, FT-IR and Electronic absorption spectra. On the basis of characterization results, molecular formula of these hetero-binuclear complexes has been proposed as [M^a M^b L^x O] where M^a = Cu²⁺, M^b = Rb⁺ / Cs⁺, L = N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) Dianion L' = Acetyl salicylate, and x = 3 / 0.5 for [CuEohacpRbAp] and [CuEohacpCsAp] respectively. Studies reveal that molecular geometry of these hetero-binuclear complexes is distorted square planar or pseudo-tetrahedral and the adducts are non-electrolytic and paramagnetic in nature

Keywords: N,N'-1,2-Ethylenebis(o-hydroxyacetophenoniminato) Copper(II), Acetyl salicylic acid (ASPIRIN), Synthesis, Structure Elucidation, Distorted square planar, Pseudo-tetrahedral, Non-electrolytic, Paramagnetic

I. INTRODUCTION

In recent years a number of binuclear metal complexes have been synthesized from Schiff bases of di-primary amine and carbonyl compound as these Schiff bases have ability to act as “di-nucleating ligand” [1-8]. Binuclear metal complexes derived from Schiff bases show massive potential in pharmacology and chemotherapy. Bimetallic complexes often show significantly improved antibacterial, antiviral, anti-cancer, anti-tubercular and antifungal properties [9-14]. Very little work has been done on synthesis of hetero-binuclear complexes with one of the metal centers as Rubidium or Caesium [15, 16]. D. Prakash et al has reported the synthesis of mixed ligand complexes of Rb and Cs salts of some organic acids like o-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol and 1-nitroso-2-naphthol with picolinic acid [17]. Priya Kumari et al has reported about the synthesis of a series of hetero binuclear complexes of general composition M_aL. M_bL' where M_a = Ni, M_b = Rb or Cs, L = N, N'-1, 2 – ethylenebis(salicylaldehyde) or N, N'



– 1,2-propylenebis (salicylaldehyde), $L' =$ deprotonated o-nitrophenol / 2, 4-dinitrophenol / 2, 4, 6-trinitrophenol / 1-nitroso-2-naphthol / 8-hydroxyquinoline. M_aL is the Schiff base complex of Ni(II) derived from ethylenediamine or propylenediamine with Salicylaldehyde. They have proposed Ni (II) Schiff base complex as N_2O_2 type, and this metal chelate of Schiff base acts as bidentate ligand and co-ordinates through the phenolic oxygen atoms. On the basis of spectral studies and magnetic moment, they report for Schiff base ligands (NiES, NiPS) and most of their binuclear adducts square planar geometry with co-ordination number 4 for Ni^{2+} ion. However, in case of some binuclear adducts due to high magnetic moment value they have suggested octahedral or tetrahedral structure [1]. In the present investigation hetero-binuclear complexes have been synthesized from Rubidium and Caesium salts of Acetyl Salicylic acid (ASPIRIN) and Copper (II) Schiff base derived from Ethylenediamine and ortho-hydroxyacetophenone. These novel hetero-binuclear complexes were obtained as non-hygroscopic crystalline solid and in good yield. The synthesized complexes have been characterized using various physico-chemical techniques such as Elemental analysis, Solubility, Melting Point, Magnetic moment and Molar conductance measurements, FT-IR and Electronic absorption spectra. On the basis of the characterization results structure and geometry of these synthesized complexes have been proposed. In future, there is ample scope of further research towards the applications of these synthesized complexes for the welfare of humankind and society such as 'Use in cooperative catalysis', 'Biological & Medicinal Mimicry', 'Design and development of drug for therapeutic use in order to minimize side effects of Aspirin', 'Anti-microbial, anti-fungal, anti-cancer activity'.

II. MATERIALS AND METHODS

2.1 Materials and Instrumentation

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

2.2 Methods

2.2.1 Synthesis of Schiff base N,N'- ethylenebis(ortho-hydroxy acetophenonimine) (Eohacp) derived from ethylenediamine and ortho-hydroxy acetophenone

In ethanolic solution of o-hydroxyacetophenone, ethylenediamine was added drop by drop with continuous stirring in 2:1 molar proportion. Yellow coloured solid Schiff base was precipitated out, washed with little ethanol, dried and kept in desiccator over anhydrous CaCl_2 .

2.2.2 Synthesis of Copper Schiff base N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato)copper(II) complex, $[\text{CuEohacp}]$

Two equimolar solutions of Schiff base and Cupric acetate monohydrate were prepared separately. In Cupric acetate solution Schiff base solution was added with constant stirring. Warmed below 40°C for 20-25 minutes. Brown (Web) coloured crystalline solid precipitated out. Precipitate was filtered, washed with little ethanol dried and kept in desiccator over anhydrous CaCl_2 .



2.2.3 Synthesis of Hetero-binuclear complexes [CuEohacpRbAp] and [CuEohacpCsAp] from Rubidium/Caesium acetyl salicylate and Copper (II) Schiff base N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato)copper(II) [CuEohacp]

Two equimolar solutions of Copper Schiff base N, N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato)copper (II) and Rubidium/Caesium acetyl salicylate in ethanol were prepared. The two solutions were mixed together and refluxed for 30 minutes at 40-50°C and cooled to ice temperature when the complex was separated out. Precipitate was filtered and washed with little ethanol, dried and kept in a desiccator over anhydrous CaCl₂.

III. EXPERIMENTAL RESULTS

3.1 Physical and Elemental analysis

The synthesized complexes are coloured, non-hygroscopic, crystalline solid and are stable in air at room temperature. These complexes do not decompose up to 250°C and are fairly stable. These synthesized hetero-binuclear complexes are insoluble in water and ethanol, and are soluble in acetone, DMF and DMSO. The physical and elemental analysis data of these synthesized complexes are presented in TABLE – 1.

TABLE – 1: Physical and Elemental analysis data

Synthesized Complex	Colour	Yield (%)	m.p (°C)	Elemental Analysis Data in % (w/w)							Empirical Formula
				C	H	N	O	Cu	Rb	Cs	
[CuEohacpRbAp]	Dark Grey (XII)	68	230	47.98	4.57	4.03	21.17	9.10	12.91		CuRbC ₂₇ H ₃₁ N ₂ O ₉
[CuEohacpCsAp]	Grullo	72	228	47.78	3.82	4.03	14.97	9.10		20.21	CuCsC ₂₇ H ₂₆ N ₂ O _{6.5}

The experimental elemental analysis data of these synthesized hetero-binuclear complexes are in good agreement with their suggested stoichiometries.

3.2 Molar Conductance Measurement

Molar conductance of 10⁻³M solution of the synthesized complexes [CuEohacpRbAp] and [CuEohacpCsAp] in DMF was measured at 20(±0.5)°C and was found to be 11.20 S.Cm².mole⁻¹ and 11.10 S.Cm².mole⁻¹, respectively. Low value of molar conductivity of these complexes [CuEohacpRbAp] and [CuEohacpCsAp] indicates their covalent nature.

TABLE – 2: Molar Conductance of Synthesized Complexes at 20(±0.5)°C

Synthesized Complex	Solvent	Molar Conductance (S.Cm ² .mole ⁻¹)	Type of Electrolyte
[CuEohacpRbAp]	DMF	11.2	Non-electrolyte
[CuEohacpCsAp]	DMF	11.1	Non-electrolyte

3.3 Magnetic Moment Measurement

Effective magnetic moment, μ_{eff} of the synthesized complexes [CuEohacpRbAp] and [CuEohacpCsAp] at 301 K is found to be 1.92 B.M. and 1.94 B.M., respectively. Both the synthesized complexes are paramagnetic with one unpaired electron in central metal ion. Cu²⁺.



3.4 FT-IR Spectra

FT-IR Spectrum of each of the synthesized complexes, [CuEohacpRbAp] and [CuEohacpCsAp] was recorded in the range 4000 – 400 cm^{-1} . The FT-IR spectrum of the complex [CuEohacpRbAp] is given in Figure-1, and FT-IR spectrum of the complex [CuEohacpCsAp] is given in Figure-2.

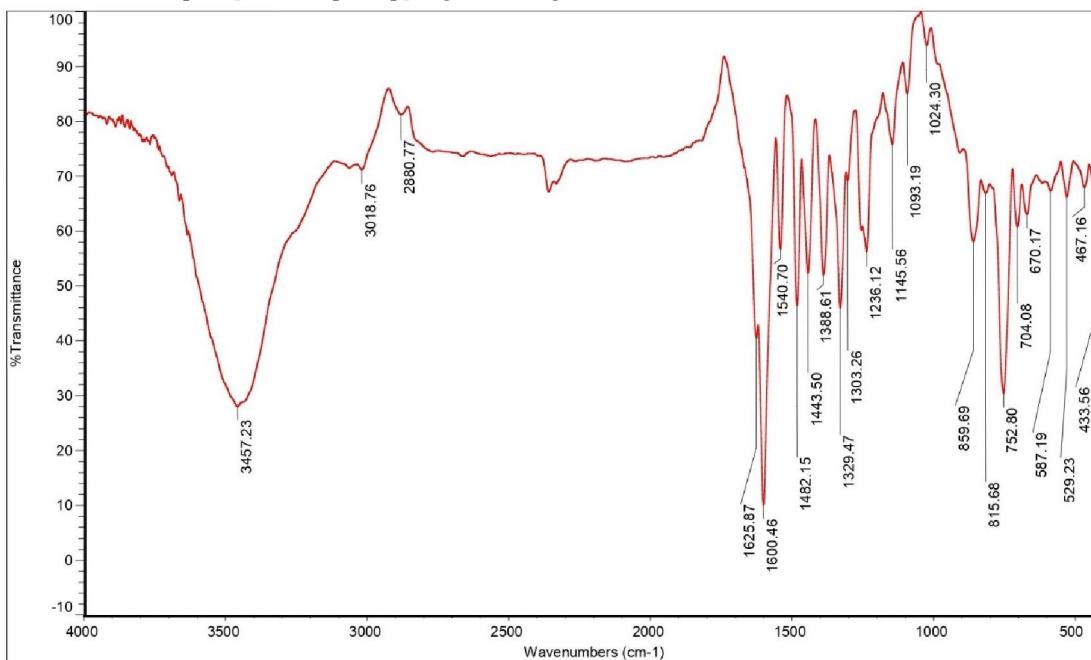


Figure-1: FT-IR Spectrum of the Complex [CuEohacpRbAp]

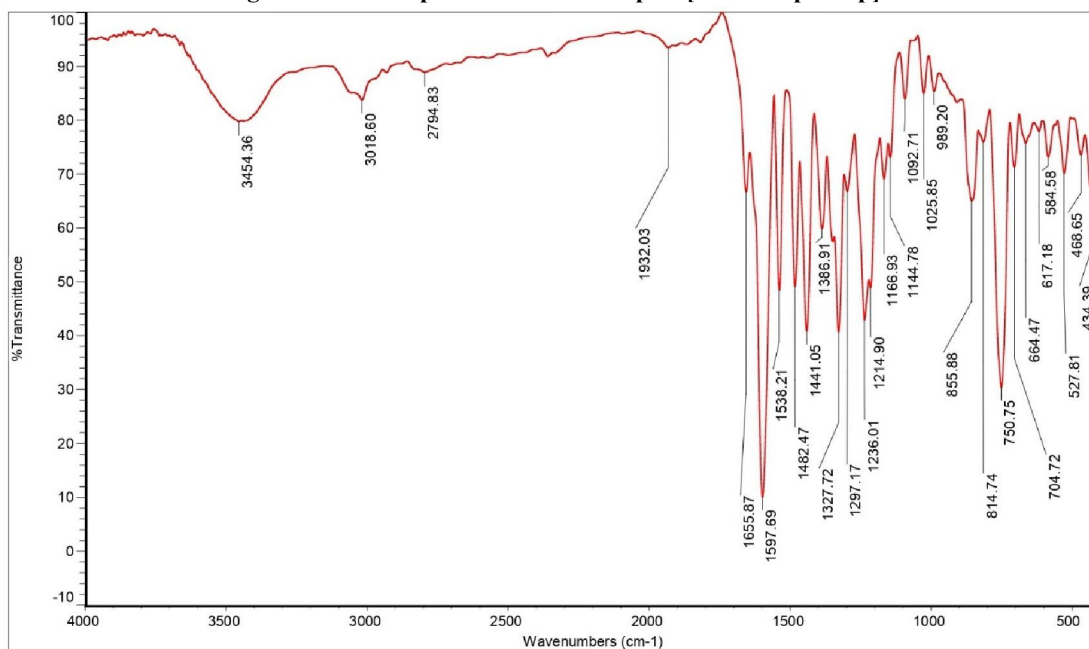


Figure-2: FT-IR Spectrum of the Complex [CuEohacpCsAp]



3.5 Electronic Absorption Spectra

Electronic absorption spectrum of 10^{-4} M solution of each of the complexes [CuEohacpRbAp] and [CuEohacpCsAp] was recorded between 200 -900 nm. Band positions in electronic spectrum of the complex [CuEohacpRbAp] has been summarized in TABLE.3 and band positions in electronic spectrum of the complex [CuEohacpCsAp] has been summarised in TABLE.4.

TABLE.3:Band Positions in Electronic Absorption Spectrum of [CuEohacpRbAp]

Absorption Band Position (in cm^{-1})	Assignment
Broad band ranging 231 – 408 nm with a peak at $\lambda_{\text{max}} = 381$ nm and a shoulder at 340 nm	(1) Intraligand transitions: (a) Benzene Chromophore $\pi \rightarrow \pi^*$ transition (b) Azomethine Chromophore $\pi \rightarrow \pi^*$ transition (c) Co-ordinated azomethine $n \rightarrow \pi^*$ transition (2) Ligand to Metal Charge Transfer (LMCT) (3) $d \rightarrow d$ transition
Band with a peak at $\lambda_{\text{max}} = 552$ nm	$d \rightarrow d$ transition

TABLE.4:Band Positions in Electronic Absorption Spectrum of [CuEohacpCsAp]

Absorption Band Position (in cm^{-1})	Assignment
Broad band ranging 231 – 408 nm with a peak at $\lambda_{\text{max}} = 385$ nm	(1) Intraligand transitions: (a) Benzene Chromophore $\pi \rightarrow \pi^*$ transition (b) Azomethine Chromophore $\pi \rightarrow \pi^*$ transition (c) Co-ordinated azomethine $n \rightarrow \pi^*$ transition (2) Ligand to Metal Charge Transfer (LMCT) (3) $d \rightarrow d$ transition
Band with a peak at $\lambda_{\text{max}} = 550$ nm	$d \rightarrow d$ transition

IV. DISCUSSION

4.1 Interpretation of FT-IR Spectra

Absorption band position of certain chemical bonds of interest have been identified in FT-IR Spectrum of Aspirin, [CuEohacp] and Synthesized complexes [CuEohacpRbAp] and [CuEohacpCsAp], and is summarized in TABLE.5. FT-IR spectrum analysis reveals a very strong band at 1600 cm^{-1} and 1597 cm^{-1} for [CuEohacpRbAp] and [CuEohacpCsAp], respectively which is assigned for $\nu_{\text{C=N}}$ stretching [18]. The $\nu_{\text{C=N}}$ stretching band in [CuEohacp] FT-IR spectrum appears at 1602 cm^{-1} . Many workers in various Schiff bases have reported $\nu_{\text{C=N}}$ stretching band for uncoordinated azomethine (C=N) in the range $1650 - 1690 \text{ cm}^{-1}$ [19]. The shift of the absorption band of $\nu_{\text{C=N}}$ stretching towards lower wave number indicates coordination of the imine nitrogen to the Cu^{2+} ion during [CuEohacp] complex formation [19, 20]. This is further substantiated by the presence of new bands in the region $529 - 670 \text{ cm}^{-1}$ assignable to $\nu_{\text{N-M}}$ stretching vibrations. Sharp, medium to weak bands in the range $500 - 700 \text{ cm}^{-1}$ have been reported for nitrogen-metal ($\nu_{\text{N-M}}$) stretching vibrations [21]. The absence of sharp characteristic absorption band in the region



3600 – 3700 cm^{-1} due to phenolic O – H stretching vibrations and also the absence of broad band in the region 3200 – 3300 cm^{-1} due to intermolecular hydrogen bond, indicates deprotonation during formation of copper complex of Schiff base [CuEohacp].

TABLE.5

Chemical Bond	Mode of Vibration	Absorption Band Position (in cm^{-1})			
		Aspirin	[CuEohacp]*	[CuEohacpRbAp]	[CuEohacpCsAp]
O – H Carboxylic	Stretching	2649br, 2821 br	NA	NP	NP
C – O Carboxylic	Stretching	1313 s	NA	1443 s	1441 s
C = O Carboxylic	Stretching	1591 s	NA	1600 s	1597 vs
C = O Ester	Stretching	1684 s	NA	1625 s	1655 s
C – O Ester	Stretching	1265 s	NA	1329 s	1327 s
C – O Phenolic	Stretching	NA	1234 s	1303 s	1297 s
C = N Azomethine	Stretching	NA	1602 s	1600 s	1597 s

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

A sharp ir absorption band appears at 1303 cm^{-1} and 1297 cm^{-1} in case of [CuEohacpRbAp] and [CuEohacpCsAp], respectively which is assigned for phenolic C - O stretching vibrations. However, phenolic C – O stretching vibrations absorption band in complex [CuEohacp] appears at 1234 cm^{-1} . A strong absorption band in region 1200 – 1350 cm^{-1} has been reported for phenolic C – O stretching mode by research workers [4, 23, 24, 25, 26]. Shifting of phenolic C – O stretching vibration towards higher wave number indicates coordination of phenolic oxygen atom to Rb^+/Cs^+ ion during hetero-binuclear complex [CuEohacpRbAp] / [CuEohacpCsAp] formation from ligand [CuEohacp]. This fact is further substantiated by the presence of oxygen – metal bond stretching vibration ($\nu_{\text{O-M}}$) bands in the region 433 – 467 cm^{-1} / 434 – 527 cm^{-1} in case of [CuEohacpRbAp]/ [CuEohacpCsAp]. Absence of absorption band of carboxylic O – H bond (Str) in [CuEohacpRbAp] and [CuEohacpCsAp] indicates deprotonation of carboxylic O – H bond during Rubidium and Caesium salt formation, and shift of absorption band of carboxylic C–O (Str) towards higher wave



number in [CuEohacpRbAp] and [CuEohacpCsAp] as compared to aspirin further substantiates the fact of deprotonation of carboxylic O – H and conversion of it into O – Rb/O-Cs. There is no change in absorption band position of carboxylic C = O (Str) in FT-IR spectra of Aspirin and [CuEohacpRbAp]/[CuEohacpCsAp] which indicates non-involvement of oxygen atom lone pair of carboxylic C = O in coordination during complex [CuEohacpRbAp]/[CuEohacpCsAp] formation. However, slight shift of absorption band of ester C = O (Str) towards lower wave number from aspirin to [CuEohacpRbAp]/[CuEohacpCsAp] indicates presence of hydrogen bonding between ester C = O group and H₂O (water of crystallisation). On comparison of FT-IR spectrum of Aspirin and [CuEohacpRbAp]/[CuEohacpCsAp], 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/Caesium during complex [CuEohacpRbAp]/[CuEohacpCsAp] formation. This fact is supported by the presence of oxygen-metal bond stretching vibration (ν_{O-M}) bands in the region 433 – 467 cm^{-1} . A broad band at 3457 cm^{-1} / 3454 cm^{-1} indicates presence of H₂O as water of crystallisation in [CuEohacpRbAp]/[CuEohacpCsAp] molecule.

4.2 Interpretation of Electronic Absorption Spectra

Band positions in Electronic Absorption Spectra of [CuEohacpRbAp] and [CuEohacpCsAp] have been summarised in TABLE.3 and TABLE.4, respectively. The electronic absorption spectrum of the complex [CuEohacpRbAp] shows a broad band ranging 231 – 408 nm with a peak at $\lambda_{\text{max}} = 381$ nm and a shoulder at 340 nm, and the electronic absorption spectrum of the complex [CuEohacpCsAp] shows a broad band ranging 231 – 408 nm with a peak at $\lambda_{\text{max}} = 385$ nm. This is due to (i) Intraligand transitions such as $\pi \rightarrow \pi^*$ transitions in Benzene and Azomethine chromophores, $n \rightarrow \pi^*$ transition in coordinated azomethine (ii) Ligand to Metal Charge Transfer (LMCT). Non-appearance of any band in the region 600–1000 nm in the spectra of the complexes [CuEohacpRbAp] and [CuEohacpCsAp] excludes possibility of octahedral geometry around Cu^{2+} ion. A single band appears at 552nm in the electronic spectrum of [CuEohacpRbAp], and at 550 nm in the electronic spectrum of [CuEohacpCsAp]. Presence of single band in the region 400 – 600 nm has been reported for a square planar geometry about Cu^{2+} ion in Copper (II) complexes [23, 25, 27]. Thus, band at 552nm in the electronic spectrum of [CuEohacpRbAp] and band at 550 nm in the electronic spectrum of [CuEohacpCsAp], is indicative of a ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition which is in conformity to a square planar geometry.

4.3 Interpretation of EAS data with Magnetic moment measurement

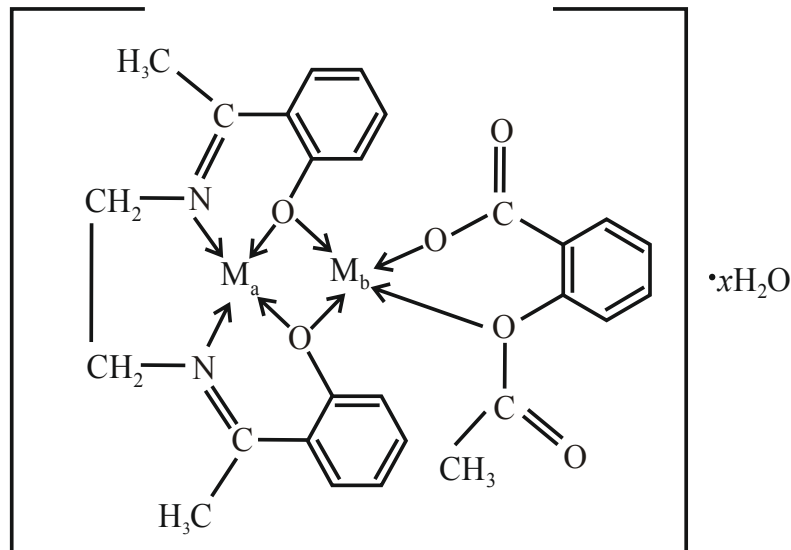
In a completely undistorted tetrahedron, Cu(II) should have a magnetic moment at room temperature of about 2.2 B.M. and an undistorted square planar geometry around Cu^{2+} ion should have a magnetic moment value at room temperature of about 1.77 B.M.[8]. However, magnetic moment value of 1.92 B.M./1.94 B.M. at 301K for [CuEohacpRbAp]/[CuEohacpCsAp] indicates a distortion from planar towards tetrahedral symmetry [8]. Further, appearance of d – d transition band at 552nm/550 nm supports distortion from planar towards tetrahedral geometry about Cu^{2+} ion in the complex as increasing distortion from planar towards tetrahedral symmetry causes a steady shift of d – d transition band to lower energy. Gruber et al [8] reported a distortion from planar towards tetrahedral geometry, i.e., Pseudo-tetrahedral geometry about copper (II) for CuTSB where shows a d – d transition band at 588nm. Therefore, geometry about Cu^{2+} ion in [CuEohacpRbAp] and [CuEohacpCsAp] is distorted square planar or say pseudo-tetrahedral. Magnetic moment of 1.92 B.M./1.94 B.M. indicates paramagnetic nature of the complexes [CuEohacpRbAp] and [CuEohacpCsAp] with one unpaired electron.

V. CONCLUSION

The hetero-binuclear complexes synthesized from N,N'-1,2-ethylenebis(o-hydroxyacetophenoniminato)copper(II) [CuEohacp] and rubidium/Caesium salt of Acetyl salicylic acid (ASPIRIN) are non-electrolytic, paramagnetic with one unpaired electron and adducts have Empirical Formula $\text{CuRbC}_{27}\text{H}_{31}\text{N}_2\text{O}_9$ and $\text{CuCsC}_{27}\text{H}_{26}\text{N}_2\text{O}_{6.5}$, respectively. The geometry of each of the hetero-binuclear complex molecules about Cu^{2+} ion is distorted square planar or pseudo-



tetrahedral. There is no change in geometry about Cu^{2+} ion during adduct formation from copper Schiff base complex [CuEohacp]. On the basis of the investigative results and discussions the following general structure is proposed for the hetero-binuclear complexes [CuEohacpRbAp] and [CuEohacpCsAp]:



Where $M_a = \text{Cu}^{2+}$, $M_b = \text{Rb}^+ \text{ or } \text{Cs}^+$, $x = 3 \text{ or } 0.5$

Figure-3: Proposed Structure of Synthesized Hetero-binuclear Complexes

Copper Schiff base $\text{N,N}'$ -1,2-ethylenebis(ortho-hydroxyacetophenoniminato) copper(II) acts as "bidentate ligand" in the complexation reaction forming adducts [CuEohacpRbAp] and [CuEohacpCsAp]. The general formula of the adducts [CuEohacpRbAp] and [CuEohacpCsAp] is $[M_a \cdot L \cdot M_b \cdot L'] \cdot x \text{H}_2\text{O}$

where $M_a = \text{Cu}^{2+}$, $M_b = \text{Rb}^+ \text{ or } \text{Cs}^+$

$L = \text{N,N}'$ -1,2-ethylenebis(ortho-hydroxyacetophenoniminato) Dianion,

$L' = \text{Acetyl salicylate}$, and $x = 3 \text{ or } 0.5$, respectively.

VI. CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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