Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 14 Issue 08, August - 2025

N_2O_2 Type Complex N, N'–1,2–Ethylenebis (Salicylaldiminato) Copper (II) as Potent Ligand in Synthesis of Heterobinuclear Complexes with Rubidium and Caesium Salts of Acetyl Salicylic Acid (ASPIRIN)

Sanjay Kumar
Department of Chemistry, Patna Science College, Patna University, Patna, INDIA
ORCID iD: https://orcid.org/0000-0003-0617-1743

ABSTRACT: **N, N'–1,2–ethylenebis(salicylaldiminato) Copper(II) complex [CuES] has been prepared using Schiff base N, N'-ethylenebis(salicylaldimine) [ES]. This complex [CuES] has been used to synthesize in pure state novel hetero binuclear complexes, [CuESRbAp] and [CuESCsAp], using Rubidium and Caesium salts of Acetyl Salicylic Acid (ASPIRIN), respectively. The structure elucidations of these synthesized red coloured solid hetero binuclear complexes have been carried out using various physico-chemical techniques viz. Solubility, Elemental analysis, Magnetic property, Molar conductance measurement, UV-Visible and FT-IR spectroscopy. From the obtained data, the distorted square planar or pseudo-tetrahedral geometry has been suggested for both these hetero binuclear complexes with a general formula $[M_a\ L\ M_b\ L']$.xH_2O Where $M_a = Cu^{2+}$, $M_b = Rb^+/Cs^+$, L = N,N'-1,2-ethylenebis(salicylaldiminato) dianion, L' = Acetyl salicylate, and x = 2/1.5 for the adducts [CuESRbAp] and [CuESCsAp], respectively.**

Keywords: **N, N'–1,2–ethylenebis(salicylaldiminato) Copper(II), [CuESRbAp], [CuESCsAp], Aspirin, Distorted square planar or pseudo-tetrahedral geometry**

1. INTRODUCTION

Complexes containing N_2O_2 type ligand structure[1] are capable of holding two metal centres in close proximity, one of transition metal and other of alkali / alkaline earth metal[2-3]. Synthesis of such hetero-binuclear complexes has been of great attraction for the researchers because of their biological importance[4-9] and their greater permeability than metal ions. Transition metals play vital role whereas Rb and Cs may act as potassium analogue, in living organisms. Acetyl salicylic acid (Aspirin) is a common non-steroidal anti-inflammatory drug (NSAID). In the present paper Copper (II) complex, N, N'–1,2–ethylenebis(salicylaldiminato) Copper(II) synthesized from tetra dentate N_2O_2 donor type Schiff base derived from condensation of Ethylenediamine and Salicylaldehyde, has been described as a potent ligand towards the formation of hetero-binuclear complex with Rubidium and Caesium salt of Acetyl salicylic acid (ASPIRIN). The synthesized hetero-binuclear complexes have been characterized using various physico-chemical techniques, and on the basis of observations structure and molecular formula have been proposed. Further investigations may be helpful in drug design from these synthesized complexes or their modified forms in order to increase efficacy of ASPIRIN.

2. 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 Copper 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). Electronic absorption spectrum of 10^{-4}M solution of the complexes was recorded between 200 -900 nm by Shimadzu UV-Visible Spectrometer Model UV-2450 using UV Probe 2.32 software. FT-IR Spectrum of synthesized complexes was recorded on Thermo Nicolet Avatar 370 in the range 4000 – 400 Cm^{-1} by KBr beam splitter.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 14 Issue 08, August - 2025

Synthesis of N, N'–1,2–ethylenebis(salicylaldiminato) Copper(II)
Schiff base N, N'-ethylenebis(salicylaldimine) [ES] was prepared from the reaction between Salicylaldehyde and Ethylenediamine in 2:1 molar ratio. Ethylenediamine was added drop by drop in ethanolic solution of Salicylaldehyde with continuous stirring which resulted with yellow coloured precipitation. Yellow coloured solid Schiff base [ES] was obtained by crystallisation process. Ethanolic solutions of Schiff base [ES] and cupric acetate monohydrate were mixed in 1:1 molar ratio and refluxed at 40^0C for 10 minutes. Antique bronze coloured crystalline solid of N, N'–1,2–ethylenebis(salicylaldiminato) Copper(II) [CuES] was precipitated out. Precipitate was filtered, washed with little ethanol and dried.

Synthesis of Hetero-binuclear complexes from Rubidium and Caesium salt of Acetyl salicylic acid (ASPIRIN) and Copper (II) Schiff base N, N'–1,2–ethylenebis(salicylaldiminato) Copper(II)
Ethanolic solutions of Rubidium acetyl salicylate or Caesium acetyl salicylate and Copper (II) Schiff base [CuES] in 1:1 molar ratio were mixed together and refluxed for 30 minutes at about 40 - 50^0C and cooled to ice temperature when the complex was separated out. Precipitate was filtered, recrystallized and dried.

3. RESULTS AND DISCUSSION

The synthesized hetero-binuclear complexes, [CuESRbAp] and [CuESCsAp], are red coloured, non-hygroscopic crystalline solid and are stable in air. These complexes are insoluble in water and benzene but are soluble in co-ordinating solvents DMF and DMSO. Melting point measurements of these synthesized complexes reveal that these complexes do not decompose up to 230^o **C** and are fairly stable. The experimental elemental analysis data of these synthesized hetero-binuclear complexes are in good agreement with their suggested stoichiometries. [Table – 1].

TABLE 1: Physical and Analytical Data of the Synthesized Complexes

Synthesized Complex	Colour	Yield (%)	m.p. (^{o}C)	Elemental Analysis Data in % Obs. (Cal)						
				C	H	N	O	Cu	Rb	Cs
[CuESRbAp]	Red	77	223	47.47 (47.58)	3.92 (3.97)	4.43 (4.44)	20.12 (20.30)	9.91 (10.07)	14.15 (13.56)	
[CuESCsAp]	Red	75	227	44.57 (44.85)	3.55 (3.59)	4.13 (4.19)	18.13 (17.94)	9.29 (9.49)		20.25 (19.87)

3.1. Molar Conductance Measurement

Molar conductance of 10^{-3}M solution of these synthesized complexes in DMF was measured at $20(\pm0.5)^0$C [Table 2]. A very low value of molar conductance (<10 $S.Cm^2.mole^{-1}$) suggests non-existence of any ion outside co-ordination sphere and, hence, their non-electrolytic nature[10-15].

TABLE 2: Molar Conductance Data of the Synthesized Complexes

Synthsized Complex	Solvent	Molar Conductance ($S.Cm^2.mole^{-1}$)	Type of Electrolyte
[CuESRbAp]	DMF	9.9	Non-electrolyte
[CuESCsAp]	DMF	9.5	Non-electrolyte

3.2. Magnetic Moment Measurement

Effective magnetic moment (μ_{eff}) of synthesized hetero-binuclear complexes [CuESRbAp] and [CuESCsAp] at 301K are 1.91 B.M. and 1.90 B.M., respectively. The result suggests these hetero-binuclear complexes to be paramagnetic in nature with one unpaired electron.

3.3. Electronic Absorption Spectra

Band positions in electronic absorption spectra of the complexes [CuESRbAp] and [CuESCsAp] have been summarised in TABLE – 3.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 14 Issue 08, August - 2025

TABLE 3: Band Positions in EAS of the Synthesized Complexes

[CuESRbAp]		**[CuESCsAp]**	
Wave number,nm	Absorbance	Wave number, nm	Absorbance
200	0.410	207	0.496
246	0.541	300	0.602
353, sh	0.640	354, sh	0.659
412, p	0.653	425, p	0.672
507	0.458	493	0.580
592, p	0.496	592, p	0.619

Study of Hetero-binuclear complex [CuESRbAp] Spectrum reveals broad band ranging 246 – 463 nm with a peak at λ_{max} = 412 nm and a shoulder at 353 nm which has been assigned to (1) Intraligand transitions such as Benzene Chromophore $\Pi \rightarrow \Pi^*$ transition, Azomethine Chromophore $\Pi \rightarrow \Pi^*$ transition and Co-ordinated azomethine $n \rightarrow \Pi^*$ transition, and (2) Ligand to Metal Charge Transfer (LMCT). Similarly, in case of [CuESCsAp] spectrum, the broad band ranging 207 – 496 nm with a peak at λ_{max} = 425 nm and a shoulder at 354 nm, has been assigned for (1) Intraligand transitions such as Benzene Chromophore $\Pi \rightarrow \Pi^*$ transition, Azomethine Chromophore $\Pi \rightarrow \Pi^*$ transition and Co-ordinated azomethine $n \rightarrow \Pi^*$ transition, and (2) Ligand to Metal Charge Transfer (LMCT). Appearance of no band in the region 600 – 1000 nm in UV-Visible spectra of [CuESRbAp] and [CuESCsAp] excludes possibility of octahedral geometry around Cu^{2+} ion. In case of Cu(II) complexes, presence of single band in the region 400 – 600nm has been reported for a square planar geometry about Cu^{2+} ion[15-19]. The band at 592nm in the electronic spectra of [CuESRbAp] and [CuESCsAp] is indicative of a $^2B_{1g} \rightarrow {}^2A_{1g}$ transition which is in conformity to a square planar geometry.

3.4. Interpretation of EAS data in correlation with Magnetic moment measurement

Both in the case of hetero-binuclear complexes [CuESRbAp] and [CuESCsAp], magnetic moment value of 1.91 B.M. and 1.90 B.M. at 301K respectively, indicate a distortion from planar towards tetrahedral symmetry[4]. 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.[4]. Further, appearance of d – d transition band at 592nm 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[4] 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 [CuESRbAp] and [CuESCsAp] is distorted square planar or say pseudo-tetrahedral and these are high spin complexes.

3.5. FT-IR Spectra

Absorption band position of certain chemical bonds of interest in FT-IR Spectrum of Aspirin, [CuES], [CuESRbAp], and [CuESCsAp] have been summarised in Table 4.

Table 4: Absorption Band Positions in FT-IR Spectra

Chemical Bond	Mode of Vibration	Absorption Band Position (in cm^{-1})			
		Aspirin	[CuES]	[CuESRbAp]	[CuESCsAp]
O – H Carboxylic	Stretching	2649 br, 2821 br	NA	NP	NP
C – O Carboxylic	Stretching	1313 s	NA	1467 s	1447 s
C = O Carboxylic	Stretching	1591 s	NA	1599 s	1599 s
C = O Ester	Stretching	1684 s	NA	1644 s	1644 s
C – O Ester	Stretching	1265 s	NA	1327 s	1329 s
C – O Phenolic	Stretching	NA	1294 s	1317 s	1305 s
C =N Azomethine	Stretching	NA	1649 vs	1634 vs	1629 vs

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

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 14 Issue 08, August - 2025

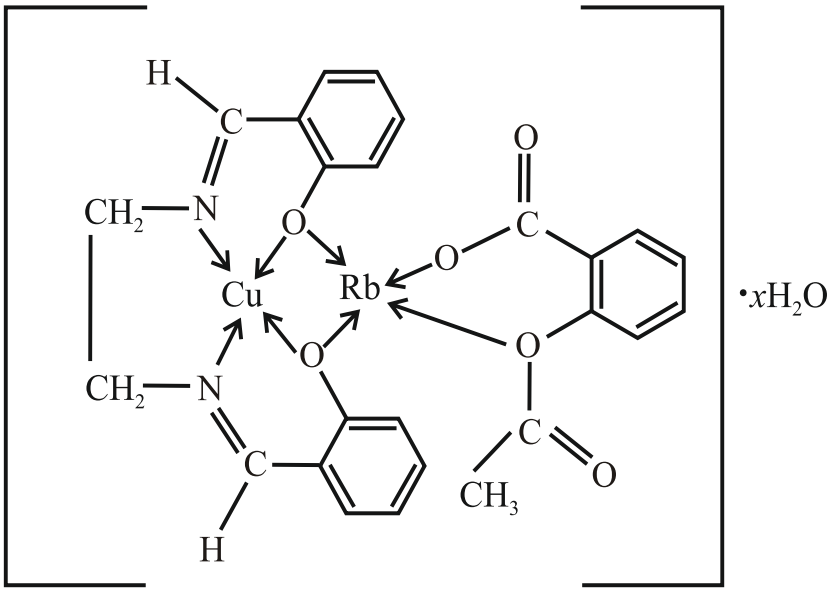
Many workers in various Schiff bases have reported $\nu_{C=N}$ stretching band for uncoordinated azomethine (C=N) in the range 1650 – 1690 Cm^{-1}.[20] FT-IR spectrum analysis reveals a very strong band at 1649 cm^{-1} in [CuES], at 1634 cm^{-1} in [CuESRbAp] and at 1629 cm^{-1} in [CuESCsAp] which has been assigned for $\nu_{C=N}$ stretching[21]. The shift of the absorption band of $\nu_{C=N}$ stretching towards lower wave number indicates coordination of the imine nitrogen to the Cu^{2+} ion during [CuES], [CuESRbAp] and [CuESCsAp] complexes formation[22,20]. This fact is further substantiated by the presence of new bands in spectra of complexes [CuES], [CuESRbAp], and [CuESCsAp] in the region 571 - 647 Cm^{-1} assignable to ν_{N-M} stretching vibrations.[23] 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 in the spectra of [CuES], [CuESRbAp] and [CuESCsAp] indicate deprotonation of phenolic O - H during formation of these complexes. Shifting of sharp ir absorption band for phenolic C - O stretching vibrations towards higher wavenumber has been assigned for coordination of phenolic oxygen atom to Rb^+ ion / Cs^+ ion during hetero-binuclear complex [CuESRbAp] and [CuESCsAp] formation from ligand [CuES].[24-27] This fact is further substantiated by the presence of oxygen – metal bond stretching vibration (ν_{O-M}) bands in the region 430 – 498 Cm^{-1}.

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. 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 / O - Cs.[28] No major shift in absorption band position of carboxylic C = O (Str) in FT-IR spectra of Aspirin and synthesized hetero-binuclear complexes indicates non-involvement of oxygen atom lone pair of carboxylic C = O in coordination during these complexes formation. However, slight shift of absorption band of ester C = O (Str) towards lower wave number in the spectra of aspirin to [CuESRbAp] / [CuESCsAp] 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 [CuESRbAp] / [CuESCsAp], 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 these hetero-binuclear complexes formation. This fact is supported by the presence of oxygen-metal bond stretching vibration (ν_{O-M}) bands in the region 430 – 498 Cm^{-1}. A broad band at 3450 Cm^{-1} / 3453 Cm^{-1} indicates presence of H_2O as water of crystallisation in [CuESRbAp] / [CuESCsAp] molecule.

4. CONCLUSION

From the above results and discussions, it is summarised that geometry about Cu^{2+} ion in case of both the synthesized hetero-binuclear complexes is Distorted Square planar or Pseudo-tetrahedral with co-ordination number 4. These results further suggest that Copper Schiff base N, N'-1,2-ethylenebis(salicylaldiminato) copper (II) acts as bidentate ligand while coordinating with Rubidium atom or Caesium atom through oxygens of its phenolic C – O. Both the synthesized hetero-binuclear complexes have water of crystallisation molecules with general formula [Ma L M_b L']$.xH_2O$ where M_a = Cu^{2+}, M_b = Rb^+ / Cs^+, L = N,N'-1,2-ethylenebis(salicylaldiminato) dianion, L' = Acetyl salicylate, x = 2 for [CuESRbAp] and x = 1.5 for [CuESCsAp]. The suggested structure for these synthesized hetero-binuclear complexes is shown in the following figure.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 14 Issue 08, August - 2025



ACKNOWLEDGEMENT

Author is grateful to Civil Engineering Department IIT Patna, SAIF CSIR-CDRI LUCKNOW, SAIF STIC COCHIN and SAIC TEZPUR UNIVERSITY for doing elemental analysis, UV-Visible, FT-IR spectral analysis and magnetic measurements.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

REFERENCES

1. H. Naeimi; M. Moradian, Efficient Synthesis and Characterization of Some Novel Nitro-Schiff Bases and Their Complexes of Nickel(II) and Copper(II), Journal of Chemistry, **2013**, 1, 1-8 http://dx.doi.org/10.1155/2013/701826 .
2. C. E. Xanthopoulos; M. P. Sigalas; G. A. Katsoulos; C. A. Tsipis; C. C. Hadjikostas; A. Terzis; M. Mentzafos, Synthesis and magnetic properties of a binuclear copper(II) complex with a.mu.-1,2-squarato coordination mode. Crystal structure of (a.mu.-1,2-squarato)bis[(N-(2-(diethylamino)ethyl]salicylidenaminato)aquacopper(II)] hydrate, Inorganic Chemistry, **1993,** 32 (17), 3743-3747.
3. S. Kumar, Studies on Heterobinuclear Complexes Derived from Rubidium and Caesium Salts of Acetyl Salicylic Acid (ASPIRIN) with N,N'-1,2-ethylenebis(5-nitrosalicylalaldiminato) Nickel(II), Oriental Journal of Chemistry, **2022**, 38(1), 193-197.
4. S. J. Gruber; C. M. Harris; E. Sinn, Binuclear Metal Complexes. XV. Copper(II) and Nickel(II) Complexes of Binucleating Ligands Derived From 3-Formyl-salicylic Acid and Diamines, Journal of Inorganic and Nuclear Chemistry, **1968**, 30, 1805-1830.
5. D. Prakash; A. K. Gupta; R. N. Shukla; A. K. Yadav, Mixed Ligand Complexes of Rb and Cs metal salts of some Organic acids with Picolinic Acid, Oriental Journal of Chemistry, **2002**, 18(2), 287-290.
6. D. Prakash; C. Kumar; S. Prakash; A. K. Gupta; K. R. R. P. Singh, Synthesis, spectral characterization and antimicrobial studies of some new binuclear complexes of Cu(II) and Ni(II) Schiff base, Journal of Indian Chemical Society, **2009**; 86(12): 1257–1261.
7. Elena Mas-Marz; Jose A. Mata; Eduardo Peris, Triazolediylidenes: A Versatile Class of Ligands for the Preparation of Discrete Molecules of Homo- and Hetero-Binuclear Complexes for Improved Catalytic Applications, Angew. Chem. Int. Ed., **2007**, 46, 3729 –3731
8. Brameshwar; A. K. Gupta; Poonam; B. Kumar, Binuclear Alkali Metal Complexes with Ni(II) & Cu(II) metal chelates of 2, 5 – Dihydroxy-1,4-Benzoquinone, Acta Ciencia Indica, **2015**, XLI C, 4, 183-188.
9. E. Pahontu; D.-C. Ilies; s. Shova; C. Paraschivescu; M. Badea; A. Gulea; T. Rosu, Synthesis, characterization, crystal structure and antimicrobial activity of Copper(II) complexes with the Schiff base derived from 2-Hydroxy-4- Methoxybenzaldehyde, Molecules, **2015,** 20(4), 5771– 5792.
10. S. Prakash; A. K. Gupta; S. Prakash; D. Prakash, Studies on some Hetero Binuclear Copper(II) Schiff Base Complexes, Oriental Journal of Chemistry, **2020,** 36(5), 955 - 959.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 14 Issue 08, August - 2025

11. C. Kumar, Synthesis, characterization and biological evaluations of heterobinuclear complexes of Cu(II) and Ni(II) Schiff base of ethylenediamine and o-hydroxyacetophenone with alkali metal salts of o-nitrophenol, Journal of Indian Chemical Society, **2017**, 94,857-861.
12. Fasina; M. Tolulope; O. Olorunfemi, Synthesis, Characterization and antimicrobial activity of some transition metal complexes of Schiff base derived from o-phenylenediamine and 5-nitrosalicylaldehyde, Der Pharma Chemica,**2014**, 6(4), 18-22.
13. W. J. Geary, Coordination Chemistry Review, 1**971**, 7, 81.
14. A. A. Ahmed; S. A. BenGuzzi; A. O. Agoob, Synthesis and Characterization of some N_2O_2 – schiff bases and their metal complexes, RASAYAN J. Chem., **2009**, 2(2), 271 – 275.
15. R.P.A. Bhoopathy; M. Malathy; R. Jayalakshmi; R. Rajavel, Synthesis, Characterisation, Magnetic interactions and Biological applications of Homo and Hetero Binuclear Schiff Base Complexes; International Journal of Pharmaceutical, Biological and Chemical Sciences, **2016**, 5(2), 11-22.
16. Fasina; Tolulope M.; Olorunfemi O., Synthesis, Characterisation and antimicrobial activity of some transition metal complexes of Schiff base derived from o-phenylenediamine and 5-nitrosalicylaldehyde, Der Pharma Chemica, **2014,** 6(4), 18-22.
17. F. S. Nworie, Bis(Salicylidene) Ethylenediamine (Salen) and Bis (Salicylidene) Ethylenediamine-Metal Complexes : from structure to biological activity, Journal of Analytical and Pharmaceutical Research, **2016**, 3(6), 1-10.
18. Aziz Ahmed; Ram Ashray Lal, Synthesis, characterization and electrochemical studies of copper(II) complexes derived from succinoyl- and adipoyldihydrazones, Arabian Journal of Chemistry, **2017**, 10(1), S901 – S908.
19. M H C Dewi; H Syaima; S Wahyuningsih; W W Lestari; S B Rahardjo, Synthesis and characterization of complex of copper(II) with Hydantoin, Journal of Physics: Conference Series, **2023**, 2556, 1 – 7.
20. U.Sani, Synthesis, Characterisation and Antimicrobial activity of Nickel (II) complexes with a Schiff base derived from salicylaldehyde and phenylhydrazine, Centrepoint Journal (Science Edition), **2011**, 17(2), 113-118.
21. A. Nagajothi; A. Kiruthika; S. Chitra; K. Parameswari, International Journal of Research in Pharmaceutical and Biomedical Sciences, **2012,** 3(4), 1768-1778.
22. Netral Pal Singh; Poonam Saini; Asvini Kumar; Krishna Kumar, Synthesis and spectroscopic characterization of some novel Schiff base complexes of Ru(III) and their biological screening, International Journal of Scientific and Engineering Research, **2014**, 5(3), 557-561.
23. Najla H. Taher; Akram A. Mohammed, Synthesis and Characterisation of some New Binuclear Complexes of Schiff Base as a Dibasic Tetradentate ligand, Iraqui National Journal of Chemistry, **2011**, 42, 207-216.
24. Shiva Shakti; P.M. Mishra; Satyendra Kumar Mishra; Ajay Kumar Jha, Synthesis and Characterization of Complexes of 2-Hydroxy-3-nitro acetophenyl thiosemicarbazone with Some 3d Series Transition Metals, Asian Journal of Chemistry, **2010**, 22(7), 5013 – 5018.
25. Vithal Jadhav; J. H. Deshmukh, Spectral study of Cu(II), Co(II) and Zn(II) metal ion complexes of Schiff Base, Journal of Emerging Technologies and Innovative Research, **2023**, 10(4), 9 – 11.
26. Ramadan M. Ramadan; Hadeel H. El-Shalakany; Mostafa A. Sayed, Structural and biomedical investigations of novel ruthenium schiff base complexes, Scientific Reports, **2025**, Article number: 18546, https://doi.org/10.1038/s41598-025-03147-9
27. Shuyeb Ahmad Khan; Sharad Saxena, Physico-chemical studies on titanium (III) complexes of polydentate Schiff bases, Oriental Journal of Chemistry, **2008,** 24(3), 1107-1110.
28. Abhay Nanda Srivastava; Netra Pal Singh; Chandra Kiran Shriwastaw, Synthesis and Characterisation of bioactive binuclear transition metal complexes of a Schiff base ligand derived from 4-amino-1H-pyrimidin-2-one, diacetyl and glycine, Journal of the Serbian Chemical Society; **2014**, 79(4), 421-433.