

Synthesis of Co (II) metal complex of 2-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenylpropanoic acid

Madhukar P. Shinde¹, Raghunath B. Toche^{1*}, Satish M. Chavan^{1,2}, P. J. Tambade³

¹Organic Chemistry Research Center, Department of Chemistry, K.R.T. Arts, B.H. Commerce and A. M. Science College, Shivajinagar, Gangapur Road, Nashik- 422 002, (MS), India.

²Department of Chemistry, R.N.C. Arts, J.D.B. Commerce and N.S.C. Science College, Nashik- (MS), India.

³Department of Chemistry, Arts, Science and Commerce College, Nandgaon.

Corresponding Author Email: raghunath_toche@rediffmail.com

ABSTRACT

Co (II) complex of 2-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenylpropanoic acid was synthesized from Co(OAc)₂ with the ligand in stoichiometric 1:1 ratio. This complex was characterized by analytical and spectroscopic methods.

KEYWORDS: 2-Hydroxy-1-naphthaldehyde, L-phenylalanine, Schiff's Base, Co (II) complex, Antimicrobial activity

INTRODUCTION

German chemist Hugo Schiff In 1864 [1] developed a new class of organic compounds and these active and well-designed organic compounds were designated as "Schiff Base Ligands" by Cozzi [2]. When α -amino acid was condensed with aldehyde to form Schiff base having azomethine ($-\text{RC}=\text{N}-$) linkage. The Schiff base metal complexes plays significant role in biology [3,4], analytical chemistry [5,6] and industry [7,8]. Schiff base ligand co-ordinated as tridentate ligand through phenoxy oxygen, carboxy oxygen and azomethine nitrogen atom. Fe (III) complex of 2-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenylpropanoic acid was prepared and structure of complex was demonstrated by physicochemical and spectral methods [9]. Bushra and co-workers prepared Vanadyl complexes by reacting Schiff base obtained from 2-hydroxybenzaldehyde and L-phenylalanine and found that complex is non-electrolyte but biological active [10]. Cu (II) complex of Salicylaldehyde-L-phenylalanine Schiff base was prepared by Mihela Mureseanu *et al* [11] and used as novel catalyst for oxidation of cyclohexane alongwith H_2O_2 . Rare earth inner transition metal Lanthanum (III) complex was prepared and octahedral geometry was predicted by S.D. Ballal *et al* [12]. A novel six coordinated Ru (II) complex was prepared by Jiao Geng *et al* from chiral bis-Schiff base ligand obtained from L-phenylalanine and terephthalaldehyde [13]. Fe (III) complex of Schiff base of L-phenylalanine was synthesized and catalytic performance at different reaction conditions were studied by S. Ahmed [14]. An eco-friendly synthesis of L-phenylalanine Schiff base in absence of organic solvent was done by A. Aghao [15].

In this paper we have focused on the synthesis and characterization of tridentate Schiff base ligand 2-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenylpropanoic acid obtained by condensation of L-phenylalanine with 2-hydroxy-1-naphthaldehyde. The ligand has been used to obtain Co (II) complex in 80-85% yield. This complex was characterized by analytical and spectroscopic methods.

MATERIALS AND METHODS

All reagents used were of analytical reagent type and were used without further purification. Analytical grade solvents were used without further purification. 2-Hydroxy-1-naphthaldehyde, L-phenylalanine, Cobalt acetate were purchased from Sigma Aldrich, Merck and Spectrochem chemicals. Melting points were determined on a Gallenkamp melting point apparatus. The ^1H (300 MHz) and ^{13}C (75MHz) NMR spectra were recorded on a Bruker Avance II 500 MHz Spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS), and multiplicities are given as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. EDS analysis was performed at CIF, SPPU, Pune-7. Mass spectra were recorded on a Shimadzu LC-MS:EI QP 2010A mass spectrometer with an ionization potential of 70eV. Elemental analyses were performed on Quest flash 1112 Series EA Analyzer at SAIF, Punjab University, Chandigarh. Reactions were monitored by thin layer chromatography (TLC), carried out on 0.2 mm silica gel 60 F₂₅₄ Merck plates using UV light (254 and 366 nm) for detection.

RESULTS AND DISCUSSION

IR Spectrum:

The characteristic vibrations of free ligand were shifted when it was reacted with metal to form complex. The IR spectrum of ligand showed band at 1624 cm^{-1} which is due to ($\nu\text{ C}=\text{N}$) confirming the formation of Schiff base [16]. The band of ($\nu\text{ C}=\text{N}$) at 1624 cm^{-1} in ligand was shifted to 1616 cm^{-1} in complex which indicate the coordination of azomethine group through its nitrogen atom [16]. The absorptions at 1597 cm^{-1} and 1405 cm^{-1} are attributed to asymmetric and symmetric ($\nu\text{ COO}$) bands respectively in the IR spectrum of ligand. These bands are shifted to lower frequency 1446 and 1396 cm^{-1} upon complexation. This indicates co-ordination of azomethine nitrogen and oxygen atom of carboxylate group to the metal ion.

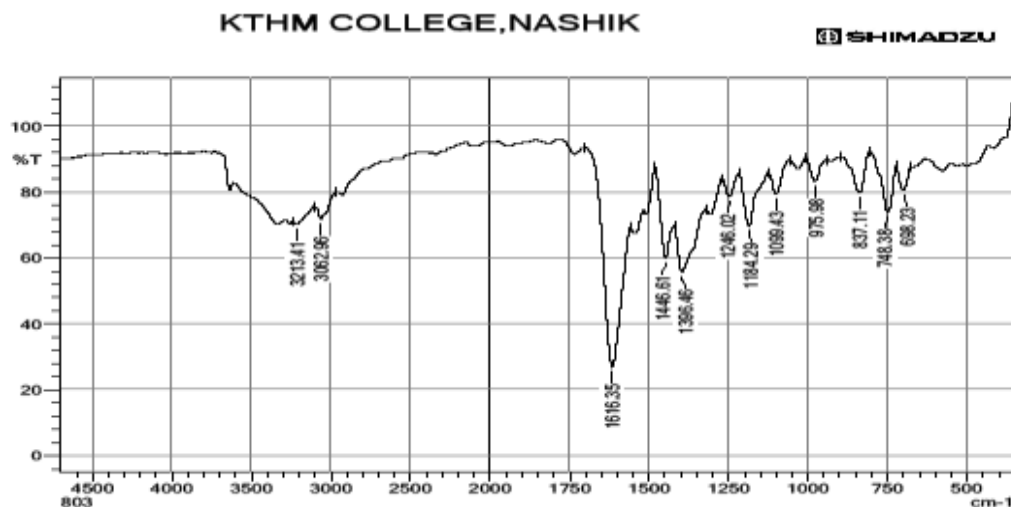


Fig. 1 IR spectrum of complex: $\text{C}_{40}\text{H}_{32}\text{CoN}_2\text{O}_6$

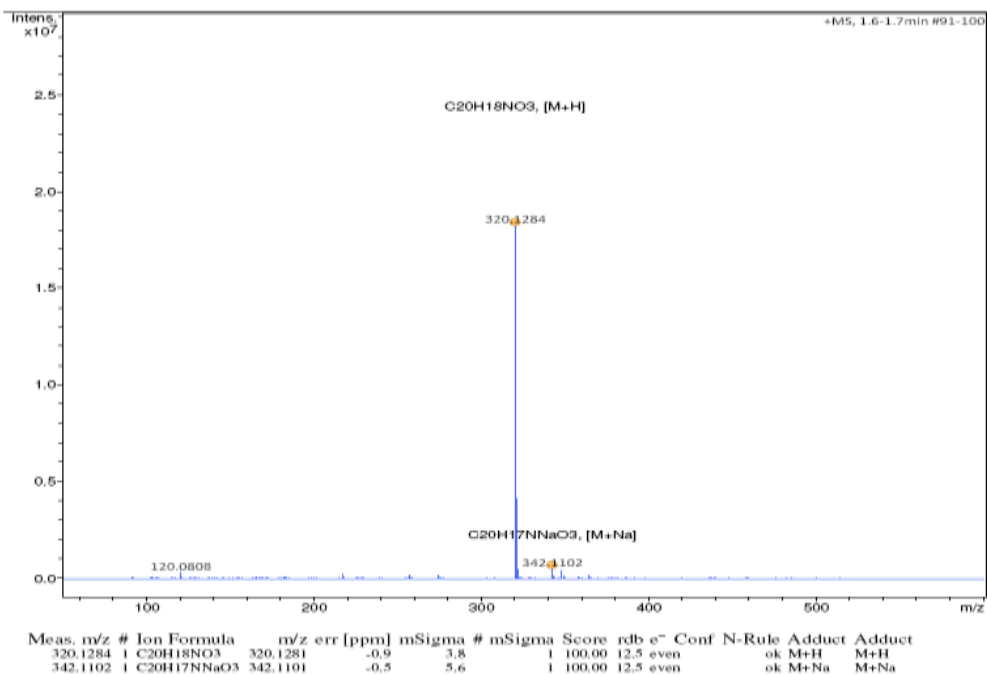


Fig. 2 Mass Spectrum of ligand

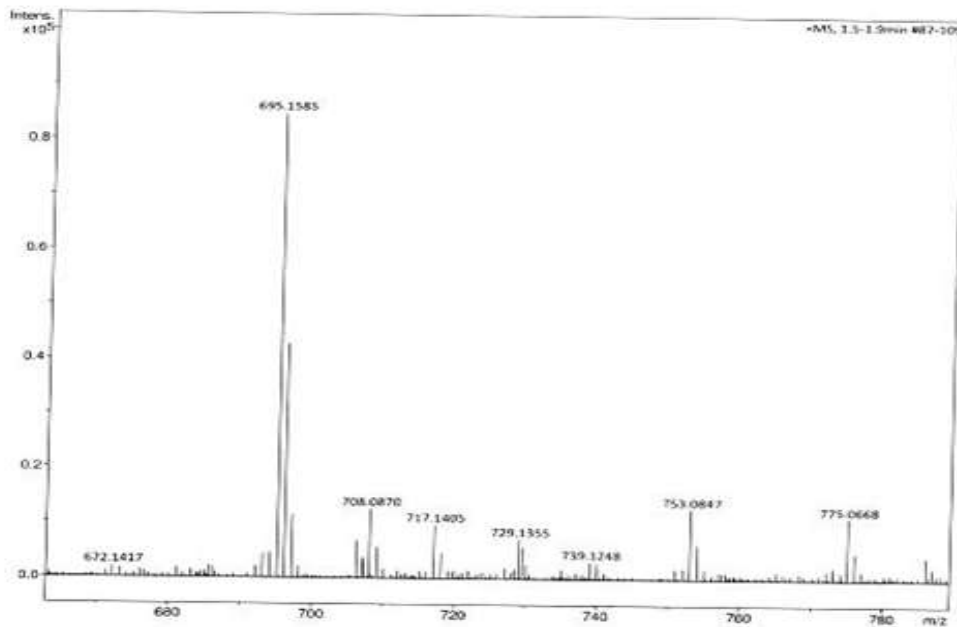


Fig.3 Mass Spectrum of complex: C₄₀H₃₂CoN₂O₆

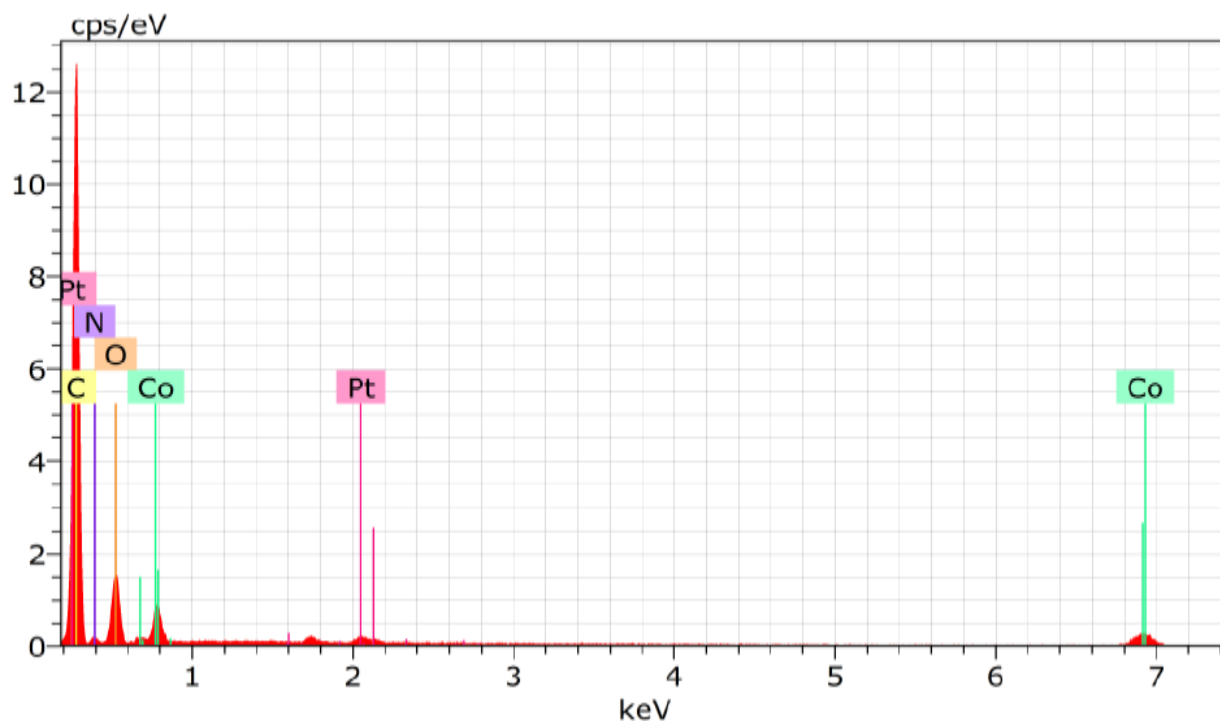
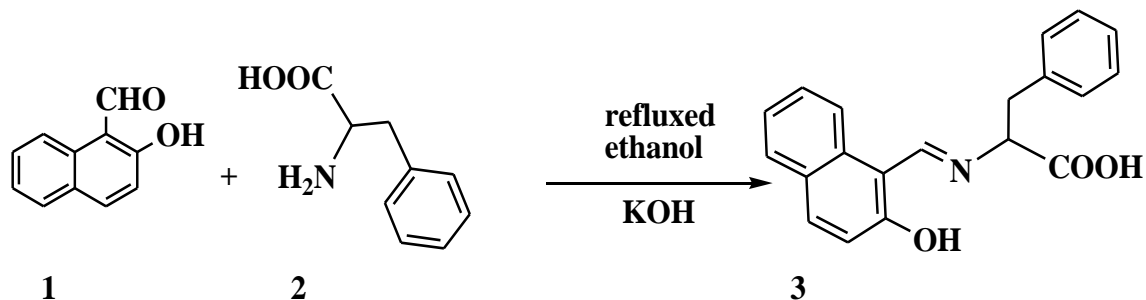


Fig. 4 EDS of complex: $C_{40}H_{32}CoN_2O_6$

EXPERIMENTAL

Synthesis of Schiff base ligand: (E)- 2-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenylpropanoic acid: ($C_{20}H_{17}NO_3$)

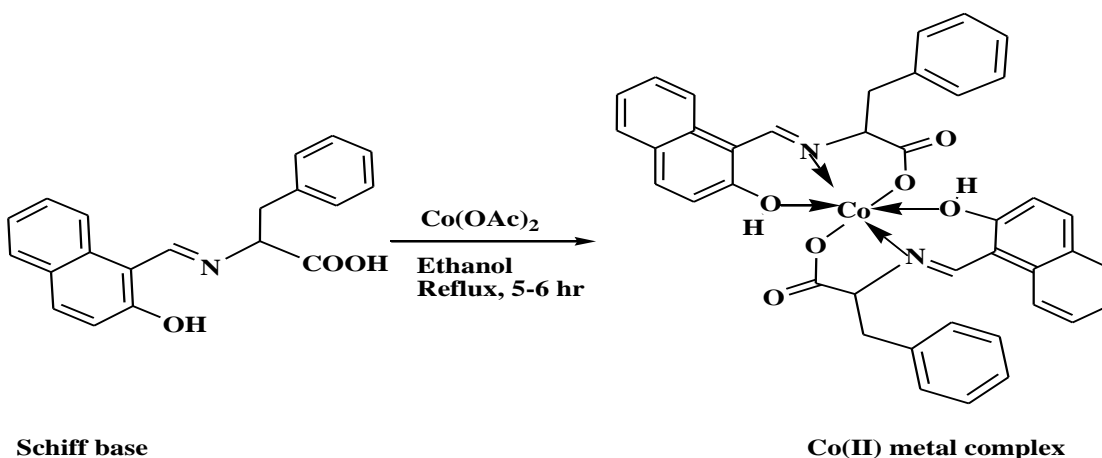
2-Hydroxy -1- naphthaldehyde (1.72g, 0.01 mol) was dissolved in 50 mL ethanol and stirred at room temperature and then it was added with stirring into 25 ml (0.0165g, 0.01 mol) L-phenylalanine containing 0.01 mol KOH. The reaction mixture was refluxed for about 3 hr. (**Scheme 1**) A yellow grain mass was separated, filtered and washed with anhydrous ethanol. It was recrystallized with methanol and then dried in vacuum over fused $CaCl_2$. The structure of ligand was determined on the basis of spectral and analytical data and compared to literature values [17]. Yield 80 %; m.p. 170°C (Decomposition) Lit m.p. 170 °C (Decomposition) [17]



Scheme 1: Synthesis of 2-hydroxy 1-naphthaldehyde based Schiff's base

Synthesis of complex: C₄₀H₃₂CoN₂O₆

M (II) complexes of this Schiff's base was synthesized having M: L stoichiometry 1:1. 0.01 M of cobalt acetate and Schiffbase (E)- 2-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenylpropanoic acid: (C₂₀H₁₇NO₃) in anhydrous ethanol (15 mL) was added with constant stirring in to the solution of 0.01 M solution of Schiff base and refluxed at 70 °C for overnight (**Scheme 2**). The red precipitate obtained after filtration was washed with ethanol and then with diethyl ether and dried in air



Scheme 2 Complex Formation Reaction of Schiff's base with transition metal

Spectral Data for complex: C₄₀H₃₂CoN₂O₆

Color: Red; Mol wt. 695.63; M.P. 232 °C; IR (KBr) ν cm⁻¹: 1616 (C=N), 1396 (COO⁻), 574 (M-N), 497 (M-O) MS (m/z): 695.16 Anal. Calcd C-69.06, H-4.64, N- 4.03 Co- 8.47 found C- 65.14, N-5.95, Co-8.81

CONCLUSION

The structural studies of the metal complex are discussed herein in the light of elemental analysis, 1H-NMR, IR, electronic spectra and mass spectra. It is concluded that the Schiff base coordinating through the azomethine nitrogen and carboxylate oxygen.

ACKNOWLEDGEMENT

The authors are thankful to UGC,WRO, Pune for financial support to this research project; Savitribai Phule Pune University, Pune, IIT, Powai, Bombay, SAIF, Punjab University, Chandigarh for spectral analysis and M.V.P. Samaj and Principal, K.R.T. Arts, B.H. Commerce and A. M. Science College, Shivajinagar, Gangapur Road, Nashik- 422 002, (MS), India for facilities.

REFERENCES

- [1] Schiff, H.; (1864), Ann. Suppl., 3, 343.
- [2] Cozzi. P.G.; (2004), Metal-Salen Schiff base complexes in catalysis: practical aspects, Chem. Soc. Rev., 33, 410.

- [3] Nath, M; Yadav, R. Spectral studies and in vitro antimicrobial activity of new organotin (IV) complexes of Schiff bases derived from amino acids. *Bull. Chem. Soc. Jpn.* 1997,70: 1331-1337
- [4] Cohan, Z.H.; Praveen, M; Ghaffar, A. Synthesis , characterization and biological role of anions (nitrate, sulphate, oxalate and acetate) in Co(II), Cu (II) and Ni (II) metal chelates of some Schiff base derived amino acids. *Synth. React. Inorg. Met.-Org. Chem.* 1998,28(10):1673-1687
- [5] Thankarajan, N; Mohanan, K. Potassium N-(2-hydroxy-1-naphthylidene)glycinate as gravimetric reagent for thorium (IV). *J. Indian Chem. Soc.* 1985, LXII: 81-82.
- [6] El-Brosy, A.M.; Al-Ghaman, S.M. High performance liquid chromatographic determination of some amino acids after derivatization with 2-hydroxy-1-naphthaldehyde. *Analyst* 1997,122:147-150.
- [7] Polbom, F.K; Robl, C; Beck, W. Metal complexes of biologically important ligands, LXXVIII. Synthesis of palladium complexes of ferrocenyl-substituted amino acid derivatives. *Can. J. Chem.* 1995, 73:1164-1174.
- [8] Tarafder, M.T.H.; Khan, A.R. Peroxo complexes of molybdenum (VI), tungsten (VI), uranium (VI), zirconium (IV) and thorium (IV) ions containing tri-dentate Schiff bases derived from salicylaldehyde and amino acids. *J. Indian Chem. Soc.* 1997, 74:489-491.
- [9] Al-Shaheen J. Amira Al-Mula A. Miaa. Schiff Base Complexes of Fe (III) Derived from Amino Acids. *Res. J. Chem. Sci.* 2014; Vol. 4(8): 25-32
- [10] Bushra K Al-Salami*, Amel H Mohammed and Kahtan A Askar. Synthesis & Characterization of New Schiff Bases Derived From 2-hydroxybenzaldehyde & Amino Acids and Their Vanadyl Complexes. *Res. J Pharm, Biol Chem Sci*, 2014, 5(4) :1457-1472
- [11] Mihaela Mureşeanu , Irina Georgescu , Livia Elena Bibire , Gabriela Cârjă. CUII (Sal-Ala)/MgAILDH and CUII(Sal-Phen)/MgAILDH as novel catalytic systems for cyclohexene oxidation by H₂O₂. *Catalysis Communications*, 2014, 54: 39–44
- [12] SD. Ballal, DG. Kolhatkar and MN Deshpande. Synthesis and spectroscopic characterization of la(iii), ce(iii) metal complexes with phenylalanine. *Int J Res Pharm Chem*, 2016, 6(4): 806-810
- [13] Jiao Geng , Kun Zhang , Yu-Xin Peng , Li Wang,Wei Huang. A ruthenium(II) complex having a ligand undergoing partial C = N cleavage and unusual double-bond shift and nonchirality. *Inorganic Chemistry Communications* 40 (2014) 112–115
- [14] S. Merajuddin Ahmed, Ahmed T. Mubarak, M. Mujahid Alam and Halima A. Al-Ahmari. Cyclohexane Oxidation: Synthesis of Iron (III)-Amino Acid and Amino Acid Schiff Base Complexes and Their Catalytic Activity Evaluation. *American Chem Sci Journal*, 2014,4(5): 600-615
- [16] Arvind K. Aghao, Dnyandeo M. Janrao and Siddharth D. Janrao. Synthesis and characterization of some novel schiff base ligands derived from 3- hydroxyquinoxaline-2-carboxaldehyde. *Der Chemica Sinica*, 2015, 6(3):68-72
- [17] Hasan A. E., Transition metal complexes of bidentate ligand N-aminoquinolino -2-one and anthranilic hydrazide, *Res. J. Chem. Sci.* (2013), 3(12), 50-53
- [18] Laila H. Abdel-Rahman a Rafat M. El-Khatib , Lobna A.E. Nassr, Ahmed M. Abu-Dief
- [19] Fakhr El-Din Lashin. Design, characterization, teratogenicity testing, antibacterial, antifungal and DNA interaction of few high spin Fe(II) Schiff base amino acid Complexes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 111 (2013) 266–276