International Journal of Chemistry Studies
ISSN: 2581-348X; Impact Factor: RJIF 5.44
Received: 03-09-2020; Accepted: 17-09-2020; Published: 06-10-2020
www.chemistryjournal.in
Volume 4; Issue 4; 2020; Page No. 04-06

Studies of newly synthesized Ni (ii) complex with ligand acid hydrazide

Dhirendra Kumar Chaudhary[1*], **Babu Nand Chaudhary**[2]
[1] Research Scholar, Department of Chemistry, LNMU, Darbhanga, Bihar, India
[2] Associate Professor, Department of Chemistry, MLSM. College, Darbhanga, Bihar, India

Abstract

In this paper, a coordination compound with transition metal Ni (II) has been prepared by the reaction between selected transition metal ions Ni (II) with newly synthesized acid hydrazide ligand. Thereafter, solubility, melting point, conductivity and spectral analysis have been studied. After analysis four coordinated square planar structure of the complex has been confirmed.

Keywords: Schiff base, acid hydrazide, spectral analysis.

1. Introduction

A Schiff base named after Hugo Schiff [1]. is a compound with the general structure as:

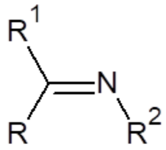

Fig 1

Schiff bases are common ligands in coordination chemistry. The imine nitrogen is basic and exhibits π-acceptor properties. The ligands are typically derived from alkyl diamines and aromatic aldehydes [2].

In this paper, we have reported, transition metal Ni (II) complex of Schiff base derived from salicylaldehyde and derivatives of benzoic acid hydrazide.

Materials and Methods

Preparation of Ligand

Reacttion Scheme

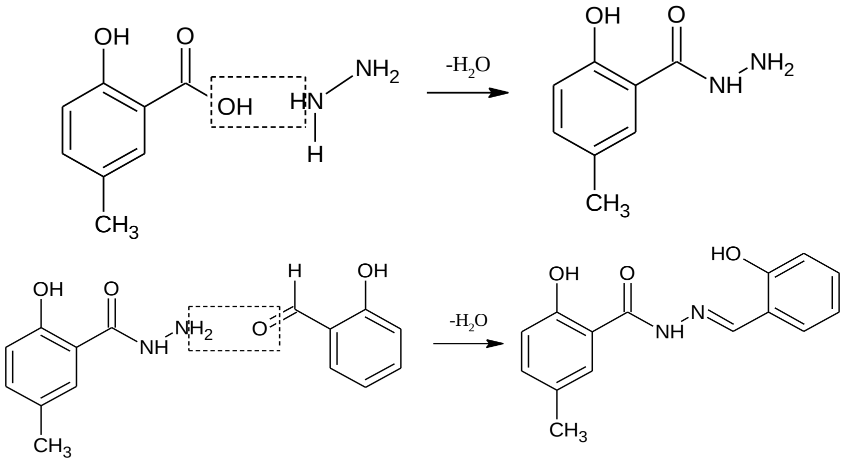

Fig 2

Procedure

At first 2-hydroxy-5-methylbenzoic acid hydrazide was prepared. In order to obtain this acid hydrazide, stoichiometric amount of 5-chloro-2-hydroxybenzoic acid was carefully added to a stirred pre-warmed methanolic solution of hydrazine. The reaction mixture was refluxed at 70 °C for 2 h in a closed system. Consequently, the resultant mixture was cooled to room temperature and then concentrated to a volume of 20 ml. The solid product formed was recovered by filtration, washed with methanol and dried in a desiccator over anhydrous $CaCl_2$ at ambient temperature. The resulting pale yellow coloured solid was filtered. The solid was washed with ethanol three times repeatedly. The purity of ligand was checked by elemental analysis and melting point.

Preparation of Acid hydrazide Solution

A 0.05 M methanolic solution of 2-hydroxy-5-methylbenzoic acid hydrazide was prepared by adding 0.405 g of 2-hydroxy-5-methylbenzoic acid hydrazide in 50 ml of methanol.

Preparation of hydrazine Solution

A 0.05 M methanolic solution of 2-hydroxybenzaldehyde (salicylaldehyde) was prepared in 50ml of methanol.

Preparation of Complex

Stoichiometric amount of 2-hydroxy-5-methylbenzoic acid hydrazide was carefully added to a stirred pre-warmed methanolic solution of 2-hydroxybenzaldehyde (salicylaldehyde). The reaction mixture was refluxed at 70 °C for ~2 h in a closed system. Consequently, the resultant mixture was cooled to room temperature and then concentrated to a volume of 20 ml. The solid product formed was recovered by filtration, washed with methanol and dried in a desiccator over anhydrous $CaCl_2$ at ambient temperature. The resulting yellow coloured solid was filtered. The solid was washed with ethanol three times repeatedly. The purity of ligand was checked by elemental analysis and melting point. It was also characterized by IR and ^{1}HNMR spectral studies.

Table 1: Elemental analysis of the compound is given as

L	% of C	% of H	% of N
Calculated	66.67	5.18	10.37
Found	66.38	5.09	10.19

Preparation of Complex

Preparation of Solution

A methanolic solution of transition metal Ni (II) chloride of 0.5 M strength was prepared by mixing appropriate amount of Ni (II) chloride in 10 ml of ethanol in a dried beaker with continuous stirring. A methanolic solution of ligand N^1-salicylidene-5-methyl-2-hydroxybenzoicacid hydrazide (L) of 0.5 M strength was prepared by mixing 1.35 g of ligand with 10 ml of ethanol in a dried beaker with continuous stirring.

Both solutions were filtered to remove any insoluble residue left.

Preparation of complex

A warm stirred methanolic solution (30 ml) of the ligand (0.01mol) was added in a 250 ml round bottom flask containing the metal (II) salt solution and fitted with a water condenser in a dropwise manner. The mixture was stirred vigorously for 20 minutes and refluxed over a steam bath at 70 °C for 2 hours. Consequently, the resultant solution was left overnight in a fume cupboard at ambient temperature until all traces of the solvent had evaporated. The solid formed, washed with methanol and dried over anhydrous calcium chloride in a vacuum desiccator. The yellowish blue precipitate was washed successively with distilled water, ethanol, and diethyl ether.

Table 2: Elemental analysis

	% of Ni	% of C	% of H	% of N
Calculated	16.16	49.56	3.58	7.71
Found	16.01	49.24	3.51	7.61

Results and Discussion

The transition metal Ni (II) complex of ligand N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide is anhydrous as supported by analytical and spectral studies. The complex is soluble in acetone, DMSO and DMF and insoluble in Water, alcohol and ether. The molar conductance of the complex has been recorded in nitrobenzene in digital systonic conductivity meter-304. The complex is non electrolytic in nature because it showed very low value of its molar conductance. Magnetic moment of the complex is in good agreement with the theoretical value calculated by Van-Vleck. Analytical data, magnetic moment, molar conductance and color of the complex are given in following table.

Table 3

Complex with L^2	Colour	Boiling point (^{0}C)	Λ_m (Ohm^{-1} cm^2 mol^{-1})	Ìeff (in B.M.)
[Ni(L)Cal]	Green	210	7.5	Dia.

IR Spectral Analysis

The infrared spectrum of the ligand N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide showed that the vibrational frequency due to the phenolic OH group that appeared in the spectrum of the ligand at 3558 cm^{-1} for N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide had disappeared in the spectrum of the complex. This may be due to the displacement of its proton during the condensation process of complex formation [9].

The ν (NH) of the uncoordinated NH groups appeared as a shoulder at 3270 cm^{-1} in spectra of the ligands N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide and at 3350 cm^{-1} in spectra of the Ni (II) complex[10]. The IR spectra of the free ligand show the characteristic >C=N (azomethine group) bands in the 1625 cm^{-1} region which are shifted to lower frequencies in the spectra of the metal complex (1575 cm^{-1}) [11].

This ν(C=N) shift to in the complex by about 35 cm^{-1} indicates the involvement of azomethine nitrogen in the coordination sphere with the metal ions for all the complexes as well as lack of carbonyl group from original substituted benzohydrazide compound [12].

The stretching vibration of the phenolic ν(C-O) observed at regions 1225 cm^{-1} in the free ligands undergo a hypochromic shift to 1317 cm^{-1} regions in the complexes upon complexation.

This shifts further confirms the coordination of the phenolic oxygen leading to the formation of C-O-M bond [13]. (where M= Fe^{2+}). The vibrational frequency at 1695 cm^{-1}, is due to carbonyl stretching vibration in the ligand N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide molecule. This carbonyl frequency is shifted downwards in the spectra of transition metal Ni (II) complex indicating the coordination has taken place through oxygen atom of C=O group [14].

Further, the appearance of new bands at 839 cm^{-1} and 815 cm^{-1} suggests ν(M-O) and ν(M-N) linkage, respectively [15]. The bands observed at ~1576 cm^{-1} is due to the ν(C-C) stretching of the aromatic ring systems. In the metal Schiff base complex, most of the bands shift observed in the wave number region 1379-1436 cm^{-1} and 1240-1259 cm^{-1} are in agreement with the structural changes observed in the molecular carbon skeleton after complexation [16]. Which cause some changes in (C–C) bond lengths.

Valuable evidence concerning the environment of the functional group's coordination to the metal atoms through azomethine nitrogen and phenolic oxygen atoms has been obtained from the FT-IR spectra.

Conclusion

IR analysis of the ligand indicates that the ligand N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide behaves as uninegative tridentate ligand having coordinating sites phenolic oxygen, carbonyl oxygen and azomethine nitrogen. The coordination sites may be shown as:

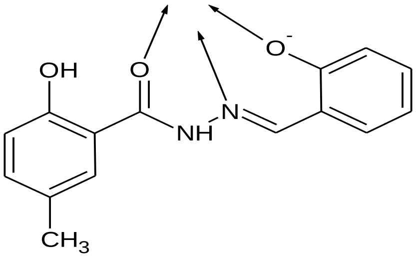

Fig 3

The analysis of electronic spectrum of the complex formed by the ligand N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide with Ni (II) ion indicates that the complex is four coordinated square planar geometry. Further, elemental analysis indicates that the complex is formed by 1:2 ratios of the metal Ni (II) and ligand N^1-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide. Thus the structure of the newly synthesized complex may be shown as:

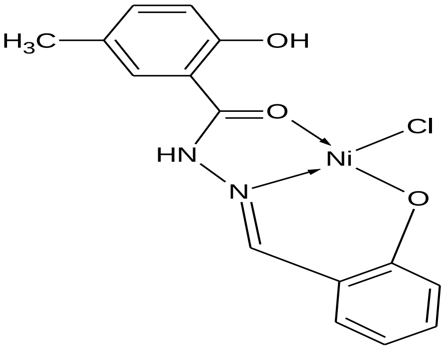

Fig 4

References

1. S Patai Ed. "The Chemistry of the Schiff Base," Interscience, New York, N.Y, 1997.
2. Chudek Foster, Young J. Chem. Soc, Perkin Trans, 1985; 2:1285.
3. Eliot AC, Kirch JF. Annual Review of Biochemistry. 2004; 73:383-415.
4. Frost A, Musulin BJ. Chem. Phys. 1953; 21:572.
5. Nozaki H, Takaya H, Moriceti S, Noyori R. Tetrahedron. 1968; 24(9):3655-3669.
6. Uribe FJ, Am J. Chem. Soc. 1975; 131, 13:4570-4571.
7. Zimmerman HE. Tetrahedron. 1982; 38:753-8.
8. Parsaee Z, Mohammadi KJ. Mol. Struct. 2017; 1137:512-23.
9. Kher SK, Sahni Kumari V, Kapoor RN, Inorg. Chem. Acta. 1979; 37:121.
10. Divaria M, Orioli PL. Acta Crystallogr, Soc. 1968; 24:1269.
11. Wester D, Palenik GJ, Am J. Chem. Soc. 1973; 95:6505.
12. Figgis BN, Hitchman MA. Ligand Field Theory and its Applications, Wiley-VCH, New York, 2000, 181-183.
13. Peter Atkins, Julio de Paula. Physical Chemistry, 9th ed., Oxford Univ. Press, 2010, 521.
14. Burger K. Coordination Chemistry Experimental Methods; Butterworth, London, 1973.
15. Nyholm RS, Inorg J. Nucl. Chem, 19588, 401.
16. Perguson J. Rev. Pure and applied Chem, 1964, 14.