Study of pH dependent coordination behaviour of some pyrazine derivative

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Abstract:-

The coordination complexes of Co (II) and Ni (II) were prepared from bidentate Schiff base. The Schiff base ligand was synthesized by the condensation of thiosemicarbazide and pyrazine-2-carbaldehyde in an alkaline medium. The ligand and its complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, solubility, infrared and ESR.The metal-ligand found to be 1 :2 in all the metal complexes. The magnetic susceptibility revealed that all the complexes are paramagnetic in nature. The infrared spectra suggested that the Schiff base behaves as bidentate ligand and coordinate with nitrogen and sulphur atoms. The molar conductivity data of the complexes in DMF indicate they are non-electrolytes. On the basis of magnetic susceptibility and electronic spectral study, geometry of complexes was proposed to be octahedral.

Keywords: - Semi carbazide, pyrazine-2-carbaldehyde, metal salts, Schiff base.

INTRODUCTION

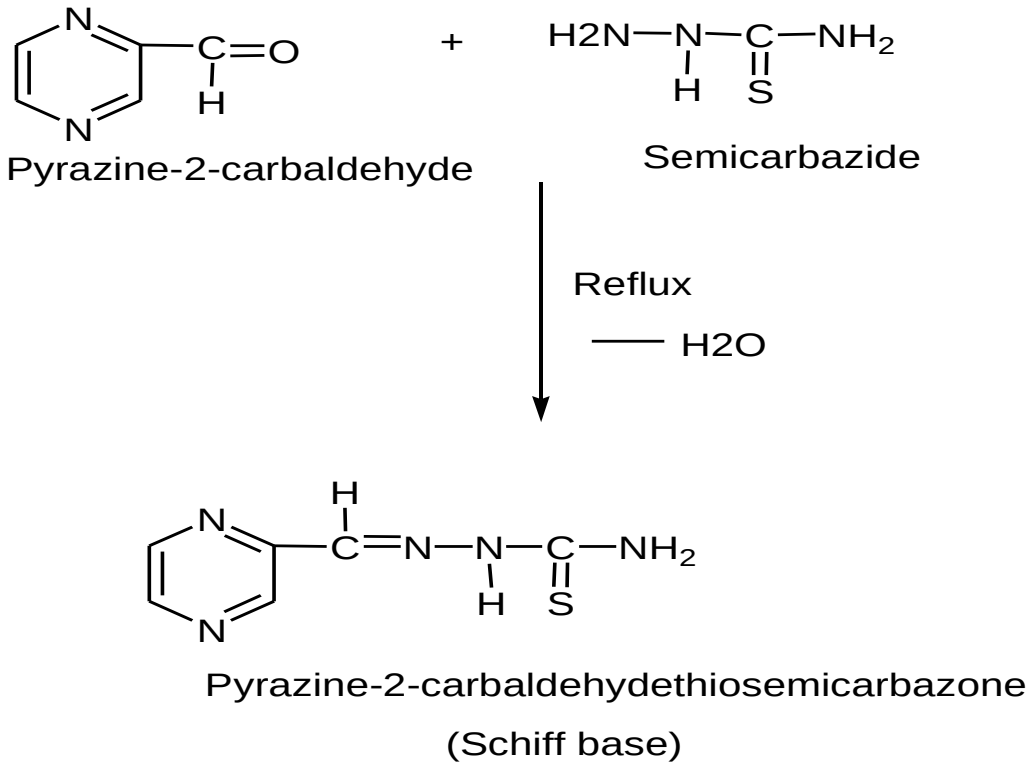
Schiff bases are the most important class of organic compounds synthesized from the condensation of a primary amine with active carbonyl compounds. Schiff bases may be represented as R─CH═N─R′ where R and R′ may be alkyl, aryl or heterocyclic. Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes due to effective conjugation. Plants and animals require Cu for normal growth and metabolism. Schiff bases and their metal complexes are used in catalyst, antimicrobials, antioxidants, dyes optical materials and analytical chemistry. Vanillin is used as flavoring agent in sweet foods and beverages. Due to chelation transition metal Schiff base complexes are more stable and have wide applications in antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory. Schiff base ligands acts as chelating ligands and their biological activity enhanced on coordination. Pyrazines are most important classes of heterocyclic compounds that can be obtained naturally or can be synthesized chemically. Pyrazine is a weaker base than pyridine and pyrimidine. Pyrazine and alkyl pyrazine are flavour and aroma compound found in baked and roasted goods. Pyrazines gained attention from the food industry as important ingredients in raw and roasted foods. I report here the Study of pH dependent coordination behavior of some pyrazine derivative.

MATERIALS AND METHODS

The chemicals used in the present work were of Anal-R grade and were used without further purification. The elemental analysis (C, H, N and S) data was obtained using CHNS Perkin-Elmer elemental analyzer. The molar conductivity of the complexes in DMF solution (10^{-3}M) were measured by using DI-909 digital conductivity meter. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR spectrophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using Hg [Co (SCN)$_4$] as a calibrant. The electronic spectra of the complexes were recorded by using Shimadzu model UV-1601 spectrophotometer in DMSO solution.

Synthesis of Schiff base Ligand:

The Schiff base ligand pyrazine-2-carbaldehyde thiosemicarbazone was prepared by the condensation of pyrazine-2-carbaldehyde with semi carbazide in an alkaline medium. The reaction mixture was refluxed for 2-3 h. The resulting solution produced faint orange crystalline solid on cooling in the freezer. The melting point of Schiff base ligand was obtained to be 54^0c. The compound found to be stable at upon storage.



Synthesis of metal (II) Complexes:

The metal (II) complexes were prepared by mixing (50 ml) ethanolic solution of metal (II) chlorides with the (50 ml) ethanolic solution of Schiff base in a metal-ligand ratio 1:2. The resulting mixture was refluxed on water bath

for 2-3 h. The complex obtained in each time was cooled, filtered and washed with acetone and recrystallized with ethanol and dried over anhydrous KOH in a desiccator.

RESULTS AND DISCUSSION

The analytical and physical properties of Schiff bases and their metal (II) complexes are given in Table-1. The spectral, analytical, theoretical and magnetic data validated the molecular formula and structures of the synthesized Schiff base ligand and metal (II) complexes. All metal (II) complexes are coloured and stable in air. All experimental data obtained strongly confirmed with theoretical data and were in agreement with suggested elemental analysis for all the synthesized complexes. The metal ligand ratio in all the metal complexes have 1:2. Molar conductance and magnetic moment data of metal (II) complexes are given in Table 2. The lower molar conductance values of metal (II) complexes in DMF solution indicate their non-electrolytic in nature. All metal (II) complexes are paramagnetic in nature due to unpaired electrons present in d-orbital of metal (II) ion.

The I.R spectral data of Schiff base ligand and metal (II) complexes are given in Table 3. The band appeared at 1620 cm^{-1} is characteristics of the azomethine group present in the Schiff base ligand. This band was shifted to lower frequency (1590 – 1595 cm^{-1}) in all the metal (II) complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. A broad band at 1230 cm^{-1} is present in pyrazine ring of Schiff base ligand and it remains unshifted in the metal complexes, which indicates nitrogen atoms of pyrazine ring is not involved in coordination to the metal ion. A sharp band due to ν(C-S) furan appears at 1020 cm^{-1} in the Schiff base, which shifted to lower frequency (980 – 1000 cm^{-1}) in all the metal (II) complexes, which indicates the coordination of the thiosemicarbazone sulphur to metal ion in complexes.

Table 3. IR spectral data of Schiff base ligand and its metal (II) complexes

Compounds	ν(C=O)	ν(C=N)	ν(C-S)
Schiff base	1670	1620	1020
$[Co(L)_2Cl_2]$	-	1590	980
$[Ni(L)_2(OAc)_2]$	-	1595	1000

The electronic absorption spectra of metal (II) complexes recorded in DMF solution. The electronic spectra of the Co(II) Complex shows three bands at 12660, 16425 and 19610 cm^{-1} assigned to $4T_{1g}(F) \rightarrow 4T_{2g}(F)$, $4T_{1g}(F) \rightarrow 4A_{2g`}(F)$ and $4T_{1g}(F) \rightarrow 4T_{1g}(P)$. These data and the magnetic moment value of 4.82 B.M, which suggested the octahedral geometry of Co(II) complex. The Ni (II) complex shows three bands at 10480, 12682 and 19650 cm^{-1} assigned $3A_2g(F) \rightarrow 3T_{2g}$,$3A_{2g}(F) \rightarrow 3T_{1g}(F)$and $3A_{2g}(F) \rightarrow 3T_{1g}(P)$ .These data and the magnetic moment value of 2.88 B.M, which suggested octahedral geometry of Ni(II) complex.

CONCLUSION

The Schiff bases derived from pyrazine-2-carbaldehyde and thiosemicarbazide have been synthesized. The metal complexes were characterized by micro elemental analysis, molar conductivity, magnetic susceptibility, FTIR, and electronic absorption spectra. The metal (II) complexes are coloured and stable in air. In the metal complexes the

metal -ligand ratio found to be 1:2. The magnetic susceptibility revealed that all the complexes are paramagnetic in nature. The infrared spectra suggested that the Schiff base behaves as bidentate ligand and coordinate with nitrogen and sulphur atoms. The molar conductivity data of the complexes in DMF indicate they are non-electrolytes. On the basis of magnetic susceptibility and electronic spectral study, geometry of complexes was proposed to be octahedral.

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