

Mannich Bases and their Metal Complexes: A Review

Abstract

It is well known that Mannich bases and their transition metal complexes play a very important role in the field of coordination chemistry because of their wide range of applications in various fields. An attempt has been made to present a categorical and summarized review of literature on various parameters and analytical measurements which were used for the structural and spectral studies of the Mannich bases and their metal complexes has been discussed in this chapter.

Keywords: Mannich Bases, Metal Complexes, Transition

Introduction

A detailed survey of literature on magnetic measurements, ultraviolet, mass, NMR, infrared, electronic, ESR, X-ray spectral studies and antimicrobial studies of Mannich bases and their transition metal complexes is reviewed as follows:

Magnetic Measurements

The study of magnetic properties of materials is a basic requirement for understanding electronic behavior in condensed matter¹. The study of these interactions among electrons requires magnetic measurement at low temperatures and high magnetic fields.

Many types of magnetometers have been developed and are now commercially available. They have been extensively reviewed by *Foner*²⁻³ and can be divided into two categories: (i) those employing direct techniques (Guoy, Faraday, Kahn balances); (ii) those based on indirect techniques. The vibrating sample magnetometer (VSM) developed originally by *Foner*³, has however, been the most successful for low temperature and high magnetic field studies of correlated electron systems due to its simplicity, ruggedness, ease of measurement and reasonably high sensitivity.

*Nyholm*⁵, *Mitra*⁶ and *Figgis*⁴ have discussed the magnetic measurements of first row transition metal ions in detail earlier. The theories advanced by *Van-Vleck*⁷, *Pauling*⁸ and *Kotani*⁹ appear to provide reasonable explanation for low moments in terms of increased orbital coupling in compounds of heavy metals. *Konig et al.*¹⁰ have also presented the complete theory of paramagnetism in transition metal ions for various electronic configuration in cubic and lower symmetry fields.

*Agarwal and Lal*¹¹ synthesized ternary complexes of nickel (II) and cobalt (II) with Mannich base ligand 8-aceto-7-hydroxy-4-methyl-6-(p,p'-amino phenyl) amino methyl coumarin as primary and β mercapto resorcylic acid and thiosalicylic acid as secondary ligand. The *magnetic moment* and spectral data suggested an octahedral configuration for these complexes.

*Pancholi and Joshi*¹² synthesized chromium (III) complexes from 2-amino-4-phenylthiazole or 2-amino-5-methyl-4-phenylthiazole and bromosalicylaldehyde. These complexes were characterized by using elemental analysis, *magnetic susceptibility measurements*, electronic and infra-red spectral studies. On the basis of these studies, octahedral geometry has been assigned for these complexes. Recently *Nakamura et al.*¹³ and *Patel et al.*¹⁴ also reported the high spin octahedral manganese (II) complexes having the magnetic moment values in the range of 5.7-5.9 B.M.

*Agarwal et al.*¹⁵ synthesized cobalt (II) and nickel (II) complexes of 4[4-(4-dimethylaminobenzalidene) amino]antipyrine and characterized them by spectral, *magnetic* and thermal studies. *Agarwal and Kumar*¹⁶ studies the cobalt (II) complexes of Mannich base derived from 3-(dimethylaminomethyl) indole and vertraldoxime. The *magnetic moment*



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value for their complexes is 4.21 B.M., which is less than the spin only value.

*Kavlakoglu et al.*¹⁷ synthesized copper (II) complex of pentadentate binucleating ligand. *Magnetic susceptibilities* of the complexes in the solid state were measured over the temperature range 4.6-308K. The observed and calculated magnetic moments decrease from a value of 2.57 B.M. at 308K to 0.25 B.M. at 4.6K, indicating a moderate intramolecular antiferromagnetic exchange interaction.

Ultraviolet Spectral Studies

Ultraviolet absorption spectroscopy¹⁸ deals with the measurement of energy absorbed when electrons are promoted to higher energy levels. An ultraviolet spectrum is eventually a graph of light absorbance versus wavelength in the range of ultraviolet region. Such a spectrum can often be produced directly by a more sophisticated spectrophotometer.

The importance of ultraviolet spectroscopy in functional group analysis is limited by the fact that the spectrum contains only a small number of bands. Its advantage over infrared spectra is the higher sensitivity, which permits the examination of very dilute solutions¹⁹.

*Lawska et al.*²⁰ synthesized Mannich bases and assessed their acid-base equilibria by *ultraviolet spectroscopy*. Results were discussed on the basis of intramolecular interactions between different substituents in phenol ring and protonation of the methylamino groups in amino acids.

The intermolecular proton transfer in Mannich and Schiff bases was studied by *Koll*²¹ with the help of *ultraviolet-visible* spectra. He reported that the proton transfer tautomer in Schiff bases have a different type of chromophore than in Mannich bases, where $-CH_2-$ group prevents direct coupling between acid and base centre.

*Abid and Azam*²² synthesized a series of 21 new 1-N-substituted cyclised pyrazoline analogues of thiosemicarbazones by cyclisation of Mannich bases with thiosemicarbazides of variegated nature. The chemical structure of the compounds were proved by UV, IR, ¹H-NMR, ¹³C-NMR spectroscopic data and elemental analyses.

*Joshi and coworkers*²³ synthesized Mannich bases with heteroaromatic ring system employing Mannich reaction of isonicotinyl hydrazide with various sulphonamides/secondary amines. They were analyzed by elemental analyses and characterized by UV, IR, ¹H-NMR spectroscopic studies.

Mass Spectral Studies

Mass spectroscopy is a name for a collection of techniques that are used to measure the abundance and masses of ions in the gas phase. The term mass spectroscopy is now a misnomer. It came about because the early data were collected as images on photographic plates and looked like spectra, with a number of separate parallel lines on the film.

The structure of the new products were confirmed by NMR, elemental analysis, X-ray and *mass spectral data*. *Verma and Rastogi*²⁴ carried out

Mannich reaction in the presence of formaldehyde and various heterocyclic secondary amines on indolinones. Their structure were established on the basis of elemental analysis, IR, NMR and *mass spectral studies*.

*Wang and coworkers*²⁵ synthesized seven Mannich bases by the reaction of 3-pyridyl-4-amino-5-marcato-1,2,4-triazole with aromatic aldehydes and furfuraldehyde. All the prepared compounds in the *mass spectra* revealed the predominant fragmentation resulting in the formation of ion at $m/z = 178$ as the strongest spectral line.

*Farghaly et al.*²⁶ prepared three novel series of pyrazolo[3,4-b]quinolines. The structure of these Mannich bases were elucidated by elemental analyses, IR, ¹H-NMR and *mass spectral studies*²⁷.

Nuclear Magnetic Resonance Spectral Studies

Nuclear magnetic resonance (NMR) spectroscopy is probably the single most important physical tool available to the chemist today. The concept that nuclei possess a magnetic moment was proposed by *Pauli*²⁸ in 1924 to account for the hyperfine structure observed in atomic spectral lines.

The successful use of NMR spectroscopy as an analytical tool depends upon the extraction of the fundamental parameters from the spectrum. The analysis of an NMR spectrum in terms of the chemical shifts and coupling constants is the most important step in the application of NMR spectroscopy.

*Pandeya et al.*²⁹ synthesized Mannich bases of norfloxacin by reacting them with formaldehyde and several isatin derivatives. Their chemical structures have been confirmed by means of IR, ¹H-NMR data and elemental analysis.

*Birader et al.*³⁰ synthesized the transition metal complexes of N-salicylideneaniline-4-sulphonamide which were characterized by elemental analysis, IR and PMR data. The PMR spectra of ligand showed a sharp singlet at δ 12.80 ppm due to phenolic OH, multiplet in the region δ 6.7 to 8.0 ppm due to aromatic protons and singlet at δ 3.21 ppm due to NH₂ proton of sulphonamide groups. On complexation these peaks were shifted upward indicating the coordination of ligand through metal ion.

*Suyaji and coworkers*³¹ studied the NMR spectra of cobalt (II) complexes of benzoic acid [(furan-2-yl)methylene]hydrazide. The ¹H-NMR spectra were recorded in CDCl₃ and showed few field signals respectively at δ 11.23, δ 11.35, δ 9.03 and δ 8.9 ppm for various protons present in the ligand. The resonance signal due to CH₃ protons presenting the ligand occur at δ 2.38 ppm respectively.

Infra-Red Spectral Studies

Infra-red spectroscopy is another one of the most successful analytical method which offers the possibility of chemical identification. The infra-red spectra of organic and inorganic is mainly divided into three general regions: functional group region (4000-1500 cm⁻¹), fingerprint region (1500-650 cm⁻¹) and aromatic region (650-200 cm⁻¹). The spectrum is usually most complex in the region 1500-650 cm⁻¹ ranges. Identification of all bands is usually not possible and commonly is not attempted.

The region between 200 and 650 cm^{-1} is also useful for inorganic and organometallic compounds. The vibrations involving metals and metal ions occur in that region. *Nakamoto*³² has given a detailed account of the characterization of metal organic and organometallic complexes using *infra-red spectral data*.

*Comainta and coworkers*³³ synthesized Mannich bases from ortho-hydroxyacetophenones. Most of the Mannich bases were transformed into oximes by treatment with hydroxylamine hydrochloride. The *IR spectra* of Mannich base exhibit an intense absorption band at 1640-1650 cm^{-1} due to the involvement of the carbonyl group in an intramolecular hydrogen bond with the neighbouring phenolic hydroxy group.

*Joshi and Khosla*³⁴ synthesized some Mannich bases of sulphonamides and nicotinamides showing *IR bands* at 3450, 3100, 1660, 1600 and 1385 cm^{-1} respectively which were assigned to amino group of sulphonamide, C-H of pyridine nucleus, C=O group of amide, NH of -CONH group and S=O group of sulphonamide.

*Kamalakanan and Venkappaya*³⁵ synthesized some cobalt (II) and nickel (II) chelates of Mannich bases. The *infra-red spectrum* of these complexes exhibit a broad band in the region 3427-2900 cm^{-1} due to $\nu_{(\text{N-H})}$.

Electronic Spectral Studies

The electronic absorption spectrum often provides quick and reliable information about the arrangement of ligands around the metal ions. It is possible to determine point group symmetries in the coordination sphere and also assign possible coordination, geometric and linkage isomers from the electronic spectra.

*Shah et al.*³⁶ prepared ternary complexes of iron (III) and manganese (II) with newly synthesized tridentate Mannich bases of phenylalanine and bromosalicylaldehyde. These complexes have been characterized by elemental analyses, spectral (IR) and *electro-chemical studies*.

*Gupta and coworkers*³⁷ studied the *electronic spectra* of cobalt (II), nickel (II) and copper (II) complexes of Mannich base, 2,5-bis (benzylaminomethyl)hydroquinone. These complexes exhibited three absorption bands at 10350, 21550 and 22220 cm^{-1} , which may be assigned to the transitions ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ (F), ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ (F) and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$ (P) in cobalt (II)-BAH, 10270, 15650 and 27220 cm^{-1} in nickel (II)-BAH due to the transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (F), ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P) and 10000, 10869 and 11363 cm^{-1} in copper (II)-BAH due to the transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ respectively. These findings were in good agreement with octahedral geometry of the complexes.

Electron Spin Resonance Spectral Studies

Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) spectroscopy is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion.

A survey of literature on ESR spectroscopy revealed that major amount of work has been performed related to the compounds of paramagnetic metal ions belonging to 3d-transition series.

*Karthikeyan et al.*³⁸ synthesized binuclear copper (II) complexes derived from 2,6-[(N-phenylpiperazin-1-yl)methyl]-4-substituted phenols and characterized by spectral studies. *EPR studies* indicated very weak interaction between the two copper atoms. Synthesis, reduction, optical and *EPR spectral properties* of a series of new binuclear copper (II) complexes containing bridging moieties with new proline based binuclear pentadentate Mannich base ligands were described by *Sougandi et al.*³⁹.

*Takashi and coworkers*⁴⁰ studied the *ESR spectra* of series of polyamine copper (II) complexes. *ESR parameters* were found to be correlated with the coordination mode of the complex. Moreover, linear relationships between *ESR parameters* and stability constants of the copper (II) complexes were observed.

Aim of the Study

Mannich bases have biological activities such as antimicrobia, antiHIV, anticancerous, analgesics, antiarrhythmic and anticonvulscent activities. Mannich bases derived from heterocyclic system and heterocyclic aldehydes and their metal complexes were synthesized by various researchers during the last two decades.

Hence, in the present work, it is thought of interest to synthesize some new heterocyclic Mannich bases and their transition metal complexes and screen them for their antimicrobial activities.

In the present work, we are presenting the use of Mannich bases derived from 2-amino thiazole / 2-amino-6-methylpyridine with p-hydroxybenzaldehyde capable of forming ONN and ONS arrangement with equal ease and attempts have been made to throw light on the possible structures, their applications to contribute to an ultimate understanding of their mode of action in nature. We are also interested in the study of coordination compounds of the synthesized Mannich bases with view of their importance in biological systems. The microbial studies of these complexes showed that these complexes are more potent than their parent ligands.

Conclusion

On the basis of above review of literature, there is a wide scope to research on Mannich bases and their metal complexes.

Endnotes

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