CHAPTER-III

SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES OF 2-HYDROXY-NICOTINIC ACID AND 2-HYDROXY-6-METHYL-NICOTINIC ACID WITH Mn(II), Co(II), Ni(II) AND Cu(II)
III.1 Introduction

Nicotinic acid is an essential water-soluble vitamin of B-complex (vitamin-B₃), also known as niacin, occurring in various animal and plant tissues. Nicotinic acid and its derivatives are potent biological chelating ligands as most of them have N, S, and O donor atoms that can act as coordinating sites for metal ion coordination. Nicotinic acid derivatives have versatile coordinating modes and many of these ligands forms 3D metal-organic framework i.e. supramolecular association with metal via hydrogen bonding, π-π interaction and metallophilic interaction. Like these ligands their metal complexes also have many important biological activities such as antibacterial, antifungal, antiviral, antitumor, anti-inflammatory, antimycobacterial etc. and are also found to be pharmacologically and physiologically active (1-3).

![Nicotinic Acid](image)

Figure III.1 Structure of Nicotinic Acid (Pyridine-3-carboxylic Acid)

III.1.1 Nicotinic Acid: Biological Significance and Effects on Human Health

Nicotinic acid is essential for many biological processes namely for the production of energy, signal transduction, regulation of gene expression and involvement in the synthetic pathway of lipids (4-5). It is required by the body for the formation of coenzymes NAD⁺/NADH and NADP⁺/NADPH. These coenzymes play an important role in tissue respiration and in glycogen, lipid, protein, amino acid and purine metabolism and are required for many cellular redox reactions. A basic
effect of nicotinic acid is the inhibition of fat-mobilizing lipolysis in adipose tissue leading to a lowering of plasma free fatty acids, which has many metabolic implications (6-7).

Nicotinic acid also acts as an antihyperlipidemic drug and as effective HDL cholesterol raising agent for reduction of cardiovascular risks. It effectively reduces serum concentrations of total cholesterol, low-density lipoprotein (LDL) cholesterol, very low density lipoprotein (VLDL) cholesterol, and triglycerides, and increases concentrations of high-density lipoprotein (HDL) cholesterol. It has been suggested that the marked lowering of serum cholesterol seen during treatment of dyslipidemia with nicotinic acid results from hepatotoxicity (8-10).

Nicotinic acid deficiency results in pellagra, a condition characterized by dermatitis, stomatitis, gastrointestinal disorders with nausea, vomiting, and diarrhea and central nervous system symptoms including headaches, dizziness and an occasional toxic psychosis. However, overdose of it causes significant physiological side effects including peripheral vasodilatation with flushing, itching and occasional bruising (11).

Nicotinic acid is also a potent vasodilator, probably by a direct action on smooth muscle cells. It produces cutaneous vasodilatation, itching of the skin, facial flushing, and sensation of feeling hot, pounding in the head, gastric irritation, diarrheal, raised aminotransferase activities, hyperglycaemia, and hyperuricemia. These adverse effects and adverse reactions limit its acceptability for many patients (12).

Narang et al. synthesized a new series of nicotinic acid benzylidene hydrazides. All synthesized compounds were characterized by elemental analysis $^1$H-NMR and Vibrational spectroscopic methods. The whole
series of derivatives was screened in-vitro for anti-mycobacterial, antiviral and antimicrobial activities. Enhanced anti-mycobacterial activity was noticed when halogens i.e. electron-withdrawing groups are attached at para-position of phenyl ring of the derivatives. Also concluded that the derivatives containing dimethoxy and nitro groups are found more effective against tested microbial strains of *S. aureus*, *B. subtilis*, *E. coli*, *C. albicans*, and *A. niger*. QSAR analysis reveals that antibacterial activity is governed by second order molecularity connectivity index and the overall antimicrobial activity of the benzylidene hydrazide derivatives is governed by first order Kier’s alpha shape index (13).

### III.1.2 2-Hydroxy Derivatives of Nicotinic Acid

2-Hydroxynicotinic acid or 2-Hydroxypyridine-3-carboxylic acid (H$_2$nicO) is a pyridine analogue of Salicylic acid and a constitutional isomer of 3-Hydroxypicolinic acid. It is one of the most studied hydroxyl derivative of nicotinic acid because of its versatile chemistry and uses in many fields like pharmaceuticals and agrochemicals. It shows a wide pattern of metal coordination, with transition metals and lanthanides both, as it is a multifunctional compound. It can form a wide range of coordination compounds including mononuclear and polymeric chains; even in some cases three dimensional supramolecular assemblies are also reported. Structures of 2-Hydroxynicotinic acid and 2-Hydroxy-6-methylnicotinic acid are shown in figure III.1.2. It has some unique features like keto-enolic tautomerization and polymorphism which are discussed below.
**Figure III.1.2** Structure of 2-Hydroxynicotinic Acid (H$_2$nicO) (a) and 2-Hydroxy-6-methylnicotinic Acid (H$_2$6MnicO) (b)

**III.1.2 (a) Keto-enolic Tautomerism of 2-Hydroxynicotinic Acid**

In hydroxy derivatives of nicotinic acid, presence of OH group at either of the neighbouring positions (either at 2 or at 6), with respect to the pyridine nitrogen atom, imparts several interesting characteristics to the derivatives. Enol-ketonic tautomerization is one such characteristic of H$_2$nicO. This special characteristic of H$_2$nicO is used to characterize it and makes it versatile in various chemical processes. Sun et al. (14) investigated that in H$_2$nicO the labile H-atom of the OH group (at position-2) is in very close proximity to the basic N-atom of pyridine ring and can be easily transferred to it, forming the keto-tautomer (2-oxo-1H-pyridine-3-carboxylic acid). The keto-tautomer is more stable, favoured in solid state, as it is stabilized by intramolecular H-bonding between the COOH and ketonic group.

Enol-ketonic tautomerism in solution phase also studied frequently because of its many interesting features. Saleh and co-workers have studied the acid-base equilibrium of H$_2$nicO, in water-ethanol medium, and it was suggested that H$_2$nicO is exists as keto-tautomer in solution phase too. The keto tautomer of H$_2$nicO is also stabilized by resonance and exists predominantly in a zwitter-ionic form in solutions at pH range 3-10.5 (15).
Dogra investigated the excited state intramolecular transfer of proton in enolic form of \( \text{H}_2\text{nicO} \), to give the keto-tautomer, in various solvents and at different pH values using a variety of spectroscopic methods and quantum chemistry calculations. Dogra suggested that due to this enol-ketonic tautomerization very less amount of enolic \( \text{H}_2\text{nicO} \) is present in the used solvents, unless there was an adjustment of acid-base concentration or pH value of the medium (16). Quintal et al. (17) reported that enol-ketonic tautomerization, of the same fashion, is also present in 2-mercaptonicotinic acid (\( \text{H}_2\text{nicS} \)).

\[
\begin{align*}
\text{2-Hydroxypyridine-3-Carboxylic acid} & \quad \leftrightarrow \quad \text{2-Oxo-1H-pyridine-3-Carboxylic acid}
\end{align*}
\]

**Figure III.1.2 (a) Enol-keto Tautomers of 2-Hydroxynicotinic Acid**

**III.1.2 (b) Coordination modes of 2-Hydroxynicotinic Acid**

Investigation of coordination modes of \( \text{H}_2\text{nicO} \) is the most interesting part of the study of its metal complexes. \( \text{H}_2\text{nicO} \) contains three functional groups viz. pyridyl nitrogen, -COOH and -OH. Hence \( \text{H}_2\text{nicO} \) behaves like a potential chelating/bridging ligand with multiple coordinating sites. According to Stephens and Orwig (18) \( \text{H}_2\text{nicO} \) undergoes mono or di-de-protonation to give \( \text{HnicO}^- \) and \( \text{nicO}^{2-} \) in basic medium depending on pH values. These mono-anionic and di-anionic forms have strong metal-coordination tendency using the pyridyl N-atom, two carboxylate oxygen atoms and the oxygen atom at position-2, which leads formation of wide variety of metal complexes including three
dimensional supramolecular assemblies and polymeric metal-organic frameworks.

The various reported coordination modes of monodeprotonated ligand HnicO$^-$ are (i) monodentate (involving pyridine N-atom) (19) (ii) $N,O$-chelation (involving the pyridine nitrogen and the oxygen at position-2, forming a four member chelate ring) (20) (iii) $O,O'$-chelation or salicylato type chelation (involving the oxygen atom of COO' group and the oxygen at position-2 i.e. phenolate oxygen, forming a six member chelate ring) (21) (iv) $O,O',O''$- chelating-bridging mode (involving the one of the oxygen atom of COO' group and the phenolate oxygen for chelation and other oxygen of carboxylate group for bridging) (22) (v) $N,O,O'$- chelating-bridging mode (salicylato type chelation via one of the oxygen atom of COO' group and the phenolate oxygen and bridging using pyridine N-atom) (23).

![Coordination modes of HnicO$^-$](image)

**Figure III.1.2 (b) Different reported Coordination modes of 2-Hydroxynicotinic acid**
III.1.2 (c) Polymorphism of 2-Hydroxynicotinic Acid

Out of many hydroxy derivatives of nicotinic acid viz. 2-hydroxy, 4-hydroxy, 5-hydroxy and 6-hydroxynicotinic acid, only the 2-hydroxynicotinic acid (H$_2$nicO) is reported to exist in four different crystalline forms i.e. it shows polymorphism. According to Long et al. it is possible because H$_2$nicO undergoes transfer of hydroxy proton to N-atom of pyridine ring and forms the more stable keto-tautomer, even in solid state. The wide range of H-bonds possible among molecules of keto tautomer creates different packing pattern of the molecules in crystal and thereby generating the four different polymorphic forms. All the four polymorphs were obtained from commercial sample of H$_2$nicO by slow crystallization using different solvents (water and organic) in presence or absence of additives. Mostly p-TsOH, DCMA and 2-CNICA were used as additives. pH changes, nature of solvent and additive added plays an important role in the generation of these polymorphs. These polymorphic forms were distinguished by XRD method. Four polymorphs are result of different packing patterns as they have same unit cells. They are monoclinic, centro-symmetric and have almost same density. Using condensed Fukui functions and the Dual descriptor, sites for possible H-bonding were identified. DFT and Thermal studies used to correlate the thermal stabilities of the polymorphs. Hirshfeld surface analysis also confirms the role of H-bonding and π-π interactions in maintaining the crystal structures of the polymorphs (24).
III.2 Experimental

III.2.1 Materials

The synthesis of various ligands used during study has been described in chapter II. In order to synthesize complexes of 2-Hydroxynicotinic acid and 2-Hydroxy-6-methylnicotinic acid with Mn(II), Co(II), Ni(II) and Cu(II), A.R. grade MnCl₂.4H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂ were procured from Sigma-Aldrich with other solvents and used as received without further purification.

III.2.2 Synthesis of Complexes of H₂nicO and H₂6MnicO with Mn(II), Co(II), Ni(II) and Cu(II).

To synthesize these complexes conventional method as well as microwave irradiation method was used. A comparison between these methods is shown in tables III.3.A and III.3.B for both the ligands, respectively.

(a) Synthesis by conventional method

To prepare complexes, 2.0 mmol (0.08 g) of NaOH were dissolved in 10 mL of distilled water and 2.0 mmol of the ligand (0.278 g of H₂nicO, 0.306 g of H₂6MnicO,) were added, respectively. The pH value of the solution was maintained to 7-8.5 with aqueous solution of NaOH or a suitable acid, respectively. 1 mmol of divalent metal chloride (0.198 g of MnCl₂.4H₂O, 0.238 g of NiCl₂.6H₂O, 0.238 g of CoCl₂.6H₂O and 0.135 g of CuCl₂) were dissolved in 5 mL of distilled water. The solution of respective metal chloride was added slowly into the basic solution of H₂nicO and H₂6MnicO, with constant stirring. The reaction mixture was placed on a magnetic stirrer (with heating) with constant stirring for 3-4 hours at room temperature and the precipitate formed during this
procedure was filtered off. The precipitate was washed with water-ethanol mixture. Basic medium with pH range 7-8.5 was maintained because it favours the monodeprotonation to form the ligand 2-Hydroxynicotinate (HnicO\textsuperscript{-}) and monodeprotonation is required to break the strong intramolecular H-bonding present in the keto form of 2-hydroxy nicotinic acid.

(b) Synthesis by microwave method

As an alternative, a novel method of synthesis has been developed as per the principles of green chemistry, in which, either the reaction mixture was irradiated in a domestic microwave at 600 W for 2-4 minutes on alumina bed or reaction mixture in the solvent or the slurry of reaction mixture was exposed in a microwave reactor at 600 W maintaining different time intervals with respect to occasional and or definite inspection of TLC data. The mixture was cooled to room temperature and poured into ice chilled methanol and dried in vacuum over P\textsubscript{2}O\textsubscript{5} (25).

The solid precipitate obtained in both the methods was separated and crystallized. Crystals were purified and recrystallized with alcohol and dried under vacuum.

III.3 Results and Discussion

III.3.1 Physical Measurements

The complexes of H\textsubscript{2}nicO and H\textsubscript{2}6MnicO with 3d transition metals Mn(II), Co(II), Ni(II) and Cu(II) are light coloured powdrous material and found stable at room temperatures for a long period of time. These complexes are soluble in DMSO, DMF, partially soluble in ethyl alcohol, methyl alcohol and insoluble in water and other solvents. The elemental
estimations gave satisfactory results. The physical and analytical data of complexes are given in Table III.3.A and Table III.3.B.

III.3.2 IR Spectral Analysis

Infrared absorption frequencies for both ligands (H$_2$nicO and H$_2$6MnicO) and their metal complexes are reported in the Table III.3.C and Table III.3.D with their tentative assignments and the respective vibrational spectra are shown in figures III.3.C.1 to III.3.C.4 and III.3.D.1 to III.3.D.4. A careful study and comparison of infrared spectra of free ligands and their metal complexes imply that the ligands behaves as bidentate and the metal ion is coordinated through the salicylate moiety using the carboxylate and phenolate oxygen atoms.

The strong band in the region 1730-1740 cm$^{-1}$, in IR spectrum of ligands, assigned to the $\nu$(C=O) stretch of COOH group, is absent in the spectrum of complexes, which confirms the coordination of respective oxygen atom to the metal (26). In complexes, the carboxylate form of the monodeprotonated ligand is confirmed by the two bands in the region 1635-1640 and 1376-1381 cm$^{-1}$ for Mn(II), 1624-1629 and 1376-1377 cm$^{-1}$ for Co(II), 1626-1630 and 1374-1391 cm$^{-1}$ for Ni(II), 1630-1631 and 1354-1371 cm$^{-1}$ for Cu(II), which are assigned to $\nu_{as}$(COO$^-$) and $\nu_s$(COO$^-$), asymmetric and symmetric stretch, respectively (27-28). In case of ligands, another strong band, centred at 1645 cm$^{-1}$ for H$_2$nicO and at 1640 cm$^{-1}$ for H$_2$6MnicO, is assigned to the $\nu$(C=O) stretch of the amide group of these ligands. The strong and broad band in complexes, due to $\nu_{as}$(COO$^-$) stretch, can be assumed as a mixed band with $\nu$(C=O) stretch of the amide group (29). This shifting of the band due to $\nu$(C=O) stretch of the amide group, in form of the mixed band, towards lower frequency in the complex confirms the metal coordination via oxygen atom of the amide group (30-31). The shift ($\Delta$) between $\nu_{as}$(COO$^-$) and $\nu_s$(COO$^-$), for
all complexes, is almost in the same range (235 cm\(^{-1}\) to 277 cm\(^{-1}\)), shows the coordination through COO\(^-\) ion in unidentate mode (32-33).

The \(\nu(N-H)\) stretch, in-plane \(\delta(N-H)\) bending and out-of-plane \(\gamma(N-H)\) bending (at 3231, 1550, 539 cm\(^{-1}\) for \(\text{H}_2\text{nicO}\) and at 3131, 1540, 581 cm\(^{-1}\) for \(\text{H}_2\text{6MnicO}\)) respectively, in the free ligand, are also present in the spectra of the complexes, at almost same range, showing the pyridine nitrogen protonation in these complexes. In the IR spectra of all complexes, absorption of medium intensity in the region 400-500 cm\(^{-1}\), may be attributed to \(\nu(M-O)\) stretching (34-35).

These observations support the final structural conclusions of the complexes and the mode of bonding in them.

**III.3.3 Electronic Spectral and Magnetic Studies**

Electronic spectra of all the metal complexes of \(\text{H}_2\text{nicO}\) and \(\text{H}_2\text{6MnicO}\) are recorded using DMSO or DMF as solvent and at \(10^{-3}\) to \(10^{-2}\) molar concentration of samples and presented in the figures III.3.E.1 to III.3.E.4 and figures III.3.F.1 to III.3.F.4, respectively. Characteristic absorbance bands, their tentative assignments and the results of magnetic studies are reported in tables III.3.E and III.3.F. The magnetic and electronic spectral data are in relevance with proposed geometry of the complexes.

**Mn(II) Complexes**

The ground state term for Mn (II), a d\(^5\) system, in high spin electronic configuration which has five unpaired electrons in d orbitals is \(^6S\). As there are no excited states of sextet spin multiplicity, spin allowed d-d transitions are not expected. Also for octahedral complexes these transitions are Laporte forbidden. So all the d-d transitions in high spin
octahedral Mn(II) are doubly forbidden; Laporte forbidden and Spin forbidden. Hence the colour of the Mn(II) complexes are either light or have no colour (36). The ground state of the high spin octahedrally coordinated Mn (II) ion is $^6A_{1g}$. Thus the electronic transitions from $^6A_{1g}$ ground state are extremely weak with very low intensities (37-38). There are eleven possible excited state for $^6A_{1g}$ ground state of Mn(II) among which four excited states (i.e. $^4G$, $^4F$, $^4P$ $^4D$) have quartet spin multiplicity.

The electronic spectrum of the brown Mn(II) complexes showed three spectral bands in the region 18083-18099, 24785-26110 and 27586-28409 cm$^{-1}$. These absorbance bands may be assigned to the spin forbidden transitions $^6A_{1g} \rightarrow ^4T_{1g},(^4G) (v_1)$, $^6A_{1g} \rightarrow ^4T_{2g},(^4G) (v_2)$ and $^6A_{1g} \rightarrow ^4A_{1g},^4E_g (^4G) (v_3)$ respectively. The third transition is the most intense and lies in the range of the ligand transitions and is very difficult to identify. These transitions indicates the octahedral geometry around Mn(II) ion (39-42).

Manganese in its bivalent oxidation state forms both high spin (S=5/2) and low spin (S=1/2) Complexes. Half filled d-orbitals have additional stability so manganese(II) generally forms high spin complexes which have an orbitally degenerate $^6S$ ground state term and it is reported for high spin Mn(II) compounds with d$^5$ configuration, the magnetic moment values are in the range 5.65 - 6.10 B.M (36).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are given in table III.3.E and table III.3.F. All the manganese (II) complexes have magnetic moment values in the range 5.80-5.85 BM indicating the
presence of five unpaired electrons and hence these are high spin octahedral complexes (43).

**Co(II) Complexes**

In an octahedral field of Co (II), d⁷-system, three spin allowed are anticipated because of splitting of the free ion, ground ⁴F and the accompanying ⁴P term. The ground state term for high spin octahedral Co(II) (d⁷ electronic configuration) is ⁴T₁g. However in the high spin octahedral systems the ⁴A₂g (F) level is usually close to the ⁴T₁g (P) level and transition to these levels are close together. All transitions in Co(II) complexes are spin allowed transitions unlike Mn(II) complexes.

Co(II) complexes of H₂nicO and H₂6MnicO exhibit absorption bands in the region 11764-11904, 18099-18115 and 20597-20833 cm⁻¹ which are attributed to the transitions ⁴T₁g (F) → ⁴T₂g (F) (ν₁), ⁴T₁g (F) → ⁴A₂g (F) (ν₂) and ⁴T₁g (F) → ⁴T₁g (P) (ν₃) respectively, indicative of octahedral geometries for the Co(II) complexes. The highest energy transition ⁴T₁g (F) → ⁴T₁g (P) (ν₃) is generally merge with ligand transitions. Since ⁴A₂g state is derived from a t₂g⁴ e_g⁴ electronic configuration and the ⁴T₁g (F) ground state is derived from t₂g⁵ e_g⁴ configuration, the ⁴T₁g (F) → ⁴A₂g (F) (ν₂) transition is essentially a two electron process, it is therefore weaker by about a factor of 10⁻² than the other transitions and often appears as a shoulder. One characteristic transition for octahedral environment around Co(II) ion is ⁴T₁g (F) → ⁴T₂g (F) (ν₁) which generally occurs in the near IR region. (44-45).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are presented in table III.3.E and table III.3.F. The magnetic moments of the complexes lies in the range 4.70-5.81 BM, which correspond to three unpaired
electrons. This indicates a quartet ground state term $^4F$ ($S = 3/2$) which is the case of Co (II) ($d^7$) and it may be obtained weak field octahedral configuration (46).

**Ni(II) Complexes**

Ni(II) is the only common $d^8$ ion and its spectroscopic and magnetic properties have accordingly been extensive studied. In a cubic field three spin allowed transitions are expected because of splitting of free ion, ground $^3F$ term and the presence of the $^3P$ term. Ni(II) is a $d^8$ system where $^3A_{2g}(F)$ is the ground state. The excited states with same multiplicity are $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$. The electronic absorption spectra of the Ni (II) complexes were recorded at room temperature using DMSO as solvent.

The electronic spectrum of the present Ni(II) complexes of $H_2nicO$ and $H_26MnicO$ showed three spin allowed bands in the region 12254-12322 cm$^{-1}$($v_1$), 16529-16583 cm$^{-1}$($v_2$) and 25673-25873 cm$^{-1}$($v_3$) which are assignable to tentative assignments viz. $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$. These transitions suggests the octahedral geometry of Ni(II) complexes. The lowest energy transition ($v_1$) occurs almost in the near IR region. (47-48).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are presented in table III.3.E and table III.3.F. The magnetic behaviour of bivalent nickel complexes depends upon the nature of the ligand and geometry of the complexes. Ni(II) complexes show the magnetic moment value in the range of 3.08-3.3 BM which is correspond to two unpaired electrons and consistency with octahedral environment around Ni (II). Both the Ni (II)
complexes exhibit paramagnetic behaviour due to the presence of two unpaired electrons (49-50).

**Cu(II) Complexes**

Copper has electronic configuration [Ar] (3d^{10}) (4s^1) and in its bivalent state it shows a configuration of [Ar] 3d^9. Octahedral Cu (II) complexes are almost invariably distorted. This is entirely consistent with the operation of Jahn-Teller effect because the ground state electronic configuration of Cu(II) ion in an octahedral field \( t_{2g}^6 e_g^3 \), \( ^2E_g \). It has an odd number of electrons in \( e_g \) orbitals. This distortion renders their absorption spectra to be quite complex. In Cu(II) complexes, tetragonal distortion either by elongation (z-out) or compression (z-in) will lead to stabilization of Cu(II) complexes. However experimental measurements show that the distortion is generally elongation along the z-axis (51).

Cu (II) gives rise to only one free ion ground term \( ^2D \), which is twofold spin and orbitally degenerate. \( ^2D \) free ion term is split into ground state \( ^2E_g \) and excited state \( ^2T_{2g} \) terms. In a perfect octahedral \( d^9 \) complex, a single absorption band with good intensity corresponding to the spin allowed transition \( ^2E_g \rightarrow ^2T_{2g} \) is expected in the region 11000-16000 cm\(^{-1}\). On distortion to \( D_{4h} \) symmetry, these terms further splits as shown in the figure below. Excitation can now occur from the ground state \( ^2B_{1g} \) to the \( ^2A_{1g}, ^2E_g \) and \( ^2B_{2g} \). In case of extreme distortion leading to the square planar geometry a multiple band with three components corresponding to the three transitions is observed (52).

In the present case of Cu(II) complexes, with \( H_2\text{nico} \) and \( H_2\text{6MnicO} \), a single asymmetric broad band, in the region 10309-14286 cm\(^{-1}\), is observed. The broadness of the band confirms the splitting of octahedral free ion terms (\( ^2E_g \) and \( ^2T_{2g} \)) into new terms \( ^2B_{1g}, ^2A_{1g}, ^2E_g \) and
\(^2\)B\(_{2g}\) on distortion to \(D_{4h}\) symmetry and the expected three transitions \(^2\)B\(_{1g}\), \(\rightarrow ^2\)A\(_{1g}\), \(^2\)B\(_{1g}\) \(\rightarrow ^2\)E\(_{g}\) and \(^2\)B\(_{1g}\) \(\rightarrow ^2\)B\(_{2g}\). The broadness of the band may be because these transitions are similar in energy thus giving rise to only one broad band. These data suggest John-Teller distortion i.e. a tetragonally distorted octahedral geometry around Cu(II) ion (53-56).

A high intense peak in the range 25773-26109 cm\(^{-1}\) present in electronic spectra of both the Cu (II) complexes which is assigned for Cl→Cu(II) charge transfer band (LMCT) (57-60).

Figure III.3.3 Splitting of Octahedral free ion term on Jahn-Teller Distortion for \(d^9\) configuration

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are presented in table III.3.E and table III.3.F. The magnetic behaviour of bivalent copper complexes depends upon the nature of the ligand and geometry of the complexes. The Cu (II) complexes of H\(_2\)nicO and H\(_2\)6MnicO show magnetic moment in the range 1.87-1.92 BM, is slightly higher than the spin-only value 1.73 BM expected for one unpaired electron, which offers possibility of an octahedral geometry (61).
### Table III.3.A

**Physico-chemical Data of Complexes of H$_2$nicO with Mn(II), Co(II), Ni(II) and Cu(II).**

(C.M. = Conventional method, M.M. = Microwave method)

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Complexes</th>
<th>Color</th>
<th>M.P. (°C)</th>
<th>Reaction Period</th>
<th>Yield %</th>
<th>Elemental Analysis Calculated (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C.M. Hrs.</td>
<td>M.M. Min.</td>
<td>C.M.</td>
</tr>
<tr>
<td>1</td>
<td>Na$_2$[Mn(HnicO)$_2$Cl$_2$]</td>
<td>Brown</td>
<td>254</td>
<td>3.5</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$[Co(HnicO)$_2$Cl$_2$]</td>
<td>Pink</td>
<td>252</td>
<td>3.4</td>
<td>3.5</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>Na$_2$[Ni(HnicO)$_2$Cl$_2$]</td>
<td>Light green</td>
<td>260</td>
<td>4.1</td>
<td>2.5</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>Na$_2$[Cu(HnicO)$_2$Cl$_2$]</td>
<td>Light blue</td>
<td>263</td>
<td>4.0</td>
<td>4.2</td>
<td>50</td>
</tr>
</tbody>
</table>
Table- III.3.B
Physico-chemical Data of Complexes of H$_2$6MnicO with Mn(II), Co(II), Ni(II) and Cu(II)
(C.M. = Conventional method, M.M. = Microwave method)

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Complexes</th>
<th>Color</th>
<th>M.P. (°C)</th>
<th>Reaction Period</th>
<th>Yield %</th>
<th>Elemental Analysis Calculated (Found)%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C.M. Hrs.</td>
<td>M.M. Min.</td>
<td>C.M.</td>
</tr>
<tr>
<td>1</td>
<td>Na$_2$[Mn(H$_6$MnicO)$_2$Cl$_2$]</td>
<td>Brown</td>
<td>255</td>
<td>4.2</td>
<td>3.0</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$[Co(H$_6$MnicO)$_2$Cl$_2$]</td>
<td>Light pink</td>
<td>250</td>
<td>3.3</td>
<td>2.5</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>Na$_2$[Ni(H$_6$MnicO)$_2$Cl$_2$]</td>
<td>Off green</td>
<td>258</td>
<td>3.2</td>
<td>3.5</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>Na$_2$[Cu(H$_6$MnicO)$_2$Cl$_2$]</td>
<td>Bluish white</td>
<td>261</td>
<td>3.4</td>
<td>3.6</td>
<td>48</td>
</tr>
</tbody>
</table>
Table- III.3.C
Vibrational Spectral Assignments (cm\(^{-1}\)) of Complexes of H\(_2\)nicO with Mn(II), Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>Ligand/Complexes</th>
<th>Carbonyl group</th>
<th>Carboxylate group</th>
<th>(\Delta)</th>
<th>N-H group</th>
<th>(\nu(M-O))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu(C=O)^a)</td>
<td>(\nu(C=O)^b)</td>
<td>(\nu_{as}(COO^-)^c)</td>
<td>(\nu_s(COO^-))</td>
<td>(\nu(N-H))</td>
</tr>
<tr>
<td>(H_2)nicO</td>
<td>1740 (\text{(vs,br)})</td>
<td>1645 (\text{(vs,br)})</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Na_2[Mn(HnicO)_2Cl_2])</td>
<td>-</td>
<td>-</td>
<td>1640 (\text{(vs,br)})</td>
<td>1376(s)</td>
<td>264</td>
</tr>
<tr>
<td>(Na_2[Co(HnicO)_2Cl_2])</td>
<td>-</td>
<td>-</td>
<td>1629 (\text{(vs,br)})</td>
<td>1376(s)</td>
<td>253</td>
</tr>
<tr>
<td>(Na_2[Ni(HnicO)_2Cl_2])</td>
<td>-</td>
<td>-</td>
<td>1630 (\text{(vs,br)})</td>
<td>1374(s)</td>
<td>256</td>
</tr>
<tr>
<td>(Na_2[Cu(HnicO)_2Cl_2])</td>
<td>-</td>
<td>-</td>
<td>1631 (\text{(vs,br)})</td>
<td>1354(s)</td>
<td>277</td>
</tr>
</tbody>
</table>

\(a = \nu(C=O)\) stretch of COOH group, \(b = \nu(C=O)\) stretch of the amide group, \(c =\) mixed absorption band of \(\nu_{as}(COO^-)\) and \(\nu(C=O)\) of the amide group, \(\nu_s =\) symmetric stretch, \(\nu_{as} =\) asymmetric stretch, \(\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)\), \(\text{vs} = \text{very strong}, s = \text{strong}, m = \text{medium}.\)
### Table- III.3.D

Vibrational Spectral Assignments (cm\(^{-1}\)) of Complexes of H\(_2\)6MnicO with Mn(II), Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>Ligand/Complexes</th>
<th>Carbonyl group</th>
<th>Carboxylate group</th>
<th>(\Delta)</th>
<th>N-H group</th>
<th>(\nu(M-O))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu(C=O)^a)</td>
<td>(\nu(C=O)^b)</td>
<td>(\nu_{as}(COO)^c)</td>
<td>(\nu(COO^\prime))</td>
<td>(\nu(N-H))</td>
</tr>
<tr>
<td>H(_2)6MnicO</td>
<td>1730 (vs,br)</td>
<td>1640 (vs,br)</td>
<td>-</td>
<td>-</td>
<td>3100</td>
</tr>
<tr>
<td>Na(_2)[Mn(H6MnicO)(_2)Cl(_2)]</td>
<td>-</td>
<td>-</td>
<td>1635(vs,br)</td>
<td>1381(s)</td>
<td>254</td>
</tr>
<tr>
<td>Na(_2)[Co(H6MnicO)(_2)Cl(_2)]</td>
<td>-</td>
<td>-</td>
<td>1624 (vs,br)</td>
<td>1377(s)</td>
<td>247</td>
</tr>
<tr>
<td>Na(_2)[Ni(H6MnicO)(_2)Cl(_2)]</td>
<td>-</td>
<td>-</td>
<td>1626 (vs,br)</td>
<td>1391(s)</td>
<td>235</td>
</tr>
<tr>
<td>Na(_2)[Cu(H6MnicO)(_2)Cl(_2)]</td>
<td>-</td>
<td>-</td>
<td>1630 (vs,br)</td>
<td>1371(s)</td>
<td>259</td>
</tr>
</tbody>
</table>

\(a = \nu(C=O)\) stretch of COOH group, \(b = \nu(C=O)\) stretch of the amide group, \(c = \) mixed absorption band of \(\nu_{as}(COO^\prime)\) and \(\nu(C=O)\) of the amide group, \(\nu_s = \) symmetric stretch, \(\nu_{as} = \) asymmetric stretch, \(\Delta = \nu_{as}(COO^\prime) - \nu_s(COO^\prime)\), \(vs = \) very strong, \(s = \) strong, \(m = \) medium.
### Table- III.3.E

Magnetic Moments and Electronic Spectral Data of Complexes of H$_2$nicO with Mn(II), Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>$R_f$ value</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>Electronic Bands (cm$^{-1}$)</th>
<th>Tentative assignments</th>
<th>Expected Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na$_2$[Mn(HnicO)$_2$Cl$_2$]</td>
<td>(0.88)$^b$</td>
<td>5.80</td>
<td>18083, 24785, 28409</td>
<td>$^6$A$<em>{1g}$→$^4$T$</em>{1g}$ ($^3$G), $^6$A$<em>{1g}$→$^4$T$</em>{2g}$ ($^3$G), $^6$A$<em>{1g}$→$^4$A$</em>{1g}$, $^4$E$_g$ ($^4$G)</td>
<td>Octahedral</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$[Co(HnicO)$_2$Cl$_2$]</td>
<td>(0.74)$^d$</td>
<td>4.81</td>
<td>11904, 18115, 20833</td>
<td>$^4$T$<em>{1g}$ (F)→$^4$T$</em>{2g}$ (F), $^4$T$<em>{1g}$ (F)→$^4$A$</em>{2g}$ (F), $^4$T$<em>{1g}$ (F)→$^4$T$</em>{1g}$ (P)</td>
<td>Octahedral</td>
</tr>
<tr>
<td>3</td>
<td>Na$_2$[Ni(HnicO)$_2$Cl$_2$]</td>
<td>(0.85)$^b$</td>
<td>3.08</td>
<td>12254, 16529, 25873</td>
<td>$^3$A$<em>{2g}$ (F)→$^3$T$</em>{2g}$ (F), $^3$A$<em>{2g}$ (F)→$^3$T$</em>{1g}$ (F), $^3$A$<em>{2g}$ (F)→$^3$T$</em>{1g}$ (P)</td>
<td>Octahedral</td>
</tr>
<tr>
<td>4</td>
<td>Na$_2$[Cu(HnicO)$_2$Cl$_2$]</td>
<td>(0.60)$^a$</td>
<td>1.92</td>
<td>10414-14286 cm$^{-1}$ (Asymmetric broad band)</td>
<td>$^2$B$<em>{1g}$→$^2$A$</em>{1g}$, $^2$B$<em>{1g}$→$^2$B$</em>{2g}$, $^2$B$_{1g}$→$^2$E$_g$</td>
<td>Distorted Octahedral</td>
</tr>
</tbody>
</table>

Table- III.3.F

Magnetic Moments and Electronic Spectral Data of Complexes of H₂6MnicO with Mn(II), Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>R_f value</th>
<th>µ_eff (BM)</th>
<th>Electronic Spectral Bands (cm⁻¹)</th>
<th>Tentative assignments</th>
<th>Expected Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂[Mn(H₆MnicO)₂Cl₂]</td>
<td>(0.80)ᵇ</td>
<td>5.85</td>
<td>18099, 26110, 27586</td>
<td>⁶A₁g → ⁴T₁g (F), ⁶A₁g → ⁴T₂g (F)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>⁶A₁g → ⁴A₁g, ⁴E₂g (F)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Na₂[Co(H₆MnicO)₂Cl₂]</td>
<td>(0.68)ᵈ</td>
<td>4.70</td>
<td>11764, 18099, 20597</td>
<td>⁴T₁g (F) → ⁴T₂g (F), ⁴T₁g (F) → ⁴A₂g (F)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>⁴T₁g (F) → ⁴T₁g (P)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Na₂[Ni(H₆MnicO)₂Cl₂]</td>
<td>(0.58)ᵇ</td>
<td>3.30</td>
<td>12322, 16583, 25673</td>
<td>³A₂g (F) → ³T₂g (F), ³A₂g (F) → ³T₁g (F)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>³A₂g (F) → ³T₁g (P)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Na₂[Cu(H₆MnicO)₂Cl₂]</td>
<td>(0.75)ᵃ</td>
<td>1.87</td>
<td>10309-14286 cm⁻¹ (Asymmetric broad band)</td>
<td>²B₁g, → ²A₁g, ²B₁g → ²B₂g</td>
<td>Distorted Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>²B₁g → ²Eｇ,</td>
<td></td>
</tr>
</tbody>
</table>

Figure III.3.C.1 Vibrational Spectrum of Na$_2$[Mn(HnicO)$_2$Cl$_2$]
Figure III.3.C.2 Vibrational Spectrum of Na$_2$[Co(HnicO)$_2$Cl$_2$]
Figure III.3.C.3 Vibrational Spectrum of Na$_2$[Ni(HnicO)$_2$Cl$_2$]
Figure III.3.C.4 Vibrational Spectrum of Na$_2$[Cu(HnicO)$_2$Cl$_2$]
Figure III.3.D.1 Vibrational Spectrum of Na$_2$[Mn(H6MnicO)$_2$Cl$_2$]
Figure III.3.D.2 Vibrational Spectrum of Na$_2$[Co(H6MnicO)$_2$Cl$_2$]
Figure III.3.D.3 Vibrational Spectrum of Na$_2$[Ni(H6MnicO)$_2$Cl$_2$]
Figure III.3.D.4 Vibrational Spectrum of Na$_2$[Cu(H6MnicO)$_2$Cl$_2$]
Figure III.3.E.1 UV-visible Spectrum of Na₂[Mn(HnicO)₂Cl₂]
Figure III.3.E.2 UV-visible Spectrum of Na$_2$[Co(HnicO)$_2$Cl$_2$]
Figure III.3.E.3 UV-visible Spectrum of Na$_2$[Ni(HnicO)$_2$Cl$_2$]
Figure III.3.E.4 UV-visible Spectrum of Na$_2$[Cu(HnicO)$_2$Cl$_2$]
Figure III.3.F.1 UV-visible Spectrum of Na$_2$[Mn(H$_6$MnicO)$_2$Cl$_2$]
Figure III.3.F.2 UV-visible Spectrum of Na₂[Co(H₆MnicO)₂Cl₂]
Figure III.3.F.3 UV-visible Spectrum of Na₂[Ni(H₆MnicO)₂Cl₂]
Figure III.3.F.4 UV-visible Spectrum of Na$_2$[Cu(H$_6$MnicO)$_2$Cl$_2$]
III.4 Conclusion

IR spectral studies has shown that both ligands 2-Hydroxynicotinic acid (\(\text{H}_2\text{nicO}\)) and 2-Hydroxy-6-methylnicotinic acid (\(\text{H}_2\text{6MnicO}\)), in their monodeprotonated form (\(\text{HnicO}^-\) and \(\text{H6MnicO}^-\)), behave as bidentate ligands in complexes with Mn(II), Co(II), Ni(II) and Cu(II). Both ligands follows \(O,O\)-chelation mode i.e. coordinating via the oxygen atom of carboxyl group and the oxygen atom present at position-2. Vibrational spectroscopic analysis also confirms the enol-keto tautomeric existence of 2-Hydroxynicotinic acid 2-Hydroxy-6-methylnicotinic acid. The electronic spectral assignments are characteristic to the geometries adopted by metal ion in ligand environments. The metal complexes of Mn(II), Co(II) and Ni(II) adopts octahedral geometry while the Cu(II) complex found to have tetragonally distorted octahedral environment around the metal ion.

Magnetic susceptibility measurements at room temperature exhibit paramagnetic character for all complexes. The observed magnetic moments for the complexes suggesting six coordinated geometry around metal ions. The complexes synthesized by novel green method are at par with conventional synthesis and in all cases yield was found to be better than conventional synthesis.
Figure III.4.1 Tentative Structure of Complex of $\text{H}_2\text{nicO}$ where $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$ and $\text{Cu(II)}$

Figure III.4.2 Tentative Structure of Complex of $\text{H}_2\text{6MnicO}$ where $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$ and $\text{Cu(II)}$. 
III.5 References


