A REVIEW ON COORDINATION BEHAVIOUR AND BIOACTIVITY OF METAL COMPLEXES OF NICOTINIC ACID AND ITS DERIVATIVES

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ABSTRACT

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. Like these ligands, their metal complexes also have many important biological activities such as antibacterial, antifungal, antiviral, antitumor, anti-inflammatory etc. and are also found to be pharmacologically and physiologically active. Many such metal complexes of nicotinic acid and its derivatives have supramolecular association i.e. 3D framework structure via hydrogen or covalent bonds. The most relevant papers recently published are reviewed with an attempt to focus the bioactivity and structure of such metal complexes along with some related applications.

KEYWORDS: Nicotinic acid, biological activity, hydrothermal, supramolecular, hydrogen bonds, schiff bases.

INTRODUCTION

Pyridine derivatives possess a diverse array of bioactivities as well as playing crucial roles for physiological functions.¹⁻⁴ They have been extensively used as ligands in the formation of coordination compounds as medicinal agent.⁵ The most striking one to our interest is nicotinic acid (NA) or pyridine-3-carboxylic acid, also known as vitamin B₃ (niacin), which is essential for many biological processes namely for the production of energy.⁶ signal
transduction, regulation of gene expression and involvement in the synthetic pathway of lipids. It also acts as an antihyperlipidemic drug and as effective HDL cholesterol raising agent for reduction of cardiovascular risks. Nicotinic acid plays fundamental roles on the productions of essential coenzymes NAD\(^+\)/NADH and NADP\(^+\)/NADPH. NAD\(^+\) and NADP\(^+\) which are required for many cellular redox reactions. 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, \(\pi\)-\(\pi\) interaction and metallophilic interaction. This can be used as a power crystal-engineering tool for constructing and tailoring metal-organic architectures with desirable applications. The studies on the co-ordination complexes of nicotinic acid and its derivatives reveal their antiviral, antifungal, anti-inflammatory, antitumor and and antibacterial activity. This review will be focused mainly on the structure and bioactivities of transition metal complexes of nicotinic acid and its various derivatives which includes mainly Amides, Hydroxy, Mercapto, Chloro, and Hydrazides.

**STRUCTURE, COORDINATION MODES AND BIOACTIVITIES OF METAL COMPLEXES OF NICOTINIC ACID AND ITS DERIVATIVES**

Scheme1: Structure of nicotinic acid and some of its derivatives viz Amide, 2-Hydroxy, 2-Mercapto, 2-Amino, 6-Methyl-2-hydroxy, 5-Chloro and Hydrazide.

**Metal Complexes of Nicotinic Acid**

Osowole et al. synthesized and characterized mixed ligand metal(II) complexes of Niacin and \(m\)-Toluic acid. The complexes are all covalent, with a 6-coordinate octahedral geometry. The room temperature magnetic moment confirms that the metal complexes are magnetically dilute with the exception of the Cu(II) complex which is antiferromagnetic with a room temperature magnetic moment of 1.69 B.M. The Co(II) And the Ni(II) complexes have broad-spectrum antibacterial activities against *B. cereus, E. coli, P. mirabilis, P. aeruginosa,*
K. oxytoca and S. aureus with inhibitory zones range of 21.0-49.0 mm and 21.0-37.0 mm respectively, proving their potentials as broad spectrum antibacterial agent.\[16\]

Dilip et al. prepared and characterized the transition metal complexes of nicotinic acid and nitrite ion. Five complexes were prepared with Cr(III), Co(II), Ni(II), Cu(II) and Cd(II). IR Spectra confirm the coordination of pyridine nitrogen of the nicotinic acid with the metal ion. The analytical data suggest that nicotinic acid acts as a monodendate ligand, and the complexes are in distorted octahedral geometry for the chromium, cobalt and nickel complexes and tetragonal for the copper and pseudo tetrahedral for the cadmium complexes. The conductance data suggests that the nitrite complexes are non ionic in nature and 1:0 electrolytes.\[17\]

Coordination compounds of Cu(II) chloride, bromide, thiocyanate and sulphate with nicotinic acid (NA), nicotinamide (NICA) and isonicotinamide (INA) were prepared by Ahuja et al. and characterized spectroscopically. IR data indicates the coordination through carbonyl oxygen in complexes of INA and NICA whereas in complexes of NA It reveals the coordination through pyridine ring nitrogen only to Cu(II) ions.\[18\]

Some complexes of chlorides and bromides of Mn(II), Fe(II), Co(II), Ni(II) and Cu (II) with nicotinic acid and nicotinamide were synthesized by Allan et al. [1979]. These complexes had stereochemistry ML₂X₂ with the exception of bis-nicotinamide manganese(II)chloride which has one molecule of water of crystallisation.\[19\]

Suksrichavalit et al. [2008] reported the synthesis of novel mixed ligand complexes of copper with nicotinic and other select carboxylic acids (Phthalic, Salicylic and Anthranilic acids). The tested copper complexes exhibited superoxide dismutase (SOD) mimetic activity and antimicrobial activity against B. subtilis ATCC 6633, with a minimum inhibition concentration of 256μg/mL. Copper complex of nicotinic-phthalic acids (CuNA/Ph) was the most potent with a SOD mimetic activity of IC50 34.42 μM. The SOD activities were observed to correlate well with the theoretical parameters as calculated using density functional theory (DFT) at the B3LYP/LANL2DZ level of theory. Interestingly, the SOD activity of the copper complex CuNA/Ph was positively correlated with the electron affinity (EA) value. The two quantum chemical parameters, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), were shown to be appropriate for understanding the mechanism of the metal complexes as their calculated energies show
good correlation with the SOD activity. Moreover, copper complex with the highest SOD activity were shown to possess the lowest HOMO energy. These findings demonstrate a great potential for the development of value-added metallovitamin-based therapeutics.\[[20]\]

One year later [2009], the same authors\[[20]\] have reported the synthesis of three novel copper complexes with nicotinic acid as the primary ligand along with 2-substituted pyridines: 2-hydroxypyridine, 2-aminopyridine and picolinic acid. In these tetragonally distorted complexes, Nicotinic acid behaved as a bidentate ligand, which utilized the ring N-atom of pyridine and the carbonyl group of carboxylic acid. These copper complexes were shown to possess superoxide dismutase (SOD) and antimicrobial activities. The copper complexes exerted SOD activity in range of 49.07–130.23 mM. Particularly, copper complex of nicotinic acid with 2-hydroxypyridine was the most potent SOD mimic with an IC\(_{50}\) of 49.07 mM. In addition, the complexes exhibited antimicrobial activity against *Bacillus subtilis* ATCC 6633 and *Candida albicans* ATCC 90028 with MIC range of 128–256 mg/mL. The SOD activities were well correlated with the theoretical parameters as calculated by density functional theory at the B3LYP/LANL2DZ level of theory. Interestingly, the SOD activity of the copper complexes was demonstrated to be inversely correlated with the electron affinity, but was well correlated with both HOMO and LUMO energies. The vitamin–metal complexes described in this report are great examples of the value-added benefits of vitamins for medicinal applications.\[[21]\]

Al-Saif and co-workers [2012] presented a simple but clever paper that reports the synthesis, spectroscopic, magnetic and thermal studies of ten metal complexes of vitaminB3/Niacin(NA) with Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), Pt(IV) and Au(III). In complexes of Mn(II), Co(II), Pd(II), and Pt(IV) both of two NA ligand coordinates one metal ion to form four or six coordinated structures, while in compound of Au(III), one NA ligand coordinate to Au\(^{+++}\) ion to form a square-planar geometry with N-bonded pyridine ligand, and (Fe(III), Ni(II), Cu(II), Zn(II)) complexes have 1:1 structures. The magnetic and electronic spectral studies support an octahedral geometry for all the complexes except Zn(II), Pd(II), Cd(II) and Au(III) complexes which exhibit tetra-dentate geometry. Biological studies were observed in term antimicrobial activities of target complexes against Gram-positive (*B. subtilis* and *S. aureus*) and Gram negative (*E. coli* and *P. aeruginosa*) and two strains of fungus (*A. Flavus* and *C. albicans*). The complexes showed more activity than free ligand. Cytotoxic and antitumor activity of palladium(II), platinum
(IV) and gold(III)nicotinamide complexes were tested against breast carcinoma cells MCF-7 cell line.\[22\]

Vicens et al., have reported the synthesis of three new nicotinic acid complexes of Cr (III) in very mild conditions. The D NMR study of the d\(_2\) nicotinic acid complexes reveals that nicotinic acid is bound to chromium (III) through the carboxylic group in all cases. The ternary complex with histidine shows zero fields splitting in its EPR spectrum indicating a distorted octahedral geometry for this complex.\[23\]

Liu and co-workers have reported the hydrothermal reaction of Ni(NO\(_3\))\(_2\), NaN\(_3\), and nicotinic acid (Hnic) yielded a 3-D supramolecular framework complex, [Ni\(_{1.5}\)(N\(_3\))(nic)\(_2\)(Hnic)]\(_n\) (I) with unusual magnetic properties. In 1, Hnic and nic\(^{-1}\) coexist and show different coordination modes (\(\mu_2\)-Hnic-N,O, \(\mu_2\)-nic-N,O and \(\mu_3\)-nic-N,O,O bridging Ni(II) ions), and azide groups adopt \(\mu\)-1,1 (EO) bridging mode linking Ni(II) ions with an unusual Ni-N-Ni angle.\[24\]

Chen et al. have carried out a study on four metal–organic co-ordination framework in the Cd\(^{II}\)–L–NCS\(^{-}\) system through covalent or hydrogen bonds using potentially bridging nicotinic acid derivatives L [nicotinic acid (HL\(_1\)), nicotinamide (L\(_2\)), isonicotinamide (L\(_3\)), or isonicotinate (L\(_4\))] In [Cd(SCN)\(_2\)(HL\(_1\))\(_2\)]. HL\(_1\) each pair of cadmium(II) ions is bridged by two inversely related \(\mu\)-NCS-N,S ligands to form infinite chains with the remaining two trans positions of six-co-ordinated Cd atoms being occupied by two HL\(_1\) ligands, which form head-to-head double hydrogen bonds using the uncoordinated carboxyl groups between adjacent chains to form two-dimensional layers. Weak S---S interactions between the NCS\(^{-}\) ligands extend the layers into a three-dimensional framework with the channels enclosing HL\(_1\) guest molecules, which are interlinked into chains through O--H---N hydrogen bonds. [Cd(SCN)\(_2\)(L\(_2\))\(_2\)].H\(_2\)O 2 and [Cd(SCN)\(_2\)(L\(_3\))\(_2\)] 3 are interesting in that they contain unprecedented 16-membered [Cd\(_4\)(\(\mu\)-SCN-N,S)\(_4\)] rings in the two-dimensional sheets. Between the sheets N--H---O amide–amide hydrogen bonds extend the two-dimensional layers to three-dimensional structures. [Cd(SCN)(L\(_4\))(H\(_2\)O)] 4 exhibits two-dimensional wave-like networks with bridging NCS\(^{-}\) and L\(_4\) ligands using both ends in co-ordination. The results demonstrate that the structures of the Cd\(^{II}\)–L–NCS system deeply depend on the nature of the nicotinic acid derivatives L.\[25\]
A recent paper by Fazary et al. [2016] presents the synthesis and characterization of twelve novel mixed ligand complexes formed between a metal ion (Cu(II), Cd(II), Mn(II), Fe(III), Ni(II), Pb(II)) and vitamins (B3 and B9) as primary ligands, and glycine as secondary ligand. The presence of coordination water molecules in the complex was also supported by TG/DTG thermal analysis. Spectral data IR, $^1$H-, $^{13}$C-NMR confirmed the participation of pyridine nitrogen and non-participation of carbonyl oxygen of the NA ligand in the coordination process. All complexes exhibited moderate cytotoxic activities against the four human cancer cell lines (HEp-2 human laryngeal carcinoma, Daoy human medulloblastoma, MCF-7 human breast adenocarcinoma, and Wi Dr human colon adenocarcinoma). Also the most metal complexes showed moderate antioxidant activity, while cadmium and lead complexes of both vitamins exhibited weak antioxidant activities.\cite{26}

![Scheme-2: Structure of mixed ligand complex involving nicotinic acid (NA).](image)

In a recently published paper by Nair et al. [2015], the crystallisation of cobalt (II) nicotinate tetrahydrate (C$_6$H$_5$NO$_2$Co.4H$_2$O as single crystals by gel method is reported for the first time. The 3D supramolecular crystal structure is stabilised by the intermolecular hydrogen bonding as revealed by the single crystal XRD data. FT-IR analysis indicates that metal atoms are co-ordinated through two pyridine nitrogen and four water molecules. The porosity of the complex offers the potential for adsorption and storage of gases.\cite{27}

Vanchesan et al. have reported synthesis of two zero-valent metal carbonyl complexes fac-[M(CO)$_3$(NIC)$_3$] (where M = Mo, W; 3, 4; NIC = Nicotinic acid) and characterized spectroscopically. The IR spectrum of complex 3 exhibits three CO stretching bands and 4 shows two CO stretching bands in addition to a carboxylic-carbonyl stretching band. The possibility of fac/mer isomerisation in complex 3 has been studied by IR spectroscopy in various solvents.\cite{28}
Transition metal hydrazine complexes of pyridine–3-carboxylic acid and pyridine–4-carboxylic acid were synthesized by Kanchana et al. and assigned octahedral geometry based on the spectroscopic studies. Where hydrazine acts as bidentate bridging ligand and pyridine-3-carboxylic acid and pyridine-4-carboxylic acid acts as monodentate ligands to the metal via carboxylate ion coordination. Antimicrobial screening was carried out for the synthesized complex against bacteria (E. coli and S. aureus) and fungi (C. albicans and A. fumigates). The binding of the complexes with herring sperm DNA was also carried out for the complexes.\(^{[29]}\)

Toma and co-workers have reported the synthesis and isolation of new TlCl\(_3\) complexes with nicotinic acid (Hnic) and isonicotinic acid (Hinic). The molecular structures of [TlCl\(_2\)(nic)(Hnic)] (1) and [TlCl(inic)\(_2\)Cl\(_0.6\)C\(_2\)H\(_5\)OH] (2) are determined by single-crystal XRD, IR, Raman and multinuclear NMR (\(^{1}\)H, \(^{13}\)C, \(^{205}\)Tl). The coordination polyhedron in compounds 1-2 is pentagonal bi-pyramidal, i.e. TlCl\(_2\)NO\(_4\) in 1, and TlClNO\(_4\) in 2, respectively. O,O’,N Bridging ligands result in a polymer chain for 1 and a supramolecular associations in 2.\(^{[30]}\)

Maurya et al. have synthesized some novel cyanonitrosyl complexes of mono-valent chromium, formed by the interaction of K\(_3\)[Cr(NO)(CN)\(_5\)].H\(_2\)O with nicotinamide (NICAM), isonicotinamide (INAM), N-methylnicotinamide (N-MeNICAM), nicotinic acid (NA), isonicotinic acid (INA) and 2-aminonicotinic acid (2AmNA). The complexes have the empirical formula [Cr(NO)(CN)\(_2\)(L)\(_2\)(H\(_2\)O)] (L = NICAM, INAM, N-MeNICAM, NA, INA, 2AmNA). Chromium(I) has a low spin d\(_5\) configuration in all these complexes. The significant positive shifts in pyridine ring breathing vibrations, in the complexes, indicates the coordination of these ligands via pyridine ring nitrogen only.\(^{[31]}\)

**Metal Complexes of Mercapto-Nicotinic Acid and Derivatives**

Pd(II) and Pt(II) complexes of 2-mercaptonicotinic acid (MENA) of formulae [M\(_3\)(MENA)\(_3\)]Cl\(_3\)] were synthesized and characterized by Marchal et al. In palladium complex the molecule has a ternary symmetry, and mercaptonicotinic acid coordinates in a bidentate (N, S) mode to each palladium ion. The sulphur atom acts as a bridge between two palladium atoms. The fourth coordination site in the plane square geometry of the Pd (II) is occupied by a chloride ion.\(^{[32]}\)

Xanthopoulou et al. have synthesized a novel triphenylin (IV) derivative of 2-mercaptopoticin acid (H\(_2\)mna) of formula \{[(C\(_6\)H\(_5\))\(_3\)Sn]\(_2\)](mna),[(CH\(_3\))\(_2\)CO]\} and
characterized by elemental analysis and $^{13}$C-NMR, and FT-IR spectroscopic techniques. Complex contains two triphenyltin moieties linked by a doubly de-protonated 2-mercaptonicotinic acid. It is an example of a pentacoordinated $\text{Ph}_3\text{SnXY}$ system with an axial-equatorial arrangement of the phenyl groups at Sn. The complex exhibits potent, \textit{in vitro}, cytotoxicity against sarcoma cancer cells (mesenchymal tissue) from the Wistar rat, polycyclic aromatic hydrocarbons (PAH, benzo[a]pyrene) carcinogenesis.\textsuperscript{[33]}

Zachariadis et al. have reported that Silver(I) chloride reacts with 2-mercapto-nicotinic acid (H$_2$mna) in the presence of an excess of triethylamine in DMSO to form a hexanuclear, water soluble, cluster of formula $\{[\text{Ag}_6(\mu_3-\text{Hmna})_4(\mu_3-\text{mna})_2]^2.[(\text{Et}_3\text{NH})^+]^2.\text{(DMSO)}^2.\text{(H}_2\text{O})\}$ (I). The entire molecule is ionic and consists of a double anionic hexa-nuclear cluster and two protonated triethylamine counter cations while it is solvated by two DMSO and one water molecule. Extended inter-molecular hydrogen bonding \textit{via} O---H-N contacts links the molecules forming a supramolecular two dimensional network. Complex I was evaluated for anti-HIV-RT activity. It was found to inhibit the human immunodeficiency viral replication reverse transcriptase (HIV-RT) with calculated inhibiting concentration (IC$_{50}$) 0.01275 ± 0.00115 mg ml$^{-1}$.\textsuperscript{[34]}

Scheme 3: Thiole-thione tautomerism of H2mna

Xanthopoulou et al. have reported the synthesis and spectroscopic characterization of a new chloro-di-phenyltin (IV) complex with 2-mercapto-nicotinic acid. The complex [(C$_6$H$_5$)$_2$SnCl(HMNA)] (1) where H$_2$MNA is thioamide 2-mercapto-nicotinic acid. The ligand coordinates to the metal centre through the exocyclic sulphur and the heterocyclic nitrogen atoms, forming a four member ring. The geometry around the tin atom described either as trigonal bipyramidal or tetragonal pyramidal. The complex was found to inhibit the catalytic oxidation of linoleic acid to hydroperoxy-linoleic acid by the enzyme lipoxygenase (LOX).\textsuperscript{[35]}

Verginadis et al. tested the triorganotin compound bis[triphenyltin(IV)](3-carboxy-pyridine-2-thionato) (SnMNA), for its anti-proliferative and antitumor activities. Cytotoxic activity
was assessed by Trypan blue and 3-(4.5-dimethylthiazol-2-yl)-2.5-diphenyltetrazolium bromide assay (MTT). SnMNA exhibited potent cytotoxic effects against leiomyosarcoma cells (LMS) and human breast adenocarcinoma cells (MCF-7), which is 200 times stronger than that of cis-platin. Moreover, SnMNA induced significant apoptosis in LMS and MCF-7 cells characterized by flow cytometry analysis and DNA fragmentation. Acute and chronic toxicity studies on Wistar rats caused kidney and lung toxicity at a single dose of 80 mg/kg Body Weight (BW) or four repeated doses of 8 mg/kg body weight once per week. Furthermore, antitumor activity studies on sarcoma bearing Wistar rats revealed that SnMNA complex at four repeated doses of 5.4 mg/kg BW every three days prolonged mean survival time of the animal at 200% and decreased mean tumor growth rate (MTGR) compared to the control group ($p < 0.05$). It is noteworthy to mention that the 30% (3 out of 10) of the bearing animals were totally cured. These findings indicate that SnMNA might be a promising new antitumor agent.\cite{36}

**Metal Complexes of Hydroxy-Nicotinic Acid and Derivatives**

Dean et al. evaluated 4-Hydroxy-6-methyl-3-pyridinecarboxylic acid (DQ6) and the new compound 2,6-dimethyl-4-hydroxy-3-pyridinecarboxylic acid (DQ726) for possible application for iron(Fe) and aluminium(Al) chelation therapy. DQ6 exhibited a high coordination efficiency towards Al(III). Fe(III)/DQ6, Al(III)/DQ726, and Fe(III)/DQ726 complexes were less stable. Accordingly, the effects of the substitution at various ring positions of 4-hydroxy-3-pyridinecarboxylic acid were rationalised. Partitioning experiments at pH 7.4 showed both DQ6 and DQ726, and their Fe (III) and Al(III) complexes, to be hydrophilic. The toxicity of DQ6 and of DQ726 was investigated with human cancer cell lines and normal human primary cells: no cytotoxic effects were observed up to 0.1 mM, following a 3 days exposure.\cite{37}

![Scheme 4. Enol-keto tautomers of 2-hydroxynicotinic acid.](image)

Two promising antimycobacterium tuberculosis ruthenium (II) complexes with the deprotonated ligands 2-hydroxynicotinic acid (2-OHnicH) and 6-hydroxynicotinic acid (6-
OHnicH) were synthesized and characterized by Barbosa et al. [2015]. Spectral analysis indicates two different coordination modes depending on the hydroxypyridinecarboxylate ligand. In the complex [Ru(2OHnic)(dppb)(bipy)]PF$_6$ (1), the 2-OHnic anion is coordinated by the O,O-chelating mode (via carboxylate group and phenolate oxygen) and in the [Ru(6-OHnic)(dppb)(bipy)]PF$_6$ (2), a O-O chelation by the carboxylate group is observed for the 6-OHnic ligand. The compounds were evaluated for activity against Mycobacterium tuberculosis H$_3$7Rv ATCC 27294 using Resazurin Microtitre Assay (REMA) plate method and cytotoxicity in VERO CCL-81 cell line. All the synthesized compounds exhibited good antimycobacterial activity and a completely lack of cytotoxicity activity, indicating a good selectivity index. [38]

Xu et al. reported the template synthesis of lanthanide coordination polymers from Pr(III), Nd(III), and Gd(III) salts; 2-hydroxynicotinic acid (Hnica); and MnSO$_4$$\cdot$H$_2$O under hydrothermal conditions. In the absence of (CH$_3$)$_3$CCOONa, 1D polymers with an infinite Ln(III)-O-Ln(III) chain structure, [Pr(Hnica)(H$_2$O)$_2$SO$_4$]$_n$ (1), [Nd(Hnica)(H$_2$O)$_2$SO$_4$]$_n$ (2), and [Gd(Hnica)(H$_2$O)$_2$SO$_4$]$_n$ (3), were generated. When (CH$_3$)$_3$CCOONa was added to the synthetic systems, 2D coordination polymers {{[Pr$_3$(Hnica)$_6$(H$_2$O)$_9$]·3H$_2$O·SO$_4$·NO$_3$}}$_n$ (4), {{[Nd$_3$(Hnica)$_6$(H$_2$O)$_9$]·3H$_2$O·SO$_4$·NO$_3$}}$_n$ (5), and {{[Gd(Hnica)$_2$(H$_2$O)$_2$]ClO$_4$·H$_2$O}}$_n$ (6) were obtained. Complexes 4 and 5 are the first examples of lanthanide coordination polymers exhibiting a Kagome lattice structure, while 6 displays a rhombic grid structure. [39]

Zou et al. presented synthesis of three novel heterometallic microporous coordination polymers {M(Hnico)$_3$M´}$_n$ (1, M = Co, M´ = K; 2, M = Ni, M´ = K; 3, M = Co, M´ = Na, Hnico is the anion of 2-hydroxy-nicotinic acid) by hydrothermal reaction between M(Ac)$_2$·4H$_2$O, M´OH and a multifunctional organic aromatic H$_2$nico ligand and characterized by spectroscopic techniques. In complexes 1–3, the M$^{2+}$ ions linked three different Hnico ligand formed [M(Hnico)$_3$]’ subunit which further interlinked the six-coordination M$^{2+}$ cation constructed 3D network. The network topology of 1–3 can be simplified a rare 3D (4, 4)-connected (4$^{12}$6$^3$) net. [40]

Three new coordination polymers, namely [Mn$_2$(5-phenoxonicotinato)$_2$] (1), [Cd$_2$(5 phenoxonicotinato)$_2$] (2), and [Fe$_2$(5-phenoxonicotinato)$_2$] (3), have been synthesized under hydrothermal conditions and characterized structurally through single-crystal X-ray diffraction by Yang et al. The structure of compound 1 can be described as a 3D metal-organic framework which is constructed by two kinds of crystallographical unique Mn
cations and one kind of \(\mu_6\)-phenoxonicotinato bridging ligand, featuring a 6,6-connected \(\{3 \cdot 4^{10} \cdot 6^6\}\) \(\{4^9 \cdot 6^6\}\) topology structure. Compounds 2 and 3 are also isostructural with 1.\[41\]

Soares-Santos et al. [2003] prepared new lanthanide complexes of 2-hydroxynicotinic acid (H\(_2\)nicO) \([\text{Ln(HnicO)}_2(\mu\text{-HnicO})(\text{H}_2\text{O})]\_n\text{H}_2\text{O}\) (Ln = Eu, Gd, Tb, Er, Tm). The crystal structures of the \([\text{Tb(HnicO)}_2(\mu\text{-HnicO})(\text{H}_2\text{O})]\_1.75\text{H}_2\text{O}\) (1) and \([\text{Eu(HnicO)}_2(\mu\text{-HnicO})(\text{H}_2\text{O})]\_1.25\text{H}_2\text{O}\) (2) complexes were determined by X-ray diffraction. The 2-hydroxynicotinate ligand coordinates through O,O-chelation to the lanthanide(III) ions as shown by XRD and the IR, Raman and NMR spectroscopy results.\[42\]

The same authors \[42\] have also prepared and characterised Samarium (III) complexes of 3-hydroxypicolinic acid (HpicOH) and 2-hydroxynicotinic acid (H\(_2\)nicO) in order to emphasize coordination modes of H\(_2\)nicO. The crystal structures of \([\text{Sm(HnicO)}_2(\mu\text{-HnicO})(\text{H}_2\text{O})]\_5\text{H}_2\text{O}\) reveals the three crystallographically unique HnicO' ligands appear with both phenolic and carboxylic acid groups deprotonated and coordinated to the Sm\(^{3+}\) centres, in a typical O,O-chelating coordination fashion.\[43\]

Yue et al. have synthesized three new Mn(II) complexes \([\text{Mn(HnicO)}_2(\text{H}_2\text{O})]\_2\) (1), \([\text{Mn}_2(\text{HnicO})_2\text{SO}_4(\text{H}_2\text{O})_2]\_n\) (2), and \([\text{NaMn(HnicO)}_3]\_n\) (3) (HnicO = 2 hydroxynicotinic acid) and determined their structure by X-ray diffraction. For complex 1, the mononuclear units with two bidentate HnicO' ions and two water molecules are assembled into a 3D architecture via hydrogen bonding and \(\pi-\pi\) interactions. For 2, Mn (II) ions are connected by \(\mu_3\)-HnicO' and \(\mu_2\)-SO\(_4\) 2- bridging ligands, producing a 2D (6,3) coordination network. For 3, binuclear Na(I)–Mn(II) units with three carbonyl oxygen bridges are interlinked by carboxylate groups, resulting in a 3D six-connected coordination network with distorted \(\alpha\)-Po topology.\[44\]

Quintal et al. presented a study to investigate coordination modes of 2-hydroxynicotinic acid in second- and third row transition metal complexes. For this purpose new Pd(II), Pt(II), Re(V), Mo(VI) and W(VI) complexes of 2-hydroxynicotinic acid (H\(_2\)nicO), \(\text{trans-}[\text{PdCl(HnicO)}(\text{PPh}_3)\_2]\_0.75\text{CH}_3\text{CN}\) (1), \([\text{K[PdCl(HnicO)}_2]\_\text{H}_2\text{O}\) (2), \([\text{Pd(HnicO)}_2(\text{bipy})]\) (3), \(\text{cis-}[\text{PtCl(HnicO)}(\text{PPh}_3)\_2]\_0.75\text{CH}_3\text{OH}0.5\text{H}_2\text{O}\) (4), \([\text{PtCl(HnicO)}(\text{bipy})]\) (5), \(\text{cis-}[\text{ReO}_2(\text{HnicO})(\text{PPh}_3)]\) (6), \([\text{Na}_2[\text{Mo}_2\text{O}_6(\text{HnicO})_2]\_\text{H}_2\text{O}\) (7), \([\text{Na}_2[\text{Mo}_4\text{O}_{12}(\text{HnicO})_2]\_\text{2H}_2\text{O}\) (8) and \([\text{Na}_2[\text{W}_2\text{O}_6(\text{HnicO})_2]\_\text{5H}_2\text{O}\) (9) have been prepared. The crystal structures of 1 and 4, were determined by X-ray diffraction and shows the HnicO' ligand coordinated to palladium or platinum through the nitrogen atom of the pyridine ring only and in the case of rhenium,
molybdenum and tungsten, a possible N,O-chelation with the adjacent oxygen atom. Infrared, Raman, $^1$H and $^{13}$C{$^1$H} NMR spectroscopic data for the complexes are presented and are in agreement with the crystallographic results.$^{[45]}$

An interesting insight into the coordination modes of 2-hydroxynicotinic acid in its Co(II) and Cu(II) complexes has been presented by Miklovic and co-workers. They reported synthesis and characterization of Cu(II) and Co(II) octahedral complexes [M(2-OHnic)$_2$(H$_2$O)$_2$] (2-OHnic is 2-hydroxynicotinato), [Cu(6-OHnic)$_2$(H$_2$O)$_2$] (6-OHnic is 6-hydroxynicotinato) as well as [Co(H$_2$O)$_6$](6-OHnic)$_2$. Based on IR spectra, O,O-asymmetrically chelating coordination of the carboxyl groups as well as ionic coordination of 6-OHnic and chelating O,O-coordination (through the oxygen atom of the carboxyl group and the oxygen atom of the amide group) of keto(amide) tautomer of 2-OHnic were supposed. The system of hydrogen bonds predominantly stabilizes the keto(amide) tautomer of both 2-hydroxynicotinic acid and 2-OHnic anion in the cobalt(II) complex. Intermolecular hydrogen bonds (between the oxygen atom of the amide group and the hydrogen atom of the NH group) interconnect two neighbouring molecules of 2-OHnicH forming dimers. Cobalt(II) in complex [Co(2-OHnic)$_2$(H$_2$O)$_2$] has nearly a regular compressed tetragonal bipyramidal arrangement.$^{[46]}$

De-Cai et al. reported synthesis of two complexes Cu(HnicO)$_2$, and Ni(HnicO)$_2$(H$_2$O)$_2$ by hydrothermal reaction and characterized structurally. There is extended 3D framework structure i.e. supramolecular formation in both complexes due to N-H---H and C–H---O hydrogen bonds.$^{[47]}$

**Metal Complexes of Amino-Nicotinic Acid and Derivatives**

Toma et al. have carried out study on synthesis and supramolecular structure of 2-aminonicotinatodimethylthallium(III), [TlMe$_2$(2anic)]$_n$. In the complex [TlMe$_2$(2anic)]$_n$, each 2anic$^-$ ligand bridges two [TlMe$_2$]$^+$ moieties, being strongly bound to one via the two oxygen atoms of the carboxylate group and less strongly to the other via the pyridine nitrogen atom. The polymeric chains so formed are associated through Tl–O$^{ii}$ secondary bonds in a two-dimensional supramolecular arrangement in which each 2anic$^-$ ligand interacts with three metal centres.$^{[48]}$
Soares-Santos et al. reported synthesis of new complex of Tb (III) with 2-aminonicotinic acid (Hanic), [Tb(anic)3]-0.5Hanic-7H2O, in which metal coordination occurs through N,O donor atoms as confirmed by vibrational frequencies and elemental analysis.[49]

Three new coordination polymers (CPs) based on rigid ligand 5-Aminonicotinic acid (5-anaH), [Cd(5-ana)2](H2O)2 (1), [Cd(5-ana)(HCOO)] (2) and [Cu(5-ana)2] (3), have been synthesized by Jiang et al., under different solvent media and temperatures. 1 is a 2D (4,4)-connected layered structure which contains 1D open channel. 2 shows a 2-nodal (3,5)-connected 3D framework. While 3 displays a 3D (3,6)-connected homochiral framework. The significant structural differences between these CPs are related to the reaction solvents, temperatures and metal cations. The different emission bands of 1 and 2 may be assigned to the coordination diversities of the Cd2+ ion centers and the rigid differences of these Cd2+ coordination frameworks.[50]

Nawaz et al. synthesized 2-aminonicotinic acid (2-ANA) complexes with metals such as Co(II), Fe(III), Ni(II), Mn(II), Zn(II), Ag(I),Cr(III), Cd(II) and Cu(II) in aqueous media. Spectroscopic data indicates that the carboxylate oxygen and the primary amino group of 2-ANA are chelated to the metal ions. The metal complexes showed varied antibacterial, fungicidal and nematicidal activities. The silver and zinc complexes showed highest activity against B. subtilis and B. licheniformis respectively. F. oxysporum was highly susceptible to nickel and copper complexes whereas M. phaseolina was completely inert to the complexes. The silver and cadmium complexes were effective against the root-knot nematode M. javanica.[51]

Greenawayet al. investigated synthesis and characterization of three complexes with a potent nonsteroidal anti-inflammatory drug niflumic acid {2-[3-(trifluoromethyl)phenyl] aminonicotinic acid} with formula [Cu(niflumato)L] (L=H2O, DMSO=dimethylsulfoxide, DMF=N,N-dimethylformamide). Each Cu(II) ion in [Cu2(DMSO)2(m-niflumato)4] is coordinated to an apical dimethylsulfoxide-O atom on the one hand and to the equatorial carbonyl and carboxylic-O atoms of two crystallographically independent niflumate moieties and their centrosymmetric counterparts on the other hand. Niflumic acid and its various copper complexes significantly inhibited polymorphonuclear leukocyte (PMNL) oxidative metabolism, as assessed by chemiluminescence and O2- generation measurement. This effect was dose-dependent. All copper complexes exerted a similar inhibiting effect which was always significantly higher than that exerted by the parent drug.[52]
Abu-Youssef et al. carried out synthesis and spectroscopic characterization of five new silver complexes, \( \text{Ag}_2\mu-O,O'\text{(2-aminonicotinium)}_2(\text{NO}_3)_2 \) (1), \( \text{Ag}(\text{isonicotinamide})_2\mu-O,O'\text{(NO}_3\text{)}_2 \) (2), \( \text{Ag}(\text{ethyl nicotinate})_2(\text{NO}_3) \) (3), \( \text{Ag}(\text{ethyl isonicotinate})_2(\text{NO}_3) \) (4), and \( \text{Ag}(\text{methyl isonicotinate})_2(\text{H}_2\text{O})(\text{NO}_3) \) (5). The antimicrobial activities of these complexes were screened using 12 different clinical isolates belonging to four pathogenic bacteria, \( S.\text{aureus}, S.\text{pyogenes}, P.\text{mirabilis}, \text{and Ps. Aeruginosa} \), all obtained from diabetic foot ulcers. These tested bacteria were resistant for at least 10 antibiotics commonly used for treatment of diabetic foot ulcers. Compounds 1 and 2 had considerable activity against \( P.\text{Aeruginosa} \) (MIC values 2-8 µg/mL), compound 3 against \( S.\text{aureus} \) (MIC 4-16 µg/mL) and \( S.\text{pyogenes} \) (MIC 2-4 µg/mL), and also 3 and 5 against \( P.\text{mirabilis} \) (MIC 1-16 µg/mL). All complexes were non-toxic for daphnia at concentrations above 512 µg/mL overnight.

**Metal Complexes of Nicotinic Acid Hydrazide and Derivatives Including Schiff’s Bases**

Hueso-Urena et al. evaluated and reported the synthesis and spectroscopic characterization of complexes of Ni(II), Cu(II), Zn(II) and Cd(II) containing hydrazones derived from 6-amino-5-formyl-1,3-dimethyluracil and nicotinic and isonicotinic acid hydrazides. In all cases, the complexes appear to be monomeric and four-coordinated, with three binding sites occupied by the dinegative tridentate ligand, which makes two five- and six-membered chelate rings and the fourth position occupied by either water or ammonia. The coordination of the organic ligand takes place through the deprotonated N(6) atom from the 6-amino group, the N(51) azomethine atom and the O(52) oxygen from the hydrazide moiety. Spectral data indicate that neither carbonyl oxygen atoms from the uracil ring nor the endocyclic nitrogen atom from pyridine are involved in the coordination to the metal.

Balasubramaniyan et al. developed the mixed Ligand complexes of Cr(III), Co(II), Ni(II) and Hg(II) with nicotinic acid hydrazide(NHA) and azide ion as ligands. From the obtained analytical, IR and NMR spectral data the formulae of the complexes are \( \text{Cr}_2(\text{NHA})_3(\text{N}_3)_6 \), \( \text{Co}(\text{NHA})_2(\text{N}_3)_2 \), \( \text{Ni}(\text{NHA})_2(\text{N}_3)_2 \) and \( \text{Hg}(\text{NHA})(\text{N}_3)_2 \). The antifungal activities of complexes compared with those of pure Ligand NHA. All the complexes show less activity against the tested fungus such as \( A.\text{flavus, A.niger, C.albicance, A.oryzae and A.sojae} \).

Hussaina et al. reported and synthesized a series of 15 metal based \([\text{Cu(II), Co(II) and Ni(II)}]\) complexes with novel \( \text{N}^-\text{[-(5-hydroxy-2-nitrophenyl)-methylidene]pyridine-4-carboxylhydrazide} \) (L1), \( \text{N}^-\text{[-1-(2,5-dihydroxyphenyl)ethylidene]pyridine-3-carboxylhydrazide} \) (L2), \( \text{N}^-\text{[-1-(5-chloro-2-hydroxyphenyl)ethylidene]pyridine-3-carboxylhydrazide} \) (L3), and \( \text{N}^-\text{[-1-(5-}
chloro-2-hydroxyphenyl)ethylidene]pyridine-4-carbohydrazide (L4) and N’-[1-(2, 5-dihydroxyphenyl)ethylidene]-3-hydroxybenzohydrazide (L5) Schiff bases and screened for antioxidant and cytotoxic activities. All these complexes exhibited strong antioxidant activity against DPPH radical. Antibacterial activity assay exhibited MIC values of these compounds comparable to standard drugs for both Gram-positive (B. subtilis, S. aureus) and Gram-negative bacteria (S. sonnei, E. coli, Ps. aeruginosa and S. typhi).\textsuperscript{[56]}

M. Syed Ali Padusha et. al. \textsuperscript{[2014]} designed a Schiff base of Nicotinic acid hydrazide with the aim to develop novel antimicrobial agent of synthetic origin having broad spectrum of activity and high potency. The Schiff base (E)-N’-(thiophen-2-ylmethylene)nicotinohydrazide (TCNH), synthesized by the condensation of nicotinic acid hydrazide and thiophene-2-carboxaldehyde, was treated with Metal chlorides [Mn(II), Co(II), Cu(II) and Zn(II)] to prepare the complexes of TCNH. IR frequencies of (\(-\text{C}=\text{O}\)) and (\(-\text{C}=\text{N}\)) of the ligand are shifted to lower value by 10-48 cm\(^{-1}\) in the spectra of the complexes, which indicate the involvement of O atom of carbonyl group and N atom of azomethine (-CH=N-) linkage in binding with metal ions. Thus, it is concluded that the ligand acts as a neutral bidentate manner in all the complexes. Further, TCNH and its metal complexes were tested against three pathogenic micro organism S.aureus, E.coli and A.niger. All the metal Complexes exhibit higher antibacterial activities than the free ligand.\textsuperscript{[57]}

After one year [2015], the same authors\textsuperscript{[57]} derived a bidentate ligand nicotinicacid-furan-2-ylmethylene-hydrazide from furan-2-aldehyde and nicotinic acid hydrazide and also synthesized its metal complexes with Mn(II), Co(II), Cu(II) and Zn(II). The spectral studies confirm the electrolytical nature and octahedral geometry of the complexes. Further the Antimicrobial screening of ligand and its metal complexes showed their excellent activity. The zone of inhibition of metal complexes is comparably higher than the free ligand.\textsuperscript{[58]}

Chohan et al. evaluated and reported preparation of nicotinic acid derived Schiff bases and their transition metal [Co(II), Ni(II) and Zn(II)] complexes [M(L)\(_2\)] with octahedral geometry and their characterization by physical, spectral and analytical data. The Schiff bases act as deprotonated tridentate ligands for the complexation of the above mentioned metal ions. For determining the effect of metal ions upon chelation, the Schiff bases and their complexes have been screened for antibacterial activity against several pathogenic strains of E. coli, S. aureus and Ps. aeruginosa. The new metal derivatives reported here were more bactericidal against one or more bacterial species as compared to the uncomplexed Schiff bases.\textsuperscript{[59]}
Tajudeen et al. presented a study that deals with the synthesis, spectral characterization of Cu metal complexes, \([L_2CuClO_4].ClO_4\), with Schiff base of isoniazid, pyrazinamide an anti-tubercular drug, and benzhydrazide, nicotinohydrazide. Spectral data reveals that ligand binds the metal ion in a bidentate fashion with N, O coordination to copper(II) ion. Thus, bonding sites are the azomethine nitrogen and the carbonyl oxygen atoms. The antibacterial study indicated that the synthesized Cu(II) complexes showed appreciable activity with that of the standard. Whereas, the anti-tubercular activity was found to be relatively less than that of the standard used.\(^{[60]}\)

A rapid, efficient, clean and environmentally benign exclusive synthesis of Schiff bases as new ligands has been developed Srivastava et al. through condensation reaction of 2-aminonicotinic acid with salicyldehyde, 5-nitrosalicyldehyde, 5-bromosalicyldehyde and 5-methoxysalicyldehyde efficiently in a water suspension medium using acid catalyst with excellent yields under microwaves irradiation. All the Schiff bases were tridentate (NNO donor) ligands that were used for complexation with Co(II), Ni(II) and Zn(II) ions.

Scheme 5: Structure of the investigated complexes (where \(R = \text{ Where } R = H, 5-\text{Br}, 5-\text{NO}_2 \& 5-\text{OCH}_3 \) and \(M = \text{Co(II), Ni(II) or Zn(II)}\)).

All the ecofriendly synthesized Schiff bases and their metal complexes were characterized by analytical and spectral methods. The synthesized Schiff bases and their transition metal complexes were evaluated for their \textit{in vitro} antibacterial activity against four Gram-negative and two Gram-positive bacterial stains by the agar-well diffusion method. Schiff bases were found to exhibit either no or low to moderate activity but all the complexes exhibited varied vigorous activity against different bacteria. Schiff bases which were inactive before complexation became active and less active became more active upon coordination with mentioned bivalent transition metal ions.\(^{[61]}\)
Mishra et al. presented a condensation method to synthesize Bidentate and tridentate (NO), (ONO) Schiff bases by condensing methyl isobutyl ketone with 2-amino-4-chlorophenol and 2-hydroxy acetophenone with isonicotinic acid hydrazide. The 1:1 or 1:2 metal complexes prepared by interacting these Schiff bases with metal ions \textit{viz.} Ni(II), Cu(II). These compounds have been synthesized by conventional as well as microwave methods and characterized by elemental analysis, FT-IR, UV-Vis, ESR, molar conductance, thermal analysis and X-ray diffraction. The Schiff bases and metal complexes show good activity against the Gram-positive bacteria; \textit{S. aureus} and Gram-negative bacteria; \textit{E. coli} and fungi \textit{A. niger} and \textit{C. albicans}. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the Schiff bases.\textsuperscript{62}

**Metal Complexes of Methyl-Nicotinic Acid and Derivatives**

Aakeriyy et al. described synthesis and crystal structures of (6-methylnicotinic acid) (6-methylnicotinato) silver(I), Di(6-methylnicotinic acid) silver(I) nitrate, (2-chloro-6-methylnicotinato) silver(I), Di(2-chloro-6-methylnicotinic acid) silver(I) nitrate, and (2-methylnicotinic acid) (2-methylnicotinato) silver(I). These coordination complexes were with very similar ligands but their resulting structures are quite different, in part due to the degree of protonation of the nicotinic acid ligand(s). The structures vary from coordination polymers to hydrogen-bonded coordination dimers, to linear structures linked by anion-carboxylic acid hydrogen bonds. This study illustrates some of the difficulties involved in predicting hydrogen-bonded networks in transition-metal systems which contain carboxylic acid moieties and coordinatively unsaturated metal ions.\textsuperscript{63}

Two new complexes derived from 6-methylnicotinic acid: (Mn(C\textsubscript{7}H\textsubscript{6}NO\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}), \textbf{1} and ([Ni(C\textsubscript{7}H\textsubscript{7}NO\textsubscript{2})\textsubscript{2}-Cl\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}].4H\textsubscript{2}O), \textbf{2} have been synthesized and characterized by Luo et al.. In complex \textbf{1}, the Mn(II) ion exhibits a distorted octahedral geometry and featured with 1D chain, while the Ni(II) ion in complex \textbf{2} exhibits a regular octahedral geometry and featured with intricate 3D motif. We further compared the molecular Hirshfeld surface and fingerprint plot analysis of ligand 6-methylnicotinic acid in complexes 1 and 2 with the individual 6-methylnicotinic acid, for the purpose of investigating the influence of different metals on the intermolecular interaction around 6-methylnicotinic acid. Which revealed that the closest contacts of these two complexes were dominated by H---H, H---O, N---H, C--H--π and π---π (C--C) interactions, and the complexation with transition metals lead to the increase of C--H---π interactions while the decrease of H--H, N--H, and π---π interactions.\textsuperscript{64}
Kukovec et al. reported the synthesis of Co(II) metal complex with 6-methylnicotinic acid, namely [Co(C7H6NO2)2(H2O)4].4H2O and described coordination modes of the ligand. The Co(II) ion is octahedrally coordinated by two 6-methylpyridine-3-carboxylate ligands in axial positions and by four water molecules in the equatorial plane. There are also four uncoordinated water molecules. The 6-methylpyridine-3-carboxylate ligands are bound to the Co(II) ion in a monodentate manner through a carboxylate-O atom. There is one strong intramolecular O–H---O hydrogen bond, and six strong intermolecular hydrogen bonds of type O–H---O and one of type O–H---N in the packing, resulting in a complex three dimensional supramolecular structure.[65]

Scheme 6: Structure of [Co(C7H6NO2)2(H2O)4].4H2O

Metal Complexes of Halo-Nicotinic Acid

Li et al. have synthesized seven Zn(II) coordination complexes with 5-halonicotinic acids (HL- X, X = F, Cl, or Br) with different synthetic approaches, including layer diffusion or stirring method in an ambient environment and solvothermal synthesis at 100°C. Assembly of HL-F with Zn(II) under different conditions will yield the same 2D network of [Zn(L-F)2]n (1). Interestingly, three distinct complexes, a 3D framework {[Zn2(L-Cl)4(H2O)](H2O)8}n (2) and two 2D pseudo-polymorphic isomers {[Zn(L-Cl)2](H2O)1.5}n (3) and {[Zn2(L-Cl)4](H2O)}n (4) can be obtained by reacting HL-Cl with Zn(II) under layer diffusion, stirring, and solvothermal conditions, respectively. Furthermore, replacing the –Cl substituent with –Br on the HL-X ligand will also afford three diverse coordination assemblies of 3D {[Zn2(L-Br)4(H2O)](CH3OH)2.5}n (5), mononuclear [Zn(HL-Br)2(H2O)4][L-Br]2 (6), and 2D {[Zn(L-Br)2](H2O)1.15}n (7) depending on the synthetic pathways. Beyond the significant influence of the synthetic approach, which will lead to the formation of various crystalline products, the halogen substitution effect of HL-X ligands on the coordination motifs has also been demonstrated.[66]
ACKNOWLEDGEMENT
One of the author Suresh Kumar Verma gratefully thanks to The University Grant Commission (UGC), CRO, Bhopal (India) for awarding Teacher Research Fellowship (TRF).

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