PART-I

Metal complexes with pyridine-4-carboxylic acid derived ligands

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A literature survey: Coordination driven or/and H-bonded 1D, 2D and 3D frameworks of metal complexes of pyridine based ligands.

The field of “crystal engineering” originated with the self-assembly in organic solids into multidimensional frameworks using intermolecular interactions such as hydrogen bonding, $\pi \cdots \pi$ contacts, halogen-halogen interactions and van der Waals forces.\(^1\) The term “crystal engineering” was first put forward by Schmidt in the context of the study of the solid-state photodimerization of cinnamic acid.\(^{1(a)}\) The original idea was the design of crystals in which organic molecules could adopt a relative orientation suitable for topochemical reactions. Since then the field has developed enormously, encompassing all branches of vertical division of chemistry, especially inorganics and organometalics. The participation of coordination and organometallic complexes has revolutionised the whole concept of self-assembly phenomenon.\(^2\)\(^{-13}\) As emphasized by Jin et al.,\(^{12(f)}\) the presence of transition metal ions in the frameworks leads to the creation of “functional materials”\(^3\)\(^{,13}\) in the field of catalysis,\(^14\) porosity,\(^15\) magnetism,\(^16\) luminescence,\(^17\) conductivity,\(^18\) sensing,\(^19\) nonlinear optics\(^20\) and chirality.\(^21\) Furthermore, the varied coordination geometries adopted by these metal centers guide the direction of propagation of the network resulting in frameworks with interesting topologies.

The main strategies for assembling molecules in a required fashion so as to guide the properties of crystalline materials are through coordination polymerization or intermolecular hydrogen bonding or a combination of both.\(^2\)\(^{-12}\) The coordination complexes in which the multidentate ligands act as bridges between metal centers giving rise to coordination polymers\(^2(c)\),\(^3(a)\) or “metal-organic frameworks” (MOF’s) were the pioneers in the field of so called “inorganic crystal engineering”. The “adhesive” or glue for the inorganic supramolecular synthesis, binding these metal centers is the coordinate-covalent bond. The ligand connecting successive metal centers must be a bridging organic group. At least in one extended dimension the metal atoms must solely be bridged by this organic ligand. Furthermore, at least one carbon atom must lie between the donor atoms. The last requirement excludes groups such as organyloxides RO’, organophosponates RPO$_3^{2-}$ or organosulfonates RSO$_3^-$ which bridge with their one “inorganic” end group only, from giving rise to
coordination polymers. Infinite metal-ligand assemblies where the metal-organic connectivity is interrupted by “inorganic” bridges, such as \(-(R,H)O–, –Cl–, –CN–, –N_3–, -(R,O)PO_3–\) and \(-(R,O)SO_3–\) or where an extended inorganic metal-ligand network is lined by only terminal organic ligands are called organic–inorganic hybrid-materials.\(^{22}\)

One drawback to coordination-polymer chemistry is that their synthesis depends on polymerization events, which can lead to materials with poor solubility and unpredictable structures. Alternatively, the coordination complexes where polymerization is not possible by coordinate covalent bond, intermolecular hydrogen bonding is employed as binding force to self assemble complex molecules into multidimensional frameworks. While hydrogen bonds are not normally as strong as coordinate-covalent interactions, Wuest and coworkers,\(^{4(a)}\) constructed a hydrogen bonded crystalline host–guest material that is strong enough to withstand a substantial amount of guest removal. Mingos and coworkers\(^{4(b)}\) were the first to use H-bonding as a tool for multidimensional framework expansion in coordination complexes. Since then several groups have used hydrogen bond in the crystal engineering of transition-metal systems.\(^{5-7}\)

The direction of propagation of the framework resulting from coordination polymerization or hydrogen bonding is dictated by the coordination geometry adopted by the metal center. Thus for the creation of 1D, 2D or 3D networks one must make appropriate choice of combination of metal ion and the bridging ligand. For example, silver(I) ions are ideal for generating 1-D architectures as they frequently adopt a linear coordination geometry, Pt(II) and Pd(II) which prefer square planar geometry are suitable for 2-D networks, and so on. The transition metals such as Cu(II), Co(II) or Ni(II) which are capable for adopting varied coordination modes/geometries are always expected to form multidimensional networks with interesting topologies.

The choice of ligand is also a very crucial factor in creation of networks along with the geometry adopted by metal center. The ligands having metal coordinating sites along with H-bonding functionalities are ideal for framework expansion. Ligands having good hydrogen bond donors, such as amide nitrogen and hydroxy oxygen atoms, and good hydrogen bond acceptors, such as pyridine, pyrimidine, pyrazine, pyrazole and imidazole nitrogen atoms and carboxylate and carboxamide oxygen atoms, are very suitable for such an approach (Figure 1). Among these, the pyridine monocarboxylic acids and their amide derivatives (nicotinic acid, isonicotinic acid,
nicotinamide and isonicotinamide), are very versatile ligands from crystal engineering point of view (Figure 1). These ligands have the structural adaptability for both the metal-ligand coordination as well as the H-bonding (Scheme 1). The complexes of these ligands self assemble into 1D, 2D or 3D frameworks using H-bonding or

Figure 1: Some frequently encountered ligands used for the formation of frameworks among metal complexes (C. Janiak, 2003).
coordination polymerization\textsuperscript{9-11} or a collaborative effort of both.\textsuperscript{9(a),11(a)} The coordination geometry of metal ion along with the nature of bridging ligand decides the direction of extension of these architectures.

![Coordination Modes and H-Bonding Modes Diagram]

\textbf{Scheme 1} (Ashwini Nangia, 2004)\textsuperscript{11(a)}

Among pyridine monocarboxamides, the pyridine-2-carboxamide employs both the pyridine nitrogen atom and the carbonyl oxygen atom forming a five membered stable chelate ring. The coordination is mainly through pyridine nitrogen atom in nicotinamide (pyridine-3-carboxamide) and isonicotinamide (pyridine-4-carboxamide) as no such five membered ring can be formed in these cases owing to the meta and para position of the pyridine nitrogen with respect to the carboxamide side arm, respectively.\textsuperscript{5,7} However these can also act in a bidentate bridging fashion between metal centers giving rise to coordination polymers.\textsuperscript{9-11}

The work done in PART-1 of this thesis comprises of assembling extended architectures (1D, 2D or 3D) of metal complexes of pyridine-4-carboxylic acid (isonicotinic acid) derived amide ligands using coordination polymerization and/or intermolecular hydrogen bonding. In this chapter, a review of the literature of self assembling of metal complexes into networks has been made with main stress on complexes containing pyridine based ligands. While going through various examples of 1D, 2D and 3D networks the term “coordination polymer” should not be confused
with networks formed through intermolecular hydrogen bonding interactions. Coordination polymers as described earlier are metal-ligand compounds that extend “infinitely” into one, two or three dimensions via more or less covalent metal-ligand bonding with a ligand molecules acting as bridges between successive metal centers. The H-bonded networks are formed on the basis of hydrogen bonding interactions between complex molecules using ligand functionalities. In many cases solvent molecules and counterions such as nitrates, perchlorates, triflates etc. also enable metal complex to self assemble into multidimensional networks by taking part in hydrogen bonding in the crystal lattice.

![Diagram](image)

**Scheme 2** (Struart L James, 2003)

The dimensionality and topology of any assembled architecture depends upon the geometry adopted by the metal ion in the complex as well as on the number and location of binding sites on the polydentate ligands (Scheme 2). For example, Ag(I) coordination complexes are ideal for forming 1D networks (coordination as well as H-bonded) as they prefer to adopt linear geometry. The use of the rigid rod like bi-exodentate ligands (Scheme 3) such as pyrazine, 4,4′-bipyridine, pyridine-4-carboxamides etc. further enhances the chances of obtaining a 1D linear polymer
For example, in case of a Ag(I) complex [Ag(isonicotinamide)][BF$_4$], the ligand pyridine-4-carboxamide (isonicotinamide) acts in a bidentate bridging mode between Ag(I) centers using both the pyridine nitrogen and carbonyl oxygen atoms to form a 1D coordination polymer on the basis of linear N$_{pyd}$-Ag-O$_{amide}$ bonding. In this complex, Ag(I) forms coordination bonds with pyridine N and amide O acceptors (Ag-N 2.18 Å, Ag-O 2.20 Å, N-Ag-O 165.4°, C-O-Ag 130.7°) to produce a linear coordination polymer along the $c$-axis. Isolation of this 1:1 Ag(I)-isonicotinamide network was the first example of N$_{pyd}$-Ag-O$_{amide}$ linkage in coordination polymers exhibiting proton/silver mimicry with respect to diacid-isonicotinamide complex. Similarly, Ag(I) forms another one dimensional coordination chain with an isonicotinamide derivative namely, N-pyridin-3-ylisonicotinamide. In this complex $\{(\text{Ag(3-pia})(\text{PF}_6))_n \}$ (3-pia = N-pyridin-3-ylisonicotinamide), the neighbouring Ag(I) centers linearly coordinated by two 3-pia ligands, resulting in one-dimensional chains. Each Ag(I) atom is linearly coordinated by two nitrogen atoms of the 3-pia ligands, carbonyl pyridine (N$^C$) and amino pyridine (N$^N$), leading to the electronically asymmetrical Ag(I) center. All Ag(I)-N distances are similar: Ag(1)–N(1) = 2.110(4), Ag(1)–N(5) = 2.114(4), Ag(2)–N(2) = 2.135(4), and Ag(2)–N(4) = 2.129(4) Å.

The ligands such as pyrazine (pyz) and 4,4′-bipyridine (bpy) further enhances the chances of formation of 1D coordination polymers. The pyrazine molecules act in
a bidentate bridging fashion between Ag(I) centers to form a one dimensional coordination polymer involving both the nitrogen atoms for coordination to metal centers. The crystal structure of the 1:1 silver nitrate-pyrazine complex consists of almost planar-kinked 1D chains of the type [-Ag-NC₄H₄N-] with Ag-N distances of
$2.213 \pm 0.014 \text{ Å}$ and N-Ag-N' angles of $159.2 \pm 0.9^\circ$. The next nearest neighbors of Ag(I) are two oxygens of a nitrate group at $2.720 \pm 0.021 \text{ Å}$ and two other nitrate oxygens at $2.943 \pm 0.017 \text{ Å}$. The chains are held together by weak or van der Waals interactions. Bosch et al. presented the synthesis and characterization of three one-dimensional coordination polymers formed on self-assembly of Ag(I) complexes with substituted pyrazines. A linear double-stranded coordination polymer was formed on self-assembly of 2,3-bis(3’5’-dimethylphenyl)pyrazine with silver(I) tetrafluoroborate. An essentially linear double-strand coordination polymer was formed on self-assembly of 2,3-bis(3’5’-dimethylphenyl)pyrazine with silver(I) trifluoromethanesulfonate. In contrast a helical silver-pyrazine coordination polymer with extensive intrastrand $\pi$-stacking was formed on self-assembly of 2,3-diphenylpyrazine with silver(I) trifluoroacetate.

Similar role in connecting Ag(I) centers to form a one-dimensional coordination polymers is performed by 4,4’-bipyridine ligands in few complexes. In complex $[\text{Ag(bpy)}][\text{PhCB}_9\text{H}_9](\text{CH}_3\text{CN})$, (where bpy = 4,4’-bipyridine), bpy ligand molecules to connect various Ag(I) centers to give an infinite linear coordination 1D chain. The crystal structure consists of a $[\text{PhCB}_9\text{H}_9]^-$ anion, a silver cation coordinated to a bpy ligand, and an uncoordinated acetonitrile solvent molecule, 4(a). The Ag(I) has two coordinate bonds to two bpy ligands in a near-linear fashion, with an angle N(1)-Ag(1)-N(2) of $177.42(15)^\circ$ and with Ag-N distances of Ag(1)-N(1) 2.132(4) and Ag(1)-N(2) 2.144(5) Å. Each bpy ligand bridges between two Ag(I) centers to give an infinite linear coordination chain, 4(b)-(c). The chains group together in pairs, with the Ag(I) center of one chain positioned directly above the center of the C4-C4’ bond of the 4,4’-bipyridine of the second chain at a closest Ag···C distance of 3.585 Å. The extended structure of this complex shows the pairs of $[\text{Ag(bpy)}]^+$ 1D chains occupying channels created by the packing of the acetonitrile molecules and $[\text{PhCB}_9\text{H}_9]^-$ anions, 4(b), (boron atoms are indicated in red colour while hydrogens are green).

In the complex catena-(bis(μ$_2$-4,4’-bipyridine)-di-silver(I) 4-aminobenzoate nitrate monohydrate) the alternating Ag(I) and 4,4’-bipyridine ligands give rise to a slightly distorted linear coordination chain, which is further extended into a two-dimensional layer through the completely overlapping and off-set stacking interactions, 5.
The transition metals such as Cu, Co, Ni etc. are capable of adopting various geometries like tetrahedral, octahedral, square planer, squarepyramidal etc and thus 1D, 2D and 3D architectures are expected with interesting topologies. However, the ligands such as mentioned in scheme 3 favour the formation of 1D networks. In case of a Cu(II) complex \([\text{Cu(C}_5\text{H}_4\text{ClNO)}_2(\text{pyrazine})(\text{H}_2\text{O})_2](\text{ClO}_4)_2\), the successive octahedral copper(II) centers are linked with each other through coordinating pyrazine ligands to form a 1D chain running parallel to \(b\) axis, 6.\(^{12(f)}\)

In complexes of the type \([\text{M(sac)}_2(\mu–\text{pyz})(\text{H}_2\text{O})_2]_n\) \([\text{M} = \text{Zn(II)}, \text{Cd(II)}\) and pyz = pyrazine, and sac = saccharinate\] the metal(II) ions are octahedrally coordinated by two sac, two aqua and two pyz ligands. The Zn(II) and Cd(II) ions are six–
coordinate with two aqua, two sac and two pyz ligands forming a distorted MN₄O₂ core. The structure of both complexes consists of linear chains with alternating [M(sac)₂(H₂O)₂] units and bridging pyz ligands, extending along the crystallographic a axis. The sac ligands are N-coordinated, while the pyz ligands are bridges between the successive metal centers, leading to one dimensional linear chains, 7. 12(g)

The pyrazine ligands are also able to bridge between dinuclear chromium entities in case of another 1D coordination polymer, catena-tetrakis(µ₂-Acetato-O,O’)-
In case of complexes of the type \([M_2(bza)_4(2-mpz)]_n\) \(\text{bza} = \text{benzoate; 2-mpz = 2-methyl pyrazine; } M = \text{Rh(II) or Cu(II)}\) the 2-methyl pyridine ligand molecules are able to bridge between dinuclear Rh(II) or Cu(II) units.\(^{12(i)}\)

Similarly, in complex \([\text{Co(NCS)}_2(H_2O)_2(4,4'-\text{bipyridine})] \cdot 4,4'\text{-bipyridine},\) the 4,4'-bipyridine molecules play a similar role in constructing the 1D linear chain. \(^{9,12(j)}\) In this 1D coordination polymer the cobalt centers are bridged by 4,4'-bipyridine (bpy) ligands, resulting in the formation of a linear Co-bpy-Co chain. In addition to two bpy ligands the cobalt centers are bonded to two SCN groups and two water molecules. Both the the NCS groups and water molecules occupy the terminal positions in the elongated octahedron around each Co(II) center. The molecular dimensions around the metal center suggest two short Co-O (H\(_2\)O) bonds (2.096(2) Å), two short Co-N (NCS) bonds (2.095(2) Å), and two long Co-N (bpy) bonds (2.162(2) Å). The NCS group is almost linear (N-C-S 178.6(3)\(^\circ\)).

In case coordination polymers like \([\text{Cu}_2(\text{RCO}_2)_4(\text{nic})]_n\) \(\text{nic} = \text{nicotinamide},\)\(^{10(c)}\) and \([\text{Cu}_2(\text{ClCH}_2\text{CO}_2)_4(\text{denic})]_n\) \(\text{denic} = \text{N,N-}\)
diethylnicotinamide)\(^{(a)}\) the ligands are able to bridge in a bidentate fashion between dinuclear paddle-wheel units giving rise to coordination polymers, 10. The crystal structure of \([\text{Cu}_2(\text{RCO}_2)_4](\text{nic})]_n\) shows that the complex is an extended coordination chain of alternating dinuclear paddle-wheel units of the bridging tetracarboxylate type \(\text{Cu}_2(\text{RCO}_2)_4\) and nicotinamide molecules. The variation in nicotinamide coordination in the polymeric chain can be described by the following formula: \(-[\text{Cu}_2(\text{RCO}_2)_4]-(\text{nic}-\text{N},\text{O})-[\text{Cu}_2(\text{RCO}_2)_4]-(\text{nic}-\text{O},\text{N})-\).

Similar is the case with \([\text{Cu}_2(\text{CICH}_2\text{CO}_2)_4](\text{denic})]_n\) complex, which represents the first example of copper(II) carboxylates where \(\text{N},\text{N}\)-diethylnicotinamide molecule acts as a bidentate bridging ligand connecting dinuclear paddle-wheel units. In both these systems both the copper ions in a dinuclear entity coordinate to the same type of donor atoms with \([\text{N}_{\text{pyd}}\cdot\text{Cu} \cdots \text{Cu} \cdot \text{N}_{\text{pyd}}]\) or \([\text{O}_{\text{amide}}\cdot\text{Cu} \cdots \text{Cu} \cdot \text{O}_{\text{amide}}]\) coordination mode.

The complex catena-((μ\(^2\)-1,4-bis((Pyrid-3-yl)carbonyl)piperazine)-bis(isothiocyanato) bis(methanol)-cobalt(II)) is a 1D coordination polymer which rides on \(\text{N}_{\text{pyd}}\cdot\text{Co} \cdot \text{N}_{\text{pyd}}\) coordination bonding. In complex \([\text{Cu}(\text{saccharinato})_2(\text{nicotinamide})(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})\), the Cu(II) centers are bridged by pyridine-3-carboxamide (nicotinamide) molecules to form a one dimensional extended structure, 11.\(^{(c)}\)
The pyridine-2,6-dicarboxylic acid also known as dipicolinic acid is also an important ligand from crystal engineering point of view. Apart from usual O-N-O tridentate coordination mode, it can also act as bridge between metal centers to form networks. In complex [Zn(pydc)(tapt)]ₙ (H₂pydc = 2,6-pyridinedicarboxylic acid, tapt = 1,4,8,9-tetranitrogen-trisphene), the Zn(II) center is octahedral with a mer arrangement of three nitrogen atoms and three oxygen atoms from a chelating tapt ligand and two different pydc ligands in two perpendicular planes. The pydc ligands coordinate in only one way, which is tridentate (O, N, O) chelate and monodentate bridging coordination mode to link two Zn(II) ions to form a one-dimensional chain, in which the 2-carboxyl group bridges two adjacent Zn(II) ions in a anti-anti coordination mode, 12.¹²(k)

When the successive metal centers are connected by a pair of ligand molecules instead of a single ligand molecule, 1D double chains/tapes are formed. The formation of such double chains/tapes has been reported in case of complex [Co(cpoa)₂(H₂O)₂].[Co(bpy)(H₂O)₄]·2H₂O (where H₂cpoa = 4-carboxyphenoxyacetic acid, bpy = 4,4′-bipyridine), 13.¹²(0) The complex contains two crystallographically independent Co(II) centers, 13(a). Co1 is coordinated by two nitrogen atoms from two bpy ligands and four oxygen atoms from four water molecules, while Co2 is
coordinated by four oxygen atoms of four cpoa$^{2-}$ anions and two oxygen atoms from two water molecules. In case of Co1 metal centers, the bpy ligands acting in a bidentate bridging fashion between adjacent Co(II) ions leads to the formation of a 1D [Co(bpy)(H$_2$O)$_4$]$^{2+}$ linear chain, 13(b). On the other hand, in case of Co2 metal centers, the H$_2$cpoa ligands are completely deprotonated and the two carboxylate groups of the cpoa$^{2-}$ anions display bis(monodentate) mode. The successive metal centers are connected with each other by a pair of anti parallel oriented ligands leading to the formation of a 1D [Co(cpoa)(H$_2$O)$_2$]$^{2-}$ double chain, 13(c).
One dimensional coordination chains are also reported for complexes in which the counterions play the role of bidentate bridging ligand connecting successive metal centers. In a nicotinamido (nia) complex of the thiocyanate mercury(II) [Hg(SCN)$_2$(nia)$_n$], the SCN entities connect various Hg(II) centers while the nicotinamide ligands coordinate in a monodentate fashion, 14.$^{12(m)}$

![Diagram 14](image14.png)

In case of complexes [Co(µ-NCS)$_2$(nicH)$_2$·(nicH)] and [Ni(µ-NCS)$_2$(H$_2$O)$_2$(isonicH)$_2$](isonicH)$_2$·2H$_2$O (where nicH is nicotinic acid, isonicH is isonicotinic acid) the successive metal centers are connected by a pair of antiparallel oriented SCN ligands leading to the formation of a 1D double chain, 15. The nicotinine acid ligands coordinate to the metal center in a monodentate fashion through pyridine nitrogen atom.$^{12(n)}$

![Diagram 15](image15.png)
In case of H-bonded 1D chains, some Ag(I) isonicotinamides produced linear assemblies: the ligands create a linear coordination complex with Ag(I) and this geometry is propagated into chains through self-complementary amide–amide interactions, respectively, 16.\textsuperscript{5(c)} The \textit{cis} relationship between amide functionalities in linear Ag(I)-nicotinamide complexes leads to the formation of 1-D ladders, 17.\textsuperscript{5(b)} The parallel 1D chains as well as the cross linking between them are both propagated through intermolecular hydrogen bonding interactions.
The pyridine-based ligands have also been used in the supramolecular assembly of platinum and palladium complexes to give one dimensional chains. Nicotinic acid, and isonicotinic acid complexes of Palladium generate infinite chains, propagated by acid-acid hydrogen bonding interactions, 18, 19. 12(o) With nicotinic acid zig-zag chain is formed, 18 due to the meta position of carboxylic group with respect to pyridine nitrogen while in case of isonicotinic acid a straight chain is formed, 19 owing to para arrangement of both. Bis-nicotinamide and bis-isonicotinamide platinum–phosphine complexes both cis and trans, exhibit hydrogen bonded chains, 20. 12(p) Similarly, Brammer et al. reported linear tapes of PtCl₂ with 3-picolinamide, 21. 6(a)
Bera et al. reported the formation of four dirhodium and dirhenium complexes with isonicotinamide and nicotinamide ligands which consist of individual M2 building blocks that form a polymeric network in the solid state as a result of self-complementary hydrogen bonds, 22.\textsuperscript{7(b)} The use of the isonicotinamide ligands results in the formation of linear structures, while the nicotinamide ligands form structures with a zig-zag or sinusoidal pattern, 23.
The Pt(II) or Pd(II) complexes are ideal for 2D expansion as the metal center is favourable to adopt square planar geometry. These two dimensional assemblies, which can be thought of mimicking clays and zeolites, are of interest due to their potential uses in host–guest chemistry, with application in storage, separations or catalysis. Aakeröy et al. reported the synthesis of an overall neutral complex, from isonicotinic acid and tetrachloroplatinate which creates a square grid network via charge-assisted OH⋯O hydrogen bonding interactions, 24. The square planar geometry of Pt(isonicotinate)$_2$(isonicotinic acid)$_2$ is propagated in two directions, yielding two crystallographically unique hydrogen bonded nets with large square holes. The nets interpenetrate in three mutually perpendicular planes, and the remaining cavities (5 Å° in diameter) are occupied by water molecules. One advantage of using neutral complexes is that, since no counter-ions are present, there is more space available for guest molecules and no possibility for unpredictable hydrogen bonding due to the counter-ion. However, 2-D motifs are also produced via catemeric amide–amide interactions in linear Ag(I)-nicotinamide salts when ‘spherical’ counterions such as [BF$_4$]$^-$ and [PF$_6$]$^-$ are used, 25.

Ni(II) complexes of isonicotinamide and 4-aldoximepyridine leading to frameworks based on intermolecular hydrogen bonding interactions have also been reported. 5(a) The oxime structure is particularly interesting, as the OH⋯O hydrogen bonds connect Ni(II)(4-aldoximepyridine)$_4$ ions into grid-like sheets, resulting in hourglass-shaped holes. The holes are blocked by overlap of the sheets, but channels remain that host uncoordinated 4-aldoximepyridine molecules. In case of Ni(II)-nicotinamide complexes the 2D network is not built on the usual complementary amide-amide H-bonding interactions but the overall expansion is governed by the participation of the amide moiety in H-bonding, 26.

The asymmetric unit of compound [{Ag(isonicotinamide)$_2$}(1,5-NDS)⋅2H$_2$O, (where 1,5-NDS = 1,5-naphthalenedisulfonate) contains two independent Ag centers, 27(a). Each Ag center is coordinated with two pyridine nitrogen atoms from two different isonicotinamide ligands with Ag–N = 2.134(3) – 2.154(3) Å as well as one sulfonate oxygen atom with Ag–O = 2.574(4) – 2.496(3) Å, respectively resulting in a H-shaped dimeric unit. The Ag center adopts a distorted trigonal configuration. The dimeric units are connected through intermolecular hydrogen bonds to form neutral extended sheets. Two major supramolecular synthons are observed in the assembled sheet, 27(b). The smaller synthon is constructed
through the amide amino group and the 1,5-NDS sulfonate group (N–H⋯O = 2.978(5) and 2.941(5) Å). The larger one, is built from the head-to-head amide–amide
interaction (N–H···O5 = 2.947(4) and 2.922(4) Å), as well as the amide-1,5-NDI hydrogen bonds (N–H···O5 2.978(5) Å. The lattice water molecules are intercalated between the layers via hydrogen bonding interaction with the amide group (N–H···O5 = 2.897(5) Å).
Two dimensional networks propagated by metal ligand coordination bonding are also reported in case of pyridine monocarboxylic acid based ligands. The compound \([\text{Cu}_2(\text{CN})(\text{in})(\text{Hin})]_n\) (in = isonicotinate; Hin = isonicotinic acid), based on fused chair shaped \([\text{Cu}_6(\mu_3\text{isonicotinic})_2(\mu_3\text{isonicotinate})_2(\mu_3\text{cyanide})_2]\) hexagons, is a rare example of a triple interpenetrated two-dimensional ligand-to-metal coordinative bonding network and simultaneously a triple interpenetrated three-dimensional hydrogen bonding network.\(^{12(q)}\)

Among 2D networks formed by coordination polymerization involving corresponding amide analogue, Moncol \textit{et al.} reported the crystal structure of \([\text{Cu}(\text{CCl}_3\text{CO}_2)_2(\text{isonicotinamide})_2(\text{H}_2\text{O})_2]\cdot2\text{H}_2\text{O}\) consisting of a 2D metal–organic framework, \(^{28}\textit{9(a)}\). The ligand isonicotinamide acts in a bidentate bridging fashion connecting metal centers and a 2D network is formed upon N\textsubscript{pyd}-
Cu-N_{pyd} and O_{amide}-Cu-O_{amide} bonds across the metal centers. Strong intramolecular hydrogen bond interactions involving an axial coordinated water molecule and a carboxylic oxygen atom stabilize the molecular structure. Similar role is played by the nicotinamide ligand in another 2D coordination polymer, catena-(bis(µ₂-nicotinamide-N,O)-diaqua-manganese(II) diperchlorate), with ligand nicotinamide coordinating in a bidentate bridging fashion between Mn(II) centers 29_{12(r)}.
In case of another 2D coordination polymer $[\{\text{Ag}(3\text{-pia})_2\} \cdot (\text{PF}_6)_n$ (3-pia = N-pyridin-3-yl-isonicotinamide), the Ag(I) atoms coordinated by four 3-pia ligands, resulting in two-dimensional sheets, 30. The Ag(I) center is coordinated by four nitrogen atoms of 3-pia ligands, two (carbonyl pyridine) N$^C$ and two (amido pyridine) N$^N$, in a distorted tetrahedral fashion, with N–Ag(I)–N angles of 97.4(2)–132.0(1)$^\circ$. The distances of Ag(I)–N$^N$ (Ag(1)–N(2) = 2.441(4) Å and Ag(1)–N(5) = 2.351(4) Å)
are greater than those of Ag(I)–N$^C$ (Ag(1)–N(1) = 2.273(4) Å and Ag(1)–N(4) = 2.266(3) Å); the distances are typical of those found in tetrahedral Ag(I) complexes.

The pyrazine ligands acting in a bidentate bridging fashion between Co(II) centers in complex [Co(NCS)$_2$(pyz)$_2$] leads to the formation of a 2D sheet, 31. The 2D sheets/layers are further stacked along the c axis with an interlayer separation of 6.31 Å. Locally, Co sits on a 2/m site and a mirror plane passes through NCS. Co is in a compressed octahedral environment with four long Co-N (pyrazine) bonds (2.210(2) Å) and two short Co-N (NCS) bonds (2.050(3) Å). The pyrazine ring is canted to the Co-N4 plane at an angle of 64°. The NCS group is almost linear with an N-C-S angle of 178.0(3)°. The connection between Co atoms and NCS groups are bent with a
C(1)-N(2)-Co angle of 158.8(3)°. In complex [Co(NCS)$_2$(H$_2$O)$_2$(bpy)].bpy (bpy = 4,4'-bipyridine), the bpy molecules play a similar role in constructing the 1D linear chain while changing the solvent from ethanol to ether in [Co(NCS)$_2$(bipy)$_2$]-2(CH$_3$CH$_2$)$_2$O a 2D network is formed, $^{32,j}$.
The structure of a copper(II) complex containing bipyridine ligands, \([\text{Cu}(4,4\text{-bpy})(\text{phmal})]_n \cdot 2\text{H}_2\text{O}\) [where (phmal) = phenylmalonate dianion, (bpy) = 4,4'-bipyridine] consists of chains of carboxylate(phenylmalonate)-bridged copper(II).
ions which are linked through bismonodentate bpy ligands to produce a sheet like 2D polymer growing in the bc plane, 33.\textsuperscript{12(s)} Rectangles with dimensions of 11.08-4.99 Å\(^2\) are repeated within each layer, the longer edge corresponding to the bpy ligand (c axis), whereas the shorter side is defined by the phenylmalonate-carboxylate group (b axis). The separation between adjacent layers is 8.64 Å. The layers are not stacked parallel along the a axis but form an angle of 17.807(6)° with the normal plane vector. They are staggered in the ABCABCABC trend and the nearest neighbors are shifted by c/3 from each other. The structure of another complex [Cu(bpy')(phmal)(H\(_2\)O)]\(_n\) [where (phmal) = phenylmalonate dianion; bpy' = 2,4'-bipyridine] consists of a sheetlike arrangement of \textit{trans}-aqua(2,4'-bipyridine)copper(II) units bridged by phenylmalonate ligands running parallel to the ac plane, 34.\textsuperscript{12(s)} A corrugated square grid of copper atoms results where the bpy' terminal ligands are alternatively located...
above and below each layer and, at the same time, inversely to the position of the phenyl group of the phmal ligand. These sheets are stacked parallel along the $b$ axis but rotated 90° through this axis in a twisted fashion (i.e., odd units in the same position and even units rotated by 90°) exhibiting the ABABAB sequence clusters containing $syn$–$syn$ bridging carboxylate and end-on azido linker. As mentioned, in this 2D coordination polymer the bpy' ligand molecules do not act as bridges between successive metal centers as the ligand no longer behaves like a rigid rod like biexodentate ligand as in case of 4,4'-bipyridine.

The pyridine based ligands are also involved in creation of 3D frameworks through coordination polymerization or intermolecular hydrogen bonding. The reaction between Co(NO$_3$)$_2$·6H$_2$O and substituted pyridylcarboxylic acid [nicotinic acid (Hnic) or trans-3-pyridylacrylic acid (Htpa)] in the presence of NaN$_3$ under
hydrothermal conditions yielded \([\text{Co}_{1.5}(\text{nic})_2(\text{Hnic})(\text{N}_3)]_n\), 35 and \([\text{Co}_{1.5}(\text{tpa})_2(\text{N}_3)(\text{H}_2\text{O})]_n\), respectively. Both complexes are 3D complicated coordination polymers. The basic repeating units in both of the complexes are Co3 trinuclear. In a similar manner, the hydrothermal reaction of Ni(NO\textsubscript{3})\textsubscript{2}, NaN\textsubscript{3}, and nicotinic acid (Hnic) yielded a 3-D supramolecular framework complex, \([\text{Ni}_{1.5}(\text{N}_3)(\text{nic})_2(\text{Hnic})]_n\), 36. The metal centers in \([\text{Co}_{1.5}(\text{nic})_2(\text{Hnic})(\text{N}_3)]_n\) and \([\text{Ni}_{1.5}(\text{N}_3)(\text{nic})_2(\text{Hnic})]_n\) are linked with each other through nicotinate and N\textsubscript{3} bridges.
Xu et al. reported the first mixed metal Zn/Cu coordination polymer, [Zn$_3$Cu$_2$(IN)$_8$] (HIN = isonicotinic acid) which was synthesized under hydrothermal conditions. The three dimensional structure has a novel topological metal-organic framework, which is built up by Zn$^{2+}$, Cu$^+$ and isonicotinate molecules to generate an open-framework with an unusual helical $[-\text{Zn(Cu)-IN-}]_n$ chains along the $b$ axis.\(^{12(v)}\)

Two new 3D zinc carboxylates Zn$_2$(suc)(ina)$_2$ (suc = succinate, ina = isonicotinate) and Zn$_2$(fum)(ina)$_2$ (fum = fumarate) have been synthesized under the hydrothermal condition. Both complexes featuring the [Zn$_2$(CO$_2$R)$_4$] subunit formed by mixed tetracarboxylate, are interlinked by carboxylate-aromatic amine ligands (isonicotinate) to construct 2D sheets, which are further pillared by rigid or flexible dicarboxylates ligands (suc or fum) into 3D framework.\(^{12(w)}\)

An octahedral metal center bonded to six pyridine-based ligands would provide an ideal situation for the constructing 3-D hydrogen bonded networks but steric constraints usually prevent the formation of hexapyridyl complexes. Thus there are few examples of three-dimensional assemblies constructed from ligand-based hydrogen bonds only. One of the first 3D hydrogen-bonded coordination networks was also happen to be a host network. In this case, octahedral Co(III) ions are coordinated to three equivalents of 2,2'-bipyridyl-5,5'-dicarboxylic acid (H$_2$dcdbpy) through the bipyridyl nitrogen atoms. The resulting neutral complex, Co(Hdcdbpy)$_3$ contains three mono-deprotonated ligands. The 3D grid network is propagated via carboxylic acid–carboxylate interactions. In this structure there are two interpenetrating lattices of opposite chirality but small channels remain, which are filled with solvent molecules.\(^{12(x)}\)

Munakata et al. provided an early report of a 3D hydrogen bonded array of coordination complexes.\(^{12(y)}\) They synthesized tetrahedral Cu(I) complexes of 3-cyano-6-methyl-2-pyridinone, in which the metal ion is coordinated to the cyano group and different counter-ions were used to test the reproducibility of the motif. With smaller counter-ions such as [ClO$_4$]$^-$ and [BF$_4$]$^-$, catemeric NH···O pyridone–pyridine interactions generate a 3D hydrogen bonded net work. With larger counter-ions such as [PF$_6$]$^-$ and [O$_3$SCF$_3$]$^-$, self-complementary NH···O hydrogen bonds generate a diamondoid motif. Another example of a 3D network was observed by Aakeröy et al. when trigonal Ag(I)isonicotinamide complexes generated a ThSi$_2$-like interpenetrating structure via catemeric amide–amide interactions,\(^{37.5(c)}\) The combination of isonicotinamide with AgBF$_4$ or AgClO$_4$, respectively, led to
isostructural compounds [tris(isonicotinamide) silver(I) tetrafluoroborate and tris(isonicotinamide)- silver(I) perchlorate], containing two 3-D interpenetrating nets of three-co-ordinate silver(I) ions linked by N-H···O hydrogen bonds between adjacent isonicotinamide ligands.

Combination of coordination polymerization and H-bonding

Discrete molecules of a coordination complex undergo self-assemble phenomenon based on H-bonding interactions. Coordination polymers of various metals are formed with ligands having favoured geometry for acting in a bridging bidentate fashion between metal centers. Increasing dimensionality of systems by combining both coordination polymerization as well as H-bonding has become an interesting field of work and the pyridine based ligands play a very important role in it. Such a combination of coordination-polymers and ligand-based hydrogen bonds has also been used by a number of groups. There are some advantages to this approach, as it combines the strength of the coordination network, and the flexibility, imparted by the softer hydrogen bond interactions.

The pyridine based ligands having carboxylic or amide moieties in them are of immense importance in this field. The pyridine nitrogen as well as the amide/acidity acid oxygen take part in coordination simultaneously to form a bridge between metal centers and propagate the expansion in various directions. The direction of propagation depends upon the geometry adopted by the metal ion and the bridging ligand used. The role of these ligands in H-bonded based self assembly is well established. These ligands have efficient metal coordination sites for coordination polymerization and also peripheral H-bonding functionalities. Hydrogen bonds involving, for example, solvent molecules or coordinated aquo and ammonia ligands
also play a very important role in expansion of the lattice structure as in some cases these entities hold the coordinated structures (1D chains or 2D layers) together to achieve the next dimension.

In case of coordination polymers like \([\text{Cu}_2(\text{RCO}_2)_4]\text{(nic)}\)_n (where nic = nicotinamide),\(^{10(c)}\) \(9\) and \([\text{Cu}_2(\text{ClCH}_2\text{CO}_2)_4]\text{(denic)}\)_n (where denic = diethylnicotinamide)\(^{9(a)}\) the metal-ligand coordinated 1D coordination chains are held together by intermolecular H-bonding to form two dimensional sheet structure. The coordinating ligands are themselves the source of the hydrogen bonding functionalities. Nangia \textit{et al.} reported a similar sheet structure of \([\text{Ag}(\text{isonicotinamide})_2][\text{BF}_4]_n\) having linear tapes of (pyridyl)N-Ag-O(amide) coordinated chains connected via N-H···F hydrogen bonds.\(^{11(a)}\) Fowler, Lauher and coworkers used such combinations of coordination polymers and H-bonding to increase dimensionality in case of Ag(I) complexes of pyridyl-derivatized ureas and oxalamides.\(^{2(e)}\) The coordination-polymers were created by bridging pyridine-like ligands and tetrahedrally- coordinated Ag(I) ions, and an overall 3-D network was created by complementary NH···O hydrogen bonds between ligands.

The compound, \([\text{Ag}(\text{C}_8\text{H}_5\text{O}_4)(\text{isonicotinic acid})]\)_n, contains one Ag\(^1\) atom, one phthalate ligand and one isonicotinic acid molecule in the asymmetric unit. Each Ag atom is three coordinated in a T-shaped geometry by two O atoms and one N atom from one phthalate ligand and two isonicotinic acid ligands. The isonicotinic acid ligand bridges two Ag atoms, forming a one-dimensional chain. Adjacent chains are linked by Ag—Ag interactions, leading to a double-chain. These double-chains are further linked via hydrogen bonds into a 2D (two-dimensional) layer.\(^{12(e)}\)

Batten \textit{et al.} reported complexes of the type \(M(\text{tcm})_2(\text{H}_2\text{O})_2\cdot\text{Me}_4\text{pyz}\) (\(M = \text{Co, Ni}\); tcm = tricyanomethanide, C(CN)_3\(^-\), Me_4pyz = tetramethylpyrazine) in which one-dimensional coordination polymer chains of \(M(\text{tcm})_2(\text{H}_2\text{O})_2\) are linked into 3D networks by hydrogen bonding between the chains and the intercalated Me_4pyz molecules, and between the chains themselves.\(^{2(e)}\) Very weak magnetic coupling is observed for the high-spin d\(^7\) and d\(^8\) ions with no evidence of long-range order. The crystalline inclusion compounds of \([\text{Ni(SCN)}_2(\text{isonicotinic acid})_2].\text{G}\) (G = aromatic guest) are constructed by stacking identical 2D host layers. The SCN- ligands acting in a bridging bidentate fashion between Ni\(^{2+}\) ions thereby connecting successive metal centers to form 1D coordinated chains. The 2D (two dimensional) layer is formed by amide-amide hydrogen bonding interactions between these 1D coordinated chains,
In case of [{\text{Cd(SCN)}_2(isonicotinic acid)}_2].isonicotinic acid, each pair of cadmium ions is bridged by two inversely related $\mu$-NCS$^-\cdot$N,$\cdot$S ligands to form infinite chains with the remaining two trans positions of six-co-ordinated Cd atoms being occupied by two isonicotinic acid ligands, which form head-to-head double hydrogen bonds using the unco-ordinated carboxyl groups between adjacent chains to form two-dimensional layers, Aakeröy et al. reported the formation of three dimensional networks involving isonicotinamide ligands. The $[{\text{Cu(L)}_n}]_1$ 1D polymeric chains are held together by amide-amide hydrogen bonds between isonicotinamide ligands (L) to give a 2D sheet structure. The cross linking of such successive sheets by short N-H$\cdots$I(Cu) hydrogen bonds opens up a three dimensional network.
Applications and future scope

The metal containing supramolecular networks are associated with many magnetic, electronic, zeolitic, catalytic and optical properties. Furthermore, the metal ions display a wide range of coordination geometries that impart structural elements not usually present in organic compounds. Thus, the presence of metal ions provides
greater flexibility in constructing “functional materials” with valuable properties having specific dimensions and topologies. Among many attributes of metal embedded networks is magnetism.\textsuperscript{16} The paramagnetic metal centers in metal ligand complexes are associated with some kind of magnetic phenomenon. This however is not sufficient to characterize a material as magnetic as there has to be some exchange between such metal centers to ensure some substantial magnetic effect, magnetism being a cooperative phenomenon.\textsuperscript{16(d)} Increasing the dimensionality from an isolated metal-ligand cluster to a 1D, 2D or 3D network provide us with a large number of metal centers at distances within which some kind of magnetic exchange can take place between these moment carriers so as to be able to show some substantial magnetic phenomenon. Thus, in fulfilling the purpose of attaining a network embedded with metal ions we actually move from an isolated magnetic cluster with a small magnetic effect to a classical bulk magnet having cooperative magnetic effect.

The general view of the strength of the interaction between the moment carriers, based on experimental observations is that it decreases with the number of intervening bonded atoms between the moment carriers. For example, the critical ordering temperatures for the three magnetic metals of the first row transition metals range between 560 and 1380 K, while for oxides (one atom bridge) of the same metals it does not exceed 900 K and for compounds with two-atom bridges (e.g., cyanide) it is below 350 K. On increasing the number of atoms in the bridge to three (e.g., dicyanamide and azide) the transition temperatures do not get higher than 50 K.\textsuperscript{16(e)-(g)} No long range magnetic ordering is observed above 2 K when the connection is through four-atom bridges. Furthermore, the transition temperature decreases in the order 3D>2D>1D.\textsuperscript{16(e)} The presence of water, hydroxide and carboxylate that form the connections between the magnetic centers is also very common in networks especially in case of cobalt.

Therefore in light of the above discussion, the magnetic phenomenon associated with frameworks built on various types of ligands such as based on carboxylates or pyridine (or other ligands useful in framework expansion) has been the focus of interest for the past couple of years. The magnetic studies on metal chloride 4,4′-bipyridine adduct complexes \([\text{MCl}_2(\text{bpy})]_n\), \(\text{M} = \text{Fe}, \text{Co}, \text{Ni}\) suggest that the metal-metal intrachain exchange interaction is ferromagnetic, while the metal-metal interchain coupling is antiferromagnetic. In cobalt(II) nicotinate frameworks based on dicobalt carboxylate unit \(\text{Co}_2(\text{H}_2\text{O})(\text{C}_6\text{H}_4\text{O}_2\text{N})_4 \cdot 0.5\text{CH}_3\text{-CH}_2\text{OH} \cdot 0.5\text{H}_2\text{O}\) and
Co$_2$(H$_2$O)(C$_8$H$_4$O$_2$N)$_4$·C$_6$H$_5$CH$_2$OH, the magnetic exchange coupling constant indicate the antiferromagnetic nature within the cobalt dimer in both the cases.$^{16(h)}$ A 2D coordination polymer Co$_3$(OH)$_2$(pa)$_2$(ina)$_2$ (pa = 3-(1H-benzimidazol-2-yl)propanoic carboxylate, ina = isonicotinate) shows antiferromagnetic interaction within mixed-geometries-based trinuclear Co(II)$T_d$−Co(II)$O_h$−Co(II)$T_d$ cluster.$^{16(i)}$ A single carboxylate bridged chain in Co$_2$(mpda)(H$_2$O)$_6$·H$_2$O (mpda = 1,2,3,4-benzenetetracarboxylate behaves as paramagnets$^{16(j)}$ while the compound $\{[\text{Co}_3\text{Cl}_4(\text{H}_2\text{O})_2][\text{Co}(\text{Hbbiz})_3]\}_n$ is the first molecule-based magnet of the $2,2'$-bibenzimidazole ligand.$^{16(k)}$

The last decade has seen enormous research efforts in the syntheses and studies of metal containing frameworks. The field of coordination polymers continues to expand exponentially. A major portion of work dealing with coordination polymers still describes and analyzes the metal-ligand and packing geometry through single-crystal X-ray structural investigations in terms of crystal engineering, structure design or control of architecture. Even after so much work done in this field, still, an accurate prediction of the overall crystal structure is usually not possible. One obstacle is the weak but numerous non-covalent interactions and their poor directionality involving the ligands and non-covalently bound anions, cations as well as solvent (guest) molecules. A metal-ligand combination can give rise to two or more different structures, even with the same stoichiometry of all components. This is termed polymorphism or supramolecular isomerism. Subtle factors from the crystallization conditions, such as solvent, temperature, time, concentration, anions, pH-value play a role. Thus, considerable research energy is dedicated towards understanding the self-assembly process between metal ions or secondary building units derived therefrom and multidentate ligands. The design and the properties of the ligand itself can be a research initiative of its own. The synthesis or self-organization of coordination polymers is achieved by combining the appropriate metal salt and ligand in a suitable solvent under mild or at the most hydrothermal conditions. Even though much effort is still devoted to the preparation and structure determination of a crystalline sample, a final goal is to design properties of the polymeric assemblies of transition metal complexes with applications to material science as catalytic, conductive, luminescent, magnetism etc. The future will show which of the above mentioned or maybe even other, not yet recognized, applications are in there for metal-organic coordination networks.
Present work

Review of the literature on the preceding pages shows that a lot of quality work has been done regarding the self assembling of pyridine based ligands such as pyrazine, 4,4′-bipyridine, nicotinic acid, isonicotinic acid, nicotinamide and isonicotinamide. The work involving nicotinamide and isonicotinamide attract immense importance as they have structural adaptations for forming framework through coordination polymerization and non covalent interactions such as hydrogen bonding, π···π etc. A closer look at the literature also shows that the fully substituted amide derivatives of pyridine carboxylic acids such as N,N-dialkylnicotinamides provide the necessary rigidity, binding sites and intermolecular interactions to allow the creation of frameworks.

However, we have not encountered any studies reported in the literature on the investigation of coordination behavior of such fully substituted amide derivatives of isonicotinamide. Therefore in the present work we report the synthesis, structure and properties of N,N-dialkylisonicotinamide ligands and their complexes with transition metal ions in chapter 2 of PART-1. The M(II)-N,N-dialkylisonicotinamide complexes form frameworks through coordination polymerization or H-bonding or using the combination of both the forces. The synthesized complexes have been studied by using single crystal X-ray crystallography as a major tool. Extensive use of UV-Vis, IR, and thermal analysis has been made for characterization of complexes. Furthermore, in light of the above mentioned significance of magnetism in metal containing frameworks, in the present work in depth magnetic measurements (variable temperature magnetic susceptibility, epr etc.) on few of the complexes were also made.
References


