

COORDINATION COMPOUND METAL COMPOUND

VADIVEL.G

Research Scholar

M.Phil Chemistry

Bharath Institute Of Higher Education And Research

Mail Id : gvjana1978@gmail.com

Dr. G. PADMAPRIYA

Associate Professor & Head, Department Of Chemistry

Bharath Institute Of Higher Education And Research

Address for Correspondence:

VADIVEL.G

Research Scholar

M.Phil Chemistry

Bharath Institute Of Higher Education And Research

Mail Id : gvjana1978@gmail.com

Abstract

Inorganic, analytical, organic, environmental, and industrial chemistry all fall under the umbrella of coordination chemistry. In the area of coordination chemistry, extensive research is being conducted, and many articles are released every month. The term "coordination chemistry" is a relatively new one. Coordination compounds were in use long before they were characterised, although there is no precise date for when they first appeared in chemistry. The discovery of the orange-colored cobalt ammine compound $\text{CoCl}_3 \cdot 6\text{NH}_3$ by Tassaert in France in 1798 from an ammoniacal solution of cobalt chloride (CoCl_2) exposed to air was a watershed moment in coordination chemistry. The separation of this new chemical from the mixture of two previously saturated compounds puzzled scientists at the time, but it took another hundred years or more for them to explain Tassaert's finding. Many theories were proposed, the most famous of which being Christian Wilhelm Blomstran's Chain Idea, which was adopted and expanded by Sophus Mads Jorgensen to explain the characteristics of cobalt and platinum amines, but the theory failed to explain many facts and was discarded. Alfred Werner's notion of coordination compounds and his general explanation of how they work [1] is possibly the most important conceptual contribution to

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inorganic chemistry, similar in both direct and indirect effect to organic chemistry's concept of the tetrahedral carbon atom. In a lengthy article [2], Alfred Werner defined the fundamentals of coordination chemistry, for which he was awarded the Nobel Prize in Chemistry in 1913, the first Nobel Prize in the branch of Inorganic Chemistry, "in recognition of his work on the linkage of atoms in molecules, by which he has thrown new light on earlier investigations and opened up new fields of research, especially in inorganic chemistry" [Werner established a comprehensive theory capable of describi Since its dissemination and general acceptance throughout the decades of 1890 and 1910, it has provided a key foundation for coordination compounds and classical chemistry. Werner's complexes captivated chemists for decades afterward, and they were crucial in the development of coordination chemistry.

INTRODUCTION

Crystal engineering of coordination polymers is one of the most active research fields in coordination, supramolecular, and materials chemistry. Organic ligands join metal cation centres in a coordination polymer, which might be inorganic or organometallic. MOFs, or metal-organic frameworks, are a subclass of these that consist of coordination networks with organic ligands and possible voids [5]. The structure and content of coordination polymers are classified in a variety of ways, with dimensionality being one of the most important classifications. A structure can be classed as one-, two-, or three-dimensional depending on how many directions in space the array spans. A one-dimensional structure extends in a single dimension, a two-dimensional structure extends in a plane, and a three-dimensional structure extends in all three dimensions [6]. Coordination polymers are frequently made through self-assembly, which requires crystallisation of a metal salt with a ligand. Some of the synthetic processes used to generate coordination polymers include solvent layering (slow diffusion), slow evaporation, and slow cooling. Van der Waals forces, - interactions, hydrogen bonding, and the stabilisation of pi bonds by polarisation bonds all play a part in defining metal-ligand complexes, in addition to the coordination link produced between the metal and the ligand. These intermolecular forces are weak and have a high equilibrium distance as compared to covalent connections (bond length). In most coordination polymers, a ligand will donate a lone pair of electrons to a metal cation and form a coordination

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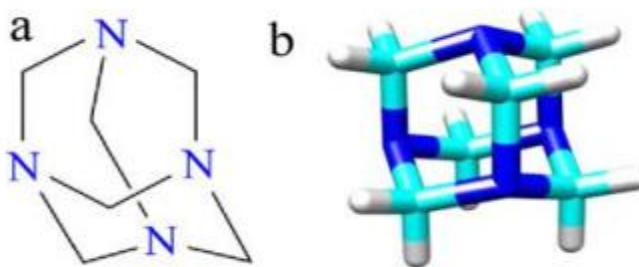
complex through a Lewis acid/base link. When a ligand has the capacity to establish numerous coordination bonds and serve as a bridge between several metal centres, coordination polymers are produced. Monodentate ligands are those that can only create one coordination bond. Polydentate ligands are those that create numerous coordination bonds, resulting in coordination polymers. Polydentate ligands are significant because they reveal the path to the creation of an endless array by connecting numerous metal centres together. Chelation is the process of polydentate ligands forming numerous bonds to the same metal. Because they do not provide a location for the network to continue, monodentate ligands are also known as terminal. Coordination polymers are often made up of a mix of poly- and monodentate ligands, as well as bridging, chelating, and terminal ligands. A ligand may be made up of almost any atom having a single pair of electrons. Polypyridines, phenanthrolines, hydroxyquinolines, and polycarboxylates are all common ligands in coordination polymers. Binding sites for oxygen and nitrogen atoms are common, although sulphur and phosphorus have also been identified. Hard soft acid base theory (HSAB) tends to follow ligand and metal cation patterns. This means that bigger, more polarizable soft metals will preferentially coordinate with larger, more polarizable soft ligands, whereas tiny, non-polarizable hard metals will preferentially coordinate with small, non-polarizable hard ligands. Ligands may be either flexible or stiff in nature. A stiff ligand lacks the ability to spin around bonds or reposition itself inside a structure. Flexible ligands can bend, spin, and realign themselves around bonds. This adds to the structure's diversity. Aside from the metal and ligand used, there are a slew of additional variables that influence the coordination polymer's structure. Most metal centres, for example, are positively charged ions that exist as salts. The salt's counterion may have an impact on the overall structure. Silver salts such as AgNO₃, AgBF₄, AgClO₄, AgPF₆, AgAsF₆, and AgSbF₆, for example, are all crystallised with the same ligand, but the structures differ in terms of the metal's coordination environment and the dimensionality of the whole coordination polymer [7]. As dyes, luminous species, electrical conductors and semi-conductors, magnetic materials displaying magnetism such as ferromagnetism, antiferromagnetism, and ferrimagnetism, and sensors, coordination polymers have a wide range of uses. Different N-donors, including as diamines and polypyridine derivatives, have been used as building blocks and linkers for the formation of coordination networks among the various organic ligands. The creation of novel organic

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compounds with adjustable characteristics for application in crystal engineering is currently being researched [8-22].

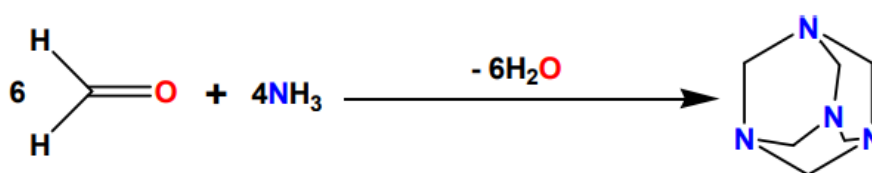
Hexamethylenetetramine (hmt)

Hexamethylenetetramine (hmt) also known as hexamine, methanamine, urotropine and 1,3,5,7-Tetraazatricyclo [3.3.1.1] decade is a simple heterocyclic compound with the formula $(\text{CH}_2)_6\text{N}_4$ and possesses a cage like structure (Scheme I-1) resembling adamantane (a colorless, crystalline cycloalkane with formula $\text{C}_{10}\text{H}_{16}$). Hmt was discovered by Alexander Mikhaylovich Butlerov in 1859 and its crystal structure was determined by Dickinson & Raymond in 1923



Scheme I-1. (a) Structural formula and (b) X-ray crystal structure of hmt, $(\text{CH}_2)_6\text{N}_4$

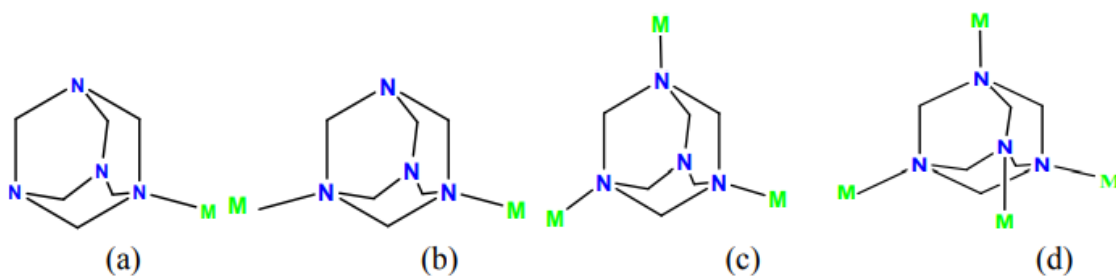
It possesses a symmetric tetrahedral cage-like structure, with nitrogen atoms as "corners" and methylene bridges as "edges." Unlike crown ethers or bigger cryptand structures, there is no empty space accessible in the interior for binding additional atoms or molecules, despite the molecular form resembling a cage. Hmt is prepared industrially by combining formaldehyde and ammonia (Scheme I-2).



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Scheme I-2. Formation of Hmt.

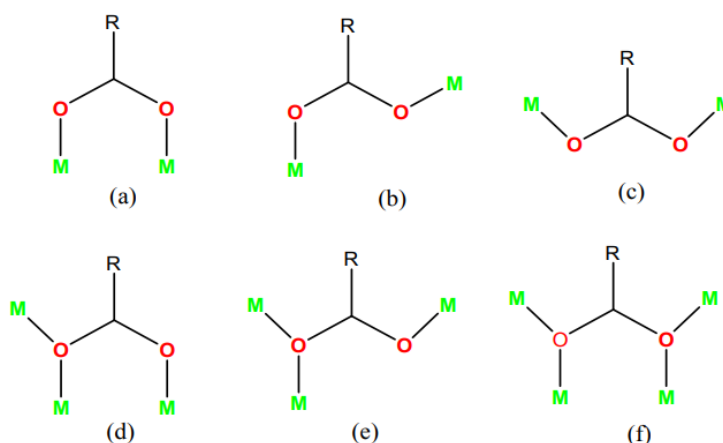
The reaction may take place in both a gaseous and a liquid state. At 280 °C, it sublimes in vacuum. Hmt offers a wide range of applications. Other chemical substances, such as polymers, medicines, and rubber additives, benefit from it. Hmt is also utilised in the production of powdered or liquid phenolic resins and phenolic resin moulding compounds as a hardening component. These materials are used as binders in a variety of applications, including brake and clutch linings, abrasive products, non-woven textiles, moulded components, and fireproof materials. The mandelic acid salt is used to treat urinary tract infections (generic methenamine mandelate). At an acidic pH, it decomposes into formaldehyde and ammonia, the formaldehyde of which is bactericidal; the mandelic acid adds to this activity. To keep urine acidic, vitamin C (ascorbic acid) or ammonium chloride are frequently employed. Formaldehyde is particularly well suited for long-term preventative therapy of urinary tract infection since bacteria can not develop resistance to it; nevertheless, it should not be used in the case of renal insufficiency. Campers, hobbyists, the military, and aid organisations utilise hexamine fuel tablets, which contain hmt and 1,3,5-trioxane, to heat camping meals or military supplies. Hmt is also used as a food ingredient and preservative. Hmt is used as a reagent in the Duff reaction (formylation of arenes), the Sommelet reaction (conversion of benzyl halides to aldehydes), and the Delepine reaction (synthesis of amines from alkyl halides). Hmt is the building block for RDX, hexamine dinitrate, and HMTD. As a simple and prospective tetradentate ligand, it displays a variety of coordination modes in ligating metal ions, including monodenticity, bidenticity, tridenticity, and tetradenticity (Scheme I-3), resulting in a variety of metal–hmt complexes with intriguing architecture.



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Scheme I-3. Ligational motif of Hmt (CH₂)₆N₄ (a) Monodenticity (b) Bidenticity (c) Tridendicity (d) Tetradenticity

From solitary molecules to complex 3D network polymers, carboxylate ligand chemistry has always supplied a wealth of examples [13,21]. More importantly, because the carboxyl entity may (and frequently does) engage in several bridging modes (Scheme I-4) [such as the ubiquitous syn-syn, anti-anti, and syn-anti (Scheme I-4-a,b,c); the less-common 1,1,3-3- (Scheme I-4-d); the rare 1,1-2- (Scheme I-4-e) and the 1,1,3,3-4- (Scheme I-4-f) Many transition-metal complexes have been discovered to have molecular magnetism, spin canting, spin glasses, and metamagnetic characteristics at low temperatures. [119-123]. The simplest but well-known example of carboxylate bridged coordination complex is [Cu₂ (μ-CH₃COO)₄(H₂O)₂]. The magnetic study of this complex has been explored by Bleaney and Bowers [124]. A few years ago R. Mukherjee et al. reported a family of acetate bridged trinuclear homo-metal Ni(II) complex and hetero-metal Ni(II)-Mn(II), and Ni(II)-Co(II) complexes and explored their magneto-structural behavior [125].



Scheme I-4. Binding motifs of carboxylates

Choice of Metals

Complex formation is a fairly universal phenomena, although it is especially noticeable among transition metal ions. “Elements with partially filled d shells as elements or in any of their frequently occurring oxidation states,” according to the widest definition. [1]. The chemistry of the transition elements differs from that of the other so-called main group

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elements in a number of ways, the most significant of which are listed below. Because transition metals often form compounds in two or more oxidation states, redox chemistry, including electrochemistry, is critical. The bulk of transition element compounds have visible spectra, which may be coloured, and the interpretation of these spectra can reveal a lot about their electrical structures. Due to the presence of one or more unpaired electrons in many transition element compounds, they exhibit intriguing and frequently beneficial magnetic characteristics. Aside from the three important points mentioned above, transition metals have a variety of coordination geometries, such as octahedral, tetrahedral, square planar, pyramidal, and so on; they have ligand field effects; they form chelated complexes; most M^{2+} and higher oxidation states are borderline or hard acids, and they generally prefer borderline or hard bases, such as O and N-donor groups; and they form pol Many solid compounds have intriguing electrical characteristics, as well as the potential to engage in catalysis and an essential role in biological processes, due to their changing oxidation states. In addition, the existence of an unpaired electron causes the metal atom/ion to be paramagnetic. The spin-spin interaction within multinuclear transition metal complexes causes ferromagnetism, antiferromagnetism, ferrimagnetism, and other intriguing magnetic characteristics. Ferromagnetic materials may sometimes exhibit molecular magnetism and be utilised in electrical devices. From catalysis to anticancer medicines, metal coordination complexes offer a broad range of technical and commercial uses [132]. The current thesis focuses on the synthesis and characterization of hexamethylenetetramine coordination compounds, including carboxylates such as acetate, phenylacetate, and benzoate, as well as isomeric 2-, 3-, and 4-nitrobenzoates with transition metals such as copper (II), nickel (II), zinc (II), and cadmium (II) (II). As a result, the following sections provide an overview of the general chemistry of these five metal ions.

Copper Copper has three potential oxidation states, the most stable of which is Cu(II), and only a few Cu(III) compounds have been discovered to far [133]. The Cu(I) state, which corresponds to the d^{10} structure, is very stable in solid state but quickly disproportionates into Cu (0) and Cu in aqueous media (II). The increase in hydration energy of the smaller Cu^{2+} ion over the larger Cu^+ ion readily overcomes the total of first and second ionisation energies, resulting in Cu^{2+} in solution. The +3 state, which corresponds to the d^8 configuration, is stable in a square planar environment and isoelectronic with nickel(II),

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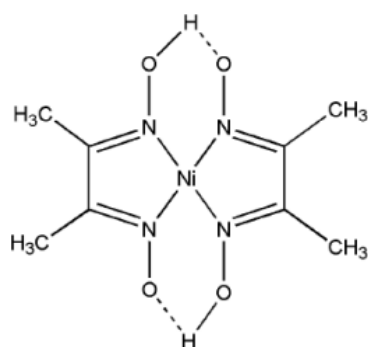
although its chemistry is less extensive than that of nickel(II) [134]. The higher ionisation energy, which cannot be readily balanced by other variables, is to blame for the scarcity of Cu(III) chemistry. In the trivalent oxidation state, it only forms a few compounds, some of which have been studied in both solution and solid form. Dithiocarbamates, 1, 2-dithiolates, biuret and its derivatives, oxamide, periodate, tellurate, peptides, and various tetradentate nitrogen-donor macrocycles are among the ligands that stabilise copper(III) [135]. Copper(II) is known for forming complexes, although it is hesitant to adopt conventional octahedral or tetrahedral geometry. Due to the existence of significant Jahn-Teller distortion, the amplitude of the splitting of the electronic energy levels in copper(II) complexes is greater than in other first row transition metals. In Cu (II) complexes, the metal-ligand interaction is often ionic, which promotes the stability of the Cu(II) state through the significant Jahn-Teller distortion. Strong exchange coupling between paramagnetic centres has been reconciled using dinuclear copper(II) complexes with extended bridging systems with azide, carboxylate, and phenolate [136]. Among the transition metal ions implicated in biological processes, copper is the third most abundant element [137-138]. Copper is a bio-essential element having chemical properties that are really unique in its two important oxidation states [139-142]. Copper atoms are linked to protein molecules in a variety of key redox enzymes, including hemocyanin, superoxide dismutase, and blue copper proteins. Copper(II) complexes containing amino acids have been shown to have anti-inflammatory and anti-ulcer properties [143]. Copper ions have been discovered in the active sites of several metalloproteins, which are engaged in critical biological electron transfer processes as well as molecular oxygen redox reactions. [144-145].

Nickel

Nickel's chemistry is vast and essential, with oxidation states ranging from -1 to +4. To far, just a handful of nickel(IV) species have been discovered [146]. The negative charge on the oximato oxygen plays a significant role in the partial neutralisation of the positive charge on the metal ion in nickel (IV) complexes of oxime ligands through inductive transmission and sigma (σ) donation. The nickel complexes with a +4 oxidation state that have been studied are octahedral and diamagnetic, with a low spin t_{2g}^6 structure similar to NiF_4 , which is a powerful oxidizer. Mononuclear Ni(III) compounds, such as $NiBr_3(PR_3)_2$,

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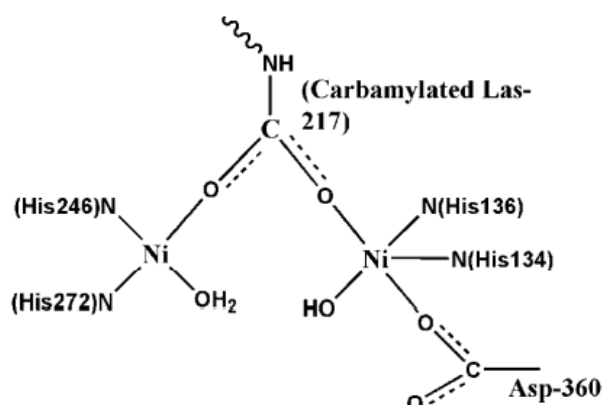
K_3NiF_6 , and others, are also instances [133]. Some nickel-containing enzymes have a +I oxidation state, but it is best represented by tetrahedral phosphines like $[Ni(PPh_3)_3X]$, which are paramagnetic, as predicted for the d^9 structure, and stable. Withdrawing ligands, such as CO, produce zero-valent nickel compounds. Important catalytic precursors are Ni(0) complexes with phosphine ligands. The carbonyl anion $[Ni_2(CO)_6]^{2-}$ contains Ni(-I). The most common oxidation state of nickel is +2, which is found in all of the above-mentioned oxidation states. Square planar Ni(II) complexes with extremely strong field ligands are diamagnetic, whereas octahedral complexes with two unpaired electrons in the e_g orbital are paramagnetic. Tetrahedral Ni(II) complexes with bulky ligands are also paramagnetic. An absorption band in the region of 450-600 nm may be seen in the electronic spectra of square planar nickel(II) complexes. $Ni(DMG)_2$ (Scheme I-5) is a well-known red-colored square planar Ni(II) complex (H_2DMG = dimethylglyoxime).



Scheme I-5. structure of $[Ni(DMG)_2]$.

Nickel compounds are of great interest because they are widely used in the design and preparation of new magnetic materials, as well as from a bioinorganic standpoint because nickel centre is an essential component of at least four enzymes: urease, carbon monoxide dehydrogenase (CODH, or acetyl coenzyme A synthase), hydrogenase, and methyl-Scoenzyme M reductase. The final one has a redox active group as a prosthetic group. NiN₄ macrocycle (factor F430). The active site structure of the urase containing two nickel atoms where one is tetra coordinated another one is pentacoordinated (Scheme I-6)

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Scheme I-6. Active site structure of the dinickel centre in Urease.

Zinc

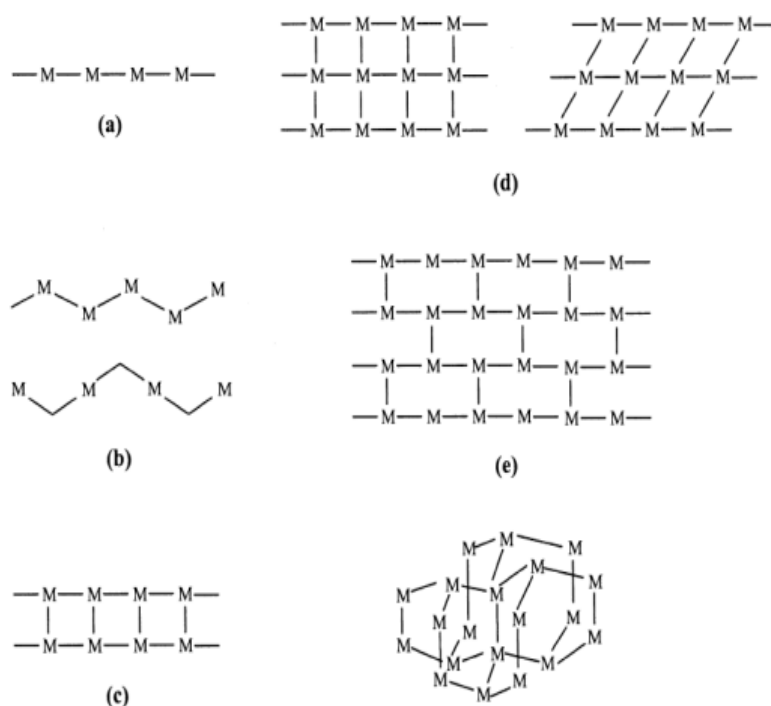
Because of its d10 electronic configuration, the metal ion Zn(II) is ideally suited for the creation of different coordination polymers, since it allows for a wide range of coordination numbers and geometries that are not reliant on ligand field stabilisation but rather on ligand size and charge. The coordination of N, O, and S donor atoms is possible due to its borderline hardness. Furthermore, the Lewis acid nature of Zn(II) complexes may be used to activate coordinated substrates [147]. Zinc is required for all forms of life and is a trace element in all biological systems, including humans. Zinc is required for proper growth and development, and it has been shown to reduce the duration of the common cold in adults [148]. It also has curative and preventive benefits on infectious illnesses such as pneumonia and malaria. Zinc's power stems from its involvement in enzymes that serve both structural and catalytic purposes. There are approximately 300 zinc enzymes, including representatives for each of the major enzyme groups [148], including hydrolases, ligases, lyases, isomerases, oxidoreductases, and transferases. Zinc's characteristics that make it so helpful in biological systems may be described as follows: Zinc possesses borderline hardness, which allows nitrogen, oxygen, and sulphur ligands to interact favourably, and zinc binds tightly to proteins.

Because the divalent zinc ion is very resistant to oxidation and reduction, it does not participate in redox processes.

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Zinc prefers a tetrahedral environment over an octahedral environment in enzymes, which increases both the Lewis acidity of the zinc centre and the Brnsted acidity of a coordinated water molecule.

Because Zn^{2+} has a d_{10} structure, zinc complexes are not affected by ligand field stabilisation, and coordination number and shape are solely determined by ligand size and charge. When coupled to Zn^{2+} , anions like OH^- , OR^- , and SR^- maintain their nucleophilic nature, with only Mn^{2+} , Fe^{3+} , and Cu^{2+} performing better [149].



Scheme I-7. Some topological types of coordination polymers (a) Linear chain, (b) Zigzag chain, (c) Ladder structure, (d) Square and Rhombic grid, (e) Brick wall and (f) Diamond related grid.

The general lability of zinc complexes makes the formation of coordination complexes reversible which facilitates ligands and metal ions to rearrange during the process

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of polymerization to give highly ordered architecture. Thus zinc can form 1D, 2D and 3D polymers and some of the topologies are exhibited in the Scheme I-7 [150]. In some cases the same type of ligands can lead to completely diverse coordination arrays. A problem encountered in case of zinc coordination complexes is the lack of spectroscopic properties of the metal ion as the exceptionally stable Zn^{2+} ion does not participate in redox reactions but advances in molecular biology and spectroscopic techniques such as fluorescence can overcome the problem [151].

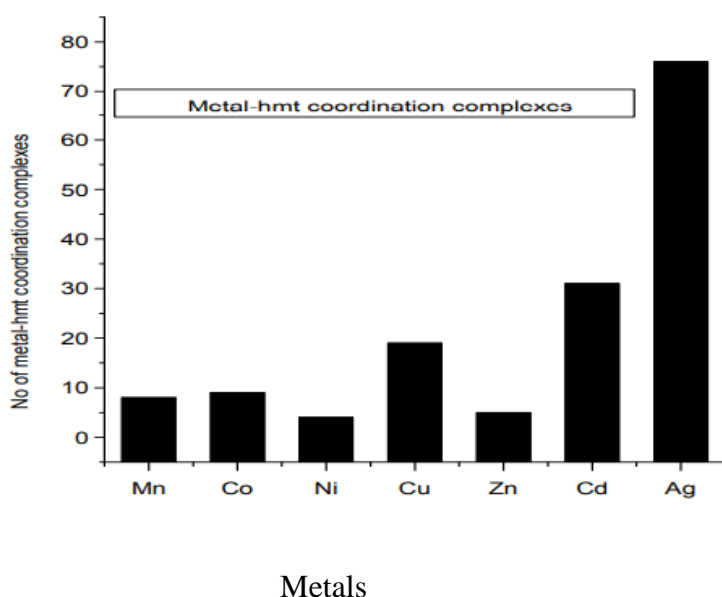
Cadmium

Cadmium chemistry has long been a hot topic of study. Because of its size and d_{10} electronic structure, the metal ion $Cd(II)$ is ideally suited for the production of different coordination polymers [63]. Due to the inadequate shielding given by the electrons of the filled 3d orbitals, the size of $Cd(II)$ is relatively small, and therefore the tiny ion will have a larger ion-dipole contribution in bonding to ligands in the complex building process [152]. A full $(n-1)$ d-shell is therefore more readily distorted or polarised by ligand electrons than filled np orbitals, resulting in a higher nuclear charge for a ligand on $Cd(II)$. However, since $Cd(II)$ -orbitals are fully filled, LFSE will not stabilise its complexes. The $Cd(II)$ ion is resistant to back-bonding due to its d_{10} electronic structure, and complexes containing π -acceptor ligands are uncommon. Because the geometry of $Cd(II)$ complexes prevents any stabilisation and the LFSE is zero, the stereochemistry is controlled by the ligands' steric needs as well as the size and polarising power of the cation. Unlike zinc, cadmium does not seem to be an important trace element in biosystems; rather, it is a very poisonous element to a broad range of living creatures, including humans.

Complexes with heterometallic elements We utilised group 2 $Ca(II)$ and group 12 $Zn(II)$ as hetero-metal ions in the production of hetero-metallic complexes. They were chosen as hetero-metal ions because $Zn(II)$'s d_{10} configuration is associated with a flexible coordination environment, allowing metal geometries in resulting hetero-metallic complexes to vary from tetrahedral to trigonal bipyramidal or square pyramidal to octahedral, as well as severe distortion of the ideal polyhedron. As a consequence, the potential for producing complexes with various nuclearities, molecular geometries, and topologies has increased.

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Due of the general lability of the d10 metal ion complexes, the metal ions and ligands may rearrange throughout the polymerization process to produce highly organised network architectures [149]. Both ions are non-toxic and physiologically relevant, and intriguing complexes with fascinating coordination patterns may be produced using hmt. Silver-based networks account for almost half of the metals that form polymers with hmt, followed by cadmium, copper, mercury, cobalt, zinc, manganese, nickel, sodium, and lead [26]. Silver chemistry has the most structures (76) among the metal-hmt coordination polymers, according to the Cambridge Structural Database, followed by cadmium (31), copper (19), cobalt (9), manganese (8), zinc (5), and nickel (4). (figures in brackets correspond to the number of known structures reported containing polymers of hmt) (Scheme I-8).

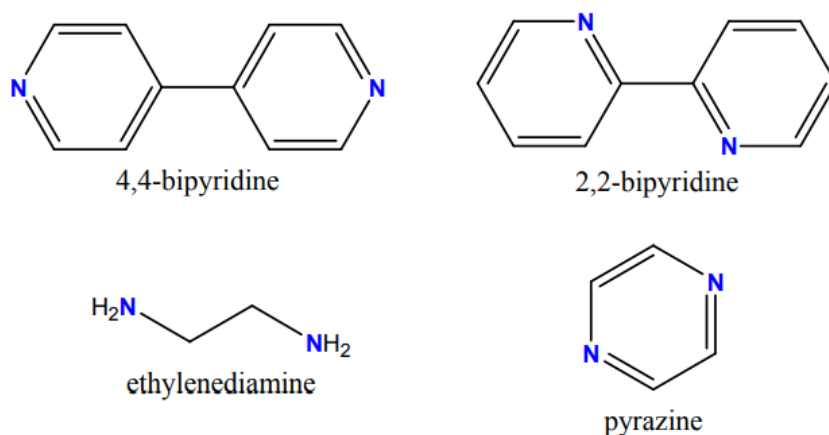


Scheme I-8. Number of known structures of metal ions containing polymers of hmt

A few heterometallic networks have also been discovered, however they all contain hmt moieties that are coordinated to just one metal. Versatile hmt serves as a linker or spacer, pillar or connection, stabiliser, and/or supporting ligand in all of these networks. In fact, the Cambridge Structural Database (CSD) shows approximately 500 structurally defined compounds containing hmt [26], including over 150 coordination polymers with a variety of

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topologies and characteristics. However, when compared to polymeric networks made from other typical N-donor ligands as 4,4-bipyridine, 2,2-bipyridine, ethylenediamine, and pyrazine (Scheme I-9) [26], the number of instances is much lower. Difficulties in synthesising and regulating the coordination number of hmt as well as the kind of metal-organic framework that results, as well as hmt polymers' thermal and solvent stability are perhaps responsible for this fact. The number of polymers with hmt and metal carboxylates are also rather scarce and even among them the vast majority have silver as the metallic ion [25,26,37,41,44,46,48-50,55,61,63, 71,157]. Given the fact that this emerging area of research on coordination polymers of hmt has been explored to a lesser extent, the present dissertation intends to report the synthesis, X-ray crystal structure determination, structural characterization, DFT calculation and magnetic behavior of a few coordination compounds of hmt with some metal carboxylates. Along with hmt, among the metal ions engaged are Cu(II), Ni(II), Zn(II) and Cd(II) while Zn(II)-Ca(II) ions are involved in the hetero-metallic complexes; carboxylates utilized are acetate, phenylacetate, benzoate and isomeric 2-, 3-, 4-nitrobenzoates.



Scheme I-9. Common Nitrogen-donor ligands.

CONCLUSIONS

To make coordination polymers, we employed four distinct dicarboxylate bridged linear dinuclear copper (II) nodes and hexamethylenetetramine (hmt) as a spacer in this thesis. X-ray single crystal structural investigation of $[\text{Cu}_3(2\text{-nbz})_6(2\text{-hmt})]_n$ (1),

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[Cu₃(pa)₆(3-hmt)]_n (2), [Cu₃(4-nbz)₆(3-hmt)]_n (3), and [Cu(3-nbz)₂(4-hmt)]_n (3). n[H₂O] (4) Complex 1 is a one-dimensional zigzag polymer, complex 2 and 3 are two-dimensional polymers with fused hexagonal rings, and complex 4 is a very rare example of a self-assembled diamondoid coordination polymer [2- nbz = 2-nitrobenzoate, pa = phenylacetate, 3-nbz = 3-nitrobenzoate, and 4-nbz = 4-nitrobenzoate]. The current work is unusual in that it has been feasible to create all potential topologies (angular, pyramidal, and tetrahedral) using linear dinuclear copper(II) carboxylate as a node and hmt as a spacer while only slightly altering the nonfunctional component of the aromatic carboxylic acids. Complexes 2 and 3 are the first instances of 2D polymeric structures with fused hexagonal rings, and complex 4 is the second example of a diamondoid structure created by linear dicopper nodes with 3-hmt and 4-hmt as spacers.

Three new Ni(II) compounds generated from hexamethylenetetramine and 2-, 3-, or 4-nitrobenzoic acids were synthesised and structurally characterised. The zigzag chain 1D coordination polymers (6 and 8) have been created for two isomeric nitrobenzoates (2-nbz, 4-nbz), but a monomeric molecule 7 has been generated when employing the 3-nbz building block. The presence of a non-coordinated 3-nbzH that forms hydrogen bonds with hmt prevents hmt from bridging and a coordination polymer from forming in 7. As a result, the location of a nitro group in 2-, 3-, or 4-nbzH, which is utilised as an auxiliary ligand source, alters the structure and dimensionality of the nickel hmt compounds, which include a 0D complex 7 and 1D coordination polymers 6 and 8. The expansion of 6–8 via traditional H-bonds into topologically separate H-bonded 1D chains (7), 2D layers (6), or 3D networks is also an important aspect (8).

Finally, the complete study looks into 21 homo-metallic and hetero-metallic polynuclear complexes generated by hexamethylenetetramine (hmt); carboxylates (benzoate, phenylacetate, acetate, or 2-,3-,4-nitrobenzoates); and metal ions, Cu(II), Ni(II), Zn(II), Cd(II), Cu(II), Ni(II), Zn(II). The synthesis, structural characterisation, and single crystal X-ray diffraction investigation have all received a lot of attention. The work's novelty consists in the creation of a number of remarkable and rather unusual polymeric complexes with intriguing structural topologies. The following are some of the most important characteristics: (a) Two extremely unusual instances of self-assembled diamondoid coordination polymers

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are created using dinuclear copper(II) 3-nitrobenzoate and benzoate as linear nodes and the ligand hmt as a linker. The Cu(II) ions are antiferromagnetically connected through the syn-syn carboxylate bridges in the non-interpenetrating cubic diamondoid coordination polymer of hmt with linear dicopper benzoate species, according to the magnetic investigation. Copper(II) created the first instances of 2D polymeric structures with fused hexagonal rings using phenylacetate and 4-nitrobenzoate anions. Copper(II) complexed with 2-nitrobenzoate is a one-dimensional zigzag polymer in which hmt works as an angular spacer.

(b) When two isomeric nitrobenzoates (2-nitrobenzoate, 4-nitrobenzoate) are used as building blocks, zigzag chain 1D coordination polymers are formed, whereas when using the 3-nitrobenzoate building block, a monomeric compound is formed, due to the presence of a non-coordinated 3-nitrobenzoic acid molecule forming hydrogen bonds with hmt, restricting the bridging mode of hmt and the formation of The location of a nitro group in 2-, 3-, or 4-nitrobenzoates utilised as an auxiliary ligand source affects the structure and dimensionality of the resultant nickel hmt compounds. The topological analysis of supramolecular networks driven by conventional H-bonds is also included in the research.

(c) When hmt and Zn(II) are combined, 3-nitrobenzoate creates a new 1D structure with four different types of bridges: 2-hmt, 2-carboxylato, 2-OH, and 3-OH, making it the first metal ion in which both hydroxide and hmt operate as bridging ligands. With 2-nitrobenzoate, the first paddlewheel compound of Zn(II) and hmt has been observed. Bridging hmt with 2 coordinating mode forms a dinuclear complex with 4-nitrobenzoate.

(d) Zn(II) coordination complexes with hmt and benzoate or acetate have been observed in two self-assembled forms. The presence of a distinct water hexamer in the supramolecular assembly of the benzoate complex is the first time such a water hexamer has been seen in a Zn(II)-hmt coordination complex.

(e) Two Zn(II) heterometallic polymers containing hmt and benzoate are described, which are the first instances of such complexes in which weak forces, such as lone pair–, –, and CH– interactions, play a crucial role in stabilising the observed structures..

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