

Review Paper

Highlights on Magneto-structural Correlations and Crystal Engineering: A Blessing of Modern Coordination Chemistry: A Review

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Abstract:

The crystal engineering of metal-organic hybrid coordination networks is now a growing field. By choosing structural ligands and the proper coordination geometry of metal ions as a building block can furnish a series of novel networks with exciting numerous crystal structures. The investigation of magnetic properties of molecule-based magnetic materials (1D, 2D and 3D) has become a fascinating subject in the fields of condensed matter physics, material chemistry as well as inorganic and biological chemistry. The preparation of multifunctional molecule-based materials that exhibit unusual magnetic, optical and electrical properties is one of the issues of fundamental research. This can be applicable to the design and preparation of new molecular materials exhibiting expected magnetic properties, such as molecule-based magnets, or to the investigation of the structure of the active sites of the metalloproteins with interesting paramagnetic centers. The amine complexes of metal ions like Cu(II), Ni(II), Cd(II) and Zn(II) etc possessing different bridging anions like Cl⁻, Br⁻, I⁻, SCN⁻, SeCN⁻, N₃⁻, different carboxylates etc are of special interest to the modern coordination chemists. The majority of works in the field of modern coordination chemistry are based on the controlled assembly of donor and acceptor building blocks in order to generate supramolecules. In the present discussion the target is to focus on some novel works in the past days regarding structural features and to some extent magnetic properties of some synthesised novel metal complexes by various research groups all around the world.

Keywords:, Amine complex, Dicarboxylate, Molecular magnetism and Supramolecule.

Introduction

At the very early stage, coordination chemists were deeply involved in synthesis of metal complexes and characterized them using the then instrumental facilities. They in general reported simple molecules and never thought of complicated molecules due to the limitations of instrumental facility. But as days go on they learnt new concepts, which directed them to synthesise difficult molecules one after another. But during last three decades, coordination chemistry was also focused on all polynuclear complexes. In recent years much research has been devoted to the synthesis and characterization of 1, 2 and 3 dimensional polymeric coordination compounds. The crystal engineering of metal-organic coordination polymers is now a maturing field. Advanced crystal engineering by selecting structural ligands and the coordination geometry of transition metal ions as a building block may give a series of novel frameworks with various interesting crystal structures. To a modest extent it has been possible to design rationally and build structures in different dimensions. The general strategy for designing such materials relies on the use of multidentate N- or O- donor ligands which have the capacity to bridge between metal centers to form polymeric structures. Here anion also played an essential part of the coordination network and amine functioned as a blocking ligand or spacer. Generally, in the amine deficient complexes of metal [Cu(II), Ni(II), Cd(II) and Zn(II) etc] possessing different anions [Cl⁻, Br⁻, I⁻, SCN⁻, SeCN⁻, N₃⁻, C₄O₄²⁻ (anion of squaric acid), anions of carboxylic acids etc] are of special interest to the coordination chemists, where the amine leaves maximum one to four positions in the primary sphere of metal and the remaining coordination sites are usually filled by anions functioning as unidentate/bidentate/polydentate ligands in order to achieve various geometry and coordination number depending on metal ions.

Construction of solid state materials that exhibit structure-function correlation requires knowledge of the relative orientation of the physically / chemically active components, with respect to each other, in the solid framework. However, this has been one of the most difficult aspects to control in material synthesis mainly due to the vast number of possible orientations a molecule may possess in the crystal lattice. Two types of interaction have been exploited in the construction of polynuclear metal complexes: i) coordinate covalent bond connecting metal centers and appropriate ligand types, and ii) hydrogen bonds in organic solids¹⁻¹⁰. In the specific case of coordination polymers, the expectation is that the geometry of the metal will be propagated through the bridging ligand, which may be

organic spacers (4,4'-bipyridine, pyrazine, 1,2-bis(4-pyridyl) ethane, di or tricarboxylates etc) or inorganic anions, e.g., halogen, pseudohalogen (SCN⁻, SeCN⁻, N₃⁻) or C₄O₄²⁻ etc. Self-assembly is currently the most efficient approach towards the design of one- two- and three-dimensional organic/ inorganic hybrid material of potential utility in the fields of catalysis¹¹, nonlinear optics¹², molecular magnetic materials¹³, electrical conductivity¹⁴, molecular recognition¹⁵ etc.

The supramolecular framework systems that result from the utilization of coordination, semi-coordination, hydrogen bonding and the effects of different counter ions in the process of self assembly is now a growing field in current research. The vast majority of current work centres around the controlled assembly of donor and acceptor building blocks in order to generate an entirely 'supramolecular polymer', i.e., a material held together solely by non-covalent interactions and such systems can be remarkably robust.¹⁶ This approach is fundamentally limited by the intrinsic strength of the constituent interactions which are markedly weaker than covalent or ionic bonds.

Molecular magnetism is the field of research concerning the chemistry and physics of molecules and molecular assemblies. The main feature of this subject deals with molecular systems exhibiting bulk physical properties. Molecular compounds possessing a spontaneous magnetization below a critical temperature were reported during the 1980s. These path finding reports motivated chemists to explore this field of research and in result a large number of molecular based magnets have been characterized.

In the early stage the synthesis of molecular based magnets were based on metal complexes of transition metal ions with the majority of copper(II). Syntheses of several Cu(II) and Ni(II) dinuclear hydroxo-, oxo-, acetato-, oxalato- etc bridged complexes and their variable temperature (up to 4 K) magnetic study was well explored. Several theories were also put forwarded by different scientists on the structural factors responsible for magnetic behavior.

Literature Review

Recent studies on the syntheses, structures and magnetic properties of ordered polynuclear complexes opened a new perspective in the field of molecular magnetism. Coordination polymers with open framework structures, which bridge the molecular and atomic solids, possess potential functions such as enantiomer separation, chiral synthesis, ligand exchange and selective catalysis. Their network topologies based on molecular building blocks are usually controlled and modified by the selection of the coordination geometry of the central metal, the structural chemistry of the organic ligands, the character of the solvent used and the ratio of the metal salt to the organic ligand.

Using different organic spacers, in particular, the dicarboxylic acids as super exchange pathways between the paramagnetic metal centres are of growing interest in the field of molecular magnetism. The superexchange phenomenon is closely related to the bridging conformations adopted by the carboxylate group in polynuclear systems.^{17,18} Magnetic studies on structurally characterized carboxylato-bridged copper(II) complexes reveal that strong and weak antiferromagnetic interactions are mediated by the *syn-syn* and *anti-anti* bridging mode respectively whereas *syn-anti* carboxylate bridged copper(II) complexes, which have been reported so far, usually exhibit ferromagnetic coupling^{17,18}. These ligands have been extensively studied due to its promising application to areas of technology such as magnetic recording as these carboxylates exhibit a variety of chelating abilities as manifested by the formation of dinuclear, tetranuclear, 1D and 2D copper(II) coordination polymers. In the preliminary stage the major studies are performed with oxalate bridged Cu(II) complexes, displaying both strongly and weakly antiferromagnetically coupled metal centres¹⁹. Benzoic acid-

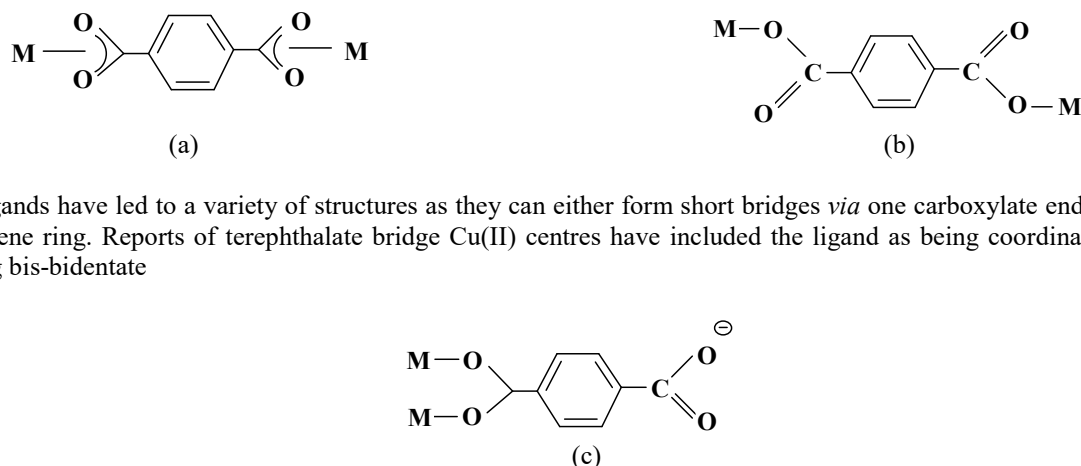


Fig 1. (a) or bis-monodentate (b) or bridging bis-monodentate (*syn-syn*) (c) fashion²⁰.

But, one-, two- and three- dimensional magnetic systems, using the dicarboxylates, such as, fumarate, maleate, malonate, adipate, succinate etc as superexchnging media are frequently cited in literature. Among them malonate dianion as bridging ligand is really

versatile due to the structural complexity in its metal complexes showing simultaneous adoption of chelating bidentate and different carboxylato – bridging coordination modes (Figure 2)

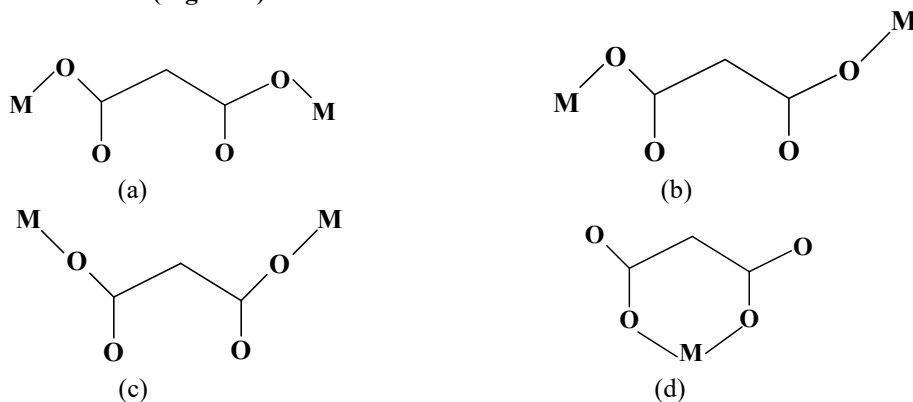


Fig 2: (a) syn-syn, (b) syn-anti, (c) anti-anti, (d) bidentate chelate.

The species, $[\text{Cu}(\text{mal})_2]^{2-}$ actually allowed the preparation of dimers²¹, trimers²² and one-²³ and two-²⁴ dimensional polymeric complexes whose structures and magnetic characteristics are subject of investigation. Li *et al.*²⁵ in 1997, synthesised the self-assembled two-dimensional square network, $[\text{Cu}_2(\text{mal})_2(\text{H}_2\text{O})_2(4,4'\text{-bpy})] \cdot \text{H}_2\text{O}$ (Figure 3), comprising both flexible malonate dianion and rigid 4,4'-bipyridine moiety. It is particularly interesting in this polymeric complex that four Cu(II) ions and four flexible malonate groups form a small planar square and four six-membered chelate rings *via* self assembly. Such a phenomenon is called “flexible self-assembly of supramolecules”.

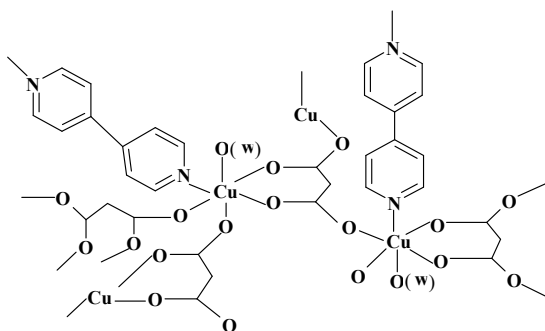


Fig 3: Two-dimensional square network in $[\text{Cu}_2(\text{mal})_2(\text{H}_2\text{O})_2(4,4'\text{-bpy})] \cdot \text{H}_2\text{O}$.

Muro *et al.*,²⁴ in 1998, studied structurally, magnetically and thermally the two dimensional malonato complexes, $[\text{MM}'(\text{mal})_2(\text{H}_2\text{O})_4]$ ($\text{M}=\text{Ba}/\text{Sr}$ and $\text{M}'=\text{Cu}/\text{Mn}$) (Figure 4). In copper analogue each copper(II) species is distorted octahedral and alkaline earth ions resemble a distorted antiprism. The other complexes are isostructural. Magnetic measurements show two-dimensional ferromagnetic and antiferromagnetic interactions for the copper(II) and manganese(II) phases respectively.

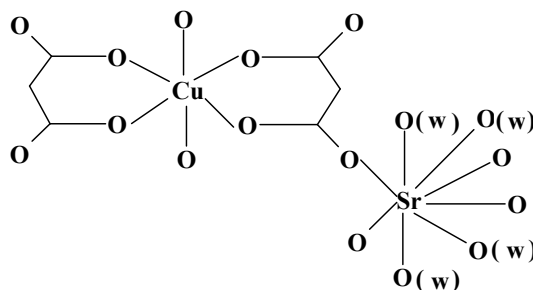


Fig 4: Environments of Cu(II) and Sr(II) in polynuclear malonate bridge heterometallic complex, $[\text{CuSr}(\text{mal})_2(\text{H}_2\text{O})_4]$.

Lightfoot *et al.*,²⁶ in 1999, hydrothermally synthesised the three dimensional malonate bridged polymeric network, $[\text{Co}_2(\text{mal})_2(\text{bpy})(\text{H}_2\text{O})_2]$ (bpy=4,4'-bipyridine) (Figure 5). The complex being composed of Co-mal sheets which are pillared by bridging bidentate bpy molecules.

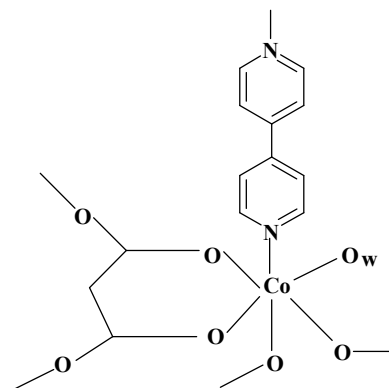


Fig 5: Building unit of $[\text{Co}_2(\text{mal})_2(\text{bpy})(\text{H}_2\text{O})_2]$.

In 2000, Ruiz-Perez *et al.*²⁷ reported magnetic coupling through the carbon skeleton of malonate in two polymorphs of $\{[\text{Cu}(\text{bpy})(\text{H}_2\text{O})][\text{Cu}(\text{bpy})(\text{mal})(\text{H}_2\text{O})]\}(\text{ClO}_4)_2$ (bpy=2,2'-bipyridine) (Figure 6). The structures of the two polymorphs are made up of uncoordinated perchlorate anions and malonate bridged zigzag Cu(II) chains. The magnetic behaviour of the two polymorphs in the temperature range 2.0-290K is very close and it corresponds to an overall ferromagnetic coupling [J_1 (through OCO carboxylate) is $+4.6\text{cm}^{-1}$ and J_2 (through OCCCO) is -4.2cm^{-1}].

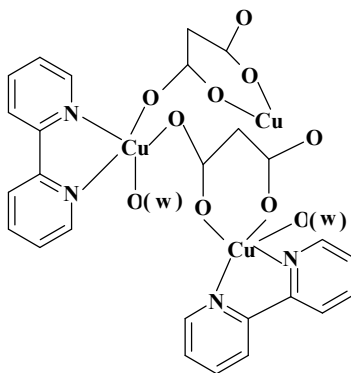


Fig 6: View of one of the polymorphs of $\{[\text{Cu}(\text{bpy})(\text{H}_2\text{O})][\text{Cu}(\text{bpy})(\text{mal})(\text{H}_2\text{O})]\}(\text{ClO}_4)_2$.

Polynucleation *via* fumarate is scanty in literature. But fumarate displays versatile bridging modes towards the metal ions producing one-, two- and three- dimensional polynuclear architectures. Magnetic superexchange between the paramagnetic metal centres is significant through fumarate.

Ray Chaudhuri *et al.*²⁸ have synthesised a novel three dimensional homometallic ferrimagnet, $[\text{Ni}_3(\text{fum})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]_n(2\text{H}_2\text{O})_n$ (Figure 7). The entire framework is formed by ribbons of fused nickel (II) octahedral units. This is the first reported 3D homometallic ferrimagnetic compound that orders magnetically at 6K.

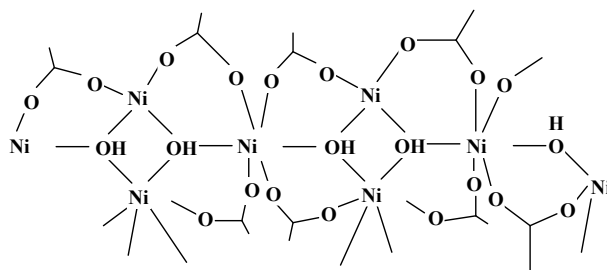


Fig 7: Three dimensional framework of $[\text{Ni}_3(\text{fum})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]_n(2\text{H}_2\text{O})_n$.

Magnetically sound polymeric metal complex formation using the bridging capability of succinate dianion ($C_4H_4O_4^{2-}$) is now frequently available in literature. Like other dicarboxylates, this dianion is capable of affording interesting bridging motifs. Kitagawa *et al.*²⁹ synthesised and characterised structurally and magnetically the coordination polymers of Cu(II), $[Cu_2(bpm)(C_4H_4O_4)_{0.5}(ClO_4)_2(OH)(H_2O)_2]_n$ and $\{[Cu(bpm)_{1.5}(C_4H_4O_4)_{0.5}](ClO_4)(H_2O)_2\}_n$ (Figure 8), using succinate dianion as flexible bridging entity (bpm = 2,2'-bipyrimidine and $C_4H_4O_4^{2-}$ = succinate dianion).

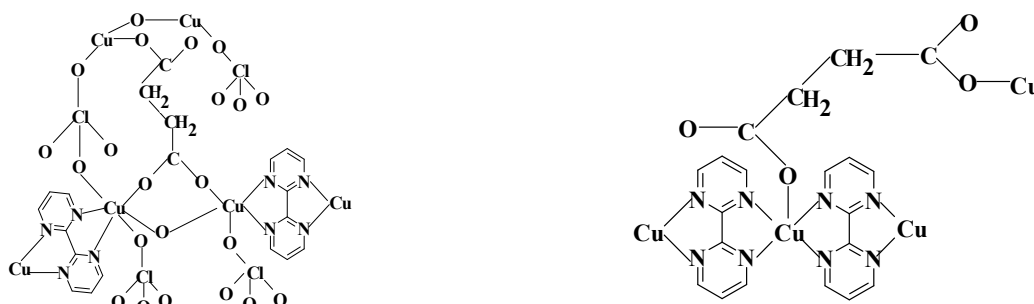


Fig 8: Molecular skeleton of $[Cu_2(bpm)(C_4H_4O_4)_{0.5}(ClO_4)_2(OH)(H_2O)_2]_n$ and $\{[Cu(bpm)_{1.5}(C_4H_4O_4)_{0.5}](ClO_4)(H_2O)_2\}_n$.

The most thoroughly investigated dinuclear compounds by far are those involving Cu(II) ions, where the interaction occurs between two local doublet states. Considering the existence of magnetic interaction between two metal ions through the bridging ligand for a system with two Cu(II) ions (noted as A and B) in the same molecular entity, bridged by a diamagnetic ligand capable of transmitting magnetic interaction between A and B then the local spin $S_A = 1/2 = S_B$ are not two good quantum numbers.³⁰ The good spin quantum numbers are $S = 0$ and 1. If E_0 and E_1 be the energies of the two pair states then due to electrostatic interaction E_0 is not equal to E_1 , but separated by a energy gap (J) which is defined as $J = E_0 - E_1$. J commonly known as coupling parameters. If the spin singlet ($S = 0$) is the ground state then $E_0 < E_1$ so J is negative, the interaction is known as antiferromagnetic and when the triplet state ($S = 1$) is ground state then $E_1 < E_0$, J is positive and the interaction is known as ferromagnetic. The J value for dinuclear Cu(II) system is generally calculated by fitting χ_M versus T data using the Bleaney-Bowers equation (eq. 1)^{30,31}.

$$\chi_M = 2Ng^2\beta^2(1-\rho)[3 + \exp(-J/kT)]^{-1}/kT + Ng^2\beta^2\rho/2kT + N\alpha \quad \dots\dots(1)$$

Where ρ is the molar fraction of non-coupled species.

Dimeric Cu(II) complexes using halogen (Cl, Br) bridge are both structurally and magnetically well characterised in literature. Metal-metal interactions in these complexes can be studied through experimental results or theoretical treatments. Bulk magnetic susceptibility measurements constitute the principal means by which metal-metal interactions between paramagnetic transition metal ions have been identified and studied.

Marsh *et al.*,³² in their studies on five coordinated dimeric bis(μ -chloro)copper(II) complexes of the type $[CuA_2Cl_2]_2$ and $[CuLCl_2]_2$ (A and L are monodentate and bidentate ligands, respectively), have found the strong correlation between the $2J$ value and the structural parameter ϕ/R (ϕ is the Cu-Cl-Cu bridging angle and R is the larger Cu-Cl bridge bond distance). However, in the case of the bis(μ -bromo)copper(II) dimers, Landee and Greeney³³ have shown that the dominant factor controlling the superexchange strength is not related to the bridging angle but instead to the amount of distortion within the copper basal plane.

Hodgson *et al.*,³² in 1983, published the structural and magnetic characterisation of bis(μ -chloro)bis[chloro(N,N,N'-triethylethylenediamine)copper(II)], $[Cu(Et_3en)Cl_2]_2$ (Figure 9). The geometry around each chloro bridged copper atom is distorted trigonal bipyramid. Magnetic susceptibility and EPR data give evidence for exchange coupling with the best fit to the data of the magnetisation expression for a pair of exchange coupled $S = 1/2$ ions yielding $g = 2.092$ and $2J = +0.06 \text{ cm}^{-1}$.

Willett *et al.*,³⁴ in 1988, reported the magnetic and structural correlation in dimeric $[(C_5H_5N)NH_2]_2Cu_2Cl_6$ and $[(C_5H_5N)NH_2]_2Cu_2Br_6 \cdot H_2O$ (Figure 10). The two compounds contain similar species, with each copper ion having a distorted trigonal-bipyramidal geometry involving four halide ions and the amino nitrogen from the pyridinium ion. The results of magnetic susceptibility measurements (2-280K) reveal ferromagnetic coupling within the chloride dimer and substantial antiferromagnetic coupling in the bromo analogue.

In 1990, Chiari *et al.*,³⁵ presented the exchange interactions in a novel Cu(II) linear chain compound, $[Cu_2(1,4\text{-diazacycloheptane})_2Cl_4]$ (Figure 11) possessing ladder like structure. Each dimer is related to its two nearest neighbours along the axis by crystallographic inversion symmetry and is connected to each of them by two Cu-Cl---H-N-Cu hydrogen bonding interactions resulting one dimensional network of hydrogen bonds. Antiferromagnetic coupling ($J = -6 \text{ cm}^{-1}$, $g = 2.13$) is observed between the adjacent copper(II) centres.

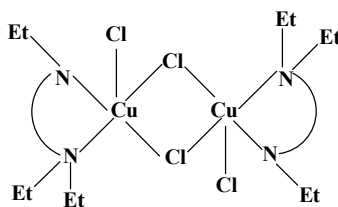


Fig 9: Structural view of $[\text{Cu}(\text{Et}_3\text{en})\text{Cl}_2]_2$

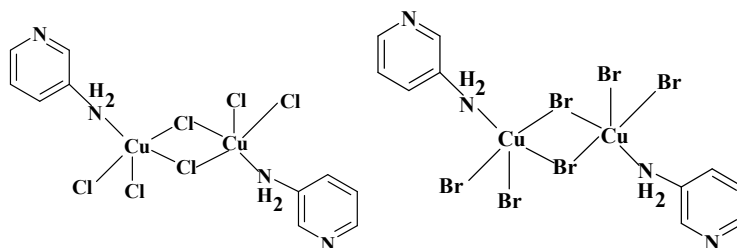


Fig 10: Chloro and bromo analogues of $[(\text{C}_5\text{H}_5\text{N})\text{NH}_2]_2\text{Cu}_2\text{X}_6$

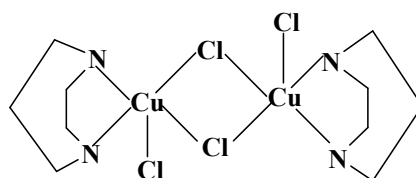


Fig 11: Dimeric moiety in linear chain ladder, $[\text{Cu}_2(1,4\text{-diazacycloheptane})_2\text{Cl}_4]$.

The copper(II) complexes containing $\mu\text{-OH}$ with $[\text{Cu}(\mu\text{-OH})_2\text{Cu}]_n$ core structure are abundant and extremely similar from a structural point of view and structural homogeneity has allowed the establishment of a well-behaved magneto-structural correlations³⁶⁻⁴⁰. The replacement of the OH by OR ligands produces structural distortions yielding complexes with different type of geometries. Manohar *et al.*,⁴¹ crystallographically identified the “stepped-cubane” structure for the Cu_4O_4 core in $[\text{Cu}_4\text{L}_2(\text{bipy})_4(\mu_3\text{-OH})_2][\text{ClO}_4]_2$ (Figure 12),

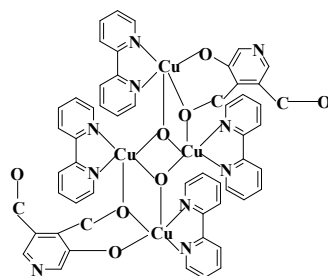


Fig 12: View of the molecular framework in $[\text{Cu}_4\text{L}_2(\text{bipy})_4(\mu_3\text{-OH})_2][\text{ClO}_4]_2$ (where HL=5-hydroxy-6-methylpyridine-3,4-dimethanol and bipy=2,2'-bipyridine.)

Polynuclear coordination network formation is extremely facilitated by the bridging capability of chalcogenocyanate ion, XCN^- , where X=S (thiocyanate), Se (selenocyanate). SCN^- is a highly versatile ambidentate bridging ligand (Figure 13) having both S and N donor centers towards self assembly. The versatility of SCN^- is well explored in the Cd(II), Ni(II) and Cu(II) systems.

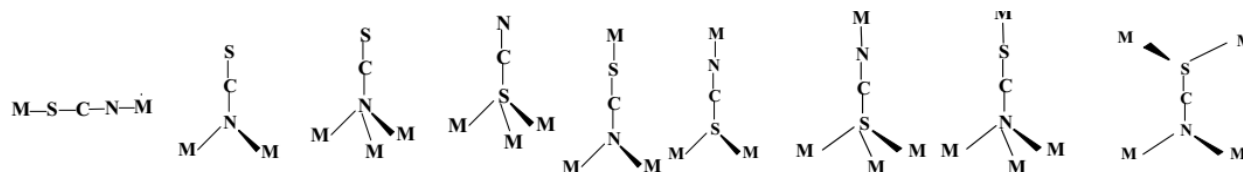


Fig 13: Bridging modes of thiocyanate anion.

Ray Chaudhuri *et al.*, reported a number of interesting polymeric triamine complexes of cadmium(II) using thiocyanate as a bridging ligand.^{42,43,44} The clathrates, $[\text{Cd}_3(\text{L})_2(\text{NCS})_6]_n \cdot n\text{H}_2\text{O}$ (**Figure 14**) [$\text{L}=\text{bis}(2\text{-aminoethyl})\text{amine}$ and $\text{bis}(2\text{-aminoethyl})\text{methylamine}$] are new types of three dimensional polymeric structures having cadmium centres linked to each other *via* NCS bridges in such a way that two types of cadmium environments (one involving only N-donor and the other only S-donor atoms) are synthesised showing the symbiotic phenomena.^{43,44}

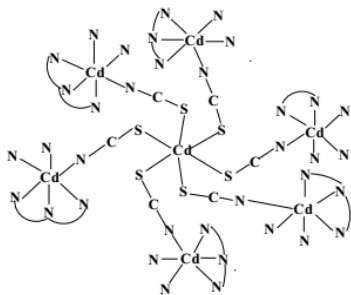


Fig 14: Symbiotic phenomenon in $[\text{Cd}_3(\text{dien})_2(\text{NCS})_6]_n \cdot n\text{H}_2\text{O}$.

A hyperbranched network, $[\text{Cd}(\text{aepn})(\text{NCS})_2]_n$ (**Figure 15**) [$\text{aepn}=(2\text{-aminoethyl})(3\text{-amionopropyl})\text{amine}$] has been synthesised in a single step in which 'propylenic' arm of the ligand as well as thiocyanate act as bridging ligand.⁴²

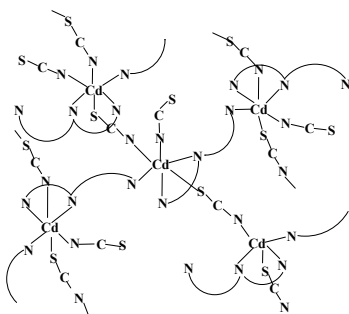
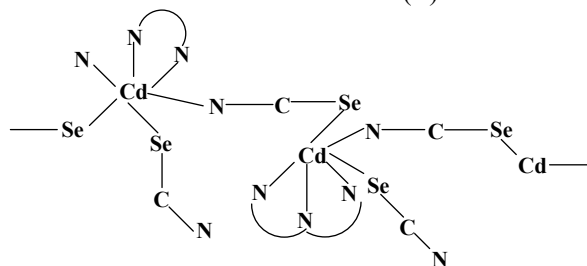


Fig 15: View where SCN as well as aepn functioning as bridging ligand in $[\text{Cd}(\text{aepn})(\text{NCS})_2]_n$.

Polynucleation of Cd(II) through selenocyanate is extremely scarce in literature. But Ray Chaudhuri *et al.*⁴⁵ have published the syntheses and crystal structures of two new selenocyanate bridged supramolecular coordination compounds of cadmium(II), $[\text{Cd}(\text{medien})(\text{SeCN})_2]_n$ (**(a)**) ($\text{medien}=\text{N}^{\text{N}}$ -methyl diethylenetriamine) and $[\text{Cd}_2(\text{iprdien})(\text{SeCN})_4]_n$ (**(b)**) ($\text{iprdien}=\text{N}^{\text{N}}$ -isopropyl diethylenetriamine)³¹ (**Figure 16**). In the complex (**a**) each octahedral cadmium(II) unit of a one dimensional coordination chain contains one pendent selenocyanate, binding through selenium and these pendant selenocyanate form mutual relationships with other chains through H-bonding interactions giving rise to a infinite two dimensional sheet. Complex (**b**) reveals two dimensional infinite coordination polymer having alternate N-bonded octahedral cadmium(II) and Se-bonded tetrahedral cadmium(II) centres



showing symbiosis .

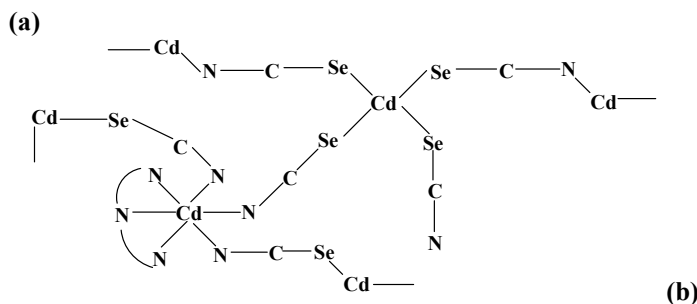


Fig 16: View of (**a**) SeCN bridged 2D hydrogen bonded infinite sheet and (**b**) 2D symbiotic infinite network.

Conclusion

The design and synthesis of coordination polymers and supramolecules with specific network (*e.g.* H-bonding, π - π interactions *etc.*) *via* self-assembly is a promising route which leads to the formation of molecular materials in general. These materials not only generate new insights into structural diversity but also exhibit encouraging potential applications in fields of catalysis, nonlinear optics, molecular magnetic materials, electrical conductivity, molecular recognition *etc.*

Recommendations

From the above review work, it is very clear that synthesising the polynuclear inorganic–organic hybrid networks with numerous interesting molecular properties is a challenge for a modern coordination chemist. By introducing several types of blocking and bridging ligands the probability of obtaining magnificent polymeric molecular entities with extraordinarily structural and magnetic properties will make the field of complex chemistry research endless. For this reason, till date, young researchers, day by day, exploring molecular beauty and definitely it will be endless.

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