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Review

Spacer directed metallo-supramolecular assemblies of pyridine carboxylates

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ABSTRACT

N,O-donating spacers are members of a class of ambidentate donors used in supramolecular self-assemblies. The skeletal adaptability and coordination flexibility of these ligands enable them to support a myriad of discrete molecular systems and extended network materials. This review focuses on pyridinecarboxylates as a representative of N,O-hetero-donating spacers and describes their recent developments in the coordination assemblies and highlights their functions and potential applications.

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1. Introduction

Following the success in the application of supramolecular chemistry [1–3] in the construction of a new generation of materials such as Metal-Organic Frameworks or MOFs [4–8] and coordination polymers [9–14], much interest has developed in the study of these new materials. Many reviews on their development, uses and applications have surfaced in recent years [2,4,8,10,15–22]. In this review, we present the application of an emerging class of spacers in supramolecular self-assembly, *viz.* the hetero-donating N,O-type ligands, with pyridinecarboxylates as a representative. One of the main foci on the design of a new generation of materials is the use of ligands or spacers to create specific molecular frameworks with desirable features or functions. A typical example of such an application is the development of molecular analytical and sensing devices. This is achieved by introducing synthons that have built-in functional units that are photoactive, electroactive, solvatochromic, etc. This unique ability to introduce purposeful components at the molecular level into an organized supramolecular architecture has fueled the excitement on the emergence of modern applications in areas such as supramolecular photonics, electronics, magnets, etc.

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The use of bidentate ligands to support supramolecular assemblies is common as the donors provide an easy way to bring the metal moieties together through straightforward Lewis acid-base interactions. Their use also helps to control the assembly process by blocking certain propagation pathways through the occupation of otherwise active coordination sites. Accordingly, a range of homo-donating ligands such as bipyridine, terpyridine and pyridine derivatives [15,23–29], di-, tri-pyrazolyl [28,30], di-, tri- and poly-carboxylates [7–10,17,31–34], etc. have been widely used. Many of these spacers support the formation of MOFs that have excellent clathrating and catalytic abilities, as well as functional qualities such as luminescence, magnetism or electro-activity. As the assembly becomes more demanding and gains sophistication, there is an increasing need to have a higher level of selectivity in the assembly process. This leads to the emergence of self-differentiating components such as hetero-donating functions typified by hybrid spacers [35], among which N,O donors such as the 4-pyridinecarboxylate (isonic) [36–45] are among the earliest candidates. The presence of different donor sites leads to possible complications arising from linkage isomerism, which often presents an experimental challenge in purification, isolation and identification. At the same time, the presence of different donor sites also raises the prospect of self-selection and self-recognition that are essential tools in MOF designs.

There are many forms of hybrid spacers that are typified by the hetero-donor functions, such as C,N-, N,O-, N,P-, N,S-, O,S-, etc. The extreme cases are those with donors that are in stark contrast in characters, e.g. σ and π, covalent and electrostatic, acceptor and donor, soft and hard, terminal and chelating, 2-e and multi-electron donation, etc. This suits bimetallic systems that are inherently contrasting, such as intermetallic (s/p-d, s/p-f, d-f) systems, early- and late metals, saturated and unsaturated metals, etc. At the other end of the spectrum, there are similar, or even the same, metal spheres that are differentiable only by the donor groups that they carry, which could be chemically analogous such as –NHR vs. –NH_2, etc. In the self-organization process, the latter donors exhibit only very subtle electronic or steric effects in selecting their metal partners. More common are those donors that have similar characteristics (such as hardness) but show sufficient selectivity to differentiate metals of related properties, such as the isoelectronic Rh(I)/Pd(II) and Pt(II)/Au(III). Typical examples of such are the N,O donors such as amino acids [46–48], amino-alkoxides [49], carboxyimidazoles [50–52], pyrazine carboxylates [53–57], pyridine alkoxides [58–60], pyridine ketones [61,62], pyridine esters [63], pyrimidine carboxylates [64,65], pyridine carboxylates [31,35–45,66–79] and pyrazole carboxylates [80,81]. With two different but compatible donor atoms, the ligands are able to exercise metal selectivity even in homometallic system or heterometallic pairs that are structurally analogous, such as Co(I)/Ni(II). The introduction of such hybrid spacers is a natural way to create asymmetry in an otherwise symmetrical network. This paves a convenient mechanism to create chiral and conducting materials.

2. Adaptable pyridinecarboxylate ligands

Among the earliest assemblies with N,O-spacers are the Zn(II) pyridine tartrate systems reported by Kim et al. which demonstrate both chiral separation and catalytic ability [82] (see Section 9). The use of pyridinecarboxylates rapidly gained popularity among hybrid spacers, especially the N,O-donors.

This review will focus on pyridinecarboxylates as a representative class of hybrid spacers in metallo-supramolecular assembly. Pyridinecarboxylic acids exist as solids at room temperature and atmospheric pressure. Isonicotinic acid (4-pyridinecarboxylic acid, *abbrev.* isonic) takes the neutral form in the crystalline state, with the molecules linked in infinite chains through O–H···N hydrogen

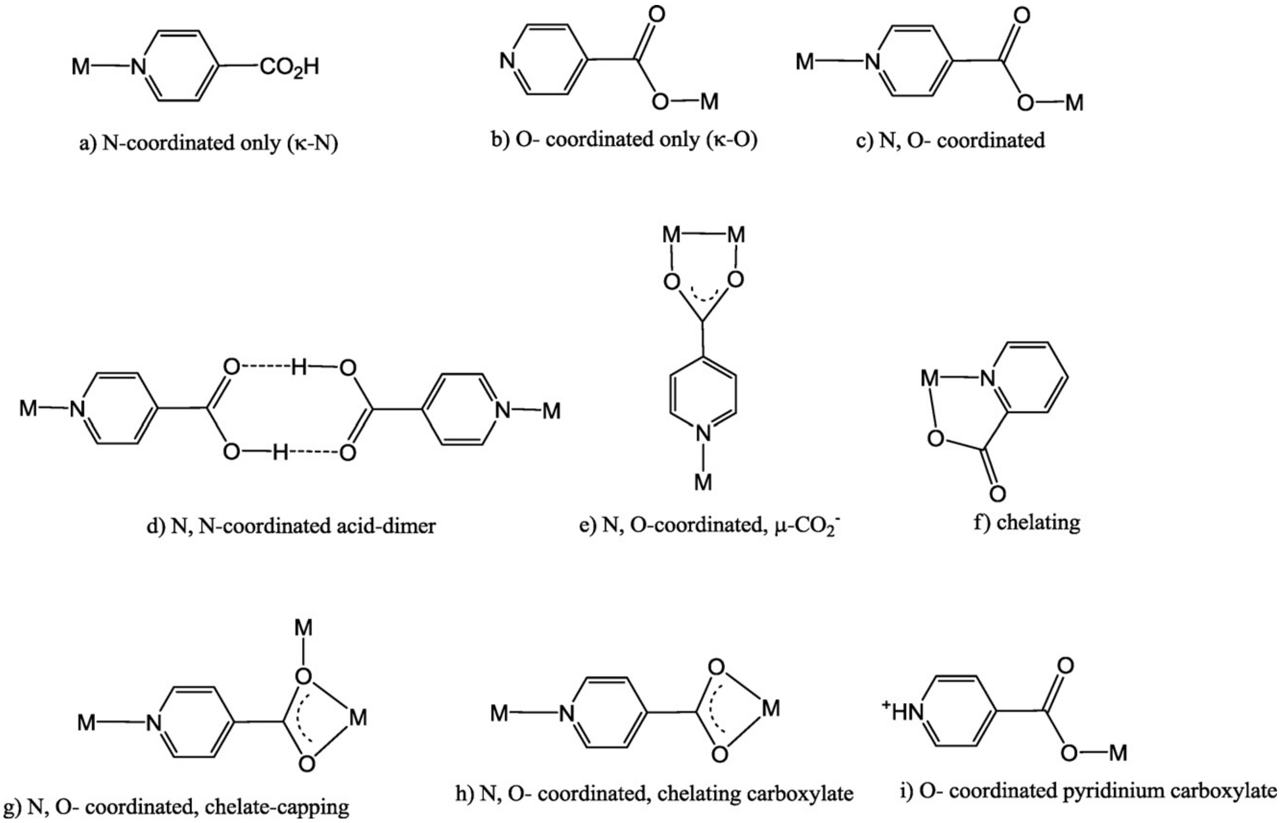

Fig. 1. (a–i) Different coordination modes of the pyridinecarboxylate ligands.

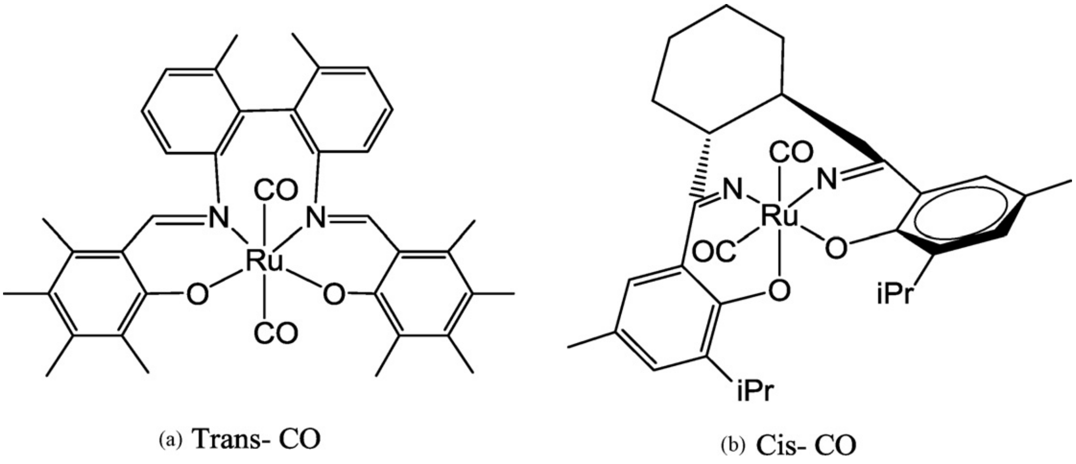

Fig. 2. Related Ru(II) complexes with [N,N,O,O] tetradentate salicylidene diamine ligand and trans (a) or cis (b) carbonyl [94].

bonds [83]. Nicotinic acid (3-pyridinecarboxylic acid, *abbrev.* nic), also known as niacin (vitamin B_3), has the acid functionality in the β-position. Like isonicotinic acid, its molecules are also linked in infinite chains by hydrogen bonding in the solid state [84]. Picolinic acid (2-pyridinecarboxylic acid, *abbrev.* pic) has the acid functionality in the α-position. All these three pyridinecarboxylic acids are soluble in water and sparingly soluble in MeOH. Their pK_a in water is about 4.84 [85]. Other variants of pyridinecarboxylic acids have different R groups (CH_2, C_2H_2, C_6H_4, etc.) inserted between the pyridine and carboxylic acid moieties.

Highlighted in this review are the typical features and unique properties of pyridinecarboxylic acids among other hybrid ligands. Included in the description are some types of N,O ligands selected for comparisons. Carboxylate is one of the most versatile ligands known in coordination chemistry [7–10,17,33,34,50,78,86]. It spans across the extremes of being non-coordinating to multidentate, taking advantage of the (weakly) basic lone pairs on both carboxyl oxygen atoms. This versatility is further strengthened by its prowess in H-bonding [31,66,67] (Fig. 1(d)), which is a key component in many supramolecular assemblies. Carboxylic acid is a proton donor, but its deprotonated carboxylate form is potentially a proton acceptor and Lewis base. This adds an extra level of flexibility for assemblies carried out in different solvents and with metals of different acidity. The carboxylate functionality as a ligand is also known to possess multiple binding modes, from monodentate to bidentate, terminal to multi-metal coordination (di-, tri- and tetra-bridging, etc.). Such multiple coordination possibilities of the ligand impart structural variation to the assembled materials. Both pyridine and carboxylate are σ donors but the former generally has higher π accepting ability. Pyridine is strictly monodentate whereas carboxylate can potentially fluctuate between mono- and bidentate, as well as shuttling among the terminal, chelating, bridging, capping and even free state. This mobility and flexibility enable the ligand to self-select the metals and self-organize the resultant framework. The presence of both pyridine and carboxylate functions therefore gives these ligands maximum prowess to cope with the demands of different metals and adapt to different forms of metal connections [31,71,72,74–76,87–89] (Fig. 1). The pyridine donicity can be further adjusted by the nature and position of the substituent on the heterocyclic ring whilst the ligand character of carboxylate is also influenced by the electronic state of the pyridine ring. In conjunction, they thus have a simple and yet powerful mechanism to meet the geometric demands of the metals and the topological demands of the network.

The possibility for placement of the carboxylate at the α-, β- or γ-position with respect to the pyridine nitrogen is a key feature that allows these ligands to support supramolecules of different frameworks. For example, α-substitution tend to favor chelates and complexes of low nuclearities whereas γ-analogues would maximize the separation between the metals and hence ideal for topologies such as square and rectangles, and generate polymers and open networks with lattices of high-porosity. Those with β substituents would promote oligomers of smaller cavities. These different levels of electronic and steric control are key in the exploration of different functional assemblies, which will be illustrated below.

The coordination dynamics of pyridinecarboxylate can be significantly enhanced when a bridgehead, commonly $-(CH_2)_n-$, is introduced between the pyridine and carboxylate moieties [36,37,39,42,44]. This adds another dimension of skeletal flexibility to cope with different demands of bridging configurations.

A distinct feature of pyridinecarboxylates is their amenity for metalloligand construction [12,37,39,45,90–92]. This is achieved by using metal substrates with limited coordination unsaturation so that only one of the two donor functions is engaged. It “forces” the formation of a dangling donor, which can be either pyridine or carboxylate. Although pyridine may be a stronger ligand in terms of higher σ donicity complemented by π accepting ability, carboxylate is superior in its chelating and multi-electron donation abilities. It is also possible to envisage the carboxylate to keep its parent acid state, thus protecting it from coordination. This represents a simple method to create metalloligand acids as shown in Fig. 1(a). The other extreme is the zwitterion in which the ligand is carboxylate bound with a pyridinium end (Fig. 1(i)).

Another unique property of pyridinecarboxylate is that even when the ligand is in a stable bidentate bridging state with N,O-coordination, there is still a carboxyl oxygen that is pendant (Fig. 1(c)). This oxygen is weakly basic but sufficient to capture a foreign oxophilic and acidic metal if the stereoconformational conditions are met. This fulfils the basic criterion to be a supramolecular metal sensor. Since carboxylate in some systems is known to switch facilely and reversibly between the chelating and monodentate modes, it can be envisaged that such a sensor can be built on a reversible model whereby the incoming metal can trigger a chelate opening. Under low metal concentration, or in the presence of a metal sponge, the process can be reversed. This offers a potentially new approach to metal sensing (see Sections 7 and 8).

3. Mononuclear complexes

Mononuclear complexes are commonly formed by chelation of the hetero-donors (Fig. 1(f)) or when one of them is protected, e.g.

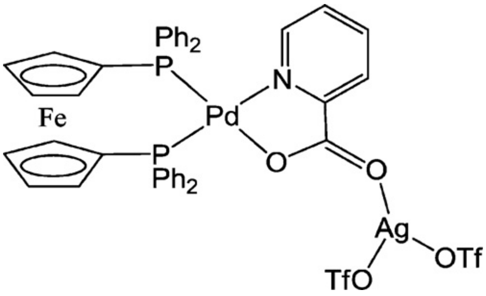

Fig. 3. Exocyclic coordination of carboxyl oxygen in [Pd(pic)(dppf)]$^+$ to $[Ag(OTf)_2]^-$ [42].

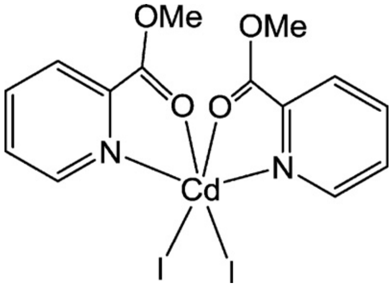

Fig. 5. A stable [N,O] pyridine-ester ligand in $[CdI_2(\text{methylpicolinate})_2]$ [63].

by protonation (Fig. 1(a) and (i)). Other N,O-donating ligands with neighboring donor sites also easily give chelates, such as in picolinate [42,75], 2-pyridineacetate (2-PyOAc) [89], pyridine esters [63], hydroxyindamine [93], carboxyimidazole [51,52], pyrazine-2-carboxylate [53–57], 2-pyridinemethoxide [59], threoninate [76], and related multidentate ligands [94] (Fig. 2). Although the vast majority of these chelates are unreactive, the presence of a pendant carboxyl oxygen, such as that in picolinate, could show sufficient basicity towards metals that are highly acidic such as Ag$^+$ (Fig. 3) [42]. This type of supramolecules has ion sensing potential, which will be described in Section 8.

Pyridine donating monodentate ligands with free carboxylic acid ends are potential metalloligands upon deprotonation, thus providing a viable pathway to heterometallic complexes [37,71] (Fig. 4). The ester form of the ligand [63] (Fig. 5) provides a feasible means of protection of the carboxyl group from coordination but subsequent activation by ester hydrolysis is problematic since it is typically conducted in an acid medium which can destroy the ligand coordination. Base hydrolysis is also not ideal since many common bases could also displace and eject the pyridinecarboxylate. As a result, usage of the ester protected pyridinecarboxylates to prepare metalloligands is not the desirable synthetic path.

Most of the known pyridinecarboxylate-based metalloligands are O-donating as the pyridine is metal-bound. Among the few exceptions are [Ni(nic)(tetramethyltriazacyclododecene)]$^+$ [71] (Fig. 6) and $Mo_2(\text{isonic})(\text{formadinate})_3$ [78] in which the active donor comes from the pendant pyridine, enabling the complexes to serve as nitrogen metalloligands.

4. Low-nuclearity assemblies

The γ-substituted pyridines are not conformationally suited for the spacer to be doubly bridging because they tend to force the metals to be directly opposite one another in a linear fashion (*vide infra*). This imposition however can be relaxed when a bridgehead such as methylene is introduced between the pyridine ring and carboxylate. This is exemplified in the dinuclear complex in which a 16-membered ring is enclaved by the two bridges (Fig. 7) [37,39,42].

Without the bridgehead, the assembly would drive towards the singly bridging form, with only one bridge across two metal centres as illustrated in Fig. 8 [68], as opposed to a doubly bridged system in Fig. 7. This is especially the case when there is only one available vacant site at the metal. This can be circumvented by pre-forming a hetero-bridge with a more acute bite, such as dppm, before the pyridinecarboxylate is introduced. When this is used with linear d^{10} metal such as Au(I), it brings the two metals and the associated donor pendants to neighborhood [45,78] (Fig. 9). Activation and coordination of the distal carboxylate or pyridine end could then lead to heterometallocyclic ring formation, thus offering an alternative to the linearly aligned system as given in Fig. 8.

When there are two vacant sites at the metal available for propagation, it commonly leads to ring or chain complexes. If the sites are orthogonal, as in d^8 species, triangular, square and rectangular rings are typically formed. This is illustrated in the formation of trinuclear $[Pt(\text{nic})(\text{dppf})]_3{}^{3+}$ and $[Pd(\text{isonic})(\text{dppf})]_3{}^{3+}$. Nicotinate is conformationally more adapted than isonic to meet the imposition from the more acute internal angle of the triangular d^8 metal rings. Use of a more linearly rigid γ-ligand would result in a complex square–triangle equilibrium which is hard to resolve synthetically [72]. An example of such dynamic competition is found in $[Pd(\text{isonic})(\text{dppf})]_n{}^{n+}$ which is triangular in solution but converts readily to the square form upon solvent removal [72]. Similar use of β-ligands to drive towards molecular triangles is also found in other related ligands such as pyrimidine formates [95] (Fig. 10). The second nitrogen on the pyrimidine ring is free but its coordination potential to create suprametallo-aggregates has not been fully exploited.

The molecular square or rectangle is the expected outcome for rigid γ-ligands with d^8 metals with *cis*-coordination sites, typically represented by $[Pt_4(\text{isonic})_4(P–P)_4]^{4+}$ (P–P = diphosphine or

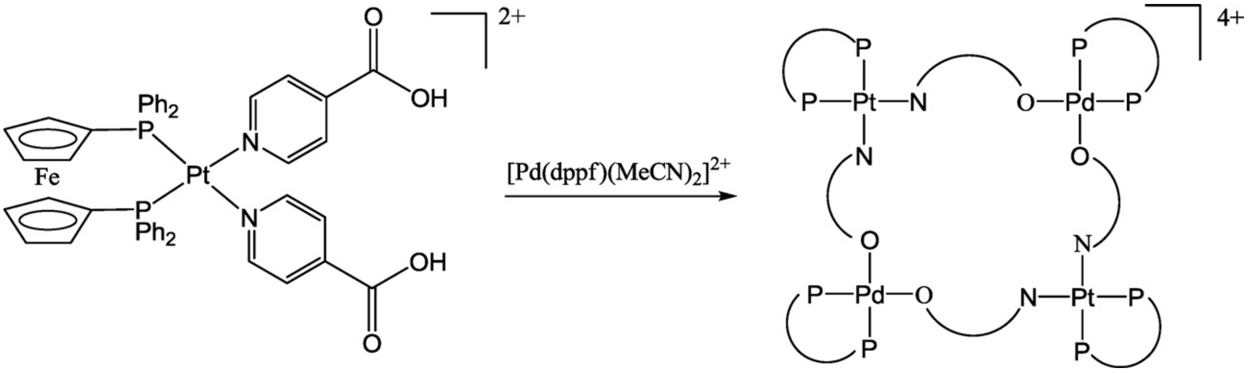

Fig. 4. Formation of a mixed-metal square complex from $[Pt(\text{isonic})_2(\text{dppf})]^{2+}$ as a metalloligand.

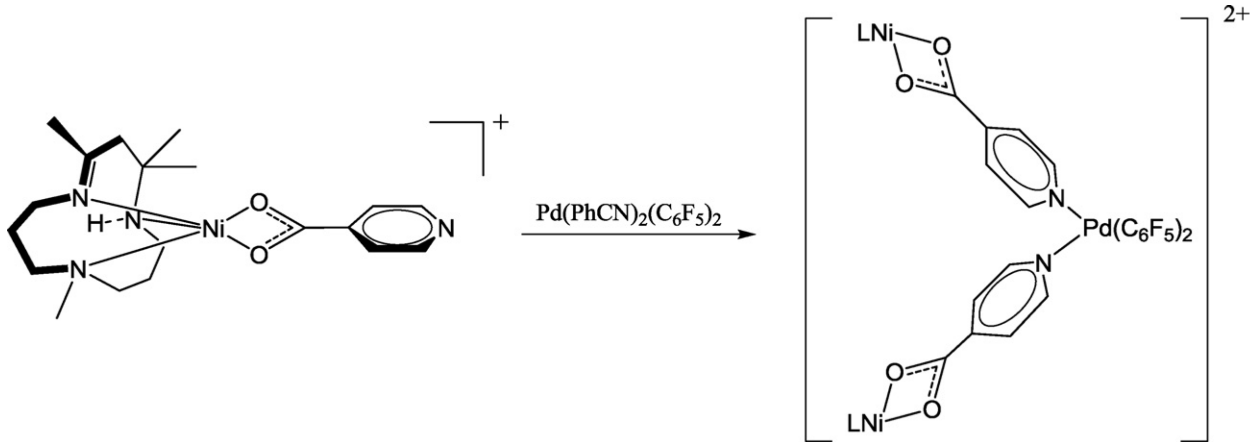

Fig. 6. An unusual pyridine pendant in $[Ni(nic)(L)]^+$ (L = tetramethyltriazacyclododecene) [71].

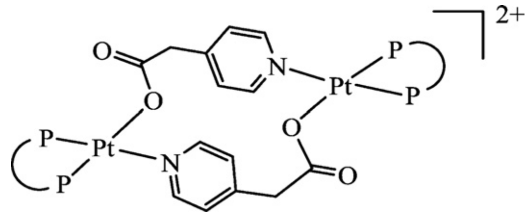

Fig. 7. Dinuclear $[Pt_2(4\text{-}PyOAc)_2(dppf)_2]^{2+}$ ring complex [37].

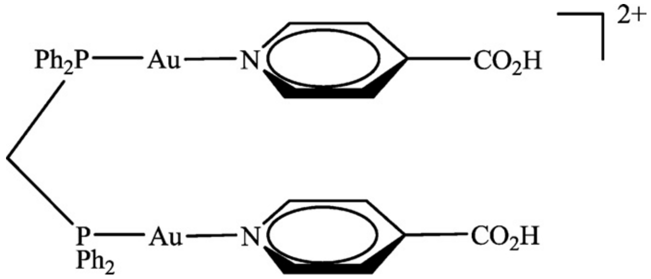

Fig. 9. Dinuclear $[Au_2(isonicH)_2(dppm)]^{2+}$ with the two free carboxylic acid moieties brought to proximity by the dppm bridge [45].

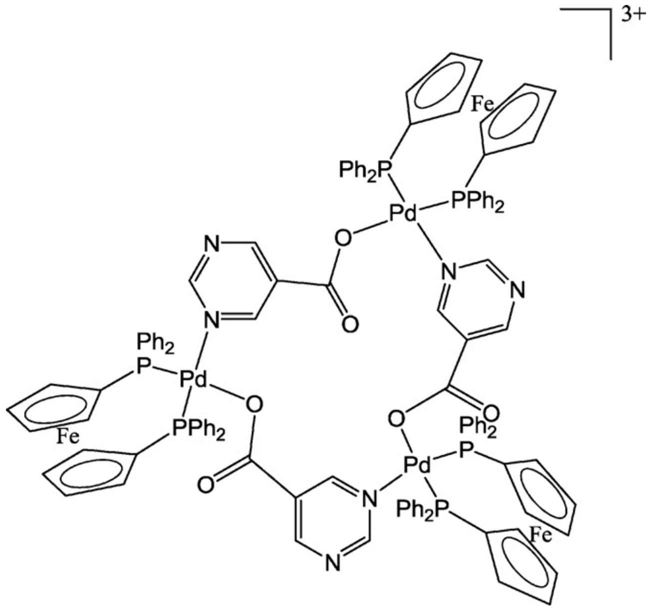

Fig. 10. Triangular $[Pd_3(\text{pyrimidine formate})_3(dppf)_3]^{3+}$ with one of the pyrimidine nitrogen atoms uncoordinated [95].

bis-monophosphines) [38,42] (Fig. 11). The yield of the square however could be complicated by polymer formation which is also skeletally favored by the ligand, as exemplified in the formation of $[Pd(isonic)(dppf)]_n^{n+}$ (Fig. 12) and $[Pd(PyAcr)(dppf)]_n^{n+}$ (4-pyridineacrylate = PyAcr) [42].

The square isomer, with a lower nuclearity, should be entropically favored, but the polymer formation is usually driven by precipitation. Their intermediate oligomeric forms, such as M_x (x = 6–10) assemblies, are rarely observed or isolated.

5. Oligomeric and polymeric assemblies

A convenient method to prepare assemblies of higher nuclearity is to use dinuclear building blocks as corner units. A good example is found in the assembly of an extraordinary tricationic hexanuclear triangular ring $[Au_6(isonic)_3(dppf)_3]^{3+}$. This is configured by three Au···Au axes at the corners of and perpendicular to the triangular plane bordered by the three isonic edges (Fig. 13) [40]. Each of the latter cascades across and down the two Au···Au axes, as schematically shown in Fig. 14. A key element of this hexanuclear triangle is the aurophilic Au···Au axis, without which the gold atoms would have little incentive to align in pairs at the corners of the triangle. The analogous Ag(I) assembly, with much weaker argentophilic interactions, gives a hint on how the assembly would look like when closed-shell attractive interactions are not dominant (Fig. 15). In this assembly, both of the carboxyl oxygen atoms are engaged,

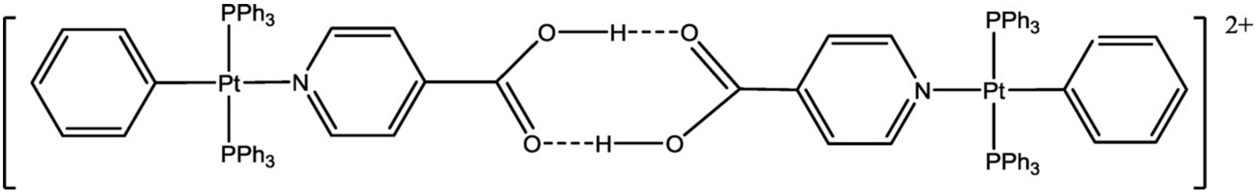

Fig. 8. Dinuclear $[Pt_2(isonicH)_2(C_6H_5)_2(PPh_3)_4]^{2+}$ with H-bonded isonic acid as an extended spacer [68].

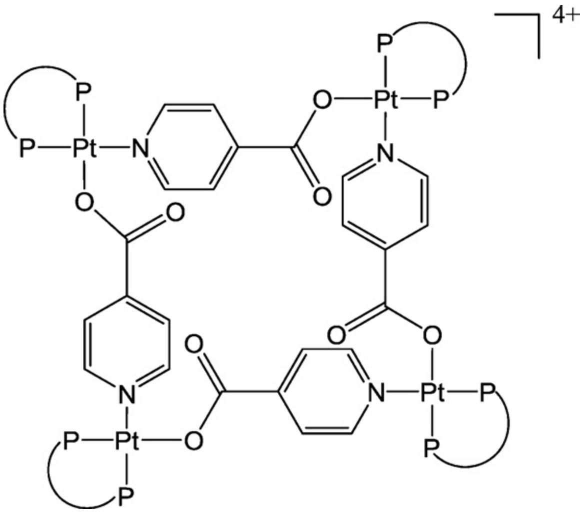

Fig. 11. Tetranuclear square-like $[Pt_4(isonic)_4(P–P)_4]^{4+}$ complex [42].

thereby the pyridinecaboxylate functions as a μ_3-capping ligand, two of which form a 14-membered rectangle-like ring with two silver atoms. This assembly also demonstrates the higher propensity for Ag(I) to form 3-coordinate complexes than Au(I) and thus more likely to take advantage of the multi-donating capacity of pyridinecarboxylates. It also illustrates how the carboxylates can span across two non-interactive metal centres that are pulled apart by a ligand as large as dppf (1,1′-(diphenylphosphino)ferrocene) [96]. This provides further evidence of the remarkable ability of pyridinecarboxylates to adapt to its environment.

The bridging mode of pyridinecarboxylates does not necessarily impose a metallocyclic ring formation. This is an important attribute for the use of a particular spacer to achieve diversity in its assemblies. A good example is found in the formation of an open-aggregate $[Ag_5(nic)_2(dppf)_2]^{3+}$ in which the five Ag(I) centers are held together by the pyridinecarboxylates but without being constrained by any ring formation (Fig. 16). This is accomplished by the fusion of two non-bonding metal triangles at a linear d^{10} metal center (C–O–Ag–Ag–O with C–O–Ag, Ag–Ag and Ag–O–C each forming one side of a triangle). Comparison of this with the Ag_4 moiety depicted in Fig. 15 suggests that carboxylate can also span over a large range of M–M distances [Dppf bridged Ag···Ag distance in Ag_4 depicted in Fig. 15: 3.809 Å (ave.) and Ag_5 in Fig. 16: 3.3030 Å (ave.)] [43]. Such bridging/binding modes of the carboxylate have been extensively studied in the literature [11,14,31]. These attributes enable the spacer to support different assemblies and networks. The diversity is further enhanced in d^{10} metals which can self-select a local geometry (linear, trigonal planar, tetrahedral) and with or without M–M interactions. Such multi-level flexibility offers a myriad of possibilities of supramolecular frames. Further evidence is obtained from the isolation of $[Ag_4(nic)_2(dppm)_4]^{2+}$ complex, in which two dppm bridges help to lock the two Ag(I) centers into close proximity (Fig. 17). Even in such a constraint situation, the carboxylate can adapt to be the third bridge. This is remarkable considering the contrasting sizes and bites of dppm and carboxylate. The outcome is a large metallocyclic cavity bordered by the two spacers and four silver atoms. This structure is also an example of co-existence of 18-electron tetrahedral and 16-electron trigonal planar Ag(I) within a framework. It is also an illustration for a 3D M_4 box construction from d^{10} metals and pyridinecarboxylate bridges, thus providing a contrast to the 2D M_4 square construction from d^8 metals described earlier. Comparison of this with the similar dppf assembly also demonstrates the ability of the spacer to adapt to both open and closed forms of aggregation.

Such an Ag_4 closed ring structure as in $[Ag_4(nic)_2(dppm)_4]^{2+}$ can in principle open up to give its nuclearity isomer in form of $[Ag_4(isonic)_2(dppm)_4]_n{}^{2n+}$ polymer (Fig. 18). This is achieved by a simple conformational re-orientation such that the carboxylate bridge is “face-on” to the $[Ag_2(dppm)_2]$ ring and “edge-on” at the pyridine end to give both 16-e and 18-e Ag(I), thus providing an effective configuration for polymeric propagation. An unusual variant is to use one of the bridging carboxyl oxygen to link two Ag_2 moieties, thereby releasing the pyridine to coordinate to an additional, and unique linear Ag(I) center. The latter can then connect through pyridine to the neighboring unit. This results in a very unusual form of polymeric pentamer, which belongs to a new class of materials termed polymer of oligomer (POLO) [43] (Fig. 19). This form of framework is sufficiently flexible to accommodate other pyridineformates. For example, a similar POLO is formed when isonic is replaced by nic or a longer and skeletally more flexible chain such as 3-pyridinepropionate ($PyPrO_2$) (Fig. 20) [43].

Other polymeric complexes formed from non-pyridinecarboxylate N,O-spacers include the Cd(II) L-proline

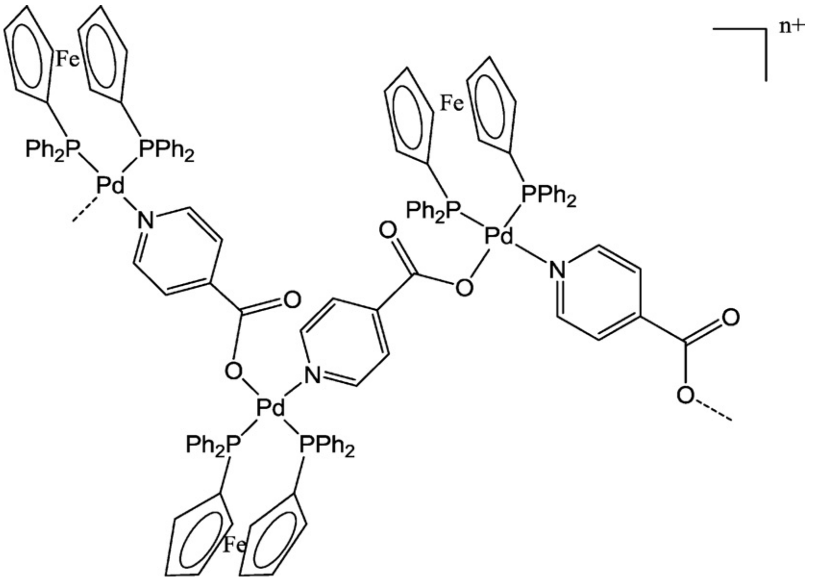

Fig. 12. A segment of polymeric $[Pd_n(isonic)_n(dppf)_n]^{n+}$ [42].

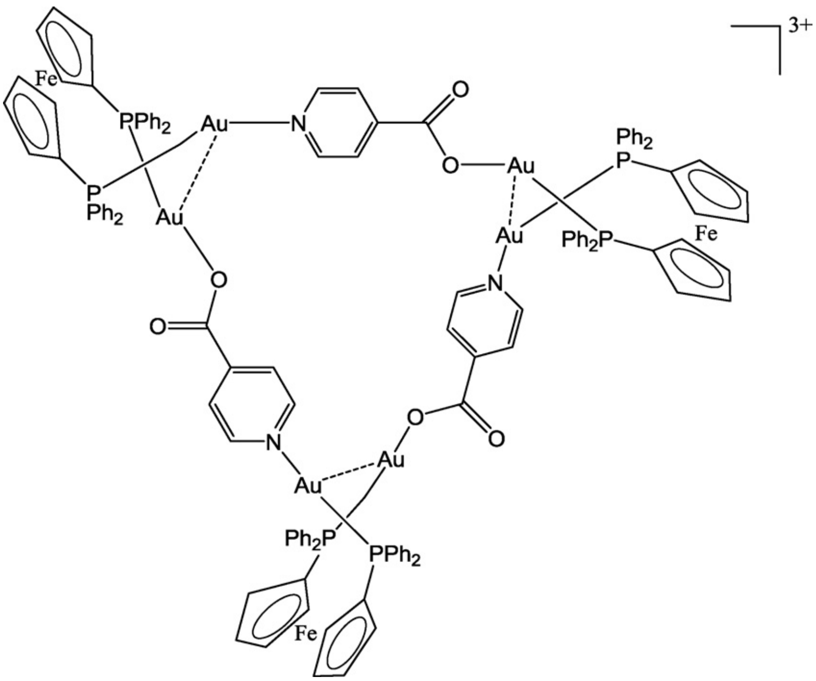

Fig. 13. Chiral $[Au_2(isonic)(dppf)]_3{}^{3+}$ triangular ring complex [40].

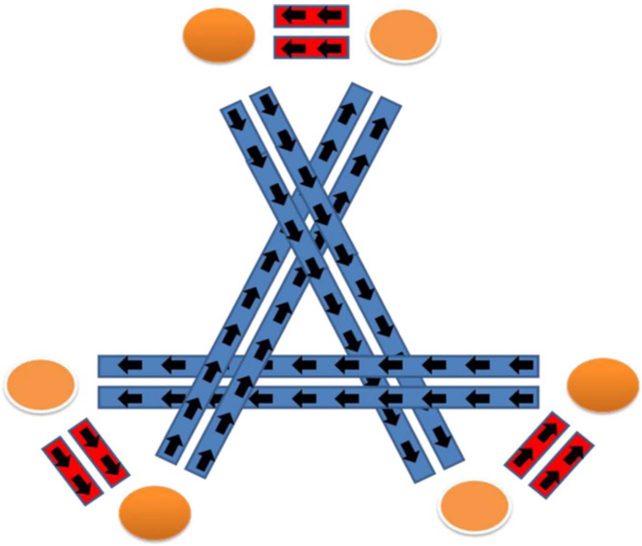

Fig. 14. Schematic drawing of hexanuclear triangular $[Au_2(isonic)(dppf)]_3{}^{3+}$ with the blue "down-riding escalators" representing the isonic spacer and the red "up-riding lifts" representing the Au···Au axis. The Au···Au axes are perpendicular to the triangular plane of the isonic ligands.

polymeric complex (Fig. 21) reported by Rosseinsky et al. [47] and a Cd(II) dicarboxyimidazole polymer by Fang and Zhang (Fig. 22) [51]. Use of natural amino acids to construct MOFs is uncommon as their small bite sizes tend to put the N and O donors groups in close proximity, resulting in chelates of low nuclearity rather than bridging or extended networks. The Cd(II) L-proline polymer is a rare success with the ligand serving a dual chelating and bridging role across the metals. The carboxylate bridge facilitates propagation of the polymer chain.

6. Network complexes

γ-Substituted pyridinecarboxylate (or pyridine-4-carboxylate) is structurally and conformationally adapted to singly-bridge metals. Such conformational adaptation provides an effective means to construct zig-zag coordination polymers, including heterometallic polymers. This is exemplified in the formation of the $[PtCu(isonic)_2(dmpda)(H_2O)_5]_n(NO_3)_n$ (dmpda = 2,2′-dimethyl-1,3-propanediamine) (Fig. 23(b)) network from $[Pt(NC_5H_4CO_2)(dmpda)]$ in which the Pt(II) selects the pyridine nitrogen and leaves the carboxylate to be the tether group (Fig. 23(a)). The latter is stabilized by intermolecular H-bonding between the diamine hydrogen atom of one molecule to the carboxylate of the neighboring molecule [88].

In homometallic systems such as those of square planar d^8 metals, the bridging ligand can be ideal edges for squares with the

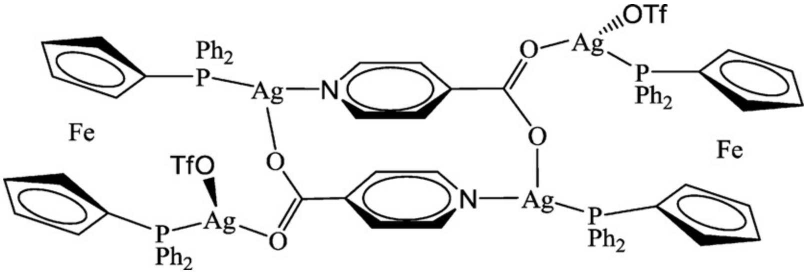

Fig. 15. Rectangular $Ag_4(isonic)_2(OTf)_2(dppf)_2$ ring complex [43].

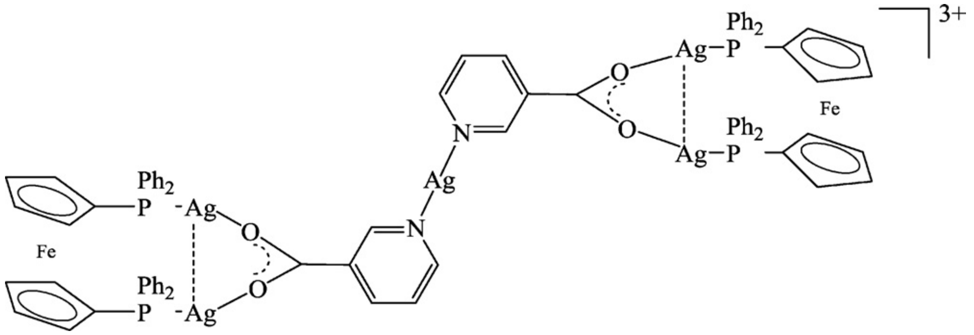

Fig. 16. $[Ag_5(nic)_2(dppf)_2]^{3+}$ complex [43].

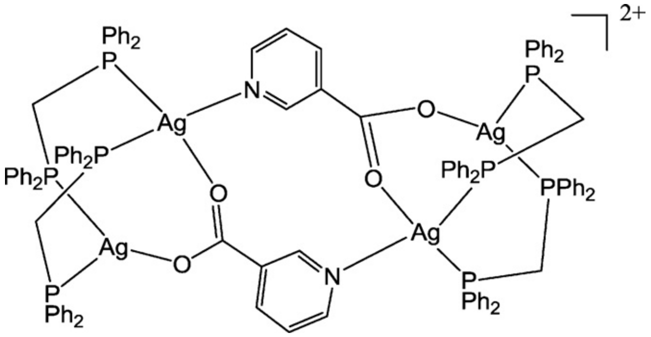

Fig. 17. $[Ag_4(nic)_2(dppm)_4]^{2+}$ complex [43].

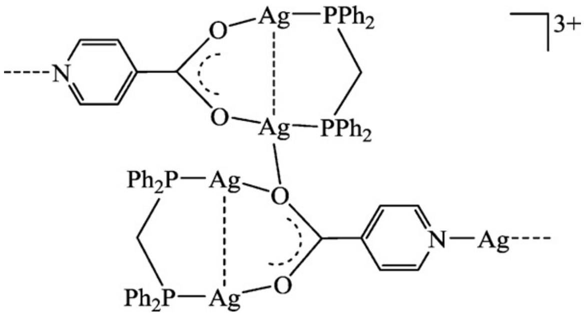

Fig. 19. Repeating unit of polymeric $[Ag_5(isonic)_2(dppm)_2]_n{}^{3n+}$ [43].

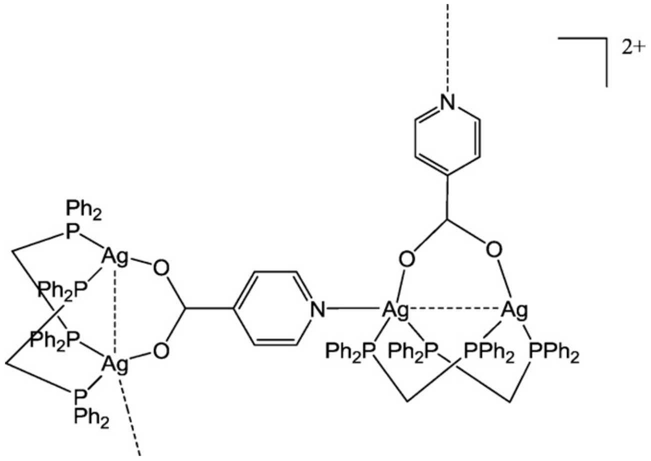

Fig. 18. A segment of $[Ag_2(isonic)(dppm)_2]_n{}^{n+}$ polymeric complex, showing two repeating units [43].

metal occupying the corners. This is found in $[Pt(isonic)(dppf)]_4{}^{4+}$ (Fig. 11) [38]. Other similar pyridinecarboxylates with coordinated pyridine and carboxylate ends have emerged recently [35,72,73]. However, the preference of Pt(II) to the pyridine nitrogen is exemplified in the assembly of a 2D binary isonic network which shows clearly that in the absence of any co-ligand, the d^8 metal self-selects the pyridine over the carboxylate (Fig. 24). To circumvent the formation of a reactive carboxylate pendant, one of the two carboxylates is protonated such that the carboxylate ends can be stabilized by H-bonding. Through these H-bonds, the framework cris-crosses to give a mesh of fused squares with large cavities (15 Å × 15 Å) [69]. Inclined interpenetration of (4,4) nets in three mutually perpendicular planes occurs in this case. Effectively, the system uses H-bonding to promote inter-spacer interaction, thereby lengthening the polygonal edges thus creating open spaces and minimizing unnecessary repulsive interactions among the metal spheres. This provides an effective means to the assembly of materials of high-porosity. A similar pattern is found in $[Ni(SCN)_2(isonicH)_2]_n$ except that both carboxylate ends are protonated, such that dual H-bonding is evident [67] (Fig. 25). The cavity dimensions in the Ni networks are about 5.5 Å × 16.3 Å. The electroneutrality is maintained in the assembly even though all the

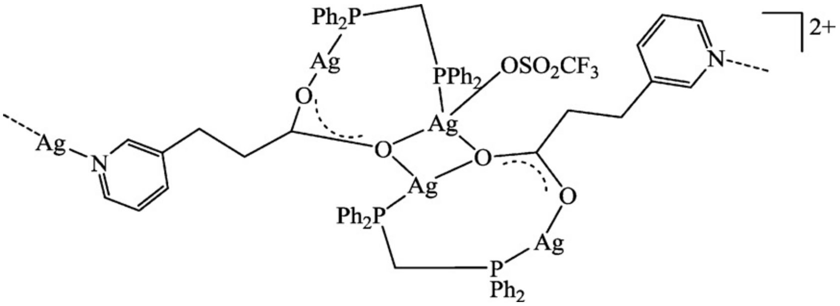

Fig. 20. Repeating unit of polymeric $[Ag_5(PyPrO_2)_2(OTf)(dppm)_2]_n{}^{2n+}$ [43].

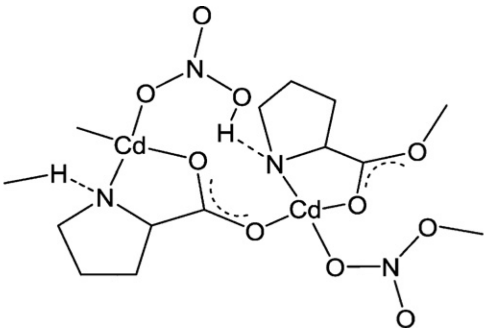

Fig. 21. A segment of [Cd(L-proline)(nitrate)(bipy)]$_n$ polymer (omitting bipy for clarity) [47].

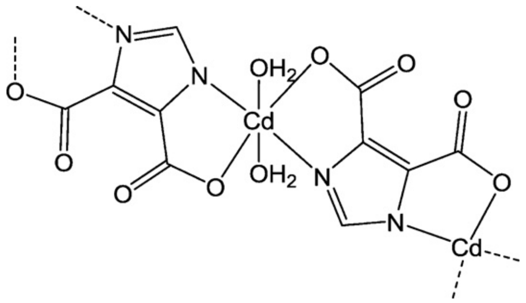

Fig. 22. Repeating unit of [Cd(dicarboxyimidazole)$_2$(H_2O)$_2$]$_n$ [51].

carboxylates are protonated because of the presence of anionic co-ligands such as thiocyanate. This demonstrates another capability of pyridinecarboxylates in supporting supramolecules from neutral to ionic states. Unlike Pt(II), the Ni(II) sphere is octahedral, thereby allowing an orthogonal arrangement of two sets of spacers in a network of fused rectangles.

Linear or T-shaped d^{10} metals such as Au(I) can also be used to assemble porous networks with pyridine carboxylates. This is prepared from a metalloligand such as [Au_2(dppf)(PyAcrH)$_2$]$^{2+}$ (Fig. 26) The *anti* orientations of the two pyridineacrylic acid residues promote an open network to accommodate the triflate anions which then H-bond with the neighboring ferrocenyl hydrogen and weakly link with the gold centers. These inter-ionic forces connect the Au_2 moieties to yield polymer chains, whose solid-state packing reveals a porous network with clathrating ability for $CHCl_3$ (Fig. 27) [40].

Some uncommon network complexes may also be formed using pyridinecarboxylates in the deprotonated form. The heterometallic Gd(III)-Cu(I) mixed-ligand complex [Gd_{14}(μ_6-O)(μ_3-OH)$_{20}$(isonic)$_{22}$$Cu_6Cl_4$($H_2O$)$_8$]$_n$, reported by Yang *et al.* is an example of an isonic-supported network (Fig. 28) [79]. The 3D network comprises a $Gd^{III}{}_{14}$ cluster linked to two Cu_2 units and another two Cu atoms by 22 bridging isonic bonded to Gd(III) and Cu(I) through carboxylate and pyridine respectively. Each Gd_{14} aggregate is held together by oxo- and hydroxo-bridges. Two forms of coordination modes of the carboxylate – through one or two carboxyl oxygen – are evident. Similar networks have been obtained with yttrium and dysprosium [79].

Binary pyridinecarboxylate complexes are most amenable to give network complexes because of the multiconnectivity at both metal and ligand sites. Typical examples are [M(isonic)$_2$]$_n$ (M = Zn, Cd) (Fig. 29) [31].

Formation of network complexes using dicarboxylates such as pyridine dicarboxylate [11], pyrazine dicarboxylate (Fig. 30) [80,81], pyrimidine dicarboxylate [65,97], and terpyridine carboxylates such as 3,5-dicyano-4-(4-carboxyphenyl)-2,2′:6′4″-terpyridine [98–100] is more common. The higher number of donor sites naturally raises the network connectivity. Other N,O-spacers for network construction include pyrazine carboxylates. The presence of two basic nitrogen atoms on these heterocycles presents a straightforward model to build connected structures. When the donors are *trans* or *anti* oriented, their ability to juxtapose the metals across the diagonal ends favors zig-zag and cross-linked polymers (Fig. 31).

7. Small molecular clathrate

The host–guest chemistry of Ni(II) pyridine carboxylate complexes has been extensively studied by Sekiya et al. [66,67,101]. The cavities in the Ni(II) isonicH network [Ni(SCN)$_2$(isonicH)$_2$]$_\infty$ (Figs. 25 and 32) [67] can accommodate a large number of different types of organic compounds, e.g. perylene, anthracene, naphthalene, azabenzene, styrene, etc. Planar molecules are compatible with the cavity shape. The aromaticity also facilitates π–π interaction between the guest and the isonic spacer, thereby strengthening

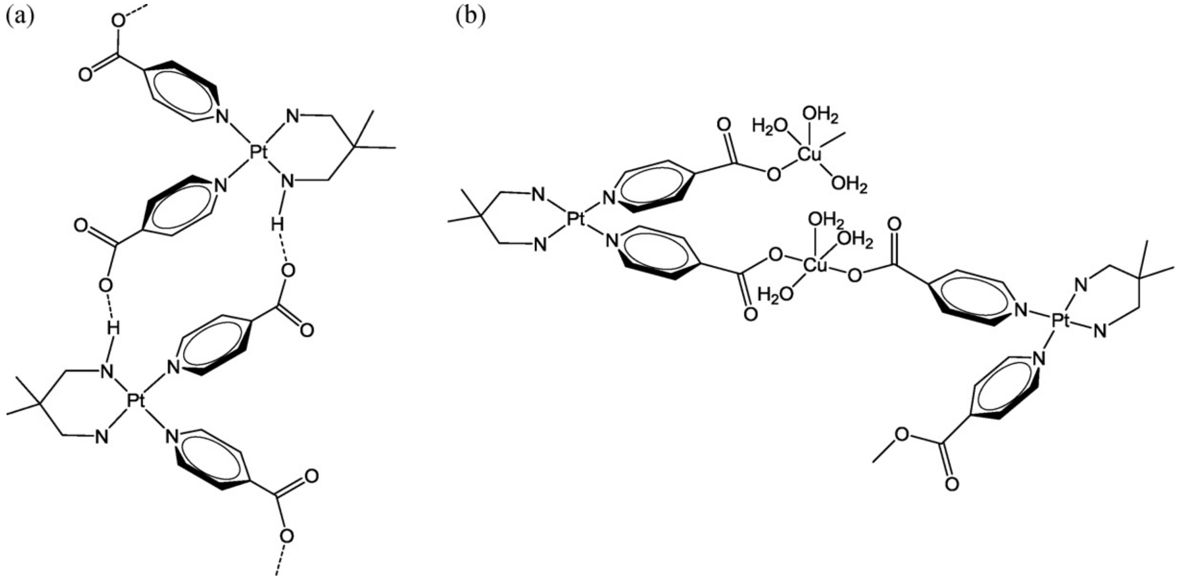

Fig. 23. (a) Zwitterionic Pt(isonic)$_2$ building block showing N-coordinating isonic; (b) a segment of the [PtCu(isonic)$_2$(dmpda)(H_2O)$_3$]$^{n+}{}_n$ polymer [88].

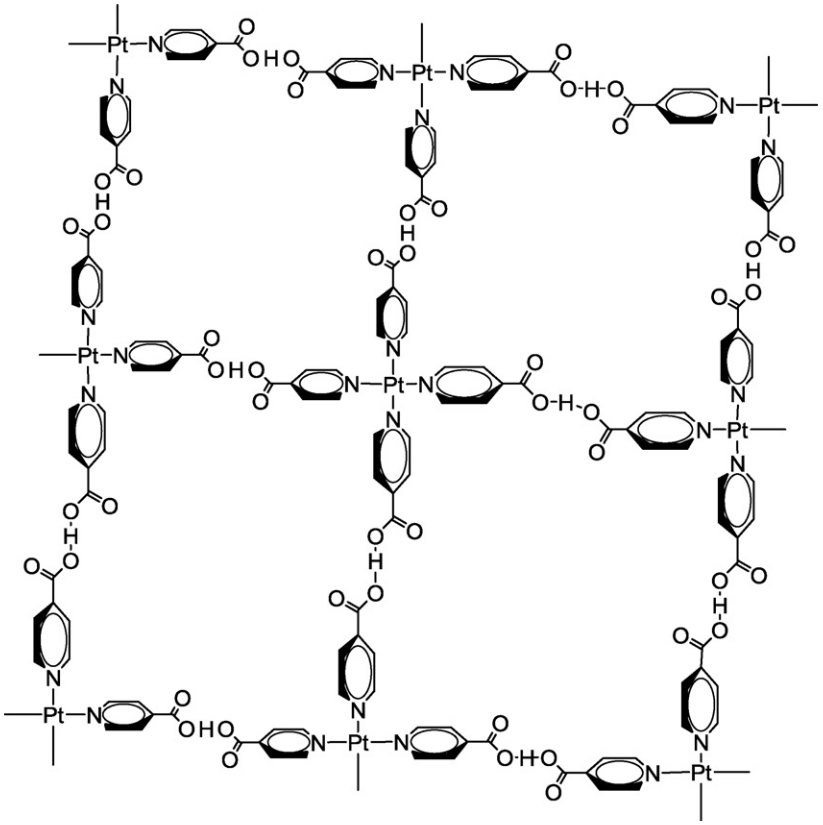

Fig. 24. [Pt(isonicH)$_2$(isonic)$_2$]$_n$ network complex with edges elongated through H-bonding between the carboxylates [69].

the host–guest association. Apart from the cavities, the spaces sandwiched by the 2D network layers also provide additional room for the guests. The large number of pore spaces in this network enables it to serve as an effective sponge or carrier, for aromatic organic compounds.

H-bonding is another common driving force for clathration. This is witnessed when H-bond donors such as $CHCl_3$ come into contact with pyridinecarboxylate networks such as [Au$_2$(PyAcr)(dppf)]$_n$(OTf)$_{2n}$ (Figs. 26 and 27) [40]. The inward directing carbonyl groups of the PyAcrH ligand helps the network capture $CHCl_3$ molecules. This is however not unique in network complexes but also found in discrete ring molecules such as [M(nic)(dppf)]$_3^{3+}$ (M = Pd, Pt (Fig. 33)). The $CHCl_3$ molecule is too bulky to be encapsulated in the ring cavity but perches on top of it [42]. Without the embracing effect, the stability of the host–guest complex depends significantly on the strength of the multi-centered H-bonding. Other small molecules with strong H-bonding tendency such as H_2O, MeOH, EtOH are also potential guests in these pyridinecarboxylate frameworks [36,42]. Such interactions are however not observed in networks constructed using homo-donor spacers that do not have H-bond acceptors such as terpyridine.

8. Ion clathrate and sensing

Pyridinecarboxylate assemblies could use the weakly basic carbonyl oxygen atoms for secondary capture of guest within the assemblies. The convergence of the carboxyl groups is typically not present in poly-carboxylate assemblies such as those of bicarboxylates [50,102] (*vide infra*). In [Pd$_2$(PyOAc)$_2$(dppf)$_2$] [Ag(OTf)$_2$]$_2$, the exo-directing carbonyl groups enable the ring to serve as a molecular host where the guests molecules are held outside the host framework by dative bonding from the carbonyl oxygen to Ag$^+$ (Fig. 34) [39]. This is an unusual form of clathration as most molecular frameworks capture their guests using lattice cavity or endocyclic encapsulation. This form of adduct allows frameworks with small cavities to host large guests. Molecular frameworks

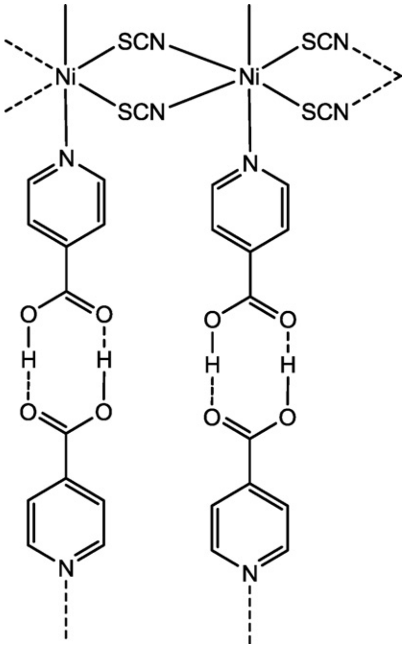

Fig. 25. [Ni(SCN)$_2$(isonicH)$_2$]$_n$ network with dual-hydrogen bonding across both carboxylic acids [67].

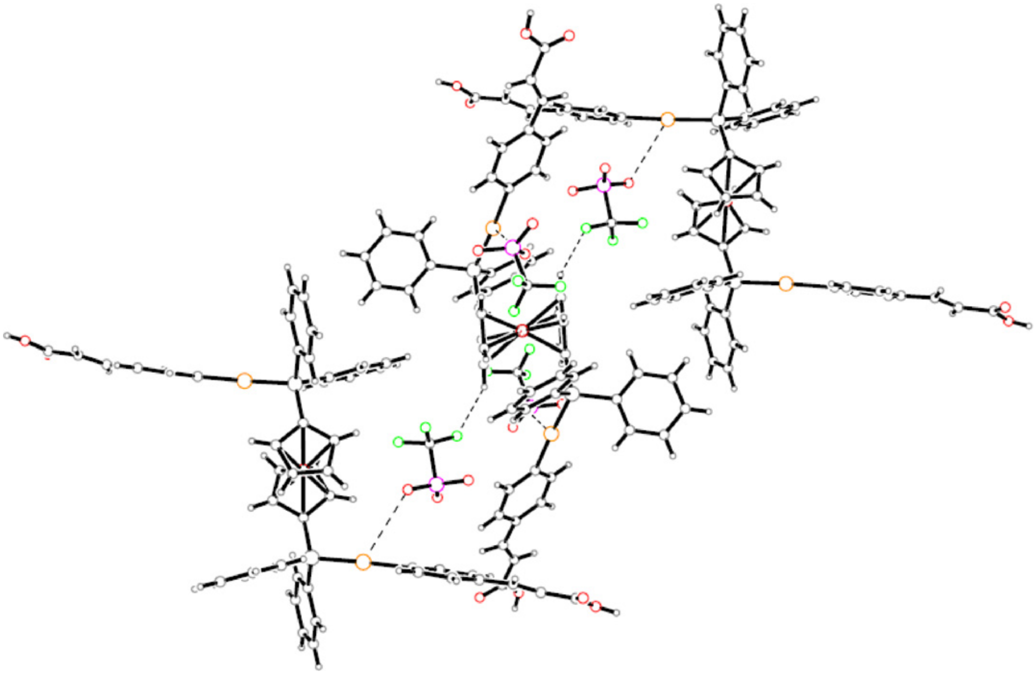

Fig. 26. Ball and stick model of [Au_2(dppf)(PyAcrH)$_2$](OTf)$_2$, showing ionic interactions between [Au_2(dppf)(PyAcrH)$_2$]$^{2+}$ cation and triflate anions to give a polymeric chain [40].

constructed using simple homo-donor ligands such as the poly-pyridine or poly-carboxylate type building blocks generally do not display such hosting properties. The former contains no spare donor to capture any guest except by the usual van der waals interactions in the framework cavities. When the latter contains carboxyl pendants, they are typically directed towards the framework cavity which generally defines the guest size and shape [50,102]. Most poly-carboxylate frameworks are also assembled with carboxylates that are either bridging or chelating such that free and active carboxyls are rare [7,9–11,17,32,33,50,86,103].

With the right choice of spacer chain length and stereogeometry, the conformation of the ring and its cavity size can be tuned and controlled. This in turn affects the type of guest captured and the mode of encapsulation. When the spacer chain length is increased and the substituent changed from *para*- to *meta*- as in 3-pyridinepropionate (PyPrO$_2$) assemblies, the free carbonyl groups

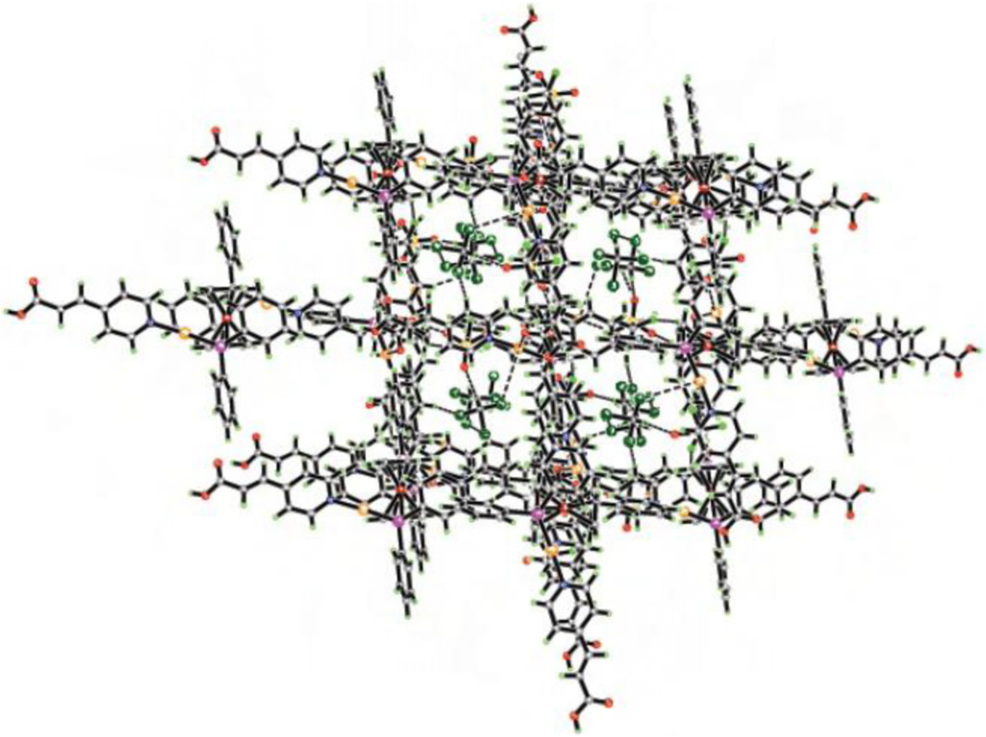

Fig. 27. ORTEP diagram (50% thermal ellipsoids) of [Au_2(dppf)(PyAcrH)$_2$](OTf)$_2$ network showing clathrated $CHCl_3$ molecules in cavities [40].

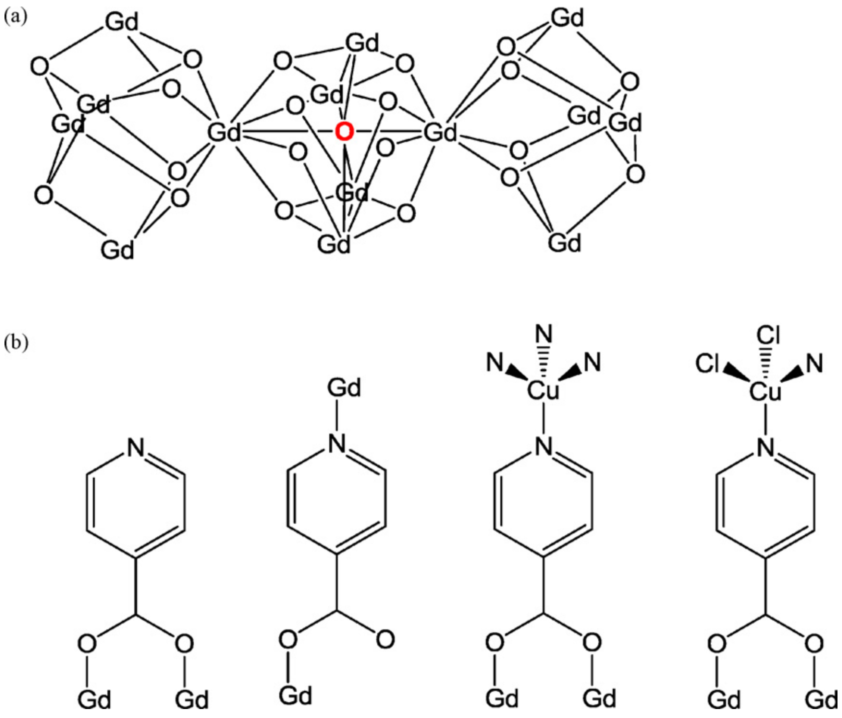

Fig. 28. (a) The Gd_{14} core of $[Gd_{14}(\mu_6\text{-O})(\mu_3\text{-OH})_{20}(\text{isonic})_{22}Cu_6Cl_4(H_2O)_8]_n$ network (H atom of OH not shown for clarity, μ_6-O shown in red). (b) Coordination modes of the bridging isonic ligands in the Gd network [79]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

on the spacer are directed towards (and upwards) the ring center, thus promoting endo- (rather than exo) hosting of guest. This allows the guest to be anchored on the carbonyls on top of the ring cavity. This form of attraction induces metal ion selectivity. For example, $[Pt(PyPrO_2)(P\text{–}P)]_2{}^{2+}$ (P–P = dppf, 2 × PPh_3) selects $[Na(OTf)_2]^-$ from a mixture of Na^+, K^+ and Ca^{2+} ions through dative bonding (Fig. 35). Yet, $[Pd(PyPrO_2)(dppf)]_2{}^{2+}$ shows higher affinity towards Ca^{2+} [44]. On the other hand, Pd(II)-pyridineacetate described earlier preferentially attracts Ag^+. This form of metal ion binding is reversible. The alkali and alkaline earth metal guests can be removed from the adduct by 18-crown-6 without destroying the host framework. These properties demonstrate the potential for these assemblies to be developed as single-molecular sensors for metal ions with high sensitivities and selectivities [77,104].

In the 3-pyridineformate (nic) triangles constructed with Pd(II) and Pt(II) [42], the carbonyl groups are directed towards the centre of the ring cavity as compared to the pyrimidine carboxylate or nic triangles by Mukherjee et al. [73,95], which show the carbonyls directed away from the ring centre in the solid-state structures. The carbonyl convergence allows the ring to function as a "molecular claw" to capture either a small solvate molecule such as $CHCl_3$ (Fig. 33) or capture a metal complex such as $[Na(OTf)_3(H_2O)_3]^{2-}$

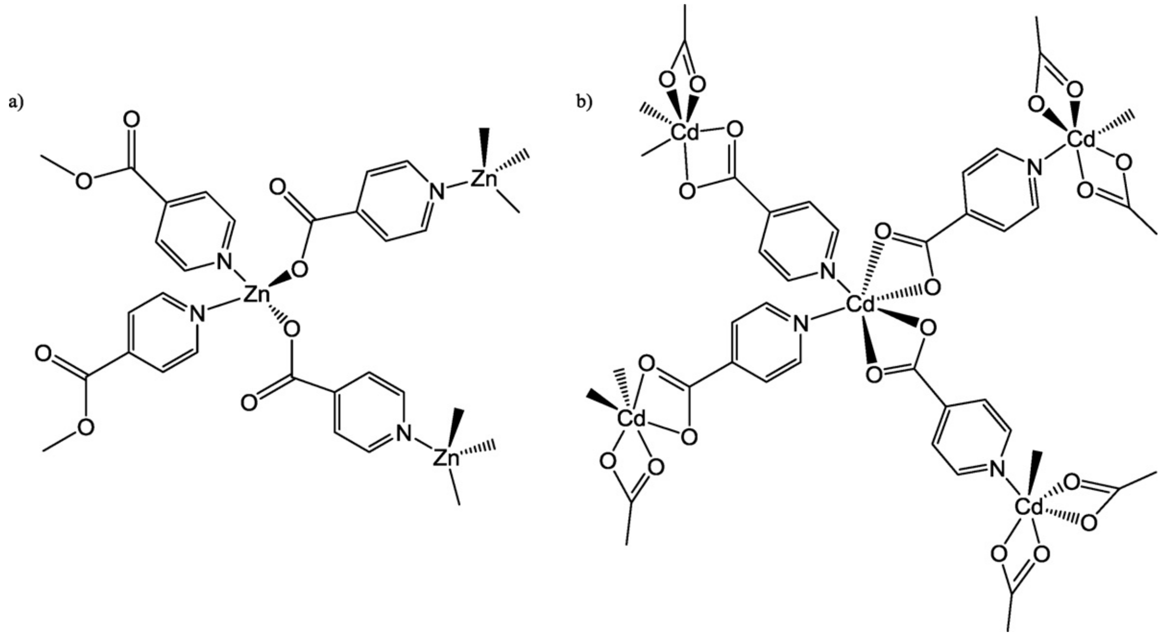

Fig. 29. $[M(\text{isonic})_2]_n$ (M = Zn (a), Cd (b) network complexes) [31].

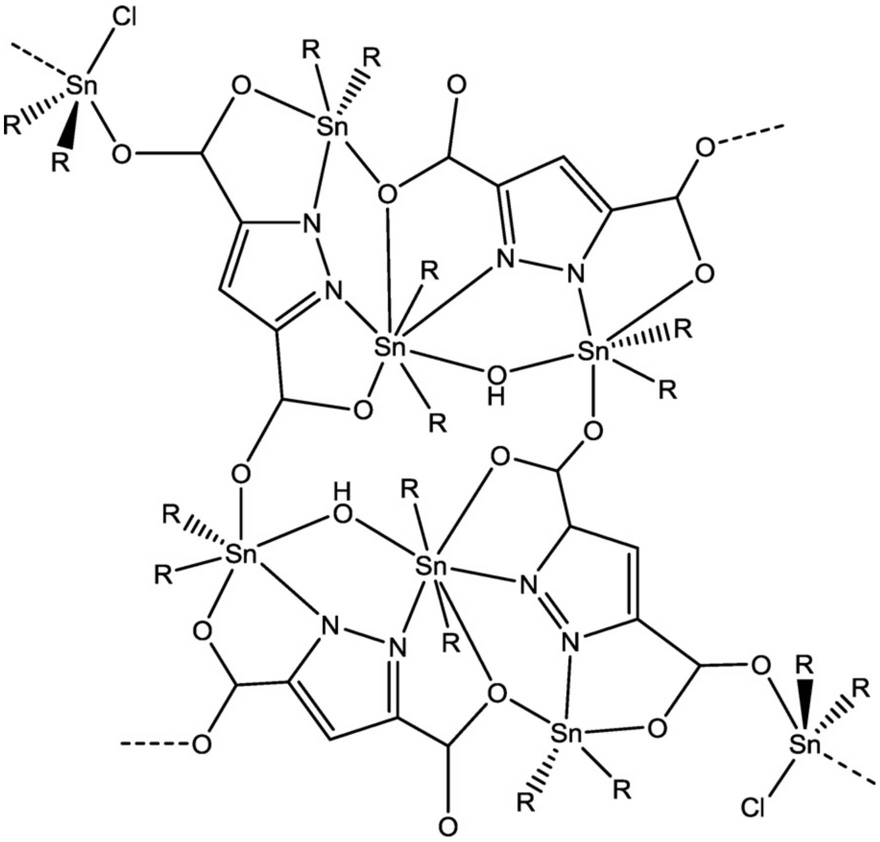

Fig. 30. Repeating unit of a tin pyrazine dicarboxylate network complex [80].

at the centre of the cavity via hydrogen bonding. The upward-centre directing carbonyls allow even large complexes such as the Na^+ complex to be captured (Fig. 36) [42]. The shorter 3-pyridineformate ligands necessarily bring the metal centres closer together and hence steric crowding would prevent *exo*-hosting like that seen in the pyridineacetate complex in Fig. 34 to occur even if the carbonyls are directed away from the ring [42].

Apart from molecular rings, non-ring complexes may also function as hosts for acidic guests under favorable conditions, for example in the presence of stereo-directing donor groups. This is witnessed in mononuclear $[Pd(pic)(dppf)]^+$ in which the basic carbonyl group is directed away from the core of the molecule, such that the complex can effectively function as metalloligand without significant steric inhibition. This carbonyl is sufficiently basic to coordinate to Ag(I) in the $[Ag(OTf)_2]^-$ guest ion (Fig. 3). The Pt(II) analogue of this assembly however does not show such ligating ability [42]. This form of complexation resembles more the usual form of complexation and less in typical host–guest adduct formation which relies on *endo* or lattice encapsulation. Nevertheless, the examples given in Figs. 3 and 34 provide examples how large guests can be exocyclically bound.

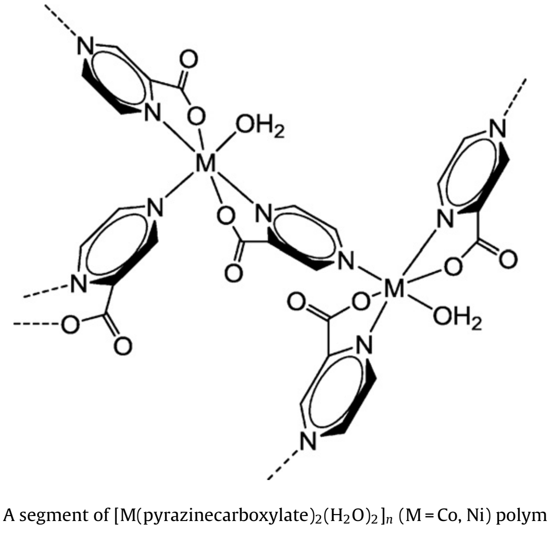

Fig. 31. A segment of $[M(pyrazinecarboxylate)_2(H_2O)_2]_n$ (M = Co, Ni) polymer.

Other than discrete molecular hosts, network assemblies of pyridinecarboxylates can also function as multi-site hosts as found in many MOF systems. Severin et al. recently reported a Rh(III) and Ir(III) pyridine-3,5-dicarboxylate network that contains triangular pore spaces with converging carbonyls for hosting of K^+ ions (Fig. 37) [105]. The *meta*-substituted carboxylates help to create a triangular cavity that is somewhat similar to that in $[Pt(nic)(PPh_3)_2]_3{}^{3+}$ (Fig. 36). The converging carbonyls are also responsible for the capture of metal ions. The conjunctive use of dicarboxylates and metals with more than two accepting sites allow for network propagation.

In the absence of a multi-donor site spacer such as pyridine dicarboxylate, extensive hydrogen bonding in the pyridinecarboxylic acid ligands may also promote 3D network formation such as that in $[Ni(isonic)(isonicH)(H_2O)_3]_n{}^{n+}$ (Fig. 38) [36]. Without robust ligands such as phosphines to block certain coordination sites, use of an octahedral metal can promote network propagation in the 3D space which can accommodate triflate anions.

9. Other applications

Other pyridinecarboxylate complexes such as $Tb_2(isonic)_6(H_2O)_4$ show luminescent activities [106]. Pyrimidine dicarboxylate and pyridine dicarboxylate networks of Cu(II), Co(II),

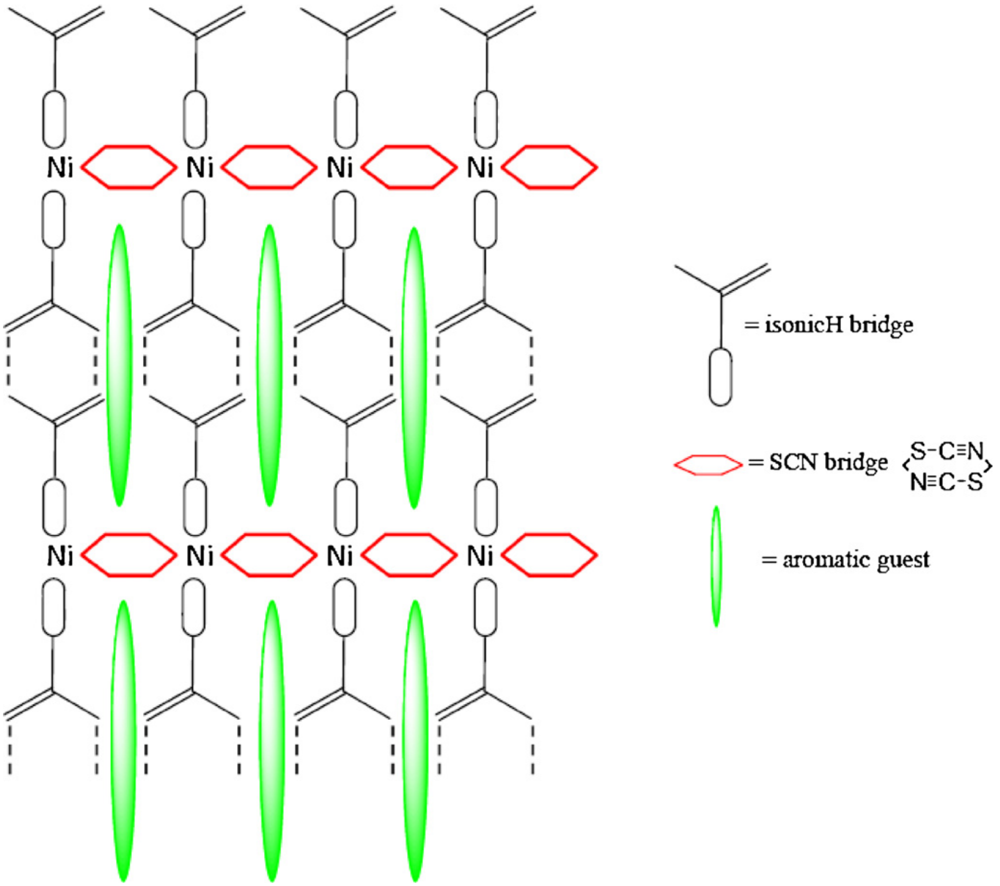

Fig. 32. Schematic diagram of $[Ni(SCN)_2(isonicH)_2]_\infty$ with encapsulated guests in cavities [67].

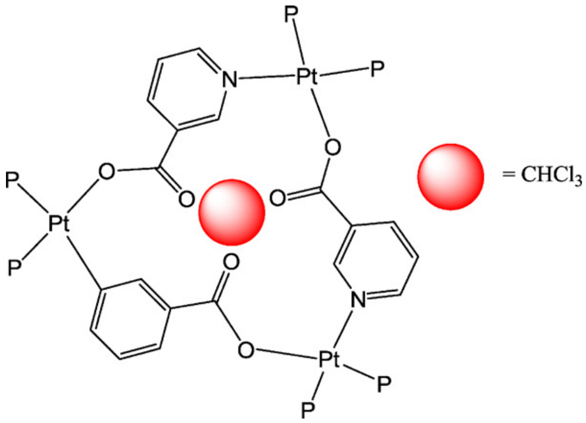

Fig. 33. $[Pt(nic)(dppf)]_3^{3+}$ showing an encapsulated $CHCl_3$ which is hydrogen-bonded to carboxyl oxygen atoms [42]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

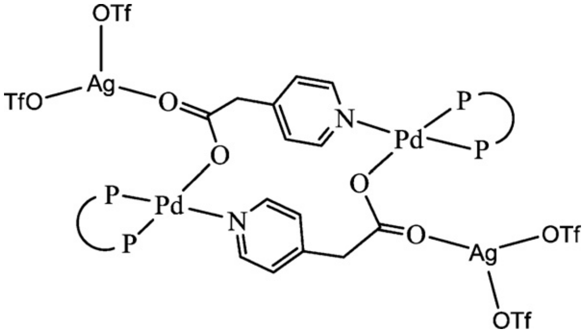

Fig. 34. $[Pd_2(PyOAc)_2(dppf)_2]^{2+}$ ring with a $[Ag(OTf)_2]^-$ guest on each carbonyl [39].

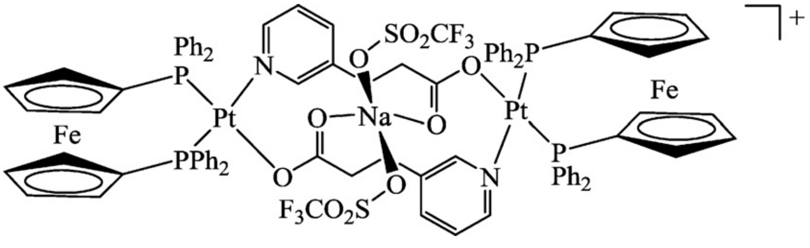

Fig. 35. $[Pt_2(PyPrO_2)_2(dppf)_2]^{2+}$ ring with a $[Na(OTf)_2]^-$ guest captured at the centre of ring cavity [44].

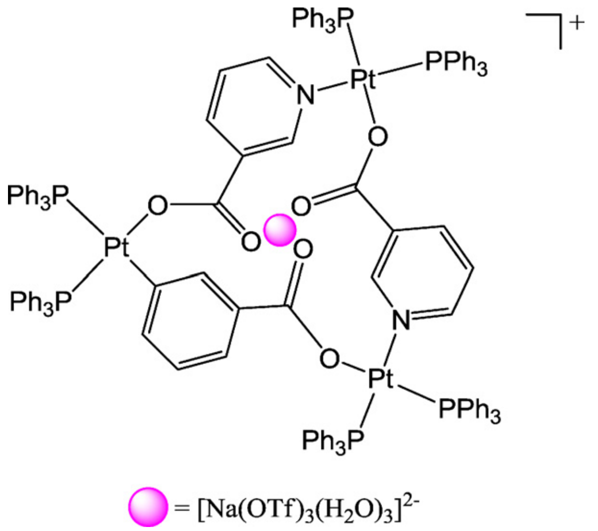

Fig. 36. Trinuclear $[Pt_3(nic)_3(PPh_3)_6]^{3+}$ complex with a $[Na(OTf)_3(H_2O)_3]^{2-}$ complex ion captured at centre [42]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

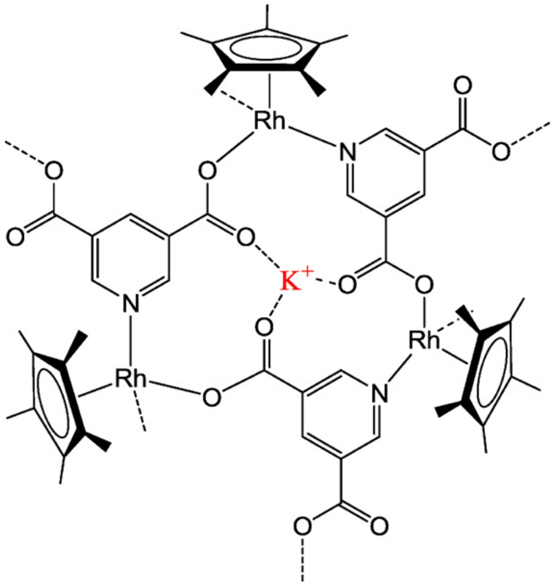

Fig. 37. $[(C_5Me_5)_3Rh_3(pyridine\text{-}3,5\text{-}dicarboxylate)_3]_n$ with K^+ guest [105]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

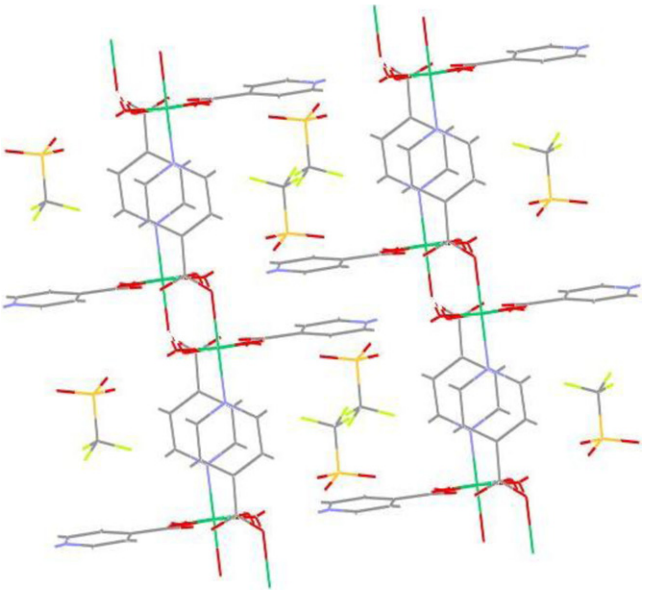

Fig. 38. Wireframe packing diagram for $[Ni(isonic)(isonicH)(H_2O)_3]_n(OTf)_n$, showing two layers of network with encapsulated triflate anions in between the layers [36].

Ni(II) and Fe(II) have also been shown to be magnetically active [12,65,97,107]. The robust bipyridine-tetracarboxylate networks $\{[Zn_2(L)]{\cdot}4H_2O\}$ exhibit permanent porosity even upon solvent removal. The frameworks also display gas uptake properties such as hydrogen and methane (1 wt% H_2 at 4 bar and 77 K, 3 wt% CH_4 at 9 bar 298 K) [99,100]. Cu(II) pyridine-2,3-dicarboxylate network exhibits preferential CO_2 uptake over other gases such as O_2 and N_2 [11,108], which paves the way for usage of pyridinecarboxylate MOFs for atmospheric CO_2 removal.

Catalytic activities have also been reported in some N,O-donor complexes. Oxidation of methylquinolines using Pd(II) pyridinedicarboxylic acid complexes have been reported [108]. The pyridine tartrate network complex of Zn(II) also actively catalyse enantioselective transesterification reactions. Treatment of 2,4-dinitroacetate with the Zn pyridine tartrate catalyst and a large excess of racemic 1-phenyl-2-propanol resulted in the formation of corresponding ester with 8% enantiomeric excess. Treatment of the same ester with ethanol in carbon tetrachloride at 27 °C resulted in the formation of ethyl acetate in 77% yield (Fig. 39) [82]. The Cu(II) pyrazinedicarboxylate porous coordination polymer by Kitagawa et al. contains nano channels that can be used for polymerization of mono-substituted acetylenes with high E-selectivity [109] in the olefin units of the resultant poly(acetylene).

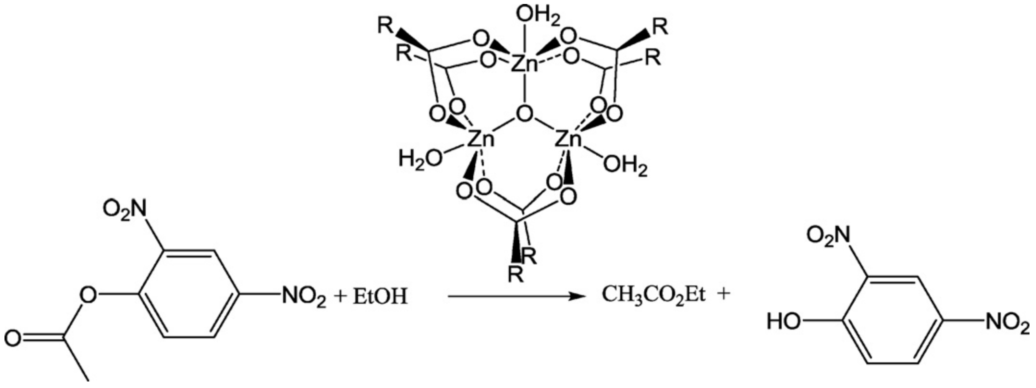

Fig. 39. Transesterification reaction of 2,4-dinitroactate with Zn pyridinetartrate network complex [82] (only the secondary building block of network is shown).

10. Concluding remarks

The use of pyridinecarboxylates in molecular complexation demonstrates the synthetic utility and value of hetero-donating spacers in supramolecular and network assemblies. The different donor groups show some, albeit limited, metal selectivity and specificity. The ease of adjustment of the spacer length and relative orientations of the donor sites however provides a powerful means of access to a myriad of framework constructions. This fuels the development of pyridine carboxylates as stereo-directing spacers in functional MOF's. The molecular and ionic clathrating abilities of these materials have been demonstrated. The next challenge is to develop a reliable method to shape the supramolecular framework, control its porosity and direct its carboxyl pendants through chemical manipulations of the spacers. Such success would lay the foundation for these materials to be applied in challenging areas such as gas storage, pollutant scavengers, chemical separation, toxin sponge, etc. Another challenge is the development of hetero- and intermetallic polymers and network materials. Most of the supramolecular and MOF constructs are based on homometallic systems. The mixed-metal pyridinecarboxylate complexes described herein have provided a model for these constructions. Emergence of such materials would benefit the development of site-selective catalysis and hybrid photo-materials. This review also gives a glimpse on the use of higher donating spacers such as pyridine dicarboxylates to raise the network connectivity and conductivity. This would provide an impetus in the development of novel molecular magnets and electronics.

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