# Lanthanide–transition metal coordination polymers based on multiple N- and O-donor ligands

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Lanthanide-transition metal (Ln–M) coordination polymers have attracted extensive interest because they exhibit novel physical properties originating from the interactions between distinct metal ions. This review mainly describes our recent work in the design of Ln–M coordination polymers through the assembly of different metal ions and organic ligands, especially the ligands with multiple N- and O-donor atoms. Many of these crystalline Ln–M materials exhibit intriguing structural motifs and interesting magnetic properties.

## Introduction

The design and construction of coordination polymers with unique structural motifs and tunable physical properties has attracted extensive interest in supramolecular chemistry and

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materials chemistry.[1–3] A number of desired architectures have been generated by design and allowing the assembly of molecular or ionic components through supramolecular interactions. Such interactions include coordination bonds between ligands and metal centers, Coulombic attractions and repulsions between ions, van der Waals forces, π–π contacts and hydrogen bonding. These different interactions offer a practical way to synthesize target materials, from building blocks to superstructures. A judicious choice of the supramolecular links allows the bottom-up approach to extended networks (coordination polymers) through the connections between polydentate ligands and metal centers. The study in this field has provided numerous examples of rationally designed one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) polymeric structures possessing specific pore sizes and types through the assembly of molecular building units.[4] Many Ln–M coordination polymers have been reported,[5] which possess not only interesting structural motifs but also significant properties, such as chemical sensor functions,[6] fluorescence[7] and catalysis.[8] Their magnetic properties have also attracted attention owing to the unique 3d–4f magnetic exchange interactions.[9–12] In addition, the high coordination number of Ln(III) ions renders structural flexibility and may increase thermal stability, which are critical to the practical application of Ln–M coordination polymers.

Recently, we have begun to explore the syntheses and characterization of Ln–M coordination polymers by using ligands with mixed N- and O-donor atoms. Systematic studies have been carried out on the assembly of tailored ligands and lanthanide and transition metal ions under different reaction conditions. By employing the hydrothermal method, a series of Ln–M coordination polymers with fascinating structures and unusual magnetic properties has been successfully synthesized.
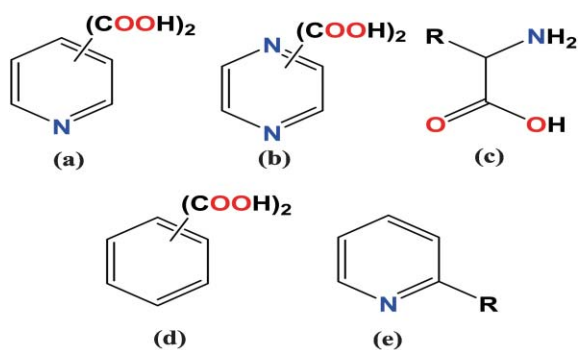
### Ligands with different donor atoms

To generate target coordination polymers by design, a judicious choice of ligands provides a way of controlling supramolecular interactions. In general, the ligands with certain features, such as rigidity and symmetry, are suitable for obtaining coordination polymers. The recognition of donor atoms by metal ions provides a potential approach to the

preparation of heterometallic coordination polymers. It is well known that lanthanide ions have high affinity and prefer to bind to hard donor atoms, whereas many later d-block transition metal ions prefer to be coordinated by soft donor atoms. To combine lanthanide and transitional metal ions in lattice packing, multidentate ligands containing $N$- and $O$-donor atoms are usually employed in the construction of Ln–M coordination polymers (Scheme 1). Thus, pyridine carboxylate ligands, such as pyridine-2,5-dicarboxylic acid (2,5-H$_2$pydc) and pyrazine-2,4-dicarboxylic acid (2,4-H$_2$pzdc) were considered. These types of ligands possess several interesting characteristics: (a) the carboxylate groups may be completely or partially deprotonated, resulting in rich coordination modes; (b) the pyridine rings provide not only $N$-donor atoms but also rigidity, which assists in the generation of crystalline products; (c) the carboxylate groups can rotate in a limited way, so it may connect metal ions in different directions. Thinking along these lines, we pioneered the study of the assembly of the suitable pyridine carboxylate ligands, lanthanide and transition metal ions, and isolated successfully a series of Ln–M coordination polymers with intriguing structural motifs and magnetic properties.

Amino acids have both $O$- and $N$-donor atoms (carboxylate and amino groups). In comparison with pyridine carboxylate ligands, amino acids have more flexibility and less steric hindrance. The study of the complexes with amino acids, which are among the most important biological ligands, has contributed to the understanding of the biological nature. Exploring the assembly of amino acids, such as proline and glycine, with lanthanide and transition metal ions, the results show that amino acids exhibit a good ability to act as bridge or chelating ligands for formation of the Ln–M coordination polymers.[13] Thus, the introducing amino acids into the lanthanide and transition metal reaction system is expected to generate Ln–M coordination polymers with interesting structures, for instance, heteronuclear clusters as building blocks in the discrete or the polymeric state.

If mixed ligands containing $N$- or $O$-donor atoms are used in the assembly process, the distinctive recognition of lanthanide and transition metal ions by hybrid donor atoms separately is expected to result in coordination polymers with novel, interesting structures. Thus, isophthalate (ip) as the angular carboxylate ligand and 2,2′-bipyridine (bpy) as a pyridine-like ligand were used for the preparation of Ln–M coordination polymers. As expected, a series of Ln–M coordination polymers with fascinating structures and magnetic properties has been obtained.

## Discrete heterometallic clusters

Recently, we have focused on the syntheses of high-nuclear Ln–M clusters with amino acids as ligands, and a series of lanthanide–copper polynuclear clusters had been reported.[13–18] For instance, if glycine (or L-alanine) and acetic acid are used together in the assembly process, discrete Ln–M complexes consisting of thirty-nuclear cluster cations [Sm$_6$Cu$_{24}$($\mu_3$-OH)$_{30}$(Gly)$_{12}$(Ac)$_{12}$(ClO$_4$)(H$_2$O)$_{16}$]·(ClO$_4$)$_9$·(OH)$_2$·(H$_2$O)$_{31}$ (**1**) and [Ln$_6$Cu$_{24}$($\mu_3$-OH)$_{30}$(Ala)$_{12}$(Ac)$_6$(ClO$_4$)(H$_2$O)$_{12}$]·(ClO$_4$)$_{10}$·(OH)$_7$·(H$_2$O)$_{34}$ (Ln = Tb **2**, Gd **3**, Dy **4**, Sm **5**, and La **6**) can be obtained.[15] All of these clusters have a Ln$_6$Cu$_{24}$ octahedral skeleton. In **1**, six Sm(III) ions with an average distance of 7 Å are located at the vertices of the octahedron, and the twelve inner Cu(II) ions are located at the midpoints of the octahedral edges (Fig. 1). Each cation also has twelve outer Cu(II) ions. Each Sm(III) ion interconnects two outer Cu(II) ions by virtue of one outer $\mu_3$-OH$^-$ and two glycinato ligands. Sm(III) ions are nine-coordinated in a monocapped square antiprismatic geometry. The inner Cu(II) ions are six-coordinated in a distorted octahedral geometry. With regard to outer Cu(II) ions, two are four-coordinated in a square–planar geometry and the others are five-coordinated in square-pyramidal geometries. Glycinato ligands chelate two Cu ions and one Sm ion through the carboxylate and amino groups. Acetate ligands adopt both bidentate and monodentate coordination modes. The interesting structural feature of the cluster is that an encapsulated distorted ClO$_4^-$ anion lies at the center of the octahedron. Although a detailed study is still needed, the encapsulated ClO$_4^-$ anion seems to act as a template, which directs the formation of the novel high-nuclear cluster structure. Owing to rich coordination modes and



**Scheme 1** Selected ligands for the preparation of Ln–M coordination polymers.
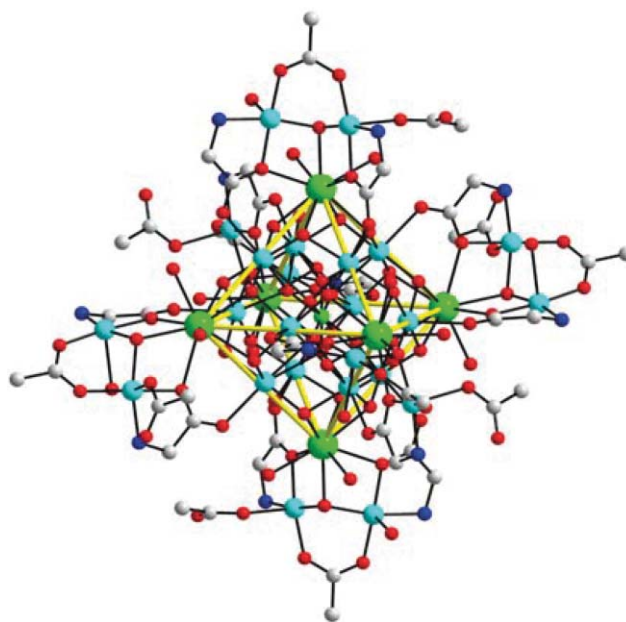


**Fig. 1** The octahedral skeleton of Sm$_6$Cu$_{24}$ cluster in **1** (Sm ions: green balls; Cu ions: cyan balls; virtual edges: yellow lines).

different donor atoms, amino acid ligands can engage numerous Sm(III) and Cu(II) ions into one system, resulting in a high-nuclear cluster. Compounds 2–6 are isostructural and have almost the same $Ln_6Cu_{24}$ cluster as that of 1 except that L-alanine replaces glycinato and only six bidentate acetate ligands are involved (Fig. 2). The acetate ligand only has a carboxylate group with coordination sites, which cannot bridge adjacent large high-nuclear clusters, and acts as a terminal ligand. In addition, the coordination sites of all the amino acid ligands in a cluster are completely occupied, resulting in no possibility of extension. Thus, the Ln–M clusters in 1–6 are discrete leading to a discontinuous packing structure (Fig. 3).

Heterometallic Ln–M complexes have the nature of magnetic exchange interactions between 3d and 4f metal ions, and are good models to investigate the 3d–4f magnetic interactions. In addition, high coordination number of lanthanide ions renders structural flexibility and may increase the thermodynamic stability. Thus, Ln–M coordination polymers possess practical importance in the design and development of intriguing magnetic materials.[19,20] Magnetic properties of these systems possessing 3d–4f metal ion interactions were investigated. For 3, $Gd_6Cu_{24}(\mu_3\text{-}OH)_{30}$ core is fascinating, and the magnetic data can be interpreted on the basis of weak ferromagnetic Gd–Cu interactions ($\theta = 0.59$ K).

### One dimensional chain structures

There are only few examples of Ln–M coordination polymers with one dimensional chain structures reported.[21] The
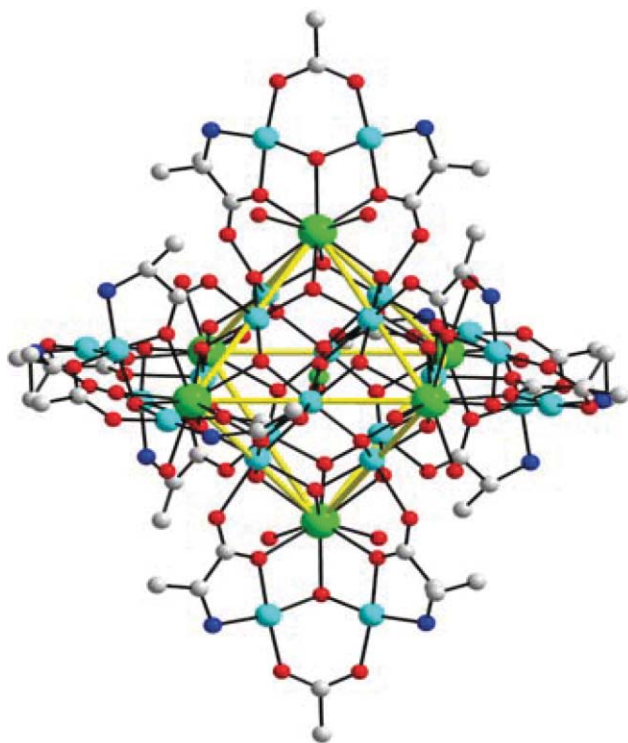


**Fig. 2** The octahedral skeleton of $Ln_6Cu_{24}$ (Ln = Tb, Gd, Dy, Sm, La) cluster in 2–6 (Ln ions: green balls; Cu ions: cyan balls; virtual edges: yellow lines).
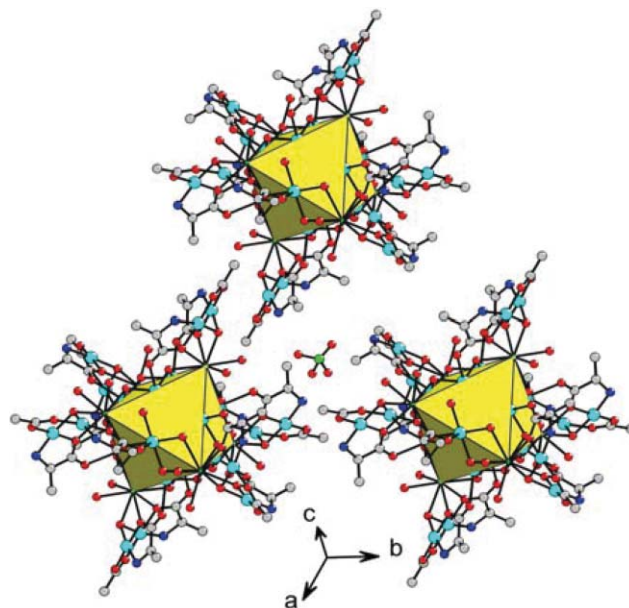


**Fig. 3** Packing structure of 2 (octahedral skeleton: yellow polyhedrons; Cu ions: cyan balls).

hydrothermal reactions of lanthanide oxide, pyridine-2,5-dicarboxylic acid (2,5-$H_2$pydc), and Cu(II) oxide or Cu(II) salts generates several Ln–Cu coordination polymers. It is observed that different Cu(II) salts and crystal growth conditions remarkably influence the structure of the final product. When copper acetate is the precursor, Cu(II) ions are readily coordinated to nitrogen atoms of 2,5-pydc ligands. Thus, the hydrothermal reactions of $Ln_2O_3$ (Ln = Er, Gd), Cu(OAc)$_2$·2H$_2$O and H$_2$-2,5-pydc in a molar ratio of 1 : 2 : 4 gave rise to two isostructural Ln–M coordination polymers with high a Cu–Ln ratio (3 : 2): [{Er$_2$Cu$_3$(2,5-pydc)$_6$(H$_2$O)$_{12}$}·4H$_2$O]$_n$ (7) and [{Gd$_2$Cu$_3$(2,5-pydc)$_6$(H$_2$O)$_{12}$}· 4H$_2$O]$_n$ (8).[21] Compound 7 displays a one-dimensional (1D) chain structure. The chain consists of two building blocks, [Er$_2$Cu$_2$(2,5-pydc)$_4$(H$_2$O)$_{12}$] and [Cu(2,5-pydc)$_2$], which are linked with each other through Er–O bonds. Each Er(III) ion is coordinated by eight oxygen atoms in a hexagonal bipyramidal geometry, as shown in Fig. 4. The chain can also be viewed as two building blocks [Cu(2,5-pydc)$_2$] and [Cu(2,5-pydc)$_2$(H$_2$O)] connected by Er(III) centers, in which each Er(III) center connects one [Cu(2,5-pydc)$_2$] and two [Cu(2,5-pydc)$_2$(H$_2$O)] units. The 1D chains are linked by hydrogen bonding to form layer structures which are further stacked by hydrogen bonding to form a three dimensional (3D) supramolecular architecture.

### Two dimensional layer structures

It is interesting that another product [Gd$_2$Cu$_2$(2,5-pydc)$_4$-(H$_2$O)$_8$·Cu(2,5-pydc)$_2$·12H$_2$O]$_n$ (9) with a different structure can be obtained following the same synthetic procedure for 8. Compound 9 has a sandwich-like structure consisting of infinite layered cation [Gd$_2$Cu$_2$(2,5-pydc)$_4$(H$_2$O)$_8$]$^{2+}$ and discrete anion [Cu(2,5-pydc)$_2$]$^{2-}$ and water molecules (Fig. 5).[21] The structure of the cation can be viewed as
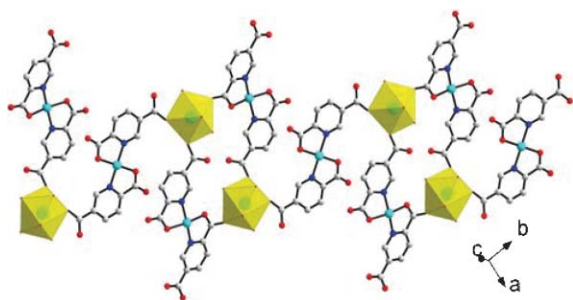
**Fig. 4** 1-D chain structure of **7** (Er ions: yellow polyhedrons; Cu ions: cyan balls).

[Cu(2,5-pydc)$_2$] units connected by Gd(III) ions, where the Cu(II) ion is four-coordinated in a distorted square planar geometry and the Gd(III) ion is eight-coordinated in a hexagonal bipyramidal geometry, leading to a 2-D cation layer. The discrete [Cu(2,5-pydc)$_2$]$^{2-}$ anions are located between adjacent cation layers to form sandwich-like structures, which are further consolidated by hydrogen bonds formed between water oxygen atoms and uncoordinated pydc oxygen atoms, resulting in a 3D supramolecular architecture (Fig. 5).

The hydrothermal reaction of Gd$_2$O$_3$, AgNO$_3$, H$_2$-2,5-pydc in a molar ratio of 1 : 4 : 5 yielded light-yellow crystals of coordination polymer [Gd$_2$Ag$_2$(2,5-pydc)$_4$(H$_2$O)$_4$]$_n$ (**10**). The crystallographic analysis revealed that the structure of **10** consists of 2D layers.[22] Each Gd(III) ion is coordinated by two nitrogen and six oxygen atoms in dodecahedral geometry, while the Ag(I) ion is coordinated by one chelate and two monodentate carboxylate groups in a nearly T-shaped fashion. 2,5-pydc ligands act as three-connectors to link Gd(III) and Ag(I) ions, resulting in a 2D layer containing rectangular cavities (Fig. 6). The 2D layers are further stacked through both hydrogen bonds and π–π stacking interactions to form a 3D supramolecular architecture.

In the absence of bridging ligands such as 2,5-H$_2$pydc, the auxiliary ligand acetate can meet the demand of lanthanide ions for a high coordination number, but can only act as terminal resulting isolated structure.[15] Thus, the assembly
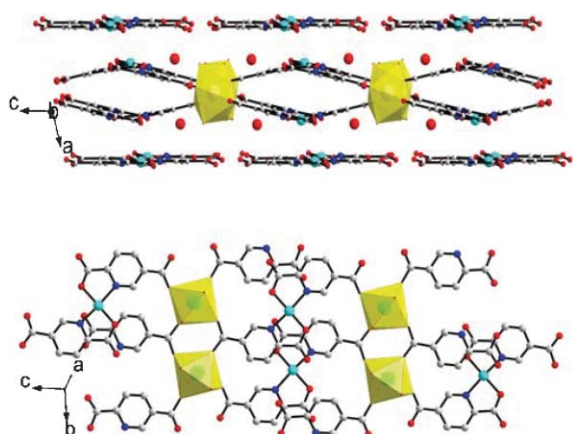


**Fig. 5** Packing structure (top) of **9** and layered cation (bottom) (Gd ions: yellow polyhedrons; Cu ions: cyan balls).
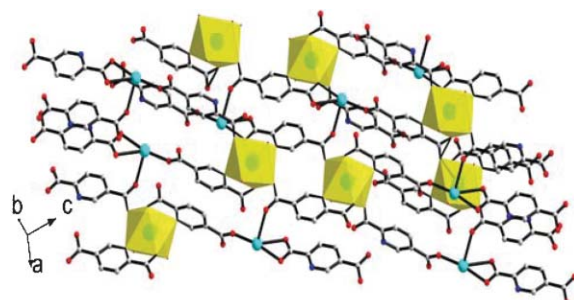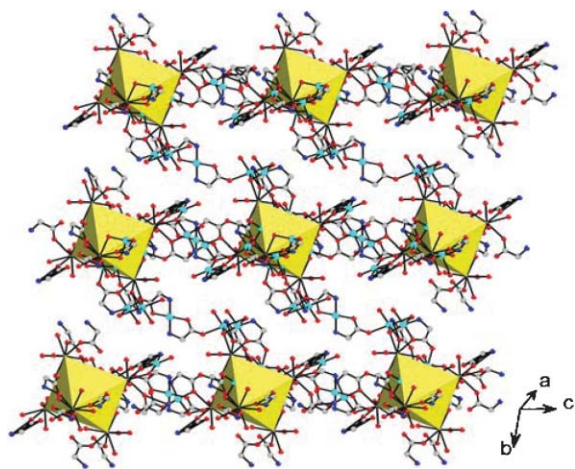


**Fig. 6** View of the 2D layer in **10** (Gd ions: yellow polyhedrons; Ag ions: cyan balls).

system consisting of only amino acid ligands, lanthanide and transition metal ions are explored. Three isostructural 2D Ln–M coordination polymers, Na$_2$[Ln$_6$Cu$_{27}$(Gly)$_{20}$(μ$_3$-OH)$_{30}$-(H$_2$O)$_{22}$(ClO$_4$)](ClO$_4$)$_{23}$(H$_2$O)$_{28}$ (Ln = Er **11**, Eu **12**, Gd **13**, gly = glycine), were isolated successfully.[23] The most striking structural feature of compounds **11**–**13** is the presence of high-nuclear heterometallic Ln$_6$Cu$_{24}$ clusters acting as nodes. Taking compound **11** as a typical example, the Er$_6$Cu$_{24}$ octahedral-like cluster cation can also be viewed as a huge Er$_6$Cu$_{12}$ octahedron (inner core) with pseudocubic $O_h$ symmetry and twelve outer Cu(II) ions (Fig. 7), which is very similar to that of **1**. There is also an encapsulated ClO$_4^-$ anion at the centre of the Er$_6$Cu$_{12}$ octahedron. The template role of this anion is further confirmed by the unsuccessful attempt to synthesise analogous structures with Cl$^-$ as the anion. Owing to the lack of acetate terminals, outer Cu(II) ions have unoccupied coordination sites, which are made use of by Gly ligands to link the discrete clusters. In consequence, four Er$_6$Cu$_{24}$ nodes are connected through six *trans*-Cu(Gly)$_2$ bridges to form a grid unit, which is extended through edge-sharing resulting in a 2D coordination layer (Fig. 8).
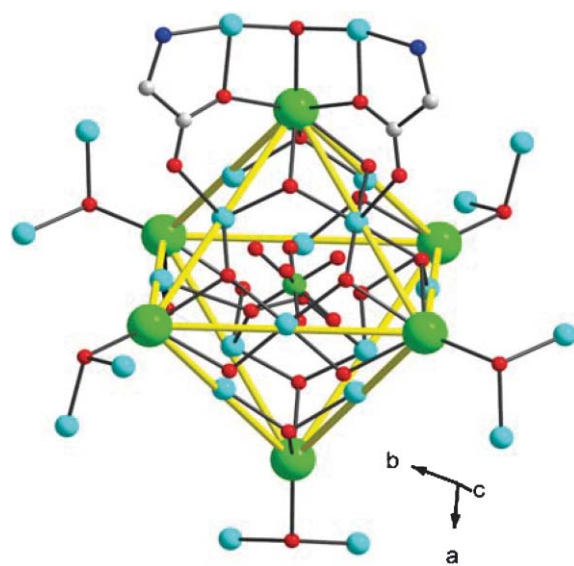


**Fig. 7** The metal framework of the Er$_6$Cu$_{24}$ node in **11**, showing Er ions (large green balls), Cu ions (middle cyan balls) and virtual edges (yellow lines).
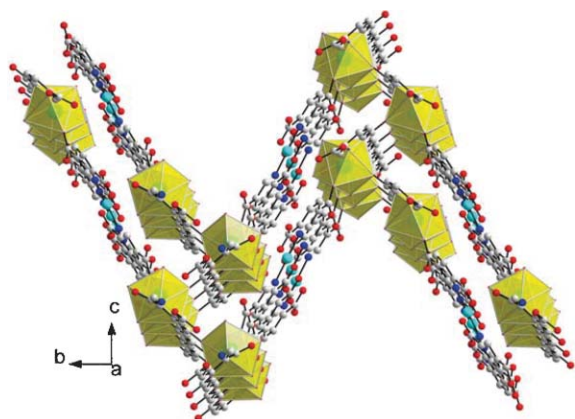
**Fig. 8** View of the 2D layer in **11–13**. (Ln$_6$Cu$_{24}$ node: yellow polyhedron; Cu ion: cyan ball).

### Three dimensional network structures

If CuO was used as precursor in the similar synthetic procedure of **7**, the reaction rate of CuO may be comparable with that of Ln$_2$O$_3$. Consequently, *N*-donor atoms of 2,5-pydc ligands are bound simultaneously by Ln(III) and Cu(II) ions leading to three isostructural 3D coordination polymers with low Cu–Ln ratio (1 : 2): [{Ln$_4$Cu$_2$(2,5-pydc)$_8$(H$_2$O)$_{12}$}·4H$_2$O]$_n$ (Ln = Sm **14**, Gd **15**, Er **16**). The structure of **14** consists of a 3D network with [Sm$_4$Cu$_2$(2,5-pydc)$_8$(H$_2$O)$_{12}$] building blocks, which are linked head to tail resulting in a infinite zigzag chain.[22,24] The neighbouring chains are further connected to generate the 2D wave-like units (Fig. 9), which are further connected with each other by 2,5-pydc ligands to form the final 3D networks. The 2D wave-like unit can also be viewed as Sm–Cu ladders, in which the rungs are formed by [Cu(2,5-pydc)$_2$] species and the sidepieces by Sm(III) chains. The sidepieces of the neighboring ladders are linked by pydc *via* Sm–O bonds to yield the wave-like unit. The Er–O and the Er–N bonds of **16** are slightly shorter than those of **14** and **15** owing to lanthanide contraction.

When the precursor was pyridine-2,4-dicarboxylic acid (2,4-H$_2$pydc) instead of pyridine-2,5-dicarboxylic acid, the similar

synthetic procedure with that of **14** gave rise to two 3D coordination polymers: [Gd$_2$Cu(2,4-pydc)$_4$(H$_2$O)$_6$]$_n$ (**17**) and [Sm$_2$Cu$_3$(2,4-pydc)$_6$(H$_2$O)$_6$]$_n$ (**18**).[25] Compound **17** has a 3D network structure (Fig. 10), in which each Gd(III) ion is seven-coordinated in a pentagonal bipyramidal geometry. Each Cu(II) ion is chelated by adjacent N and O atoms from two pydc ligands in a square planar geometry. The structure comprises two building blocks [Gd(2,4-pydc)$_3$(H$_2$O)] and [Cu(2,4-pydc)$_2$]. Two adjacent [Gd(2,4-pydc)$_3$(H$_2$O)] units are linked together through sharing pydc ligands to form a 2D wave-like layer. The 2D layers are further connected Gd-O bonds to form the final 3D network. Compound **18** also has a 3D network structure. Each Sm(III) ion is coordinated by eight oxygen atoms in a dodecahedral geometry. One Cu(II) ion is five-coordinated in a slightly distorted square pyramidal geometry. While the other Cu(II) is four-coordinated in an octahedral geometry (Fig. 11), the structure of **18** can also be viewed as consisting of linear trinuclear Cu$_3$(2,4-pydc)$_6$ units and Sm(III) linkers. Every two Cu$_3$ units are linked head to tail through the bonds between Cu ion and 2,4-pydc O atoms resulting in a linear chain, which are further connected by
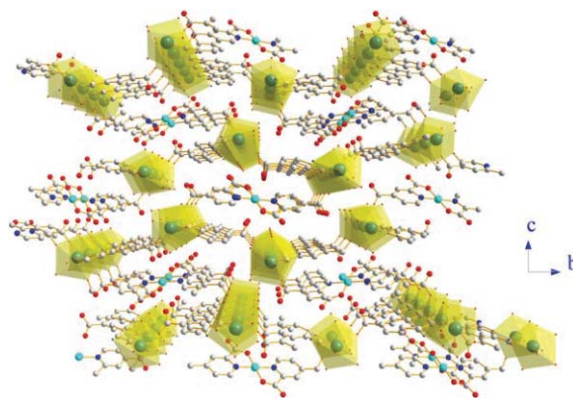


**Fig. 10** View of 3D network in **17** (Gd ions: yellow polyhedrons; Cu ions: cyan balls).



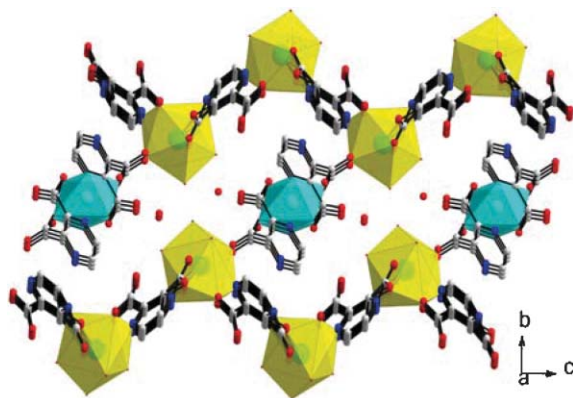**Fig. 9** Wave-like structure of **14** (Sm ions: yellow polyhedrons; Cu ions: cyan balls).
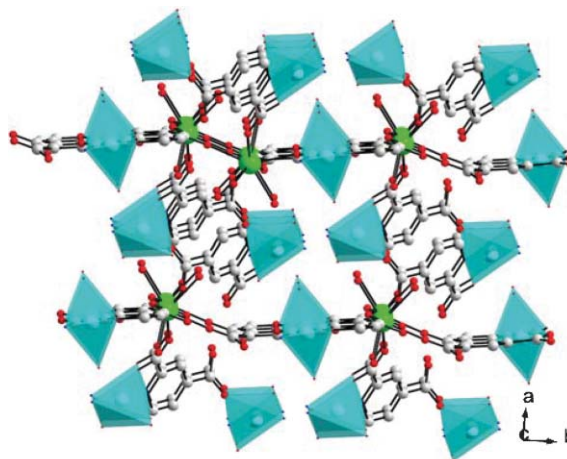


**Fig. 11** View of 3D network in **18**, showing different coordination polyhedra of Cu ions (Cu ions: cyan polyhedron; Sm ions: green balls).

Sm(III) linkers through the Sm–O(2,4-pydc) bonds to form the final 3D network.

To obtain more diverse Ln–M coordination polymers, the assembly of analogous ligand pyrazine-2,3-dicarboxylic acid (2,3-$H_2$pzdc) with metal ions was explored. The hydrothermal reactions of $Ln_2O_3$, $Zn(NO_3)_2 \cdot 6H_2O$, $H_2$pzdc and $H_2O$ resulted in three isostructural coordination polymers $[Ln_2Zn(2,3\text{-pzdc})_4(H_2O)_6 \cdot 2H_2O]_n$ (Ln = Gd **19**, Nd **20**, Sm **21**).[26] The structures of **19–21** possess 3D brick-like networks containing $Ln_2Zn(2,3\text{-pzdc})_4(H_2O)_6$ building blocks. Each Ln(III) ion is coordinated by seven oxygen and two nitrogen atoms in a tricapped trigonal prismatic geometry. The zinc(II) ions are bonded by four oxygen and two nitrogen atoms in an octahedral geometry. The above building blocks are further extended through polydentate 2,3-pzdc ligands to form a zigzag chain. 2,3-pzdc ligands adopt two coordination modes to link Gd(III) ions. One is the chelated mode, which connects the zigzag chains into a 2D layer. The other has a mono-dentate mode, in which the 2D layers are linked into a brick-like 3D network (Fig. 12). Each brick-like channel accommodates two water molecules as guests.

The assembly of amino acids, lanthanide and transition metal ions also gives diverse 3D coordination polymers. When the assembly of amino acids, lanthanide and transition metal ions were carried out, the 3D Ln–M coordination polymers, formulated as $\{[Sm_6Cu_{29}(\mu_3\text{-OH})_{30}(Gly)_{24}(ClO_4)(H_2O)_{22} \cdot (ClO_4)_{14} \cdot (OH)_7 \cdot (H_2O)_{24}\}_n$ (**22**) and $\{[Nd_6Cu_{30}(\mu_3\text{-OH})_{30}(Pro)_{24}(ClO_4)(H_2O)_{21}] \cdot (ClO_4)_{12} \cdot (OH)_{11} \cdot (H_2O)_6\}_n$ (**23**) (Gly = glycine and Pro = L-proline), were isolated.[27] 35-Nuclear complex **22** has a primitive cubic net-like structure and 36-nuclear complex **23** has a face-centred cubic network type structure. Being analogous to **1**, both complexes utilize the $Ln_6Cu_{24}$ octahedral clusters as nodes and *trans*-Cu(amino acid)$_2$ groups as bridges. Each $Sm_6Cu_{24}$ unit in **22** is connected through ten *trans*-Cu(Gly)$_2$ bridges to six neighboring $Sm_6Cu_{24}$ units (being four in **1**), and extends along three dimensionalities resulting in a 3D cubic network. Thus, the quasi-rectangular channels with dimensions of about 7 × 31 Å$^2$ are formed (Fig. 13). When the chiral L-proline was used as a precursor instead of glycine, a 3D coordination polymer **23** in chiral space group $P2_13$ was obtained consequently. In contrast to **22**, each $Nd_6Cu_{24}$ unit is connected to twelve, not six, neighboring $Nd_6Cu_{24}$ units through twelve *trans*-Cu(Pro)$_2$ bridges, resulting in a cubic close packed network (also known as face-centred cubic) in **23**. The steric effect originating from the side chain of L-proline is responsible for the clear difference between the structures of **22** and **23**.

If the oxygen-donor and the nitrogen-donor ligands are introduced separately in reactions with lanthanide and transition metal ions, coordination polymers with more diverse structures are expected to form. Thus, we have also explored the assembly of isophthalate (ip), 2,2′-bipyridine (bpy), lanthanide and transition metal ions. The hydrothermal reaction of $Gd_2O_3$, $Cu(NO_3)_2 \cdot 3H_2O$, $H_2$ip and bpy in a molar ratio of 1 : 2 : 1 : 2 at 170 °C yielded crystals of $[\{Gd_4(ip)_7(H_2O)_2\}\{Cu(bpy)_2\}_2]_n$ (**24**). The structure of **24** consists of charged cages containing two encapsulated $[Cu(bpy)_2]^+$ cations, respectively (Fig. 14).[28] Each Gd(III) ion is eight-coordinated to furnish a dodecahedral geometry. Two independent Gd(III) ions are linked by two μ-oxygen atoms from separate carboxylate groups to form the $Gd_2O_2$ building unit. Eight $Gd_2O_2$ units are linked by ip ligands to generate a
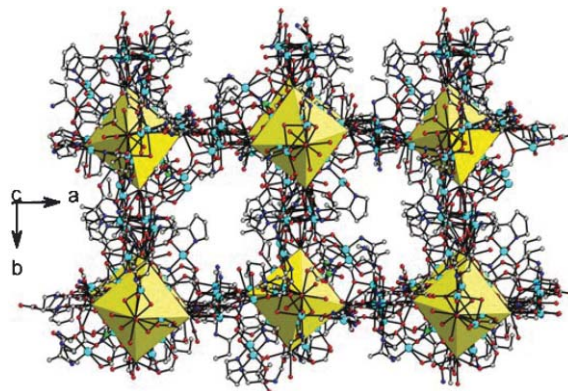


**Fig. 13** View of 3D channel-like network in **22** ($Sm_6Cu_{24}$ node: yellow polyhedron; Cu ion: cyan ball).



**Fig. 12** View of 3D network in **19–21** (Zn ions: cyan polyhedron; Ln ions: yellow polyhedron).
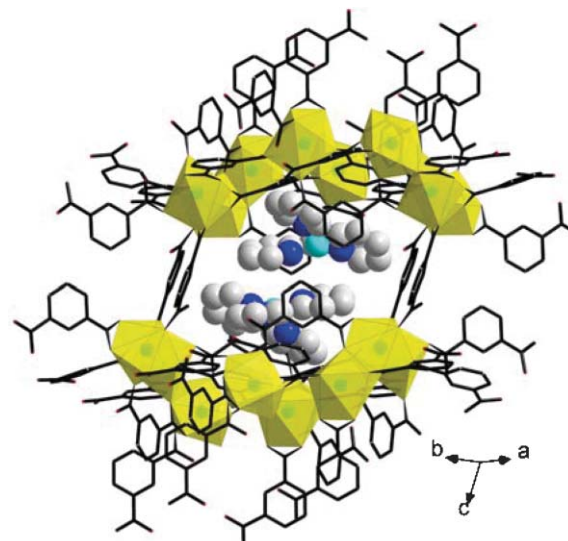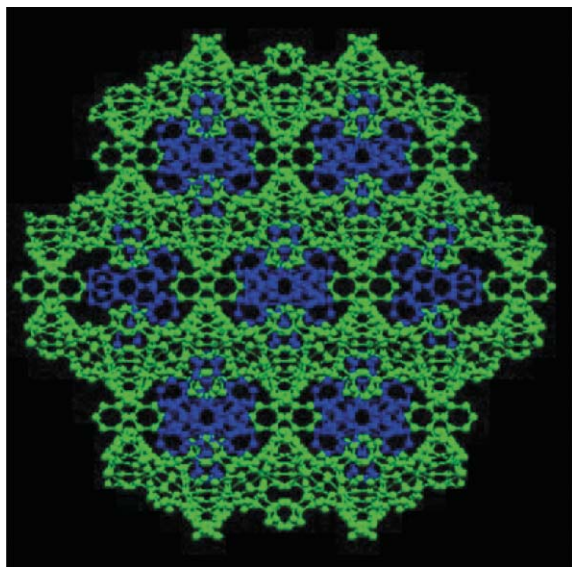


**Fig. 14** View of polymeric cage with two encapsulated $[Cu(bpy)_2]^+$ cations in **24** (Gd ions: yellow polyhedrons; Cu ions: cyan balls).
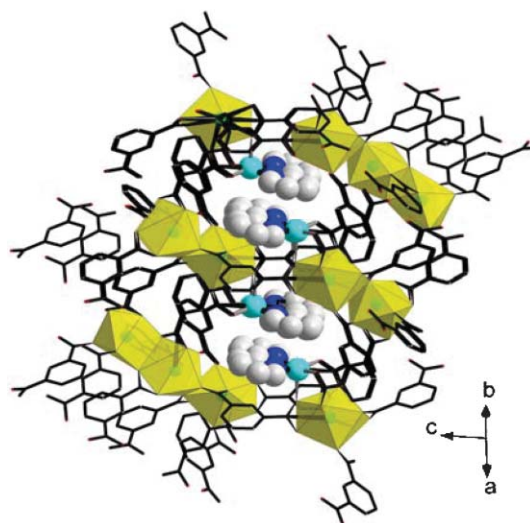
large charged cage (*ca.* 11.5 × 14.9 × 16.5 Å$^3$), in which two [Cu(bpy)$_2$]$^+$ cations in a distorted tetrahedral geometry are trapped as charge-compensating guests. Unusually, two trapped guests (about 11.0 Å diameter) adopt the encapsulated mode because they are larger than the largest effective pore of cage (*ca.* 9.78 Å diameter). The cationic guests are further stabilized by π–π stacking interactions and van der Waals forces. The inclusion cages are connected by ip ligands to form a 3D cavitary framework (Fig. 15). The compound **24** represents the first 3D framework containing multi encapsulated complex cations within a charged cage, which is different from other inclusion complexes.

Clearly, Cu(II) was reduced to Cu(I) by the excessive bpy during the hydrothermal synthesis of **24**. In an attempt to synthesize Gd(III)-Cu(II) analogue by using a smaller amount of bpy, a similar reaction was carried out with the molar ratio of Gd : Cu : H$_2$ip : bpy (1 : 2 : 1 : 1), and yielded successfully [Gd$_3$Cu(ip)$_5$(Hip)(bpy)]$_n$·nH$_2$O (**25**).[28] Each Gd(III) ion is also eight-coordinated in a dodecahedral geometry. Ip ligands link Gd(III) and Cu(II) ions to form a 3D open-framework containing irregular cavities (*ca.* 11.4 × 8.10 Å$^2$). [Cu(bpy)]$^{2+}$ cations are alternately bonded to the inner backbone of the Gd-ip cavity (Fig. 16). The structures of **24** and **25** imply that copper ions and bpy ligands form complex cations first, and then cations serve as structure-directing templates.

For **24**, the observed $\chi_M T$ values of 30.9 cm$^3$ mol$^{-1}$ K at 300 K is slightly smaller than the expected value of 31.5 cm$^3$ mol$^{-1}$ K for a noninteracting Gd(III)$_4$Cu(I)$_2$ complex, implying the presence of global antiferromagnetic interactions. $\chi_M T$ decreases slightly to 29.0 cm$^3$ mol$^{-1}$ K at 12 K, and then dramatically decreases to 25.8 cm$^3$ mol$^{-1}$ K at 5 K (Fig. 17). Considering the structure of **24** and lack of an orbital angular momentum of Gd(III) ion, the spin-coupled dimer model (H = $-J$S$_{Gd}$·S$_{Gd}$) was applied to perform a quantitative analysis, indicating very weak antiferromagnetic interaction between closest Gd(III) ions ($J = -0.09$ cm$^{-1}$). For **25**, the observed



**Fig. 16** View of polymeric cavity with inside-bonded [Cu(bpy)]$^{2+}$ cations in **25** (Gd ions: yellow polyhedrons; Cu ions: cyan balls).

$\chi_M T$ values of 24.2 cm$^3$ mol$^{-1}$ K at 300 K is slightly larger than the expected value of 24.0 cm$^3$ mol$^{-1}$ K for a noninteracting Gd$_3$Cu complex. $\chi_M T$ increases above 50 K and reaches the maximum 24.4 cm$^3$ mol$^{-1}$ K around 10 K, and then decreases to 23.9 cm$^3$mol$^{-1}$K at 5 K (Fig. 17). Considering the separations between adjacent metal ions, a linear octanuclear model containing one spin-coupled Gd(III)–Gd(III) dimer (i), two spin-coupled Gd(III)–Cu(II) dimer (ii) and two uncoupled Gd(III) ions was applied to perform a quantitative analysis leading to $J_i = -0.159$ cm$^{-1}$ and $J_{ii} = 2.07$ cm$^{-1}$. The result indicates that the Gd(III)–Gd(III) interaction is weak antiferromagnetic, while the Gd(III)–Cu(II) interaction is ferromagnetic. The weak ferromagnetic Gd–Cu interactions were observed in **25** which included two spin-coupled Gd–Cu dimer, and a quantitative analysis leaded to a positive coupling constant ($J = 2.07$ cm$^{-1}$).

## Conclusion

In summary, a series of Ln–M coordination polymers have been successfully synthesized based on organic or



**Fig. 15** Charged cavity network (green) and encapsulated complex cations (blue) of **24**.
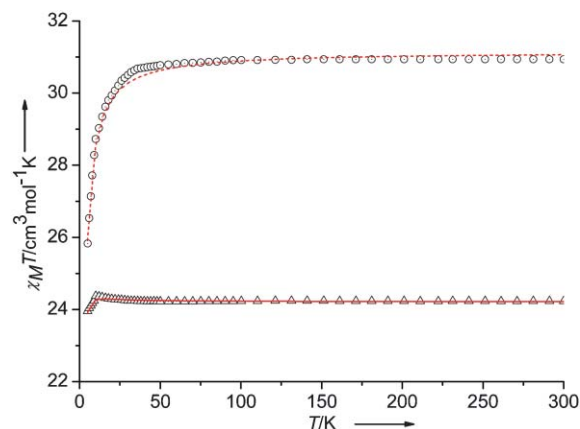


**Fig. 17** $\chi_M T$ *vs.* $T$ curves for **24** (○) and **25** (Δ).

organometallic building blocks, which contain *N*- and/or *O*-donor atoms. There are several factors, such as precursor anion, pH value, molar ratio, reaction medium *etc.*, that play important roles in the final structure and crystal growth of Ln–M coordination polymers. For instance, careful selection of a second solvent (such as acetic acid) will adjust the pH value of reaction mixture, which favors the isolation of the crystalline Ln–M coordination polymers. With regard to pyridine carboxylate ligands, they contain both different donor atoms and the rigid pyridyl ring, which favor the formation of Ln–M coordination polymers with Ln–L–M building units. For amino acids, they are flexible and show less steric hindrance in comparison with pyridine carboxylate ligands. Thus, the introduction of amino acids is expected to give the Ln–M coordination polymers with novel high-nuclear heterometallic clusters as nodes (compounds **1**–**6**, **11**–**13**, **22**, **23**). If polydentate ligands with *N*- or *O*-donor atoms are introduced respectively, the assembly of Ln–M coordination polymers will be more difficult but more interesting comparing with the above two types of ligands (compounds **24**, **25**). In some cases, transition metal ions and one ligand can form complexes first, and then act as structure-directing templates to favor the formation of extended networks with interesting structural motifs. Although we can make use of the concept of crystal engineering to make crystals with a purpose, we cannot generate the target Ln–M coordination polymers freely. The difficulty in obtaining Ln–M coordination polymers may be attributed to the fact that 3d and 4f ions have distinctly different chemical behaviors and the difficulty of seeking a suitable reaction condition allowing mixed *N*- and *O*-donor ligands to coordinate lanthanide and transition metal ions at the same time. This remains a challenge for scientists to better understand and master the significant factors during the assembly process of Ln–M coordination polymers. The Ln–M coordination polymers have rich magnetic properties, but the magnetic interactions involving lanthanide ions is still far from being theoretically interpretable mainly owing to the complications from the orbital contribution.
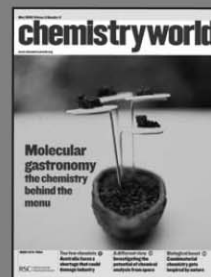
## Acknowledgements

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