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Lanthanide co-ordination frameworks: Opportunities and diversity

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Abstract

Significant successes have been made over recent years in preparing co-ordination framework polymers that show macroscopic material properties, but in the vast majority of cases this has been achieved with *d*-block metal-based systems. Lanthanide co-ordination frameworks also offer attractive properties in terms of their potential applications as luminescent, non-linear optical and porous materials. However, lanthanide-based systems have been far less studied to date than their *d*-block counterparts. One possible reason for this is that the co-ordination spheres of lanthanide cations are more difficult to control and, in the absence of design strategies for lanthanide co-ordination frameworks, it is significantly more difficult to target materials with specific properties. However, this article highlights some of the exciting possibilities that have emerged from the earliest investigations in this field with new topological families of compounds being discovered from relatively simple framework components, including unusual eight, seven and five-connected framework systems. Our own research, as well as others, is leading to a much greater appreciation of the factors that control framework formation and the resultant observed topologies of these polymers. As this understanding develops targeting particular framework types will become more straightforward and the development of designed polyfunctional materials more accessible. Thus, it can be seen that lanthanide co-ordination frameworks have the potential to open up previously unexplored directions for materials chemistry. This article focuses on the underlying concepts for the construction of these enticing and potentially highly important materials.

Keywords: Co-ordination frameworks; Co-ordination polymer; Crystal structure; Lanthanides; Ligands

1. Introduction

The development of co-ordination framework materials is an area of intense current interest [1–3] owing to the need not only to understand how crystalline and ordered materials may be engineered [4], but also to elucidate the underlying processes of self-assembly [5]. As the arrangement of individual components within a material will determine its macroscopic properties, the rational design of multi-dimensional and multi-functional molecular architectures is of great importance for the targeted synthesis of new materials. A range of new co-ordination polymer materials showing solvent-inclusion [6–9], gas adsorption [9–11] characteristics or with electronic [12] or non-linear optical properties [13] having been reported.

The majority of reported networks have been produced using the building-block methodology [14] in which cationic metal centres are linked by linear bridging ligands. Owing to their differing co-ordination connectivities and geometries the choice of metal centre dictates the architecture of the resultant framework materials. Thus, two-fold linear connectivity leads to 1-D chains, three-fold T-shaped and four-fold square planar connectivities afford 2-D sheets, while four-fold tetrahedral and six-fold octahedral centres give 3-D-networks. The building block methodology is particularly attractive as it provides a relatively simple conceptual framework to work within and allows the extrapolation of the basic principles of co-ordination

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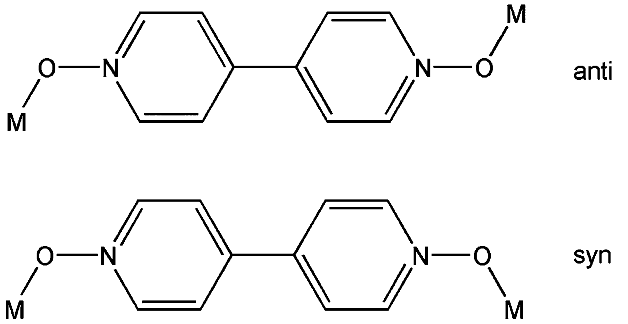
chemistry, i.e., co-ordination numbers and preferred geometrical arrangements of metal cations and ligand geometries.

This strategy is limited by either ligand design or more usually by the co-ordination preferences expressed by the metal cation used. The vast majority of co-ordination frameworks reported thus far incorporate *d*-block metals centres and the majority of co-ordination frameworks are thus limited inherently by the geometries that these metals adopt. The most common framework connectivities are two, three, four and six reflecting the common co-ordination geometries in tetrahedral, square-planar and octahedral complexes, and in some cases co-ordination sites are blocked by additional ligating molecules (e.g., co-ordinating anions) that block polymer-propagation in a given direction. In terms of framework design and ultimately materials design, the co-ordination preferences of *d*-block transition metals represent, to some extent, a limiting factor for the preparation of some materials. For example, it is difficult to envisage the general preparation of framework materials with connectivities of greater than six since co-ordination numbers higher than six for *d*-block centres are relatively rare and are limited to specific metal/ligand combinations, e.g., $[Mo(CN)_8]^{x-}$ [15]. Some examples of five-connected frameworks are known with *d*-block metals but they are very much the exception and usually unanticipated. It is however worth noting that the significant successes reported thus far in preparing functional co-ordination frameworks for storage, magnetism or luminescence have been achieved with co-ordination framework systems incorporating *d*-block metal centres.

Lanthanide co-ordination frameworks also offer attractive properties in terms of their potential applications and material properties. In particular, systems with luminescent [16,17], non-linear optical [16a] and porous [17,18] properties have been investigated. However, lanthanide-based systems have been far less studied to date than their *d*-block counterparts. It is not necessarily clear why this is the case, but one possible explanation is that the co-ordination spheres of lanthanide cations are difficult to control and in the absence of design strategies for lanthanide co-ordination frameworks it will be difficult to target materials with specific structure and hence properties. Bearing these issues in mind, we have recently extended the synthesis of co-ordination frameworks to include metal centres of higher connectivities by utilising lanthanide(III) centres with seven, eight and nine co-ordinate geometries. Although lanthanide cations may be difficult to control they offer some attractive features, notably a higher connectivity and also greater co-ordinative flexibility which often leads to unanticipated but remarkable structures which are highly unlikely to be encountered when using more predictable *d*-block metal ions.



Scheme 1. *Anti*- and *syn*-conformations of 4,4′-bipyridine-*N,N′*-dioxide when co-ordinated to lanthanide metal centres.

During our studies we have focussed on lanthanide co-ordination frameworks with the ligand 4,4′-bipyridine-*N,N′*-dioxide (L), although other pyridine *N*-oxide ligands have been studied and confirmed the successful application of this strategy. In our studies 4,4′-bipyridine-*N,N′*-dioxide has been chosen due to the excellent hard acid/hard base complementarity of the lanthanide cations and the *N*-oxide donor, and, also because the small steric size of this ligand which avoids crowding at the metal centre and encourages high-connectivity. 4,4′-bipyridine-*N,N′*-dioxide (L) can bridge metal centres in both *anti*- and *syn*-conformations (Scheme 1) and can form 'double-bridges' as well as single bridges. In our experience the 4,4′-bipyridine-*N,N′*-dioxide acts most commonly as a μ_2-bridge but exceptions are known in which a μ_3- or μ_4-bridging modes are adopted [16–19]. Although lanthanide co-ordination frameworks with three- [21], four- [20] and six-connected [21] topologies can be prepared, it can also be seen from the following selected examples that combining mixtures of lanthanide(III) centres and L successfully generates complex frameworks based on high co-ordination numbers and connectivity. The examples highlighted here give a glimpse of what may be possible with lanthanide-based co-ordination frameworks and the large range of new framework systems that are awaiting discovery.

2. Highly connected frameworks: Eight and seven-connected systems

Networks derived from eight-connected lanthanide nodes have been prepared as both 3-D frameworks [22,23] and, perhaps surprisingly, as bilayer [23] network structures.

Three distinct groups of 3-D frameworks with eight-connected topologies have been identified, (a) $\{[La(L)_4](CF_3SO_3)_3 \cdot 4.2MeOH\}_\infty$ [22] and $\{[Ln(\text{pyrazine-}N,N'\text{-dioxide})_4](ClO_4)_3\}_\infty$, ($Ln = La$, Ce, Pr, Sm, Eu, Gd, Tb or Y) [24]; (b) $\{[La(L)_4](ClO_4)_3 \cdot MeOH \cdot 4CHCl_2CHCl_2\}_\infty$ [23] and (c) $\{[Ln(L)_4](CF_3SO_3)_3 \cdot$

$4MeOH \cdot C_2Cl_4\}_\infty$ (Ln = Yb or Eu) [23]. In all three compound groups the lanthanides are co-ordinated exclusively by bridging 4,4′-bipyridine-*N,N*′-dioxide (L) or pyrazine-*N,N*′-dioxide ligands that act as bridges between adjacent lanthanide nodes in the extended framework structures. It is also worth noting that in all three structural types the interlayer bridging L molecules are located equally on opposite sides of the metal centre co-ordination polyhedron.

The structure observed for $\{[La(L)_4](CF_3SO_3)_3 \cdot 4.2MeOH\}_\infty$ [22] and $\{[Ln(\text{pyrazine-}N,N'\text{-dioxide})_4](ClO_4)_3\}_\infty$, ($Ln$ = La, Ce, Pr, Sm, Eu, Gd, Tb or Y) [24] is relatively simple. Each La(III) centre is co-ordinated in a compressed square anti-prismatic geometry by eight L molecules which bridge to eight different neighbouring La(III) centres forming a 3-D *bcc* type framework of $4^{24}6^4$ topology, as in CsCl (Fig. 1). This net can alternatively be described in terms of a series of intersecting 4^4 nets [25].

The structures of $\{[La(L)_4](ClO_4)_3 \cdot MeOH \cdot 4CHCl_2CHCl_2\}_\infty$ [23] and $\{[Ln(L)_4](CF_3SO_3)_3 \cdot 4MeOH \cdot C_2Cl_4\}_\infty$ (M = Yb or Eu) [23] are far more complex than the simple CsCl-like net observed above. The asymmetric unit of the latter $\{[La(L)_4](ClO_4)_3\}_\infty$ contains only one unique La(III) centre, which adopts an approximately dodecahedral homoleptic LaO_8 co-ordination environment. Each La(III) centre is linked to eight adjacent metal centres to form a 3-D eight-connected framework structure which is *not* of the familiar CsCl-type. The structure of CsCl consists exclusively of tetragonal motifs with $4^{24}6^4$ topology (Fig. 1), while the structure of $\{[La(L)_4](ClO_4)_3\}_\infty$ contains triangular and pentagonal subunits and exhibits $3^34^{15}5^86^2$ topology (Fig. 2). The structures of CsCl-topology and of $\{[La(L)_4](ClO_4)_3\}_\infty$ consist of two parallel (4^4) nets (Figs. 1 and 2) cross-linked by zig-zag chains. However, the relative displacement of the linking zig-zag chains differs significantly between the two structural types. In CsCl-like frameworks the parallel 4^4 nets are displaced only by translation, while in $\{[La(L)_4](ClO_4)_3\}_\infty$ these nets are displaced by translation and by a rotation of 61.5°. Furthermore, in CsCl-like nets zig-zag chains on both sides of a (4^4) net are mutually parallel, and bridge across the diagonal of the (4^4) net. In $\{[La(L)_4](ClO_4)_3\}_\infty$, however, the zig-zag chains bridge the axial direction of one (4^4) net and the diagonal of the next.

The structures of $\{[Ln(L)_4](CF_3SO_3)_3\}_\infty$ (M = Yb or Eu) [23] are binodal (i.e., there are two chemically distinct nodes X and Y within the lattice), each metal centre being 8-co-ordinate. The structure is extremely complex but can be regarded as comprising a four-connected sub-net of $SrAl_2$ topology that is further intersected by two sets of (4^4) nets that intersect at two distinct eight-connected nodes (with stoichiometry XY_2) leading to a framework of $(3^54^{14}5^9)\,(3^54^{13}5^{10})_2$ topology (Fig. 3). The observation that this network forms with both Yb(III) and Eu(III) suggests that a range of related materials might show this topology.

The eight-connected bilayer structure $\{[La_2(L)_{7.3}(CH_3OH)(H_2O)_{0.4}](CF_3SO_3)_6\}_\infty$ [23] is also formed from eight-co-ordinate lanthanide nodes, although two independent La(III) centres are observed, one surrounded by eight L molecules while the other is ligated by seven L molecules and a MeOH molecule. Both nodes adopt tetragonal anti-prismatic co-ordination geometries with four of the bridging ligands used to generate a 4^4-net. The remaining L molecules are all

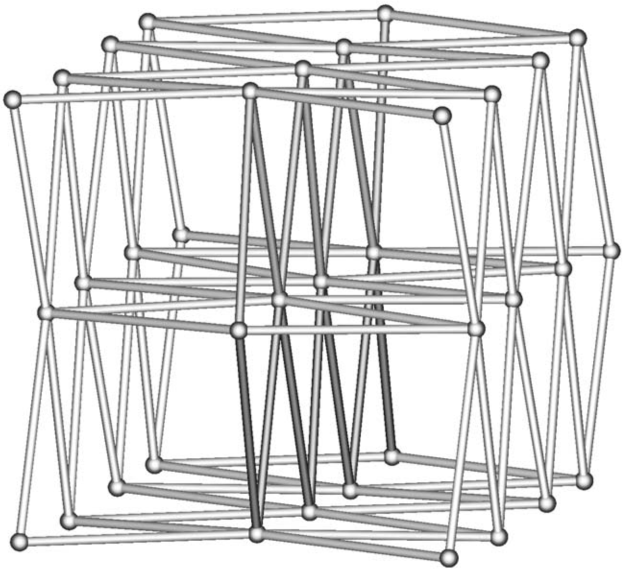


Fig. 1. Schematic representations illustrating the different links between the 4^4-nets in the eight-connected 3-D networks of $\{[La(L)_4](CF_3SO_3)_3 \cdot 4.2MeOH\}_\infty$.

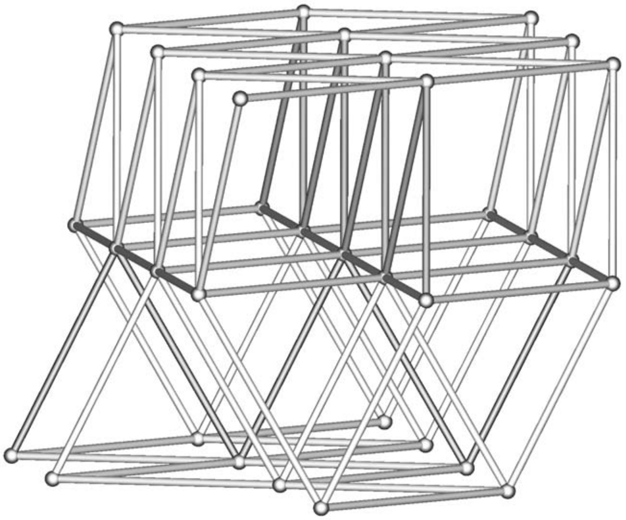


Fig. 2. Schematic representations illustrating the different links between the 4^4-nets in the eight-connected 3-D networks of $\{[La(L)_4](ClO_4)_3 \cdot MeOH \cdot 4CHCl_2CHCl_2\}_\infty$.

located on the same side of the net linking to a second 4^4-net to give a bilayer motif (Fig. 4). This arrangement affords three and four-fold bridges from seven- and eight-connected centres, respectively, between the two 4^4-nets.

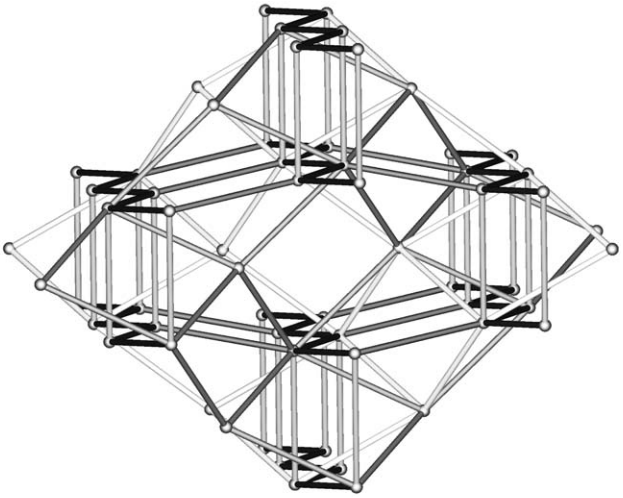


Fig. 3. Schematic representations illustrating the interlinking of the two 4^4-nets and the interconnected 6^3-nets in $\{[M(L)_4](CF_3SO_3)_3 \cdot 4MeOH \cdot C_2Cl_4\}_\infty$ (M = Yb or Eu).

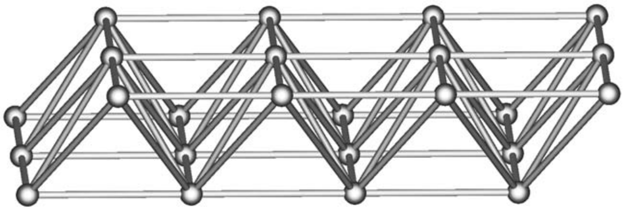


Fig. 4. Schematic representations of an eight-connected bilayer structure observed in $\{[La_2(L)_{7.3}(CH_3OH)(H_2O)_{0.4}](CF_3SO_3)_6\}_\infty$.

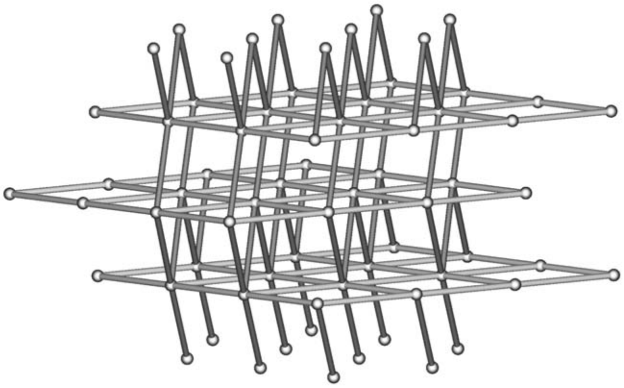


Fig. 5. Schematic representations illustrating the different links between the 4^4-nets in the seven-connected 3-D network of $\{[La(L)_4](BPh_4)(ClO_4)_3 \cdot 2.75MeOH\}_\infty$.

Framework structures containing seven-connected centres are extremely rare in materials chemistry and it is difficult to envisage how such structures would be achieved with co-ordination frameworks if a lanthanide-based system were not used. Thus far only two have been reported and of these, the bilayer structure discussed above has the seven-connected junction occurring in conjunction with an eight-connected centre. In $\{[La(L)_4](BPh_4)(ClO_4)_3 \cdot 2.75MeOH\}_\infty$ [22], however, a lattice derived from a unique seven-connected La(III) centre is formed. The La(III) in this complex is co-ordinated by eight L molecules, six of which form single bridges to six neighbouring La(III) centres, while the remaining two form a 'double bridge' to a single neighbouring La(III) centre (Fig. 5) producing a network structure that comprises intersecting (4^4) and (6^3) nets.

3. Unusual topologies and new framework families: Five-connected systems

Five-connected networks are relatively rare amongst co-ordination frameworks but have been successfully prepared using lanthanide building blocks. As lanthanide cations exhibit high, co-ordination numbers the formation of five-connected structures requires some of the available co-ordination sites to be blocked and we have successfully achieved this by using co-ordinating anions such as carboxylates or halide ligands.

Two examples of 3-D co-ordination frameworks derived from five-connected lanthanide metal centres have been reported [26], and both contain metal centres containing 'blocking' chemical moieties. In both cases the networks are composed of 2-D 6^3-nets, that use three of the bridging L molecules, which are linked in differing fashions using $[La(L)]_\infty$ zig-zag chains. In the case of $\{[La_4L_{10}(MeOH)_{10}Cl_3]Cl(BPh_4)_8 \cdot 22MeOH\}_\infty$ [26], the interplanar bridging L molecules linking the 6^3-nets form zig-zag chains, which are alternately distributed on either side of the net (Fig. 6a). On the other hand, the interplanar bridging L molecules linking the 6^3-nets in the uninodal $\{[LaL_{2.5}(MeOH)\{Ph_2B(OMe)_2\}](BPh_4)_2 \cdot 4.5MeOH\}_\infty$ [26], form zig-zag chains, which are arranged such that every pair alternates on opposing sides of the 6^3-nets (Fig. 6b). Structurally, these two lattices (Fig. 6a and b) may be regarded as isomers, having $4^6 6^2 8^2$ and $4^4 6^4$ topologies, respectively.

An example of a 2-D bilayer structure has also been reported in $\{[La(L)_{2.5}(CH_3OH)_2(C_7H_{11}CH_2CO_2)](BPh_4)_2 \cdot 2.7CH_3OH\}_\infty$ [27]. In this lattice the five-connected topology is achieved by co-ordination of a chelating carboxylate anion and two molecules of MeOH at a nine-co-ordinate La(III) node leaving five sites to bind bridging molecules of L. In this case four of the molecules of L afford a 2-D 4^4 net which is then

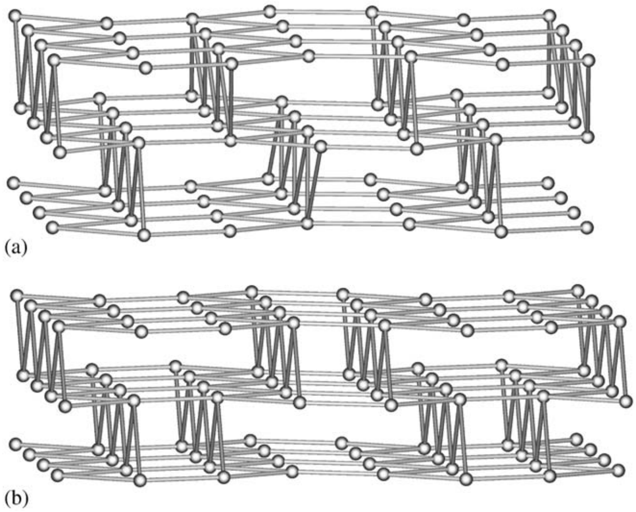


Fig. 6. Schematic representations illustrating the linking of the 6^3-nets in the five-connected 3-D networks of (a) $\{[La_4L_{10}(MeOH)_{10}Cl_3]Cl(BPh_4)_8 \cdot 22MeOH\}_\infty$ and (b) $\{[LaL_{2.5}(MeOH)\{Ph_2B(OMe)_2\}](BPh_4)_2 \cdot 4.5MeOH\}_\infty$.

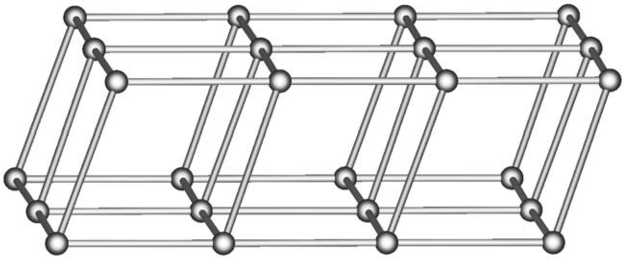


Fig. 7. Schematic representations of a five-connected bilayer structure as observed in $\{[La(L)_{2.5}(CH_3OH)_2(C_7H_{11}CH_2CO_2)](BPh_4)_2 \cdot 2.7 CH_3OH\}_\infty$.

linked to a symmetry-related net by the remaining bridging L molecule, thus affording a 2-D five-connected bilayer structure (Fig. 7).

4. Summary

It is clear from the highly unusual structures described above that lanthanide cations offer a huge variety of possible framework targets that would be highly difficult, if not impossible, to prepare with *d*-block metal cations. However, the somewhat unpredictable nature and lability of lanthanide cation nodes leads to both exciting opportunities and to difficulties in targeted materials synthesis. Research is leading to a much greater appreciation of the factors that control framework formation and the resultant topology. As this understanding develops it will become easier to target particular framework types and then to develop applications from these new and highly unusual materials. Thus, it can be seen that lanthanide coordination frameworks have the potential to open up new directions for new materials chemistry and as such the underlying concepts for the construction are enticing and potentially highly important.

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