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New Approaches to the Analysis of High Connectivity Materials: Design Frameworks Based upon 4^4- and 6^3-Subnet Tectons

ROBERT J. HILL, DE-LIANG LONG,
NEIL R. CHAMPNESS,*
PETER HUBBERSTEY,* AND
MARTIN SCHRÖDER*
School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

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ABSTRACT
Coordination framework polymers derived from lanthanide metal ions with *N*,*N*′-dioxide ligands (4,4′-bipyridine-*N*,*N*′-dioxide, pyrazine-*N*,*N*′-dioxide, 1,2-bis(pyridin-4-yl)ethane-*N*,*N*′-dioxide, *trans*-1,2-bis(pyridin-4-yl)ethene-*N*,*N*′-dioxide) exhibit such intricate architectures that a new strategy is required to appreciate and understand their structures. Rather than analyzing the overall structure in terms of the connectivity of individual metal nodes, which can lead in some cases to extremely complex topological treatments, our new strategy is based on the visualization of the structures as combinations of interconnected layered 2-D sheets or subnet tectons. Despite the diversity and relative complexities of many of the structures discussed here, they can all be described by the interconnection of just two types of 2-D subnet tectons, 4^4 square grids or 6^3 hexagonal grids. The interconnection of these layered sheets with bridging *N*,*N*′-dioxide molecules gives rise to both 2-D bilayer and 3-D network extended structures depending upon the relative dispositions of the interconnecting *N*,*N*′-dioxide ligands. Thus, 2-D bilayers result when the *N*,*N*′-dioxide ligands that bridge two subnet tectons are located on the same side of the sheet, while 3-D networks are formed when the bridging *N*,*N*′-dioxide ligands are located on both sides of the sheet. This analysis allows ready identification and interpretation of some of the most highly connected and complex architectures yet observed in materials chemistry.

1. Introduction

The development of metal–organic coordination 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] Because the arrangement of individual components within a material will determine its macroscopic properties and function, the rational design of multidimensional and multifunctional molecular architectures is of great importance for the targeted synthesis of new materials for solvent inclusion[6–9] or gas adsorption[9–11] characteristics or materials with electronic[12] or nonlinear optical properties.[13] The majority of the networks reported thus far have been produced using a building-block methodology[14] in which cationic metal centers are linked by bridging ligands. Owing to their differing coordination numbers and geometries, the choice of metal center often dictates the architecture of the resultant framework materials. For example, two-fold linear connectivity leads to 1-D chains, three-fold connectivity leads to brickwall or hexagonal networks, four-fold square-planar connectivities often afford 2-D sheets, while four-fold tetrahedral and six-fold octahedral centers give corresponding 3-D-networks. Recently, we have extended this work to include metal centers of higher coordination numbers and connectivities

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Robert J. Hill graduated with a M.Sci. Honours Degree in Chemistry from the University of Nottingham in 2001. He is currently a graduate student completing his Ph.D. on the synthesis and structures of coordination framework polymers.

De-Liang Long was born in Hunan, China. He received his B.Sc. and M.Sc. degrees in chemistry from Wuhan University and completed his Ph.D. under the direction of Professor Xin-Quan Xin at Nanjing University in 1996. After a postdoctoral appointment at Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, in 1999 he held the Royal Society KC Wong Fellowship working with Professor Martin Schröder at the University of Nottingham. He is currently a Research Fellow at the University of Glasgow, U.K. His interests are in inorganic synthesis, coordination chemistry, and cluster-based materials.

Neil Champness is Professor of Chemical Nanoscience at the University of Nottingham. He began his academic career at the University of Southampton with a B.Sc. in Chemistry (1989) and Ph.D. (1993), under the supervision of Prof. W. Levason. Following postdoctoral studies in Southampton with Dr. G. Reid, he moved to the University of Nottingham in 1995 as a Teaching Fellow in Inorganic Chemistry. He took up a Lectureship in Inorganic Chemistry in 1998 and was promoted to Reader in Chemistry in 2003. He was appointed to the Chair of Chemical Nanoscience in 2004. His research is concerned with molecular organization, including the understanding of solution-phase self-assembly processes, surface supramolecular assembly, and organization in the solid-state via crystal engineering. Particular targets of his work are guest molecular entrapment and nanostructure formation in solid, solution, or surface environments with an emphasis on applications in information storage and sustainable energy sources.

Peter Hubberstey is a Reader in Inorganic Chemistry at the University of Nottingham. He began his academic career at the University of Nottingham with a B.Sc. in Chemistry (1965) and Ph.D. (1968), under the supervision of Prof. C. C. Addison. Following postdoctoral studies at Brookhaven National Laboratory with Prof. A. W. Castleman, he returned to the University of Nottingham in 1970 to take up a Lecturership in Inorganic Chemistry with subsequent promotions to Senior Lecturer and Reader. Coordination chemistry has been his primary interest since 1985, and he has extensive experience of ligand design as applied initially to small molecule analogues of biologically significant metallo-proteins and metallo-enzymes including hemocyanins, nitrite reductases, and ascorbate oxidases and subsequently to metal-containing multidimensional frameworks based on either coordinate or hydrogen-bonded supramolecular interactions. In his earlier career, his major interests centred on nonaqueous solvents, particularly the application of electrical resistivity techniques to the elucidation of the reaction chemistry of solutes dissolved in liquid alkali metals.

Martin Schröder gained his B.Sc. in Chemistry from the University of Sheffield (1975), Ph.D. and DIC from Imperial College, University of London (1978), under the supervision of Professor W.P. Griffith, and after postdoctoral fellowships at the ETH (Professor Eschenmoser) and the University of Cambridge (Professor Lewis), he was appointed in 1982 to a Senior Demonstratorship at the University of Edinburgh. He was subsequently promoted to Lecturer, Reader, and Professor and in 1995 moved to his present position as Head and Professor of Inorganic Chemistry at the University of Nottingham. He is currently Head of the School of Chemistry. He has been a Visiting Professor at the University of Toronto, University of Otago, and the Louis Pasteur University, Strasbourg. He has published some 350 publications and is a Fellow of the Royal Society of Edinburgh (FRSE) and a Fellow of the Royal Society of Chemistry (FRSC). His research awards include the RSC Corday-Morgan Medal and Prize in 1991, a Royal Society of Edinburgh Support Research Fellowship in 1991–1992, the RSC Tilden Lecturer in 2001, and the RSC award for the Chemistry of Transition Metals in 2003. In 2005, he was awarded a Royal Society Wolfson Merit Award. His research interests span the coordination and redox chemistry of macrocycles, metal–organic framework polymers, structural and functional models for hydrogenase enzymes, and the development of metal salt binding and extraction agents.

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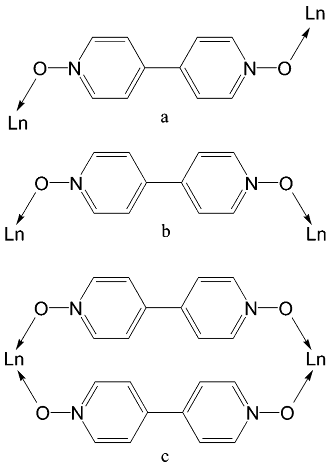
Scheme 1. Anti (a) and Syn Conformations (b) of and Double-Bridge Formation (c) by 4,4′-Bipyridine-*N,N′*-dioxide Bound to Lanthanide Metal Centers



by utilizing lanthanide(III) centers with seven, eight, and nine coordinate geometries. To avoid steric crowding at the metal center, our approach has been to replace 4,4′-bipyridine with less sterically demanding and more coordinatively flexible ligands such as 4,4′-bipyridine-*N,N′*-dioxide (L), which can bridge metal centers in both anti (Scheme 1a) and syn conformations (Scheme 1b) and can form "double-bridges" (Scheme 1c), as well as single bridges (Scheme 1a,b). In all but one of the lanthanide−4,4′-bipyridine-*N,N′*-dioxide compounds considered in this Account, the ligand acts as a μ_2-bridge as shown in Scheme 1. In the exception,[15] 4,4′-bipyridine-*N,N′*-dioxide acts as a μ_4-bridging ligand. Other structures also exist in which other *N,N′*-dioxides act as μ_3- or μ_4-bridging ligands to link Ln(III) centers.[16−18] The Ln^{3+}−oxygen donor combination is effective in framework construction owing to the complementarity of the hard metal cationic acid and hard donor base. Thus, reaction of lanthanide(III) salts and L successfully generates complex frameworks showing high coordination numbers and unprecedented high connectivities. The choice of anion and solvent medium can be critical in these reactions. For example, strongly coordinating anions and solvent molecules may occupy coordination sites of the metal center thereby reducing the number of available coordination sites and lowering the connectivity of the metal center.

The network polymers produced by combination of lanthanide(III) centers and L exhibit a wide range of structures, which, like all other inorganic−organic coordination frameworks, can be classified topologically by consideration of the angles at each node of the network.[19] For nets built up from a set of identical nodes (so-called uninodal nets), the number of angles at each node, defined by pairs of edges, differs with the connectivity of the net; thus, the nodes in 3-, 4-, and 6-connected nets have 3, 6, and 15 angles, respectively. Since each angle is contained in a circuit with *N* other nodes, the net can be characterized by a "Schläfli" symbol[20] that defines the number of nodes in the shortest circuit associated with each of the angles. For example in a 4-connected diamond-type net where all six angles are equivalent and form part of six-membered circuits,[21] the symbol would be 6^6. Alternatively, if two of the angles were involved in four-membered circuits and four in eight-membered circuits as in the PtS-type structure,[22] the symbol would be $4^2 8^4$. These are relatively simple topologies; more intricate architectures have extremely complex topological treatments.

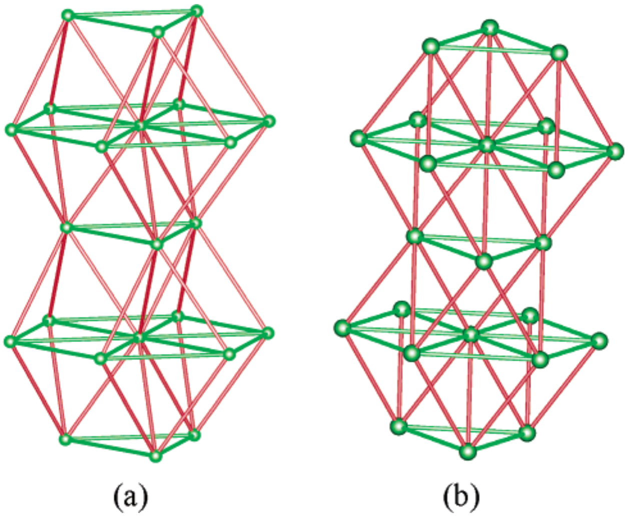


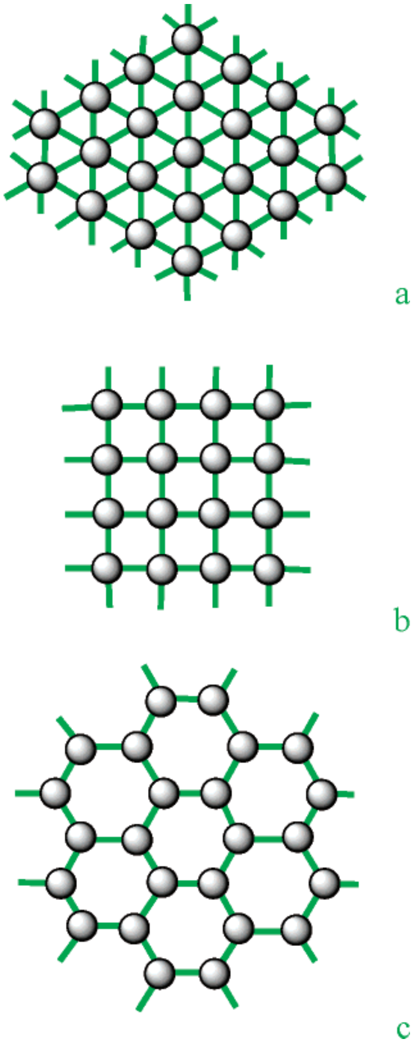
FIGURE 1. Identification of 3^6-nets in (a) hexagonal and (b) cubic close-packed structures.

Rather than considering a coordination polymer as an independent framework to which a discrete topology can be assigned, we have adopted a new strategy to identify architectural trends by regarding the polymers as constructed from interconnected layered 2-D sheets, which we term subnet tectons. This approach permits easier visualization of and simplifies structural interpretation of high connectivity structures. Furthermore, it allows the identification of families of structures and their relationships to one another by defining the subnet tectons from which they are constructed.

The simplest 2-D sheets, which comprise just one kind of regular polygon, are so-called regular "tilings" or "tessellations".[23] There are three common architectures, which are based on triangles, squares, and hexagons. Since six triangles, four squares, and three hexagons meet at a node in a 2-D network, giving angles of 60°, 90°, and 120°, the corresponding Schläfli symbols are 3^6, 4^4, and 6^3, respectively (Scheme 2).

Before further consideration of these materials, it is appropriate to consider the familiar structures of the elements to illustrate the approach that we adopt. The majority of metals adopt 12-coordinate close-packed structures, either hexagonal close-packed[24] or cubic close-packed (face-centered cubic).[25] Both can be described as being formed from parallel 3^6 nets with each center providing six links to centers in adjacent nets (Figure 1), three on each side. Whereas for hexagonal close-packed structures, these six links lead to centers arranged in a trigonal prismatic geometry (Figure 2a), for cubic close-packed structures, the centers are arranged in a trigonally

Scheme 2. 2-D Nets with (a) 3^6, (b) 4^4, and (c) 6^3 Topologies



elongated octahedral geometry (Figure 2b). The hexagonal symmetry of the former system gives rise to a single set of parallel 3^6-nets; the cubic symmetry of the latter system results in four sets of parallel 3^6-nets.

Other metals adopt eight-coordinate body-centered cubic structures.[26] This arrangement can be described as being formed from parallel 4^4-nets with each center providing four links to centers in adjacent nets, two on each side. These links form an independent series of parallel 4^4-nets aligned at 90° to the original net (Figure 3). 4^4-Nets can also be identified in the six-coordinate structure of α-polonium [the rock-salt (NaCl) structure with both cation and anion replaced by polonium atoms]. In this case, however, the parallel series of 4^4-nets are interconnected by just two links, one on each side of the net (Figure 4).

Elements that adopt four-coordinate geometries include lighter group 14 elements, which adopt diamond or diamond-type structures.[27] Both cubic and hexagonal (lonsdaleite) forms of the diamond structure are known; the former is equivalent to the zinc blende (ZnS) structure, while the latter is equivalent to the wurtzite (ZnS) structure with both cation and anion replaced by carbon atoms. Cubic and hexagonal forms can be described as being derived from puckered 6^3-nets, each center providing a single link to centers in adjacent nets, the direction of the link alternating with neighboring centers. The principal difference between the two forms is the linking of the six-membered rings, all of which adopt the chair conformation (Figure 5), although it should be noted that some six-

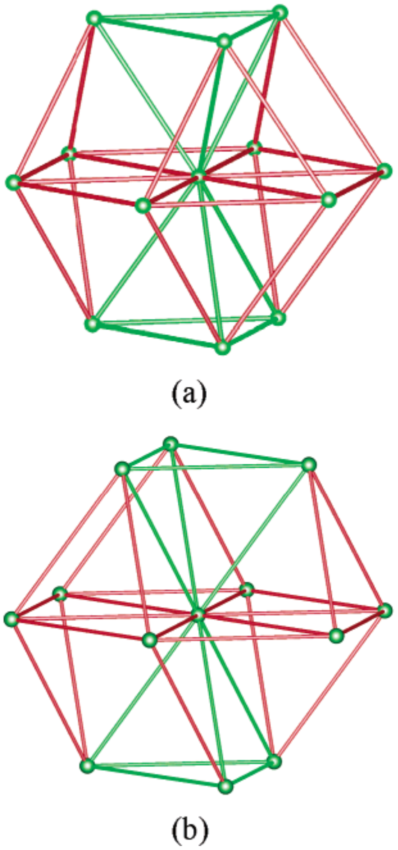


FIGURE 2. Linking of 3^6-nets in (a) hexagonal and (b) cubic close-packed structures.

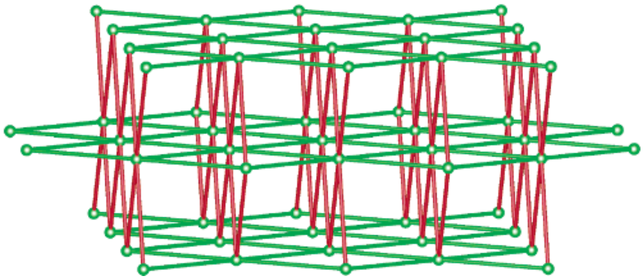


FIGURE 3. Identification of 4^4-nets in body-centered cubic structures.

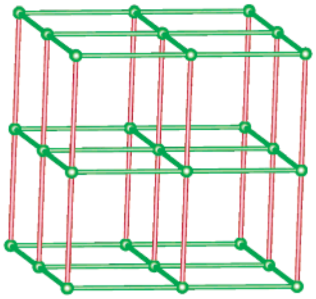
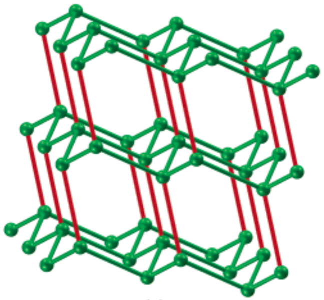


FIGURE 4. Identification of 4^4-nets in α-polonium.


(a)

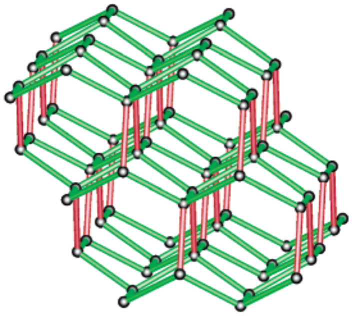

(b)

FIGURE 5. Identification of 6^3-nets in (a) cubic and (b) hexagonal diamond-type structures.

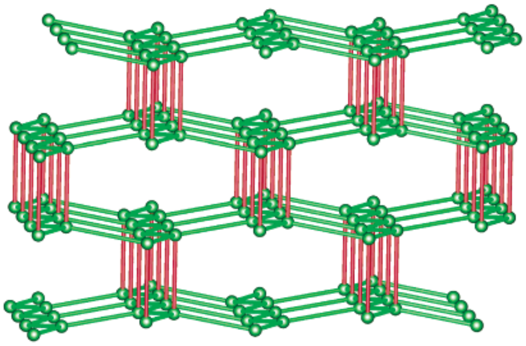


FIGURE 6. Identification of 6^3-nets in $SrAl_2$-type structures.

membered rings in lonsdaleite adopt boat conformations. A further linking of 6^3-nets is found in $SrAl_2$-type structures (Figure 6).

Elements that adopt three-coordinate geometries include carbon, as graphite, and the heavier group 15 elements.[28] Although they all form 6^3-nets, that of graphite (Figure 7) is planar whereas those of group 15 elements are puckered. As for the group 14 elements, two forms, in this case termed rhombohedral and orthorhombic, are known for the group 15 elements (Figure 8). The difference lies in the way the rings, which again adopt chair conformations, are linked to generate the 6^3-net. Graphite forms a planar 6^3-net while puckering occurs in the 6^3-nets observed in the diamond-type and group 15 element structures owing to the difference in bond angles, which is 120° (sp^2-hybridized) for graphite (trigonal planar) and ca. 109.5° (sp^3-hybridized) for the diamond-type (tetrahedral) and group 15 element (pyramidal) structures. Because four-connected metal centers are common, many metal−organic systems might be expected to adopt 6^3-net architectures.

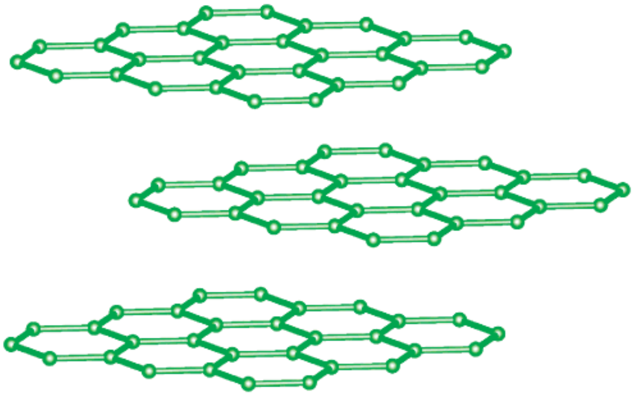
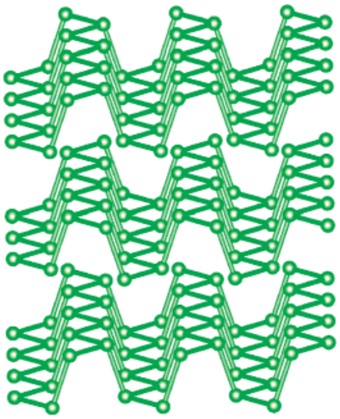


FIGURE 7. Identification of 6^3-nets in the structure of graphite.


(a)

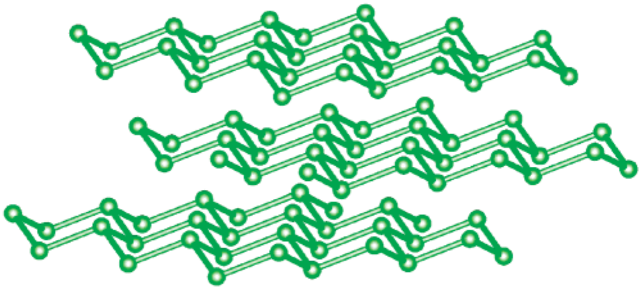
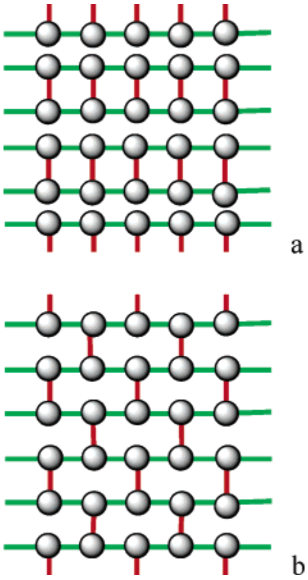

(b)

FIGURE 8. Identification of 6^3-nets in the structures of (a) orthorhombic and (b) rhombohedral phosphorus.

2. Inorganic−Organic Hybrid Structures

Inorganic−organic coordination polymers can be considered in an analogous fashion to the elements, the organic linker equating to element−element bonds. However, the situation is made much more fascinating and diverse by the fact that cationic metal centers can be coordinated by a range of ligands giving a variety of connectivities. For example, lanthanum(III) can be coordinated by four, five, seven, or eight 4,4′-bipyridine-*N*,*N*′-dioxide (L) ligands in $\{[La(L)_2(NO_3)_3]\}_\infty$,[29] $\{[La(L)_{2.5}(CH_3OH)(Ph_2B(OMe)_2)](BPh_4)_2\cdot 4.5MeOH\}_\infty$,[30] $\{[La_2(L)_{7.3}(CH_3OH)(H_2O)_{0.4}](CF_3SO_3)_6\}_\infty$,[31] or $\{[La(L)_4](ClO_4)_3\cdot MeOH\cdot 4CHCl_2CHCl_2\}_\infty$,[31] respectively. Furthermore, the bridging ligands can act independently as single bridges (Scheme 1a,b) or in pairs as double bridges

Scheme 3. Linking of 4^4-nets (Green Contacts) Formed by Five-Connected Metal Centers with the Metal Centers Disposed Such That the Interplanar Bridging (Fifth) L Molecules (Red Contacts) Are on (a) the Same Side of the Net Thus Forming a 2-D Bilayer or (b) Opposite Sides of the Net Forming a 3-D Network



(Scheme 1c) to give differing connectivities. For example, eight-coordinate La(III) centers are known to form six-fold (in $\{[La(L)_4](ClO_4)_3{\cdot}C_6H_5Cl{\cdot}CH_3OH\}_\infty$ [29]), seven-fold (in $\{[La(L)_4](BPh_4){\cdot}(ClO_4)_2{\cdot}2.75CH_3OH\}_\infty$ [32]), or eight-fold (in $\{[La(L)_4](ClO_4)_3{\cdot}MeOH{\cdot}4CHCl_2CHCl_2\}_\infty$ [31]) connectivities.

The extended structure of these materials depends in large part upon the geometry of the metal coordination center. Taking 4^4-nets as an example, it is clear that four-connected square-planar metal centers will give rise to 2-D sheet architectures, each of the four coplanar coordinated molecules of L participating in the construction of the 4^4-net. Five-connected metal centers, however, can give rise to either 2-D bilayer or 3-D network structures. Of the five coordinated molecules of L, four form the 4^4-net while the fifth is perpendicularly aligned to the net. When all the metal centers in the 4^4-nets face in the same direction, the fifth (interlayer bridging) L molecules are all on the same side of the net and a bilayer results (Scheme 3a). On the other hand, if alternate metal centers face opposite directions, the interlayer L molecules are equally arranged on both sides of the net and a 3-D network results (Scheme 3b).

For metal centers with higher connectivity, the situation is even more complex because the two interlayer L molecules can be located on either the same or opposite sides of the metal center as shown in Figure 9 for the six-connected M(III) centers in $\{[Yb(L)_3](CF_3SO_3)_3\}_\infty$ [29] and $\{[Sc(L)_3](NO_3)_3\}_\infty$.[33] When both of the interlayer bridging (fifth and sixth) L molecules are located on the same side of the coordination polyhedron, it is possible to generate 2-D bilayers (Scheme 4a) and 3-D networks (Scheme 4b) in an analogous manner as for the five-connected metal centers. When the two interlayer bridging L molecules are located on opposite sides of the coordination polyhedron, it is only possible to generate 3-D networks (Scheme 4c).

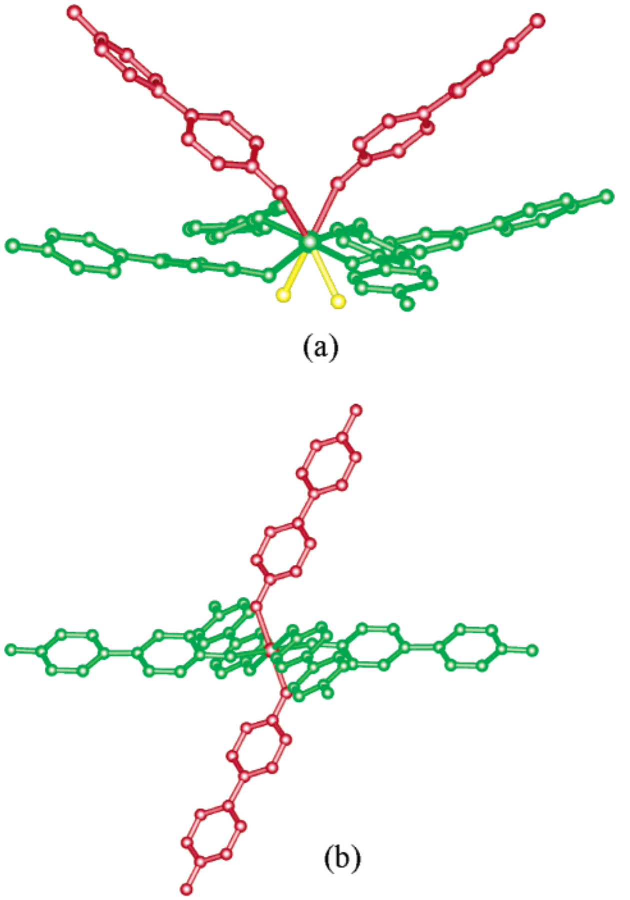
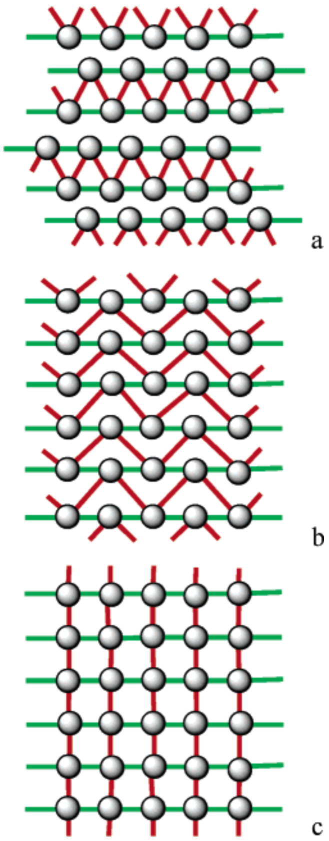


FIGURE 9. Views of the coordination geometries of the M(III) centers in (a) $\{[Yb(L)_3](CF_3SO_3)_3\}_\infty$ [29] and (b) $\{[Sc(L)_3](NO_3)_3\}_\infty$ [33] showing the disposition of the interlayer bridging L molecules on either the same (a) or opposite (b) sides of the 4^4-net.

Although similar arguments apply to systems containing metal centers with even higher connectivity, for 3-D network structures with connectivity six and greater, a significant number of bridging molecules remain following identification of a 2-D net. In some cases, these bridge the metal centers to form independent 2-D nets. For example, six-, seven-, and eight-connected Ln(III) centers form nodes within two independent and intersecting 6^3-nets, in intersecting 4^4- and 6^3-nets, and in two independent and intersecting 4^4-nets, respectively.

Because lanthanide(III) metal centers tend to have high coordination numbers, high connectivity architectures are favored. Low connectivity architectures require either the formation of double bridges, in which two bridging molecules adopt the syn conformation (Scheme 1b) rather than the more usual anti conformation (Scheme 1a) to link a single pair of metal centers (Scheme 1c), or the occupation of coordination sites by chemical moieties, such as anions or solvent molecules. However as noted above, “blocking” one face of the lanthanide(III) coordination polyhedron by chemical moieties does not ensure bilayer formation because alternate metal centers can face opposite directions to give a 3-D network. Examples of the formation of both high and low connectivity architectures are discussed in more detail in the following sections.

Scheme 4. Linking of 4^4-nets (Green Contacts) Formed by Six-Connected Metal Centers with (a, b) Both Interplanar (Fifth and Sixth) Molecules L (Red Contacts) on the Same Side of the Metal Centers Forming Either (a) a 2-D Bilayer or (b) a 3-D Network and with (c) the Two Interplanar L Molecules on Opposite Sides of the Metal Center, Thus Forming a 3-D Network



2.1. Inorganic−Organic Hybrid Structures Based on 4^4-Nets. 2.1.1. Four-Fold Connectivity. Four-fold connectivity is the minimum required for 4^4-net formation. For example, a simple 4^4-net is formed in the four-connected compound $\{[La(L)_2(NO_3)_3]\}_\infty$ [29] in which La(III) centers are coordinated by three bidentate chelating nitrate anions, as well as the four bridging L ligands, which link to form a near planar 2-D sheet (Figure 10).

2.1.2. Five-Fold Connectivity. As discussed earlier, two architectures, either a bilayer (Scheme 2a) or a network (Scheme 2b), can be envisaged for five-connected structures derived from 4^4-nets. A bilayer architecture is observed in $\{[La(L)_{2.5}(CH_3OH)_2(X)](BPh_4)_2\cdot 2.7MeOH\}_\infty$ (X = norbornyl acetate)[29] in which the nine-coordinate La(III) center is bound by five molecules of L, a bidentate chelating norbornyl acetate anion and two MeOH molecules. Of the five ligands L, four are involved in 4^4-net construction with the fifth linking the nets together (Figure 11a). Interestingly, the ligands within the 4^4-net adopt a syn conformation but are anti in the interlayer bridges. The carboxylate anion, deliberately chosen to block sufficient coordination sites of the La(III) center to encourage bilayer formation, and the MeOH molecules lie on the opposite side of the net to the interlayer bridge L. The alternative architecture in which the Ln(III) cations face opposite directions and the fifth molecule L is located on both sides of the 4^4-net to generate a 3-D network structure has not yet been observed.

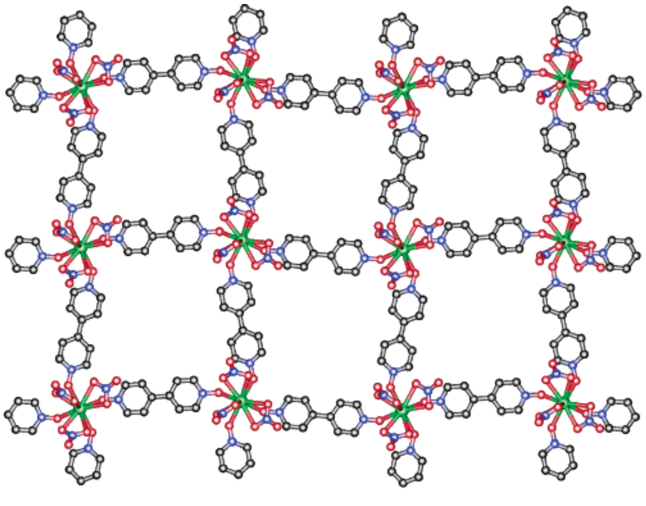


FIGURE 10. A view of the 4^4-net structure of $\{[La(L)_2(NO_3)_3]\}_\infty$.

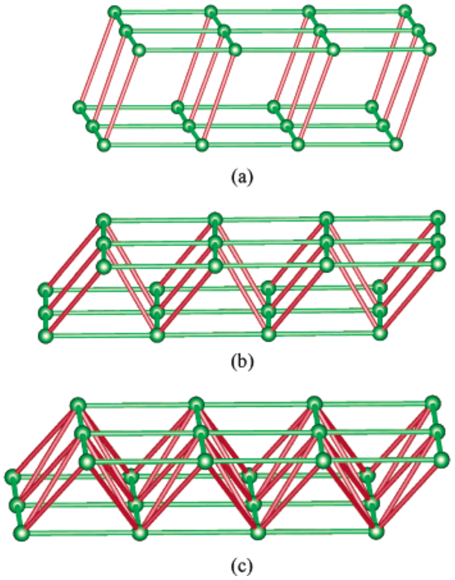


FIGURE 11. Schematic representations of (a) five-connected, (b) six-connected, and (c) eight-connected bilayers.

2.1.3. Six-Fold Connectivity. As noted earlier both bilayer (Scheme 3a,b) and network (Scheme 3c) architectures can be envisaged for six-connected structures derived from 4^4-nets. Several examples of both network types have been reported.

A family of bilayers derived from six-connected metal centers, which have either six or eight bound ligands L, has been discovered for $\{[Yb(L)_3](CF_3SO_3)_3\}_\infty$,[29] $\{[Er(L)_5](I_3)_3\cdot 0.5L\cdot MeOH\}_\infty$,[29] and $\{[La(L)_4](ClO_4)_3\cdot C_6H_5Cl\cdot CH_3OH\}_\infty$.[29] In $\{[Yb(L)_3(OH_2)_2](CF_3SO_3)_3\}_\infty$, the Yb(III) center is located in an eight-fold square anti-prismatic coordination sphere comprising six molecules of L and two "blocking" water molecules. Four ligands L lie within a 4^4-net with the two remaining molecules L bridging on the same side of the net to give the observed bilayer architecture (Figure 11b). The two water molecules, which complete the coordination sphere at Yb(III), are located

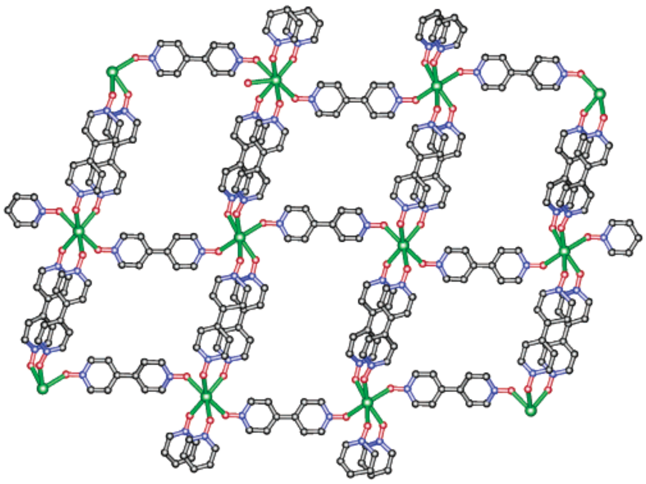


FIGURE 12. A view of the 4^4-net structure of $\{[La(L)_4](ClO_4)_3 \cdot C_6H_5Cl \cdot CH_3OH\}_\infty$.

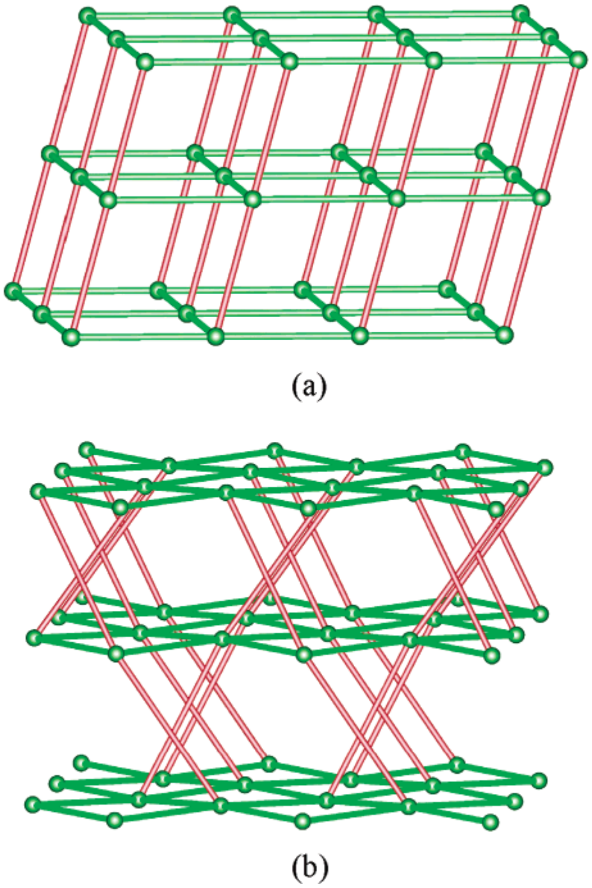
on the opposite side of the 4^4-net to the interlayer bridging ligands L and H-bond to other bilayer arrays.

The topology of $\{[Er(L)_5](I_3)_3 \cdot 0.5L \cdot MeOH\}_\infty$ [29] is very similar to that of $\{[Yb(L)_3](CF_3SO_3)_3\}_\infty$, the principal difference being the replacement of the "blocking" water molecules by pendant, nonbridging L molecules. Thus, the eight-fold square anti-prismatic coordination geometry of the Er(III) center is provided entirely by L. Four molecules L generate the 4^4-net, and two bridge on the same side of the net to separate Er(III) centers in an identical net to give the bilayer architecture (Figure 11b). The two remaining ligands L are monodentate and are located on the opposite side of the net; adjacent bilayers are thus linked through $\pi-\pi$ interactions between these pendant L molecules, which also provide the space required to accommodate the linear I_3^- anions.

Like the Er(III) center in $\{[Er(L)_5](I_3)_3 \cdot 0.5L \cdot MeOH\}_\infty$,[29] the La(III) center in $\{[La(L)_4](ClO_4)_3 \cdot C_6H_5Cl \cdot CH_3OH\}_\infty$ [29] is bound to eight ligands L in a square anti-prismatic geometry. In this case, however, six molecules of L are used to generate the 4^4-net, two bridging ligands acting independently and four acting in pairs to form "double bridges" (Figure 12). The two remaining L molecules bridge on the same side of the net to separate La(III) centers of an identical net to give a bilayer architecture Figure 11b).

Networks derived from six-connected metal centers that contain 4^4-nets can be identified in $\{[Sc(L)_3](X)_3\}_\infty$ (X = NO_3 or ClO_4),[33] $\{[Sc(L)_3](CF_3SO_3)_3 \cdot 2.7MeOH \cdot 3H_2O\}_\infty$,[33] and $\{[La(L)_4][Co(C_2H_{11}B_9)_2]_3 \cdot 0.5MeOH\}_\infty$.[32] The Sc(III) materials are included in this analysis owing to the analogous electronic configurations of Sc(III) and Ln(III) centers. As for the corresponding bilayer structures, these networks are formed by metal centers coordinated by both six and eight ligands L. However, in all four cases, the two interlayer bridging L molecules are located on opposite sides of the metal center coordination polyhedron.

The octahedral Sc(III) centers in $\{[Sc(L)_3](X)_3\}_\infty$ (X = NO_3 or ClO_4)[33] are linked to form α-polonium-type structures but with rhombohedral rather than cubic frameworks. Thus, following the description of the structure of α-polonium they can be considered to comprise parallel series of 4^4-nets with each Sc(III) center linked to two other Sc(III) centers in both adjacent nets (Figures 4 and 13a). As for the α-polonium structure, owing to the 3-fold symmetry of the rhombohedron, there are three ways (along the three crystallographic axes) of viewing this particular description of the structures of $\{[Sc(L)_3](X)_3\}_\infty$ (X = NO_3 or ClO_4),[33] the overall topology of which is $4^{12}6^3$.[33] The third Sc(III) compound, $\{[Sc(L)_3](CF_3SO_3)_3 \cdot 2.7MeOH \cdot 3H_2O\}_\infty$,[33] differs from $\{[Sc(L)_3](X)_3\}_\infty$ (X = NO_3 or ClO_4)[33] in the displacement of the linkages between the 4^4-nets (Figure 13b). The distorted octahedral geometry of the Sc(III) center results not in collinear bridges as in the α-polonium structure Figure 13a) but in alternating bridges adopting mutually inclined orientations while linking adjacent 4^4-nets (Figure 13b) as a result of which the topology changes from $4^{12}6^3$ to 4^86^68.



(a)

(b)

FIGURE 13. Schematic representations illustrating the different links between the 4^4-nets in the six-connected 3-D networks of (a) $\{[Sc(L)_3](X)_3\}_\infty$ (X = NO_3 or ClO_4) and (b) $\{[Sc(L)_3](CF_3SO_3)_3 \cdot 2.7MeOH \cdot 3H_2O\}_\infty$.

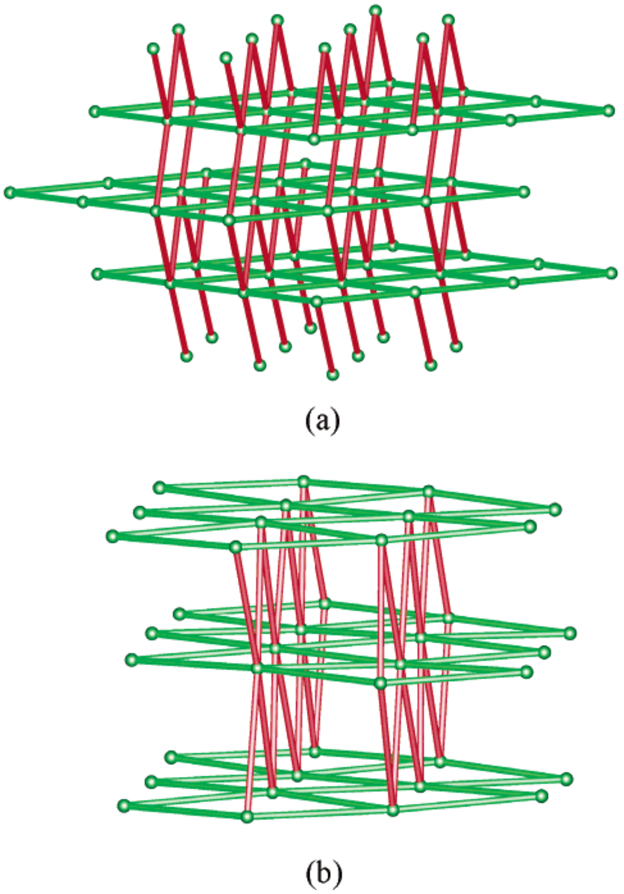
The six-fold connectivity of the structure of $\{[La(L)_4][Co(C_2H_{11}B_9)_2]_3 \cdot 0.5MeOH\}_\infty$,[32] in which the La(III) center is surrounded by eight molecules of L, arises from the presence of four single and two "double bridges" as in $\{[La(L)_4](ClO_4)_3 \cdot C_6H_5Cl \cdot CH_3OH\}_\infty$.[29] In this case, however, the structure can be considered to be either a series of parallel 4^4-nets built up from four single bridges as in $\{[La(L)_2(NO_3)_3]\}_\infty$ (Figure 10)[29] with "double bridges" linking the layers or as a series of parallel 4^4-nets built up from two single bridges and two "double bridges" as in $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{ClO}_4)_3{\cdot}\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}{\cdot}\mathrm{CH}_3\mathrm{OH}\}_\infty$[29] (Figure 12) with single bridges linking the layers. Ignoring the difference in the bridges, the structure is analogous to the α-polonium structure and has $4^{12}6^3$ topology.

The structure of the lanthanide−1,2-bis(pyridin-4-yl)-ethane-*N*,*N'*-dioxide complex $\{[\mathrm{Ln}(\mathrm{L})_3](\mathrm{ClO}_4)_3{\cdot}\mathrm{H}_2\mathrm{O}\}_\infty$ (Ln = Er or Yb)[16] is based on a six-connected Ln(III) center. It is essentially an α-polonium-type framework analogous to that formed by $\{[\mathrm{Sc}(\mathrm{L})_3](\mathrm{X})_3\}_\infty$ (X = NO_3 or ClO_4).[33]

2.1.4. Seven-Fold Connectivity. Structures containing seven-connected centers are extremely rare. Thus far only two have been reported, and of these, one occurs in conjunction with an eight-connected center and will be discussed in the next section devoted to eight-fold connectivity (section 2.1.5). Seven-connected structures containing 4^4-nets have three interplanar bridges. As noted earlier, there is thus a possibility that these molecules will link the Ln(III) metal centers to form an independent 6^3-net. This is the case in $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{BPh}_4)(\mathrm{ClO}_4)_3{\cdot}2.75\mathrm{MeOH}\}_\infty$[32] in which the unique seven-connected La(III) center is coordinated by eight ligands L, six of which form single bridges to six neighboring La(III) centers, while the remaining two form a "double bridge" to a single neighboring La(III) center. The structure can thus be considered to be a series of parallel 4^4-nets built up from four single bridges as in $\{[\mathrm{La}(\mathrm{L})_2(\mathrm{NO}_3)_3]\}_\infty$ (Figure 10)[29] with two single bridges to the adjacent net on one side and a "double bridge" to the net on the other side (Figure 14a). It is these three bridges that form the independent 6^3-subnet (see section 2.2.3). Thus, this lattice can be viewed most easily as comprising intersecting 4^4- and 6^3-nets.

2.1.5. Eight-Fold Connectivity. Networks derived from eight-connected metal centers that contain 4^4-nets adopt both bilayer and 3-D network structures. The bilayer is not generated in the same way as those observed in five- and six-connected systems because the Ln(III) coordination sphere does not include any "blocking" molecules. Instead, the four molecules L forming the 4^4-net are located on one face of the La(III) metal center and adopt syn conformations such that they generate a coplanar array, while the other four L molecules are located on a second face of the La(III) metal center and bridge to metal centers in the adjacent 4^4-net. In fact, the asymmetric unit of $\{[\mathrm{La}_2(\mathrm{L})_{7.3}(\mathrm{CH}_3\mathrm{OH})(\mathrm{H}_2\mathrm{O})_{0.4}](\mathrm{CF}_3\mathrm{SO}_3)_6\}_\infty$[31] contains two independent eight-coordinate La(III) centers. One is surrounded by eight L molecules, while the other is ligated by seven L molecules and a MeOH molecule. Both adopt tetragonal anti-prismatic La(III) coordination geometries. At each metal center, four of the bridging ligands are used to generate a 4^4-net. The remaining L molecules are all located on the same side of the net linking to a second 4^4-net to give a bilayer motif (Figure 11c). This arrangement affords three- and four-fold bridges from seven- and eight-connected centers, respectively, between the two 4^4-nets.

4^4-Nets can also be identified in three materials derived from eight-connected metal centers that adopt 3-D framework structures, namely, $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{CF}_3\mathrm{SO}_3)_3{\cdot}4.2\mathrm{MeOH}\}_\infty$,[32] $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{ClO}_4)_3{\cdot}\mathrm{MeOH}{\cdot}4\mathrm{CHCl}_2\mathrm{CHCl}_2\}_\infty$,[31] and $\{[\mathrm{Ln}(\mathrm{L})_4](\mathrm{CF}_3\mathrm{SO}_3)_3{\cdot}4\mathrm{MeOH}{\cdot}\mathrm{C}_2\mathrm{Cl}_4\}_\infty$ (Ln = Yb or Eu).[31] In all three compounds, the interlayer bridging molecules L are located equally on opposite sides of the metal center coordination polyhedron. However, they differ in their disposition with respect to the 4^4-net. Furthermore, as noted above, the fact that there are four interlayer bridging L molecules raises the possibility of the presence of independent 2-D networks. Indeed, this leads to a range of structures in which independent 4^4- and 3^6-nets have been identified.


(a)

(b)

FIGURE 14. Schematic representations illustrating the different links between the 4^4-nets in the seven- and eight-connected 3-D networks of (a) $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{BPh}_4)(\mathrm{ClO}_4)_3{\cdot}2.75\mathrm{MeOH}\}_\infty$ and (b) $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{CF}_3\mathrm{SO}_3)_3{\cdot}4.2\mathrm{MeOH}\}_\infty$, which generate 6^3- and 4^4-nets, respectively.

The structure of $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{CF}_3\mathrm{SO}_3)_3{\cdot}4.2\mathrm{MeOH}\}_\infty$[32] is relatively straightforward. Each La(III) center is coordinated in a compressed square anti-prismatic geometry by eight L molecules, which bridge to eight different neighboring La(III) centers forming a 3-D body-centered cubic type framework of $4^{24}6^4$ topology, as in CsCl. Thus, following the description of the structure of body-centered cubic arrays (Figure 3), $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{CF}_3\mathrm{SO}_3)_3{\cdot}4.2\mathrm{MeOH}\}_\infty$ can be described as being formed from parallel 4^4-nets with each center providing four links to four different centers in the two adjacent nets (Figure 14b). As for the body-centered cubic arrays (Figure 3), these four links form an independent series of parallel 4^4-nets aligned at 90° to the original net. This architecture can be compared to that discussed earlier for the seven-connected $\{[\mathrm{La}(\mathrm{L})_4](\mathrm{BPh}_4)$-

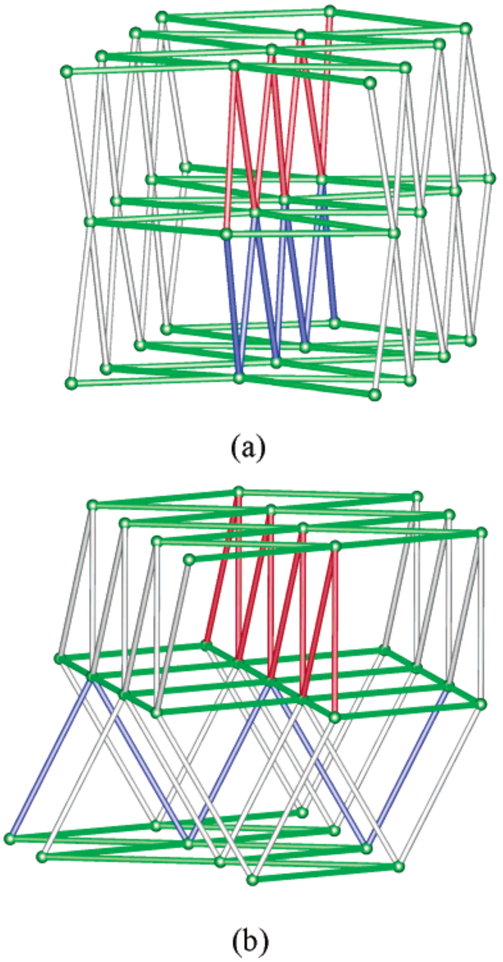


FIGURE 15. Schematic representations illustrating the different links between the 4^4-nets in the eight-connected 3-D networks of (a) $\{[La(L)_4](CF_3SO_3)_3{\cdot}4.2MeOH\}_\infty$ and (b) $\{[La(L)_4](ClO_4)_3{\cdot}MeOH{\cdot}4CHCl_2CHCl_2\}_\infty$.

$(ClO_4)_3{\cdot}2.75MeOH\}_\infty$ [32] compound (section 2.1.4). Thus, replacement of two single bridges by a double bridge results in reduction in the number of links from eight to seven and the conversion of one of the 4^4-nets, each of which requires four connections per La(III) center, with a 6^3-net, which requires just three connections per La(III) center (Figure 14a).

The structures of $\{[La(L)_4](ClO_4)_3{\cdot}MeOH{\cdot}4CHCl_2CHCl_2\}_\infty$ [31] and $\{[Ln(L)_4](CF_3SO_3)_3{\cdot}4MeOH{\cdot}C_2Cl_4\}_\infty$ (M = Yb or Eu)[31] are far more complex. Like the cubic close-packed structure of $\{[La(L)_4](CF_3SO_3)_3{\cdot}4.2MeOH\}_\infty$,[32] the structure of $\{[La(L)_4](ClO_4)_3{\cdot}MeOH{\cdot}4CHCl_2CHCl_2\}_\infty$ comprises a series of 4^4-nets linked by four L molecules, which bridge to four different centers in the two adjacent nets. The difference lies in the disposition of the 4^4-nets (green in Figure 15) and the bridging L molecules, which can be considered to form a pair of zigzag chains (red and blue in Figure 15). Whereas in $\{[La(L)_4](CF_3SO_3)_3{\cdot}4.2MeOH\}_\infty$ [32] the 4^4-nets (Figure 15a) align in the same direction allowing the zigzag chains of bridging L molecules to be coplanar (Figure 15a), in $\{[La(L)_4](ClO_4)_3{\cdot}MeOH{\cdot}4CHCl_2CHCl_2\}_\infty$ the 4^4-nets (Figure 15b) are twisted by some 61.5° with respect to one another. The zigzag chains are now no longer coplanar but are angled such that they bridge both diagonals and the sides of the 4^4-net (Figure 15b) to give a framework structure that contains triangular and pentagonal subunits within a $3^3 4^{15} 5^8 6^2$ topology.

The extended structure of $\{[M(L)_4](CF_3SO_3)_3{\cdot}4MeOH{\cdot}C_2Cl_4\}_\infty$ (M = Yb or Eu)[31] comprises three totally independent nets, two 4^4-nets and a single 6^3-net. The asymmetric unit of this binodal system contains two eight-coordinate metal centers, both of which are surrounded solely by molecules of L. One metal node (A; Figure 16a) is common to the two 4^4-nets (bound to eight ligands L). The other metal center (B; Figure 16b) is common to one 4^4-net (bound to four L ligands) and the 6^3-net (bound to three L ligands), and its coordination sphere is completed by an L molecule that links adjacent 6^3-nets to give a four-connected network of $SrAl_2$ topology (Figure 6). The disposition of the two 4^4-nets is shown in Figure 16a, while that of the interconnected 6^3-nets is shown in Figure 16b. The interlinking of the two 4^4-nets and the interconnected 6^3-nets results in an overall topology of $(3^5 4^{14} 5^9)(3^5 4^{13} 5^{10})_2$, which is shown in Figure 16c.

The structure of the isomorphous lanthanide−pyrazine-*N*,*N*′-dioxide polymers $\{[Ln(L)_4](ClO_4)_3\}_\infty$, (Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, or Y)[34] is based on an eight-connected Ln(III) center. These complexes all essentially have a body-centered cubic-type framework structure analogous to that formed by $\{[La(L)_4](CF_3SO_3)_3{\cdot}4.2MeOH\}_\infty$.[32]

2.2. Inorganic−Organic Hybrid Structures Based on 6^3-Nets. Although three-fold connectivity is the minimum theoretically required for 6^3-net formation, four-fold connectivity is the minimum known to form 6^3-nets for lanthanide−4,4′-bipyridine-*N*,*N*′-dioxide systems. Several isomorphous three-connected compounds based on Ln(III) centers linked by L molecules have been crystallized, including $\{[Er(L)_{1.5}(NO_3)_3]{\cdot}MeOH\}_\infty$,[35] $\{[Tb(L)_{1.5}(NO_3)_3]{\cdot}0.8MeOH{\cdot}0.4C_2Cl_4\}_\infty$,[36] and $\{[Tb(L)_{1.5}(NO_3)_3]{\cdot}MeOH{\cdot}0.8H_2O\}_\infty$.[36] However, instead of forming a simple 2-D 6^3-net, they adopt a more complex 2-D architecture based on a combination of four- and eight-membered rings (Figure 17).

Although not found for lanthanide−4,4′-bipyridine-*N*,*N*′-dioxide systems, a 6^3-net based on three-fold connectivity has been observed in the isomorphous lanthanide−1,2-bis(pyridin-4-yl)ethane-*N*,*N*′-dioxide polymers, $\{[Ln(L)_{1.5}(NO_3)_3]{\cdot}H_2O\}_\infty$ (Ln = Er or Yb).[16] Three such nets, which have a herringbone- or parquet-type pattern, interweave to form a matlike composite layer.

2.2.1. Four-Fold Connectivity. 6^3-Net formation in four-connected compounds normally leads to diamond-type structures (Figure 5). This is the case in the only known example of 6^3-net formation in lanthanide−*N*,*N*′-dioxide systems, $\{[Sc(L)_4(OH_2)_2](ClO_4)_3\}_\infty$,[33] in which each Sc(III) center is coordinated by four L molecules and two water molecules. This network is based upon an equimolar mixture of Sc(III) and hydrogen-bonded centers connected by molecules L, which coordinate at one end to the Sc(III) center and hydrogen-bond at the other end to water molecules to form a four-connected diamond-type subnet based on 6^3-nets (Figure 5a). A view of a

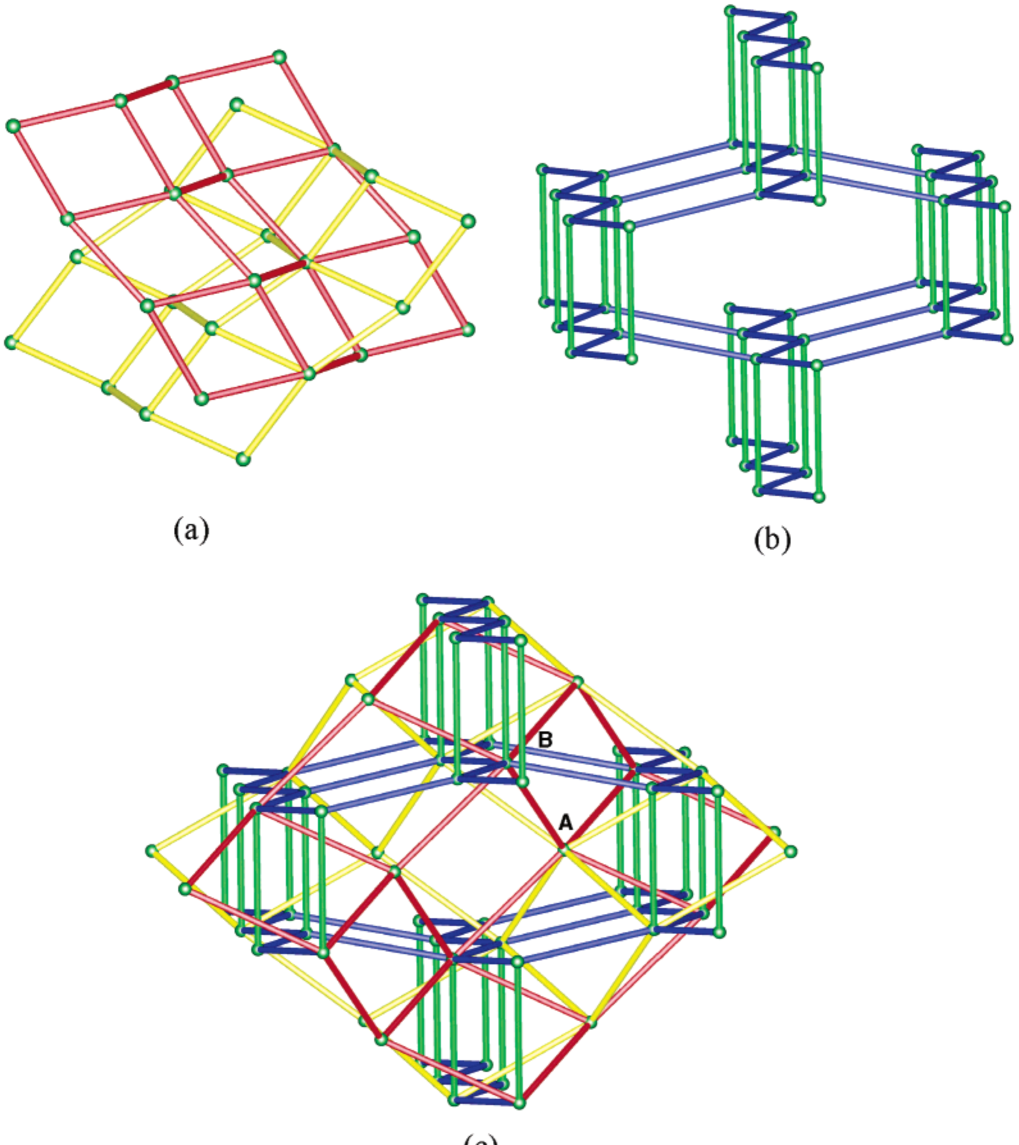


FIGURE 16. Schematic representations illustrating (a) the two 4^4-nets (red and yellow), (b) the interconnected 6^3-nets (intralayer blue, interlayer green), and (c) the interlinking of the two 4^4-nets and the interconnected 6^3-nets in $\{[M(L)_4](CF_3SO_3)_3{\cdot}4MeOH{\cdot}C_2Cl_4\}_\infty$ (M = Yb or Eu). A is the node between the two 4^4-nets, while B is the node between 4^4-nets and 6^3-nets.

6^3-net structure within $\{[Sc(L)_2(OH_2)](ClO_4)_3\}_\infty$ is shown in Figure 18. The diamond-type subnets are linked to form a single 3-D network of 4^86^7 topology (Figure 19).

2.2.2. Five-Fold Connectivity. The potential for bilayer and network formation for five-connected frameworks constructed from 6^3-nets is exactly the same as for six-connected frameworks constructed from 4^4-nets because both systems have the same number (two) of interlayer bridging L molecules. Two networks derived from five-connected metal centers that contain 6^3-nets have been crystallographically characterized.[30] They both contain metal centers containing “blocking” chemical moieties, which results in both interplanar bridging molecules L being located on the same side of the metal center. Alternate metal centers face opposite directions such that the interplanar L molecules are on alternating sides of the net forming a 3-D network. Thus, the interplanar bridging L molecules linking the 6^3-nets in the tetranodal

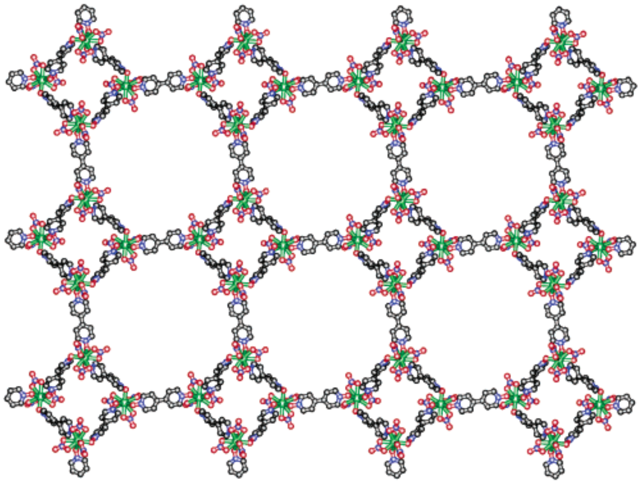


FIGURE 17. A view of the 4^18^2-net structure of $\{[Er(L)_{1.5}(NO_3)_3]{\cdot}MeOH\}_\infty$.

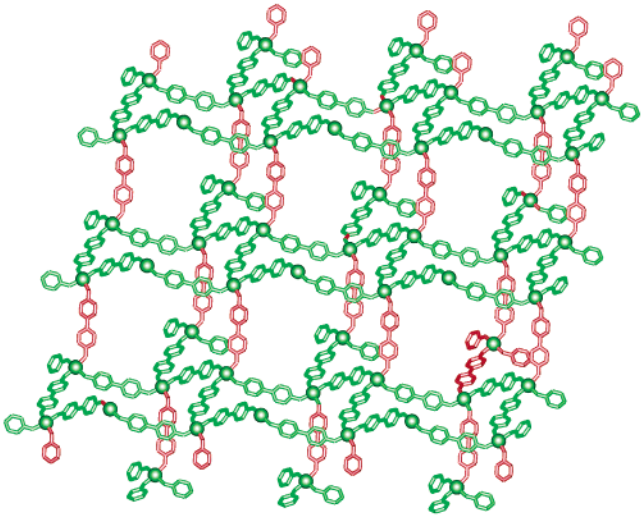


FIGURE 18. A view of the 6^3-net structure within $\{[Sc(L)_2(OH_2)](ClO_4)_3\}_\infty$.

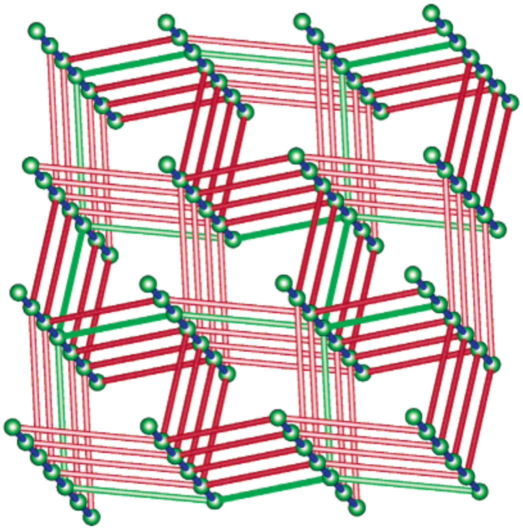


FIGURE 19. Schematic representation illustrating the relationship between the diamondoid-type subnet and oxide bridges in $\{[Sc(L)_2(OH_2)](ClO_4)_3\}_\infty$.

$\{[La_4L_{10}(MeOH)_{10}Cl_3]Cl(BPh_4)_8{\cdot}22MeOH\}_\infty$ [30] align parallel to the (0 0 1) plane and form zigzag chains, which are alternately distributed on either side of the net (Figure 20a). On the other hand, the interplanar bridging L molecules linking the 6^3-nets in the uninodal $\{[LaL_{2.5}(MeOH)\{Ph_2B(OMe)_2\}](BPh_4)_2{\cdot}4.5MeOH\}_\infty$ [30] form zigzag chains, which are arranged such that every pair alternates on opposing sides of the 6^3-nets (Figure 20b). Topologically, the two nets illustrated in Figure 20 may be regarded as isomeric pairs.

2.2.3. Seven- and Eight-Fold Connectivity. Many networks containing 6^3-nets built up from seven- and eight-connected centers can be envisaged. Thus far, however, such lanthanide−*N*,*N*′-dioxide systems are extremely rare, and only two networks containing 6^3-nets, one seven-connected, that in $\{[La(L)_4](BPh_4)(ClO_4)_2{\cdot}2.75MeOH\}_\infty$,[32] and one eight-connected, that in $\{[M(L)_4](CF_3SO_3)_3{\cdot}4MeOH{\cdot}C_2Cl_4\}_\infty$ (M = Yb or Eu),[31] have been reported. Because both networks also contain independent 4^4-nets, their structures have already been considered above. The earlier description of the seven-connected polymer (section 2.1.4) was based on the linking of 4^4-nets by three connections; here the structure is considered to be a series of parallel 6^3-nets with four bridges, two on each side of the net, to adjacent nets (Figure 21). These four bridges form the basis of the independent 4^4-net.

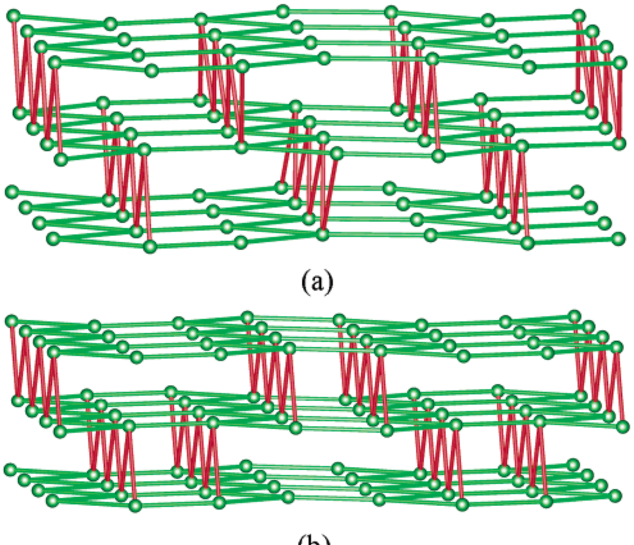


FIGURE 20. Schematic representations illustrating the linking of the 6^3-nets in the five-connected 3-D networks of (a) $\{[La_4L_{10}(MeOH)_{10}Cl_3]Cl(BPh_4)_8{\cdot}22MeOH\}_\infty$ and (b) $\{[LaL_{2.5}(MeOH)\{Ph_2B(OMe)_2\}](BPh_4)_2{\cdot}4.5MeOH\}_\infty$.

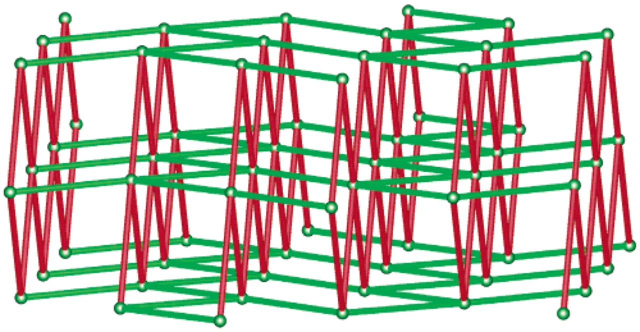


FIGURE 21. Schematic representation illustrating the linking of the 6^3-nets in the seven-connected 3-D network of $\{[La(L)_4](BPh_4)(ClO_4)_3{\cdot}2.75MeOH\}_\infty$. The four bridges give rise to an independent 4^4-net.

The eight-connected polymer $\{[M(L)_4](CF_3SO_3)_3{\cdot}4MeOH{\cdot}C_2Cl_4\}_\infty$ (M = Yb or Eu),[31] which comprises three totally independent nets, two 4^4-nets and a single 6^3-net, has been described earlier (section 2.1.5; Figure 16) and will not be considered in detail here.

3. Discussion and Conclusions

Examples of structurally characterized lanthanide−*N*,*N*′-dioxide coordination polymers are listed in Table 1. Frameworks reported with *N*,*N*′-dioxide ligands other than 4,4′-bipyridine-*N*,*N*′-dioxide, including pyrazine-*N*,*N*′-dioxide, 1,2-bis(pyridin-4-yl)ethane-*N*,*N*′-dioxide, and *trans*-1,2-bis(pyridin-4-yl)ethene-*N*,*N*′-dioxide are also included. All of the structures are delineated in terms of their

Table 1. Crystallographically Characterized Lanthanide−*N,N′*-Dioxide Coordination Polymers Listing (a) Coordination Number, (b) Number of Coordinated of *N,N′*-Dioxide Molecules, (c) Connectivity, (d) Constituent 2-D Nets, and (e) Framework Type (2-D Sheet, 2-D Bilayer, or 3-D Network)

compound[a]	a	b	c	d	e
L = 4,4′-Bipyridine-*N,N′*-dioxide					
$\{[\mathrm{La(L)_2(NO_3)_3}]\}_\infty$ [29]	10	4	4	4^4	sheet
$\{[\mathrm{La(L)_{2.5}(CH_3OH)_2(X)}](\mathrm{BPh_4})_2\cdot 2.7\mathrm{MeOH}\}_\infty$ (X = norbornyl acetate)[29]	9	5	5	4^4	bilayer
$\{[\mathrm{Yb(L)_3}](\mathrm{CF_3SO_3})_3\}_\infty$ [29]	6	6	6	4^4	bilayer
$\{[\mathrm{Sc(L)_3}](\mathrm{X})_3\}_\infty$ (X = $\mathrm{NO_3}$ or $\mathrm{ClO_4}$)[33]	6	6	6	4^4	net
$\{[\mathrm{Sc(L)_3}](\mathrm{CF_3SO_3})_3\cdot 2.7\mathrm{MeOH}\cdot 3\mathrm{H_2O}\}_\infty$ [33]	6	6	6	4^4	net
$\{[\mathrm{La_2(L)_{7.3}(CH_3OH)(H_2O)_{0.4}}](\mathrm{CF_3SO_3})_6\}_\infty$ [31]					
node A	8	7	7	4^4	bilayer
node B	8	8	8		
$\{[\mathrm{Er(L)_5}](\mathrm{I_3})_3\cdot 0.5\mathrm{L}\cdot\mathrm{MeOH}\}_\infty$ [29]	8	8	6	4^4	bilayer
$\{[\mathrm{La(L)_4}](\mathrm{ClO_4})_3\cdot\mathrm{C_6H_5Cl}\cdot\mathrm{CH_3OH}\}_\infty$ [29]	8	8	6	4^4	bilayer
$\{[\mathrm{La(L)_4}][\mathrm{Co(C_2H_{11}B_9)_2}]_3\cdot 0.5\mathrm{MeOH}\}_\infty$ [32]	8	8	6	4^4	net
$\{[\mathrm{La(L)_4}](\mathrm{BPh_4})(\mathrm{ClO_4})_3\cdot 2.75\mathrm{MeOH}\}_\infty$ [32]	8	8	7	4^4	net
$\{[\mathrm{La(L)_4}](\mathrm{CF_3SO_3})_3\cdot 4.2\mathrm{MeOH}\}_\infty$ [32]	8	8	8	4^4	net
$\{[\mathrm{La(L)_4}](\mathrm{ClO_4})_3\cdot\mathrm{MeOH}\cdot 4\mathrm{CHCl_2CHCl_2}\}_\infty$ [31]	8	8	8	4^4	net
$\{[\mathrm{Ln(L)_4}](\mathrm{CF_3SO_3})_3\cdot 4\mathrm{MeOH}\cdot\mathrm{C_2Cl_4}\}_\infty$ (Ln = Yb or Eu)[31]					
node A	8	8	8	$4^4/4^4$	net
node B	8	8	8	$4^4/6^3$	net
$\{[\mathrm{Er(L)_{1.5}(NO_3)_3}]\cdot\mathrm{MeOH}\}_\infty$ [35]	9	3	3	4.8^2	sheet
$\{[\mathrm{Tb(L)_{1.5}(NO_3)_3}]\cdot\mathrm{MeOH}\cdot 0.8\mathrm{H_2O}\}_\infty$ [36]	9	3	3	4.8^2	sheet
$\{[\mathrm{Tb(L)_{1.5}(NO_3)_3}]\cdot 0.8\mathrm{MeOH}\cdot 0.4\mathrm{C_2Cl_4}\}_\infty$ [36]	9	3	3	4.8^2	sheet
$\{[\mathrm{Sc(L)_2(OH_2)}](\mathrm{ClO_4})_3\}_\infty$ [33]	6	4	4	6^3	net
$\{[\mathrm{La_4L_{10}(MeOH)_{10}Cl_3}]\mathrm{Cl(BPh_4)8}\cdot 22\mathrm{MeOH}\}_\infty$ [30]					
node A	8	5	5	6^3	net
node B	8	5	5		
node C	8	5	5		
node D	7	5	5		
$\{[\mathrm{LaL_{2.5}(MeOH)\{Ph_2B(OMe)_2\}}](\mathrm{BPh_4})_2\cdot 4.5\mathrm{MeOH}\}_\infty$ [30]	7	5	5	6^3	net
$\{[\mathrm{La(L)_4}](\mathrm{BPh_4})(\mathrm{ClO_4})_2\cdot 2.75\mathrm{MeOH}\}_\infty$ [32]	8	8	7	6^3	net
$\{[\mathrm{M(L)_4}](\mathrm{CF_3SO_3})_3\cdot 4\mathrm{MeOH}\cdot\mathrm{C_2Cl_4}\}_\infty$ (M = Yb or Eu), node B[31]	8	8	8	$6^3/4^4$	net
$\{[\mathrm{Tb(L)(MeOH)(NO_3)_3}]\}_\infty$ [36]	9	2	2		chain[a]
$\{[\mathrm{Eu(TTA)_3(L)}]\cdot\mathrm{MeOH}\}_\infty$ [37] (TTA = thenoyltrifluoroacetonate)	8	2	2		chain[a]
$\{[\mathrm{La(TFA)_3(L)}]\}_\infty$ [38] (TFA = thenoyltrifluoroacetonate)	8	2	2		chain[a]
$\{[\mathrm{La_2(BTA)_6(L)_{1.5}}]\cdot 1.5\mathrm{H_2O}\}_\infty$ [15] (BTA = benzoyltrifluoroacetonate)	9	3	3		*b*
$\{[\mathrm{Tb(L)_{1.5}(NO_3)_3}]\cdot\mathrm{CH_2Cl_2}\}_\infty$ [36]	9	3	3		ladder[c]
$\{[\mathrm{Tb(L)_2(NO_3)_3}]\}_\infty$ [36]	9	3	2		chain[d]
L = Pyrazine-*N,N′*-dioxide					
$\{[\mathrm{Ln(L)_4}](\mathrm{ClO_4})_3\}_\infty$ (Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, or Y)[34]	8	8	8	$4^4/4^4$	net (bcc)
L = 1,2-Bis(pyridin-4-yl)ethane-*N,N′*-dioxide					
$\{[\mathrm{Ln(L)_3}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}\}_\infty$ (Ln = Er or Yb)[16]	6	6	6	4^4	net (α-Po)
$\{[\mathrm{Ln(L)_{1.5}(NO_3)_3}]\cdot\mathrm{H_2O}\}_\infty$ (Ln = Er or Yb)[16]	9	3	3	6^3	sheet
$\{[\mathrm{La(L)(MeOH)(NO_3)_3}]\cdot\mathrm{MeOH}\cdot\mathrm{CH_2Cl_2}\}_\infty$ [16]	10	3	2		*e*
$\{[\mathrm{Ce(L)_{1.5}(NO_3)_3}]\cdot 0.25\mathrm{CH_2Cl_2}\cdot 0.25\mathrm{H_2O}\}_\infty$ [17]	9	4			*f*
$\{[\mathrm{La(L)_3(OH_2)_2}](\mathrm{CF_3SO_3})_3\}_\infty$ [18]	8	6			*g*
L = *trans*-1,2-Bis(pyridin-4-yl)ethene-*N,N′*-dioxide					
$\{[\mathrm{Er(L)_{0.5}(OH_2)_3(C_2O_4)}](\mathrm{ClO_4})\cdot\mathrm{L}\cdot 6\mathrm{H_2O}\cdot 0.5\mathrm{dioxane}\}_\infty$ [16]	8	1			*h*
$\{[\mathrm{Yb(L)(MeOH)(NO_3)_3}]\}_\infty$ [17]	9	2	2		chain[a]
$\{[\mathrm{Ln(L)_{1.5}(NO_3)_3}]\}_\infty$ (Ln = Ce or Gd)[17]	10	4			*i*

[a] A 1-D chain is formed by two μ_2-bridging *N,N′*-dioxide ligands linking two-connected Ln(III) centers. [b] Each node comprises two $\{\mathrm{La(NO_3)_3}\}$ moieties and is three-connected via three tetradentate μ_4-bridging *N,N′*-dioxide molecules to form a 3-D 10^3-net. Two 10^3-nets are interpenetrated to give the extended structure. This is the only example of a lanthanide−4,4′-bipyridine-*N,N′*-dioxide system in which the ligand acts as a tetradentate μ_4-bridge. [c] A 1-D ladder is formed by three μ_2-bridging *N,N′*-dioxide ligands linking three-connected T-shaped Ln(III) centers. [d] A 1-D chain is formed by two μ_2-bridging *N,N′*-dioxide ligands linking two-connected Ln(III) centers, which are coordinated by a third pendant terminal *N,N′*-dioxide. [e] Each node comprises two $\{\mathrm{La(NO_3)_3}\}$ moieties. Two *N,N′*-dioxide molecules act as tetradentate μ_4-bridging ligands linking two pairs of La(III) centers, while two other *N,N′*-dioxide molecules act as normal bidentate μ_2-bridging ligands linking two La(III) centers to give a 4^4-net. [f] Each node comprises two $\{\mathrm{Ce(NO_3)_3}\}$ moieties. Two *N,N′*-dioxide molecules act as tetradentate μ_4-bridging ligands linking two pairs of Ce(III) centers, while two other *N,N′*-dioxide molecules act as normal bidentate μ_2-bridging ligands linking two Ce(III) centers to give a 4^4-net. Two bidentate μ_2-bridging *N,N′*-dioxide ligands link the 4^4-nets to generate an α-Po-type structure. [g] A 3-D network is formed by an equimolar mixture of μ_2- and μ_3-bridging *N,N′*-dioxide ligands linking La(III) centers. [h] A 4^4-net is formed by an equimolar mixture of *N,N′*-dioxide molecules and oxalate anions linking Er(III) centers. The *N,N′*-dioxide molecules are terminal moieties; one *N*-oxide moiety forms a coordinate bond to the Er(III) center, while the other is hydrogen-bonded to a coordinated water molecule. [i] Each node comprises two $\{\mathrm{Ln(NO_3)_3}\}$ moieties. Two *N,N′*-dioxide molecules act as tetradentate μ_4-bridging ligands linking two pairs of Ln(III) centers, while four other *N,N′*-dioxide molecules act as normal bidentate μ_2-bridging ligands linking just two Ln(III) centers. Thus, the μ_2-bridging ligands act as double bridges to give a 4^4-net structure.

connectivity and interpreted using the 2-D subnet approach. Inspection of the table shows that very few materials cannot be visualized as interconnected 2-D uninodal nets confirming the viability of our approach. Of the three uninodal nets, 3^6, 4^4, and 6^3, no examples of a linked 3^6-net are known in lanthanide−*N,N′*-dioxide materials, reflecting its unusual geometrical arrangement and requirements. Linking 4^4- or 6^3-nets gives rise to two basic framework architectures, 2-D bilayers and 3-D networks. These architectures are constructed by three different arrangements, which depend on just two parameters, (i) the arrangement of the bridging *N,N′*-dioxide ligands around the metal center and (ii) the disposition of the metal centers relative to each other. With the exception of simple 2-D nets and 1-D chains, all of the structures discovered thus far for lanthanide−*N,N′*-dioxide frameworks fall into the two categories of 2-D bilayer or 3-D network structures and can be interpreted in terms of the 2-D subnet strategy. Indeed, we suggest that the vast majority of transition metal based coordination framework structures can be interpreted in this fashion, illustrating the wide applicability of this approach.

For some high connectivity systems, two or more independent nets can be identified. For example, it is possible to envisage a seven-connected system that can be described as a 4^4-net linked by three interlayer bridging *N,N′*-dioxide molecules or as a 6^3-net linked by four interlayer bridging *N,N′*-dioxide molecules. In cases where more than one 2-D subnet occurs, the choice is arbitrary and should depend on the quality of the two nets, which can be interpreted in many ways, (i) the most symmetrical, (ii) the most planar, (iii) the most chemically sensible, or (iv) the best relationship with crystallographic planes. Ultimately, the best choice of the basic 2-D subnet is that which best aids interpretation and visualization of the extended framework structure.

In conclusion, we believe that the approach to the interpretation of complex framework materials described herein is a valuable development to aid understanding of these intricate and, in some cases, highly complex structures. Instead of considering 3-D structures solely in terms of topology via “Schläfli” symbols, our approach allows a simpler and more readily visualized description in terms of 2-D subnet tectons derived, in this case, from 4^4- and 6^3-nets.

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(25) Elements with room-temperature cubic close-packed (face-centered cubic) structures include α-Ca, α-Sr, Al, Pb, α-Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, and α-Th.

(26) Elements with room-temperature body-centered cubic structures include metals α-Li, β-Na, K, Rb, Cs, Ba, V, Cr, α-Mn, α-Fe, Nb, Mo, Ta, W, and Eu.

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