Coordination Networks

Non-Natural Eight-Connected Solid-State Materials: A New Coordination Chemistry**

De-Liang Long, Robert J. Hill, Alexander J. Blake, Neil R. Champness, Peter Hubberstey,* Davide M. Proserpio, Claire Wilson, and Martin Schröder**

Molecular and materials science has provided a wide range of topologies and connectivities in the solid state. The most common nomenclature for such systems has been based[1–3] on the idea of two-, three-, four-, or six-connected materials in one, two and three dimensions.[4–11] Connectivities of five, seven, or higher are extremely rare,[12–14] and recent studies on inorganic/organic hybrid materials, especially in the area of metal–ligand coordination framework polymers, have enriched this area substantially.[15–21] However, highly connected materials remain scarce because the construction of such systems is severely hampered by the available number of coordination sites at the metal centers and the sterically demanding nature of organic ligands. Our design is based upon the combination of high coordination number lanthanide metal centers and 4,4′-bipyridine-*N*,*N*′-dioxide ligands. The latter have flexible angular geometries at the O-donor, are complementary to hard lanthanide metal centers, and, therefore, form highly stable yet sterically flexible complex geometries. The only previously known examples of eight-connected frameworks have body-centered-cubic structures,[22–24] this structure representing the archetypal textbook lattice as found in CsCl. We report herein three unprecedented and unpredicted eight-connected networks that, for the first time, define non-CsCl topologies for eight-connected solid-state materials.

The compounds **1**–**3** have been obtained by slow diffusion of methanolic solutions of $La(CF_3SO_3)_3$, $La(ClO_4)_3$, or $Yb(CF_3SO_3)_3$, respectively, and 4,4′-bipyridine-*N*,*N*′-dioxide (L) in MeOH in a U-tube through a buffering layer of CH_2Cl_2 (for **1**), $CHCl_2CHCl_2$ (for **2**), or C_2Cl_4 (for **3**). Compound **3** can also be prepared by covering the solid metal salt $Yb(CF_3SO_3)_3$ with CH_2Cl_2 or chlorobenzene and carefully layering with a solution of L in MeOH. Single-crystal X-ray structure determinations[25] of **1**–**3** confirm that they all have polymeric structures based on networks of eight-coordinated Ln^{III} nodes linked by bridging L ligands.

$\{[La_2(L)_{7.3}(MeOH)(H_2O)_{0.4}](CF_3SO_3)_6\}_\infty$ **1**

$\{[La(L)_4](ClO_4)_3\}_\infty$ **2**

$\{[Yb(L)_4](CF_3SO_3)_3\}_\infty$ **3**

The asymmetric unit of **1** contains *two* independent La^{III} centers. Although both are eight-coordinate, their coordination spheres are different. One La^{III} center is bound by eight molecules of L, each bridging between the metal center and eight other La^{III} centers. This, therefore, defines an eight-connected node within the structure. The second Ln^{III} center is ligated with a molecule of MeOH and seven molecules of L with each of the latter bridging to seven other Ln^{III} ions. This, therefore, defines a seven-connected node. At each metal center, four of the bridging ligands are used to generate a (4,4) net in which the remaining ligands are sited on the same side of the net linking to a second (4,4) net to give the observed bilayer motif. This affords three- and fourfold bridges from seven- and eight-connected centers, respectively, between the two (4,4) nets (Figure 1) with a tetragonal antiprismatic LaO_8 coordination polyhedron at each metal center. The extended structure of **1** can be represented by the ideal network as shown in Figure 1a. This unique two-dimensional bilayer motif, therefore, comprises two parallel (4,4) square nets displaced such that the nodes of one net lie above the holes of the other with triangular subunits between the two (4,4) nets. Interestingly, such frameworks are commonly used structures in buildings such as the roofs of the IUA Congress Headquarters, London[26] and the roof of The National Theatre in Kuala Lumpur, Malaysia,[27] and are referred to as "square on square offset truss" or "octet truss". The "defects" from the idealized structure in **1** derive from the presence of seven-connected La^{III} nodes with one coordinated MeOH group in place of a bridging L (Figure 1b). Thus, two coordinated MeOH molecules are present on every adjacent pair of seven-

[*] Dr. D.-L. Long, R. J. Hill, Dr. A. J. Blake, Dr. N. R. Champness, Dr. P. Hubberstey, Dr. C. Wilson, Prof. Dr. M. Schröder
School of Chemistry
The University of Nottingham
University Park, Nottingham NG7 2RD (UK)
Fax: (+44) 115-951-3563
E-mail: Neil.Champness@nottingham.ac.uk
Peter.Hubberstey@nottingham.ac.uk
m.schroder@nottingham.ac.uk
Dr. D. M. Proserpio
Dipartimento di Chimica Strutturale e Stereochimica Inorganica (DCSSI)
Università di Milano
Via G. Venezian 21, 20133 Milano (Italy)

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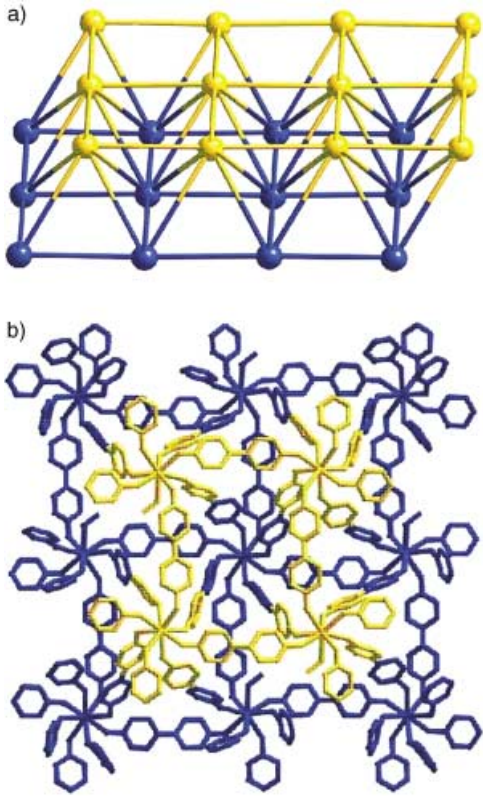

Figure 1. a) An idealized view of the eight-connected bilayer framework of **1**. b) A view of the two (4,4) nets (yellow and blue) in the double layer structure of **1**. Anions are omitted for clarity.

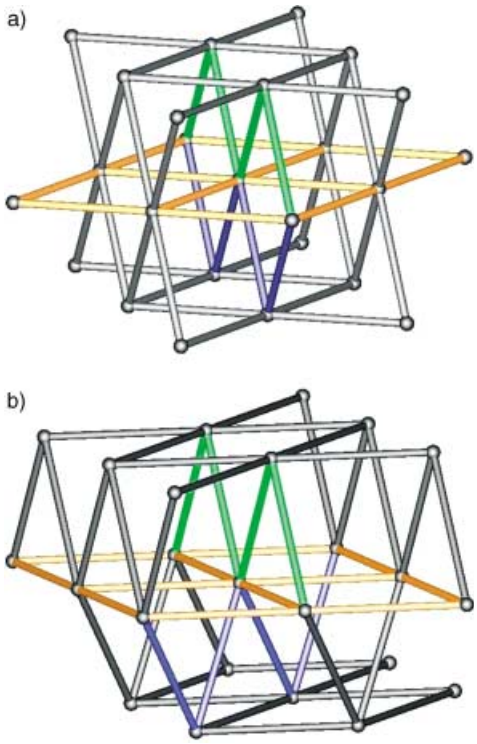

Figure 2. Schematic representations of a) the $4^{24}6^4$ topology in CsCl-type network; b) the three-dimensional eight-connected framework structure of $3^34^{15}5^86^2$ topology in **2**.

connected lanthanum centers, and are separated by a distance equivalent to that required for a bridging molecule of L. To the best of our knowledge, there is no previous example of a double layer eight-connected network. Such a unique topology may only be afforded in coordination compounds in which the flexible organic ligand can adjust to the distorted coordination sphere of the metal ion. In **1**, such flexibility is observed in the < N-O-La angles subtended at the O-donors of the bridging ligands L, which range from 122.9(6) to 147.1(4)°.

The asymmetric unit of compound **2** contains only one unique La^{III} center, which adopts an approximately dodecahedral homoleptic LaO_8 coordination environment. Each La^{III} center is linked to eight adjacent metal centers at distances of 12.9 to 13.7 Å through eight ligands L to form a three-dimensional eight-connected framework structure which is *not* of the familiar CsCl-type. The structure of CsCl consists of tetragonal motifs with $4^{24}6^4$ topology (Figure 2a), while the new structure **2** contains several triangular and pentagonal subunits and exhibits $3^34^{15}5^86^2$ topology (Figure 2). The structures of both CsCl and **2** consist of two parallel (4,4) nets (gray and yellow; Figure 2) cross-linked by zigzag chains. In CsCl the yellow net is displaced only by translation with respect to the gray net, while in **2** it is displaced by translation and by a rotation of 61.5°. Furthermore, in CsCl the zigzag chains (blue and green, Figure 2) are distributed on both sides of a (4,4) net in a parallel fashion, and bridge across the diagonal of the (4,4) net. In **2**, however, the zigzag chains bridge the axial direction of one (4,4) net and the diagonal of the next. Although there are many examples in which coordination framework topology can be directly related to the coordination geometry of the metal-based node,[4] this is not the case in the structures reported here. The fact that the M-O-N angle is flexible removes the rigid nature of what may be considered to be the metal center's extended coordination sphere thereby leading to the absence of a strict metal geometry–topology correlation.

Compound **2** crystallizes in the non-centrosymmetric space group *Cc*, and the large volume within this polar framework accommodates not only ClO_4^- ions but four molecules of $CHCl_2CHCl_2$ and one CH_3OH per metal center, comprising 26.5% of the non-hydrogen atoms in the structure.

The structure of **3** is binodal, each Yb^{III} center being eight-coordinate. The structure consists of layers of puckered and irregular (6,3) nets, each six-membered ring having two opposite angles of 84.6° and four others at 137.5°. Each (6,3) grid (red in Figure 3b) is connected to two adjacent ones (one above and one below) by ligands L perpendicular to the plane of the grid. For each six-membered ring, three of these ligands connect to the grid above and three connect to the grid below. The result is a four-connected subnet of $SrAl_2$ topology;[28,29] this arrangement is further intersected by two sets of (4,4) nets, A and B, (light blue and dark blue, respectively, in Figure 3a), which lie at an angle of 77° to each other and at an angle of 70° to the (6,3) grids. Nets A and B intersect at eight-connected nodes (X in Figure 3b) that lie between the (6,3) layers of the $SrAl_2$ subnet; additionally grids A and B also

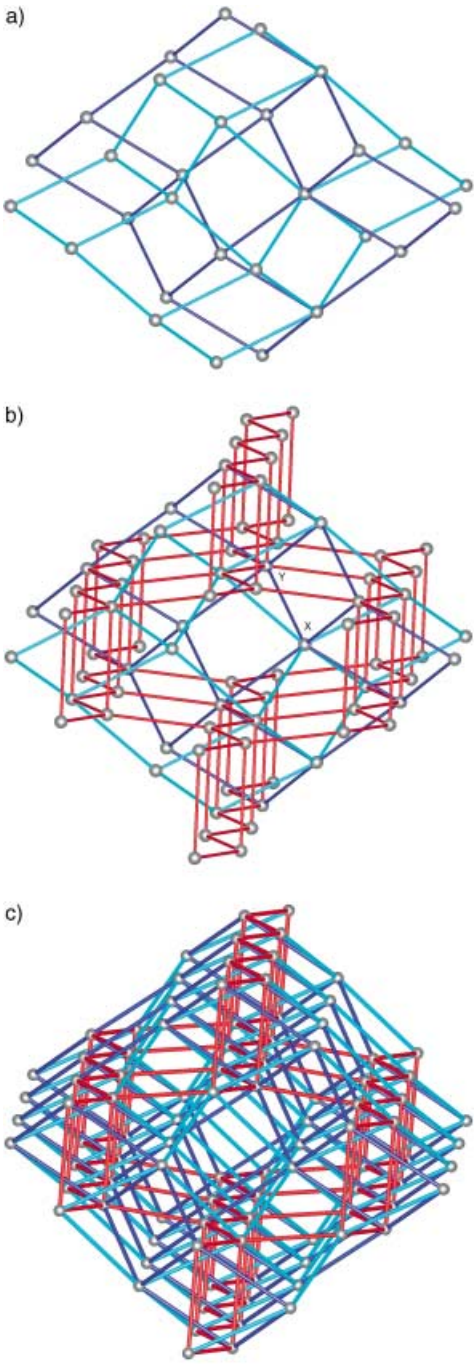

Figure 3. Views of structure and fragments of **3**: a) (4,4) nets; b) interlinking of (6,3) nets and nodes X and Y; c) complete structure. Red: $SrAl_2$ subnet; light blue: (4,4) grid A; dark blue: (4,4) grid B.

intersect the (6,3) nets independently to afford another type of node (Y in Figure 3b). Therefore, in each four-membered grid A or B, there are two opposite corners that intersect at node X with grid B or A, respectively. The other two opposite corners in grids A and B intersect at node Y with the (6,3) grid. Thus, each node Y in the $SrAl_2$ subnet is connected through four ligands within that net and by four ligands to either grid A or grid B. There are, therefore, two distinct eight-connected nodes in **3** with stoichiometry XY_2 of topology $(3^5 4^{14} 5^9)\,(3^5 4^{13} 5^{10})_2$ (Figure 3b).

Significantly, we have prepared an analogue of **3** but with Yb^{III} replaced by Eu^{III}. The structure of the network polymer $[Eu(L)_4]^{3+}$ in **4**[25] is the same as that of **3**, suggesting that a range of related materials might show this topology.

We have demonstrated herein the construction of unique highly connected solid-state materials, and have defined for the first time the structural motifs and topologies that are possible in such materials. Current work seeks to discover and define further topologies and new connectivities within metal–ligand coordination framework materials.

Experimental Section

1: $La(CF_3SO_3)_3{\cdot}x\,H_2O$ (36 mg, 0.05 mmol) and 4,4′-bipyridine-*N*,*N*′-dioxide hydrate (44 mg, 0.2 mmol) were separately dissolved in MeOH (4 mL) and added to the two branches of a U-tube, the bottom of which contained CH_2Cl_2 (4 mL) as a solvent buffer. Colorless crystals appear at the interface between CH_2Cl_2 and the metal salt solution over 10 days. Yield about 30% for **1**; elemental analysis calcd (%) for $C_{82}H_{78.4}F_{18}La_2N_{14.6}O_{39.6}S_6$ {$[La_2(L)_{7.3}(MeOH)(H_2O)_{0.4}](CF_3SO_3)_6{\cdot}3.6\,H_2O{\cdot}2\,MeOH$}: C 36.29, H 2.91, N 7.53; found: C 36.67, H 2.80, N 7.22.

2: Complex **2** was produced by a similar procedure to that for **1** but with $La(ClO_4)_3{\cdot}x\,H_2O$ instead of $La(CF_3SO_3)_3{\cdot}x\,H_2O$ and 1,1,2,2-tetrachloroethane in place of CH_2Cl_2. Yield about 25% for **2**; elemental analysis calcd (%) for $C_{49}H_{44}Cl_{19}LaN_8O_{21}$ {$[La(L)_4]{\cdot}(ClO_4)_3{\cdot}MeOH{\cdot}4\,CHCl_2CHCl_2$}: C 31.08, H 2.34, N 5.92; found: C 31.50, H 2.29, N 6.46.

3: 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (10 mg) and $Yb(CF_3SO_3)_3{\cdot}x\,H_2O$ (32 mg) were separately dissolved in MeOH (20 mL) and added to the two branches of a U-tube in which tetrachloroethylene (5 mL) had been placed. Single crystals of the complex were obtained after a period of 20 days. Alternatively, the compound can be prepared by covering the solid metal salt with dichloromethane then carefully layering a solution of the ligand in MeOH (20 mL) on top. Yield about 20% for **3**; elemental analysis calcd (%) for $C_{49}H_{48}Cl_4F_9N_8O_{21}S_3Yb$ {$[Yb(L)_4](CF_3SO_3)_3{\cdot}4\,MeOH{\cdot}C_2Cl_4$} C 34.8, H 2.7, N 6.8; found: C 34.3, H 2.7, N 7.1.

4: Complex **4** was produced by a similar procedure to that for **3** but with $Eu(CF_3SO_3)_3{\cdot}x\,H_2O$ instead of $Yb(CF_3SO_3)_3{\cdot}x\,H_2O$.

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[25] Crystal data for **1**: $C_{82}H_{78.4}F_{18}La_2N_{14.6}O_{39.6}S_6$, $M_r = 2714.17$, triclinic, $P\bar{1}$ (no. 2), $a = 16.9322(12)$, $b = 18.5089(13)$, $c = 18.7708(13)$ Å, $\alpha = 90.056(1)$, $\beta = 111.528(1)$, $\gamma = 102.210(1)°$, $V = 5328.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.692$ g cm^{-3}, $T = 150$ K, 24140 unique reflections (17751 with $I > 2\sigma(I)$), final $R_1 = 0.062$, $wR_2 = 0.176$. Some pyridine rings were treated with two-component disorder models and refined as rigid groups. Most anions were treated with two-component disorder models. The number of solvent water and methanol molecules are estimated due to their highly disordered presentation, in which partial occupancies were applied. Pyridine H atoms were placed geometrically and refined by using a riding model. No hydrogen atoms were included for disorder regions. The refinement model for compound **1** includes a disorder model in which a ligand L (occupancy 0.60) and a water molecule (occupancy 0.40) share one coordination site on the eight-connected lanthanum node. This site is centrosymmetrically related to itself in the extended framework structure. Crystal data for **2**: $C_{49}H_{44}Cl_{19}LaN_8O_{21}$, $M_r = 1893.38$, monoclinic, Cc (no. 9), $a = 13.520(2)$, $b = 22.575(3)$, $c = 23.688(3)$ Å, $\beta = 103.924(2)°$, $V = 7017.5(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.792$ g cm^{-3}, $T = 150$ K, 8566 unique reflections (7577 with $I > 2\sigma(I)$), final $R_1 = 0.044$, $wR_2 = 0.105$. Hydrogen atoms were placed geometrically and refined by using a riding model. Some 1,1,2,2-tetrachloroethane solvent molecules were treated as two-component disorder models with the occupancy for each component refined. No hydrogen atoms were included in the model for these disorder regions. Crystal data for **3**: $C_{43}H_{32}F_9N_8O_{17}S_3Yb$, $M_r = 1372.98$, triclinic, $P\bar{1}$ (no. 2), $a = 24.0460(9)$, $b = 24.1573(9)$, $c = 24.3834(9)$ Å, $\alpha = 83.861(1)$, $\beta = 61.837(1)$, $\gamma = 61.701(1)°$, $V = 10869.5(7)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.259$ g cm^{-3}, $T = 150$ K, 49683 unique reflections (33722 with $I > 2\sigma(I)$), final $R_1 = 0.103$, $wR_2 = 0.335$. The high final R values are due to large regions, occupied by solvents and anions, which could only be modeled approximately. However, this did not prevent reliable characterization of the cationic framework. Crystal data for **4**: $C_{41.33}H_{32}Cl_{1.67}EuF_4N_8O_{12}S_{1.33}$, $M_r = 1157.3$, triclinic, $P\bar{1}$ (no. 2), $a = 24.1412(12)$, $b = 24.3031(13)$, $c = 24.4706(13)$ Å, $\alpha = 84.434(1)$, $\beta = 61.742(1)$, $\gamma = 61.494(1)°$, $V = 10957.6(10)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.052$ g cm^{-3}, $T = 150$ K, 38458 unique reflections (28037 with $I > 2\sigma(I)$), final $R_1 = 0.107$, $wR_2 = 0.342$. The high final R values are due to the same factors as in the isostructural Yb analogue. For details see Supporting Information. CCDC-216447 (**1**), CCDC-216448 (**2**), CCDC-216449 (**3**), and CCDC-216450 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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