

Lanthanum Coordination Networks Based on Unusual Five-Connected Topologies

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The design and construction of inorganic coordination networks has developed rapidly in recent years.¹ Much attention has been drawn to the rational design of new network topologies, and a variety of extended frameworks has been obtained via the use of polydentate ligands, such as 4,4'-bipyridine and its derivatives, bound to d-block transition metal ions.² Recently, a few examples have appeared of lanthanide-based frameworks employing polydentate ligands such as sulfoxides,³ carboxylates,⁴ pyridones and lactams.^{5,6} Although the flexibility of the coordination sphere of lanthanide ions makes design difficult, this pliability or coordinative ambivalence, coupled with the tendency of lanthanides to adopt high coordination numbers, makes the f-block metal ions attractive for the discovery of new and unusual network topologies. We have recently developed a strategy using 4,4'-bipyridine-*N,N'*-dioxide as a bridging ligand for the construction of lanthanide coordination networks and have reported a CdSO₄-like network and an unprecedented two-dimensional structure of 4.8² topology.⁷ Although these structures are unusual, they exhibit low connectivity, four-fold and three-fold respectively, due to the presence

of coordinating nitrate anions. Therefore, we have developed a strategy to incorporate the noncoordinating BPh₄⁻ anion into lanthanide coordination networks which we anticipated would generate noninterpenetrating frameworks with large internal cavities. We report herein two remarkable lanthanide coordination polymers with unprecedented network structure that were not predicted by Wells,⁸ {[La₄L₁₀(CH₃OH)₁₀Cl₃]Cl(BPh₄)₈·22CH₃-OH}_∞ **1** and {[La_{2.5}(CH₃OH)(Ph₂B(OMe)₂)](BPh₄)₂·4.5CH₃-OH}_∞ **2** (L = 4,4'-bipyridine-*N,N'*-dioxide) consisting of unusual five-connected lanthanum nodes sustained by bridging ligands L. These structures verify that the flexible modes and high coordination of lanthanide ions suit the formation of frameworks with unusual and highly connected nodes.

Compounds **1** and **2** were obtained from the same reaction mixture by mixing methanolic solutions of LaCl₃, NaBPh₄, and L.⁹ **1** was prepared as the major species with a small proportion of crystals of **2** also being isolated. Crystals of both **1** and **2** were found to be unstable in air and decayed quickly via solvent loss. X-ray diffraction studies of **1** and **2** reveal polymeric structures based on networks of eight- and nine-coordinated La(III) centers linked by 4,4'-bipyridine-*N,N'*-dioxide ligands.¹⁰ The asymmetric unit for **1** comprises four independent lanthanum(III) centers, ten 4,4'-bipyridine-*N,N'*-dioxide ligands, four Cl⁻ ions, eight BPh₄⁻ ions, and a number of methanol solvent molecules. All of the La(III) centers act as similar five-connected nodes, although their coordination number and geometry vary. Besides their five *N*-oxide ligands, three La(III) ions are each further coordinated by a Cl⁻ ion and two methanol molecules and have a total coordination of eight, while the fourth La(III) ion is coordinated by four methanol molecules and has a total coordination number of nine, leaving the fourth Cl⁻ ion uncoordinated and engaged in hydrogen-bonding with methanol molecules. The 4,4'-bipyridine-*N,N'*-dioxide ligands bridge the metal centers and support a 3D framework structure of 4⁴6⁶ topology,^{11a} (Figure 1) which can be described by the combination of (6,3) plane nets parallel to the *ab* plane linked through zigzag chains propagating along the crystallographic *a* axis. These linking chains are alternately distributed on either side of the plane nets, thus forming large "six-metal-membered" channels of effective cross-section of ~8 × 18 Å parallel to the *a*-axis. Most of the space within the channels is occupied by the bulky BPh₄⁻ counterions, of which there are 16 per unit cell. However, despite this, the structure contains cavities which are large enough to accommodate 44 methanol molecules per unit cell and account for ~12% of the unit cell volume. Nine methanol molecules form a hydrogen-bonded chain which is terminated at both ends by solvated chloride ions.

In contrast, the asymmetric unit for **2** is quite simple with only one unique La(III) center, which acts as a five-connected node

(8) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977.

(9) Crystals of **1** and **2** were produced as follows: A solution of LaCl₃·6H₂O (0.075 g, 0.2 mmol) and NaBPh₄ (0.210 g, 0.6 mmol) in MeOH (30 cm³) was added dropwise to a solution of 4,4'-bipyridine-*N,N'*-dioxide hydrate (0.110 g, 0.5 mmol) in MeOH (20 cm³), producing a white emulsion-like precipitate, which in turn transformed to a pale yellow crystalline product over 10 h. Almost all the crystals were plate-shaped and were determined to be compound **1**. Elemental analyses are consistent with formula of **1**. A few prism-shaped crystals were selected and determined by X-ray diffraction to be compound **2**. An attempt to prepare **2** quantitatively was unsuccessful.

(10) Crystal data: {[La₄L₁₀(CH₃OH)₁₀Cl₃]Cl(BPh₄)₈·22CH₃OH}_∞ **1**, monoclinic, *Pc*, *a* = 15.134(3) Å, *b* = 47.621(8) Å, *c* = 22.431(4) Å, β = 91.947(2)°, *V* = 16156(8) Å³, *T* = 150 K, *Z* = 2, *R*₁ = 0.091, *wR*₂ = 0.230, *S* = 1.110. {[La_{2.5}(CH₃OH)(Ph₂B(OMe)₂)](BPh₄)₂·4.5CH₃OH}_∞ **2**, orthorhombic, *Pbcn*, *a* = 48.422(7) Å, *b* = 21.958(3) Å, *c* = 15.814(2) Å, *V* = 16814(7) Å³, *T* = 150 K, *Z* = 8, *R*₁ = 0.081, *wR*₂ = 0.192, *S* = 1.147.

(11) The topological symbol refers to the "shortest circuits" formed around the La connecting nodes; thus (a) for **1** the 4⁴6⁶ symbol indicates that four 4-gons and six 6-gons are adopted around each La node, (b) for **2** the 4⁶6²8² symbol indicates that six 4-gons, two 6-gons and two 8-gons are adopted around each La node.

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(1) For recent reviews regarding the development of inorganic coordination networks, see for example: (a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (c) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461. (d) Hargman, P. J.; Hargman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2639. (e) Fujita, M. *Acc. Chem. Res.* **1998**, *32*, 53.

(2) (a) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. (b) Yaghi, O. M.; Li, H.; Groy, T. L. *Inorg. Chem.* **1997**, *36*, 4292. (c) Gudbjartson, H.; Biradha, K.; Poirier, K. M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 2599. (d) Biradha, K.; Domasevitch, K. V.; Moulton, B.; Seward, C.; Zaworotko, M. J. *Chem. Commun.* **1999**, 1327. (e) Real, J. A.; Andres, E.; Munoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265. (f) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. (g) Lin, W.; Evans, O. R.; Xiong, R.-G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13272. (h) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (i) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327. (j) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Chem. Commun.* **1999**, 449. (k) Keller, S. W.; Lopez, S. *J. Am. Chem. Soc.* **1999**, *121*, 6306. (l) Wang, Q.-M.; Guo, G.-C.; Mak, T. C. W. *Chem. Commun.* **1999**, 1849. (m) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem. Eur. J.* **2000**, *6*, 156.

(3) Zhang, R.-H.; Ma, B.-Q.; Bu, X.-H.; Wang, H.-G.; Yao, X.-K. *Polyhedron* **1997**, *16*, 1123.

(4) (a) Reineke, T. M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 4843. (b) Lee, E.; Heo, J.; Kim, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2699. (c) Mao, J. G.; Zhang, H. J.; Ni, J. Z.; Wang, S. B.; Mak, T. C. W. *Polyhedron* **1999**, *18*, 1519. (d) Ma, L.; Evans, O. R.; Foxman, B. M.; Lin, W. *Inorg. Chem.* **1999**, *38*, 5837. (e) Pan, L.; Huang, X.; Li, J.; Wu, Y.; Zheng, N. *Angew. Chem., Int. Ed.* **2000**, *39*, 527. (f) Reineke, T. M.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2590. (g) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651.

(5) (a) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Chem. Commun.* **1997**, 339. (b) Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *Inorg. Chim. Acta* **1998**, *272*, 131.

(6) (a) Doyle, G. A.; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 207. (b) Carrad, L. H.; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Chem. Dalton Trans.* **1993**, 1003. (c) Goodgame, D. M. L.; Menzer, S.; Ross, A. T.; Williams, D. J. *Inorg. Chim. Acta* **1996**, *251*, 141.

(7) Long, D.-L.; Blake, A. J.; Champness, N. R.; Schröder, M. *Chem. Commun.* **2000**, 1369.

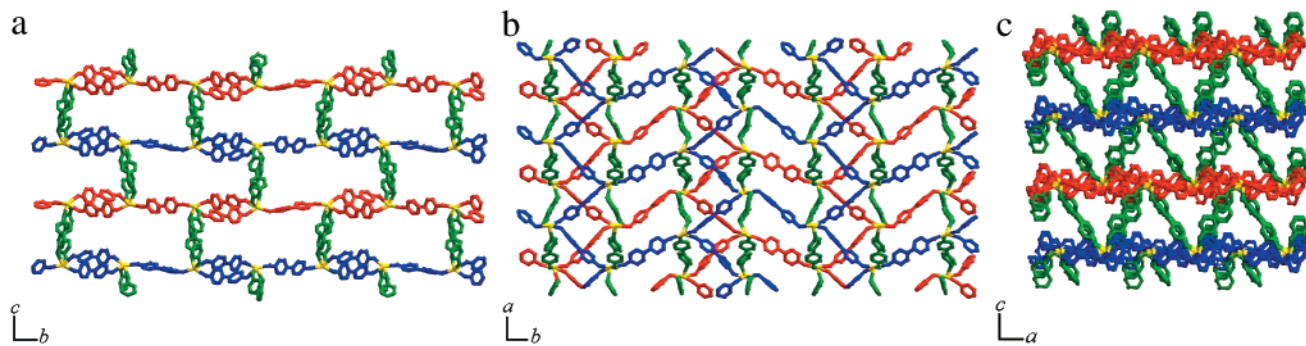


Figure 1. (a) View, along the crystallographic *a* axis, of the “six-metal-membered” channels in compound **1**. Two-dimensional (6,3) nets, viewed “side-on” (red and blue) are interlinked via zigzag chains (green). (b) View along the crystallographic *c* axis in compound **1** showing the (6,3) plane nets (laterally displaced with respect to each other, red and blue) which run parallel to the *ab* plane and are linked via zigzag chains (green) to give the 3D network observed. Similar plane nets are observed in compound **2**. (c) View along the crystallographic *b* axis in **1**, illustrating the zigzag chains (green) linking (6,3) nets.

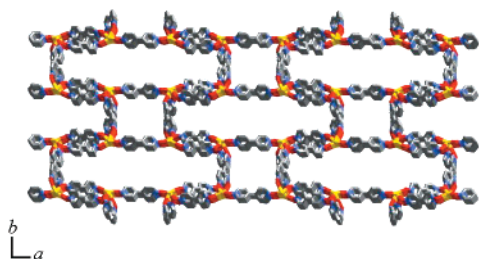


Figure 2. View along the crystallographic *c* axis in compound **2** illustrating the “eight-metal-membered” and “four-metal-membered” channels. BPh_4^- anions, MeOH solvent molecules and hydrogen atoms are omitted for clarity.

as in **1**. Besides the five 4,4'-bipyridine-*N,N'*-dioxide ligands and a methanol molecule, an unusual bidentate $[\text{Ph}_2\text{B}(\text{OMe})_2]^-$ anion was found to chelate the La(III) center. X-ray studies revealed that **2** has a 3-D structure of $4^66^28^2$ topology,^{11b} which is closely related to the 4^46^6 topology found for **1**, both of them having five-connected nodes. If **1** can be considered as consisting of plane nets joined by zigzag chains alternately distributed on opposing sides of the plane nets, then **2** is composed of similar (6,3) plane nets joined by zigzag chains with *every pair* alternating on opposing sides of the plane nets (Figure 2). In contrast to compound **1**, compound **2** has two kinds of channels, namely square “four-metal-membered” and rectangular “eight-metal-membered” ones. These two types of channel have effective cross-sections of $\sim 8 \times 8 \text{ \AA}$ and $8 \times 27 \text{ \AA}$, respectively. As in the case of **1**, most space within these channels is occupied by the bulky BPh_4^- counterions, of which there are 16 per unit cell, with the residual cavities filled by 36 methanol molecules which account for $\sim 11\%$ of the crystal volume.

The $[\text{Ph}_2\text{B}(\text{OMe})_2]^-$ anion originates from the methanolysis of BPh_4^- .¹² This is the first isolation of the intermediate product $[\text{Ph}_2\text{B}(\text{OMe})_2]^-$ from the methanolysis reaction of BPh_4^- under such mild conditions, although the final product $[\text{B}(\text{OMe})_4]^-$ has been observed in $[\text{Cd}\{\text{C}(\text{CN})_3\}\{\text{B}(\text{OMe})_4\}] \cdot 1.6\text{MeOH}$,¹³ and other intermediate products can be envisaged.

Although a large number of examples of three-, or four-connected networks based on d-block metal ions have been reported,¹ to our knowledge there are only two examples of previously known five-connected networks.¹⁴ Both of these structures have Ag(I) metal nodes, one adopting a square-

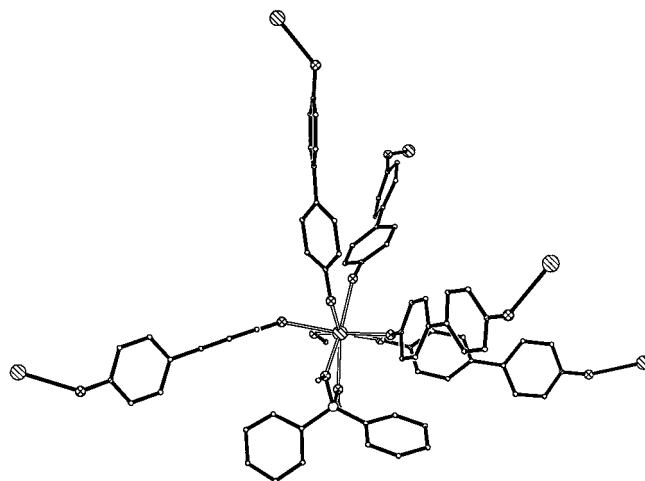


Figure 3. Coordination sphere around the La(III) centers in **2** illustrating the arrangement of the 4,4'-bipyridine-*N,N'*-dioxide ligands that bridge adjacent La(III) nodes. A similar orientation is observed in **1**. Hydrogen atoms are omitted for clarity. (Lanthanum, left-hatched; oxygen, cross-hatched)

pyramidal geometry^{14a} and the other a trigonal bipyramidal geometry,^{14b} as would be expected for five-coordinate transition metal ions. Unlike d-block metal ions, however, lanthanide ions have high coordination numbers, a property that can be employed partially as links to construct networks; furthermore, the geometry of these links is potentially widely variable. The geometry of the five links around the nodes in **1** and **2** cannot be described by any simple polyhedron since three links are coplanar and the other two occupy sites on the *same* side of the plane (Figure 3), unlike a trigonal bipyramidal geometry. It seems unlikely that d-block metal ions could generate such nodes, however distorted their shape. Therefore, it can be seen that lanthanide ions have their own, and inherently more flexible, role to play in producing new coordination frameworks. It is also clear that the anions and ligands will have an important role to play in the construction of highly connected lanthanide-based frameworks. The success in production of unusually connected compounds **1** and **2** indicates a new future direction for the development of coordination networks and the discovery of new topological constructs.

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Supporting Information Available: Numbering schemes, tables of crystallographic data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen positions (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>. JA0030461

(12) (a) Bardwell, D. A.; Jeffery, J. C.; Ward, M. D. *Inorg. Chim. Acta* **1996**, *241*, 125. (b) Bardwell, D. A.; Jeffery, J. C.; Ward, M. D. *Polyhedron* **1996**, *15*, 2019.

(13) Batten, S. R.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 636.

(14) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1895. (b) Batten, S. R.; Hoskins, B. F.; Robson, R. *New J. Chem.* **1998**, *22*, 173.