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Three-Dimensional Helical Coordination Networks of a Hexanuclear Manganese Metallamacrocycle as a Helical Tecton

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We report on helical coordination networks that were prepared using a hexanuclear manganese metallamacrocycle as a helical tecton. We were able to prepare the three-dimensional helical coordination networks using a hexanuclear manganese metallamacrocycle, [$Mn_6(lshz)_6$], as a helical tecton, where *N*-lauroyl salicylhydrazide (H_3lshz) was used as the primary building unit to generate the helical tecton as a secondary building unit. While the $4_1/4_3$ screw symmetry-linked helical coordination network was obtained when the primary building units had an *N*-acetyl group, both the $3_1/3_2$ screw symmetry-linked and the $4_1/4_3$ screw symmetry-linked helical coordination networks were obtained simultaneously in the same batch when the primary building unit had a long alkyl *N*-lauroyl group at the *N*-acetyl site.

The rational design of novel coordination networks is of great interest, because the topology of these networks can be manipulated to influence the properties and functions of the materials.[1] The common strategy for constructing coordination networks relies on the proper programming of building units made up of metal ions and organic ligands for the spontaneous self-assembly of a well-defined structural entity. The most frequently occurring structural motifs in the coordination networks are linear or bent ditopic, triangular tritopic, tetrahedral or square planar tetratopic, and octahedral hexatopic tectons.[2] Various one-dimensional, two-dimensional, and three-dimensional coordination networks have been constructed using these tectons. Among the many coordination networks known, helical coordination networks are of particular interest, owing to their potential utility in chiral separation, asymmetric catalysis, and nonlinear optic applications.[3] Organic and/or metallic tectons can be used to generate one-dimensional and two-dimensional helical coordination networks.[4] However, only a few helical tectons have been utilized for the construction of three-dimensional helical coordination networks.[5]

Many coordination networks constructed from smaller molecular units have been reported. However, coordination networks constructed from nanoscale macrocyclic secondary building units are less common. There has been a report on the construction of a three-dimensional coordination network using a dodecanuclear cadmium metallamacrocycle as the nanoscale macrocyclic secondary building unit.[6] The metallamacrocycle served as a helical tecton, and a bridging exobidentate ligand, 1,2-bis(4-pyridyl)ethene, connected the helical tecton via a $3_1/3_2$ screw symmetry to form the three-

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(1) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658. (b) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305−326. (c) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107−114. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247−289. (e) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714. (f) Bodwin, J. J.; Cutland, A. D.; Malkani, R. G.; Pecoraro, V. L. *Coord. Chem. Rev.* **2001**, *216−217*, 489−512.

(2) (a) Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91−119. (b) Kaes, C.; Hosseini, M. W.; Rickard, C. E. F.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 920−922. (c) Kondo, M.; Okubo, T.; Asami, A.; Noro, S.; Yoshitomi, T.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Seki, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 140−142. (d) Kiang, Y.-H.; Lee, S.; Xu, Z.; Choe, W.; Gardner, G. B. *Adv. Mater.* **2000**, *12*, 767−770. (e) Tadokoro, M.; Nakasuji, K. *Coord. Chem. Rev.* **2000**, *198*, 205−218. (f) Saied, O.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 14956−14957. (g) Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568−2583. (h) Yan, B.; Zhou, H.; Lachgar, A. *Inorg. Chem.* **2003**, *42*, 8818−8822.

(3) (a) Lin, W.; Evans, O. R.; Xiong, R.-G.; Wang, Z.; Wong, G. K. *Angew. Chem., Int. Ed.* **1999**, *38*, 536. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982−986. (c) Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430.

(4) (a) Han, L.; Hong, M.; Wang, R.; Luo, J.; Lin, Z.; Yuan, D. *Chem. Commun.* **2003**, 2580−2581. (b) Cave, G. W. V.; Raston, C. L. *J. Supramol. Chem.* **2002**, *2*, 317−319. (c) Jouaiti, A.; Hosseini, M. W.; Kyritsakas, N. *Chem. Commun.* **2003**, 472−473. (d) Grosshans, P.; Jouaiti, A.; Bulach, V.; Planeix, J.-M.; Hosseini, M. W.; Nicoud, J.-F. *Chem. Commun.* **2003**, 1336−1337. (e) Jaunky, W.; Hosseini, M. W.; Planeix, J. M.; De Cian, A.; Kyritsakas, N.; Fischer, J. *Chem. Commun.* **1999**, 2313−2314. (f) Zhu, L.-G.; Kitagawa, S.; Seki, K. *Chem. Lett.* **2003**, *32*, 588−589.

(5) (a) Seeber, G.; Pickering, A. L.; Long, D.-L.; Cronin, L. *Chem. Commun.* **2003**, 2002−2003. (b) Evans, O. R.; Wang, Z.; Lin, W. *Chem. Commun.* **1999**, 1903−1904. (c) Zhang, L.-J.; Xu, J.-Q.; Shi, Z.; Xu, W.; Wang, T.-G. *Dalton Trans.* **2003**, 1148−1152.

(6) Wang, R.; Hong, M.; Luo, J.; Cao, R.; Weng, J. *Chem. Commun.* **2003**, 1018−1019.

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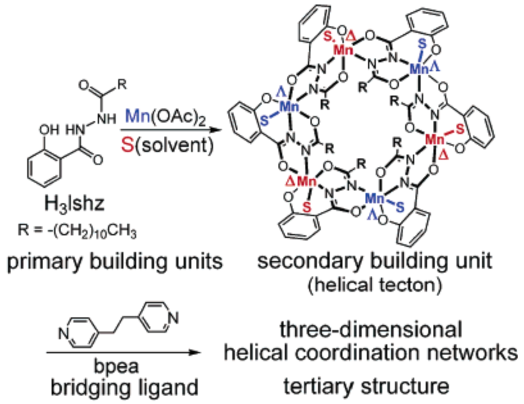
Scheme 1. Schematic Diagram of the Preparation of the Three-Dimensional Helical Coordination Networks[a]



[a] The helical tectons, the secondary building units built from H_3shz and metal ions, are linked via exo-bidentate bpea ligand to form two different tertiary structure three-dimensional helical coordination networks. The three-dimensional helical coordination networks were obtained by substitution of the coordinated solvent molecules of the hexanuclear manganese metallamacrocycle using a bpea.

dimensional helical coordination network. We have also demonstrated the construction of a three-dimensional helical coordination network using a hexanuclear manganese metallamacrocycle as the helical tecton.[7] A new type of metal cluster, a hexanuclear manganese metallamacrocycle, was prepared as a helical tecton using the pentadentate ligand, *N*-acetyl salicylhydrazide (H_3ashz), and manganese ions as the primary building units. In this three-dimensional coordination network, the hexanuclear manganese metallamacrocycle served as a helical tecton, and 1,2-bis(4-pyridyl)-ethane (bpea) connected the helical tecton via a $4_1/4_3$ screw symmetry. The coordination network contains three-dimensional solvent channels, in which the *N*-acetyl side chains are exposed to the channel.

In this study, we have introduced the lauroyl group at the *N*-acetyl group site of the primary building units to modify the hexanuclear manganese metallamacrocycle with a retention of the helical tectonic feature. We have observed the effect of the long alkyl side chain on the formation of the helical coordination network. In contrast to the construction of a three-dimensional helical coordination network using H_3ashz as the primary building unit, a similar preparation using *N*-lauroyl salicylhydrazide (H_3lshz) resulted in two different forms of crystals occurring in the same batch[8] (Scheme 1).

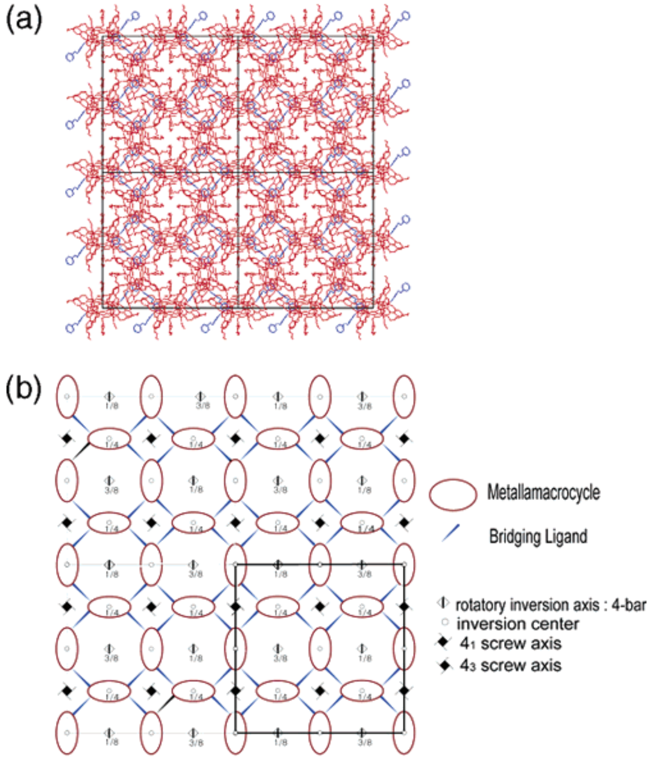


Figure 1. Diagrams of the $[Mn_6(lshz)_6(DMF)_2(bpea)_2]$ network, **1**. (a) A line drawing diagram showing that most of the channel cavities are filled with long alkyl groups. (b) A schematic diagram. Key: red = metallamacrocycle and DMF; blue = bpea.

The crystals with a rectangular morphology had an isostructural helical coordination network architecture, the same as those with H_3ashz.[9] The potential pentadentate ligand, H_3lshz, connected the metal ions via diaza linkages, as shown in Scheme 1, to construct the hexanuclear manganese metallamacrocycle as a secondary building unit. The three-dimensional coordination network, $[Mn_6(lshz)_6(DMF)_2(bpea)_2]$ (**1**), was obtained by substitution of the alternating coordinated solvent molecules of the hexanuclear manganese metallamacrocycle, $[Mn_6(lshz)_6(DMF)_6]$, using a bridging exo-bidentate ligand, bpea. The hexanuclear manganese metallamacrocycle acting as a helical tecton was connected through the bpea linkers via a $4_1/4_3$ screw symmetry, in which the long alkyl side chains of the $lshz^{3-}$ ligands were packed in the solvent channels observed in the $[Mn_6(ashz)_6(DMF)_2(bpea)_2]$ network, leaving only 16 isolated DMF solvent sites per unit cell (Figure 1).

The crystals with rhomboidal morphology had the same helical tecton, but had a completely different helical coor-

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(7) Moon, M.; Kim, I.; Lah, M. S. *Inorg. Chem.* **2000**, *39*, 2710−2711.

(8) $[Mn_6(lshz)_6(bpea)_2(DMF)_2]$, **1**, and $[Mn_6(lshz)_6(bpea)_2(DMF)_2]_3 \cdot [Mn_6(lshz)_6(DMF)_6]$, **2**: A 0.167 g (0.499 mmol) sample of H_3lshz was dissolved in 15 mL of DMF. A 0.046 g (0.250 mmol) sample of bpea was then added to the solution, which was stirred for 5 min. When all the ligands were completely dissolved, a 0.123 g (0.502 mmol) sample of manganese(II) acetate tetrahydrate was added to the solution, without the solution being stirred. The solution was allowed to stand for a week, whereupon a mixture of rectangular and rhombic-shaped dark brown crystals was obtained, 0.217 g, 91% total yield for the mixture. Anal. Calcd for $[Mn_6(lshz)_6(bpea)_2(DMF)_2] \cdot 0.5(DMF)$, **1** ($C_{145.5}H_{207.5}N_{18.5}O_{22.5}Mn_6$) (fw = 2869.46): C, 60.90; H, 7.15; N, 9.03%. Found for **1**: C, 61.06; H, 6.86; N, 9.33%. Anal. Calcd for $[Mn_6(lshz)_6(bpea)_2(DMF)_2]_3 \cdot [Mn_6(lshz)_6(DMF)_6] \cdot 9(H_2O) \cdot 7(DMF)$, **2** ($C_{585}H_{871}N_{79}O_{100}Mn_{24}$) (fw = 11929.33): C, 58.90; H, 7.36; N, 9.28%. Found for **2**: C, 58.70; H, 7.47; N, 9.26%.

(9) Crystal data for $[Mn_6(lshz)_6(DMF)_2(bpea)_2]$, **1**: 0.85 × 0.55 × 0.35 mm^3, dark brown crystals, tetragonal, $I4_1/a$, $a = b = 41.4326(5)$ Å, $c = 17.75560(10)$ Å; $V = 30480.3(5)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.298$ g cm^{-1}, μ(Mo Kα) = 0.553 mm^{-1}, $2\theta_{max} = 48.5°$. R1 = 0.0490 for 10772 reflections of $I > 2\sigma(I)$, R1 = 0.0573, wR2 = 0.1393 for all 12174 reflections. The largest difference peak and hole were 0.574 and −0.380 e·Å^{-3}, respectively. Crystal data for $[Mn_6(lshz)_6(bpea)_2(DMF)_2]_3 \cdot [Mn_6(lshz)_6(DMF)_6]$, **2**: 0.48 × 0.48 × 0.40 mm^3, dark brown crystals, hexagonal, $R3$, $a = b = 51.668(5)$ Å, $c = 20.345(3)$ Å; $V = 47035(10)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.192$ g cm^{-1}, μ(Mo Kα) = 0.533 mm^{-1}, $2\theta_{max} = 50°$. R1 = 0.0818 for 8763 reflections of $I > 2\sigma(I)$, R1 = 0.1401, wR2 = 0.2540 for all 18449 reflections. The largest difference peak and hole were 0.804 and −0.461 e·Å^{-3} respectively.

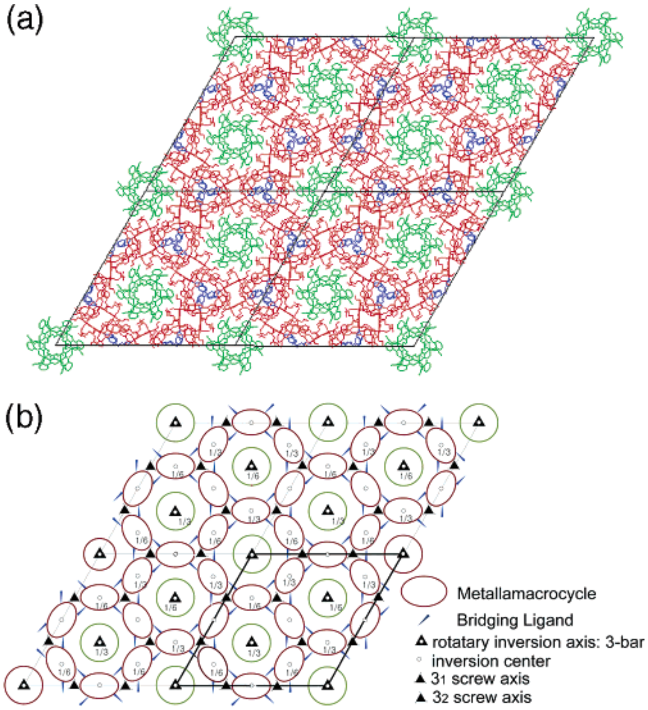

Figure 2. Diagrams of the $[Mn_6(lshz)_6(bpea)_2]_3 \cdot [Mn_6(lshz)_6(DMF)_6]$ network, **2**. (a) A line drawing diagram. (b) A schematic diagram. The one-dimensional channels run parallel to the crystallographic *c*-axis and the nonconnected metallamacrocycles are packed in the channels. Key: red = metallamacrocycle; blue = bpea; green = nonconnected metallamacrocycle.

dination network architecture, $[Mn_6(lshz)_6(bpea)_2]_3 \cdot [Mn_6(lshz)_6(DMF)_6]$, **2**.[9] The hexanuclear manganese metallamacrocycle, $[Mn_6(lshz)_6]$, in the rhomboidal crystal structure, retains the helical tectonic feature observed in the metallamacrocycle, of the helical coordination in network **1** of the rectangular crystal structure. The helical tecton with a noncrystallographic local pseudo-S_6 symmetry was in the crystallographic inversion center. As in network **1**, four of the six solvent sites in the building unit were exchanged with bpea. However, the helical tectons were networked in a different fashion, via a $3_1/3_2$ screw symmetry (Figure 2). This helical network architecture leads to the formation of large, one-dimensional channels of around 2.0 nm in diameter. The hexagonal channels running along the S_6 symmetry sites are parallel to the crystallographic *c*-axis and are occupied by unconnected $[Mn_6(lshz)_6(DMF)_6]$ hexanuclear manganese metallamacrocycles.

Thermogravimetric analysis (TGA) data for network **1** carried out in flowing nitrogen gas indicates a two-stage weight loss. The first weight loss of 1.3% occurs up to 180 °C, and corresponds to the loss of half of the DMF molecules per Mn_6 unit (calcd = 1.27%).[10] The second weight loss of around 80% from 250 to 400 °C is associated with the MnO_2 framework. The TGA data for network **2** show multistage weight losses. The first loss of 1.4% at temperatures up to 70 °C and the second weight loss of an additional 4.2% up to 190 °C correspond to the loss of nine water molecules (calcd = 1.36%), and the loss of seven DMF molecules (calc. = 4.29%) per Mn_{24} unit, respectively. The remaining multistage additional 50+% weight losses occur at $T > 210$ °C.

The crystals of network **1** are diffracting, even after heating the crystals to 180 °C. The crystals of network **2** are also diffracting after drying in air for 1 day. However, these crystals are only weakly diffracting after heating to 180 °C. When both sets of crystals were soaked in various solvents, including DMF and chloroform, they lost their crystallinity, so that it was not possible to check the guest binding inside the channels for these solvents. However, the reintroduction of DMF solvent in the dried crystals of network **2** via vapor diffusion showed a partial recovery of the diffraction intensities.

The magnetic behavior of both networks is very similar to that of the nonconnected hexanuclear manganese metallamacrocycle, $[Mn_6(lshz)_6(DMF)_6]$ ($J = -2.53(3)$ K, and the effective magnetic moment, $\mu_{eff} = 4.9(1)\ \mu_B$, per manganese center (unpublished)). The characteristic magnetic behavior of these networks is antiferromagnetic couplings. The best fit of the data of each network using a Curie–Weiss law gives rise to the exchange parameters between the neighboring centers of $J = -3.06(3)$ and $-2.93(3)$ K, and an effective magnetic moment of $\mu_{eff} = 4.9(1)$ and 5.0(1) μ_B per manganese center for networks **1** and **2**, respectively.

In conclusion, we have constructed a helical coordination network with a hexanuclear manganese metallamacrocycle as a helical tecton. While a $4_1/4_3$ screw symmetry-linked helical coordination network was obtained as the sole product when the primary building unit had an *N*-acetyl group, both a $3_1/3_2$ screw symmetry-linked and a $4_1/4_3$ screw symmetry-linked helical coordination network were obtained simultaneously in the same batch when the primary building unit had a long alkyl *N*-lauroyl group at the *N*-acetyl site.[11] Modification of the metallamacrocycle with retention of the helical tectonic feature resulted in a different coordination network architecture, but the helicity of the coordination network was preserved in a different mode.

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Supporting Information Available: X-ray crystallographic file in CIF format and TGA data for **1** and **2**, and magnetic data in the temperature range 2–300 K for $[Mn_6(lshz)_6(DMF)_6]$, **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The elemental analysis data are in conformity with TGA results.

(11) When the long lauroyl group was introduced as a side chain, the solvent channels that formed from the architecture of network **1** could barely accommodate the long alkyl side chains that may make the stability of network **1** comparable to that of network **2**.