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A Noninterpenetrating Three-Dimensional $4^6 6^9$ Iron(II) Coordination Polymer Built with a Trigonal-Antiprismatic Iron(III) Metalloligand[**]

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Research into three-dimensional (3D) coordination polymers and other relevant materials has been intensively pursued in order to develop their physical properties for use in the fields

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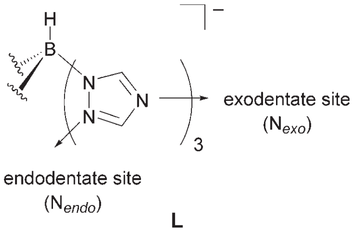
of transport, storage, separation, optics, and magnetism.[1] When manipulating multidimensional coordination polymers, good control over the structure is of great importance, so that the assembled components form the desired architectures.[2] Recently, novel metalloligands have been investigated as a means for controlling the assembly of building blocks by manipulating their structural properties.[3,4] The metalloligand should have a second coordination sphere comprised of *exo*-oriented donor atoms and *endo*-oriented donor atoms that complete the first coordination sphere of an unsaturated transition-metal moiety.[4] The geometric orientation of the second coordination sphere of the metalloligand depends on the preferred geometry of the metal ions and the nature of the ligands bearing the multifunctional groups.

The development of well-designed metalloligands is highly demanding, especially when coordination polymers with specific topologies are desired. To the best of our knowledge, only a few types of metalloligands have been so far been reported (i.e., linear,[3,5] trigonal,[4,6] and square-planar[7]) despite their great potential for fabricating specific topologies. We have focused on synthesizing novel metalloligands and their subsequent incorporation into new functional coordination polymers. Herein we present the novel metalloligand $[\mathrm{Fe^{III}}(\mathbf{L})_2]\mathrm{ClO_4}\cdot 2\,\mathrm{MeCN}$ ($\mathbf{1}\cdot 2\,\mathrm{MeCN}$) as a molecular building block. The noninterpenetrating 3D coordination polymer framework of $[\mathrm{Fe^{II}}(\mathbf{L})_2][\mathrm{Rh_2(OAc)_4}]_3\cdot x\mathbf{S}$ ($\mathbf{2}\cdot x\mathbf{S}$) was characterized by single-crystal X-ray structure analysis (**L** = hydrotris(1,2,4-triazolyl)borate anion, **S** = solvent).[8]

Reaction of K**L**[9] with $\mathrm{Fe^{III}(ClO_4)_3}\cdot x\,\mathrm{H_2O}$ in MeCN yielded orange $\mathbf{1}\cdot 2\,\mathrm{MeCN}$. Six N_{endo} atoms of two **L** complete the first coordination sphere in the terdentate mode. As a result, the iron center adopts a slightly distorted octahedral geometry (Figure 1). The magnetic moment of $\mathbf{1}\cdot 2\,\mathrm{MeCN}$, about 1.5 μ_B in the temperature range 5–300 K, implies that iron(III) is in a low-spin state (the spin-only value of the low-spin d^5 system is 1.7 μ_B). The average $\mathrm{Fe{-}N}_{endo}$ bond length of 1.95 Å is comparable to those of the low-spin $\mathrm{Fe^{III}N_6}$ complexes $[\mathrm{Fe^{III}(phen)_3}](\mathrm{ClO_4})_3$ (phen = 1,10-phenanthroline)[10] (1.974 Å) and $[\mathrm{Fe^{III}(tacn)_2}]\mathrm{Cl_3}\cdot 5\,\mathrm{H_2O}$ (tacn = 1,4,7-triazacyclononane)[11] (1.99 Å). The intrinsic structure of **L** means that the orientation of the lone-pair electrons of the N_{exo} atoms does not coincide with that of the $\mathrm{N}_{endo}{-}\mathrm{Fe^{II}}$ bonds in **1**, and hence the arrangement of the free N_{exo} atoms is not octahedral but trigonal-antiprismatic. Thus, the N_{exo} atoms are located at the vertices of a trigonal-antiprismatic building block. All free N_{exo} atoms can interact with appropriate linkers, such as a transition metal ion or an unsaturated metal complex, to afford a variety of multidimensional coordination polymers. While neutral complexes $[\mathrm{M^{II}}(\mathbf{L})_2]$[9,12] (M = Fe, Co, Ni, Cu, Zn) have similar structural properties to **1**, their use as trigonal-antiprismatic metalloligands suffers from extremely low solubility. On the other hand, metalloligand **1** has the advantage of good solubility in MeCN and $\mathrm{CH_3NO_2}$. Interestingly, in MeCN solution, **1** is easily reduced to the magenta iron(II) species $[\mathrm{Fe^{II}}(\mathbf{L})_2]$, due to the strong reducing power of the borate ligand; similar transformations were observed for $[\mathrm{Fe^{III}(Tp)_2}]^+$ (Tp = hydrotris(pyrazolyl)borate anion).[9] The addition of hydroquinone drastically facilitates the reduction of **1** in MeCN solution. The iron(III) state of **1** is somewhat more stable in the solid state. In short, the facile reduction of **1** and its good solubility make it very useful for assembling $[\mathrm{Fe^{II}}(\mathbf{L})_2]$ moieties as potential spin-crossover sites in a series of coordination polymers that may show unique spin-transition behavior.[12]



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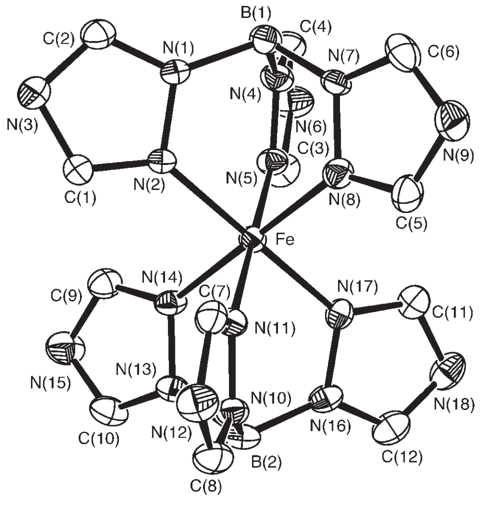

Figure 1. X-ray structure of the $[\mathrm{Fe}(\mathbf{L})_2]^+$ cation in **1**. The $\mathrm{Fe{-}N}_{endo}$ bond lengths range from 1.943(3) to 1.955(3) Å. N_{exo} atoms are at the vertices of a trigonal antiprism.

In pursuit of a novel topology built by trigonal-antiprismatic metalloligand **1**, we obtained the neutral noninterpenetrating 3D coordination polymer $\mathbf{2}\cdot x\mathbf{S}$ (**S** = MeCN and $\mathrm{CHCl_3}$) by reaction of **1** with paddle-wheel-shaped dirhodium tetraacetate ($\mathrm{Rh_2(OAc)_4}\cdot 2\,\mathrm{MeOH}$ or $\mathrm{Rh_2(OAc)_4}\cdot 2\,\mathrm{py}$). Single-crystal X-ray structure analysis revealed that $\mathbf{2}\cdot x\mathbf{S}$ crystallizes in the highly symmetric cubic space group $Ia\bar{3}d$ (No. 230). The framework results from the assembly of a dirhodium complex as a linear spacer[5d,13] and an iron(II) metalloligand acting as a six-connected uninode (Figure 2).

In **2**, the iron center adopts an octahedral geometry with an $\mathrm{Fe{-}N}_{endo}$ distance of 2.007(3) Å, which is somewhat longer than that of **1**. This implies that the iron(III) metalloligand is reduced to $[\mathrm{Fe^{II}}(\mathbf{L})_2]$, which retains its trigonal-antiprismatic geometry. All of the N_{exo} atoms are coordinated to axial sites of dirhodium moieties at a distance of 2.255(4) Å. The topology of **2** is related to a body-centered cubic structure, which has an eight-connected node in view of the occupation of the node in the lattice. If the symmetry was not taken into account, the unit cell of **2** could be considered to be comprised of eight body-centered cubic subunits, of which all lattice points are occupied by $\mathrm{Fe^{II}}$ nodes. If all the connections

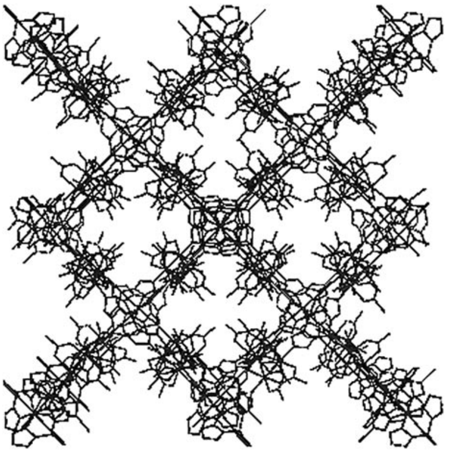

Figure 2. Perspective view of 3D noninterpenetrating framework of **2** along the crystallographic *a*/*b*/*c* axis. Hydrogen atoms are omitted for clarity.

between the nodes were intact, then an eight-connected framework could appear, like that found in CsCl. However, because the Fe^{II} node has six N_{exo} atoms that adopt a trigonal-antiprismatic binding arrangement, two *trans* connections should be omitted from the eight-connected nodes in a manner that preserves the cubic symmetry (Figure 3 a).

Then, the noninterpenetrating 3D framework of **2** is formed, which is composed of six-connected nodes. Each iron(II) center is linked to six adjacent ones at a distance of 15.077(2) Å through two triazole rings of **L** and one $Rh_2(OAc)_4$ unit. The framework of **2** can be defined as $4^6 6^9$ net by considering the iron centers as topological uninodes (Figure 3 b), though the resulting 3D net resembles the α-polonium structure viewed along all the crystallographic axes. To the best of our knowledge, this topology has never been realized before. In general, homogeneous six-connected nodes adopting octahedral geometry afford well-known primitive cubic nets,[14] which allows the α-polonium net to be described as a $4^{12} 6^3$ topology.

The 3D framework of **2** cannot be sustained out of the mother liquor. The XRD pattern of the dried solid collapses due to easy escape of solvent molecules **S** from **2**·*x* **S**, so that we could not determine the exact number of solvent molecules per iron center accommodated within the framework voids. Thus, all contributions of the disordered MeCN and $CHCl_3$ molecules were subtracted from the observed data in the diffraction pattern by using SQUEEZE in PLATON.[15] By this procedure a good framework geometry was obtained.

To inquire into the oxidation state of the iron center in dried solid **2**, we investigated the X-ray absorption structure (XAS) of **1**, **2**, and $[Fe^{II}(\mathbf{L})_2]$[9] at the Fe K-edge (Figure 4). The pre-edge absorption peaks corresponding to the 1s→3d transition provide parameters such as oxidation states, site symmetry, and covalent bond strength.[16,17] The 1s→3d pre-edge feature of **1** is very similar to that of the low-spin $[Fe^{III}(Tp)_2]^+$ complex, in which the $^2T_{2g}$ ground state has a $(t_{2g})^1(e_g)^4$ hole configuration with two allowed one-electron excited configurations (7113.6 eV). This is consistent with the results of magnetic measurements. Consequently, **1** is confirmed as a low-spin iron(III) complex. On the other hand, the single 1s→3d pre-edge absorption peak (7112.8 eV) of **2** appears to be similar to that of low-spin $[Fe^{II}(\mathbf{L})_2]$ (7112.6 eV). This can be assigned as the allowed electric quadrupole transition feature corresponding to the transition

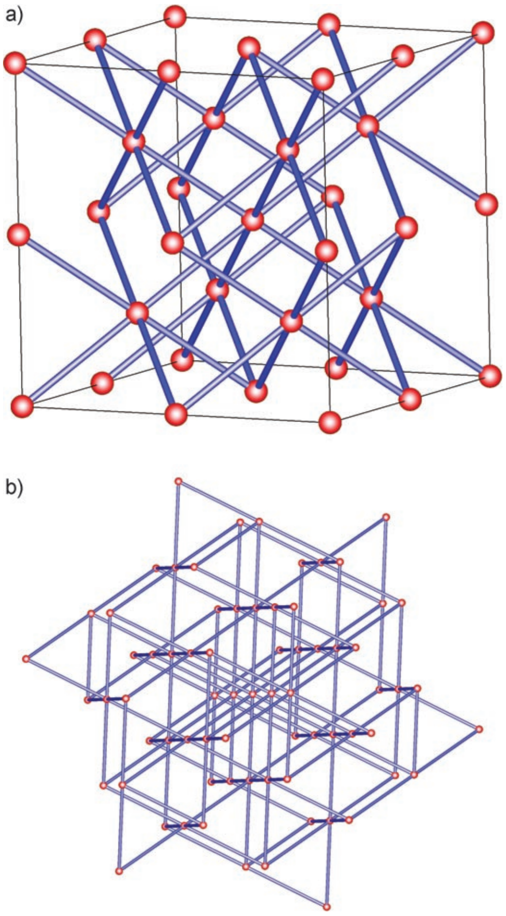

Figure 3. a) Bonding mode of the six-connected Fe^{II} nodes (red spheres) of **2** in the unit cell. b) Schematic representation of 3D noninterpenetrating six-connected framework assigned as $4^6 6^9$ topology in **2**. $Rh_2(OAc)_4$ linear spacers are represented by blue rods.

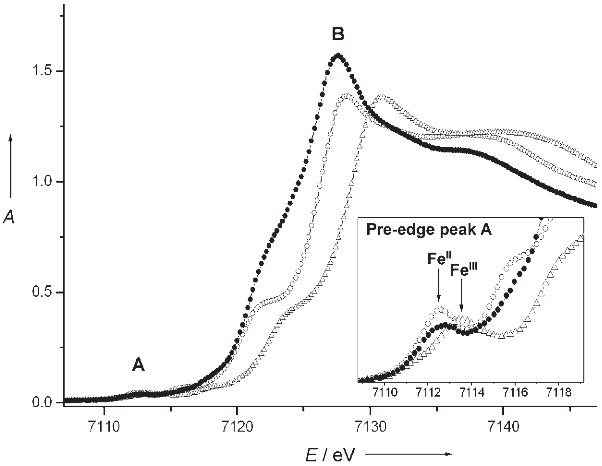

Figure 4. Fe K-edge XANES spectra of **1**·2 MeCN (△), **2** (●), and $[Fe(\mathbf{L})_2]$ (○). The inset shows an expanded view of the 1s→3d transition in the pre-edge region.

from the $^1A_{1g}$ ground state with an electronic hole configuration of $(e_g)^4$ to the ^2E_g excited state with $(e_g)^3$ as a pre-edge feature of a low-spin iron(II) complex.[16] Despite the collapse of the framework, the iron centers are still firmly confined by six N_{endo} atoms, and all N_{exo} atoms are coordinated to dirhodium moieties. This is because the decrease in peak **A** and the increase in peak **B** of **2** in intensity with respect to $[Fe^{II}(\mathbf{L})_2]$ indicate that the local structure around the octahedral iron centers of **2** is more centrosymmetric than that of $[Fe^{II}(\mathbf{L})_2]$, and less 3d–4p orbital mixing occurs.

Variable-temperature magnetic susceptibility measurements revealed that **2** shows an incomplete spin transition. For octahedral iron(II) complexes with an N_6 environment, a spin transition between the high- and low-spin states has been reported.[18] The $\chi_M T$ value expected for a full high-spin iron(II) ion could not be observed within the temperature limits (5–380 K). The spin transition was found to be gradual and incomplete without any thermal hysteresis for both increasing and decreasing temperature, which is the usual observation for mononuclear iron(II) complexes of substituted 1,2,4-triazole ligands.[19] It also is indicative of a lack of "cooperativity" caused by the collapse of the crystal lattice. At the highest temperature (380 K), the $\chi_M T$ value of 1.72 $cm^3 K mol^{-1}$ is much smaller than the theoretical spin-only $\chi_M T$ value of 3.0 $cm^3 K mol^{-1}$ for a high-spin $Fe^{II}N_6$ set.[20] The highest molar fraction of a high-spin state γ_{HS} is estimated to be 0.57. However, below 340 K low-spin states predominate over high-spin states, which corresponds to the finding that the $1s \rightarrow 3d$ pre-edge feature of **2** is very similar to that of the low-spin iron(II) complex $[Fe^{II}(\mathbf{L})_2]$ at ambient temperature. The $\chi_M T$ value decreases gradually, reaching about 0.47 $cm^3 K mol^{-1}$ at 100 K, and remains constant down to 15 K. Below 15 K the $\chi_M T$ value falls, which may be attributed to the zero-field splitting of the residual high-spin state. However, the predominance of a low-spin state at a low temperature is also confirmed by crystallographic evidence: the Fe^{II}–N bond length of 2.007(3) Å in **2** at 150 K is comparable to that of low-spin $[Fe^{II}(\mathbf{L})_2]$ (1.99 Å) rather than with that of high-spin iron(II) complex $[Fe^{II}(Tp^{3,5Me2})_2]$ (2.172 Å, $Tp^{3,5Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate anion).[21]

In summary, we have demonstrated incorporation of trigonal-antiprismatic metalloligand **1** in an unprecedented noninterpenetrating 3D $4^6 6^9$ coordination polymer. The ease of reduction and good solubility of **1**·2MeCN facilitates incorporation of $[Fe^{II}(\mathbf{L})_2]$ as a potential spin-crossover moiety in a 3D net showing spin transition. Taking advantage of **1**·2MeCN as a metalloligand, we are seeking to obtain stable multidimensional coordination polymers in order to establish a correlation of structural properties with magnetic properties.

Experimental Section

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

1·2MeCN: A solution of K**L** (0.512 g, 2 mmol) in methanol (30 mL) was added dropwise to a solution of $Fe(ClO_4)_3 \cdot x H_2O$ (0.354 g, 1 mmol) in MeOH (40 mL). The reaction mixture was stirred vigorously for 4 h. The resultant orange precipitate was separated by filtration and recrystallized from $MeCN/CHCl_3$ to afford orange crystals (0.393 g, 58.7 %). C,H,N analysis (%) calcd for $C_{16}H_{20}B_2ClFeN_{20}O_4$: C 28.71, H 3.01, N 41.85; found: C 28.41, H 2.88, N 42.03; IR (KBr): $\tilde{\nu}$ = 2565 (w, ν_{BH}), 2020 (w, ν_{MeCN}), 1146, 1110, 1086 cm^{-1} (s, ν_{ClO_4}).

2: Method A: A solution of **1**·2MeCN (0.017 g, 0.025 mmol) in MeCN (5 mL) was carefully layered over a solution of $Rh_2(OAc)_4 \cdot 2py$ (0.045 g, 0.075 mmol) in $CHCl_3$ (5 mL) in a test tube. After 2 d, red crystals of **2**·x**S** had separated, which lost their crystallinity once out of the mother liquor (0.043 g, 47.4 %). C,H,N analysis (%) calcd for $C_{36}H_{50}B_2FeN_{18}O_{24}Rh_6$ (vacuum-dried solid): C 23.84, H 2.78, N 13.90; found: C 24.01, H 2.55, N 14.37; IR (KBr): $\tilde{\nu}$ = 2528 cm^{-1} (w, ν_{BH}).

Method B: A solution of **1**·2MeCN (0.034 g, 0.05 mmol) in MeCN (5 mL) was carefully layered in a test tube with a solution of $Rh_2(OAc)_4 \cdot 2MeOH$ (0.076 g, 0.15 mmol) in $MeCN/CHCl_3$ (4:1, 5 mL). Red crystals separated after 2 d.

Fe K-edge X-ray absorption spectra were recorded on the Electrochemistry beam line (BL7C1) of the Pohang Accelerator Laboratory (PAL) with a ring current of 120–170 mA at 2.5 GeV. An Si(111) monochromator crystal was used, detuned to 85 % in intensity, to eliminate high-order harmonics. The data were collected in transmission mode with gas-filled (85 % N_2, 15 % Ar) ionization chambers as detectors. Energy calibration was carried out for all measurements by placing Fe foil in front of the third ion chamber and thus assigning the first inflection point to 7112 eV.

Magnetic measurements on a vacuum-dried sample of **2** were carried out with a Quantum Design MPMS-5 SQUID magnetometer in the temperature range 5–380 K at the Korean Basic Science Institute (KBSI) with an applied magnetic field of 0.5 T. Molar susceptibilities χ_M were corrected for diamagnetic contributions χ_D, that is, -246.44×10^{-6} $cm^3 mol^{-1}$ for **1**·2MeCN and -353.44×10^{-6} $cm^3 mol^{-1}$ for **2**.[22]

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[8] Crystal data for **1**·2 MeCN: $C_{16}H_{20}B_2Cl_3FeN_{20}O_4$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.7139(2)$, $b = 12.412(2)$, $c = 25.618(5)$ Å, $V = 2770.8(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.605$ g cm^{-1}, $\mu = 0.707$ mm^{-1}, $T = 233(2)$ K, 14766 reflections were recorded of which 5161 were unique ($R_{int} = 0.0467$). All hydrogen atoms were placed in idealized positions, and all other atoms were refined anisotropically by a full-matrix least-squares method on F^2 to give $R1 = 0.0421$ ($I > 2\sigma(I)$), $wR2 = 0.0744$, GOF = 0.975, max./min. residual electron density 0.325/–0.407 e Å^{-3}, Flack parameter 0.038(2). Crystal data for **2**·*x* **S**: $C_{36}H_{50}B_2FeN_{18}O_{24}Rh_6$ (including only well-ordered atoms), cubic, $Ia\bar{3}d$ (no. 230), $a = 34.8205(6)$ Å, $V = 42218.7(1)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.141$ g cm^{-1}, $\mu = 1.100$ mm^{-1}, $T = 150(1)$ K, 27878 reflections were recorded, of which 3119 were unique ($R_{int} = 0.043$). Disordered model crystallographic refinement converged at $R1 = 0.1101$ and $wR2 = 0.2828$ ($I > 2\sigma(I)$). After subtracting the contribution of all disordered solvent molecules to the diffraction pattern from the observed data by SQUEEZE in PLATON, final $R1 = 0.0409$ and $wR2 = 0.1149$ ($I > 2\sigma(I)$), GOF = 1.094, and max./min. residual electron density 0.589/–0.453 e Å^{-3} were obtained. CCDC-220728 and -220729 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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