

Coordination Networks with Fluorinated Backbones

Ye Gao, Brendan Twamley, and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83843-2343

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Fluorine-containing ligands 2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-yl-methyl)benzene (**1**) and 2,3,5,6-tetrafluoro-1,4-bis(2-methylimidazol-1-yl-methyl)benzene (**2**) were prepared and coordinated with AgNO_3 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, respectively, to form the following structures: 3D channel polymer $[\text{Ag}_2(\mathbf{1})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{MeOH}]_n$ (**3**), 2D sheet polymer $[\text{Co}(\mathbf{1})_3(\text{ClO}_4)_2]_n$ (**4**), 1D chain polymer $[\text{Cd}(\mathbf{1})_3(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]_n$ (**5**), and a 2D herringbone sheet polymer $[\text{Ag}(\mathbf{2})\text{NO}_3 \cdot 1.5\text{MeOH}]_n$ (**6**). The solid-state crystal structures of **3–6** were studied by single-crystal X-ray crystallography.

Introduction

Considerable growth in the area of coordination polymers has occurred over the past several years.^{1,2} Because the ligands used to bridge metal centers have become more complex, the derived networks display a wonderful diversity in both structure and properties. In general, the multiple coordination sites of the longer-chain ligands with the metal ion may form structures of higher dimensions with various sizes and shapes of cavities or channels in the assembly. By careful design of tailored ligands, various novel supramolecular architectures have been constructed. However, it is becoming increasingly evident that, despite continuous efforts to understand molecular structure and topology, the control and the challenge of predicting coordination networks have not been reduced.

A particularly promising class of ligand, where two imidazole units are interconnected by chains or groups of different types, has been explored to form open frameworks.³ 1,4-Bis(imidazol-1-yl-methyl)-benzene⁴ (bix), which has comparatively longer linkers, was a good candidate for the formation of novel supramolecular architectures. This ligand

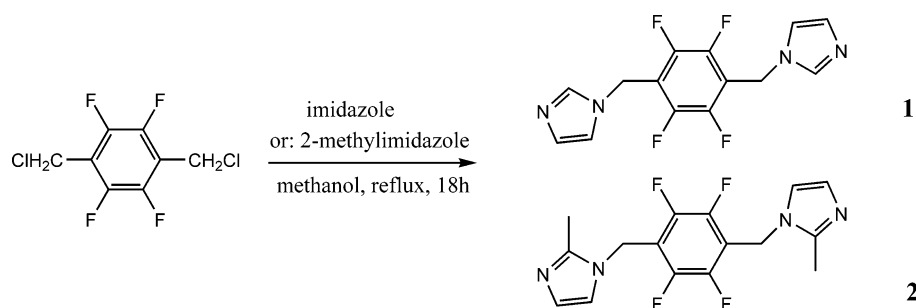
formed ordered, open networks defined by metal coordination geometries but also frequently suffered from the phenomenon of interpenetration and supramolecular isomerization^{4a–4c} leaving no void space in the solid for enclathrating guests. One strategy was to design programmed organic ligands that prevent this interpenetration.⁵ This was achieved by introducing substituents on the bix ligand.⁶ By using electron-deficient coordinated imidazolium groups and replacing electron-rich phenylene with electron-deficient tetrafluorophenylene, the resulting flexible networks are unlikely to be constricted or interpenetrated, but, because of the weak intermolecular interactions in fluorine-containing compounds, may prefer to interact with guest molecules to form clathrate compounds.^{7,8}

* To whom correspondence should be addressed. E-mail: jshreeve@uidaho.edu.

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Scheme 1

**Table 1.** Crystallographic Data and Refinement Parameters for **3–6**

	3	4	5	6
formula	C ₂₉ H ₂₆ Ag ₂ F ₈ N ₁₀ O ₈	C ₄₂ H ₃₀ Cl ₂ CoF ₁₂ N ₁₂ O ₈	C ₄₂ H ₃₈ CdF ₁₂ N ₁₄ O ₁₀	C _{17.50} H ₂₀ AgF ₄ N ₅ O _{4.50}
fw	1010.34	1188.61	1239.26	556.26
<i>T</i> (K)	86(2)	86(2)	87(2)	87(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P2</i> (1)/ <i>n</i>	<i>Cc</i>	<i>P1</i>	<i>C2/c</i>
size (mm ³)	0.31 × 0.17 × 0.15	0.39 × 0.19 × 0.02	0.35 × 0.25 × 0.12	0.28 × 0.14 × 0.08
<i>a</i> (Å)	5.8598(4)	13.6994(10)	10.2250(5)	17.5825(8)
<i>b</i> (Å)	13.2926(9)	23.8843(17)	11.5836(6)	10.6000(5)
<i>c</i> (Å)	24.0817(17)	15.1402(11)	12.1961(6)	23.1545(11)
α (deg)	90	90	103.944(1)	90
β (deg)	91.763(1)	103.591(1)	103.595(1)	105.410(1)
γ (deg)	90	90	112.743(1)	90
<i>V</i> (Å ³)	1874.9(2)	4815.2(6)	1202.80(10)	4160.3(3)
<i>Z</i>	2	4	1	8
<i>D_c</i> (Mg m ⁻³)	1.790	1.640	1.711	1.776
μ (mm ⁻¹)	1.145	0.580	0.574	1.043
<i>F</i> (000)	1000	2396	624	2232
reflns total	28 016	31 442	13 505	31 798
reflns indep.	3360 [R(int) = 0.0000]	8708 [R(int) = 0.0531]	4363 [R(int) = 0.0193]	3766 [R(int) = 0.0387]
data/restraints/params	3360/18/271	8708/38/760	4363/0/358	3766/1/297
index ranges	−7 ≤ <i>h</i> ≤ 7, 0 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 28	−16 ≤ <i>h</i> ≤ 16, −28 ≤ <i>k</i> ≤ 28, −18 ≤ <i>l</i> ≤ 18	−12 ≤ <i>h</i> ≤ 12, −13 ≤ <i>k</i> ≤ 13, −14 ≤ <i>l</i> ≤ 14	−21 ≤ <i>h</i> ≤ 21, −12 ≤ <i>k</i> ≤ 12, −27 ≤ <i>l</i> ≤ 27
R1, wR2, <i>I</i> > 2σ(<i>I</i>) ^a	0.0493, 0.1125	0.0504, 0.1065	0.0345, 0.0988	0.0339, 0.0744
GOF on <i>F</i> ²	1.070	1.031	1.014	1.077
Δρ _{min} and Δρ _{max} (e Å ⁻³)	1.257 and −1.239	0.557 and −0.382	1.606 and −0.532	0.640 and −0.763

^a R1 = Σ|*F_o* − |*F_c*|/Σ|*F_o*|; wR2 = {Σ[w(*F_o*² − *F_c*²)²]/Σ[w(*F_o*²)²]}^{1/2}.

In this paper, we report two fluorine-containing bix (Fbix) ligands 2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-yl-methyl)benzene (**1**) and 2,3,5,6-tetrafluoro-1,4-bis(2-methylimidazol-1-yl-methyl)benzene (**2**). The resultant non-interpenetration polymeric complexes formed by coordination of these ligands with metal salts, e.g., AgNO₃, Co(ClO₄)₂·6H₂O, Cd(NO₃)₂·4H₂O, are reported, as well as their solid-state structures.

Results and Discussion

The syntheses of the fluorinated ligands are relatively straightforward. **1** and **2** were prepared by reacting 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene with imidazole (2-methylimidazole) in methanol (Scheme 1).

Polymeric complexes **3–6** are obtained by reacting ligands **1** and **2** with the metal salts AgNO₃, Co(ClO₄)₂·6H₂O, and Cd(NO₃)₂·4H₂O, respectively. Crystal data and refinement parameters for complexes **3–6** are listed in Table 1.

Structure of [Ag₂(1**)₂(NO₃)₂·H₂O·2Methanol]_{*n*} (**3**).** In the nonfluorinated analogue of **3**, each ring is interpenetrated by another polymer chain, forming a rotaxane structure.^{4b} The fluorination of the bix ligand and subsequent reaction with AgNO₃, yields a different structure—a nanotubular motif

of metallorganic rings held together by interactions with the anion (H-bonding and Ag···O intermolecular contacts). Two ligands of **1** bridge two Ag centers (Ag–N, 2.140(5), 2.141(5) Å; Ag–N, 2.140(5), 2.141(5) Å; N(7)–Ag(1)–N(8), 166.53(18)°) which resulted in a bimetallic ring as the basic building block (Figure 1a). The ligands are in an eclipsed conformation. The exo channel nitrate groups link these units together via weak hydrogen bonding between adjacent methylene carbons in ligand **1** in another ring with the nitrate group (bifurcated C–H···O interactions with distances ca. 3.01 Å, see Figure 1b). There are also intermolecular Ag···O contacts of 2.84 and 2.97 Å between each ring Ag and the nitrate group, forming a double chelation of the NO₃[−] group. These interactions are within the sum of the Ag/O van der Waals radii (3.24 Å) but much longer than the covalent Ag–O bond length (ca. 2.4 Å); however, they are similar to other doubly chelated NO₃[−]/Ag systems (Ag···O 2.63–3.1 Å).⁹ They are shorter

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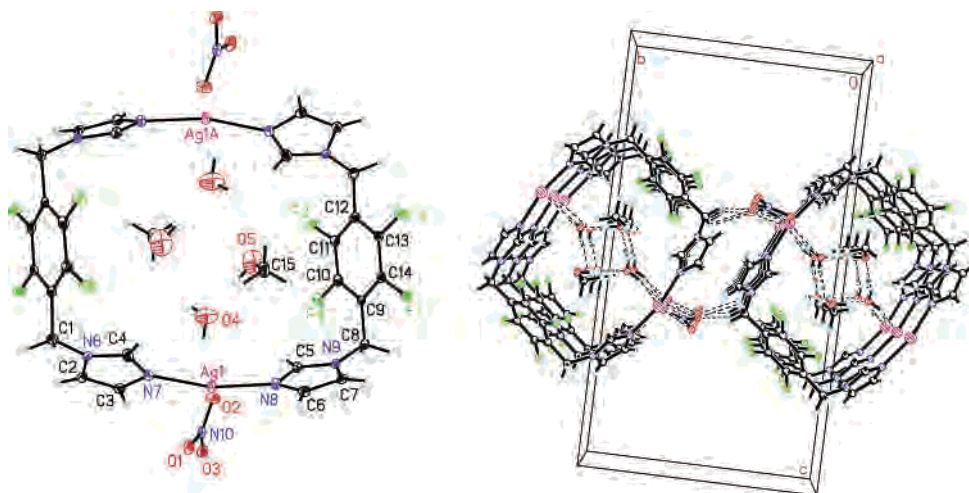


Figure 1. (a) Thermal ellipsoid (30%) plot of one $\text{Ag}_2(\mathbf{1})_2$ bimetallic ring. (b) Side view of the packing of complex **3**, showing the 3D framework and channels.

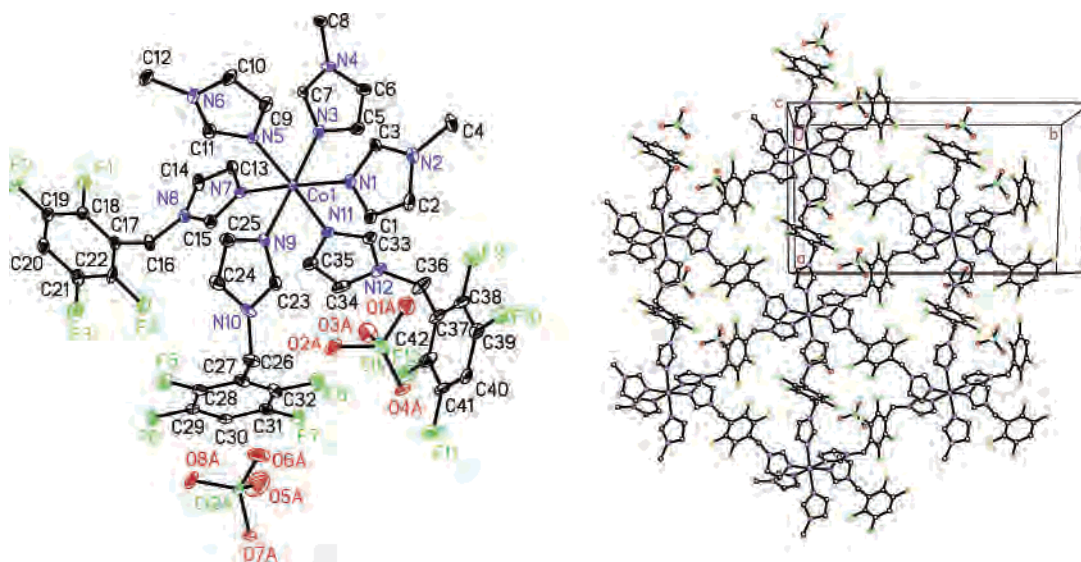


Figure 2. (a) Thermal ellipsoid (30%) plot of **4** with the atom numbering scheme. Hydrogen atoms are omitted for clarity. (b) Stacked layers in the ab plane, showing the triangular voids. Perchlorate anions have been omitted for clarity.

than the nonfluorinated analogue (2.92–3.16 Å).^{4b} This synthon forms a connective scaffolding between all the hollow bimetallic rings. The endo ring Ag–Ag distance is 8.84 Å, and the exo ring Ag–Ag distance is 5.86 Å. The angle between the silver centers in adjacent rings (angle formed by the endo–endo–exo Ag centers) is 80.7°, indicating that each tube has a ca. 10° tilt. The endo ring Ag–Ag distance is shorter than in the bix analogue (10.50 Å). This reflects the major structural difference found between **3** (Fbix) and the bix analogue. As found in **3**, the ring channel accommodates only reaction solvents (water, methanol) which do not strain the shape of the ring. The water molecule is half occupied and forms hydrogen bonds to both the Ag center (Ag–H, 2.95 Å) and the methanol (O4···O5, 2.76 Å).

Structure of $[\text{Co}(\mathbf{1})_3(\text{ClO}_4)_2]_n$ (4**).** The reaction of **1** with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ yields the coordination polymer **4** (Figure 2a). Each Co center is octahedrally coordinated by six fluorinated bix ligands (Co1–N5, 2.151(4); Co1–N11, 2.146(4); Co1–N3, 2.154(4); Co1–N1, 2.152(4); Co1–N7,

2.178(4); Co1–N9, 2.200(4) Å; N(5)–Co(1)–N(11), 176.59(16); N(1)–Co(1)–N(7), 176.58(18); N(3)–Co(1)–N(9), 176.14(17)°) and form a sheet network parallel to the ab plane (Figure 2b). The charge is balanced by perchlorate anions that occupy the pseudo-triangular voids (formed by three neighboring Co(II) ions) and are situated between the sheets. Using ligand **1** in this case does not result in an open α -polonium extended network as seen in the nonfluorinated analogue,^{4c} and each void is encapsulated by the next sheet. The Co–Co distance across the ligand bridge is 13.76 Å, (nonfluorinated analogue, 13.55 Å),^{4c} and the interchain Co–Co distance between layers is 8.16 Å.

The magnetic susceptibility (χ_M) of **4** was measured at 25 °C. The $\chi_M T$ value is 3.31 cm³ mol^{−1} K^{−1} which is significantly less than the spin-only value of 4.37 cm³ mol^{−1} K^{−1} for Co^{II} ($s = 5/2$). The value for the bix species is 5.05 cm³ mol^{−1} K^{−1} at 25 °C.^{4e} The magnetic moment (μ_{eff}) is 5.19 μ_B , which places it in the high-spin octahedral category with very high orbital contributions.

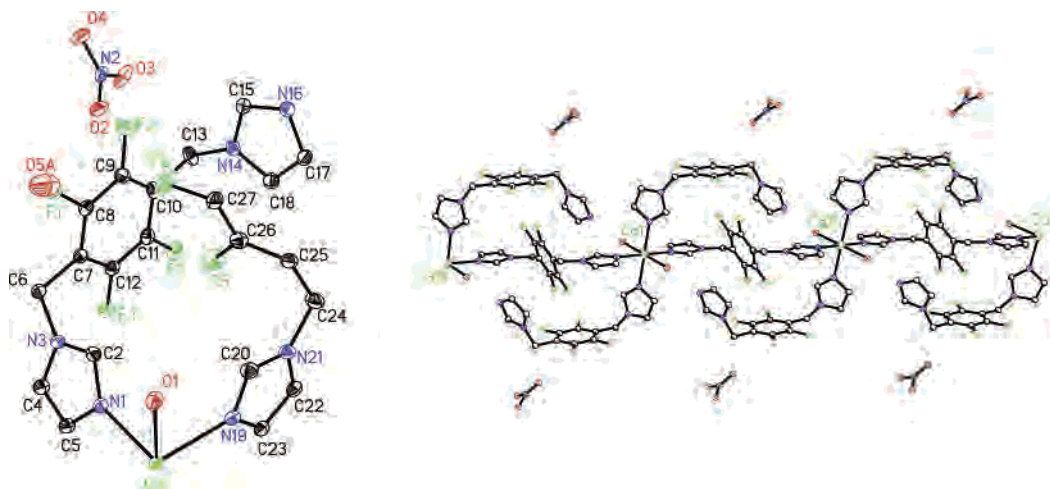


Figure 3. (a) Thermal ellipsoid (30%) plot of the asymmetric unit in **5** with the atom numbering scheme. (b) A ball-and-stick packing diagram of **5** viewed parallel to $[0 -1 2]$. Hydrogen atoms and most atom labeling are omitted for clarity.

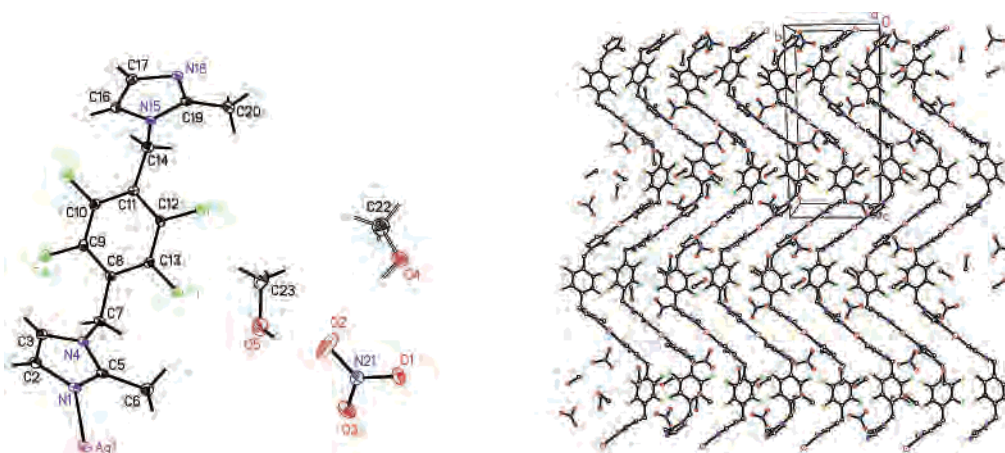


Figure 4. (a) Thermal ellipsoid (30%) plot of the asymmetric unit in **6** with the atom numbering scheme. (b) A ball-and-stick packing diagram of **6** showing the herringbone pattern of the extended sheet structure. Hydrogen atoms have been omitted for clarity.

Structure of $[\{Cd(1)_3(NO_3)_2 \cdot 2H_2O\} + 2H_2O]_n$ (5**).** The reaction of $Cd(NO_3)_2$ with **1** in a water/methanol mixture yielded **5** (Figure 3), a cadmium coordination chain polymer. This is unlike the 3D interpenetrating polymer formed from the reaction of bix with $Cd(NO_3)_2$.^{4c} In **5**, each Cd atom is trans octahedrally coordinated with four ligands and two coordinated H_2O molecules ($O(1)-Cd(1)-O(1)^i$, $N(19)-Cd(1)-N(19)$, $N(1)-Cd(1)-N(1) = 180^\circ$). Two of the trans-oriented ligands form bridging units between Cd centers. The other two fluorinated bix ligands wrap around and are coordinated, via hydrogen bonding, to the Cd coordinated water molecules ($O(1)-H(1B) \cdots N(16)$, 2.722(3) Å; 163.5°). This prevents any further association of the polymer into a higher dimensionality. The Cd–Cd vectors are aligned in the $(-2, 2, 0)$ direction. The space between the chains is occupied by lattice water molecules and the nitrate anions. The nitrate ions tie the chains together via strong hydrogen bonds with the Cd-coordinated water molecules, $OH \cdots O$, 2.713(3) Å; 168.4° . This link is assisted by the lattice water molecule which hydrogen bonds to the nitrate anion (2.9–3.4 Å). The Cd–Cd distance across the bridge is 13.0 Å, which is slightly shorter than in the nonfluorinated

analogue, 13.9–15.5 Å.^{4c} The interchain Cd–Cd distances between layers is ca. 10.2 Å.

Structure of $[Ag(2)NO_3 \cdot 1.5Methanol]_n$ (6**).** The reaction of $AgNO_3$ with **2** led to a completely different type of coordination polymer, **6** (Figure 4). Unlike tubular polymer **3** (vide supra), or the polyrotaxane network seen previously using nonfluorinated bix,^{4b} the solid-state structure of **6** shows a herringbone or zigzag chain polymer which aggregates by hydrogen bonding into sheets. The sheets are oriented along the $(-1 0 1)$ direction. The primary coordination environment around the silver center is a distorted square planar arrangement consisting of two methyl-Fbix ligands directly bonded to silver and two adjacent perpendicular ligands which are bonded to another Ag center. This results in Ag–N bonds and angles: Ag–N1, 2.109(3), Ag1–N18, 2.103(3), Ag1–N4, 3.394(4), Ag1–N15, 3.465(4) Å; N1–Ag1–N18, $172.15(10)^\circ$ and N4–Ag1–N15 $171.8(3)^\circ$. The two long Ag–N interactions are reinforced by two other interactions: hydrogen bonding and $Ag \cdots O$ interactions. The former interaction is caused by the syn conformation of the ligand which brings the methylene hydrogen atoms close to the silver (e.g., $C14 \cdots Ag1$, 3.58 Å). The latter interaction is the chelate effect of the O–N–O of the nitrate group

(Ag1···O1, 2.94; Ag1···O3, 2.79; Ag1–N21, 3.14 Å). This complex synthon arranges the polymer complex into a 2D sheet and the intersheet space is filled with solvent molecules. These methanol molecules form close hydrogen bonds to the remaining nitrate oxygen (O4···O2, 3.164(7) Å, 168.4°; O5···O2, 2.793(4) Å, 158.2°) and in turn tie the sheets together with weak hydrogen bonding from the ligand, **2**, to the methanol oxygen (C6···O3, 3.215(4) Å, 137.3°; C14···O4, 2.948(6) Å, 115.9°). The Ag–Ag distance across the ligand bridge is 12.52 Å, and the interchain Ag–Ag distances are 5.66 and 5.08 Å.

Interesting comparisons can be made when examining the structures of metal cations containing bix and fluorinated bix(Fbix) ligands and demonstrate the importance of the presence of a fluorinated phenylene group vis-à-vis its nonfluorinated analogue. It is noteworthy that the bix ligand is able to form interpenetration complexes. For example, compared with complex **3**, the nonfluorinated analogue forms a polyrotaxane complex, where Ag⁺ is 3-connected by rodlike segments and two-half-loops of the rings. For complex **5**, the nonfluorinated analogue exhibits an α -polonium topology and triply interpenetrating complexes where Cd²⁺ is coordinated with six bridging bix groups. The structure of **5** is similar to [Mn(bix)₃(NO₃)₂·4H₂O].^{4d} From a former two-pair comparison, the Fbix ligand is not apt to form interpenetration complexes. The difference between complex **4** and its nonfluorinated analogue is not as large as for **3** and **5**. Both form open three-dimensional channels, but the channels of complex **4** are triangular, while those of its nonfluorinated analogue are quadrilateral.

Thermogravimetric (TGA) measurements for **3–6** showed that they are thermally stable to 261, 313, 287, and 287 °C, respectively.

Experimental Section

General. All reagents and solvents were available commercially except for ligand **1** and **2** which are prepared according to the literature.^{4b} ¹H and ¹³C spectra were recorded in acetone-*d*₆ on a 300 MHz (Bruker AMX 300) spectrometer operating at 300.1 and 75.5 MHz, respectively. Chemical shifts are reported in parts per million relative to Me₄Si. Melting points were recorded on a differential scanning calorimeter (DSC) (TA Instruments TA10) at a scan rate of 10 °C/min. IR spectra (BioRad FTS 3000 Excalibur series) were obtained using KBr pellets. Magnetic susceptibility was measured on an Evans–Johnson Matthey balance for solids. TGA measurements were recorded on a TA Instruments TA50 as 5% weight loss temperature at a scan rate of 10 °C/min. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ, and the Shanghai Institute of Organic Chemistry.

Crystallographic Analyses. Crystals of compound **3–6** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.¹⁰ Data for **3–6** were collected at 86(2) K using a Bruker/Siemens SMART APEX instrument (Mo K α radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° per frame for 20 s, and a full sphere of data

was collected. A total of 2132 frames were collected with a final resolution of 0.73 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART¹¹ software and refined using SAINTPlus¹² on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.¹³ The structure was solved by direct methods and refined by least-squares method on *F*² using the SHELXTL program package. All atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are provided in the Supporting Information.

1 was obtained on the basis of literature methods.^{4b} A solution containing imidazole (3.40 g, 50 mmol) and 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene (1.23 g, 5 mmol) in methanol (60 mL) was heated at reflux (18 h). Removal of methanol by evaporation left a colorless syrup which was dissolved in aqueous K₂CO₃ (6.5 g, 100 mL). Upon standing, this solution yielded crystalline **1**, which was filtered, washed with water (3 × 20 mL), and dried in vacuo for 24 h. Yield: 0.93 g (60%). Ligand **1**: mp = 175.1 °C, IR (KBr): 3110, 3000, 2974, 1508, 1492, 1380, 1280, 1229, 1075, 1035, 903 cm⁻¹. ¹H NMR (300 MHz) δ 5.44 (s, 4H), 6.89 (t, *J* = 1.1 Hz, 2H), 7.08 (t, *J* = 1.1 Hz, 2H), 7.63 (s, 2H); ¹³C NMR (75 MHz) δ 146.8–147.1 (m), 144.8–145.1 (m), 138.4, 130.5, 119.9, 117.2–117.6 (m), 38.37 (t, *J* = 2.9 Hz); ¹⁹F NMR (282 MHz) δ –144.7. Anal. Calcd for C₁₄H₁₀N₄F₄: C, 54.20; H, 3.25; N, 18.06. Found: C, 54.14; H, 3.25; N, 18.06. Found: C, 54.14; H, 3.16; N, 17.90.

2,3,5,6-Tetrafluoro-1,4-bis(2-methylimidazole-1-yl-methyl)-benzene (2). The synthesis is similar to that of **1**. 2-Methylimidazole (4.10 g, 50 mmol) reacted with 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene (1.23 g, 5 mmol) gave 0.42 g, yield (25%) of **2**, mp = 197.6 °C, IR (KBr): 2990, 1508, 1493, 1427, 1360, 1275, 1076, 1021, 984 cm⁻¹. ¹H NMR (300 MHz) δ 2.48 (s, 6H), 5.32 (s, 4H), 6.89 (d, *J* = 1.2 Hz, 2H), 7.07 (d, *J* = 1.2 Hz, 2H); ¹³C NMR (75 MHz) δ 147.3–147.6 (m), 146.6, 145.3–145.6 (m), 127.7, 121.3, 116.9–117.1 (m), 38.78 (t, *J* = 2.5 Hz), 12.93; ¹⁹F NMR (282 MHz) δ –144.1. Anal. Calcd for C₁₆H₁₄N₄F₄: C, 56.81; H, 4.17; N, 16.56. Found: C, 56.65; H, 4.18; N, 16.73.

[Ag(1)NO₃·H₂O·Methanol]_n (3). The single-crystal X-ray analysis of **3** was prepared from a methanol solution (15 mL) of **1** (31 mg, 0.1 mmol) slowly layered onto a water solution (5 mL) of AgNO₃ (17 mg, 0.1 mmol) in a test tube at 25 °C. Complex **3** was obtained as colorless crystalline in 80% yield (38 mg). IR (KBr): 3439, 3123, 3015, 1503, 1492, 1354, 1284, 1232, 1089, 1034 cm⁻¹. Anal. Calcd for C₂₉H₂₆Ag₂F₈N₁₀O₈: C, 34.48; H, 2.59; N, 13.86. Found: C, 34.60; H, 2.25; N, 14.51.

[Co(1)₃(ClO₄)₂]_n (4). Complex **4** was obtained by a procedure similar to that of **3**, except that Co(ClO₄)₂·6H₂O (37 mg, 0.1 mmol) was used instead of AgNO₃ reacted with 93 mg (0.3 mmol) of **1**. **4** was obtained as a pink crystalline solid in 80% yield (98 mg). IR (KBr): 3439, 3138, 3026, 1512, 1496, 1360, 1285, 1231, 1087, 1039, 936 cm⁻¹. Anal. Calcd for C₄₂H₃₀Cl₂CoF₁₂N₁₂O₈: C, 42.44; H, 2.54; N, 14.14. Found: C, 42.14; H, 2.66; N, 14.15.

(11) SMART: version 5.625, Bruker Molecular Analysis Research Tool; Bruker AXS: Madison, WI, 2001.

(12) SAINTPlus: version 6.22, Data Reduction and Correction Program; Bruker AXS: Madison, WI, 2001.

(13) (a) Sheldrick, G. M. SADABS: version 2.01, An Empirical Absorption Correction Program; Bruker AXS: Madison, WI, 2001. (b) SHELXTL: version 6.10, Structure Determination Software Suite; Bruker AXS: Madison, WI, 2001.

(10) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1–3.

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[Cd(1)₃(NO₃)₂]_n (5). Compound **5** was prepared from a methanol solution (50 mL) of **1** (93 mg, 0.3 mmol) to which was added Cd(NO₃)₂·4H₂O (31 mg, 0.1 mmol) in 5 mL of water. The mixture was refluxed for 5 min, and the solvent was evaporated slowly. **5** was obtained as a colorless crystalline solid in 75% yield (93 mg). IR (KBr): 3434, 3134, 3010, 1514, 1493, 1412, 1318, 1288, 1238, 1088, 1037, 937 cm⁻¹. Anal. Calcd for C₄₂H₃₈CdF₁₂N₁₄O₁₀: C, 40.71; H, 3.09; N, 15.82. Found: C, 40.15; H, 2.93; N, 15.92.

[Ag(2)NO₃·H₂O·Methanol]_n (6). Compound **6** was prepared from a methanol solution (15 mL) of **2** (34 mg, 0.1 mmol) slowly layered onto a water solution (5 mL) of AgNO₃ (17 mg, 0.1 mmol) in a test tube at 25 °C. **6** was obtained as colorless crystalline solid in 70% yield (36 mg). IR (KBr): 3443, 3129, 2986, 2938, 1514, 1493, 1426, 1353, 1279, 1147, 1021, 941 cm⁻¹. Anal. Calcd for

C₃₅H₄₀Ag₂F₈N₁₀O₉: C, 37.79; H, 3.62; N, 12.59. Found: C, 36.92; H, 3.46; N, 13.03.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>. IC051608H