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Unusual Noninterpenetrating (3,6) Topological Network Assembled by Semirigid Benzimidazole-Based Bridging Ligand

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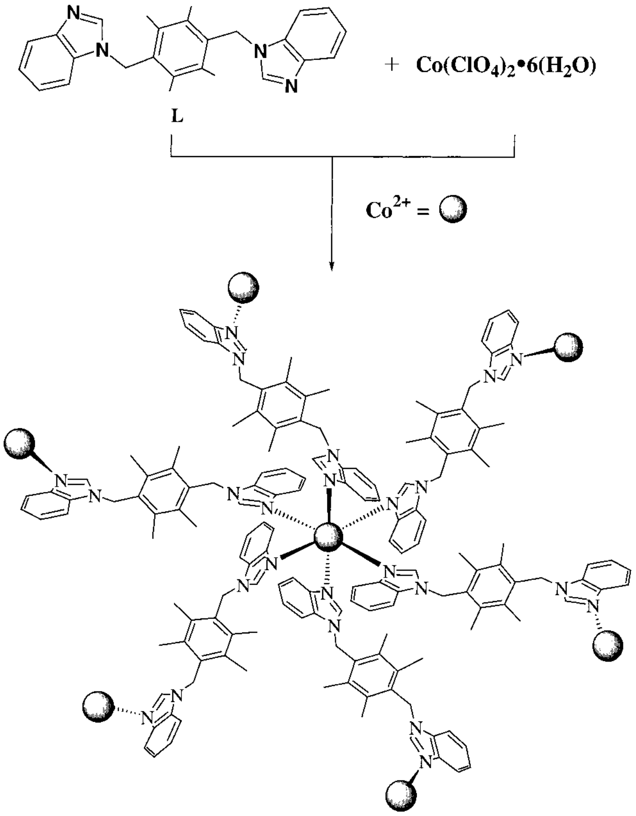
The use of metal ions to control the self-assembly of composite organic/inorganic supramolecular architectures represents one of the burgeoning fields that may offer functional solid materials for molecular selection, ion exchange, and catalysis,[1] particularly with purposeful construction of molecular aggregates, like helices, rotaxanes, catenanes, knots,[2] and the crystal engineering of polymeric coordination networks with the intriguing variety of structures and topologies.[3] By the careful design of tailored ligands, various novel supramolecular architectures have been constructed. For example, rigid polyfunctional ligands are well-known to form grids, rods, bricks, honeycombs, diamondoid nets, and other noteworthy species,[4] while flexible linear ligands may facilitate formation of helicates and other intertwined supramolecules.[5] However, it is becoming increasingly evident that despite the continuous endeavor to understand the molecular structure and topology, the control and prediction of coordination networks are still a great challenge. The rigid polyfunctional ligands take the advantage to form ordered open networks defined by metal coordination geometries but also frequently suffer from the phenomenon of interpenetration and supramolecular isomerization.[3a,b] One of the possible new strategies is to design programmed organic ligands that disfavor the interpenetration.[6] Herein we describe the synthesis and crystal structure of the coordination polymer $[\mathrm{Co}\mathbf{L}_3](\mathrm{ClO}_4)_2$, **1**, generated from a bridging ligand **L** with benzimidazole rings as arms.

Scheme 1. Preparation of **1**



The ligand 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene **L** can be easily prepared from the replacement reaction of 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene with benzimidazole. The complex was prepared by reaction of a hydrated metal salt $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ with ligand **L** in molar ratios of 1:3 in MeOH medium as shown in Scheme 1.[7] Elemental analysis suggested the composition $(\mathrm{Co}\mathbf{L}_3)(\mathrm{ClO}_4)_2$, which was further confirmed by X-ray single-crystal structural analysis.[8]

X-ray crystallographic analysis showed that complex **1** is a two-dimensional lamellar polymer. Six **L** ligands wrap around the cobalt(II) ion to give an octahedral coordination geometry that possesses a crystallographic $\bar{3}$ symmetry passing through the

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(7) Preparation of **1**. An ammount of 350 mg (1 mmol) of $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ and 1.2 g (3 mmol) of **L** were added to 15 mL of methanol, and the mixture was stirred for 30 min at room temperature. *Caution!* Perchlorate salts are potentially explosive and should be handled carefully in small amounts. After filtration diethyl ether was allowed to slowly diffuse into the filtrate to produce pale-red block crystals. Yield: 450 mg. Found: C, 64.81; H, 5.44; N, 11.73. Anal. Calcd for $\mathrm{C_{78}H_{78}Cl_2CoN_{12}O_8}$: C, 65.09; H, 5.28; N, 11.68. IR (KBr, cm^{-1}): ν 3057(m), 1600(s), 1535(m), 1392(w), 1446(w), 1411(s), 1325(w), 1279(w), 1220(m), 1099(s), 1003(m), 927(m), 809(s), 733(m), 622(s), 575(w), 469(w).

(8) Crystal data for **1**. $\mathrm{C_{78}H_{78}Cl_2N_{12}O_8Co}$, MW = 1441.35, hexagonal, space group $P\bar{3}$, $a = 13.3994(14)$ Å, $c = 10.5933(16)$ Å, $V = 1647.1(3)$ Å^3, $Z = 1$, crystal size 0.12 × 0.10 × 0.08 mm^3, 3171 unique reflections measured, final R1 = 0.0591 and wR2 = 0.1527 for 1594 observed [$I > 2\sigma(I)$] reflections.

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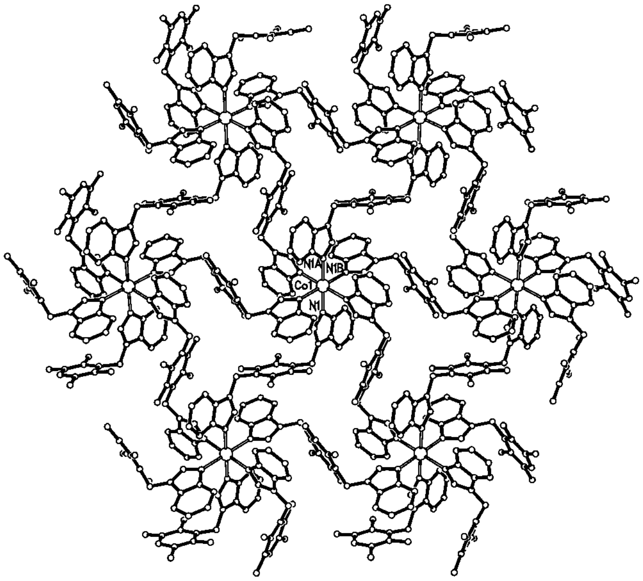


Figure 1. View of **1** down *c* axis showing radiative starlike structure. Selected bond distances (Å) and angles (deg): Co1 N1 2.200(2), N1−Co1−N1a 180.00(13), N1−Co1−N1b 86.07(8), N1a-Co1−N1b 93.93(8). Symmetry transformation used to generate equivalent atoms: (a) −*x*, −*y*, −*z*; (b) −*y*, *x* − *y*, *z*.

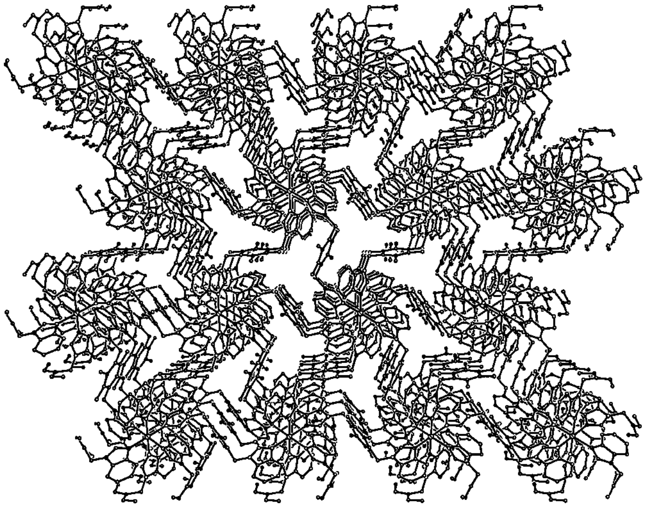
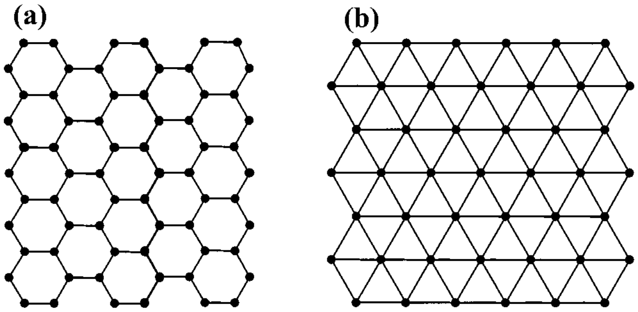


Figure 2. Face-to-face stacked layers in *ab* plane, leaving triangular channels. Perchlorate anions have been omitted for clarity.

central ion. Each ligand connects another Co(II) ion, thus generating a starlike structure as shown in Figure 1. All ligands are crystallographically identical taking C_i trans conformation with the *i* symmetry located at the center of the phenyl ring. The two benzimidazole arms of each ligand are nearly perpendicular to the base phenyl ring and disposed up and down alternately around the $\bar{3}$ axis to bridge six neighboring Co(II) ions, resulting in the lamellar structure extended in *ab* plane.

Chart 1[a]



[a] (a) (6, 3) topological net. (b) (3, 6) topological net.

It is interesting to compare the net topology of the present case with other related known examples. The octahedrally coordinated Co(II) ions usually yield a cubic lattice related to α-polonium.[3b,9] However, the present case exhibits a novel two-dimensional (3, 6) (or 3^6) topology comparable well to the well-known three-connected (6, 3) networks (Chart 1).[3b,3e,10] Each Co(II) is linked to six other radiative Co(II) ions, and every three neighboring Co(II) ions encircle a triangular hole. The semirigid ligands used here are facile to generate such lamellar structure, and the high symmetry with such close arrangement of molecules can effectively prevent interpenetrating. Instead, face-to-face stacking of such lamellar layers affords triangular channels to accommodate perchlorate anions (Figure 2). When viewed from the *a* direction, lamellar networks and perchlorate anions are stacked alternately, giving a bilayer architecture. For clarity a side view showing how the layers stack up in parallel along the *c* axis is shown in Figure S1 of Supporting Information without counterions.

In summary, a noninterpenetrating two-dimensional open network has been constructed that shows remarkable diversification from the normal framework with octahedral metal centers. The structure and topology is evidently controlled by the coordination geometry of the metal ion, and the semirigid ligand facilitates formation of a lamellar layer whose high symmetry and close packing evidently disfavor interpenetration. The anionic molecules are located between layers to separate neighboring layers. This implies the possibility of introducing other guest molecules among the layers, which has potential importance in the supramolecular materials. Further investigation is now in progress.

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Supporting Information Available: X-ray crystallographic file, in CIF format, and Figure S1 of a side view of the layer structure in **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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