Syntheses and Structures of Zn Coordination Polymers with 4,4'-Bipyridine and 4,4'-Azopyridine. Effect of Counter Anions on the Network System

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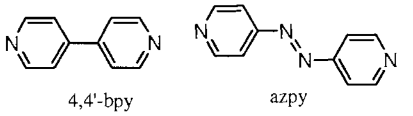
Three zinc(II) coordination polymers, $[Zn(4,4'\text{-bpy})(NCS)_2]_n$ (4,4'-bpy = 4,4'-bipyridine; **1**), $\{[Zn(4,4'\text{-bpy})(SO_4)(H_2O)_3]\cdot 3H_2O\}_n$ (**2**), and $\{[Zn_2(azpy)_2(SO_4)_2(H_2O)_3]\cdot 0.5(azpy)\}_n$ (azpy = 4,4'-azopyridine; **3**) have been synthesized and structurally characterized. **1** and **2** show assembled structure of one-dimensional chains, while **3** has a three-dimensional structure with pillared-layer type network. The important effect of counter anions on the coordination network was studied.

Synthesis and structural characterization of coordination polymers with specific network topologies are of current interest.[1] The reason for this is not only because of their potential functionalities, but also because of their intriguing structural diversity.[2] Since the no ligand-field stabilization effect of the Zn(II) ion, the geometry of the metal center, which largely affects the network structure, could be controllable by the coordination circumstance. We have succeeded in the syntheses and structural characterization of new zinc(II) coordination polymers, $[Zn(4,4'\text{-bpy})(NCS)_2]_n$ (4,4'-bpy = 4,4'-bipyridine; **1**), $\{[Zn(4,4'\text{-bpy})(SO_4)(H_2O)_3]\cdot 3H_2O\}_n$ (**2**), and $\{[Zn_2(azpy)_2(SO_4)_2(H_2O)_3]\cdot 0.5(azpy)\}_n$ (azpy = 4,4'-azopyridine; **3**), and have found that the unique effect of the counter anions on the structure of zinc(II) coordination polymer.



Scheme 1.

The reaction of $Zn(NCS)_2$ with 2 equiv. of 4,4'-bipyridine (4,4'-bpy) in H_2O/EtOH (1:1, v/v) produces **1**, whose crystal structure is shown in Figure 1.[3] The coordinations of four nitrogen atoms of two NCS^- and two 4,4'-bpy provide tetragonal geometry around this metal center. This circumstance is similar to that of monomeric compound, $[Zn(4\text{-methylpyridine})_2(NCS)_2]$.[4] The 4,4'-bpy links each zinc(II) center to afford zig-zag chain, which are arranged along the *c*-axis. Two pyridine rings of 4,4'-bpy are coplanar.

On the other hand, coordination networks with octahedral zinc(II) center are observed in **2** and **3**, which are prepared by the reaction of $ZnSO_4$ with 4,4'-bpy and azpy, respectively. **2** was synthesized by the reaction of $ZnSO_4$ with 2 equiv. of 4,4'-bpy in H_2O/EtOH (1:1, v/v). The structure is shown in Figure 2.[5] The four oxygen atoms of three waters and sulfate anion and two nitrogen atoms of 4,4'-bpy afford octahedral coordination geometry around zinc(II) center. This compound also has assembled structure of one-dimensional chains of $[Zn(4,4'\text{-bpy})]_n$. These chains run parallel in the *ab*-plane to form two-dimensional layer, which stacks along the *c*-axis with separation of about 3 Å. Two pyridine rings of the 4,4'-bpy are parallel to the *ab*-plane. The chains in the adjacent layer are rotated by 60° to provide helical staircase network. The channels created along the *c*-axis are filled with sulfate anions and crystalline water molecules, which are linked by hydrogen bondings each other. This compound is isostructural with $[Cu(4,4'\text{-bpy})(SO_4)(H_2O)_3]_n$,[6] and the assembled motif was reported in $[Ag(pytz)(NO_3)]_n$ (pytz = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine).[7]

The reaction of $ZnSO_4$ with 2 equiv. of azpy in H_2O/EtOH

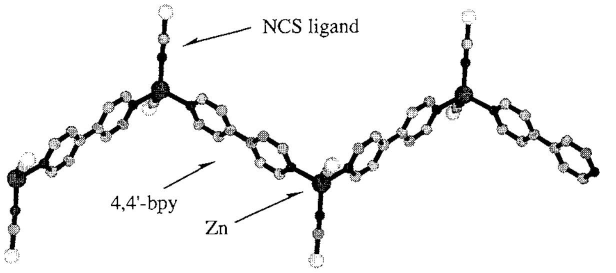


Figure 1. Crystal structure of **1**. Hydrogen atoms are omitted for clarity.

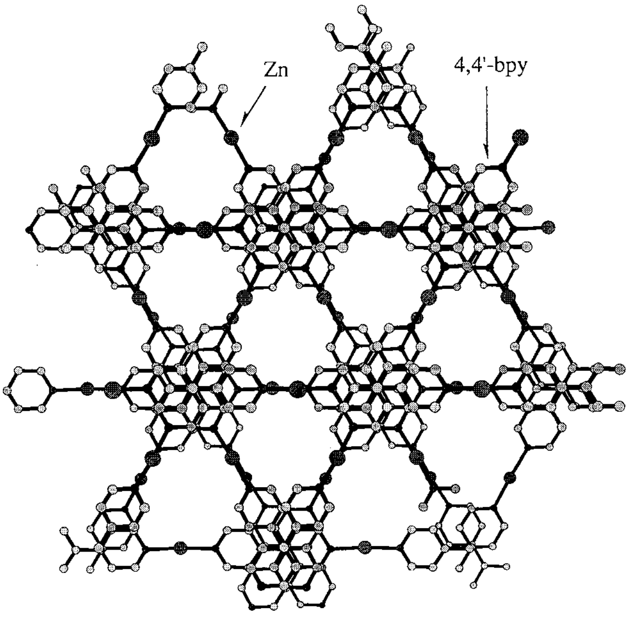


Figure 2. Crystal structure of **2** along the *c*-axis. Sulfate anions, Crystalline water molecules, and hydrogen atoms are omitted for clarity.

(1:1, v/v) provides **3**.[8] This network is comprised of the two-dimensional sheet of $[Zn_2(SO_4)_2(H_2O)_3]_n$ and azpy ligand, which bridges these sheets. The sheet structure is illustrated in Figure 3. Sulfate anions link Zn(II) atoms to provide one-dimensional chain, containing $[Zn(SO_4)]_2$ and $[Zn(SO_4)]_4$ units, which are alternatively arranged. Each chain is linked by hydrogen bonds between coordinating waters or coordinating oxygen atoms of sulfate anions to produce layer network, which is perpendicular to the *ac*-plane. (Figure 4) Each sheet is linked by azpy to produce three-dimensional structure with pillared-layer type network, having one-dimensional channels along the *a*+*c* vector with dimension of about 5 x 1 Å, which are filled with free azpy molecules.

To the best of our knowledge, this is the first example of metal-sulfate two-dimensional phase, which is constructed in the coordination network. This study demonstrates that the two significant functions of the counter anions on the construction of new coordination networks, involving regulation of the geometry of metal site and creation of the new network phases. This synthetic strategy, which control the network structure by counter anions, could lead to the new designed synthesis of coordination network. We are currently preparing the new Zn(II) coordination polymers with various counter anions and bridging ligands.

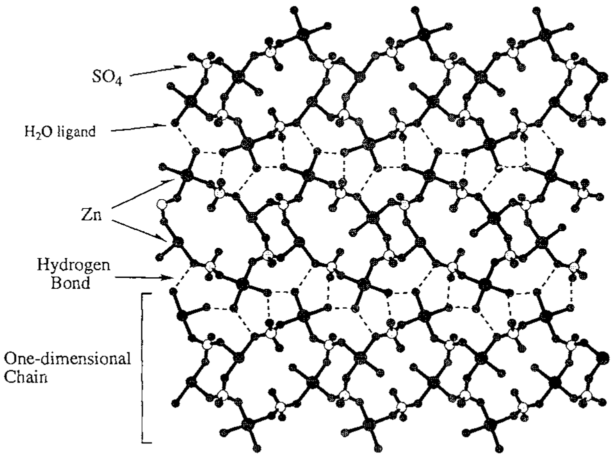


Figure 3. Two-dimensional layer of .3.

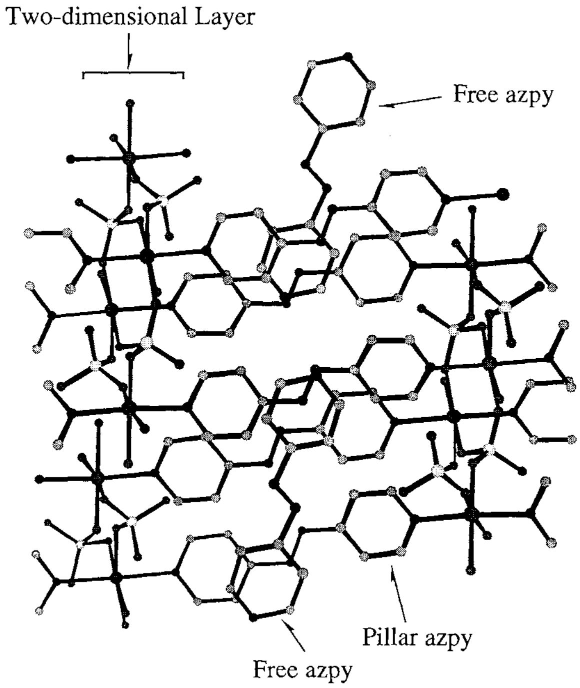


Figure 4. Crystal structure of **3**. Hydrogen atoms are omitted for clarity.

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References and Notes

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3 Crystal data for **1**: $C_{12}H_8N_4S_2Zn$, M = 337.7, monoclinic, space group *C*2/c (no. 15), a = 18.132(7), b = 5.210(3), c = 17.344(3) Å, β = 115.65(2)°, V = 1477(1) $Å^3$, Z = 4, D_{calcd} = 1.519 g/cm^3, MoKα (λ = 0.71069 Å), μ = 19.35 cm^{-1}, T = 295 K, 1962 reflections measured, 1897 independent, 984 [$I > 3\sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 88 parameters R = 0.044, R_w = 0.035.

4 J. Lipkowski, *J. Coord. Chem.*, **22**, 153 (1990).

5 Crystal data for **2**: $C_{10}H_{20}N_2O_{10}SZn$, M = 407.7, hexagonal, space group $P6_5$ (no. 170), a = 11.391(1), c = 20.921(6) Å, V = 2350.9(4) $Å^3$, Z = 6, D_{calcd} = 1.80 g/cm^3, MoKα (λ = 0.71069 Å), μ = 17.57 cm^{-1}, T = 295 , 11347 reflections measured, 1904 independent, 1431 [$I > 3\sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 192 parameters R = 0.083, R_w = 0.095.

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7 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, **36**, 2327 (1997).

8 Crystal data for **3**: $C_{25}H_{26}N_{10}O_{11}S_2Zn_2$, M = 837.4, monoclinic, space group $P2_1$ (no. 14), a = 14.679(2), b = 10.101(3), c = 19.160(3) Å, β = 96.41(1)°, V = 3015.3(8) $Å^3$, Z = 4, D_{calcd} = 1.85 g/cm^3, MoKα (λ = 0.71069 Å), μ = 18.10 cm^{-1}, T = 295 , 7591 reflections measured, 7328 independent, 4925 [$I > 3\sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 451 parameters R = 0.038, R_w = 0.043.