The First Three-Leg Ladder Coordination Polymer: $[Zn_3(OAc)_4(4,4'\text{-bpy})_3\{N(CN)_2\}_2]$

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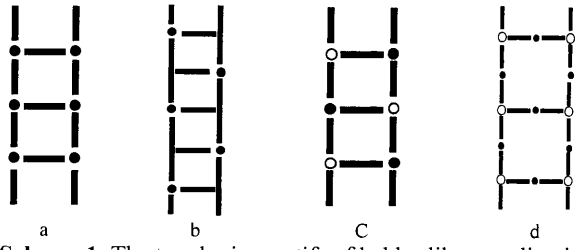
The coordination polymer $[Zn_3(OAc)_4(4,4'\text{-bpy})_3\{N(CN)_2\}_2]$ is prepared and characterized by X-ray diffraction studies, which shows a unique three-leg molecular ladder structure.

Interest in self-assembled coordination polymers with specific network topologies is expanding rapidly because of their potential properties as novel materials and fascinating structural chemistry.[1–4] Many types of interesting network topologies have been reported recently, including chain,[4] ladder,[5] grid,[6] brick wall,[7] honeycomb,[8] diamondoid,[9] rutile,[10] and α-polonium.[11] Although ladder-like coordination polymers are less well investigated comparing with other network topologies, however, the results obtained from these compounds are surprising rich from both fascinating structural and novel properties such as molecular adsorption[12] and magnetic properties[13] in the last two years. Those motifs can be classified as homometallic ladders (including normal ladder,[14] quasi ladder,[15] twist ladder,[16] and undulating ladder[17]), and heterometallic ladders (including rope-ladder[18] and alternate ladder[19]) according to the metal species. Alternatively, they can also be summarized as four



Scheme 1. The topologies motifs of ladder-like coordination polymers. (a and b are homometallic ladders, c and d are heterometallic ladders)

kinds of topology motifs (Scheme 1).

It is worth to note that all the molecular ladders mentioned above have two legs. Originally, two ligands 4,4'-bpy and $N(CN)_2^-$ were expected to react with $Zn(OAc)_2$ acted as bridges dually to construct a multi-dimensional porous molecular solid. But an unexpected novel coordination polymer: $[Zn_3(OAc)_4(4,4'\text{-bpy})_3\{N(CN)_2\}_2]$ (**1**) was obtained, and it represents the first example of a three-leg ladder

The reaction[20] of $Zn(OAc)_2{\cdot}2H_2O$ with the methanol solution of 4,4'-bpy and water solution $NaN(CN)_2$ yields clear solution from which the crystal of composition $[Zn_3(OAc)_4(4,4'\text{-bpy})_3\{N(CN)_2\}_2]$ were isolated after two weeks. An X-ray diffraction study[21] revealed that **1** adopts an infinite three-leg ladder structure. As shown in Figure 1, Zn^{II} ions located at the cross-point of the rungs and rails. Two OAc^- ligands linked two adjacent Zn^{II} ions at the same rung using $\eta^{1,1}$ and $\eta^{1,3}$ mode, respectively. Each Zn^{II} ion located at the side rails has a

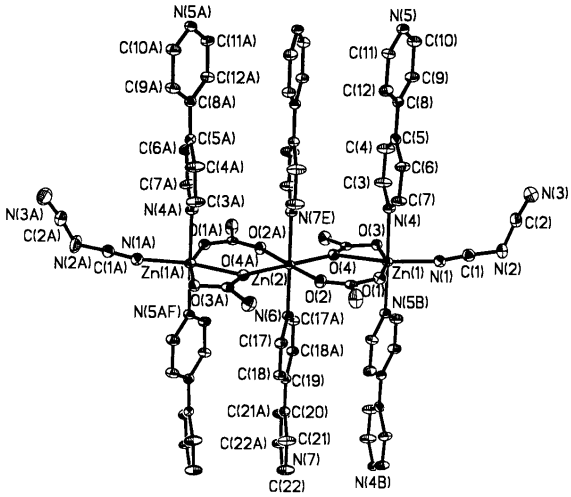


Figure 1. Section of the polymeric structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°):Zn(1)-O(1) 2.008(3), Zn(1)-O(4) 2.279(2), Zn(1)-N(1) 2.057(3), Zn(2)-O(2) 2.089(2), Zn(1)-O(3) 2.145(3), Zn(2)-O(4A) 2.146(3), Zn(1)-N(5B) 2.185(3), Zn(2)-O(4) 2.146(3), Zn(1)-N(4) 2.197(3), Zn(2)-N(6) 2.151(4), Zn(2)-N(7E) 2.181(4), O(1)-Zn(1)-N(1) 101.03(12), N(1)-Zn(1)-N(4) 89.14(12), N(1)-Zn(1)-O(3) 99.72(12) O(3)-Zn(1)-N(4) 90.56(11), O(1)-Zn(1)-N(5B) 90.71(11), N(5B)-Zn(1)-N(4) 179.31(12), N(1)-Zn(1)-N(5B) 91.55(12), O(1)-Zn(1)-O(4) 100.47(10), O(3)-Zn(1)-N(5B) 89.31(11), O(3)-Zn(1)-O(4) 58.78(9), O(1)-Zn(1)-N(4) 89.16(11), N(5B)-Zn(1)-O(4) 88.74(10), N(4)-Zn(1)-O(4) 90.61(10), O(2)-Zn(2)-O(4) 90.98(10), O(2)-Zn(2)-O(4A) 89.02(10), O(2A)-Zn(2)-N(6) 90.65(7), O(2)-Zn(2)-N(6) 90.65(7), O(4A)-Zn(2)-N(7E) 90.05(6), O(4A)-Zn(2)-N(6) 89.95(6), O(4)-Zn(2)-N(7E) 90.05(6), O(4)-Zn(2)-N(6) 89.95(6), N(6)-Zn(2)-N(7E) 180.000(1), A: -x,y,-z+1/2 B: x,y+1,z E: x,y-1,z

tetragonal bipyramid environment. Three O atoms from two OAc^- ligands and one N atom from CN^- group of $N(CN)_2^-$ form the equatorial plane. The $Zn^{II}(2)$ ion displays octahedral coordination, with the four O atoms of different OAc^- ligands in the equatorial plane. The axial positions of all the $Zn^{II}(2)$ ions are occupied by two N atoms of two different 4,4'-bpy ligands. The dicyanamide ligand possesses pseudo-C_{2v} symmetry with C≡N bond distances ranging from 1.148(5) to 1.139(5) Å. The dihedral angles between the two pyridine rings of 4,4'-bpy are 39.97(11)° (at side rails) and 17.67(21)°(at middle rail). The distance between Zn(1) and Zn(2) is 3.864(1) Å.

Space-filling view of the molecular three-leg ladder is shown in Figure 2. The compound possesses narrow twist cavities with dimensions of 3.86 × 11.4 Å enclosed by the rungs and 4,4'-bpy ligands. Scheme 2 illustrates the crystal packing of the ladders. Two infinite ladders are juxtaposed in the *bc*

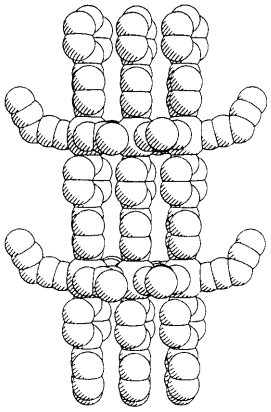
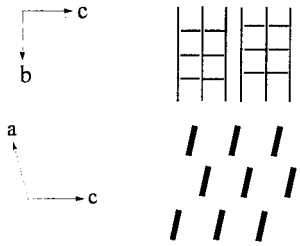


Figure 2. Space-filling views of the three-leg ladder $Zn_3(OAc)_4(4,4'\text{-bpy})_3[N(CN)_2]_2$



Scheme 2. Illustrates the crystal packing of the three-leg ladders.

plane and are offset by quarter of a "step" along *b*.

In conclusion we have prepared a unique three-leg ladder coordination polymer in which 4,4'-bpy ligands link Zn^{II} ions form rails and OAc^- ligands connect Zn^{II} ions to form rungs of the ladder. We also used other paramagnetic metal ions ($M(OAc)_2$, M = Co^{II}, Mn^{II}, Ni^{II}) instead of $Zn(OAc)_2$ to react with 4,4'-bpy and $NaN(CN)_2$, and a two-fold interpenetrated three-dimensional cobalt(II) complex $[Co(4,4'\text{-bpy})\{N(CN)_2\}_2]$ was obtained.[22] Many fascinating structures will be assembled by the two remarkably versatile building block 4,4'-bpy and $N(CN)_2^-$ ligands.

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20 Experimental: In a small flask $Zn(OAc)_2{\cdot}2H_2O$ (43.9 mg, 0.2 mmol) was dissolved in water (10 mL). A methanol solution of 4,4'-bpy (31.24 mg, 0.2 mmol) was added, followed by a water solution of $Na[N(CN)_2]$ (35.6 mg, 0.4 mmol). Well-shaped crystals of $[Zn_3(OAc)_4(4,4'\text{-bpy})_3\{N(CN)_2\}_2]$ were obtained from the mother liquor by slow evaporation at room temperature after two weeks. They were filtered off, washed with a small amount of water, and dried in air. The yield is 65%. Anal. Calcd for $C_{42}H_{36}N_{12}O_8Zn_3$: C, 48.84; H, 3.51, N, 16.27%. Found: C, 49.01, H, 3.42, N, 16.53%. Selected IR frequencies for $[N(CN)_2]$ (cm^{-1}): ν_s(C≡N), 2156; ν_{as}(C≡N), 2271; ν_s(C–N), 935; ν_{as}(C–N), 1357.

21 Crystal data: $Zn_3(OAc)_4(4,4'\text{-bpy})_3[N(CN)_2]_2$, monoclinic, space group *C*2/c, a = 21.603(1), b = 11.457(1), c = 17.798(1) Å, β =104.245(4)°, V = 4269.6(5) $Å^3$, Z = 4, D_{calc}= 1.607 Mg/m^3, μ = 1.741 cm^{-1}, 24237 reflections collections, 5058 uniqu [R(int) = 0.1104]. Data collected at room temperature on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073) at Nonius B. V. Demo Lab in Peking University. Solution was obtained by direct methods (SHELX 97) followed by successive Fourier-difference syntheses, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97). All non-hydrogen atoms were made anisotropic, while all hydrogens were assigned to calculated positions, R= 0.0506 and wR = 0.0877, S = 1.005, based on 2823 observations [$I>2\sigma(I)$].

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