Three-Dimensional Zinc(Ⅱ) Coordination Polymer with Strong Blue Fluorescent Emission Formed by Parallel Interlocking of (4,4) Two-Dimensional Networks

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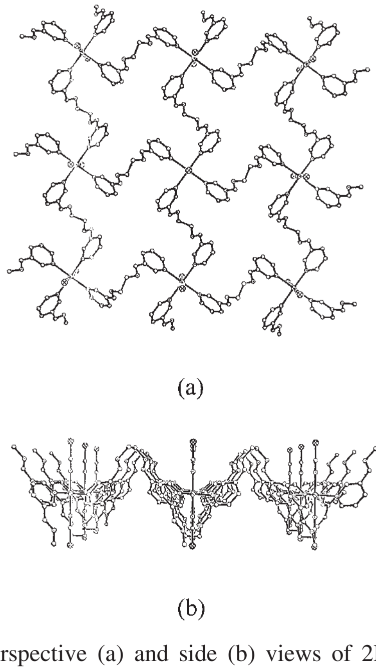
A novel coordination polymer, $[Zn(NCS)_2(L)_2]\cdot 2H_2O$, with strong blue fluorescent emission was prepared by an assembly reaction of 1,2-bis(3-pyridylmethyleneamino)ethane (L) with $Zn(ClO_4)_2$ and NaSCN. A crystallographic analysis indicates that the structure of the complex contains (4,4) two-dimensional layers, which interlock each other in parallel to form a three-dimensional framework.

In the past decade, many chemists have focused their studies on the deliberate design of coordination polymers with specific structures.[1] In particular, it has been a growing area for constructing infinite two- (2D) and three-dimensional (3D) frameworks exhibiting different degrees of interpenetration, which have recently been reviewed.[2] Intertwining of 2D motifs can occur in two different ways, namely, parallel and perpendicular or inclined interpenetrations.[2–4] However, because the bridging ligands, e.g. tricyanomethanide, phenazine, *trans*-4,4′-azobis(pyridine) (azpy) etc., used in the reported interpenetration complexes are rigid, they can form frameworks with large vacancies for interpenetrating. In contrast, flexible ligands are rarely used to construct interpenetration complexes. Here, we report for the first time on a novel interpenetrated coordination polymer, $[Zn(NCS)_2(L)_2]\cdot 2H_2O$, with a flexible ligand, 1,2-bis(3-pyridylmethyleneamino)ethane (L), formed by the parallel interlocking of 2D layers.

We studied the self-assembly of di-Schiff base and reduced di-Schiff base ligands containing 4-pyridyl groups with various metal salts, and found that they can form 1D and 2D frameworks, depending on the metal ions, counter anions etc.[5] Using new suitably designed ligands can offer the chance to produce unprecedented structures, and therefore properties and functions. As a part of our systematic research and to investigate the influence of the nature of organic ligands on the construction of metal-organic frameworks, we synthesized a new di-Schiff base ligand, 1,2-bis(3-pyridylmethyleneamino)ethane (L).

The complex $[Zn(NCS)_2(L)_2]\cdot 2H_2O$ was readily prepared by reaction of L with $Zn(ClO_4)_2$ and NaSCN. An X-ray crystallographic analysis indicates that each zinc(Ⅱ) atom is coordinated by four equatorial L ligands and two axial linear NCS^- anions, and is in a compressed octahedral environment with four long Zn–N (pyridine) bonds [2.202(4) Å] and two short Zn–N (NCS) bonds [2.103(6) Å]. Two coordinated NCS^- and the zinc(Ⅱ) atom are strictly in a line, since the angle of N–Zn–N is 180.0°. The structure of the complex contains 2D layers with (4,4) topology, as defined by Robson et al,[2b] in which four-connected nodes are provided by Zn(Ⅱ) atoms and ligand L provides connections using two terminal pyridyl groups between the nodes (Fig. 1a). All of the Zn(Ⅱ) atoms of each layer are in the same plane with a separation of 11.38 Å. A similar 2D structure with (4,4) topology was observed in $Co(NCS)_2(pyz)_2$ (pyz = pyrazine), in which pyz was used as connections.[6] It is interesting that two imine N atoms of each ligand L did not participate in the coordination with the metal atoms, and thus the L acted as a bidentate ligand to link two metal atoms, like the above-mentioned pyz and azpy. However, in contrast to the rigid and rod-like ligands of pyz and azpy, the flexible ligand L is not linear, but has a U-shape in the complex (Fig. 1b). Furthermore, all of the ligands L in the (4,4) layer lie above and under the plane defined by the zinc(Ⅱ) atoms alternately. Thus, the 2D network of the complex $[Zn(NCS)_2(L)_2]\cdot 2H_2O$ exhibits corrugated motifs, which can meet the need of possible parallel interpenetrating, which requires undulating layers.[2]

In fact, a 3D framework is formed by parallel interpenetrating 2D layers, as shown in Fig. 2. The Zn(Ⅱ) atoms in one layer sit above or below the center of grids from the adjacent layers (Fig. 2a). The uncommon mode of interpenetration observed in $[Zn(NCS)_2(L)_2]\cdot 2H_2O$ is topologically different from those which appeared in the reported complexes with parallel interpenetrating nets based on the (4,4) topology.[7] It



(a)

(b)

Fig. 1. Perspective (a) and side (b) views of 2D network structure of $[Zn(NCS)_2(L)_2]\cdot 2H_2O$, hydrogen atoms were omitted for clarity.

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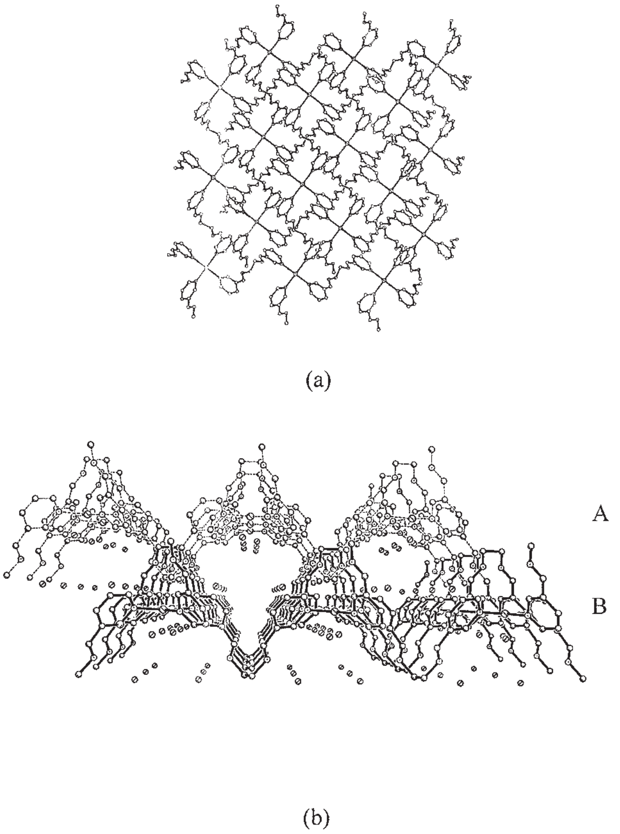

(a)

(b)

Fig. 2. Perspective (a) and side (b) views of parallel interlocking structure of two layers in $[Zn(NCS)_2(L)_2]\cdot 2H_2O$.

can be clearly seen from Fig. 2b that the middle (uncoordinated) part of ligand L below the zinc(II) plane in layer A is interlocked by the middle part of ligand L above the zinc(II) plane in layer B, and that such interlocking is repeated to form the 3D framework. The solvent water molecules, without hydrogen-bonding interactions with ligand L, occupy the vacancy between two interlocking layers. The mode of interlocking by nonbonding interactions in $[Zn(NCS)_2(L)_2]\cdot 2H_2O$ is much like that observed in catenanes. Thus, the complex could be regarded as a polycatenane.

The 2D → 3D parallel interpenetration is still a rarity.[2c] The complex reported here is the first example of an interlocked 3D structure with parallel (4,4) 2D layers. The octahedral geometric requirement of a zinc(II) atom and a steric hindrance may prevent the coordination of imine N atoms with the metal atoms. The uncoordinated diimine group and the flexibility of L may probably lead to the formation of this unusual interlocking architecture.

It is interesting that the synthesized complex shows strong photoluminescence with an emission maximum at 464 nm upon excitation at 370 nm in the solid state at room temperature, while the free ligand L exhibits fluorescent emission at 396 nm under the same conditions (Data is deposited as Document No.K02758 at the Office of the Editor of Bull. Chem. Soc. Jpn.). Thus, the emission observed in $[Zn(NCS)_2(L)_2]\cdot 2H_2O$ is tentatively assigned to intraligand fluorescence.[8,9] The red-shifted blue photoluminescence is attributed to the coordination of metal atoms to the pyridine-containing ligand, particularly the terminal pyridyl-metal coordination.[5a]

Experimental

Preparation of $[Zn(NCS)_2(L)_2]\cdot 2H_2O$. L was prepared by procedures similar to those reported for 1,2-bis(4-pyridylmethyleneamino)ethane.[5] To a solution of L (0.05 mmol, 11.9 mg) in methanol (3 mL), a solution of $Zn(ClO_4)_2$ (0.05 mmol, 13.2 mg) in methanol (2 mL) was added, and the mixture was stirred for a while. An aqueous solution of NaSCN (0.1 mmol, 8.2 mg) was added and the mixture was continuously stirred for several minutes. Colorless needle crystals were obtained through slow evaporation of the final clear solution at room temperature for a week. Yield: 68%. Anal. Cacld for $C_{30}H_{32}N_{10}O_2S_2Zn$: C, 51.91; H, 4.64; N, 20.17%. Found: C, 51.95; H, 4.75; N, 20.14%.

Crystal Structure Determination. Data collection was performed on a Smart Apex CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using Fourier techniques. All of the data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. Crystallographic data for $[Zn(NCS)_2(L)_2]\cdot 2H_2O$: $C_{30}H_{32}N_{10}O_2S_2Zn$, fw $= 694.15$, tetragonal, $I4$, $a = 11.3790(10)$, $c = 13.015(3)$ Å, $V = 1685.2(4)$ Å^3, $Z = 2$, $D_{\mathrm{calc}} = 1.368$ Mg/m^3, 4280 reflections collected, 1489 unique ($R_{\mathrm{int}} = 0.0235$), goodness-of-fit 0.994. $R1$, $wR2$ $[I > 2\sigma(I)]$ 0.0518, 0.1435; $R1$, $wR2$ (all data) 0.0543, 0.1453.

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