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Coordination pillared layers using a dinuclear Mn(V) complex as a secondary building unit

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This paper is dedicated to the memory of Alfred Werner.

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ABSTRACT

Coordination pillared layers (CPLs) are among the most attractive framework compounds displaying unique porous properties depending on their components. Three-dimensional Hofmann-type porous coordination polymers consisting of pillared cyanide-bridged layers with a tetracyanometallate anion $[M^{II}(CN)_4]^{2-}$ (M = Ni, Pd, Pt) as a secondary building unit (SBU) are the representative functional CPLs. In this paper, we report a new synthetic strategy for constructing CPLs using a new SBU linking two tetracyanometallate complexes, $[\{Mn^V(N)(CN)_4\}_2(bpy)]^{4-}$ (bpy = 4,4′-bipyridyl). The $[Mn^V(N)(CN)_4]^{2-}$ part in the SBU permits expansion of the 2-D cyanide-bridged layers and the pillar part bpy simultaneously links the layers. Two CPLs, $[M^{II}(bpy)\{Mn^V(N)(CN)_4(bpy)_{1/2}\}]\cdot MeCN\cdot H_2O$ (M = Zn, Cd), were synthesized by applying the SBU and characterized by X-ray single-crystal structural analysis and gas adsorption measurements.

1. Introduction

The field of coordination chemistry has come a long way since the breakthrough achieved by Alfred Werner more than 100 years ago. Along the way, diverse structural forms of coordination compounds, e.g. mono-, oligo- and polynuclear complexes, supramolecular assemblies, coordination polymers, etc., have been discovered, and they have exhibited wide-ranging features in inorganic, organic and catalytic chemistry, biology, pharmacology, material science, and so on. In recent years, coordination polymers having infinite structures via multidentate bridging ligands attract much attention from the aspect of long-range ordering and cooperativity of physical properties and structural functions which are not shown by discrete coordination compounds. In particular, for the past decade, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) providing flexible and regular porous frameworks have shown remarkable development as a new-generation porous material [1–7]. These compounds perform various functions: gas adsorption, gas separation, ion conductivity, heterogeneous catalyst, and so on, with diverse combinations of their components: metal ion, bridging ligand, co-ligand, and so on [8–16]. A rational design and synthesis of PCPs is one of the key challenges for achieving desirable properties and functions. In general, PCPs are obtained by a one-pot reaction of the components, e.g. hydrothermal synthesis. Modification of the components with different organic ligands and metal ions is often applied to enhance the properties of PCP [17–22]; however, it is difficult to forecast the resultant structures by the one-pot approach. To solve the problem, a post-synthetic method and a layer-by-layer method for constructing modified frameworks as hierarchical approaches have been developing recently [23–29]. For the rational construction of desirable framework, design strategies exploiting a stable small metal cluster or metal complex as secondary building units (SBUs) have been developed [30]. The SBU derives relatively predictable framework with polytopic organic linkers. Larger scale metal–organic polyhedral (MOPs) are also adopted as supramolecular building blocks (SBBs) for enhancing properties and structures of PCPs [31].

Coordination pillared layers (CPLs) consisting of two-dimensional (2-D) coordination networks and interlayer bridging ligands (pillar ligands) are the representative structures of PCPs [32–36]. The pillar ligand, e.g., pyrazine (pz), 4,4′-bipyridyl (bpy), etc., are important components in modifying the structure and porous properties. Hofmann-type metal complexes using the tetracyanonickelate anion $[Ni^{II}(CN)_4]^{2-}$ are some of the most traditional

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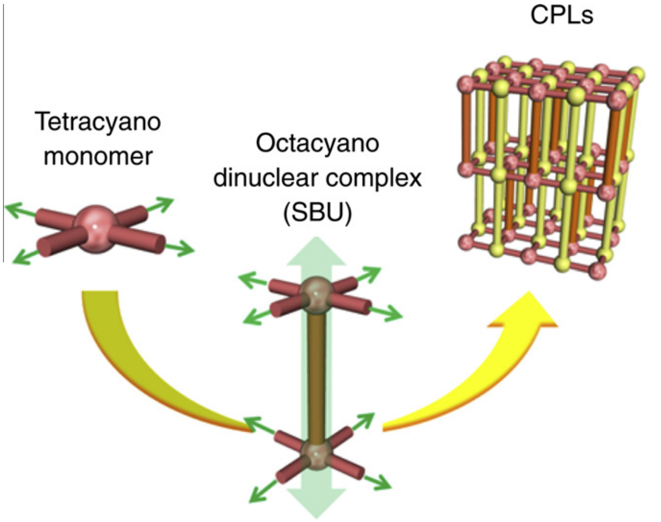
coordination polymers and show unique host–guest interactions such as solvatochromism [37–42]. Recently, CPLs based on Hofmann-type frameworks have attracted much attention. In particular, three-dimensional (3-D) Hofmann-type compounds $\{Fe^{II}(pz)[M^{II}(CN)_4]\}$ (M = Ni, Pd, Pt), which show cooperative spin transitions have been actively investigated [43–48]. These compounds have 3-D porous frameworks consisting of cyanide-bridged $Fe^{II}M^{II}$ bimetallic layers and the pillar ligand pz, and exhibit new functions coupling magnetic and adsorption properties, e.g., magnetic chemoswitching and modulation of the spin-transition temperature by guest molecules [45–48]. The tetracyanometallate SBUs play an important role in showing strong host–guest interactions as open-metal sites (OMS), however, the metal centres of OMS are limited to Ni^{II}, Pd^{II} and Pt^{II} ions at this stage. Therefore, we conceived to modify the pillared-layer-type structure by using new SBUs including the tetracyanometallate units to upgrade their functions.

Here, we focused on a tetracyanometallate complex, $[Mn^V(N)(CN)_4]^{2-}$ that was reported by Wieghardt and co-workers [49]. This compound has a distorted square planar structure like an umbrella because of the steric hindrance between the four cyano ligands and an axial nitride on the Mn^V centre. The five-coordinated Mn^V provides an OMS, which can interact with other molecules. The catalytic activity of this compound was reported by Lau and coworkers [50]. This group also adapted the $[Mn(N)(CN)_4]^{2-}$ anion as a SBU for the construction of coordination polymers, and reported 1-D and 2-D cyanide-bridged dimetallic complexes, $[\{M(L)\}\{Mn(N)(CN)_4\}\cdot solvent]$ (L = tetradentate ligands, M = Cu^{II}, Ni^{II}, Mn^{III}) [51]. Most recently, structures and thermal expansion properties of CPLs $[M(H_2O)(bpy)_{1/2}\{Mn(N)(CN)_4(bpy)_{1/2}\}]\cdot 2H_2O$ (M^{II} = Mn, Fe, Co) using the $[Mn(N)(CN)_4]^{2-}$ anion were reported by Kepert's group [52]. These compounds had wavy cyanide-bridged layers formed by the distorted shape of the $[Mn(N)(CN)_4]^{2-}$ SBU, and the M^{2+} ions were coordinated by four cyano ligands, one bpy and one water molecule. At the same time, we also investigated similar PCPs, and found that the OMS of the $[Mn(N)(CN)_4]^{2-}$ anion accepting various molecules causes the unpredictable structures. Based on these results, we designed a new SBU linking $[Mn(N)(CN)_4]^{2-}$ anion, $[\{Mn(N)(CN)_4\}_2(L)]^{4-}$ (L = bridging ligand). The OMS of the $[Mn(N)(CN)_4]^{2-}$ anion is occupied by L, and the dinuclear complex, SBU, is expected to form the 2-D networks expanded through the eight cyano groups and also act as a pillar unit for construction of the pillared-layer-type framework through the one-pot reaction (Scheme 1). Moreover, the dinuclear structure is effective in relaxing the inherent strain of the $[Mn(N)(CN)_4]^{2-}$ anion. In this paper, we report structures and guest adsorption properties of two CPLs, $[M^{II}(bpy)\{Mn^V(N)(CN)_4(bpy)_{1/2}\}]$ (M = Zn, Cd) prepared by a sequential process using the SBU, $[\{Mn^V(N)(CN)_4\}_2(bpy)]^{4-}$.



Scheme 1. A design strategy for construction of coordination pillared layers (CPLs) by using a dinuclear complex including tetracyanometallate as a secondary building unit (SBU).

2. Results and discussion

2.1. Synthesis and IR spectra

The monomer complex $[PPh_4]_2[Mn(N)(CN)_4]\cdot 2H_2O$ (**1**) was prepared as orange-pink crystals according to the literature method [49].

The crystal structure of **1** has been already reported [49]. Complex **1** has a five-coordinated distorted square pyramidal structure with an axial nitride, four equatorial cyano groups and one coordinatively unsaturated site (OMS) (Fig. 1). Complex **1** accepts other

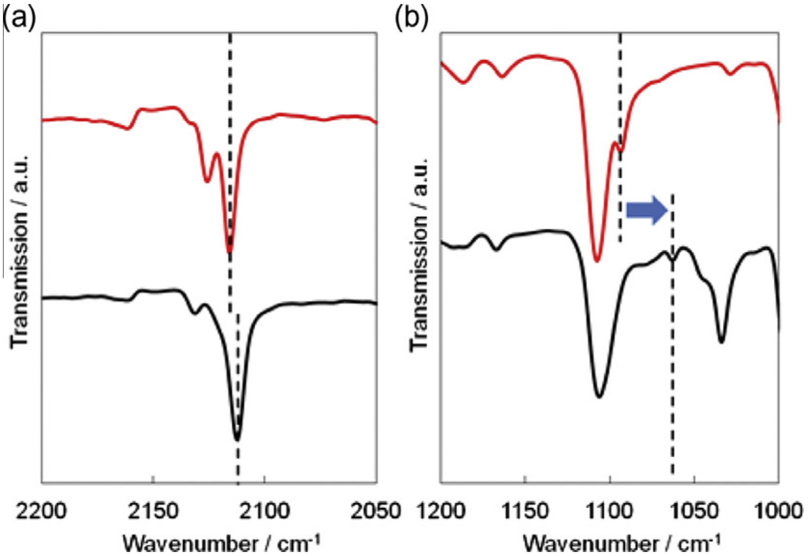


Fig. 1. Infrared spectra around (a) the $\nu(C{\equiv}N)$ and (b) $\nu(Mn{\equiv}N)$ region of **1** (red line) and **2** (black line). (Colour online.)