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Solvent effect on the structure and topology of metal-organic frameworks with the rigid tripodal star ligand 1,3,5-tris-(1-imidazolyl)benzene and lead(II) nitrate†

Jian Fan,[a] Mou-Hai Shu,[b] Taka-aki Okamura,[c] Yi-Zhi Li,[a] Wei-Yin Sun,*[a] Wen-Xia Tang[a] and Norikazu Ueyama[c]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China. E-mail: sunwy@nju.edu.cn*
[b] *School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China*
[c] *Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

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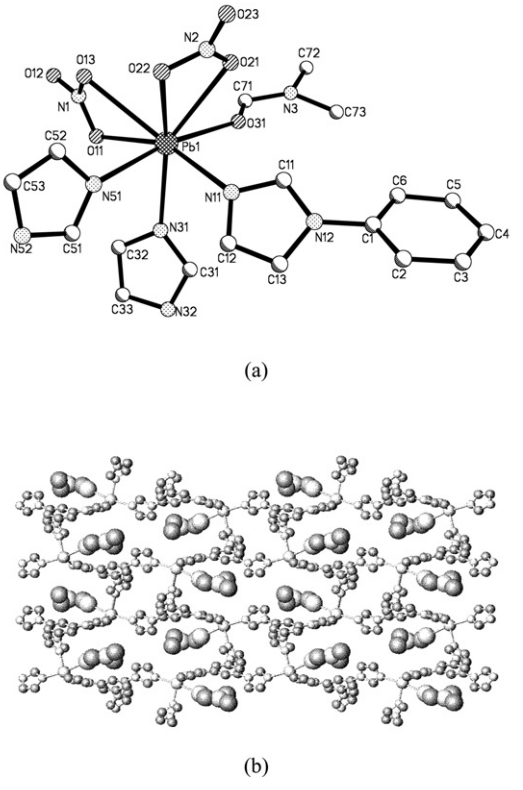
Reaction of 1,3,5-tris(1-imidazolyl)benzene with $Pb(NO_3)_2$ in DMF affords a novel metal-organic framework with 4.8^2 topology in which the DMF molecules are attached to the channel walls, while in the reaction carried out in methanol, a one-dimensional coordination polymer was obtained.

Interest in porous metal-organic frameworks (MOFs) has been driven by the prospect of generating a wide range of materials with useful properties for applications such as adsorption, ion-exchange and catalysis.[1–3] The stability of porous MOFs is a prerequisite for their use as such materials.[4] Typically, rigid ligands such as 4,4-bipyridine[5] and benzene-1,3,5-tricarboxylic acid have been deliberately chosen to construct such porous MOFs.[6]

On the other hand, lead(II) compounds have been increasingly studied owing to their possible applications in different fields, especially in environmental protection due to the toxicity of lead and in biological systems for its diverse interactions with biological molecules. In this paper, we report novel MOFs $[Pb(tib)(DMF)(NO_3)_2]$ (**1**) and $[Pb(tib)(NO_3)_2]$ (**2**) constructed from the assembly of the rigid tripodal star ligand 1,3,5-tris(1-imidazolyl)benzene (tib) with lead(II) nitrate in DMF (*N*,*N*-dimethylformaimde) and methanol, respectively, which provide nice example of structures and topologies of MOFs determined by the solvent.

The tib ligand was prepared from 1,3,5-tribromobenzene and imidazole using the Ullmann condensation reaction.[7] Complex $[Pb(tib)(DMF)(NO_3)_2]$ (**1**) was synthesized by slow diffusion of diethyl ether into a solution of tib and $Pb(NO_3)_2$ in DMF. The 2D network structure of **1** was revealed by a single crystal X-ray diffraction study. In the repeating unit of **1**, there are two nitrate ions, one lead(II) cation, one DMF molecule and one tib ligand as shown in Fig. 1(a). Each lead(II) center has a eight-coordinated environment in a holo-directed geometry, according to the discussions by Shimoni-Livny *et al.*,[8] and each nitrate anion is coordinated with Pb(II) in a bidentate mode with the Pb–O distances ranging from 2.678(6) to 2.823(15) Å. It is notable that the O atom of the DMF molecule is coordinated to Pb(II) with a Pb1–O31 distance of 2.720(15) Å. Three N atoms (N11, N31 and N51) from different tib ligands have different Pb–N distances ranging from 2.538(6) to 2.579(6) Å, which are comparable with those previously reported in complex $[Pb(timpt)(NO_3)_2]\cdot(Et_2O)_{0.417}(H_2O)_{0.167}$ {timpt = 2,4,6-tris[4-(imidazol-1-ylmethyl)-phenyl]-1,3,5-triazine}.[9] In **1**, both the Pb(II) atoms and tib ligands serve as three-connected nodes, resulting in the formation of 2D network with 4.8^2 topology as illustrated in Fig. 1(b). Compared with the (6,3) network, the 4.8^2 topology was not well-known up to now.[3b,9–10] Due to the relatively small coordination angle of N–Pb–N, ranging from 80.0(2)°



(a)

(b)

Fig. 1 (a) Coordination environment around the lead(II) atom in **1**. (b) View of the 2D 4.8^2 network of **1**, the DMF molecules are represented by a space-filling model, the hydrogen atoms and counter-ions are omitted for clarity.

† Electronic supplementary information (ESI) available: crystal packing diagram of **1**. See http://www.rsc.org/suppdata/nj/b3/b306876p/

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to 83.2(2)°, the tib ligands coordinated to the same Pb(II) atom extend within a narrow space. As a result, the imidazole groups are twisted by large angles (30.7°, 65.4° and 71.9°) with respect to the core benzene ring and the 2D network is heavily corrugated. The 2D sheet contains two kinds of metallacycles and the DMF molecules are positioned within the larger one [Fig. 1(b)]. The most striking feature of this complex is that the 2D sheets stack in a parallel mode to generate an open framework (see Fig. S1 in the Electronic supplementary information) and the solvent DMF molecules are attached the channel wall *via* a weak Pb–O coordination bond with a length of 2.720(15) Å. The remarkable openness of this MOF structure is indicated by the presence of a wide, square aperture of *ca.* 15× 6 Å^2. After removing the DMF molecules, a Platon calculation showed that the framework has 25.2% void volume.

To examine the mobility of the solvent molecules within this MOF, a thermogravimetric analysis for **1** was carried out. A weight loss corresponding to the liberation of the DMF molecules was observed below 160 °C and no weight loss was observed over the temperature range of 160–330 °C. The powder X-ray diffraction pattern of the complex without DMF obtained by heating complex **1** to 160 °C for 2 h under N_2 is sharp and essentially the same as that of complex **1** (Fig. 2). This result indicates that the porosity of **1** is retained in the absence of the DMF molecules. The stability of porous materials requires a robust framework and the rigidity of the ligand tib is responsible for the stability of complex **1**, even after removing the DMF molecules. Furthermore, when complex **1**, after removal of the DMF molecules, was immersed in an aqueous solution for one day, the resulting complex shows a weight loss in two steps: a weight loss of 2.6% below 70 °C and a further weight loss of 2.5% below 160 °C, corresponding to the liberation of two water molecules per formula unit (calcd 5.3%). As a result, one water molecule is proposed to coordinate to the Pb(II) atom in the place of the DMF molecule. No absorption was observed when **1**, after removing the DMF molecules, was immersed in tetrahydrofuran, probably due to steric hindrance.

In order to investigate the effect of solvent DMF molecules on the self-assembly process, complex [Pb(tib)$(NO_3)_2$] (**2**) was synthesized in a methanol–water system and structurally characterized. As shown in Fig. 3(a), each lead(II) was six-coordinated in a hemi-directed geometry, with two nitrate anions in bidentate and monodentate binding modes. There is an identifiable void trans to the Pb–N32, which can be seen clearly from the polyhedron presentation [Fig. 3(b)]. Although with the same metal-to-ligand ratio as complex **1**, complex **2** is composed of 1D chains, termed as a "tubular ribbon".[11] Divalent lead is known to exhibit variable coordination numbers from 2 to 10. Obviously, the coordination of the DMF molecule to Pb(II) in **1** changes the disposition of the ligands around the lead(II). It has been concluded that small cycles are favored over larger ones for entropic reasons.[12] In complex **1**, due to the presence of DMF, four tib ligands, each using two

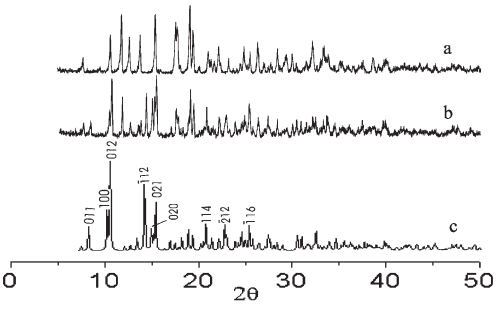
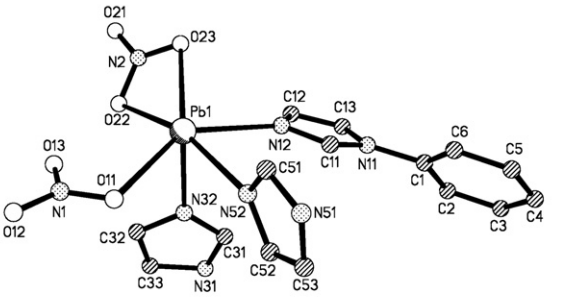
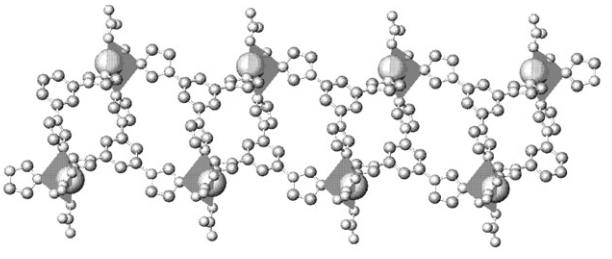


Fig. 2 X-Ray powder diffraction diagram of (a) **1** after removing the DMF molecules, (b) of **1** and (c) the simulated diagram of **1**.



(a)



(b)

Fig. 3 (a) Coordination environment around the lead(II) atom in **2**. (b) One-dimensional polymeric chain representation of complex **2**.

of their three arms, are linked by four lead(II) atoms to form a large metallacycles. In complex **2**, two kinds of metallacycles are found to result in the formation of the 1D chain, with both metallacycles being composed of two lead(II) atoms and two tib ligands.

In conclusion, two novel MOFs were obtained by assembly reactions of the rigid tripodal star ligand 1,3,5-tris(1-imidazolyl)benzene with lead(II) nitrate. The structural difference indicate that the solvents greatly affect the self-assembly process in this system. This approach of incorporating solvent molecules into MOFs provides opportunities for the design of new MOFs.

Experimental

Syntheses

Synthesis of 1. $Pb(NO_3)_2$ (16.5 mg, 0.05 mmol) and tib (13.8 mg, 0.05 mmol) were added to the DMF solution (10 ml). The mixture was stirred for half an hour and filtered. Colorless crystals were obtained by slow diffusion of diethyl ether into the above filtrate over several weeks. Yield 56%. Anal. calcd for $C_{18}H_{19}N_9O_7Pb$: C, 31.77; H, 2.81; N, 18.52; found: C, 31.65; H, 2.89; N, 18.64.

Synthesis of 2. A methanol solution (10 ml) of tib (13.8 mg, 0.05 mmol) was layered over an aqueous solution (2 ml) of $Pb(NO_3)_2$ (16.5 mg, 0.05 mmol). Colorless crystals were isolated by filtration after several weeks. Yield 63%. Anal. calcd for $C_{15}H_{12}N_8O_6Pb$: C, 29.66; H, 1.99; N, 18.44; found: C, 29.77; H, 2.10; N, 18.49.

X-Ray crystallography

The data collection for complex **1** was made on a Bruker Smart Apex CCD with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The structures was solved by direct

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methods using SHELX-97 and refined by full-matrix least-squares method anisotropically for non-hydrogen atoms. Calculations were performed on a PC-586 computer with the Siemens SHELXTL program package. The data collection for **2** was performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å) at 200 K. The structures were solved by direct methods using SIR92 and expanded using Fourier techniques. Calculations were carried out on a SGI workstation with teXsan software package.

CCDC reference numbers 206573–206574. See http://www.rsc.org/suppdata/nj/b3/b306876p/ for crystallographic files in CIF or other electronic format.

Crystal data for [Pb(tib)(DMF)$(NO_3)_2$] (1). Monoclinic, $P2_1/c$, $M = 680.61$, $a = 8.5468(8)$, $b = 11.7744(11)$, $c = 23.277(2)$ Å, $\beta = 96.143(2)°$, $U = 2329.0(4)$ Å^3, $Z = 4$, $Dc = 1.941$ g cm^{-3}, $\mu = 0.7303$ mm^{-1}, $R1 = 0.0536$, $wR2 = 0.1468$ (4221 reflections).

Crystal data for [Pb(tib)$(NO_3)_2$] (2). Triclinic, $P-1$, $M = 607.52$, $a = 8.6278(6)$, $b = 9.5870(7)$, $c = 11.5759(8)$ Å, $\alpha = 84.345(4)°$, $\beta = 84.226(5)°$, $\gamma = 75.040(4)°$, $U = 917.73(11)$ Å^3, $Z = 2$, $Dc = 2.198$ g cm^{-3}, $\mu = 0.9247$ mm^{-1}, $R1 = 0.0538$, $wR2 = 0.1340$ (3373 reflections).

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