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2D 4.8^2 Network with threefold parallel interpenetration from nanometer-sized tripodal ligand and lead(II) nitrate†

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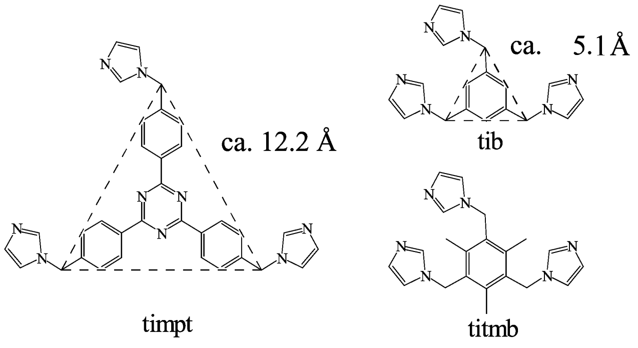
Reaction of nanometer-sized tripodal ligand 2,4,6-tris[4-(imidazol-1-ylmethyl)phenyl]-1,3,5-triazine (timpt) with lead(II) nitrate affords a novel polycatenated structure containing three interpenetrating 4.8^2 networks, in which the lead(II) atom has a hemidirected coordination geometry and a stereochemically active lone pair of electrons.

Supramolecular polymeric architectures containing topological bonds, such as polycatenanes and polyrotaxanes, have been attracting considerable interest,[1] not only because of their aesthetic structures but also due to their interesting properties and potential applications.[1,2] We are currently engaged in a systematic study of self-assembly of a series of tripodal ligands with various metal ions and are investigating the influence of the linkage mode of bridging ligands on the assembly process of supramolecular complexes.[3] Our previously reported tripodal ligands, *e.g.* 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib), 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb), in which the imidazole groups are connected *via* methylene group to the central benzene ring, have been found to form individual cages and infinite 2D networks with metal salts.[3] A novel nanometer-sized tripodal ligand 2,4,6-tris[4-(imidazol-1-ylmethyl)phenyl]-1,3,5-triazine (timpt) (Scheme 1) was designed by insertion of a rigid benzene ring between the methylene and central aromatic groups, and such large three-connecting ligand can be expected to form large frameworks with interesting topologies and structures by reactions with metal salts. We report herein a coordination polymer constructed from timpt and lead(II) nitrate, and consisting of three independent 2D polymeric sheets which interpenetrate each other in a parallel manner to generate a novel 2D polycatenated network.

The timpt ligand was prepared from 2,4,6-tris[4-(chloromethyl)phenyl]-1,3,5-triazine and imidazole.‡ The title complex, $[Pb(timpt)(NO_3)_2]\cdot(Et_2O)_{0.417}\cdot(H_2O)_{0.167}$ (**1**), was synthesized by slow diffusion of diethyl ether into the solution of timpt and $Pb(NO_3)_2$ in DMF.§ The X-ray structural analysis of **1**¶ reveals that each lead(II) center has a seven-coordinated environment as shown in Fig. 1. The Pb(II) atom lies 0.41 Å above the plane defined by the five coordinated atoms N12, O41, N32, O52 and O53, while the N22 is 1.96 Å below the plane. Three N atoms (N12, N22 and N32) from three different ligand moieties, have different Pb–N distances ranging from 2.374(5) to 2.601(7) Å. The four remaining sites are occupied by O atoms from two nitrate anions. From Fig. 1, it can be clearly seen that the coordination sphere on Pb(II) is rather one-sided. According to the discussions by Shimoni-Livny *et al.*, the coordination around the lead(II) atom described here is hemidirected with a significant void *trans* to the Pb–N22 bond, indicating a stereochemically active lone pair of electrons on Pb(II).[4]



Scheme 1

On the other hand, each timpt ligand links three Pb(II) atom to generate a 2D network structure with two different large metallacycles A and B (Fig. 2). In A, four arms from two different timpt ligands bridge two lead(II) atoms to form a 40-membered ring with a Pb···Pb distance of 18.62 Å. In B, four timpt ligands, each using two of their three arms, are

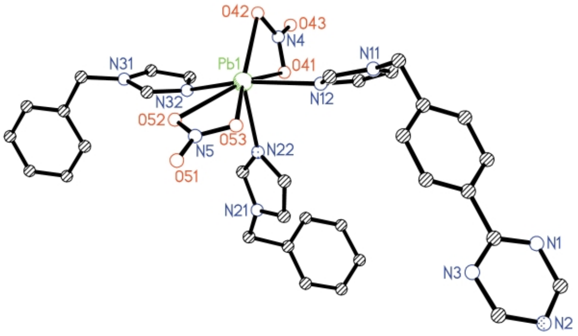


Fig. 1 Coordination environment around the lead(II) atom in **1**. Selected bond lengths (Å) and angles (°): Pb1–N12 = 2.564(6), Pb1–N22 = 2.374(5), Pb1–N32 = 2.600(7), Pb1–O41 = 2.543(6), Pb1–O52 = 2.751(6), Pb1–O53 = 2.753(5), Pb1–O42 = 2.863(6); N12–Pb1–N22 = 83.8(2), N32–Pb1–N22 = 81.3(2), O41–Pb1–N22 = 77.28(19), O52–Pb1–N22 = 84.21(19), O53–Pb1–N22 = 79.19(17), O52–Pb1–O53 = 45.33(17).

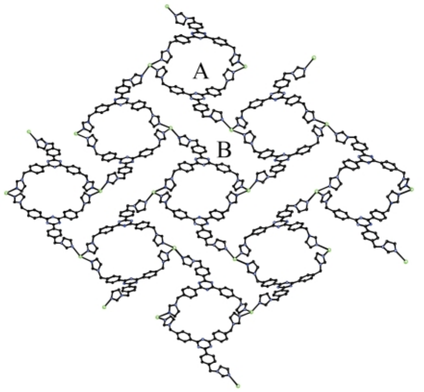


Fig. 2 2D network of 40- and 80-membered metallacycles of **1**.

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† Electronic supplementary information available: Fig. 1S. See http://www.rsc.org/suppdata/cc/b2/b207568g/

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connected by four lead(II) atoms to form a 80-membered ring. Accordingly, each 40-membered ring is surrounded by four 80-membered rings, and each 80-membered ring neighbors upon four 40-membered and four 80-membered rings arranged in a spaced manner. Namely the 2D network has a 4.8^2 topology.

The fascinating feature of the overall structure of **1** is that three such 2D networks are interpenetrating each other as illustrated in Fig. 3. Namely, three independent 2D sheets interpenetrate each other in a parallel fashion, still making an infinite 2D polycatenated network sheet. Two 80-membered rings from two different independent sheets are threaded through one of the 40-membered rings from the third sheet, and each 80-membered ring passes through four 40-membered rings from the other two sheets, thus generating a polycatenane network. This is, to our knowledge, the first structure presenting three interpenetrating 2D frameworks with tripodal ligand[5] and the second structure containing interpenetrating 4.8^2 networks.[1f,6]

In the timpt, the rigid benzene rings between the flexible imidazol-1-ylmethyl arms and the central aromatic core made the resulting metallacycles large enough to accommodate an additional two layers in a parallel manner. While in the reported tib and titmb ligands, no such large metallacycles and interpenetrating structures could be obtained since they are smaller than the timpt ligand (Scheme 1).[3] In addition, the large aromatic system in timpt ligand increases the possibility of π–π interactions which may contribute to the stability of the interpenetrating networks. Indeed, efficient parallel face-to-face π–π interactions were observed between the triazine rings with a centroid–centroid separation of 3.62 Å, and also between the triazine ring and the benzene ring with a centroid–centroid separation of 3.85 Å (Fig. S1†). Therefore the nanometer size of timpt and its flexibility provide the opportunity for the formation of the observed structure, while the other tripodal ligands, *e.g.* 1,3,5-tricyanobenzene and titmb, also connect three metal atoms to form 2D networks but without interpenetration due to their small size and rigidity.[2f,3a]

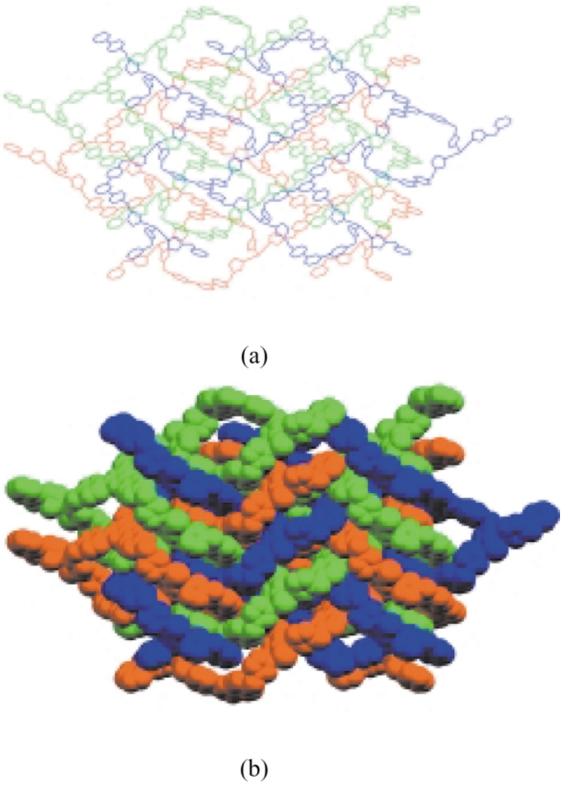

Fig. 3 Perspective (a) and space-filling (b) view of the 2D threefold interwoven polycatenane structure of **1**. Nitrate anions were omitted for clarity.

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Notes and references

‡ The timpt ligand was prepared from the reaction of 2,4,6-tris[4-(chloromethyl)phenyl]-1,3,5-triazine and imidazole in the presence of K_2CO_3 and catalytic amounts of KI in acetone and was isolated in 60% yield. ^1H NMR (DMSO-d_6, 298 K): *d* 8.68 (6H, d, H_{bz}), 7.82 (3H, s, $^2H_{im}$), 7.48 (6H, d, H_{bz}), 7.25 (3H, s, $^5H_{im}$), 6.96 (3H, s, $^4H_{im}$), 5.36 (6H, s, CH_2). H_{bz} refers to benzene-ring protons and H_{im} imidazole protons. Element analysis found: C, 72.07; H, 4.99; N, 22.96. $C_{33}H_{27}N_9$ requires C, 72.11; H, 4.95; N, 22.94%.

§ *Experimental*: A MeOH solution (10 ml) of timpt (55.0 mg, 0.1 mmol) was added dropwise to $Pb(NO_3)_2$ (33.1 mg, 0.1 mmol) in MeOH/H_2O (10 ml, v/v, 20 : 1) to give a white precipitate. After being stirred for *ca.* 15 min at room temperature, the precipitate was isolated, dissolved in DMF (10 ml) and filtered. Colorless crystals were obtained by slow diffusion of diethyl ether into the above filtrate over several days. The yield amounted to *ca.* 65%. Element analysis found: C, 45.84; H, 3.55; N, 16.81. $C_{34.67}H_{31.50}N_{11}O_{6.58}Pb$ {$[Pb(timpt)(NO_3)_2]\cdot(Et_2O)_{0.417}\cdot(H_2O)_{0.167}$} (**1**) requires C, 45.52; H, 3.47; N, 16.84%. TGA data of **1** showed that the framework is stable up to 280 °C after losing diethyl ether and water molecules with weight loss of 3.77% (calcd. 3.71%). The X-ray powder pattern of white precipitate formed immediately and **1** after removing diethyl ether and water is almost the same with that of **1** indicating that the structure of **1** is maintained without solvent molecules. The Platon calculation shows that the framework has 8.7% void volume.

¶ *Crystal data* for {$[Pb(timpt)(NO_3)_2]\cdot(Et_2O)_{0.417}\cdot(H_2O)_{0.167}$}: $M = 914.73$, monoclinic, space group $C2/c$, $a = 33.6859(7)$, $b = 7.7447(2)$, $c = 30.8578(10)$ Å. $\beta = 116.0144(11)°$. $U = 7234.8(3)$ Å^3, $Z = 8$, $D_c = 1.680$ g·cm^{-3}, $\mu = 4.727$ mm^{-1}, $F(000) = 3609$, $T = 200$ K. The data collection was carried out on a Rigaku RAXIS-RAPID Imaging Plate using graphite-monochromated Mo-Ka radiation ($\lambda = 0.7107$ Å). The structure was solved by direct method with SIR-92 and refined by full-matrix least-squares calculations. The O atom of water was refined isotropically and the hydrogen atoms on the water molecules are not located. The final $R1 = 0.0558$ [$I > 2\sigma(I)$]. CCDC 191433. See http://www.rsc.org/suppdata/cc/b2/b207568g/ for crystallographic files in CIF or other electronic format.

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