

Reversible uptake of HgCl₂ in a porous coordination polymer based on the dual functions of carboxylate and thioether†

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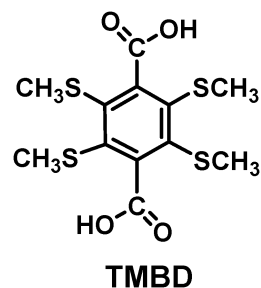
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Bifunctional tetrakis(methylthio)-1,4-benzenedicarboxylic acid and Pb²⁺ ions form a robust porous net featuring free-standing thioether groups that allow reversible uptake of HgCl₂.

Coordination polymers (aka metal–organic frameworks, MOFs)¹ present remarkable porous features and have potential applications in sorption/separation,² catalysis,³ and sensing.^{2e,4} Unlike inorganic systems, the organic linkers of porous coordination networks (PCNs) offer functional diversity and thus convenient control of the size, shape and functionality of the porous structures. Although the control of pore size or shape by tuning the organic linker has been extensively explored,⁵ functionalization of the pores by means of secondary binding units on organic linkers is gaining ever more importance. Besides the earlier studies from the groups of Lee,^{5d,6} Wuest (H-bonding nets)⁷ and Lin,^{3b} notable recent efforts include the use of 2-amino-1,4-benzene dicarboxylic acid,⁸ an azide-decorated MOF for click functionalization,⁹ and ZIF post-synthetic modification.¹⁰ A major challenge here is to choose secondary groups that refrain from significant metal complexation in the crystallization process, as such complexation could interfere with the primary groups when forming the host net.

In this regard, the combination of carboxylic and thioether functional groups as illustrated in TMBD provides appealing opportunities for functionalizing metal–organic frameworks. Specifically, the ionic, chemically hard carboxylate groups are predisposed as the primary group to interact with metal ions for network formation, while leaving the neutral, and generally weaker-binding thioether groups as free standing, secondary donors. We have recently demonstrated the viability of building an open metal–carboxylate network containing free-standing methylthio groups (*i.e.*, Zn₄O(H₂O)₃(TMBD)₃).^{11a} This particular network, however, tended to degrade upon solvent loss, and therefore precludes further studies on sorption/exchange behaviors. Herein, we report a highly robust, 3D porous coordination network compound (network composition: PbTMBD; henceforth called **1**) featuring microchannels that are extensively functionalized with methylthio groups.^{11b} To illustrate the functional significance of the thioether groups as

a secondary binding unit, we will present the reversible sorption of HgCl₂ species into the microchannels of this network. Such sorption behavior is particularly worthy of note, because the sorption studies of PCNs are often devoted to gaseous species (*e.g.*, N₂, H₂, CH₄ and CO₂)^{1a,2a–d} or small organic molecules (*e.g.*, alkanes and aromatics),^{2e–g} and the coordinative binding of metal species onto PCN matrices is just beginning to be pursued.^{3b,4f,8d,12,13}



Compound **1** was obtained by reacting TMBD with Pb(NO₃)₂ in *N,N*-dimethylacetamide (DMA) and acetonitrile (4:1, v/v) under solvothermal conditions.† X-ray single-crystal analysis reveals that **1** crystallizes in the space group *C2/c* (No. 15) and features chains of the Pb-carboxylate component integrated into a 3D open framework by the aromatic cores of the TMBD molecules, with both the Pb-carboxylate chains and the channels running along the *c* axis (see Fig. 1). The asymmetric portion of the unit cell contains 1.5 Pb²⁺ centers (Pb1 and Pb2, with Pb2 located on a C₂ axis and thus has a multiplicity of 2), 1.5 TMBD molecules (*i.e.*, from 3 centrosymmetric TMBD), and one DMA molecule and an

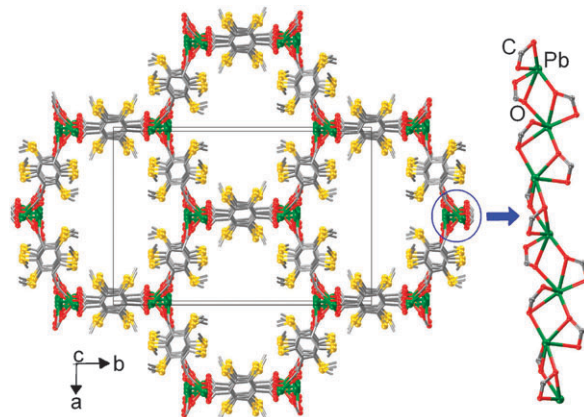


Fig. 1 View of the PbTMBD network of **1** along the channel direction (left), and a side view of the chain-like Pb-carboxylate domain (right).

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oxygen site refined as a water molecule with an occupancy factor of 0.79 (this O atom is on the C_2 axis with a multiplicity of 2): the overall formula determined from X-ray diffraction can thus be represented as $Pb_3(TMBD)_3 \cdot 2DMA \cdot 0.79H_2O$. Both Pb^{2+} ions are coordinated to six oxygen atoms of the carboxylate groups, with $Pb1-O$ distances ranging from 2.271 to 2.957 Å, and $Pb2-O$ from 2.477 to 2.597 Å—the water molecule is located at the center of the channel and is not bonded to the $Pb(II)$ ions. Pairs of $Pb1$ atoms alternate with individual $Pb2$ atoms along the Pb -carboxylate chain direction. Besides the O atoms, $Pb1$ also weakly interacts the S2 and S6 atoms at 3.646 and 3.571 Å, respectively; $Pb2$ to S3 at 3.330 Å (S1, S4 and S5 are free-standing). The association of the S atoms with the $Pb(II)$ centers is thus quite limited, and their orientation toward the channel also makes them poised for secondary donation. The channels of the as-synthesized crystals of **1** are filled with DMA and water guest molecules, and the total solvent-accessible volume of the $PbTMBD$ network is about 25.6% as calculated by PLATON.¹⁴

Thermogravimetric analysis (TGA, Fig. S1†) of the as-made sample of **1** reveals a gradual and continuous weight loss of 10.0% between 95 °C and 316 °C, corresponding to the evacuation of the DMA and water guests (calculated DMA and water proportion in $Pb_3(TMBD)_3 \cdot 2DMA \cdot 0.79H_2O$: 10.1%). The weight loss registered beyond 316 °C is precipitous and suggests a disintegrating host net. The DMA and water guests can also be removed, without collapsing the host net, by heating the as-made sample at 200 °C *in vacuo* for 5 h (see pattern c in Fig. S3†); unless otherwise indicated, all solvent-free samples of **1** in this work were similarly prepared. The guest-free framework of $PbTMBD$ thus prepared was further characterized by TGA, IR and elemental analysis, to verify the complete removal of the guest molecules (ESI†). The guest-free sample of $PbTMBD$ was then subjected to sorption studies of $HgCl_2$ —at this preliminary stage, we have chosen $HgCl_2$ because of the softness of $Hg(II)$ species (which favors interaction with the soft S atoms in **1**), its relatively good solubility in organic solvents and the environmental relevance of the Hg species. Specifically, the desolvated crystals of $PbTMBD$ and excess $HgCl_2$ in benzene were sealed in a glass tube, and then heated at 100 °C for 48 h (ESI†). After filtrating and washing with THF (to remove residual $HgCl_2$ particles from the exterior of the $PbTMBD$ network), the solid sample thus treated was subjected to the regular CHN (carbon, hydrogen and nitrogen) and ICP (inductively coupled plasma) elemental analyses, which indicated that $PbTMBD$ was impregnated with $HgCl_2$ guests (*i.e.*, 1:1 $Pb^{2+} : Hg^{2+}$ ratio, see also ESI†), and the resultant adduct can be represented as $PbTMBD \cdot HgCl_2$.

The uptake of $HgCl_2$ into the $PbTMBD$ net was also monitored by powder X-ray diffraction studies. As shown in Fig. 2, the 110 and 020 peaks almost vanish for the loaded sample (pattern b), whereas the higher angle peaks (*e.g.*, 200, 220, 330) become relatively strong. Such a drastic change in diffraction peak intensities reflects the significant increase of electron density in the channel region (*i.e.*, the system becomes less porous) as a result of the uptake of $HgCl_2$. Incidentally, the impregnated sample $PbTMBD \cdot HgCl_2$ maintains the single crystalline appearance (*e.g.*, with regards shape and transparency),

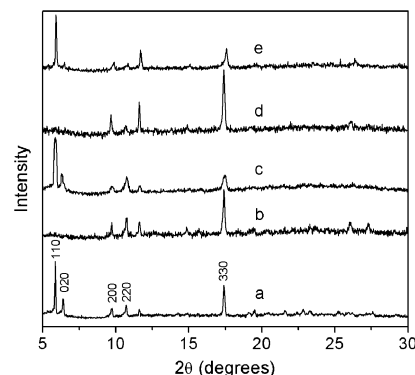


Fig. 2 X-Ray powder patterns at 298 K ($Cu K\alpha$, $\lambda = 1.5418 \text{ \AA}$) of (a) an as-made sample of **1**; (b) a $HgCl_2$ -loaded sample of $PbTMBD \cdot HgCl_2$; (c) a $HgCl_2$ -depleted sample from washing (b) with acetonitrile; (d) a sample from reloading (c) with $HgCl_2$; (e) a sample from washing (d) with acetonitrile to deplete $HgCl_2$ once again.

and a single crystal diffraction dataset was collected. The processing of this dataset revealed that the space group changed from $C2/c$ for pristine **1** to $C2/m$ for the impregnated sample of $PbTMBD \cdot HgCl_2$. The overall connectivity as well as the local coordinating features of the $PbTMBD$ host net are, however, little changed, as can be readily determined from the diffraction data. Modeling of the strong Fourier peaks in the channel region, however, proved hardly viable, and it was therefore handled by the SQUEEZE procedure in PLATON (see the ESI†). In the difference res file thus obtained, residual electron density peaks (Q peaks) of up to 48 electrons are observed. Such strong Q peaks are consistent with the presence of the heavy atoms of the $HgCl_2$ components. Specifically, the strongest Q peak is 2.685 Å away from two (chelating) S atoms on the host net, suggestive of an Hg site from the $HgCl_2$ fragments. Fig. S4 presents the structure from the difference res file, with the major Q peaks included.† Assuming that all the residual electron density within the voids is due to $HgCl_2$, the electron count within the voids obtained from SQUEEZE leads to a $Pb : Hg$ ratio of 1 : 0.96, in accord with the value of 1 : 1 obtained by ICP.

Interestingly, the majority of the $HgCl_2$ component in the $PbTMBD \cdot HgCl_2$ sample can be removed by a polar solvent such as acetonitrile, while maintaining the structural integrity of the $PbTMBD$ host net. For example, immersing the $PbTMBD \cdot HgCl_2$ crystals (about 10.0 mg) in acetonitrile (about 2.0 ml) at 60 °C for 3 days led to over 79% of the $HgCl_2$ component being removed, as shown by the regular CHN and ICP elemental analyses (see ESI†). Powder X-ray diffraction studies on the $PbTMBD$ host net thus recovered revealed that the relative intensity of the peaks was largely restored to resemble that of the pristine samples of **1**, consistent with the recovering of the porous features of the host net (pattern c in Fig. 2). Moreover, this impregnation–depletion cycle can be repeatedly executed while maintaining the crystallinity of the host net (*e.g.*, patterns d and e in Fig. 2).

To highlight the functional significance of the methythio groups for the sorption of $HgCl_2$, zinc 1,4-benzenedicarboxylate (BDC)-based MOF-5 crystals were subjected to sorption studies under similar conditions (ESI†). The powder X-ray diffraction patterns of the MOF-5 samples did not change

significantly after being treated by a benzene solution of HgCl_2 under the same conditions used for the preparation of PbTMBD-HgCl_2 (Fig. S5[†]). The ICP measurement on the HgCl_2 -treated sample also registered minimal presence of Hg species, with a measured Zn:Hg ratio being about 658:1. Such studies thus indicate that, unlike the host net of **1**, MOF-5 does not significantly take up HgCl_2 under these conditions. This is also consistent with the fact that upload of metal-containing species into MOF-5 commonly proceeds through volatile or soluble organic metal complexes.¹⁵

Similar efforts to load AgBF_4 and PdCl_2 (using common solvents such as benzene, THF) into the guest-free samples of **1** did not indicate as significant an uptake as for HgCl_2 . Introducing more binding sites in the side chain (e.g., $\text{CH}_3\text{SCH}_2\text{CH}_2\text{S}-$) and enlarging the pores may help promote the uptake of a wider range of metal species.

To conclude, the reversible adsorption of HgCl_2 observed here reflects the robustness of the host net as well as the binding efficiency of the free-standing thioether groups. Moreover, the upload of metal species provides a springboard for further functionalizing the coordination nets. For example, the uploaded metal species could serve as functional sites for solid state catalysis or sensing, or for reacting with additional guest species (e.g., H_2S) to generate a wider array of metal species within the pores. The combination of chemically soft and hard functional groups in the molecular building blocks may prove to be a generally applicable paradigm for achieving advanced structural features and functions in coordination polymers.

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Notes and references

[†] Synthesis of **1**: A mixture of $\text{Pb}(\text{NO}_3)_2$ (3.3 mg), TMBD (3.5 mg), and *N,N*-dimethylacetamide (DMA)-acetonitrile (0.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 140 °C for 48 h and cooled to room temperature at a rate of 5 °C h⁻¹. Colorless block-like crystals were obtained (4.3 mg, 70%, based on TMBD). Larger-scale preparations (e.g., with 35.0 mg of TMBD) using a larger Pyrex glass tube or Teflon reactor provided the same product in single phase purity (as checked by X-ray powder diffraction). Chemical analysis of the product $\text{C}_{44}\text{H}_{55.58}\text{N}_2\text{O}_{14.79}\text{Pb}_3\text{S}_{12}$, corresponding to $\text{Pb}_3(\text{TMBD})_3 \cdot 2\text{DMA} \cdot 0.79\text{H}_2\text{O}$, yields: calcd [C (28.48%), H (3.02%), N (1.51%)]; found [C (28.24%), H (3.00%), N (1.52%)].

Crystal data for **1**: $\text{C}_{44}\text{H}_{55.58}\text{N}_2\text{O}_{14.79}\text{Pb}_3\text{S}_{12}$, $M_r = 1855.56$, space group $C2/c$, $a = 19.900(1)$ Å, $b = 27.036(2)$ Å, $c = 12.2604(8)$ Å, $\beta = 110.896(1)^\circ$, $V = 6162.4(7)$ Å³, $Z = 4$, $D_c = 2.001$ g cm⁻³, $\mu = 8.642$ mm⁻¹, $F(000) = 3559.6$, GOF = 1.118. A total of 25561 reflections were collected and 7653 are unique ($R_{\text{int}} = 0.0352$). $R1$ ($wR2$) = 0.0329 (0.0764) for 357 parameters and 7653 reflections [$I > 2\sigma(I)$].

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