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Communication

A novel porous metal-organic framework from a new bis(acylhydrazone) ligand capable of reversibly adsorbing/desorbing water and small alcohol molecules†‡

Chun-Li Guo,[a,b] **Xiao-Zeng Li,**[*a,b] **Xing-Mei Zhang,**[a] **Lu Wang**[a] **and Li-Na Zhu**[a]

A porous metal-organic material of the doubly deprotonated form of a new bis(aroylhydrazone) ligand (L1²⁻) was self-assembled from 2,3-butanedione, isonicotinoyl hydrazine and
10 **lead nitrate. X-ray single crystal analysis revealed that six L1²⁻ and six Pb²⁺ are arranged alternately to form a metallomacrocycle in the porous material. Weak coordination bonds together with π···π interactions connect the metallomacrocycle units rather strongly into two**
15 **interpenetrating unique 3D networks. TG, PXRD and dehydration investigation showed that all the coordination and guest water molecules in the material can be removed when heated to give the activated structure with vacant pores and open Pb sites. The material can reversibly adsorb/desorb**
20 **water and small alcohol molecules.**

Porous metal-organic frameworks (MOFs) have wide application potential in catalysis,[1] gas storage[2] and separation,[2e,2f,3] ion exchange,[4] drug delivery,[5] molecular sensing,[6] and so on.[7] Therefore, the design and construction of functional porous
25 MOFs have attracted enormous attention.

The judicious selection and design of bridging ligands are among the most powerful strategies to achieve target MOFs. Various features of bridging ligands, such as coordination characteristics, shapes, functionalities, charges and rigidities are
30 closely related with the structures, properties and functions of the resulting MOFs and should be carefully considered in the ligand selection and design.[2f,7f-h] It can be deduced that bis(isonicotinoyl hydrazones) (denoted as H₂L, Scheme 1 (a)) of 2,3-butanedione, pyruvaldehyde, dibenzoyl and other compounds with two
35 adjacent active carbonyls and the deprotonated forms HL⁻ and L²⁻ (Scheme 1 (b and c)) of such bis(aroylhydrazones) would constitute a new series of bridging ligands for the construction of functional MOFs. An H₂L could be formed by the Schiff base condensation of isonicotinoyl hydrazine and the related
40 compound with two adjacent active carbonyls and could lose the protons on the amido N atoms to form the corresponding HL⁻ or L²⁻ when binding to metal ions according to the chemistry of the reported acylhydrazones.[8] Such a ligand would be able to link metal centres by tetradentately chelating a metal ion via its two O
45 atoms and two imine N atoms and coordinating to other metal
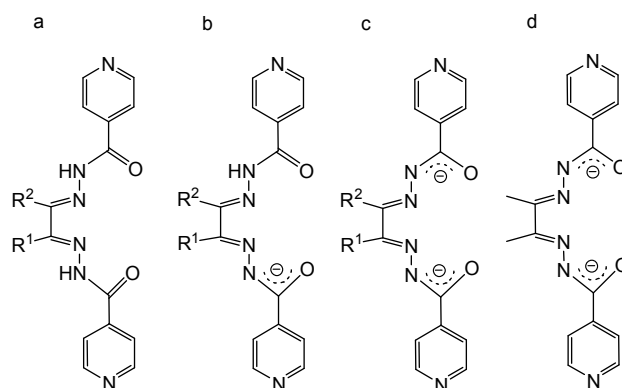
Scheme 1 (a) H₂L, (b) HL⁻, (c) L²⁻ and (d) L1²⁻

ions through its pyridine N atoms. MOFs constructed from bridging ligands with such two neighbouring acylhydrazone moieties to tetradentately chelate a metal centre have not been
50 reported to the best of our knowledge. The above tetradentate chelation would augment the metal-ligand binding strength. The negative charges on HL⁻ and L²⁻ ligands would both strengthen the metal-bridging ligand bonds and reduce or eliminate the need for other anions to balance the positive charges of the metal ions.
55 The reduction or elimination of counterions would be conductive to increasing the effective pore volumes of the MOFs. The π-systems of H₂L, HL⁻ and L²⁻ could be involved in π···π interactions,[8c,9] being possible to play a part in stabilising the resultant structures and increasing interactions with guest
60 molecules having π-systems. Interestingly, metal complexes of acylhydrazone ligands have been found to have good biological activities[8b,8c] as well as catalytic activities.[10]

The wise choice of metal ions is another potent tool to engineer the structures, properties and functions of MOFs. Pb²⁺ is
65 unique in that it has a tendency to take on hemidirected coordination geometries, especially for N and O donor atoms.[11] If Pb²⁺ ions act as the nodes of MOFs, the hemidirected coordination geometries could play roles in directing the structures of the resulting materials. Furthermore, the
70 uncoordinated sides of the Pb²⁺ nodes with hemidirected coordination geometries could be the components of the pore surfaces of porous MOFs, and thus the functions of the materials could have relevance to the exposed Pb sites. Exposed metal

centers can play key roles in many of the materials applications such as catalysis,[1d,3c,7b,7e-g] adsorption[2g,3c,6c,7e-g] and sensing.[3c,6c-e]

Herein we report a new porous MOF $\{[PbL1(H_2O)]_6 \cdot 30H_2O\}_\infty$ (1) (for $L1^{2-}$ see Scheme 1 (d)), which was obtained by slow
5 reaction of 2,3-butanedione, isonicotinoyl hydrazine, lead nitrate and triethylamine in a mixture solvent of acetonitrile and water at room temperature (see the ESI† for further details).

X-ray single-crystal diffraction analysis (ESI†) revealed that in compound 1 the ligand $L1^{2-}$ provides its two O atoms (O1 and
10 O2) and two imine N atoms (N3 and N4) to chelate a Pb^{2+} ion and coordinates to another Pb^{2+} ion using a pyridine N atom (N1) (Fig. 1 (top)). Interestingly, six such $L1^{2-}$ ligands and six Pb^{2+} ions are arranged alternately to form a metallomacrocycle with the longest Pb⋯Pb separation being 14.907(2) Å (centre-to-centre).
15 All the hexametallomacrocycles in 1 adopt the same chair conformation. The two O and three N donor atoms locate in a space smaller than half the globe around the Pb centre to form a hemidirected geometry.[11]

The O1–C11 and O2–C6 lengths (1.27(1) and 1.28(1) Å, Fig.
20 1 (middle), Table S1, ESI†) of the $L1^{2-}$ ligand in 1 are significantly longer than the C=O bonds in isonicotinoyl hydrazone ligands.[8a,8c,12] The N2–C11 and N5–C6 distances (1.33(1) and 1.33(1) Å) are shorter than their counterparts in free isonicotinyl hydrazone ligands and have C=N double bond
25 characters rather than those of typical N–C single ones. N2–N3, N4–N5, C5–C6, C7–C9 and C11–C12 are single bonds according to their lengths. The above facts imply that the bis(isonicotinoyl hydrazone) ligand in the title complex is in the doubly deprotonated form ($L1^{2-}$) and that the π-electrons originated from
30 the C=O bonds and deprotonation of the amido groups are delocalised to form two conjugated systems, one of which includes O1, C11 and N2 and the other includes O2, C6 and N5.

It is worthy to note that each metallomacrocycle in the crystal of 1 contacts with six other metallomacrocycles with close atom-
35 to-atom distances (Fig. 1 (middle and bottom), Fig. S1 and Table S2, ESI†). Between each pair of such contacting metallomacrocycles, there are two Pb⋯N_{amide} distances (Pb1⋯N5B, 2.991(8) Å) considerably longer than normal Pb–N bonds,[11a] much shorter than the sum of the van der Waals radii of
40 Pb and N atoms (3.55 Å)[13] and significantly longer than any other atom-to-atom distance in each pair of such contacting metallomacrocycles, hinting that binding interactions weaker than normal coordination bonds but stronger than van der Waals interaction exist between the contacting Pb and N_{amide} atoms.
45 Apart from the Pb⋯N_{amide} weak bonds, many other atom-to-atom distances are shorter than 3.80 Å (Fig. 1 (middle) and Table S2, ESI†) between each pair of the contacting metallomacrocycles. These contacting atoms are involved in unclosed π-systems or pyridine rings, which can take part in π⋯π
50 interactions.[8c,9] Hence, extensive π⋯π interactions occur between each pair of the metallomacrocycles with the short contacts.

Remarkably, the weak Pb⋯N_{amide} bonds and π⋯π interactions link the metallomacrocycles in the crystal of 1 into two same unique 3D networks (Figs. 1 (bottom) and 2 and Figs. S1–S3,
55 ESI†) with large pores. Intriguingly, the two unique 3D networks interpenetrate each other (Fig. 2 and Fig. S4, ESI†), which still sustains channels along the c axis with a diameter as large as that of the metallomacrocycles and filled with water molecules.
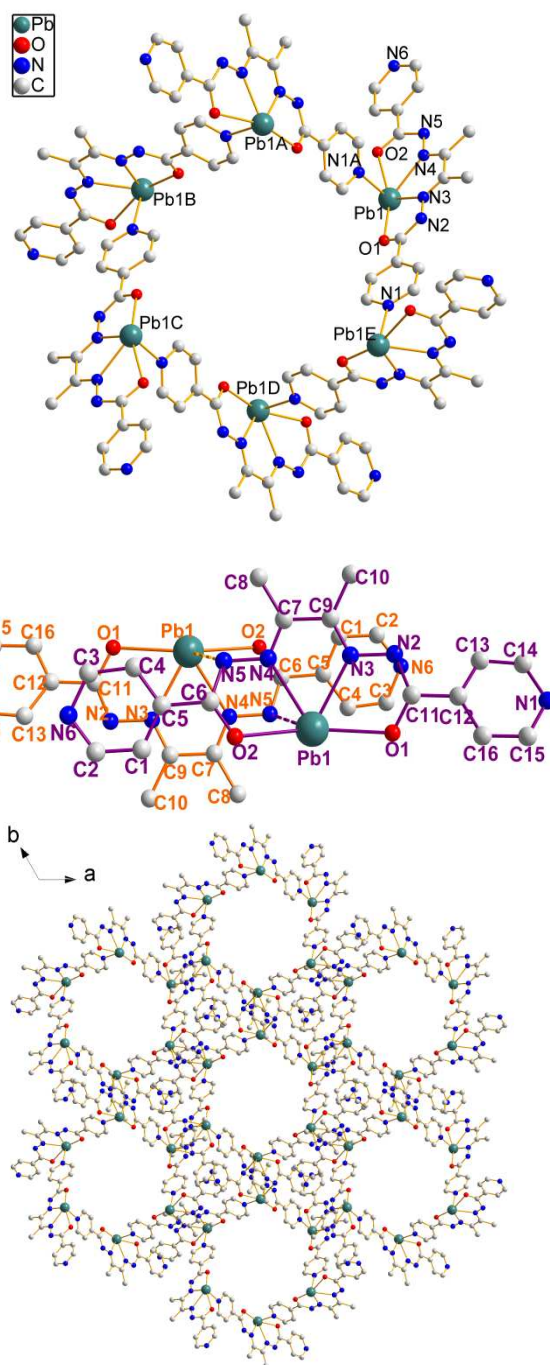

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Fig. 1 Plots showing the metallomacrocyclic unit (top), the long Pb–N_{amide}
65 bonds (dashed lines) and π⋯π stacking between the metallomacrocycle units (middle) and a metallomacrocycle contacting with six other metallomacrocycles (bottom) in the crystal of 1.

Moreover, a water O atom in 1 contact the Pb centre (Fig. 3) with a distance (Pb1⋯O10 = 3.02(2) Å) considerably longer than
70 normal O–Pb bonds[11] and considerably shorter than the sum of the van der Waals radii of Pb and O atoms (3.50 Å),[13] suggesting binding interactions weaker than normal coordination bonds but stronger than van der Waals interaction. On the other hand, the O1, O2, N2 and N6 atoms of $L1^{2-}$ is involved in hydrogen bonds
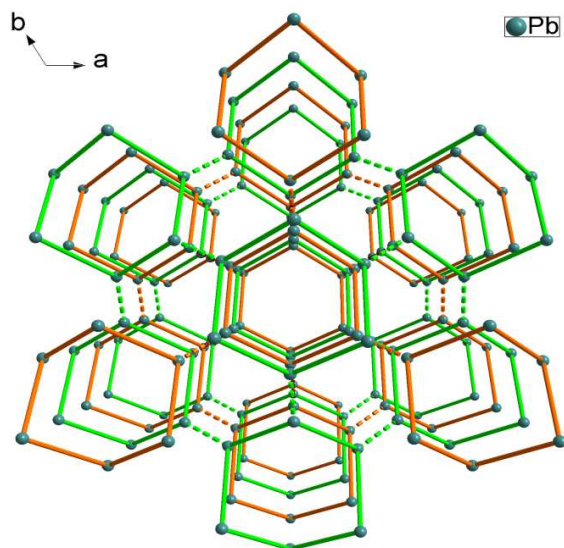75 as acceptors to bind to guest water molecules (Table S3, ESI†).

Fig. 2 Schematic representation of the two interpenetrating 3D networks (one is in amber and the other in bright green) in the crystal of **1** (Solid lines represent moieties of the bridging ligands between Pb nodes and dashed lines represent the inter-metallomacrocycle Pb···N_{amide} weak bonds and π···π interactions. Atoms other than Pb are omitted for clarity).

The above facts demonstrate the hydrophilicity of the pores in 1.

Thermogravimetric analysis (TGA) (Fig. S5. ESI†) of a polycrystalline sample of **1** displayed a weight loss of 15.02% from 25 to ca. 90 °C. This weight loss corresponds to the removal of all the water molecules (calcd 15.71%), indicating that the binding between the pore surface (including the Pb sites) and the water molecules is weak. The sample exhibited no weight loss from 90 °C to 115 °C. Then it lost weight slowly up to ca. 310 °C, meaning slow decomposition of the material. On heating further, the sample decomposed drastically.

Powder X-ray diffraction (PXRD) analyses (ESI†) of **1** displayed that the pattern recorded at room temperature matches the one simulated from single crystal diffraction data (Fig. 4), demonstrating the phase purity of the prepared sample. The PXRD patterns of **1** heated in air for 5 hours at 80, 100 and 120 °C were also measured. The outcome indicated that the porous structure was well sustained up to 100 °C at which all the water molecules were removed according to the result of the thermogravimetric analysis. Thus the Pb^{2+} nodes of the material activated at 100 °C should be exposed and should have hemidirected coordination geometries due to the departure of the water molecules weakly coordinating to the nodes in **1**.

To investigate the dehydration-rehydration behaviour of **1**, a three cycle experiment was performed. For each cycle, the
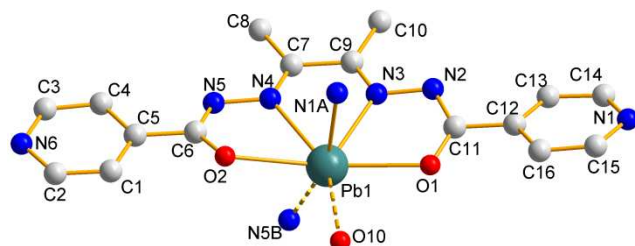

Fig. 3 Plot showing the whole coordination environment of Pb^{2+} in **1** (dashed lines represent the weak coordination bonds).
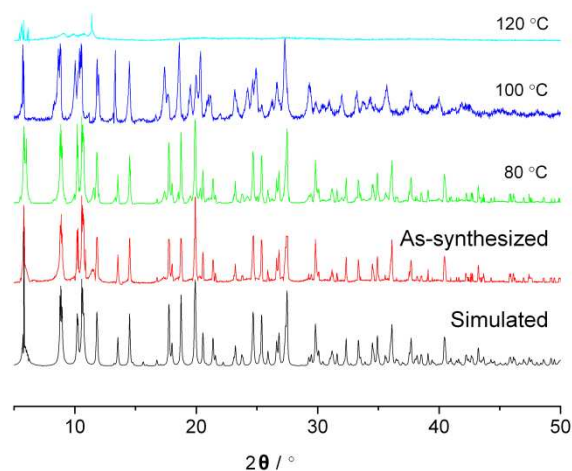

Fig. 4 PXRD patterns simulated from the X-ray single-crystal structure of **1** and recorded from samples as-synthesised and heated at different temperatures.

dehydration was carried out by heating the sample for 5 hours at 100 °C in air on the basis of the results of the TG and PXRD analyses, and the rehydration was conducted by sealing the dehydrated sample together with water (in an open beaker) in a glass desiccator at room temperature for 36 hours. Further extension of the rehydration time did not lead to any weight increase of the sample. The outcome showed that **1** has good reversibility of dehydration-rehydration with the weight losses and increases (Table S4, ESI†) being in line with the calculated water content of **1**.

The adsorption capacities of dehydrated **1** for vapours of methanol, ethanol, isopropanol and n-butanol were also studied. For all the experiments, the samples were also activated by being heated for 5 hours at 100 °C in air, and each adsorption for the corresponding vapour was performed by sealing the activated sample together with the organic liquid (in an open beaker) in a glass desiccator at room temperature for 36 hours. For each alcohol, the adsorption/desorption cycle was repeated three times. The average weight increases are 12.0%, 9.7%, 6.8% and 4.4% for methanol, ethanol, isopropanol and n-butanol, respectively, and the corresponding average weight losses are 12.1%, 9.6%, 6.8% and 4.5%, respectively (Table S5, ESI†).

The above results demonstrate that **1** has good reversibility of adsorption/desorption for vapours of water and the alcohols, which should also be related to the stability of the porous structure. The sequence of the adsorption capabilities of dehydrated **1** for the different vapours, namely water > methanol > ethanol > isopropanol > n-butanol, is against the size order of the molecules. It is imaginable that the smaller the group binding to the hydroxyl of a molecule, the less the hindrance from the group and the stronger the abilities of the hydroxyl to donate to a metal ion and to form H-bonds, which is helpful for the molecules to bind to the open Pb sites and the O and N sites in the pores of the material.

Conclusions

In conclusion, a new series of bridging ligands, bis(isonicotinoyl hydrazones) of compounds with two adjacent active carbonyls and their deprotonated forms, were designed, and a novel porous

MOF of a doubly deprotonated bis(isonicotinoyl hydrazone) bridging ligand and Pb^{2+} node was self-assembled. Weak coordination bonds together with $\pi\cdots\pi$ interactions link the metallomacrocycle units in the porous material into two interpenetrating unique 3D networks. TG and dehydration investigation suggested that all the coordination and guest water molecules in the material can be removed by being heated. PXRD analyses supported that the material sustained the porous structure after the removal of all the coordination and guest water molecules, implying that the fully dehydrated structure possessed accessible Pb sites and not only that the linkages in the metallomacrocycles are strong and rigid but also that the multiple interactions between the metallomacrocycle units present considerable connection strength and rigidity though an individual of the interactions is weak. Experiment results evidenced the material's capability of reversible dehydration/rehydration and adsorption/desorption for small alcohol molecules. The $L1^{2-}$ ligand furnishes several O and N atoms as acceptors to bind to guest water molecules via H-bonds and the Pb^{2+} node coordinates to a water molecule weakly, endowing the material with the ability to adsorb/desorb water and alcohol molecules reversibly. This work supports that both Pb^{2+} and the new bis(aroylhydrazones) would be useful for the construction of stable metal-organic frameworks with hydrophilic pore surfaces.

Acknowledgements

Notes and references

ᵃ Department of Chemistry, School of Science, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China. Tel: +86-022-27403475; Fax: +86-022-27403475; E-mail: lixiaozeng321@tju.edu.cn
ᵇ State Key laboratory of Crystal Material, (Shandong University), Jinan, 250100, P. R. China

† Electronic Supplementary Information (ESI) available: Synthesis, thermogravimetric analysis, powder X-ray diffraction analyses, adsorption/desorption invastigation, crystallographic details, figures and tables for additional structural features. CCDC reference number 972449 for **1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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§ Crystal data of **1**: $C_{32}H_{52}N_{12}O_{16}Pb_2$, M_r =1275.23, T = 293(2) K, Rhombohedral R-3, a = 29.958(4) Å, b = 29.958(4)Å, c = 15.570(3) Å, γ = 120°, V = 12102(3) Å^3, Z = 9, D_c = 1.575 g cm^{-3}, μ = 6.318 mm^{-1}, R_{int} = 0.0576, final R_1 = 0.0571, wR_2 = 0.1503 for 10643 unique reflections ($I \geq 2\sigma$).

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Chun-Li Guo, Xiao-Zeng Li, Xing-Mei Zhang, Lu Wang and Li-Na Zhu

Weak coordination and π-π interactions link the metallomacrocycles into two interpenetrating 3D networks to form the material with hydrophilic pores.