Reliability of π–π stacking interactions in crystal engineering: synthesis and structure of a hemidirected lead complex

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A new three-dimensional polymeric supramolecular Pb^{II} complex, $\{[Pb_3(bpy)_3(ip)_3](H_2O)\}_n$, (bpy = 2,2′-bipyridine and ip = isophthalate), has been synthesised and characterised. Single-crystal analysis shows that $\{[Pb_3(bpy)_3(ip)_3](H_2O)\}_n$ contains a one-dimensional chain polymeric framework and all the Pb centres with a coordination number of six possess an electron lone pair. The coordination sphere is hemidirected which gives a highly distorted geometry. The arrangement of O- and N- atoms towards Pb atoms suggests a gap or hole in the coordination geometry around these atoms. Moreover, there are three types of π–π interactions between aromatic rings and the one-dimensional chains, which are connected by these interactions to form a three dimensional supramolecular network with the channels occupied by water molecules.

Keywords: crystal structure, π–π interactions, lead, lone pair

In recent years, studies on the synthesis of metal–organic frameworks (MOFs) from transition metals and organic ligands have been extensively developed for their crystallographic diversity and potential applications in catalysis, nonlinear optics, magnetism, and molecular recognition.[1-7] Conventional "strong" π–π stacking interactions have long been recognised as being of fundamental importance in determining the supramolecular structure of metal–organic solids. It has been shown that these non-covalent interactions may be utilised in the deliberate design of metal–organic solids that possess controlled supramolecular structures, with the intention that such materials may possess specific and useful chemical and physical properties, or play a role in the binding and conformations all the way from nucleic acids and proteins to benzene.[8,9] Aromatic–aromatic or π–π interactions are important noncovalent intermolecular forces similar to hydrogen bonding. They can contribute to self-assembly or molecular recognition processes when extended structures are formed from building blocks with aromatic moieties. Hydrothermal synthesis has been demonstrated to be an effective and powerful technique for crystal growth of many coordination polymers. To investigate the potential of using these seemingly persistent and strong π–π stacking interactions in crystal engineering, we have used as ligands 2, 2'-bipyridine and 1,3-dicarboxybenzene, with aromatic rings, to obtain three separated 1-D chains in compounds resulting from hydrothermal synthesis. Furthermore, by π–π interactions, these chains organized to a 3-D supramolecular framework with the channels occupied by water molecules along the *a* direction.

In the crystal structure of **1**, there are three different $[Pb(bpy)(ip)]_n$ units and one lattice water molecule in each independent crystallographic cell (Fig. 1). In each unit the Pb^{II} atom is chelated by two N atoms of one 2, 2-bipy ligand [Pb–N 2.478(15)–2.645(17) Å] and four O atoms from two ip ligands [Pb–0 2.424(13)–2.717(13) Å]. The coordination geometry of Pb can be described as a highly distorted pentagonal bipyramid with the seventh coordination site occupied by its lone pair of electrons. The atoms N2, N4, N5 and three lone pairs of electrons occupy the axial positions of each Pb atom in its coordinated mode. The activity of the lone pair in the coordination sphere of Pb is probably due to the low coordination number and *hard* donor atoms (*e.g.*, O- and N-atoms).[10] There is a noticeable lack of solvent bound to Pb(II), which is different from the Pb^{II}–Sip (NaH_2Sip = 5-sulfoisophthalic acid monosodium salt) coordination polymers previously described.[11] Actually, the coordination sphere of

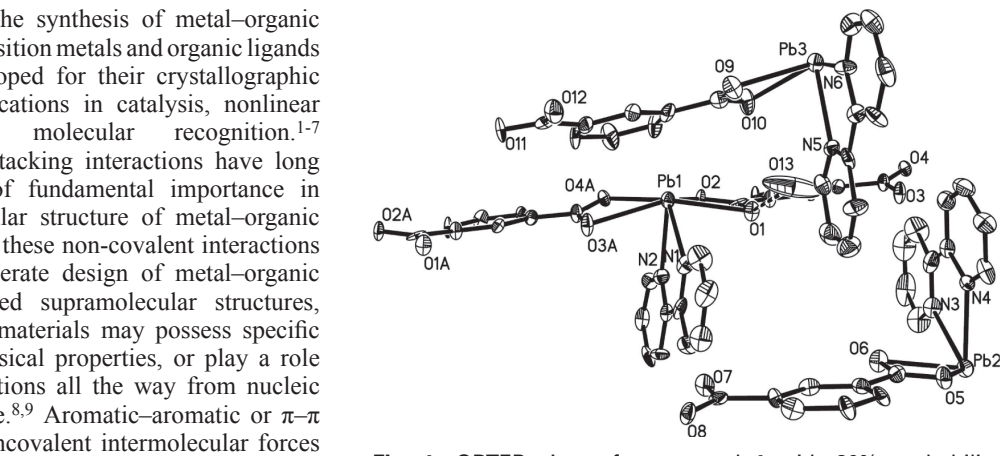

Fig. 1 ORTEP view of compound **1** with 30% probability ellipsoids (hydrogen atoms were omitted for clarity). Symmetry code: A = *x*–1, y, *z*.

Pb^{II} can be viewed as typical hemidirected, which refers to those cases in which the bonds to the ligand atoms are directed only to a part of the coordination sphere, leaving a gap in the distribution of bonds to the ligands.[12] In compound **1** the gap may provide potential supramolecular recognition sites for π–π aromatic stacking interaction. Furthermore every unit is connected by ip ligands to form 1-D separated chains along the *a* direction (Fig. 2).

The striking feature of the structure of **1** is that there are three different π–π aromatic stacking interactions, which are favourable for configuration of the framework and lead to an unpredicted 3D supramolecular structure. The first is that the aromatic pyridine rings of one chain are not symmetry-related [symmetry code: 1–*x*, 1–*y*, 1–*z* for pb1 chains; 1–*x*, 1–*y*, –*z* for pb3 chains]; adjacent chains interacts with offset face-to-face separations of *ca* 3.375 and 3.454 Å and centroid–centroid distances of 3.608 and 3.615 Å, indicating significant π–π interactions[13,14]. As a result, two types of double chain, involving Pb1 and Pb3 respectively, are generated (Fig. 3). The double chains are connected by the Pb2 chain into 2-

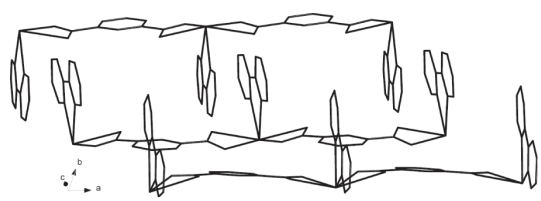

Fig. 2 Three 1-D chains in compound **1.**

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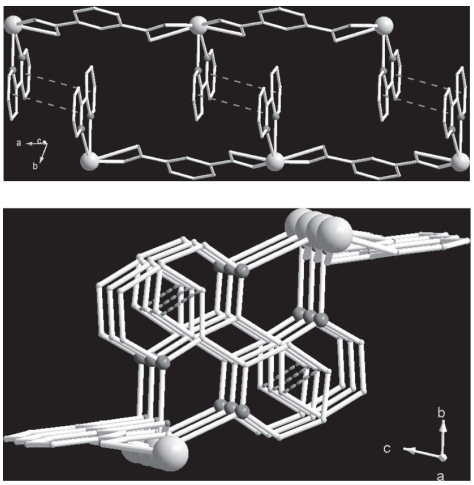

Fig. 3 The double chain connected by π–π interactions (dashed lines) viewed from *c* (top) and *a* (bottom) directions.

D molecular layers by the second π–π stacking interactions between the aromatic pyridine rings of N3–C27–C28–C29–C30–C31 and N1A–C9A–C10A–C11A–C12A–C13A, the rings of N4–C32–C33–C34–C35–C36 and N5A–C45A–C46A–C47A–C48A–C49A have offset face-to-face separations of *ca* 3.437 and 3.515 Å and centroid–centroid distances of 3.653 and 3.755 Å (Fig.4). Furthermore, a three-dimensional supramolecular network featuring channels of the title compound is formed by the last π–π stacking interactions between the benzene rings of isophthalates from the adjacent layers with offset face-to-face separations of *ca* 3.535 and 3.203 Å and a centroid–centroid distances of 4.232 and 3.971 Å. These interacting benzene rings are C2–C3–C4–C5–C6–C7 and C2A–C3A–C4A–C5A–C6A–C7A, C20–C21–C22–C23–C24–C25 and C38A–C39A–C40A–C41A–C42A–C43A, respectively. The lattice water molecule is located in the channel of the structure and is hydrogen bonded to the ip ligand (O13–O1 = 2.837 Å) (Fig. 5).

In this work, we have shown the reliability of π–π interactions in crystal engineering, in which 1-D chains with aromatic rings can be extended to give 3-D supramolecular structures. The structural motif reinforces the view that π–π interactions often have a significant influence on the supramolecular structure of metal–organic frameworks. Nevertheless, the difficulty in achieving precise control over structures using this motif is emphasised by the unpredictable nature of the synthesis.

Experimental

All chemical reagents were commercially available. Elemental analyses of C, H and N were carried out with an Elemental Vario EL III microanalyser. The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using the KBr pellet technique in the range 3200–4000 cm^{-1}.

A suitable crystal of **1** (0.10 × 0.08 × 0.06 mm) was used for X-ray analysis. Data collections were performed on a Simens Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073Å). Empirical absorption corrections were applied by using the SADABS program[15] for the Siemens area detector. The structures were solved by direct methods and refined by full-matrix least-squares methods. The Pb atoms were located from the E-map and all non-hydrogen atoms were derived from the successive difference Fourier syntheses. All the hydrogen atoms (except isolated water molecules) were calculated on the ideal positions and refined isotropically and all non-hydrogen atoms were refined anisotropically. The programs for structure solution and refinement were SHELXS-97[16] and SHELXL-97,[17] respectively. The crystallographic data, selected bond lengths and angles for **1** are listed in Tables 1 and 2.

General procedure for preparation of $\{[Pb_3(bpy)_3(ip)_3](H_2O)\}_n$ (**1**)
Compound **1** was hydrothermally synthesised under autogenous pressure. A mixture of $PbNO_3$ (0.066 g, 0.2 mmol), 2, 2-bipy (0.031 g, 0.2 mmol), ip (0.033 g, 0.2 mmol) and H_2O (12 ml) was sealed in a 20 ml Teflon-lined autoclave, which was heated to 160 °C for three days. After slow cooling to room temperature, light yellow crystals of **1** were obtained by filtration. The crystals were washed with distilled water several times and finally dried in air. Yield, 64% (based on Pb). Anal. Calcd for **1**: C, 40.52; H, 2.39; N, 5.25%; Found: C, 40.42; H, 2.32; N, 5.23%. IR (KBr pellet, cm^{-1}): 3453(w), 1690(m), 1598(vs), 1536(vs), 1477(w),1440(w),1356(vs), 1269(w), 1160(w), 1076(w) 1099(s), 934(w), 826(s), 767(m), 754(s), 713(s), 626(w).

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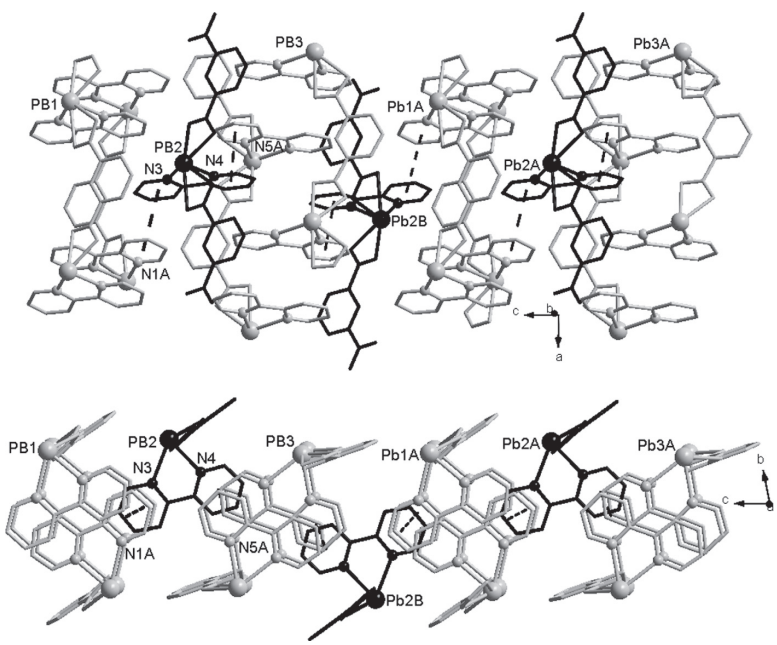

Fig. 4 2-D molecular layer connected by the second type of π–π stacking interactions (dashed lines) viewed from *b* (top) and *a* (bottom) directions.

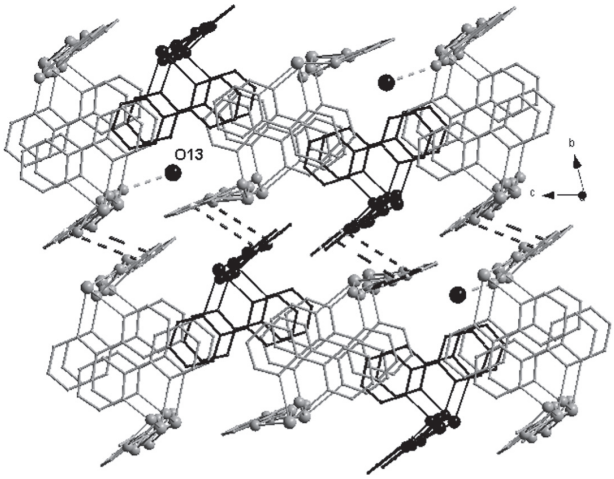

Fig. 5 Three-dimensional supramolecular network formed *via* third type of π–π stacking interactions (black dashed lines) and water molecules located in the channels by hydrogen bonds (grey dashed lines).

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Table 1 Crystal data and structure refinement for the title compound

Compound	**1**
Empirical formula	$C_{54}H_{38}N_6O_{13}Pb$
Formula weight	1600.47
Temperature (K)	273(2)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.2601(2)
b (Å)	12.4052(2)
c (Å)	20.8198(1)
α (deg)	78.8230(1)
β (deg)	88.8920(1)
γ (deg)	72.1690(1)
V (Å^3)	2472.50(6)
Z	2
D_c(g cm^{-3})	2.147
μ (mm^{-1})	10.264
F (000)	1504
θ range (deg)	1.00–25.15
Reflection collected	12699
Independent reflections	8608 [*R*(int) = 0.0544]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8608/0/645
Goodness-of-fit on F^2	1.097 Multi-scan
Absorption correction	
Final R indices [I > 2σ(I)]	R^1 = 0.0762, wR^2 = 0.1579,
R indices (all data)	R^1 = 0.1042, wR^2 = 0.1795
Largest diff. peak and hole (eÅ)$^{-3}$	1.973 and –2.036

Table 2 Selected bond lengths (Å) and angles (°) for the title compound

Pb(1)–O(2)	2.425(12)	Pb(2)–N(4)	2.478(15)
Pb(1)–O(4)#1	2.449(13)	Pb(2)–O(6)	2.619(13)
Pb(1)–N(2)	2.498(16)	Pb(2)–O(7)#2	2.690(13)
Pb(1)–O(3)#1	2.639(12)	Pb(3)–O(11)#2	2.424(13)
Pb(1)–N(1)	2.645(17)	Pb(3)–O(10)	2.467(15)
Pb(1)–O(1)	2.717(13)	Pb(3)–N(5)	2.533(15)
Pb(2)–O(5)	2.439(12)	Pb(3)–O(9)	2.586(14)
Pb(2)–O(8)#2	2.458(14)	Pb(3)–N(6)	2.636(16)
O(2)–Pb(1)–O(4)#1	80.8(4)	N(4)–Pb(2)–N(3)	65.1(5)
O(2)–Pb(1)–N(2)	76.4(5)	O(5)–Pb(2)–O(6)	51.9(4)
O(4)#1–Pb(1)–N(2)	77.1(5)	O(8)#2–Pb(2)–O(6)	128.8(4)
O(2)–Pb(1)–O(3)#1	128.3(4)	N(4)–Pb(2)–O(6)	79.6(5)
O(4)#1–Pb(1)–O(3)#1	51.5(4)	N(3)–Pb(2)–O(6)	84.2(5)
N(2)–Pb(1)–O(3)#1	74.6(5)	O(5)–Pb(2)–O(7)#2	127.0(4)
O(2)–Pb(1)–N(1)	122.0(5)	O(8)#2–Pb(2)–O(7)#2	50.2(4)
O(4)#1–Pb(1)–N(1)	124.1(5)	N(4)–Pb(2)–O(7)#2	79.6(5)
N(2)–Pb(1)–N(1)	63.2(6)	N(3)–Pb(2)–O(7)#2	82.8(5)
O(3)#1–Pb(1)–N(1)	79.9(5)	O(6)–Pb(2)–O(7)#2	158.7(5)
O(2)–Pb(1)–O(1)	50.7(4)	O(11)#2–Pb(3)–O(10)	78.2(4)
O(4)#1–Pb(1)–O(1)	130.7(4)	O(11)#2–Pb(3)–N(5)	80.6(5)
N(2)–Pb(1)–O(1)	83.0(5)	O(10)–Pb(3)–N(5)	84.2(5)
O(3)#1–Pb(1)–O(1)	156.3(5)	O(11)#2–Pb(3)–O(9)	126.2(4)
N(1)–Pb(1)–O(1)	83.2(4)	O(10)–Pb(3)–O(9)	51.8(4)
O(5)–Pb(2)–O(8)#2	78.5(4)	N(5)–Pb(3)–O(9)	76.4(5)
O(5)–Pb(2)–N(4)	77.8(5)	O(11)#2–Pb(3)–N(6)	127.9(5)
O(8)#2–Pb(2)–N(4)	78.3(5)	O(10)–Pb(3)–N(6)	128.5(5)
O(5)–Pb(2)–N(3)	127.2(5)	N(5)–Pb(3)–N(6)	62.6(5)
O(8)#2–Pb(2)–N(3)	125.1(5)	O(9)–Pb(3)–N(6)	81.3(5)

Symmetry code: #1 *x*–1, *y*, *z*; #2 x + 1, *y*, *z*.

References

1 M. Yaghi, H. Li, C. Davis, D. Richardson and T.L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.
2 Z. Li, Z.-X. Zhu, G.-H. Song, X. Qian and J. Sun, *J. Chem. Res. (S)*, 1999,66.
3 G.-L. Feng, S.-J. Ji, L.-J. Geng, B. Bian and Y. Liu, *J. Chem. Res. (S)*, 2008, 137.
4 P.J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.* 1999, **38**, 2638.
5 R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.
6 T. Li, Z.-H. Li and S.-W. Du *J. Cluster Sci.*, 2008, **19**, 323.
7 P.M. Forster and A.K. Cheetham, *Angew. Chem., Int. Ed,* 2002, **41**, 457.
8 S.K. Burley and G.A. Petsko, *J. Am. Chem. Soc.*, 1986, **108**, 7995.
9 K. Müller-Dethlefs and P. Hobza, *Chem. Rev.*, 2000, **100**, 143.
10 L. Shimoni-Livny, J.P. Glusker and C.W. Bock, *Inorg. Chem.*, 1998, **37**, 1853.
11 Q.-Y. Liu and X. Li, *Eur. J. Inorg. Chem.*, 2006, 1620.
12 J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi and A.H. White, *Aust. J. Chem.*, 1996, **49,** 1165.
13 I. Dance and M. Scudder, *J. Chem. Soc. Chem. Commun.*, 1995, 1039.
14 J. Christoph, *J. Chem. Soc., Dalton Trans*, 2000, 3885.
15 G.M. Sheldrick, A program for the Siemens Area Detector ABSorption correction, University of Göttingen, 1997.
16 G.M. Sheldrick, SHELXS97 program for solution of crystal structures, University of Göttingen, Germany, 1997.
17 G.M. Sheldrick, SHELXL97 program for Refinement of crystal structures, University of Göttingen, Germany, 1997.