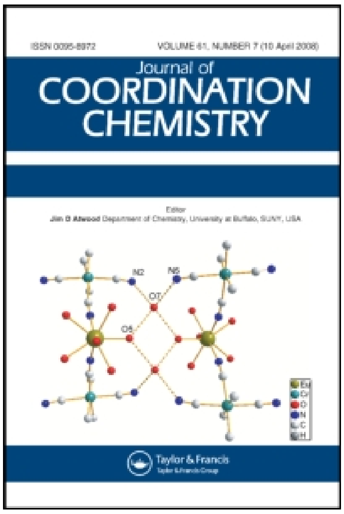

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Lead(II) complexes of *o*-phthalate including a crystal structure of a novel 2D coordination polymer, $[Pb(pht)(H_2O)]$_n

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Lead(II) complexes of *o*-phthalate including a crystal structure of a novel 2D coordination polymer, $[Pb(pht)(H_2O)]_n$

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Three new *o*-phthalate (pht) lead(II) complexes were synthesized and characterized by elemental analyses, IR, ^1H NMR, and ^{13}C NMR spectroscopy. Single crystal X-ray structural analysis of $[Pb(pht)(H_2O)]_n$ shows the complex to be a novel 2D chain polymer as a result of phthalate bridging. Coordination number of Pb(II) is eight, PbO_8, with a "stereo-chemically active" electron lone pair, and the coordination sphere is hemidirected. Packing of this compound in the solid state via π–π stacking and hydrogen bonding is discussed.

Keywords: Crystal structure; Lead(II); Phthalate

1. Introduction

Coordination polymers or hybrid inorganic–organic materials composed of metal centers bridged by organic connectors are currently under investigation [1]. Much of the interest centers on applications in gas adsorption, molecular recognition, magnetism, and photochemistry. Coordination polymers with moderate stability and high lability are also efficient catalysts in a range of chemical and biochemical processes [2]. Investigations into the synthesis of new coordination polymers using dicarboxylic acids as the spacer [3–7] show that *o*-phthalic acid (H_2pht) is a useful building block for the creation of such systems. H_2pht and its anions, $Hpht^-$ and pht^{2-} adopt a wide variety of coordination modes with metal centers; the observed architecture is the result of a subtle interplay between steric hindrance resulting from the close proximity of the two ortho-carboxylate groups and the tendency of phthalates to form the greatest possible number of metal–oxygen bonds upon complexation. So far 26 different coordination types have been observed in crystal structures containing this ligand [8]. Of these the 1,6-bridging mode, which favors the formation of coordination polymers,

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is the most common. The phthalate ligand can also take part in additional weak hydrogen bonding, stabilizing polymeric structures by forming two- and three-dimensional networks. Herein the crystal structure of one novel two-dimensional lead(II) coordination polymer, $[Pb(pht)(H_2O)]_n$, is reported.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510 P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

2.2. *Preparation of $[Pb(pht)(H_2O)]_n$ (1)*

The compound $[Pb(pht)(H_2O)]_n$ was prepared by dissolving lead(II) nitrate (0.331 g, 1 mmol) in distilled water and methanol and adding a mixture of *o*-phthalic acid (0.186 g, 1 mmol) and sodium hydroxide (0.04 g, 1 mmol) in methanol. The resulting solution was stirred and allowed to stand for some days at room temperature. Slow evaporation of the solvent at room temperature yielded suitable crystals for X-ray analysis (m.p. >300°C). The crystals were washed with acetone and air dried. IR (selected bands; in cm^{-1}): 3300–3400 m, 3050 w, 2885 w, 1616 vs, 1539 s, 1462 m, 1383 s, 1349 s, 1300 w, 925 m, 717 m. Anal. Calcd for $C_8H_6O_5Pb$: C, 24.67; H, 1.54; Pb, 53.21; found: C, 25.02; H, 1.50; Pb, 53.10. ^{1}H NMR (DMSO): δ: 7.50 (*t*, 2H), 8.14 (*t*, 2H) ppm. ^{13}C-{^{1}H} NMR (DMSO): $\delta = 130.23$, 132.37, 135.00 and 168.04 ppm.

2.3. *Preparation of [Pb(pht)(phen)] (2)*

1,10-Phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube [9] and mixtures of lead(II) nitrate (0.331 g, 1 mmol) in distilled water and sodium phthalate (0.210 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60°C, while the other was at ambient temperature. After 3 days, yellow crystals were deposited in the cooler arm which were filtered off, washed with ether and air dried (yield 53%), m.p.: 285°C. Anal. Calcd for $C_{20}H_{12}N_2O_4Pb$: C, 43.55; H, 2.17; N, 5.08; found: C, 43.61; H, 2.38; N, 5.43%. IR (cm^{-1}) selected bands: 3137 s, 3062 m, 1612 s, 1589 vs, 1579 sh, 1486 m, 1394 s, 1373 vs, 1329 m, 1267 m, 1107 m, 1075 vs, 957 m, 840 m, 656 vs, 620 m, ^{1}H NMR (DMSO): δ: 7.47 (2H, m, CH of pht), 7.40 (2H, m, CH of pht), 8.10–8.30 (m, 4H), 8.55–9.00 (m, 2H), and 9.20–9.45 (m, 2H).

^{13}C-{^1H} NMR (DMSO): δ: 124.30, 127.50, 129.40, 130.43, 133.01, 137.00, 139.30, 144.50, 149.32 and 167.22 ppm.

2.4. *Preparation of [Pb(pht)(bpy)(H_2O)] (3)*

This complex was prepared via an analogous method to that used for $[Pb(pht)(phen)]_n$. Reactant materials: 2,2′-bipyridine (bpy), lead(II) nitrate, sodium phthalate, (1 : 1 : 1), yellow crystals, m.p. >300°C. Yield 60%. Anal. Calcd for $C_{18}H_{14}N_2O_5Pb$: C, 39.63; H, 2.56; N, 5.13; found: C, 40.01; H, 2.38; N, 5.43%. IR (cm^{-1}) selected bands: 3479–3380 m, 3137 s, 3067 m, 1616 vs, 1587 vs, 1570 vs, 1539 sh, 1506 sh, 1485 m, 1385 vs, 1370 vs, 1330 m, 1071 s, 859 m, 750 s, 705 m. ^1H NMR (DMSO): δ: 7.38 (2H, m, CH of pht), 7.21 (2H, m, CH of pht), 7.65 (d, 2H), 7.80 (m, 2H), 8.25 (m, 2H) and 8.75 (d, 2H). ^{13}C-{^1H} NMR (DMSO): δ: 128.50, 129.47, 131.753, 134.37, 137.00, 140.20, 145.63, 149.93 and 168.75.

2.5. *X-ray crystallography*

X-ray measurements were made at 120(2) K using a Bruker SMART 1000 CCD area detector. The intensity data were collected within the range $3.22 \leq \theta \leq 28.00°$ using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved using the programs SHELXTL [10]. The molecular plots were prepared by using SHELXTL and ORTEP III [11].

Crystal data and refinement parameters are given in table 1. Selected bond lengths and angles are given in table 2. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in figures 1(a) and 3, respectively.

3. Results and discussion

3.1. *Synthesis*

Reaction between lead(II) nitrate and mixtures of phthalic acid and sodium hydroxide in methanol provided the crystalline material $[Pb(pht)(H_2O)]_n$. The IR spectrum of this compound shows absorption bands resulting from skeletal vibrations of aromatic rings in the 1400–1523 cm^{-1} range. The relatively weak band at around 3050 cm^{-1} is assigned to the ν(CH) mode of phthalate aromatic rings. The broad absorption band for ν(H–O) is at ca 3430 cm^{-1}, attributable to coordinated water, hydrogen bound, which is confirmed by the crystal structure. Reaction between 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy) and mixtures of lead(II) nitrate with sodium phthalate provided powdered materials analyzing as $[Pb(pht)(phen)]_n$ (**2**) and $[Pb(pht)(bpy)(H_2O)]_n$ (**3**). The IR spectra of both complexes show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1615 cm^{-1} range [12]. Strong bands in the 1616–1570 and 1385–1370 cm^{-1} regions were assigned to the asymmetric and symmetric stretching modes of

Table 1. Crystal data and structure refinement for $[Pb(pht)(H_2O)]_n$.

Identification code	$[Pb(pht)(H_2O)]_n$
Empirical formula	$C_8H_{62}O_5Pb$
Formula weight	389.32
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*21
Unit cell dimensions (Å, °)	
a	6.4379(9)
b	6.9060(9)
c	9.9125(16)
α	90
β	100.848(7)
γ	90
Volume (Å^3)	432.84(11)
Z	2
Density (Calcd Mg m^{-3})	2.987
Absorption coefficient (mm^{-1})	19.480
F(000)	352
Crystal size (mm^3)	$0.24 \times 0.14 \times 0.1$
θ range for data collection (°)	3.22–28.00
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 8$, $-13 \le l \le 13$
Reflections collected/unique	3315/1900 [R(int) = 0.0363]
Completeness to $\theta = 28.00$	98.1%
Max and min transmission	0.2461 and 0.0893
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1900/9/130
Goodness-of-fit on F^2	0.999
Final R indices [1821 rfls with $I > 2\sigma(I)$]	$R_1 = 0.0284$, $wR_2 = 0.0707$
R indices (all data)	$R_1 = 0.0294$, $wR_2 = 0.0714$
Absolute structure parameter	0.029(18)
Extinction coefficient	0.0234(16)
Largest diff. peak, hole (e Å^{-3})	1.903 and −2.142

Table 2. Selected bond lengths (Å) and angles (°) for $[Pb(pht)(H_2O)]_n$.

Pb(1)–O(3)^{i}	2.340(7)	Pb(1)–O(1)	2.706(6)
Pb(1)–O(1)^{ii}	2.474(6)	Pb(1)–O(4)^{i}	2.745(7)
Pb(1)–O(2)	2.574(6)	Pb(1)–O(2)^{iii}	2.809(7)
Pb(1)–O(5)	2.616(7)	Pb(1)–O(4)^{iv}	3.032(6)
O(3)^{i}–Pb(1)–O(1)^{ii}	73.4(2)	O(2)–Pb(1)–O(1)	49.5(2)
O(3)^{i}–Pb(1)–O(2)	72.4(2)	O(5)–Pb(1)–O(1)	143.6(2)
O(1)^{ii}–Pb(1)–O(2)	77.2(2)	O(3)^{i}–Pb(1)–O(4)^{i}	50.4(2)
O(3)^{i}–Pb(1)–O(5)	74.9(2)	O(1)^{ii}–Pb(1)–O(4)^{i}	122.3(2)
O(1)^{ii}–Pb(1)–O(5)	93.3(2)	O(2)–Pb(1)–O(4)^{i}	74.6(2)
O(2)–Pb(1)–O(5)	147.3(2)	O(5)–Pb(1)–O(4)^{i}	84.9(2)
O(3)^{i}–Pb(1)–O(1)	104.8(2)	O(1)–Pb(1)–O(4)^{i}	69.40(19)
O(1)^{ii}–Pb(1)–O(1)	121.96(18)	O(3)^{i}–Pb(1)–O(2)^{iii}	114.4(2)
O(5)–Pb(1)–O(2)^{iii}	77.4(2)	O(1)^{ii}–Pb(1)–O(2)^{iii}	165.06(19)
O(1)–Pb(1)–O(2)^{iii}	69.68(18)	O(2)–Pb(1)–O(2)^{iii}	116.81(18)
O(4)^{i}–Pb(1)–O(2)^{iii}	69.04(19)		

Symmetry codes: i: $x-1, y, z$; ii: $-x, y-(1/2), -z+2$; iii: $-x, y+(1/2), -z+2$; iv: $-x+1, y-(1/2), -z+2$.

carboxylate groups, respectively [13, 14]. The separations between the asymmetric and symmetric stretching frequencies, $\Delta\nu(\nu_{\mathrm{asym}} - \nu_{\mathrm{sym}})$ range from 246 to 185 cm^{-1}, indicative of COO^- groups from phthalate with bridging O atoms [15]. Such absorptions have already been reported for other phthalate complexes with aromatic amines (1620–1520 cm^{-1}) [16, 17].

The ^{1}H NMR spectrum of the DMSO solution of the three complexes displays two distinct absorption bands at $<$ 7.50 ppm assigned to the aromatic protons of phthalate. In complexes **2** and **3**, bands at 8.10–9.50 and 7.65–8.75 ppm are assigned to aromatic protons of phen and bpy, respectively. The ^{13}C NMR spectrum of the DMSO solution of the three complexes displays a distinct absorption bands at 168 ppm, assigned to the carboxylic carbons of phthalate and absorption bands at 124–150 ppm, assigned to the aromatic carbons.

Because of large size of lead(II) [18] and the tendency of phthalate for bridging, it is possible, nonetheless, that **2** and **3** may be considered as coordination polymers. Given the high coordination numbers and the inherently relatively weak bonding interaction of a metal such as Pb [19], this is perhaps unsurprising.

3.2. *Crystal structure of [Pb(pht)(H_2O)]*$_n$

Determination of the structure of the [Pb(pht)(H_2O)]$_n$ by X-ray crystallography (table 1) showed the compound to be a two-dimensional polymer (figure 1b). The lead atoms can be considered eight-coordinate (figure 2 and table 2) with separation between the lead atoms of 4.046 and 6.068 Å, longer than the sum of van der Waals radii [20]. Hence, a direct Pb–Pb interaction in this compound cannot be considered. Each "phthalate^{2-}" anion acts as a tetradentate ligand, connecting four Pb(II) ions. The carboxylate groups of the "phthalate^{2-}" act as both bidentate chelating, and bridging as two oxygen atoms of the carboxylate group coordinate to a lead(II) and another carboxylate group bridge to three other lead atoms, a very novel and interesting behavior of carboxylate groups (scheme 1 and figure 1b).

The coordination number of Pb [21] is from seven oxygens of three "phthalate^{2-}" anions and one coordinated water. The arrangement of the oxygen atoms suggests a gap or hole in the coordination geometry around the lead, occupied possibly by a stereo-active lone pair of electrons. The observed shortening of the Pb–O bond opposite to the putative lone pair (Pb1–O4 = 2.745(7) compared with Pb1–O4 = 3.032(6) Å adjacent to the lone pair) supports this feature [22]. The compound is linked by intermolecular hydrogen bonding (figure 3 and table 3). The coordinated –OH group of water is involved in hydrogen bonding [23], acting as hydrogen-bond donors with O atoms from adjacent "phthalate^{2-}" hydrogen-bond acceptors (table 3).

A π–π stacking [24, 25] interaction between the parallel aromatic rings belonging to adjacent chains in the complex exists as shown in figure 3. The phenyl groups are almost parallel and separated by a distance of about 3.5Å, close to that of the layers in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "edge-to-edge" types. The edge-to-edge interplanar distances are 3.547, 3.260 Å, normal for π–π stacking [26, 27]. Thus, three factors of hydrogen

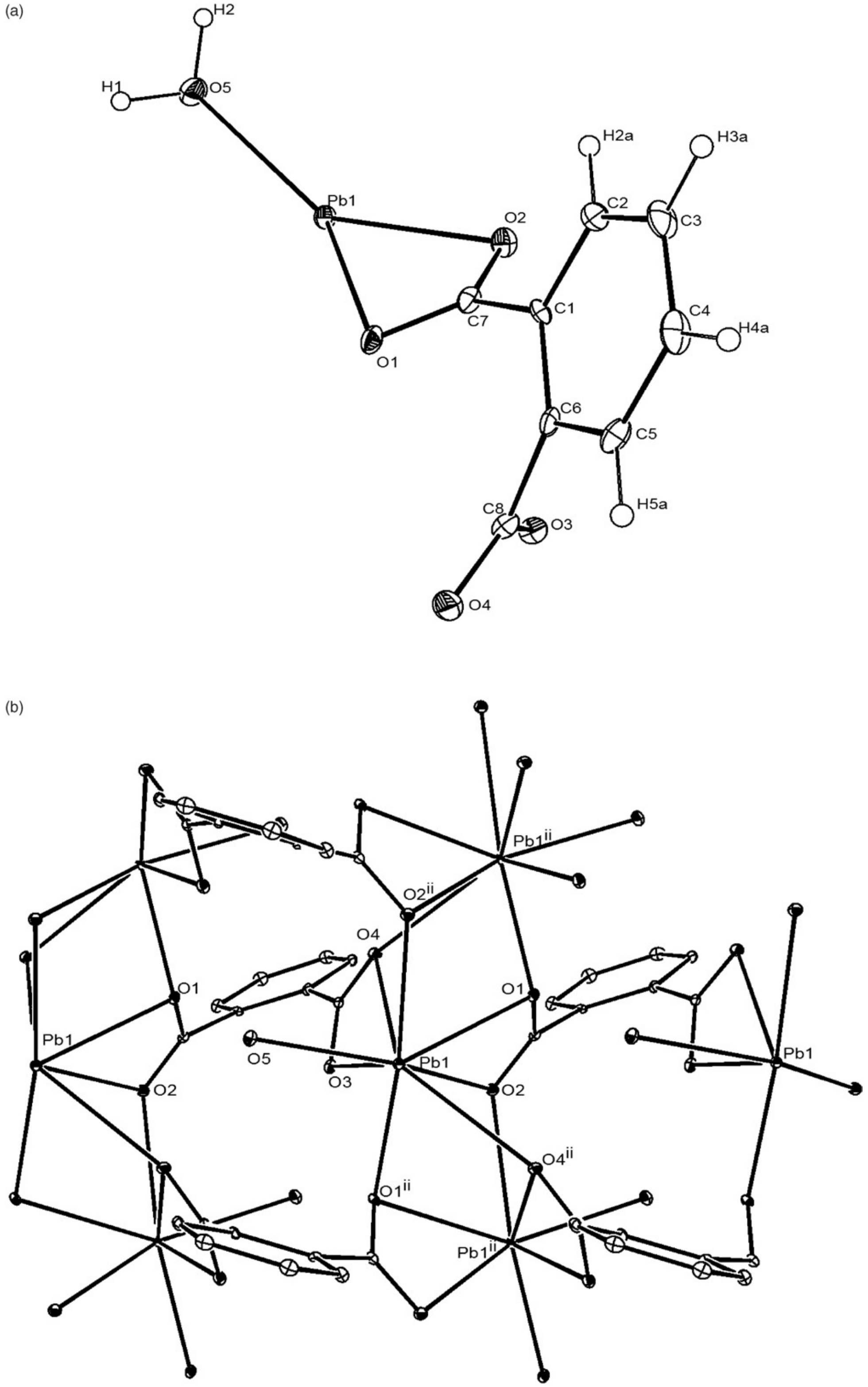


Figure 1. (a) ORTEP diagram of $[Pb(pht)(H_2O)]_n$ complex; (b) 2D-frame of the $[Pb(pht)(H_2O)]_n$ complex.

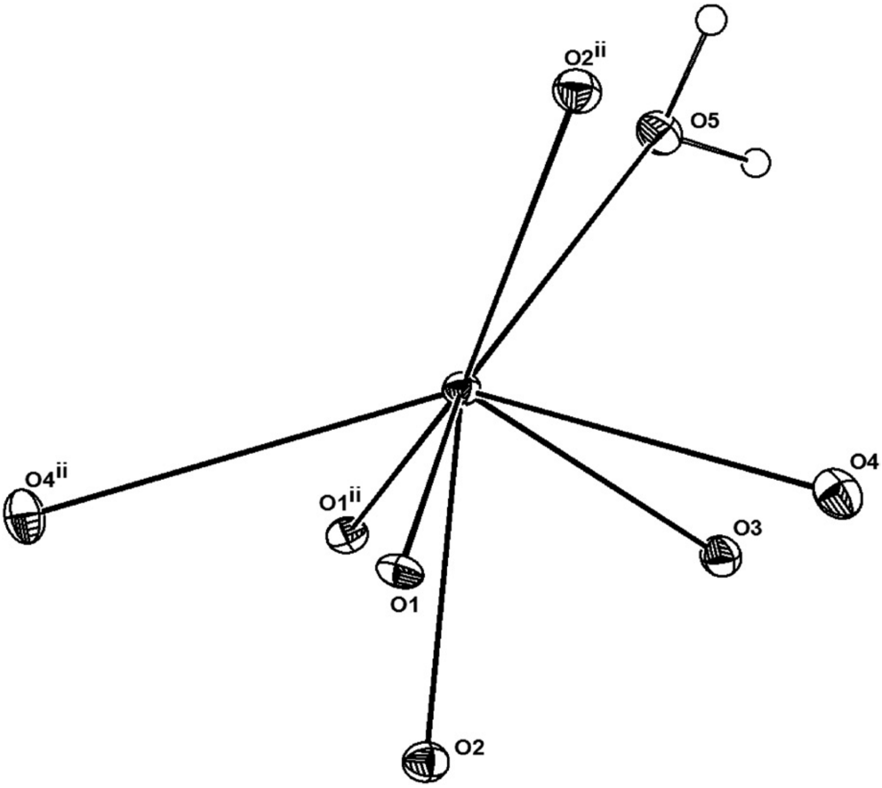
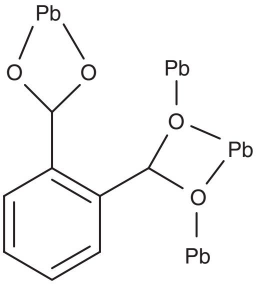


Figure 2. Environment of Pb-atoms in $[Pb(pht)(H_2O)]_n$ complex.



Scheme 1. The coordination mode of [phthalate^{2-}] ligand.

bonding, lone pair activity and π–π stacking interactions control the packing of this coordination polymer.

Supplementary material

Crystallographic data for the structures reported in the article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.

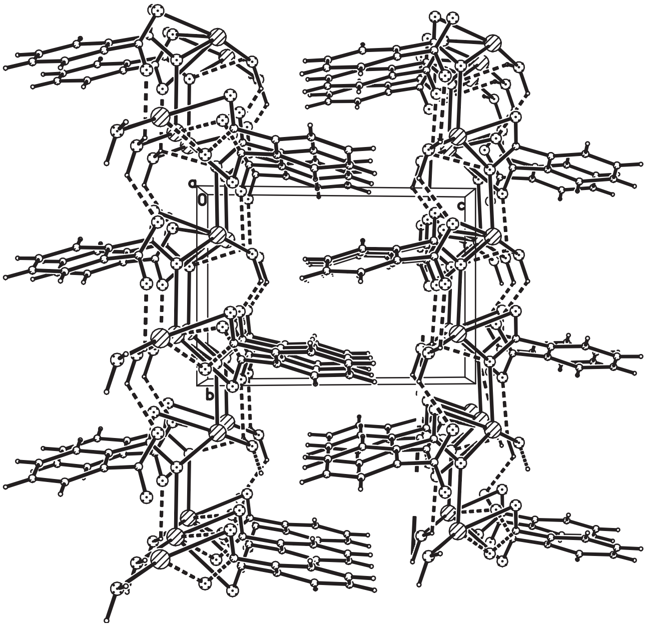


Figure 3. Unit cell of the [Pb(pht)(H_2O)]$_n$ complex, showing edge-to-edge π–π stacking interactions and hydrogen bonding.

Table 3. Intermolecular H-bonds in the structure of [Pb(pht)(H_2O)]$_n$.

D–H	d(D–H)Å	d(H···A)Å	∠DHA°	d(D···A)Å	A
O5–H1	1.020	2.154	121.40	2.823(7)	O3 $[-x, y+(1/2), -z+2]$
O5–H2	1.020	2.285	121.83	2.953(7)	O4 $[-x, y-(1/2), -z+2]$
O5–H2	1.020	2.376	130.89	3.140(7)	O1 $[x-1, y, z]$

CCDC-611663 for [Pb(pht)(H_2O)]$_n$. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 441223/336033; Email: deposit@ccdc.cam.ac.uk).

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