

A three-dimensional lead(II) coordination polymer: poly[aqua- μ -imidazole-4,5-dicarboxylato-lead(II)]

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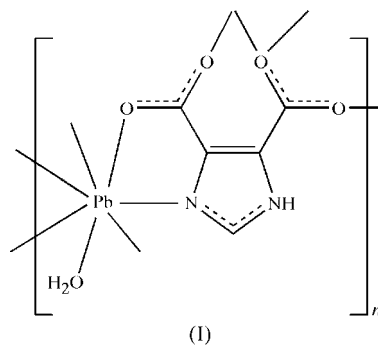
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In the title coordination polymer, $[\text{Pb}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{H}_2\text{O})]_n$, the Pb^{II} atom is seven-coordinated by one N atom and five O atoms from four individual imidazole-4,5-dicarboxylate (HIDC^{2-}) groups and one water molecule. It is interesting to note that the HIDC^{2-} group serves as a bridging ligand to link the Pb^{II} atoms into a three-dimensional microporous open-framework.

Comment

There has been considerable interest in the design and synthesis of metal-organic complexes during recent decades (Erxleben, 2003). The structures and properties of such complexes depend on the coordination habits and geometric preferences of both metal ions and bridging ligands, as well as on the influence of weaker non-covalent interactions such as hydrogen bonding. In investigations of coordination polymers that address the use of bridging multidentate ligands, the anion of 1*H*-imidazole-4,5-dicarboxylic acid (H_3IDC) exemplifies a ligand that is used in the formation of supramolecular complexes. This acid can be successively deprotonated to furnish H_2IDC^- , HIDC^{2-} and IDC^{3-} anions, these anions giving rise to a wide range of supramolecular architectures. To our knowledge, some transition metal complexes with one-dimensional chain structures of Mn, Cu and Cd complexes (Zhang *et al.*, 2004; Gao, Gu *et al.*, 2004; Gao, Liu *et al.*, 2004), two-dimensional layer structures of Mn and Fe complexes (Gao *et al.*, 2005; Xu *et al.*, 2004) and a three-dimensional Mn complex (Zhang *et al.*, 2006) have been reported to date. Compared with the extensively investigated transition metal coordination polymers, it is surprising to see the relatively small number of main group metal coordination polymers. Recently, we have reported the structures of a mononuclear calcium complex (Gao, Zhang *et al.*, 2004) and a two-dimensional brick-like layer barium coordination polymer (Zhang *et al.*, 2005). However, no three-dimensional crystal structure of a main group metal coordination polymer constructed using this acid has yet been reported. We obtained the title novel three-

dimensional lead(II) coordination polymer, $[\text{Pb}(\text{HIDC})(\text{H}_2\text{O})]_n$, (I), and its synthesis and crystal structure are reported here.



As shown in Fig. 1, the asymmetric building unit of complex (I) comprises one Pb^{II} atom, one HIDC^{2-} dianion and one coordinated water molecule. Each Pb^{II} atom is seven-coordinated by one N atom of a HIDC^{2-} anion, with a $\text{Pb}-\text{N}$ distance of 2.491 (3) Å, five O atoms from four individual HIDC^{2-} anions, with $\text{Pb}-\text{O}$ distances in the range 2.474 (3)–2.822 (3) Å, and one water molecule, with a $\text{Pb}-\text{O}$ distance of 2.739 (4) Å (Table 1). The $\text{Pb}-\text{O}4^{\text{iii}}$ [symmetry code: (iii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$] distance of 2.822 (3) Å is considerably longer, but lies within the range found for $\text{Pb}-\text{O}$ bond distances in many similar Pb^{II} coordination polymers; for example, Morsali & Mahjoub (2004) reported a $\text{Pb}-\text{O}$ range of 2.542 (10)–2.975 (9) Å.

It is interesting to note that each HIDC^{2-} anion serves as a bridging ligand to link four Pb^{II} atoms into a three-dimensional microporous structure. The HIDC^{2-} dianion in (I) shows four different coordination modes. Firstly, it binds to the Pb1 atom in an *N,O*-bidentate coordination mode through imidazole atom N1 and carboxyl atom O1, forming a five-membered chelate ring. Secondly, it coordinates to atom Pb1A [symmetry code: (A) $x, -y+\frac{1}{2}, z-\frac{1}{2}$] in an *O,O*-bidentate coordination mode through two carboxyl atoms, *viz.* O2 and

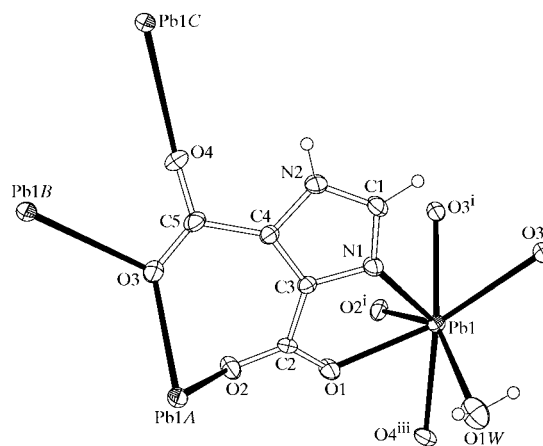


Figure 1

A plot of the title complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (A) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (B) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (C) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$.]

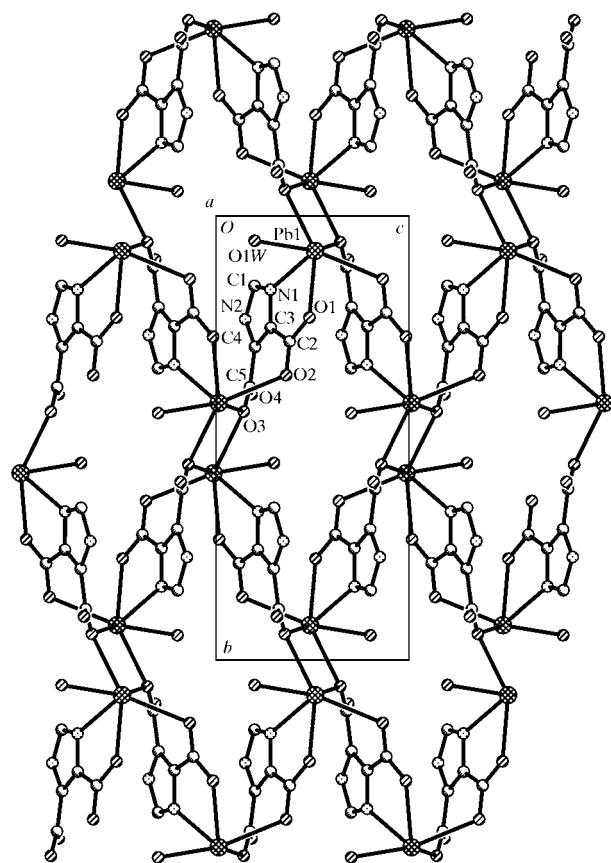


Figure 2

A packing diagram for (I), viewed down the *a* axis, showing the macrocyclic ring structure. H atoms have been omitted.

O3, generating a seven-membered chelate ring with an envelope-like conformation. Thirdly, it bridges atoms Pb1A and Pb1B [symmetry code: (B) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$] through carboxyl atom O3. In this case, a centrosymmetric four-membered (Pb/O/Pb/O) loop is formed, with a Pb...Pb distance of 4.1523 (9) Å. Fourthly, it coordinates to atom Pb1C [symmetry code: (C) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$] in a monodentate coordination mode through carboxyl atom O4. Furthermore, four such HIDC²⁻ ligands connect four Pb^{II} centres, generating a macrocyclic ring structure, with adjacent Pb...Pb distances of 6.4103 (10) and 9.1379 (16) Å (Fig. 2). As a consequence of these H₂IDC²⁻ bridges, as well as the hydrogen bonds in which all active H atoms in the structure are involved (Table 2), polymer (I) presents an extended three-dimensional microporous open-framework.

Experimental

Pb(NO₃)₂·4H₂O (4.03 g, 10 mmol), 1*H*-imidazole-4,5-dicarboxylic acid (1.54 g, 10 mmol) and NaOH (0.8 g, 20 mmol) were dissolved in an aqueous solution (25 ml). The mixture was sealed in a 50 ml Teflon-lined stainless steel bomb and held at 403 K for 5 d. The bomb was cooled naturally to room temperature and colourless prismatic crystals were obtained after several days. CHN analysis calculated for C₅H₄N₂O₅Pb: C 15.83, H 1.06, N 7.39%; found: C 15.86, H 1.08, N 7.36%.

Crystal data

[Pb(C₅H₂N₂O₄)(H₂O)]
M_r = 379.30
 Monoclinic, *P*2₁/*c*
a = 7.0301 (14) Å
b = 15.707 (3) Å
c = 6.9680 (14) Å
 β = 101.77 (3)°
V = 753.2 (3) Å³

Z = 4
D_x = 3.345 Mg m⁻³
 Mo *K*α radiation
 μ = 22.39 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.28 × 0.22 × 0.12 mm

Data collection

Rigaku R-Axis RAPID
 diffractometer
 ω scans
 Absorption correction: numerical
 (NUMABS; Higashi, 1995)
T_{min} = 0.007, *T_{max}* = 0.068

7289 measured reflections
 1717 independent reflections
 1631 reflections with *I* > 2σ(*I*)
R_{int} = 0.037
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.020
wR [*F*²] = 0.049
S = 1.00
 1717 reflections
 124 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 1.5416P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.59 e Å⁻³
 Δρ_{min} = -2.08 e Å⁻³

Table 1

Selected bond lengths (Å).

Pb1—O1	2.474 (3)	Pb1—O1W	2.739 (4)
Pb1—N1	2.491 (3)	Pb1—O3 ⁱⁱ	2.758 (3)
Pb1—O3 ⁱ	2.547 (3)	Pb1—O4 ⁱⁱⁱ	2.822 (3)
Pb1—O2 ⁱ	2.598 (3)		

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O2 ^{iv}	0.86 (3)	1.86 (3)	2.708 (4)	176 (6)
O1W—H1W2...O4 ⁱⁱ	0.85 (3)	1.95 (3)	2.705 (5)	147 (4)
N2—H6...O1 ^v	0.86	1.95	2.811 (4)	174

Symmetry codes: (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$.

H atoms on C and N atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and were refined in the riding-model approximation, with *U*_{iso}(H) = 1.2*U*_{eq}(C,N). Water H atoms were located in a difference Fourier map and refined with O—H and H...H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with *U*_{iso}(H) = 1.5*U*_{eq}(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3021). Services for accessing these data are described at the back of the journal.

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