

Poly[(*N,N*-dimethylformamide- κ O)-(μ_3 -4,4'-ethylenedibenzoato- κ^5 O, O' :- $O':O'',O'''$)(pyrazino[2,3-*f*][1,10]phenanthroline- κ^2 N⁸,N⁹)lead(II)]

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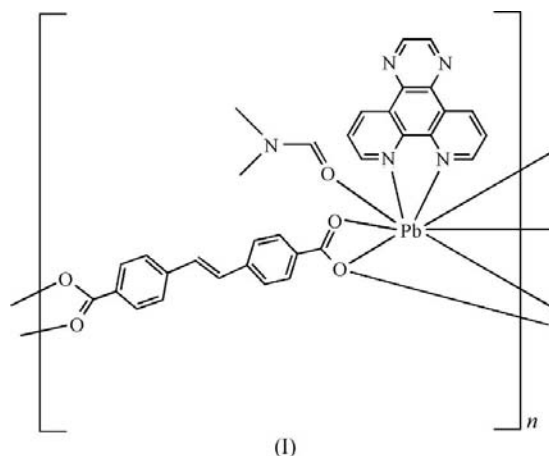
In the title Pb^{II} coordination polymer, [Pb(C₁₆H₁₀O₄)-(C₁₄H₈N₄)(C₃H₇NO)]_n, each Pb^{II} atom is eight-coordinated by two chelating N atoms from one pyrazino[2,3-*f*][1,10]phenanthroline (*L*) ligand, one dimethylformamide (DMF) O atom and five carboxylate O atoms from three different 4,4'-ethylenedibenzoate (eedb) ligands. The eedb dianions bridge neighbouring Pb^{II} centres through four typical Pb—O bonds and one longer Pb—O interaction to form a two-dimensional structure. The C atoms from the *L* and eedb ligands form C—H···O hydrogen bonds with the O atoms of eedb and DMF ligands, which further stabilize the structure. The title compound is the first Pb^{II} coordination polymer incorporating the *L* ligand.

Comment

Until recently, research on coordination polymers has focused mainly on incorporation of *s*-, *d*- and even *f*-block metal ions as the coordination centres, while less consideration has been given to metals of the *p* block (Xu *et al.*, 2005). *p*-Block metal-organic materials may be important in applications such as electroluminescent devices or organic light-emitting diodes (OLEDs), and so have stimulated much interest (Tsuboi & Sifsten, 1991; Singh & Richter, 2004). As far as the intrinsic appeal of Pb^{II} is concerned, the presence of a 6s² outer electron configuration not only leads to interesting topological arrangements, but also plays an important role in the luminescence activity of any resulting complex (Deo & Godwin, 2000; Li & Lu, 2000). Lead(II), as a toxic heavy metal, is commonly found in critical life cycles due to its widespread use in numerous industrial applications (Andersen *et al.*, 2006). The possible molecular mechanisms of the toxicity of Pb^{II} may affect several different types of protein. Therefore, good knowledge of the coordination properties of Pb^{II}, including

aspects such as the lone pair of electrons, the coordination number and the coordination geometry, is crucial for understanding the toxicological properties of lead(II).

1,10-Phenanthroline (phen) has been widely used to build supramolecular architectures because of its excellent coordinating ability and large conjugated system that can easily form π - π interactions (Wang *et al.*, 2005; Tong *et al.*, 2000; Zheng *et al.*, 2001). However, far less attention has been given to its derivatives (Yang, Ma *et al.*, 2007; Yang, Li *et al.*, 2007). Pyrazino[2,3-*f*][1,10]phenanthroline (*L*) is an important phen derivative. It possesses aromatic systems and is a good candidate for the construction of metal-organic supramolecular architectures (Wang *et al.*, 2007). To the best of our knowledge, coordination polymers constructed from a Pb^{II} dicarboxylate ligand and *L* have not been documented so far (Yang, Ma *et al.*, 2007). Here, we have selected the 4,4'-ethylenedibenzoate dianion (eedb) as an organic linker and *L* as an *N,N'*-chelating ligand, generating the title new Pb^{II} coordination polymer, [Pb(eedb)(*L*)(DMF)] (DMF is dimethylformamide), (I), the structure of which we now report.



Selected bond lengths for (I) are given in Table 1. As shown in Fig. 1, each Pb^{II} atom is eight-coordinated by two N atoms from one *L* ligand, one DMF O atom, and five carboxylate O atoms from three different eedb ligands {comprising four typical Pb—O bonds [2.352 (4)–2.707 (5) Å] and one longer Pb—O interaction [3.055 (5) Å]}. The typical Pb—O distances in (I) (Table 1) are comparable with those found in another crystallographically characterized Pb^{II} complex, *viz.* [Pb(NO₃)₂(bpno)(H₂O)]_n (bpno is 4,4'-bipyridine *N,N'*-dioxide; Xu *et al.*, 2005).

As depicted in Fig. 2, the eedb dianions bridge two neighbouring Pb^{II} centres through typical Pb—O bonds, resulting in a one-dimensional chain structure along the *b* axis. It is noted that the *L* ligands are extended on both sides of the chains. Clearly, the N-containing chelating *L* ligand plays an important role in the formation of the chain structure. Two N atoms from the *L* ligand occupy two coordination positions of the Pb^{II} atom, while the remaining coordination positions are available for eedb ligands, allowing the formation of the chain structure. Notably, if the longer Pb—O interaction [3.055 (5) Å] is considered, a two-dimensional structure is formed (Fig. 3). To the best of our knowledge, no other Pb^{II}

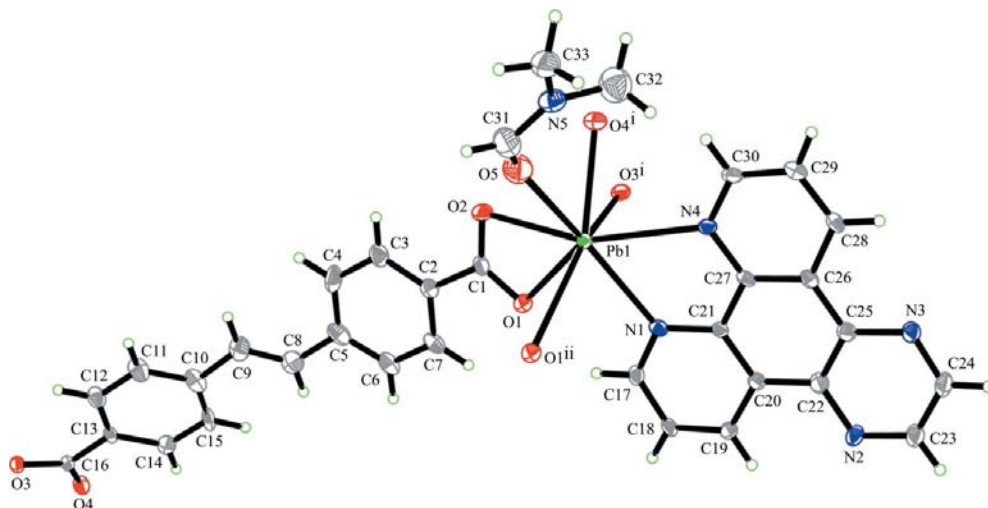


Figure 1

A view of the local coordination of the Pb^{II} cation in (I), showing the atom-numbering scheme. Only one conformation of the DMF molecule is shown. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ (ii) $-x + 1, -y + 1, -z + 1$.]

coordination polymer containing the chelating ligand L has been reported so far, although several Pb^{II} complexes including phen-like chelating ligands have been reported (Yang, Ma *et al.*, 2007). The C atoms from the L and eedb ligands form $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds with the O atoms of eedb and DMF ligands, which stabilize the structure of (I) (Table 2).

It is noteworthy that the structure of (I) is different from that of the related structure $[\text{Zn}(\text{eedb})(L)(\text{H}_2\text{O})]\cdot 0.5\text{DMF}$ (Wang *et al.*, 2008), in which the eedb dianions bridge neighbouring Zn^{II} centres to give a one-dimensional chain structure in the ab plane. In that structure, a three-dimensional supramolecular architecture is formed through two types of $\pi-\pi$ interactions between neighbouring chains. One is between the centrosymmetrically related L ligands, and the second is between L and eedb ligands. The structure of (I) is also entirely different from that of the related polymer $[\text{Cd}_2(1,4\text{-ndc})_2(L)_2]$ (1,4-ndc is naphthalene-1,4-dicarboxylate; Qiao *et al.*, 2008), in which the 1,4-ndc ligands link the Cd^{II} centres to give an interesting six-connected three-dimensional α -Po-related architecture.

The stereochemical activity of the Pb^{II} lone pair of electrons is an interesting topic and is often discussed. The geometries of Pb^{II} complexes can be classified as holo- and hemidirected. Holodirected refers to Pb^{II} complexes in which the bonds to the ligand atoms are located throughout the surface of an

encompassing sphere, while hemidirected refers to those cases in which the bonds to the ligand atoms are directed through only part of an encompassing sphere (Shimoni-Livny *et al.*, 1998). In compound (I), the central Pb^{II} atom is eight-coordinated by two N atoms, one DMF molecule and five carboxylate O atoms. The coordination of the ligands at Pb^{II} does not leave room for a lone pair of electrons. Therefore, this coordination environment can be considered somewhat holodirected. To date, several Pb^{II} coordination polymers with different phen derivatives have been reported (Yang, Li *et al.*, 2007). The Pb^{II} coordination geometry of the polymer $[\text{Pb}(1,4\text{-ndc})(\text{tcpn})_2]$ [tcpn is 2-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)naphthol] is very similar to that observed in (I). In that structure, the Pb^{II} atom is also eight-coordinated by four N atoms and four carboxylate O atoms, and the bonds to the ligand atoms are distributed throughout the surface of the encompassing Pb^{II} sphere. Therefore, the coordination environment of the Pb^{II} atom can also be considered as holodirected.

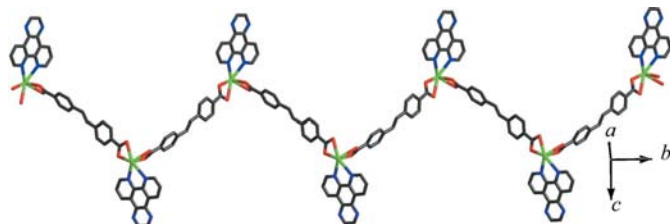


Figure 2

A view of the one-dimensional chain of (I) along the b axis.

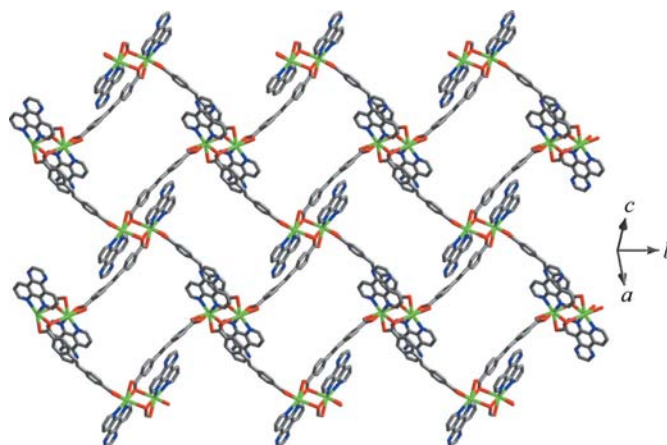


Figure 3

A view of the two-dimensional supramolecular structure of (I).

Experimental

Pb(NO₃)₂ (0.166 g, 0.5 mmol), H₂eedb (0.133 g, 0.5 mmol) and L (0.121 g, 0.5 mmol) were dissolved in a mixture of DMF (6 ml) and distilled water (8 ml). The resulting mixture was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 398 K for 5 d under autogenous pressure. The reaction system was cooled gradually to room temperature at a rate of 10 K h⁻¹. Pale-yellow crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with DMF, and dried in air at ambient temperature (yield 72%, based on Pb^{II}).

Crystal data

[Pb(C ₁₆ H ₁₀ O ₄)(C ₁₄ H ₈ N ₄)- (C ₃ H ₇ NO)]	$\beta = 102.7510 (10)^\circ$
$M_r = 778.77$	$V = 2844.8 (4) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 4$
$a = 9.0255 (7) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 25.5628 (19) \text{ \AA}$	$\mu = 5.98 \text{ mm}^{-1}$
$c = 12.6422 (9) \text{ \AA}$	$T = 295 \text{ K}$
	$0.23 \times 0.20 \times 0.18 \text{ mm}$

Data collection

Bruker APEX diffractometer	14893 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5224 independent reflections
$T_{\min} = 0.340$, $T_{\max} = 0.412$ (expected range = 0.281–0.341)	4134 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	72 restraints
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.95 \text{ e \AA}^{-3}$
5224 reflections	$\Delta\rho_{\text{min}} = -0.92 \text{ e \AA}^{-3}$
428 parameters	

Table 1

Selected geometric parameters (Å).

Pb1—O1	2.448 (4)	Pb1—O1 ⁱⁱ	3.055 (5)
Pb1—O2	2.707 (5)	Pb1—O5	3.023 (17)
Pb1—O3 ⁱ	2.352 (4)	Pb1—N1	2.594 (5)
Pb1—O4 ⁱ	2.638 (4)	Pb1—N4	2.695 (5)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C8—H8 \cdots O3 ⁱⁱⁱ	0.93	2.52	3.435 (9)	168
C15—H15 \cdots O3 ⁱⁱⁱ	0.93	2.65	3.567 (8)	170
C17—H17 \cdots O1	0.93	2.26	2.968 (8)	132
C18—H18 \cdots O5 ⁱⁱ	0.93	2.64	3.22 (2)	121
C18—H18 \cdots O5 ⁱⁱ	0.93	2.39	3.309 (11)	170
C23—H23 \cdots O2 ^{iv}	0.93	2.27	3.090 (9)	147

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

Carbon-bound H atoms were positioned geometrically, with C—H = 0.93 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. As the C—C distances of the N-heterocycle were unreasonable, the central six-carbon ring was refined as a rigid hexagon with sides of 1.39 Å. The DMF ligand is disordered over two sites each with a site occupancy of 0.5. The C=O distances were restrained to 1.25 (1) Å, N—C(=O) to 1.35 (1) Å and N—CH₃ to 1.45 (1) Å. The C, N and O atoms of each component was restrained to be nearly planar. The anisotropic displacement parameters were restrained to be nearly isotropic. The displacement parameters of the O5/O5' pair were restrained to be identical and were further restrained to be nearly isotropic. The final difference Fourier map has a large peak at 1 Å from Pb1 but is otherwise featureless.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL-Plus (Sheldrick, 2008); software used to prepare material for publication: publCIF (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3189). Services for accessing these data are described at the back of the journal.

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