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Crystal structure of *catena*-[(1,10-phenanthroline-*N*,*N*′)-bis(μ-acetato-*O*,*O*′)lead(II)], $Pb(C_{12}H_8N_2)(CH_3COO)_2$

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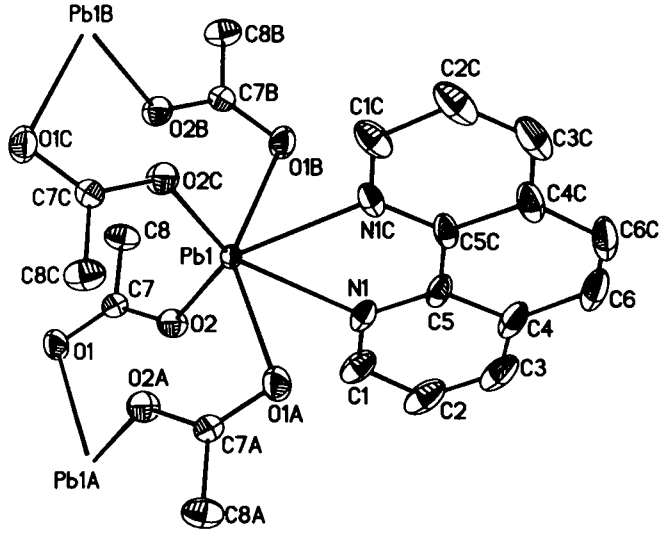

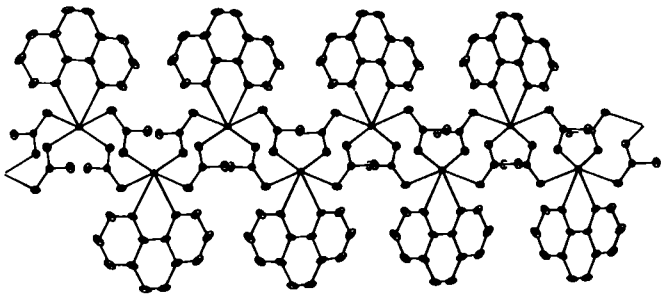

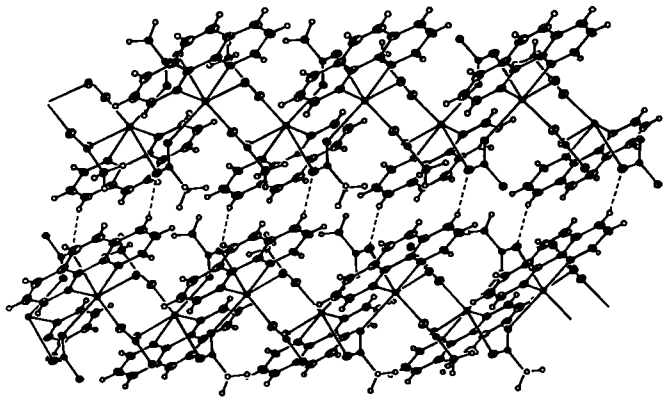

Abstract

$C_{16}H_{14}N_2O_4Pb$, monoclinic, *C*12/*c*1 (no. 15), a = 10.945(1) Å, b = 20.499(2) Å, c = 7.4643(7) Å, β = 107.653(1)°, V = 1595.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.019, $wR_{ref}(F^2)$ = 0.051, T = 291 K.

Source of material

The mixture of $Pb(CH_3COO)_2 \cdot 3H_2O$ (2 mmol) and 1,10-phenanthroline (2 mmol) was stirred into 10 mL aqueous solution at room temperature. Then the pH was adjusted to approximately 6 with 3 M NaOH. The reaction mixture was heated on a water bath, holding for 3 h at 65 °C, and then filtered. The colorless crystal was separated from the mother liquor by slow evaporation at room temperature after 18 days (yield 0.36 g, 46 %).

Discussion

As a toxic heavy metal element in biological systems and natural environment, the construction of Pb(II) organic coordination frameworks by metal coordination directed self-assembly processes has attracted extensive attention in recent years [1-4]. Pb(II) ions cannot only form coordination polymers and polynuclear complexes, but also frequently were discussed in regard to the possible stereochemical activity of the valence shell lone electron pairs [5-7]. This metal ion adapts to different coordinations as a consequence of the large ionic radius and adopts different coordination numbers. On the other hand, aromatic rings and carboxyl groups are important structural and functional elements in synthetic supramolecular architectures. They significantly devote to the intramolecular stabilization of structures and to the formation of intermolecular complexes. Moreover, hydrogen bonds also play vital roles in creating high-dimensional structure and stabilizing metal-organic coordination frameworks. Taking the aspects mentioned above into account, we investigate herein a new coordination polymer of lead(II) with 1,10-phenanthroline and acetate ligands. Although the coordination structures of Pb(II) ion with 1,10-phenanthroline and acetate ligands have been reported [8,9], such coordination mode of four acetate-bridged polymeric lead(II) complex $[Pb(phen)(CH_3COO)_2]_n$ has not been described yet.

In the crystal structure of the complex, each Pb(II) ion is six-coordinated by four oxygen atoms (the bond lengths of Pb—O1 and Pb—O2 are 2.9614(4) Å and 2.652(4) Å, respectively) from four acetate ligands and two nitrogen atoms (the bond length of Pb—N1 is 2.554(4) Å) from one bidentate phen ligand to generate a N_2O_4 distorted octahedral environment (figure, top). The Pb—O and Pb—N bond lengths are close to those found in Pb(II) complexes of 1,10-phenanthroline and acetate ligands. The coordination mode of this Pb(II) complex is quite different from other complexes containing the phen and acetate ligands [8,9]. Four ac-

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etate ligands act as bridge three Pb(II) ions and form two eight-membered rings which display a twisted non-coplanar coordination mode. Each acetate adopts the bis-monodentate coordination mode to link two adjacent Pb(II) ions forming one-dimensional chain (figure, middle). The phen ligands are alternately attached to both sides of the chain. The bond angles of N1–Pb1–O2 and O2C–Pb1–O2 are 143.4(2)° and 135.7(2)°, respectively. The arrangement of the phen and acetate ligands suggests a gap coordination around the Pb(II) ion, which might be occupied by a stereoactive lone pair of electrons on Pb(II) ion and also probably due to steric hindrance of the phen and acetate ligands. It is noteworthy that there exist weak hydrogen bond interactions between the neighboring one-dimensional chains. This is the other remarkably different from those complexes mentioned in the literature. The weak C–H···O bonds form between the carboxylate O of acetate anions and H atoms of phen groups from adjacent chain and generate two-dimensional framework structure (figure, bottom). It is the weak hydrogen bond interactions that stabilize the 2D network structure of the metal coordination compound.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.18 × 0.19 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	105.93 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4957, 1824
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1757
$N(param)_{refined}$:	106
Programs:	SHELXS-97 [10], SHELXL-97 [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.6441	0.6185	0.1827	0.103
H(2)	8*f*	0.7058	0.7132	0.3603	0.137
H(3)	8*f*	0.6602	0.8117	0.2071	0.137
H(6)	8*f*	0.5543	0.8772	–0.1031	0.145
H(8A)	8*f*	0.9092	0.4275	0.1052	0.115
H(8B)	8*f*	0.8838	0.5011	0.0489	0.115
H(8C)	8*f*	0.8276	0.4463	–0.0997	0.115

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	4*e*	½	0.555487(9)	–¼	0.0445(1)	0.0317(1)	0.0420(1)	0	0.01281(9)	0
O(1)	8*f*	0.7047(5)	0.4068(2)	0.1674(8)	0.089(3)	0.052(2)	0.123(4)	0.013(2)	0.057(3)	0.015(2)
O(2)	8*f*	0.6599(4)	0.5067(2)	0.0627(6)	0.072(2)	0.074(2)	0.067(2)	0.025(2)	0.022(2)	0.020(2)
N(1)	8*f*	0.5639(4)	0.6603(2)	–0.0596(7)	0.053(2)	0.049(2)	0.088(3)	–0.004(2)	0.024(2)	–0.025(2)
C(1)	8*f*	0.6254(6)	0.6588(4)	0.124(1)	0.065(3)	0.097(4)	0.092(4)	–0.012(3)	0.019(3)	–0.049(4)
C(2)	8*f*	0.6633(8)	0.7152(5)	0.232(1)	0.088(5)	0.130(5)	0.129(5)	–0.023(4)	0.040(4)	–0.078(4)
C(3)	8*f*	0.6346(8)	0.7734(5)	0.139(2)	0.089(5)	0.102(4)	0.176(6)	–0.038(4)	0.076(4)	–0.082(4)
C(4)	8*f*	0.5681(7)	0.7780(3)	–0.054(2)	0.085(4)	0.057(3)	0.185(6)	–0.017(3)	0.086(4)	–0.042(4)
C(5)	8*f*	0.5338(5)	0.7179(2)	–0.151(1)	0.060(3)	0.043(2)	0.140(5)	–0.009(2)	0.060(3)	–0.023(3)
C(6)	8*f*	0.5311(9)	0.8374(3)	–0.163(2)	0.118(7)	0.047(3)	0.238(9)	–0.015(3)	0.113(7)	–0.033(4)
C(7)	8*f*	0.7288(5)	0.4563(2)	0.0889(7)	0.044(2)	0.057(3)	0.045(2)	0.008(2)	0.008(2)	–0.000(2)
C(8)	8*f*	0.8480(6)	0.4579(4)	0.031(1)	0.052(3)	0.112(5)	0.068(4)	0.013(3)	0.022(3)	0.015(3)

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