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Crystal structure of poly[tetra-(μ_4 -naphthalene-1,8-dicarboxylato- $\kappa^4 O:O, O': O'': O'', O'''$)-(μ_4 -oxo- $\kappa^4 O:O:O:O$) penta-lead(II)], $C_{48}H_{24}O_{17}Pb_5$

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Abstract

$C_{48}H_{24}O_{17}Pb_5$, monoclinic, $C2/c$ (no. 15), $a = 23.8455(6)$ Å, $b = 9.4617(2)$ Å, $c = 21.0940(5)$ Å, $\beta = 115.730(1)^\circ$, $V = 4287.33(18)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0290$, $wR_{ref}(F^2) = 0.0580$, $T = 296$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of materials

All source materials, naphthalene-1,8-dicarboxylic acid ($C_{12}H_8O_4$), $Pb(NO_3)_2$ and KOH, were purchased from Jinan Camolai Trading Company. All chemicals of analytical grade were obtained from commercial sources and used without further purification. A mixture of $C_{12}H_8O_4$ (0.1 g), $Pb(NO_3)_2$ (0.1 g), KOH (0.03 g) and deionized water (15 mL) was placed in a 25 mL Teflon-lined stainless steel autoclave. Then the autoclave was sealed and heated to 160 °C under autogenous pressure for five days. After being slowly cooled to room temperature at a rate of 5 °C/h, colorless prismatic crystals were

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	$0.20 \times 0.10 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	19.65 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, ω -scans
$\theta_{\max}$, completeness:	28.2° , >97% (up to 25.2° , >99)
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13438, 5147, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4118
$N(\text{param})_{\text{refined}}$:	317
Programs:	Bruker programs [1], SHELX [2]

recovered by filtration, washed with distilled water and air dried.

Experimental details

The H atoms were placed in idealized positions with C–H bond lengths constrained to 0.93 Å, and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$.

Comment

The design and construction of coordination polymers (CPs) has been one of the most active areas of material research in recent years. Being easily and efficiently synthesized from relatively simple subunits, CPs exhibit a fascinating variety of architectures and topologies and have attracted considerable interest for their potential applications (catalysis, magnetism, electric conductivity, and nonlinear optics) as functional materials [3–5]. Most CPs are usually made by combining a conducting organic network with an inorganic magnetic component. To our knowledge, the selection of suitable organic ligands is crucial for constructing

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Pb1	0.06357(2)	0.52622(2)	0.35640(2)	0.02240(6)
Pb2	0.07585(2)	0.74678(2)	0.22217(2)	0.02423(7)
Pb3	0.000000	1.13310(3)	0.250000	0.02495(8)
C1	0.1236(3)	0.8645(6)	0.3657(3)	0.0224(13)
C2	0.1549(3)	0.9491(6)	0.4323(3)	0.0215(13)
C3	0.2191(3)	0.9462(7)	0.4631(3)	0.0312(15)
H3	0.239594	0.882215	0.446938	0.037*
C4	0.2537(3)	1.0377(8)	0.5180(4)	0.0452(19)
H4	0.296982	1.036066	0.537367	0.054*
C5	0.2246(4)	1.1288(8)	0.5431(4)	0.047(2)
H5	0.248148	1.191063	0.578896	0.056*
C6	0.1590(3)	1.1313(6)	0.5159(3)	0.0310(15)
C7	0.1289(4)	1.2250(7)	0.5425(4)	0.047(2)
H7	0.152539	1.287212	0.578257	0.057*
C8	0.0657(4)	1.2269(7)	0.5169(4)	0.046(2)
H8	0.046473	1.290516	0.534795	0.055*
C9	0.0298(3)	1.1318(6)	0.4634(3)	0.0323(15)
H9	−0.013349	1.133014	0.446006	0.039*
C10	0.0571(3)	1.0387(6)	0.4367(3)	0.0236(13)
C11	0.1227(3)	1.0379(6)	0.4602(3)	0.0210(13)
C12	0.0155(3)	0.9322(6)	0.3845(3)	0.0240(13)
C13	0.0526(3)	0.4152(6)	0.1477(3)	0.0209(12)
C14	0.1057(3)	0.3460(6)	0.1392(3)	0.0227(13)
C15	0.1068(3)	0.3635(7)	0.0753(4)	0.0296(15)
H15	0.078558	0.425053	0.042529	0.036*
C16	0.1497(3)	0.2903(7)	0.0582(4)	0.0329(16)
H16	0.150354	0.304131	0.014859	0.039*
C17	0.1895(4)	0.2006(8)	0.1050(4)	0.0427(18)
H17	0.217193	0.150786	0.093196	0.051*
C18	0.1909(3)	0.1786(7)	0.1725(4)	0.0310(15)
C19	0.1497(3)	0.2567(6)	0.1916(3)	0.0228(13)
C20	0.1241(3)	0.3378(6)	0.2916(3)	0.0203(12)
C21	0.1542(3)	0.2400(6)	0.2605(3)	0.0212(13)
C22	0.1917(3)	0.1379(6)	0.3033(3)	0.0301(15)
H22	0.191332	0.121495	0.346621	0.036*
C23	0.2311(3)	0.0563(8)	0.2837(4)	0.0447(19)
H23	0.256729	−0.012679	0.313713	0.054*
C24	0.2310(3)	0.0802(8)	0.2197(4)	0.0449(19)
H24	0.258264	0.029790	0.207431	0.054*
O1	0.000000	0.6344(5)	0.250000	0.0200(12)
O2	0.12797(19)	0.4682(4)	0.2848(2)	0.0241(9)
O3	0.0957(2)	0.2859(4)	0.3254(2)	0.0263(10)
O4	0.02198(18)	0.3453(4)	0.1736(2)	0.0241(9)
O5	0.0373(2)	0.5378(4)	0.1243(2)	0.0298(10)
O6	0.1410(2)	0.7417(4)	0.3639(2)	0.0313(11)
O7	0.08243(19)	0.9253(4)	0.3122(2)	0.0260(9)
O8	−0.0317(2)	0.9806(4)	0.3314(2)	0.0302(10)
O9	0.02589(19)	0.8041(4)	0.3944(2)	0.0284(10)

extended coordination frameworks. As one of the most fascinating ligands, naphthalene-1,8-dicarboxylic acid (1,8-nap) was selected as a cluster ligand because its four carboxylate groups may be completely or partially deprotonated, and

can act as hydrogen bond acceptors as well as hydrogen bond donors to assemble supramolecular structures. Until now, a variety of frameworks with novel topologies have been constructed by 1,8-nap ligands and metal ions, such as [Mn₂(NTC)(H₂O)₂]_n [6], [Ba(C₁₂H₆O₄)(H₂O)₂]_n [5], [Ba(μ₅-1,8-nap)]_n [7, 8], [Zn(C₁₂H₆O₄)(H₂O)]_n [9], and so on. We speculate that interesting structures can be obtained based on the 1,8-nap ligand and Pb^{II} central cation under hydrothermal conditions. In this paper, we introduce a new type of CP compound, named Pb₅O(C₁₂H₆O₄)₄, in our experiment.

Single crystal X-ray analysis shows that the title compound exhibits a one-dimensional chain structure running along the *b*-axis. It crystallizes in monoclinic space group C2/*c*. There are three Pb²⁺ cations, two deprotonated 1,8-nap ligands and a bridging O atom in the asymmetric unit (shown in the upper part of the figure). The coordination environments of three cations are different: Pb1 and Pb2 are both hexa-coordinated by five carboxylate O atoms from two (C₁₂H₆O₄)₄^{2−} ligands and one oxo ligand (the O^{2−} atom sits on a 2-fold axis), and Pb3, which sits on a special position, is octa-coordinated by eight carboxylate O atoms from four (C₁₂H₆O₄)₄^{2−} ligands. The oxo ligand bridges four Pb cations giving rise to a distorted OPb₄ tetrahedron with the O—Pb bond distances of 2.337(3)–2.377(3) Å. Interestingly, the Pb—O contacts involving carboxylate O atoms fall in the range of 2.496(5)–2.721(5) Å, which is significantly longer than these of free coordinated O atoms. The calculated total bond valences for the Pb1, Pb2 and Pb3 atoms are 1.873(2), 1.812(2), and 1.888(2), respectively, indicating an oxidation state of +2 for all cations. Within the one-dimensional chain running along the *b*-axis, the (C₁₂H₆O₄)₄^{2−} ligands are arranged so that the aromatic rings point towards the chain exterior. Thus the chains are linked by Van der Waals and C—H···π interactions into the final architecture of compound Pb₅O(C₁₂H₆O₄)₄ (cf. lower part of the figure).

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