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Crystal structure of bis[(μ_2 -4- $\cdots$ O, O' : O')-(4-hydroxybenzoato- κ^2 O, O')-(1,10-phenanthroline- κ^2 N, N')]-di-lead(II) μ -4-hydroxybenzoato- κ^3 O, O' : O' ; κ^3 O, O' : O' -bis-[(4-hydroxybenzoato- κ^2 O, O')bis(1,10-phenanthroline- κ^2 N, N')]di-lead(II)] monohydrate, $C_{52}H_{36}N_4O_{12}Pb_2 \cdot H_2O$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.18 × 0.15 × 0.12 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	14.5 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	71.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13530, 4473, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4280
$N(\text{param})_{\text{refined}}$:	327
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [4]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pb01	0.48621(2)	0.02888(2)	0.59982(2)	0.01486(6)
O1	0.54684(16)	0.1199(3)	0.71761(10)	0.0241(5)
O2	0.48805(15)	0.2951(3)	0.64403(10)	0.0220(5)
O3	0.69817(16)	0.8023(3)	0.83811(11)	0.0242(5)
H3	0.7396	0.7692	0.8644	0.036*
O4	0.66988(15)	0.1705(3)	0.58260(10)	0.0233(5)
O5	0.54817(15)	0.1857(3)	0.51039(9)	0.0202(5)
O6	0.86619(19)	0.5518(4)	0.35781(12)	0.0304(6)
H6	0.9228	0.5197	0.3611	0.046*
N1	0.33194(18)	0.1403(4)	0.54478(12)	0.0189(5)
N2	0.3284(2)	−0.0268(3)	0.65712(14)	0.0209(6)
C1	0.3328(2)	0.2258(4)	0.49147(15)	0.0228(7)
H1	0.3926	0.2557	0.4765	0.027*
C2	0.2483(3)	0.2736(5)	0.45643(16)	0.0274(8)
H2	0.2521	0.3335	0.4191	0.033*
C3	0.1606(2)	0.2311(5)	0.47796(17)	0.0307(8)
H3A	0.1037	0.2600	0.4549	0.037*
C4	0.1558(2)	0.1431(5)	0.53518(16)	0.0250(7)
C5	0.0659(2)	0.0966(5)	0.56160(19)	0.0344(9)
H5	0.0076	0.1283	0.5409	0.041*
C6	0.0636(3)	0.0089(5)	0.6151(2)	0.0352(10)
H6A	0.0041	−0.0208	0.6305	0.042*
C7	0.1528(3)	−0.0400(5)	0.64927(19)	0.0275(8)
C8	0.1556(3)	−0.1351(5)	0.70479(17)	0.0339(9)
H8	0.0980	−0.1723	0.7210	0.041*
C9	0.2425(3)	−0.1729(5)	0.73504(16)	0.0301(8)
H9	0.2450	−0.2363	0.7718	0.036*
C10	0.3282(2)	−0.1144(5)	0.70980(15)	0.0247(7)

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Abstract

$C_{52}H_{36}N_4O_{12}Pb_2 \cdot H_2O$, monoclinic, $P2_1/n$ (no. 19), $a = 13.7767(1)$ Å, $b = 7.9925(1)$ Å, $c = 21.2490(2)$ Å, $\beta = 93.1490(10)^\circ$, $V = 2336.20(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0220$, $wR_{\text{ref}}(F^2) = 0.0582$, $T = 170$ K.

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The symmetric unit of the title compound is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H10	0.3873	−0.1383	0.7311	0.030*
C11	0.2424(2)	0.0091(4)	0.62605(17)	0.0207(7)
C12	0.2443(2)	0.0998(4)	0.56734(14)	0.0192(7)
C13	0.5828(2)	0.4093(4)	0.73081(14)	0.0183(6)
C14	0.6524(2)	0.3789(4)	0.77954(15)	0.0209(7)
H14	0.6718	0.2695	0.7883	0.025*
C15	0.6928(2)	0.5075(4)	0.81484(17)	0.0209(7)
H15	0.7396	0.4853	0.8469	0.025*
C16	0.6637(2)	0.6698(4)	0.80253(14)	0.0199(7)
C17	0.5971(2)	0.7046(5)	0.75229(15)	0.0248(7)
H17	0.5797	0.8144	0.7426	0.030*
C18	0.5573(2)	0.5716(5)	0.71683(16)	0.0239(7)
H18	0.5128	0.5934	0.6833	0.029*
C19	0.5368(2)	0.2653(4)	0.69578(14)	0.0183(6)
C20	0.6977(2)	0.3088(4)	0.48567(14)	0.0167(6)
C21	0.7989(2)	0.3018(4)	0.49339(14)	0.0195(7)
H21	0.8278	0.2429	0.5272	0.023*
C22	0.8564(2)	0.3808(5)	0.45167(15)	0.0220(7)
H22	0.9237	0.3756	0.4573	0.026*
C23	0.8131(3)	0.4693(4)	0.40059(17)	0.0223(7)
C24	0.7128(3)	0.4799(4)	0.39316(16)	0.0217(7)
H24	0.6839	0.5410	0.3599	0.026*
C25	0.6557(2)	0.3996(4)	0.43521(14)	0.0201(7)
H25	0.5883	0.4062	0.4298	0.024*
C26	0.6356(2)	0.2176(4)	0.52926(14)	0.0180(6)
O7	1.05036(18)	0.4552(3)	0.34915(12)	0.0293(6)
H7A	1.1014	0.5058	0.3631	0.044*
H7B	1.0580	0.4215	0.3118	0.044*

Source of materials

A solution of Pb(CH₃COOH)₂ · 3H₂O (0.1902 g, 0.5 mmol) in distilled water (5 mL) was added to a solution of 1,10-phenanthroline (C₁₂H₈N₂, 0.0906 g, 0.5 mmol) and 4-hydroxybenzoate acid (0.1392 g, 1 mmol) in ethanol/water (*v*:*v* = 1:1, 20 mL). The mixture was stirred at 323 K and refluxed for 6 h and then a white precipitate was filtered. Bright colorless single crystals were obtained by slow evaporation of the filtrate after 3 d at room temperature, one of which was selected for an X-ray experiment.

Experimental details

Hydrogen atoms bound to C were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å. Hydroxy H atoms were refined in a similar manner, with O—H = 0.82 Å. Water H atoms were found according to the residual electron-density peaks around each water O atom and the directions of hydrogen bonds, and were then locked in position with O—H = 0.85 Å and included in the refinement with the SHELXL AFIX 3 command. *U*_{iso}(H) were set to *U*_{iso}(H) = 1.2*U*_{eq}(C or N) and *U*_{iso}(H) = 1.5*U*_{eq}(O), respectively.

Comment

The coordination chemistry of lead(II) with N and O donor ligands has been investigated in past decades as [5]. Because of its electronic configuration and size, Pb(II) exhibits various coordination numbers and geometries. A number of lead(II) complexes with different donor ligands has been synthesized and studied by X-ray crystallography [6–10].

The crystal structure of the title compound consists of dimeric units of Pb(C₇H₅O₃)₂(C₁₂H₆N₂), related by a crystallographic inversion centre (the figure), and complemented by an uncoordinated water molecule. Each Pb^{II} cation is chelated by two N atoms of 1,10-phenanthroline with Pb—N distances of 2.531(2) Å and 2.589(3) Å, and five carbonyl O atoms from three 4-hydroxybenzoate anions. The 4-hydroxybenzoate groups coordinate to each Pb^{II} ion in two different ways. Two 4-hydroxybenzoate ions behave as chelating ligands to a Pb atom, two form bridges between the two Pb atoms. The five Pb—O distances are significantly different, as are the two Pb—N distances. The shortest Pb—O distance is 2.326(2) Å and the longest is 2.920(2) Å. The weak Pb—O bridging interactions form a centrosymmetric four-membered Pb₂O₂ quadrilateral with a Pb···Pb distance of 4.305(6) Å. Molecules are linked into a two-dimensional framework by O—H···O hydrogen bonds. The packing is further stabilized by π–π interactions in the sequence of benzoate-phenanthroline-benzoate-phenanthroline of neighbouring molecules. The centroid-centroid distances between Cg1(C20–C25) and Cg2(N1/C1–C4/C12) [symmetry code: 1 − *x*, 1 − *y*, 1 − *z*] and between Cg3(N2/C10–C7/C11) [symmetry code: 1 − *x*, 1 − *y*, 1 − *z*] and Cg4(C20–C25) [symmetry code: *x*, 1 + *y*, *z*] are 3.521 Å and 3.613 Å, respectively. This combination of hydrogen bonds and π–π stacking interactions builds a three-dimensional network architecture.

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