

Supporting Information

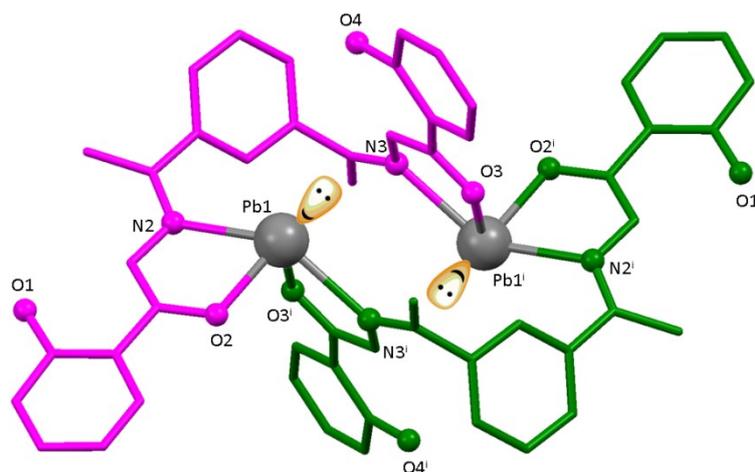
An unusual assembled Pb(II) meso-helicate showing the inert pair effect

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Experimental

Materials

All solvents, 1, 3-diacetylbenzene, salicyloyl hydrazide and the lead metal plate (ca. 2x2 cm²) are commercially available and were used without further purification.

Physical Measurements

Elemental analysis of C, H and N were performed on a FISON EA 1108 analyzer. ¹H and ¹³C/DEPT NMR spectra were recorded on a Varian Mercury 300 spectrometer and ²⁰⁷Pb NMR spectra were recorded on a Bruker AMX-500 spectrometer at 298 K, using DMSO-d₆ as deuterated solvent. Chemical shifts are expressed relative to tetramethylsilane (¹H and ¹³C NMR) and neat tetramethyllead using a saturated solution of PbPh₄ in CDCl₃ (−178 ppm) as an external reference (²⁰⁷Pb NMR). Infrared spectra were measured as KBr pellets on a BRUKER IFS-66V spectrophotometer in the range 4000-100 cm^{−1}. Electrospray ionisation (ESI- and ESI+) mass spectra were recorded on an API4000 Applied Biosystems mass spectrometer with Triple Cuadrupole analyser.

Crystal Structure Determinations

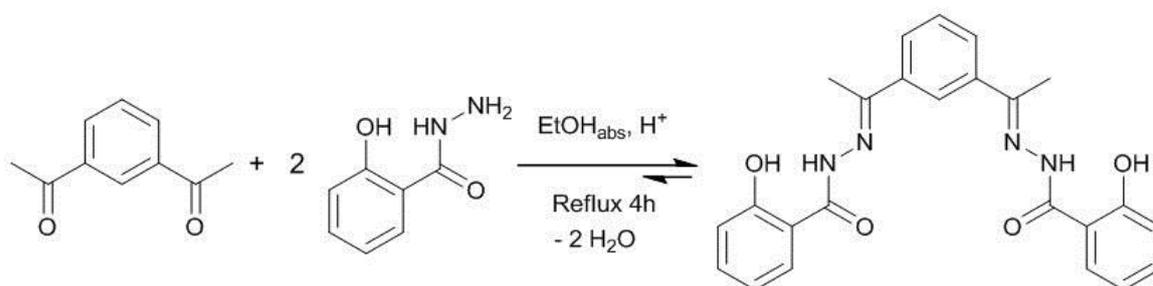
Colourless prismatic crystals of the lead(II) mesocate **2** were mounted on a glass fibre and used for data collection. Crystal data were collected at 100(2) K using a BRUKER APPEX-II CCD diffractometer. Graphite monochromated MoK(α) radiation (λ = 0.71073 Å) was used throughout. The data were processed with BRUKER SAINT¹ and corrected for absorption using SADABS.² The structures were solved by SIR-97³ and refined by full-matrix least-squares techniques against *F*² using SHELXL-97.⁴ Positional and anisotropic atomic displacement parameters were refined for all heteroatoms. The water protons were located in a difference map and their positions, with distance restraints, were refined isotropically [U_{iso}(H) = 1.2U_{eq}(O)]. Other H atoms were included as fixed contributions riding on attached atoms with isotropic thermal parameters (1.2-1.5 times those of their carrier atoms). Criteria of a satisfactory complete analysis were the ratios of "rms" shift to standard deviation less than 0.001 and no significant features in the final difference maps. Molecular graphics were done with ORTEP⁵ and MERCURY.⁶ A summary of the crystal data of **2** is listed in Table S1. Significant bond

distances and angles for **2** are summarized in Table S2 and hydrogen bond parameters are listed in Table S3.

CCDC 1487152 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

Synthesis of H₂L 1

0.21 g (1.30 mmol) of 1, 3-diacetylbenzene and 0.39 g (2.60 mmol) of salicyloyl hydrazide were dissolved in absolute ethanol (70 mL), and a catalytic amount of *p*-toluenesulfonic acid (ca. 10 mg) was added to the mixture. The reaction was stirred under reflux with a Dean-Stark trap for 4 h (Scheme S1). Finally the solution was concentrated to a volume of ca. 20 mL and cooled down to 4 °C until the formation of a white product was observed. The solid was filtered off, washed with diethyl ether and dried under vacuum. Yield: 0.5 g (90%); m.p. 160-162 °C; E. A. (Found: C, 67.1; H, 5.1; N, 13.1; C₂₄H₂₂N₄O₄ required: C, 66.9; H, 5.2; N, 13.0; S; ESI-MS (*m/z*) 429.2 [H₂L-H]⁻; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 11.90 (s, 2H, OH), 11.38 (s, 2H, NH), 8.31 (s, 1H, H₅), 8.01 (d, 1H, *J* = 7.4 Hz, H₃), 7.90 (d, 1H, *J* = 7.3 Hz, H₆), 7.52 (t, 1H, *J* = 7.6 Hz, H₄), 7.42 (t, 1H, *J* = 7.2 Hz, H₇), 7.02-6.99 (m, 2H, H₈+ H₉), 2.37 (s, 6H, CH₃); ¹³C/DEPT NMR (126 MHz, DMSO-d₆, ppm): δ 162.1 (C=O), 152.1 (C=N), 156.5 (C_{ar}-OH), 138.1-117.3 (9C_{ar}), 14.1 (CH₃); IR (KBr, cm⁻¹): ν(OH) 3440, ν(NH) 3261, ν(Amide I) 1631, ν(C=N) 1604, ν(Amide II) 1541, ν(Amide III) 1311.



Scheme S1: Synthesis of the ligand H₂L 1.

Synthesis of [Pb₂(L)₂] **2**

The lead(II) complex was synthesized by an electrochemical procedure. The electrochemical cell can be represented as Pt(-) | H₂L + CH₃CN | Pb(+). The ligand H₂L (0.05 g, 0.116 mmol) was dissolved in warm acetonitrile (*ca.* 80 cm³). Once the solution reached room temperature, a small amount of supporting electrolyte (tetraethylammonium perchlorate) was added. The solution was electrolysed at 10 mA and 13 V for 38 min. The yellow solid was filtered off, washed with diethyl ether and dried under vacuum. Caution! Perchlorate salts are potentially explosive and should be handled with care. Yield: 0.2 g (74%); $E_f = 1.0 \text{ mol F}^{-1}$; E. A. (Found: C, 44.44; H, 3.07; N, 8.63; C₄₈H₄₀N₈O₈Pb₂ required: C, 45.35; H, 3.17; N, 8.81; ESI⁺-MS (*m/z*) 637.0 [ML+H]⁺, 1272.8 [M₂L₂+H]⁺; ¹H NMR (500 MHz, DMSO-d₆, 298 K, ppm): 14.45 (s, 4H, OH), 7.80-7.63 (m, 4H), 7.97-7.86 (m, 6H), 7.47-7.22 (m, 6H), 6.89 (d, 4H, *J* = 7.1 Hz), 6.83-6.73 (m, 4H), 2.29 (s, 12H); ²⁰⁷Pb NMR (500 MHz, DMSO-d₆, 298 K, ppm): -770.7; IR (KBr, cm⁻¹): ν(OH) 3440, ν(Amide I) 1632, ν(C=N) 1605, ν(Amide II) 1540, ν(Amide III) 1311. Recrystallization from the mother liquors afforded X-ray quality crystals of **2** (CCDC 1487152).

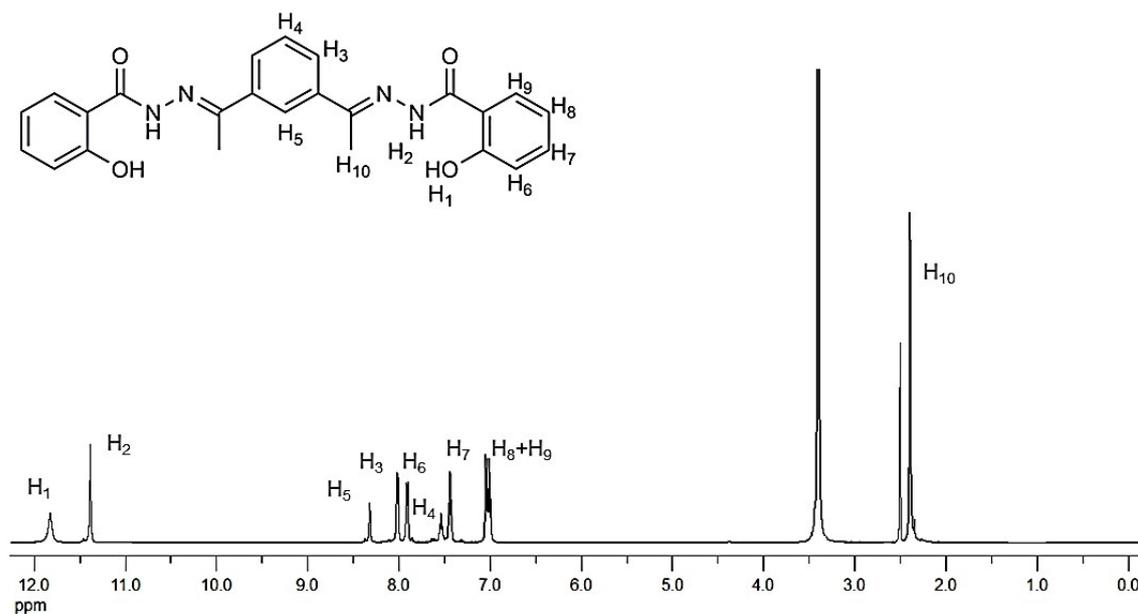


Figure S1: ^1H NMR spectrum of the ligand H_2L (**1**) recorded in DMSO-d_6 .

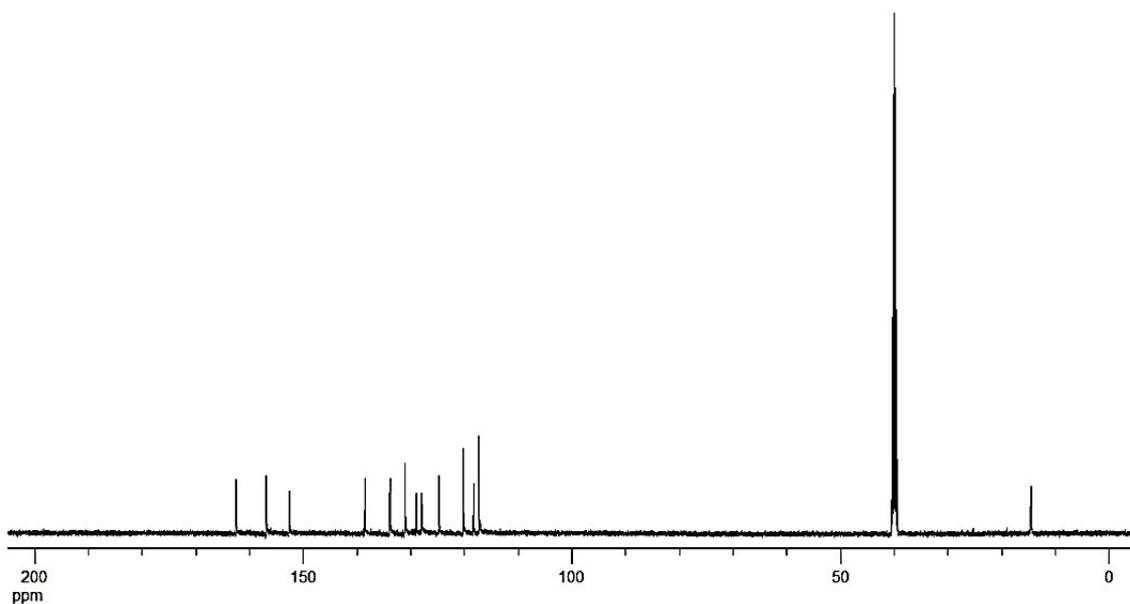


Figure S2: ^{13}C NMR spectrum of the ligand H_2L (**1**) recorded in DMSO-d_6 .

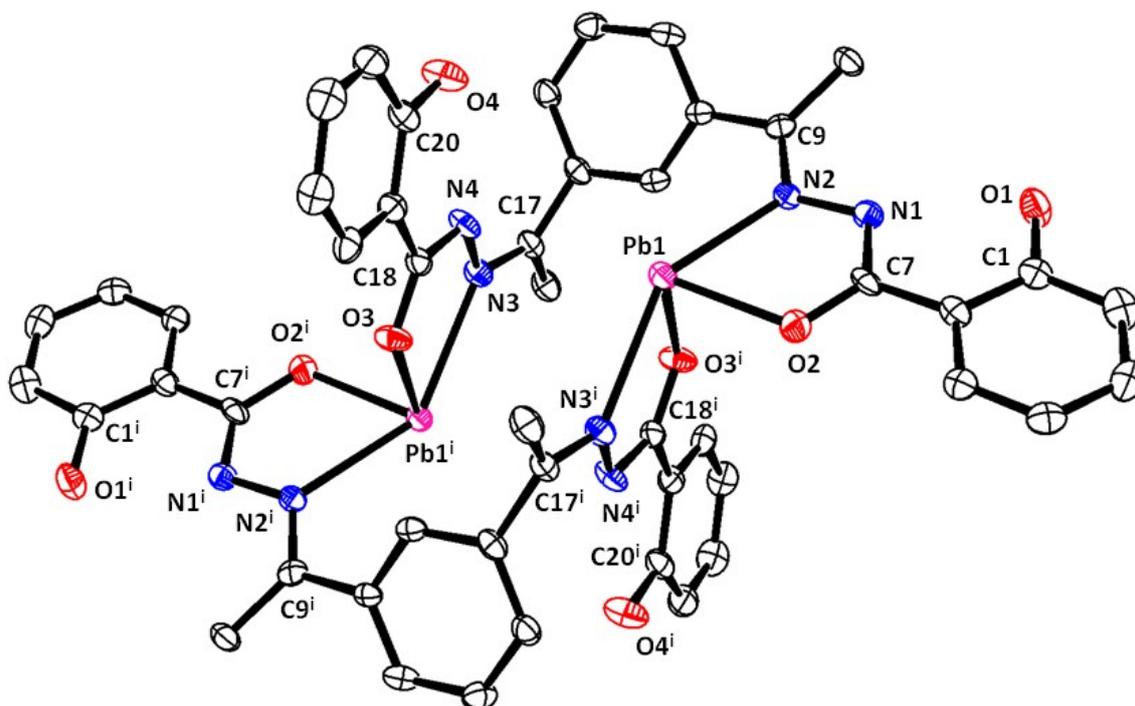


Figure S3: ORTEP diagram of the Pb(II) mesocate **2** showing ellipsoids at 50% level. Hydrogen atoms have been omitted for clarity.

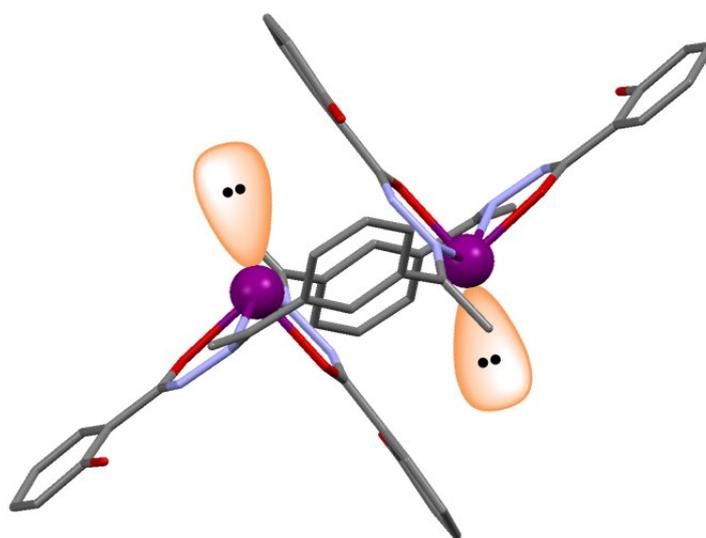


Figure S4: Stick representation of the mesocate **2** showing the antiparallel voids created by the stereochemically active lone pair in each Pb(II) ion.

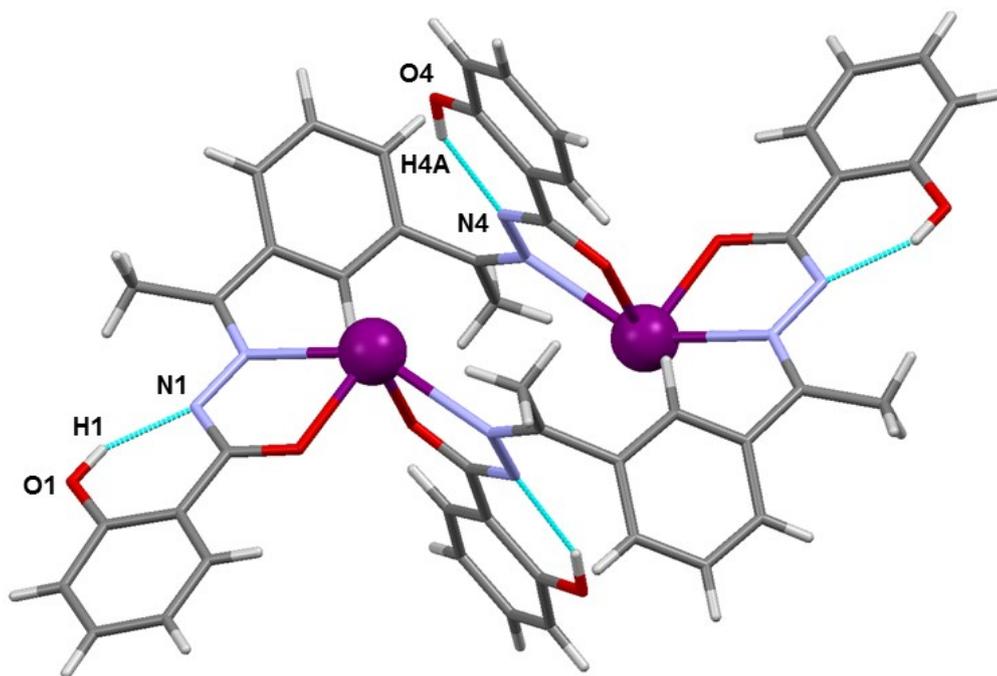


Figure S5: Classical hydrogen bond interactions observed in the mesocate $[Pb_2(L)_2]$ **2**.

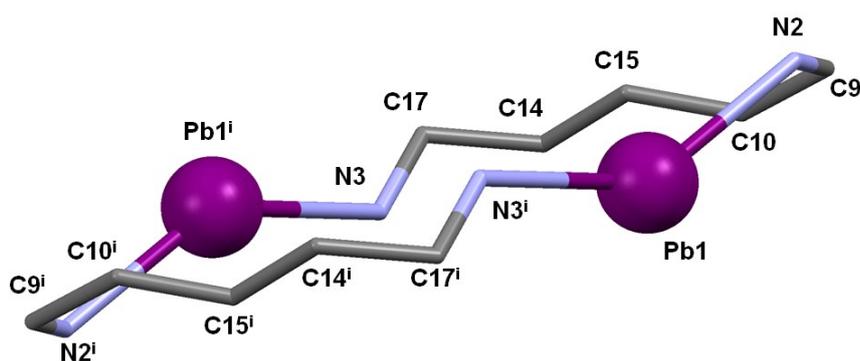


Figure S6: Chair-like conformation adopted by the 16-membered metallacycle in the Pb(II) mesocate **2**.

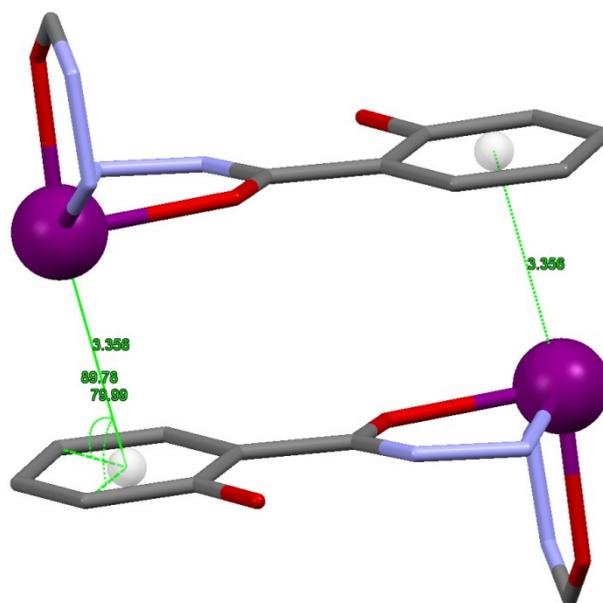


Figure S7: Pb···aryl centroid distances (Å) and angles(°) for the strong Pb···π interaction in mesocate **2**.

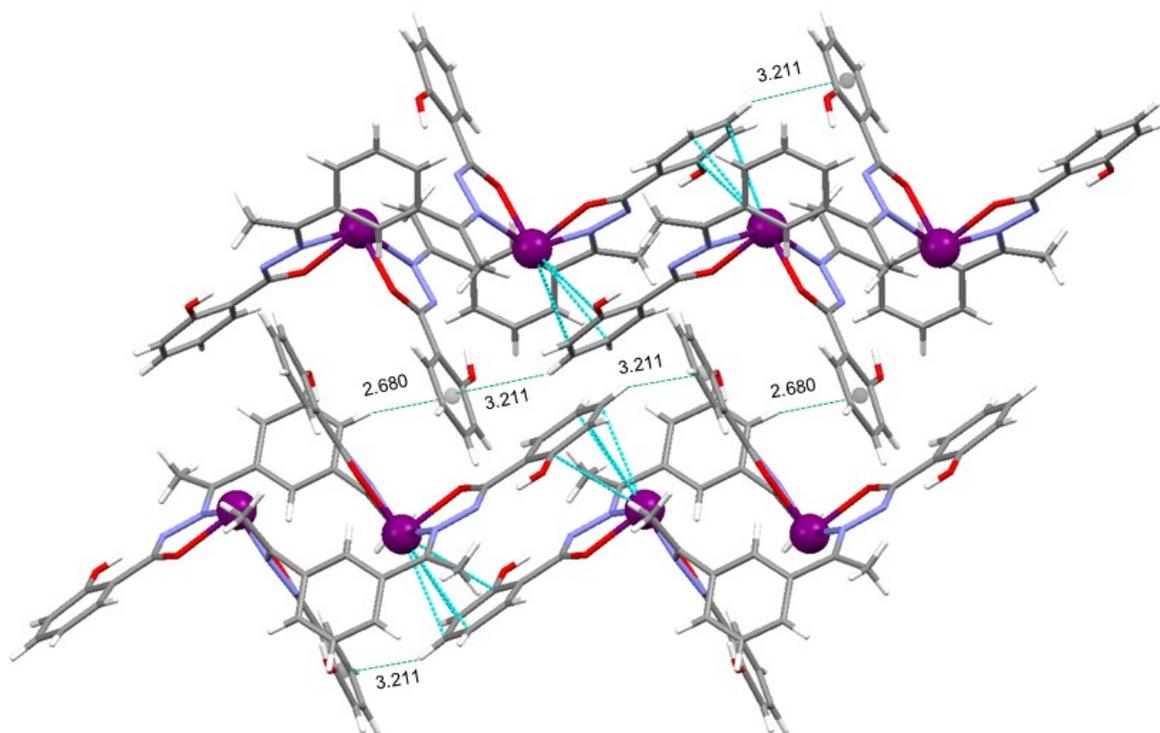


Figure S8: Intermolecular CH... π and Pb(II) lone pair... π interactions established between molecules of mesocate [Pb₂(L)₂] **2**.

Table S1: Crystallographic parameters of the lead(II) complex [Pb₂(L)₂] **2**

[Pb ₂ (L) ₂] 2			
Empirical Formula	C ₄₈ H ₄₀ N ₈ O ₈ Pb ₂	Z	4
Formula weight/ g·mol⁻¹	1271.26	Volume / Å³	2136.77 (11)
Space group	<i>P</i> 21/ <i>c</i>	Density/g·cm⁻³	1.976
Crystal system	Monoclinic	μ /mm⁻¹	7.94
Crystal size / mm	0.15 x 0.11 x 0.10	GOF	1.01
a/Å	12.4274 (4)	F(000)	1224
b/Å	10.6731 (3)	Reflections collected	25486
c/Å	17.2083 (5)	Independent reflections [R_{int}]	4708 [0.063]
α°	90	Data/restraints/parameters	4708/ 2/ 304
β°	110.584 (2)	R₁, wR₂ [I > 2σ (I)]	0.0333 [0.0612]
γ°	90	R₁, wR₂ (all data)	0.0545 [0.0676]
Temperature/ K	100	Δρ max and min /e·Å⁻³	1.18 and -0.77

Table S2: Selected bond distances [Å] and angles [°] of the lead(II) complex [Pb₂(L)₂] **2**

[Pb ₂ (L) ₂] 2					
C(1)-O(1)	1.327(6)	N(1)-N(2)	1.396(6)	O(2)-Pb(1)	2.261(4)
C(20)-O(4)	1.351(6)	N(4)-N(3)	1.407(6)	N(2)-Pb(1)	2.520(4)
N(1)-N(2)	1.396(6)	C(7)-O(2)	1.322(6)	O(3)-Pb(1)	2.260(4)
N(4)-N(3)	1.407(6)	C(18)-O(3)	1.276(6)	N(3)-Pb(1)	2.593(4)
C(9)-N(2)	1.290(6)	C(7)-N(1)	1.312(7)		
C(17)-N(3)	1.290(7)	C(18)-N(4)	1.314(7)		
C(1)-O(1)-H(10)	109.50	N(4)-N(3)-C(17)	114.90(4)	O(2)-Pb-N(3)ⁱ	88.44(13)
C(20)-O(4)-H(4O)	104.00(4)	N(1)-N(2)-Pb	113.30(3)	N(2)-Pb-O(3)ⁱ	84.62(13)
C(7)-N(1)-N(2)	112.90(4)	N(4)-N(3)-Pbⁱ	111.60(3)	O(2)-Pb-O(3)ⁱ	87.96(14)
C(18)-N(4)-N(3)	113.60(4)	C(7)-O(2)-Pb	118.60(3)	N(2)-Pb-N(3)ⁱ	142.77(13)
N(2)-C(9)-C(10)	116.20(5)	C(18)-O(3)-Pbⁱ	121.90(4)	O(3)ⁱ-Pb-N(3)ⁱ	65.98(13)
N(3)-C(17)-C(14)	120.10(5)	N(1)-C(7)-O(2)	126.80(5)	O(2)-Pb-N(2)	67.27(13)
N(1)-N(2)-C(9)	117.40(4)	N(4)-C(18)-O(3)	126.70(5)		

Symmetry operation: *i* = -*x*, -*y*, -*z*

Table S3: Classical and non-classical hydrogen bond interactions observed in the crystal packing of the Pb(II) mesocate **2**.

[Pb₂(L)₂] 2				
D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (<)
O(1)-H(1)···N(1)	0.8196	1.8192	2.545(7)	146.88
O(4)-H(4A)···N(4)	0.82(3)	1.84(4)	2.583(7)	149(5)
C(5)-H(5)···O(2)	0.9294	2.4505	2.776(7)	100.60
C(15)ⁱ-H(15)ⁱ···O(3)	0.9310	2.3086	3.119(6)	145.27

Symmetry operations: i = -x, -y, -z

Table S4: Intermolecular CH··· π interactions involved in the 3D zig-zag packing of mesocate **2**

C-H···Ring	Distance (Å)
C(13)-H(13)···C(19)-C(24)-C(23)-C(22)-C(21)-C(20)	2.680
C(3)-H(3)···C(19)-C(24)-C(23)-C(22)-C(21)-C(20)	3.261

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