Supplementary Information (SI) for CrystEngComm.

Electronic supplementary information

for

An unsymmetrically sandwiched bis(O3S2-macrocycle) lead(II) complex via an endo/exo-coordination mode

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Experimental

General procedures

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. ESI-mass spectra were obtained employing a Thermo Scientific LCQ Fleet spectrometer. The FT-IR spectra were recorded using Varian 640-IR FT-IR Spectrometer with KBr pellets. The elemental analysis was carried out using a Thermo Scientific Flash 2000 Series elemental analyser. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 500 (500 MHz). FT-IR spectra are recorded using Spectrum Two FT-IR Perkinelmer with KBr pellets

Preparation of $[Pb(L)_2(ClO_4)]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5CH_3CN$ (1).

$Pb(ClO_4)_2 \cdot 3H_2O$ (14.7 mg, 0.032 mmol) in acetonitrile (1.0 mL) was added to a solution of **L** (10.0 mg, 0.027 mmol) in dichloromethane (1.0 mL). Slow evaporation of the solution afforded a colourless crystalline product **1** suitable for X-ray analysis. Yield: 32%; IR (KBr): 2935, 2886, 1598, 1492, 1449, 1292, 1246, 1090, 1069, 1045 (ClO_4^-), 929, 764 cm^{-1}. Grinding the product for microanalysis led to removing the solvent molecules to yield a product. Anal. calc. for $C_{40}H_{48}Cl_2O_{14}PbS_4$: C, 41.45; H, 4.17. Found: C, 41.65.; H, 4.55%. Mass spectrum *m/z* (ESI): 1059 for $[Pb(\mathbf{L})_2(ClO_4)]^+$.

Caution: Since the perchlorate compound could be explosive, it should be handled with great care!

X-ray crystallographic analysis

Crystal data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection, data reduction and semi-empirical absorption correction were carried out using the software package of APEX2.[S1] All of the calculations for the structure determination were carried out using the SHELXTL package.[S2] Relevant crystal data collection and refinement data are summarised in Table S1.

CCDC 2389314 (**1**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

S1. Bruker, APEX2 Version 2009.1-0 Data Collection and Processing Software (Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008).

S2. Bruker. SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures. 2001.

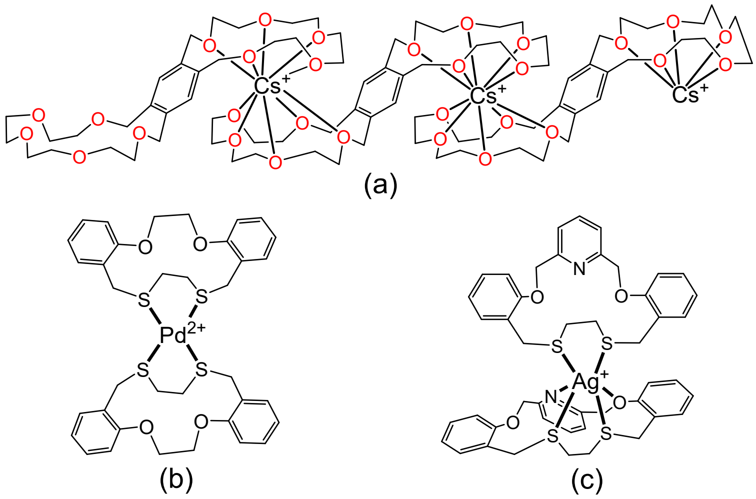
Table S1 Crystallographic data and refinement parameter of **1**

	1
Formula	$C_{83}H_{101}Cl_6NO_{28}Pb_2S_8$
Formula weight	2444.20
Temperature	173
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	2
a (Å)	15.4259(2)
b (Å)	21.5068(3)
c (Å)	15.6995(2)
α (°)	90
β (°)	112.9730(10)
γ (°)	90
V (Å^3)	4795.40(11)
D_{calc} (g/cm^3)	1.693
$2\theta_{max}$ (°)	52.00
R_1, wR_2 [$I > 2\sigma(I)$]	0.0369, 0.0745
R_1, wR_2 [all data]	0.0553, 0.0807
Goodness-of-fit on F^2	1.031
No. of reflection used [$>2\sigma(I)$]	9419 [R_{int} = 0.0726]
Refinement	42433

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**

Pb1-S1	2.9022(13)	Pb1-O1	2.854(3)
Pb1-S2	2.9897(12)	Pb1-O2	2.806(3)
Pb1-S3	2.9015(11)	Pb1-O3	2.951(1)
Pb1-S4	3.1003(12)	Pb1-O8	2.781(9)
S1-Pb1-S2	70.19(3)	S3-Pb1-O1	141.36(7)
S1-Pb1-S3	78.04(3)	S3-Pb1-O2	150.36(7)
S1-Pb1-S4	68.11(3)	S3-Pb1-O3	102.55(4)
S1-Pb1-O1	75.15(7)	S3-Pb1-O8	83.86(3)
S1-Pb1-O2	131.58(7)	S4-Pb1-O1	74.65(7)
S1-Pb1-O3	135.94(7)	S4-Pb1-O2	115.88(7)
S1-Pb1-O8	140.93(7)	S4-Pb1-O3	154.19(4)
S2-Pb1-S3	67.06(3)	S4-Pb1-O8	73.21(1)
S2-Pb1-S4	124.47(3)	O1-Pb1-O2	61.58(9)
S2-Pb1-O1	126.39(7)	O1-Pb1-O3	116.07(4)
S2-Pb1-O2	119.04(7)	O1-Pb1-O8	100.02(9)
S2-Pb1-O3	69.87(9)	O2-Pb1-O3	58.90(3)
S2-Pb1-O8	132.41(5)	O2-Pb1-O8	71.27(2)
S3-Pb1-S4	69.75(3)	O3-Pb1-O8	81.59(1)

Recently, we have reported a poly(sandwich)-type Cs^+ complex of bis-o-xylyl-(17-crown-5) as the first example of infinite sandwich-type macrocyclic complexes (Fig. S1a, see Type A in Scheme 1a).[S1] Some Pd^{2+} complexes of bis(O_2S_2-macrocycle), adopting an *edge-to-edge* mode (Fig. S1b, see Type B in Scheme 1b) were isolated via mole-ratio-controlled approaches.[S2, S3] An unsymmetrically sandwiched silver(I) complex $[Ag(L')_2]PF_6$ (L': NO_2S_2-macrocycle, Fig.S1c, see Type C in Scheme 1c) also has been reported by the Lee group as the first example of this type.[S4]



(a)

(b)

(c)

Fig. S1 Some extended sandwich-type macrocyclic complexes reported previously: (a) one-dimensional polymeric Cs^+-complex (*face-to-face*), (b) Pd^{2+}-complex (*edge-to-edge*) and (c) Ag^+-complex (*edge-to-face*).

References

S1. S. Kim, I.-H. Park, S. S. Lee, W. Sim and J. Y. Lee, *CrystEngComm*, 2020, **22**, 5601-5605.
S2. S. Y. Lee, S. Park and S. S. Lee, *Inorg. Chem.*, 2009, **48**, 11335-11341.
S3. S. Y. Lee, S. Park and S. S. Lee, *Inorg. Chim. Acta*, 2009, **362**, 1047-1052.
S4. H. J. Kim, K. F. Sultana, J. Y. Lee and S. S. Lee, *CrystEngComm*, 2010, **12**, 1494-1500.

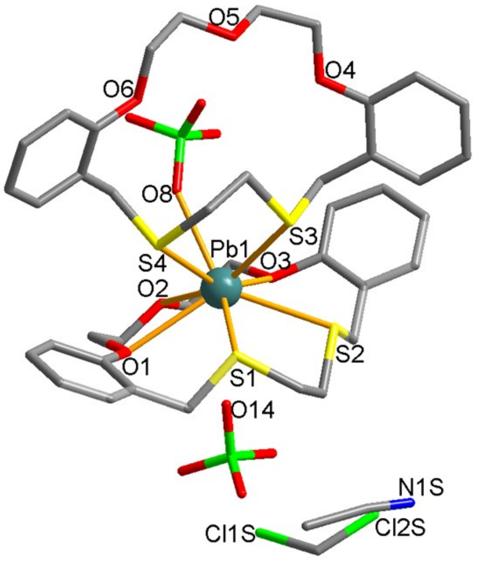
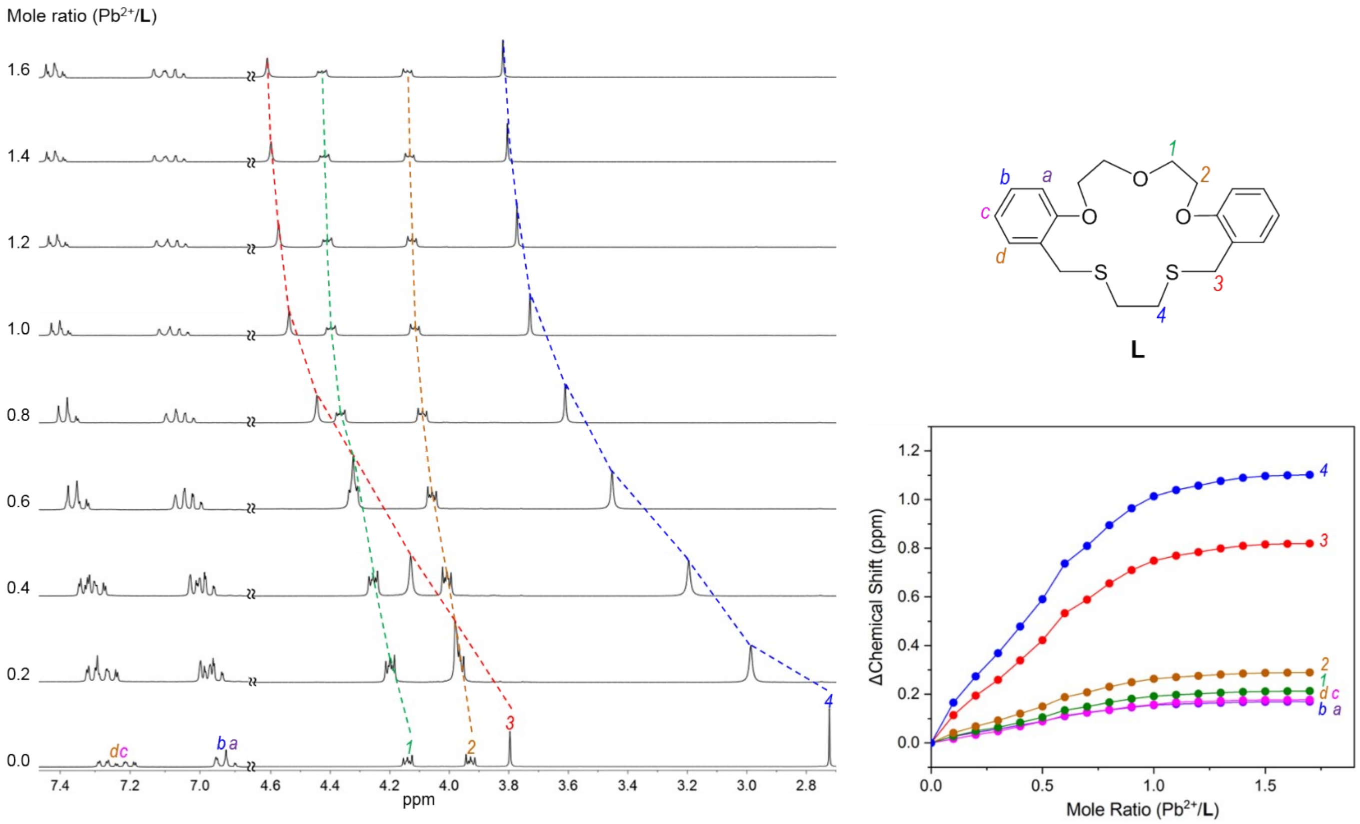
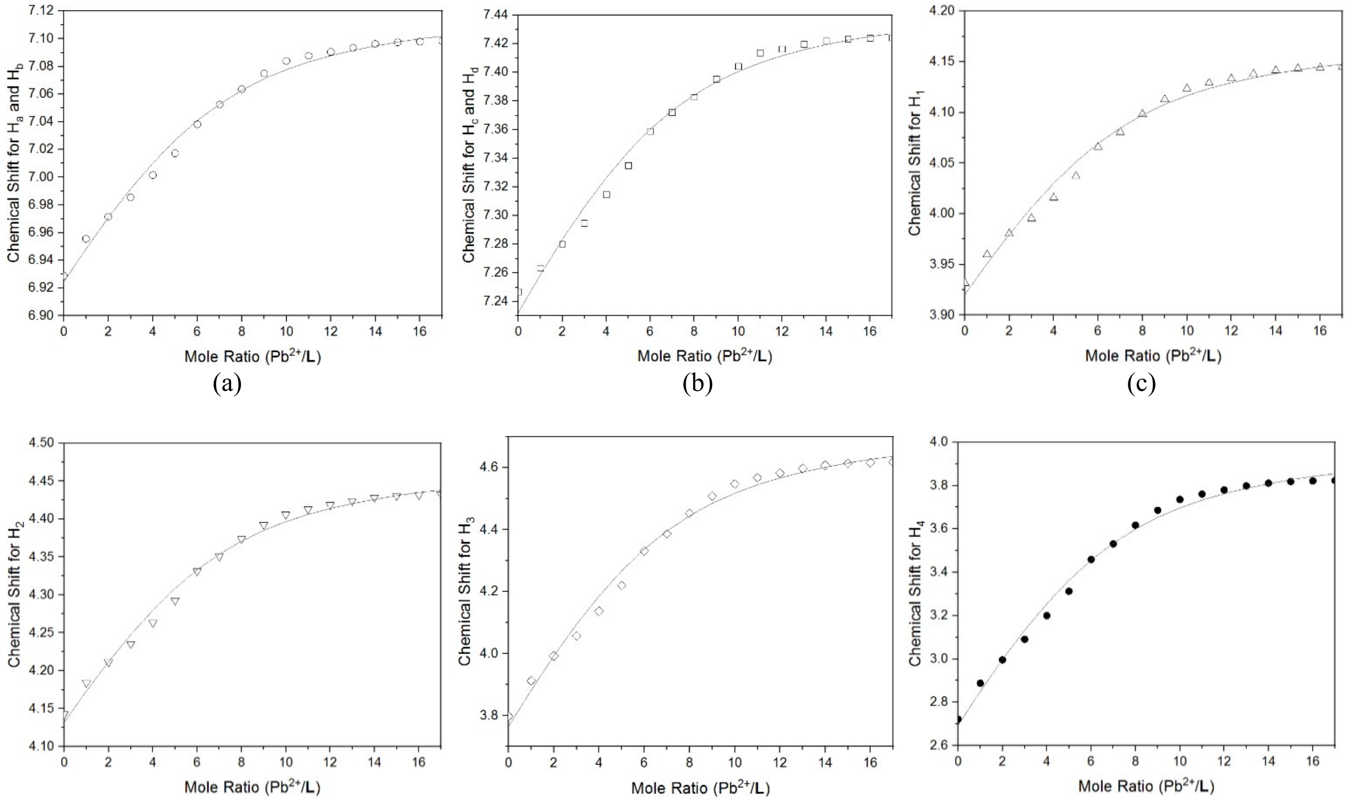


Fig. S2 Crystal structure of [Pb(**L**)$_2$(ClO$_4$)]ClO$_4$·0.5CH$_2$Cl$_2$·0.5CH$_3$CN (**1**) showing non-coordinated anion and solvent molecules.



(a) (b)

Fig. S3 (a) ^{1}H NMR titration of **L** (1.0×10^{-3} M) with lead(II) perchlorate in $CDCl_3$/CD_3CN (v/v 1:1) and (b) titration curves for each proton in **L**.



(a) (b) (c)

(d) (e) (f)

Fig. S4 HyperNMR output for (a) $H_{a,b}$, (b) $H_{c,d}$, (c) H_1, (d) H_2, (e) H_3 and (f) H_4 signals (circles, squares and triangles: experimental points, solid lines: theoretical fit for the $[Pb\mathbf{L}]^{2+}$ (1:1) model). log *K* = 5.9(5) for the 1:1 complexation.

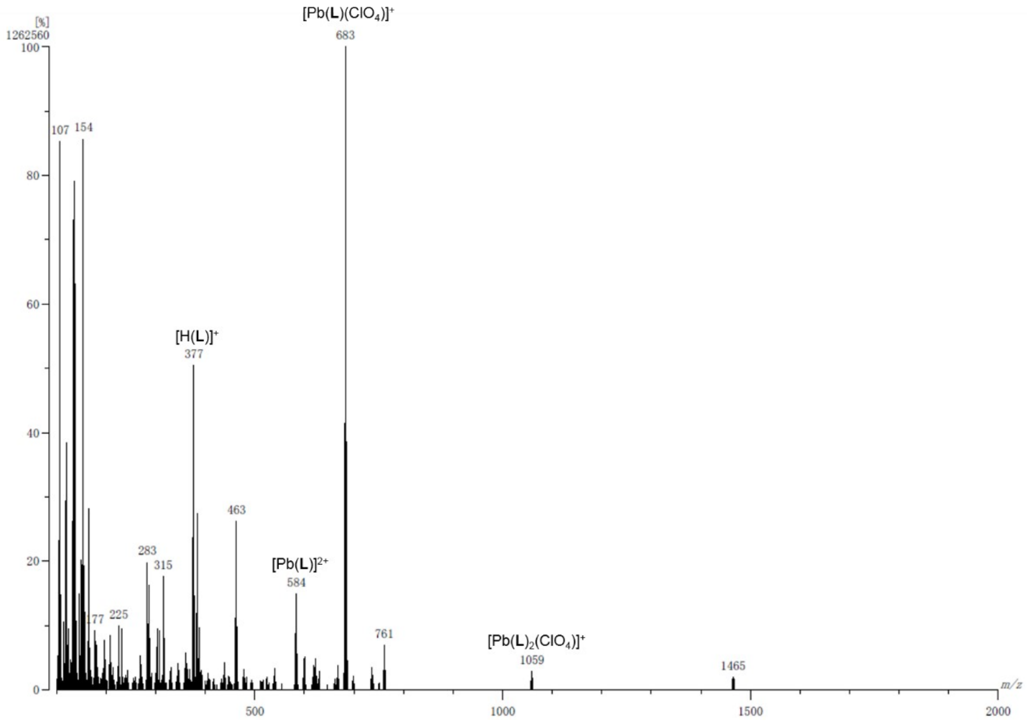


Fig. S5 FAB-mass spectrum of **1**.

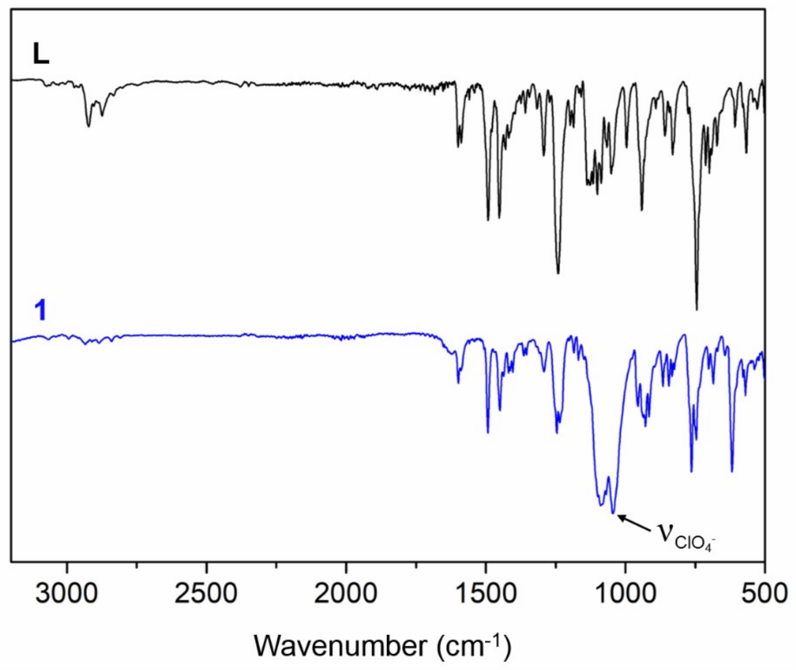


Fig. S6 FT-IR spectra of **L** and **1**.