Stereochemically Active Lead Chloride Enantiomers Mediated by Homochiral Organic Cation

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ABSTRACT

Two-dimensional ((S)-1-(1-naphthyl)ethylamineH)$_2$Pb$_4$Cl$_{10}$·2DMF (1) and ((R)-1-(1-naphthyl)ethylamineH)$_2$Pb$_4$Cl$_{10}$·2DMF (2) have been synthesized using the corresponding homochiral organic cations. The lead atoms within the structure adopt a variety of coordination geometries, with Pb(II)Cl$_6$ adopting a distorted pentagonal pyramid geometry and exhibiting stereochemically active lone-pair electrons, instead of a more typical octahedral geometry with less stereochemical activity.

Keywords Pb(II) coordination spheres, Crystal engineering, Hybrid organic-inorganic halides, Stereochemically active, Single enantiomer

1. Introduction

The rich compositional choices of hybrid organic-inorganic halides (HOIHs) offer numerous chances for materials exploration and application. Haloplumbates(II) play a significant role in HOIHs due to the flexible coordination sphere of lead(II) arising in part from the lone pair of electrons.[1-4] As a representative example, APbX$_3$ (A = small organic cation, X = halogen) provides a class of photovoltaic materials that have generated substantial interest in recent years.[5,6] Generally, Pb(II) compounds have two coordination possibilities, holodirected (Figure 1a) and hemidirected (Figure 1b), which can be distinguished according to the disposition of ligands around Pb(II).[7] A void in the coordination configuration appears for the hemidirected category, while not for holodirected.[7] Lone-pair electrons account for this difference in coordination and are stereochemically active in the void of hemidirected Pb(II) compounds, while they are stereochemically inactive (or less active) for holodirected systems.[8] The stereochemical activity of lone-pair electrons plays a critical role in materials properties, *e.g.* low thermal conductivity in PbCuSbS$_3$,[9] selectivity in the Pb(II) protein binding[10] and a phase transition in (2-MIm)SbI$_4$.[11] Hemidirected types are found for lower Pb(II) coordination numbers (2-5), while holodirected are often found for the higher coordination numbers (9-10).[7] Both hemidirected and holodirected can be found for intermediate Pb(II) coordination numbers (6-8), although in this category the hemidirected type is quite rare.[7,12]

Beyond the question of lone pair stereochemical activity, chiral HOIHs materials are intriguing because of their potential applications in ferroelectrics, piezoelectrics and non-linear optics arising from the polar structures.[13,14] In addition, the enantiomers of chiral materials with different configurations have distinct biological,[15] physical,[16] and chemical properties.[17] However, chiral structures are relatively scarce owing to the polarity elimination trend in the molecular packing.[18,19] Homochiral organic cations have, however, been used to induce chirality in HOIHs.[20-31] ((S)-C$_6$H$_5$C$_2$H$_4$NH$_3$)[PbBr$_3$] has been reported as the first chiral HOIH prepared using a single enantiomer for the organic cation.[21] In contrast, a racemic mixture of organic cations usually results in centrosymmetric structures[23,30,32] – *e.g.*, ((RS)-C$_6$H$_{11}$CH(CH$_3$)NH$_3$)$_2$[PbCl$_4$] crystallizes in the *C*2/*c* space group compared with the chiral *P*2$_1$ for ((R)-C$_6$H$_{11}$CH(CH$_3$)NH$_3$)$_2$[PbCl$_4$] and ((S)-C$_6$H$_{11}$CH(CH$_3$)NH$_3$)$_2$[PbCl$_4$].[23] It is noteworthy that flexible and symmetrical organic cations, such as pyrrolidinium- and pyrrolinium-based examples,[33-38] can induce symmetry breaking (typically not chirality) in HOIHs according to the order-disorder transition.[14] Among the fruitful organic cation families, acene alkylammoniums are very attractive. As demonstrated in our previous work,[39] the structure of acene alkylammoniums is a benefit for cation design due to the various active substitution sites, the tuneable length of the alkylamine tail and the number of fused benzene rings. All of these can be used to modify the packing or chiral nature of the organic cation and thereby the crystal structure of HOIHs.

Herein, two new layered homochiral ((S)-1-(1-naphthyl)ethylamineH)$_2$[Pb$_4$Cl$_{10}$]·2DMF (**1**) and ((R)-1-(1-naphthyl)ethylamineH)$_2$[Pb$_4$Cl$_{10}$]·2DMF (**2**) (DMF = N,N-Dimethylformamide) were achieved using (S) and (R)-1-(1-naphthyl)ethylamineH (S-NEA and R-NEA, Figures 1c and 1d) to induce chirality, respectively. Pb(II) in these two structures show four-, five- and six- coordination to Cl atoms. The Pb(II) atoms are all hemidirected with stereochemically active lone-pair electrons. The crystal structures, optical absorption and emission of the two compounds have also been studied.

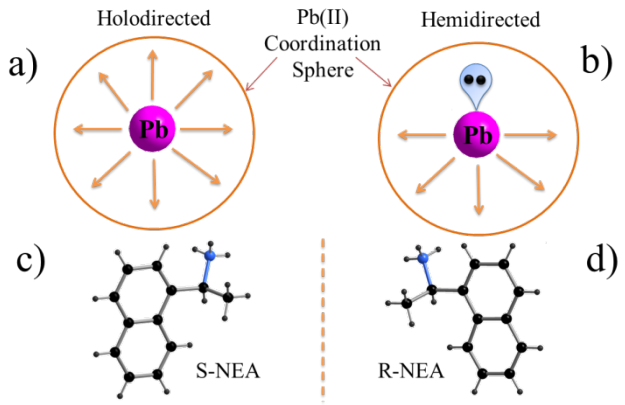

Figure 1 Schematic of the possible coordination spheres for Pb(II) (a, b) and the organic cations of **1** and **2** (c, d).

2. Materials and methods

Crystals of **1** and **2** were synthesized through solution evaporation. $PbCl_2$ (99.999% metal basis) was purchased from Alfa Aesar company. (S)-(−)-1-(1-Naphthyl)ethylamine hydrochloride (97%) (S-NEA), (R)-(+)-1-(1-Naphthyl)ethylamine hydrochloride(97%) (R-NEA) and N,N-Dimethylformamide (anhydrous, 99.8%) (DMF) were purchased from Sigma-Aldrich company. 2-butanol (99.5%) was purchased from VWR International.

Single crystal X-ray diffraction data were measured on a Bruker D8 ADVANCE Series II (Mo*Kα* radiation) at room temperature. The structures were solved and refined using Shelxl and Olex software.[40,41] Powder X-ray diffraction data were collected using a PANalytical Empyrean powder X-ray diffractometer (Cu*Kα* radiation). Optical absorption spectra measurements were performed using a Shimadzu UV-3600 spectrophotometer. The photoluminescence spectra were collected using a Horiba Jobi-Yvon LabRAM ARAMIS system at room temperature, with a 325 nm He-Cd laser excitation. The laser beam was focused through a 40× UV objective onto the crystal surface. The infrared (IR) spectra were measured in a Bruker VERTEX70 unit. The circular dichroism (CD) spectra were collected using a MOS-450 system. Thermogravimetric Analysis (TGA) was performed using a NETZSCH-STA-449F3 under the dry nitrogen atmosphere.

((S)-1-(1-Naphthyl)ethylamineH)$_2$Pb$_4$Cl$_{10}$·2DMF (1). A mixture of S-NEA (17.1 mg, 0.010 mmol) and $PbCl_2$ (13.9 mg, 0.005 mmol) was weighted in a 4 mL scintillation vial and dissolved in 0.5 ml DMF solvent. Then 1 ml 2-butanol was placed on the top of the DMF solution. No crystals formed in this clear layered solution for several days. The mixed solvents were evaporated over several months and the colorless crystals of ((S)-1-(1-Naphthyl)ethylamineH)$_2$Pb$_4$Cl$_{10}$·2DMF were found at the bottom of the vial. Crystal and structure refinement parameters for **1**: $C_{30}H_{42}Cl_{10}O_2Pb_4$, M = 1673.98, monoclinic, $P2_1$, a = 16.3182(3), b = 8.1686(1), c = 18.0061(4) Å, β = 110.944(1), V = 2241.58(7) Å^3, Z = 2, D_{calc} = 2.480 g·cm^{-3}, $F(000)$ = 1528.0, μ = 15.605 mm^{-1}, T = 296 K, 43650 reflections measured, 7893 unique reflections (R_{int} = 0.0348), 7246 observed reflections [$I > 2\sigma(I)$] with $R_1(wR_2)$ = 0.0223 (0.0551), $R_1(wR_2)$ = 0.0265 (0.0575) (all data), GOF = 0.993, flack parameter = 0.011(4), CCDC 1846208.

((R)-1-(1-Naphthyl)ethylamineH)$_2$Pb$_4$Cl$_{10}$·2DMF (2). S-NEA was replaced with R-NEA. Then using the same procedure, ((S)-1-(1-Naphthyl)ethylamineH)$_2$Pb$_4$Cl$_{10}$·2DMF was obtained. Crystal and structure refinement parameters for **2**: $C_{30}H_{42}Cl_{10}O_2Pb_4$, M = 1673.98, monoclinic, $P2_1$, a = 16.3288(4), b = 8.1696(2), c = 18.0090(4) Å, β = 110.918 (1), V = 2244.06(9) Å^3, Z = 2, D_{calc} = 2.477 g·cm^{-3}, $F(000)$ = 1528.0, μ = 15.587 mm^{-1}, T = 296 K, 27803 reflections measured, 7906 unique reflections (R_{int} = 0.0457), 6265 observed reflections [$I > 2\sigma(I)$] with $R_1(wR_2)$ = 0.0298 (0.0651), $R_1(wR_2)$ = 0.0464 (0.0723) (all data), GOF = 0.879, flack parameter = -0.016(8), CCDC 1846209.

3. Results and discussion

The title compounds are enantiomers (Figures S1a and S1b), crystallized in the $P2_1$ space group (Table S1) with flack parameters 0.011(4) and -0.016(8) for **1** and **2**, respectively. The asymmetric unit contains four Pb^{2+}, ten Cl^-, two DMF molecules and two (S or R)-NEA cations. The characteristic peaks for $-NH_2$, -CHO and benzene can be found in the IR spectra (Figure S2).

Taking **1** as a representative, their unique structures are shown in Figures 2 and 3. Pb(1) is coordinated to four chlorine atoms (Figure 2a), with two long (3.010 (2) and 3.066(2) Å) and two short (2.737(2) and 2.725(2) Å) bond lengths. The hexahedral geometry of Pb(1) is similar to the Pb coordination environment in ((R)-$C_6H_{11}CH(CH_3)NH_3)_2PbCl_4$.[23] The $Pb(2)Cl_5$ distorted square pyramid (Figure 2b), with bond lengths ranging from 2.682(2) to 3.069(2) Å, is similar to that found in the compound of $(C_9H_{14}N)_2PbCl_4$.[42] Both Pb(3) and Pb(4) are six-coordinated (Figure 2c, d), with the Pb-Cl distances ranging from 2.700(2) to 3.088(2) Å. The $Pb(3)Cl_6$ unit might be considered a highly distorted octahedron (Figure 2c). $Pb(4)Cl_6$ forms an approximate pentagonal pyramid (Figure 2d). The lone-pair electrons are sitting in the void of each Pb(1 - 4) geometry and are stereochemically active. In this analysis we don't consider the Pb-Cl bond lengths above 3.2 Å, since these are above the sum of Pb and Cl ionic radii. The bond valence calculation by Fullprof software also confirms the Pb(1 - 4) coordination number mentioned above. While most haloplumbates(II) with six-coordinated Pb(II) exhibit octahedral coordination, the pentagonal pyramids in the current structures are quite rare in haloplumbate(II) structural chemistry.[7]

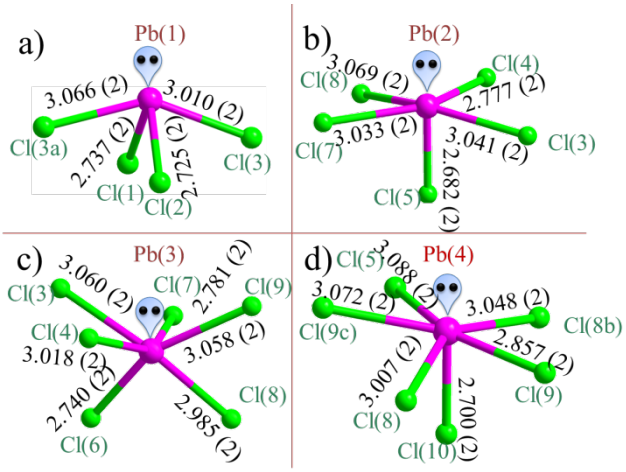

Figure 2 (a) Four-, (b) five- and (c, d) six- coordinated modes for Pb atoms in **1**. The lone-pair electrons were added in the void. The symmetry operations: a 2-*X*, -1/2+*Y*, -*Z*; b 1-*X*, -1/2+*Y*, -*Z*; c 1-*X*, 1/2+*Y*, -*Z*.

Pb(2), Pb(3) and Pb(4) are interconnected by sharing Cl(5), Cl(7) and Cl(9) to form an eight-membered Pb_4Cl_4 ring (black bonds in Figure 3a), with a Cl(8) atom in the center. The eight-membered Pb_4Cl_4 (R1) fuses with the neighboring ring (R2) by sharing the Pb(4)-Cl(9) edge to form a Pb_6Cl_6 chain. R1 and R3 in the chain are interconnected by sharing Cl(3) and Cl(4). Cl(3) atoms act as a μ4 metal-linker, connecting with two Pb(1) (blue bonds in Figure 3a), one Pb(3) and one Pb(4) to generate the $[Pb_4Cl_{10}]^{2-}$ layer. Based on the symmetry of the crystal structures, there are two 2_1 helical axes along the Pb(1)-Cl(3) and Pb(4)-Cl(9) lines (brown axes in Figure 3(a)), respectively. (S)-1-(1-naphthyl)ethylamineH cations together with DMF molecules form organic bilayers that alternate with the inorganic anion layers (Figure 3b). The chiral organic cation brings the chirality into the corresponding crystal through weak hydrogen bonds (Figure 3b).[43] CD spectra have been collected using KBr pellets (Figure S3) and the distinct Cotton effect confirms the chiral space group of compounds **1** and **2**. Using a similar strategy, (S and R)-$(C_6H_5C^*H(CH_3)NH_2)$,[20] (S and R)-$C_6H_{11}C^*H(CH_3)NH_3$,[23] (R)-3-aminopiperidine dihydrochloride,[26] mono-substituted benzylidene-1-aminopyridinium Schiff base derivative,[27] (S and R)-α-methylbenzylamine,[28] sertraline,[29] 1-(4-haloaryl)ethylammonium,[30] (R)-naphthyl-2-ethylammonium,[31] have been used to achieve chiral HOIHs.

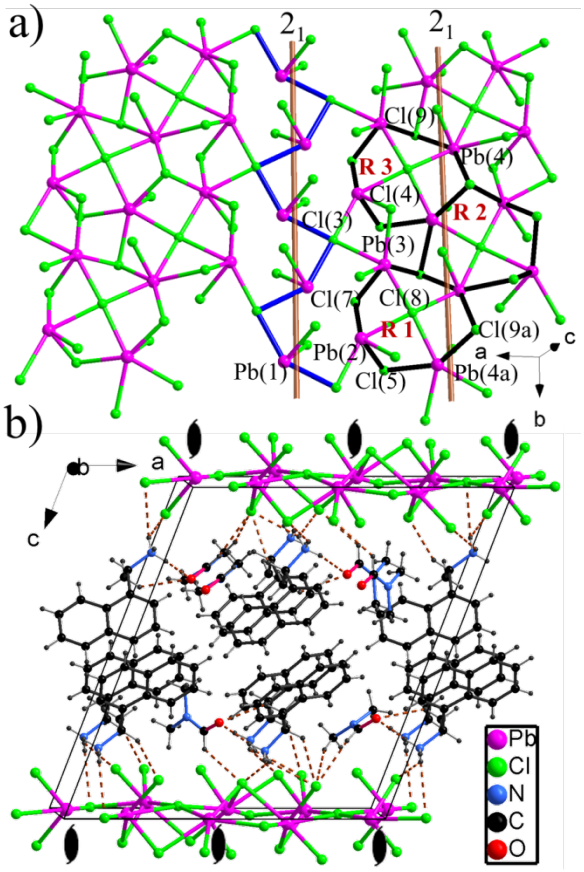

Figure 3 (a) The structure of $[Pb_4Cl_{10}]^{2-}$; (b) the packing structure of **1.** The brown dashed bonds are hydrogen bonds. The 2_1 helical axes are added in the packing structure. The symmetry operations: a 1-*X*, 1.5+*Y*, -*Z*.

The experimental powder X-ray diffraction (PXRD) patterns of **1** and **2** are in agreement with the calculated ones, which hence confirm the phase purity of **1** and **2** reactions (Figure S4). According to the TGA curves (Figure S5), compounds **1** and **2** lose one DMFmolecule (about 4%) around 70℃. They then further decompose at around 200 ℃ with a weight loss of 66%, which is attributed to the removal of DMF and S-NEA·HCl (or R-NEA·HCl).

The diffuse reflectance spectra of the title compounds were converted into the optical absorption spectra using the Kubelka-Munk function.[44,45]

$$F(R) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty},$$

where *K* is the K-M absorption coefficient, R_∞ is the diffuse reflection, and S is K-M scattering coefficient, which can be regarded as approximately a constant with respect to wavelength. Compounds **1** and **2** show an absorption edge at 315 nm (Figure 4a), consistent with the colourless nature of the crystals. The luminescence spectra of **1** and **2** are almost identical, with two emission peaks at around 450 and 530 nm. To understand the luminescence further, we compare the spectra of the title compounds with the corresponding spectra of the organic components alone (Figure 4b). The good agreement between the two sets of spectra demonstrates that the emission peaks of **1** and **2** evidently originate from the component organic cations (Figures 4b and S6). Unlike compounds with the layered $[PbX_4]^{2-}$ (X = Cl, Br, I) anion,[46] no sharp exciton peak appears from the layered $[Pb_4Cl_{10}]^{2-}$ anion of **1** and **2**.

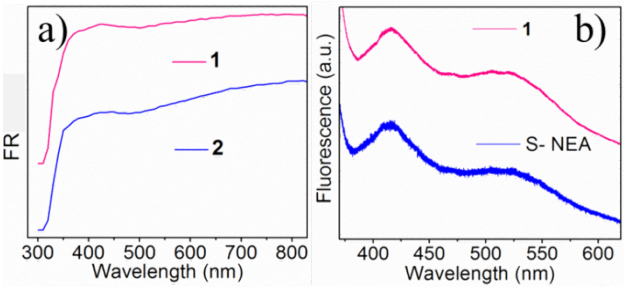

Figure 4 The optical absorption of **1** and **2** (a); the luminescence spectra of **1** and S-NEA (b).The layers in each plot have been shifted along the y axis.

4. Conclusions

Two layered homochiral compounds, ((S)-1-(1-naphthyl)ethylamineH)$_2Pb_4Cl_{10}$·2DMF and ((R)-1-(1-naphthyl)ethylamineH)$_2Pb_4Cl_{10}$·2DMF, have been achieved using the corresponding homochiral organic cations. The homochiral structures have been confirmed by CD spectra. The Pb(II) atoms have four-, five-, and six- coordination geometry in the layered $[Pb_4Cl_{10}]^{2-}$ anion. One of the six-coordinated Pb(II) atoms adopts an unusual distorted pentagonal pyramid geometry with stereochemically active lone-pair electrons. The organic components dominate the luminescence spectra of the title compounds with two emission peaks centered around 450 and 530 nm.

Conflicts of interest

There are no conflicts to declare

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Appendix A. Supplementary data

Electronic Supplementary Information (ESI) available: The tables of structure refinements, atomic coordinates and equivalent displacement parameters, the bond lengths and bond angles, the hydrogen bonds. See DOI: 10.1039/x0xx00000x

Acknowledgements

This work was supported by the National Science Foundation of China (NSFC) (Nos. 21871048, 51802039), the Award Program for Fujian Minjiang Scholar Professorship (2017) and the NSF under award number DMR-1728921.

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Supporting Information

Stereochemically Active Lead Chloride Enantiomers Mediated by Homochiral Organic Cation

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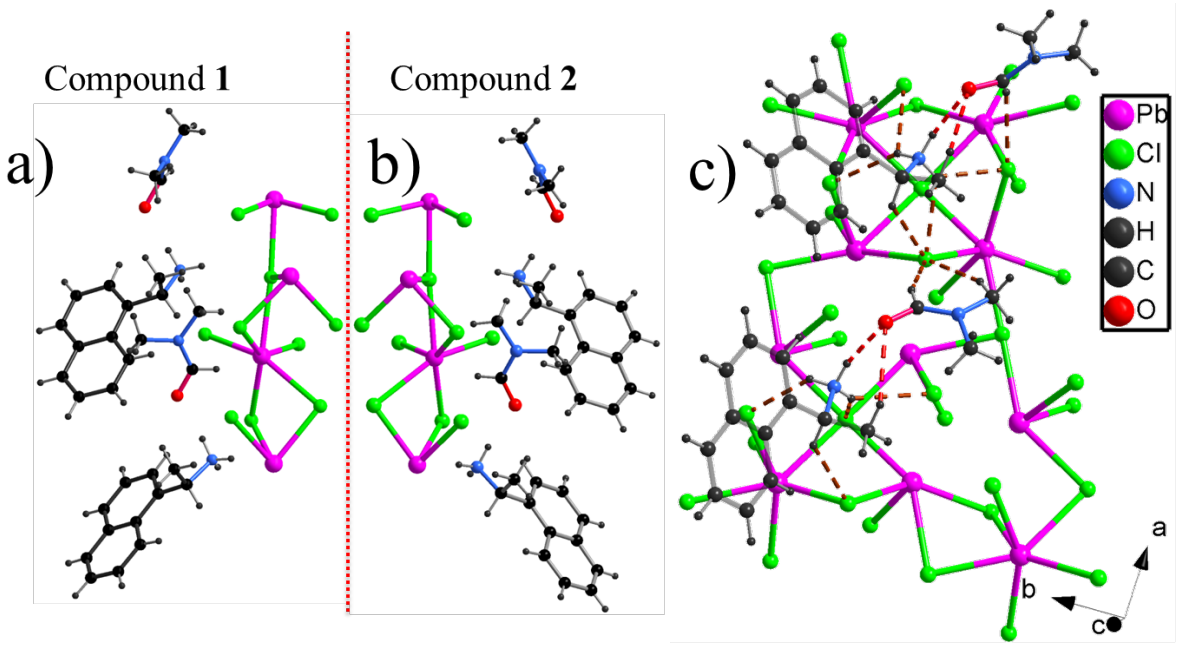

Figure S1 The asymmetric unit of **1** and **2** (a, b); the hydrogen bonds for **1** (c), shown as dashed lines.

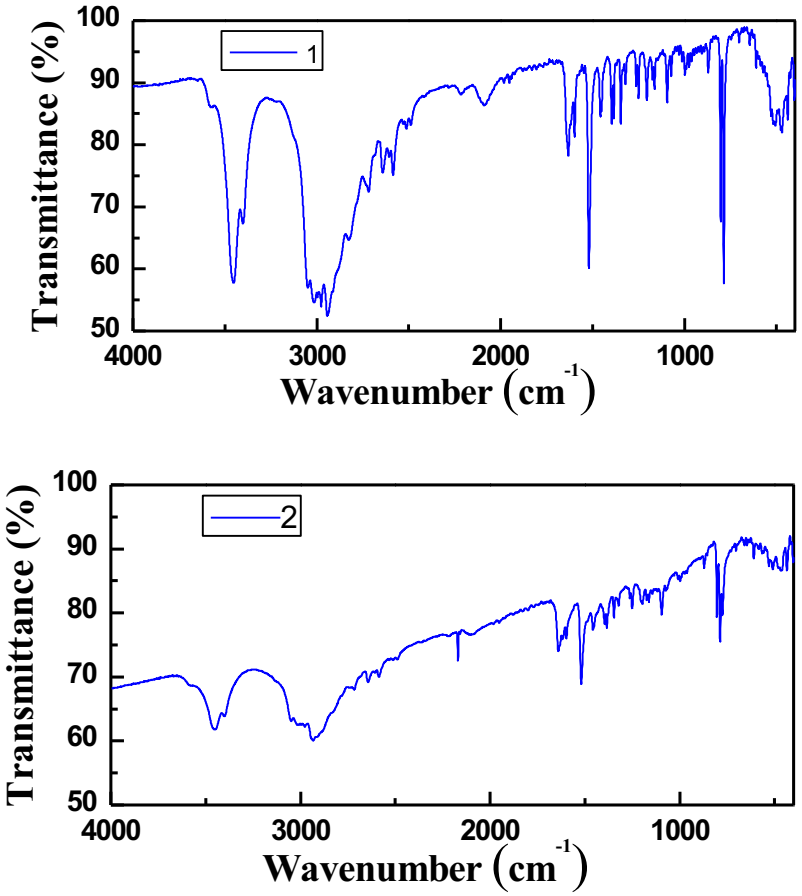

Figure S2 The IR spectra of compounds **1** and **2.** Two characteristic peaks around 3449 cm^{-1} and 3399 cm^{-1} are attributed to the stretching vibrations of -NH_2. The peaks around 2941 cm^{-1} arise from C-H stretching in the benzene ring. The double peaks around 2822 cm^{-1} and 2710 cm^{-1} are contributed by the stretching vibration of -CHO group on DMF. The four peaks (1628 cm^{-1}, 1588 cm^{-1}, 1584 cm^{-1} and 1448 cm^{-1}) are the characteristic of C=C stretching on the benzene ring. A strong peak at 787 cm^{-1} comes from the stretching vibration of ortho-substitution in the benzene ring.

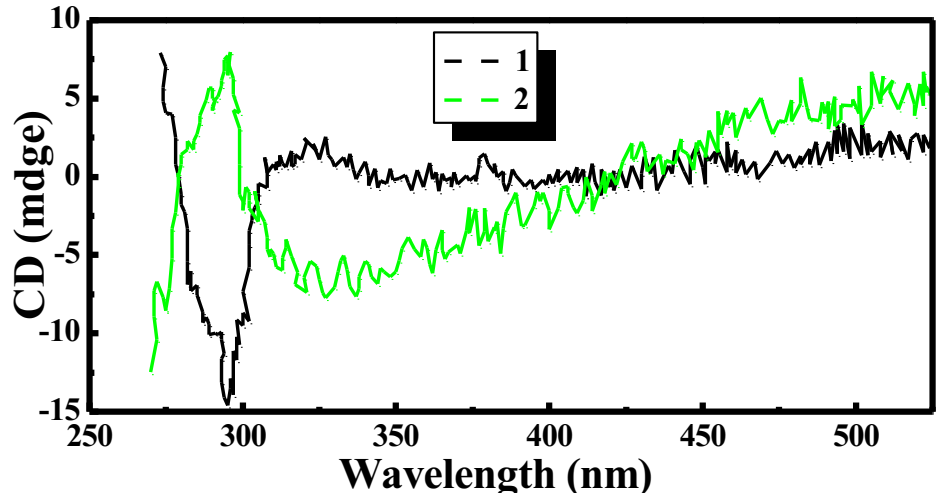

Figure S3 The transmission CD spectra on the pellets of **1** and **2**, which were mixed with KBr in a ratio of 1:100 at room temperature, respectively.

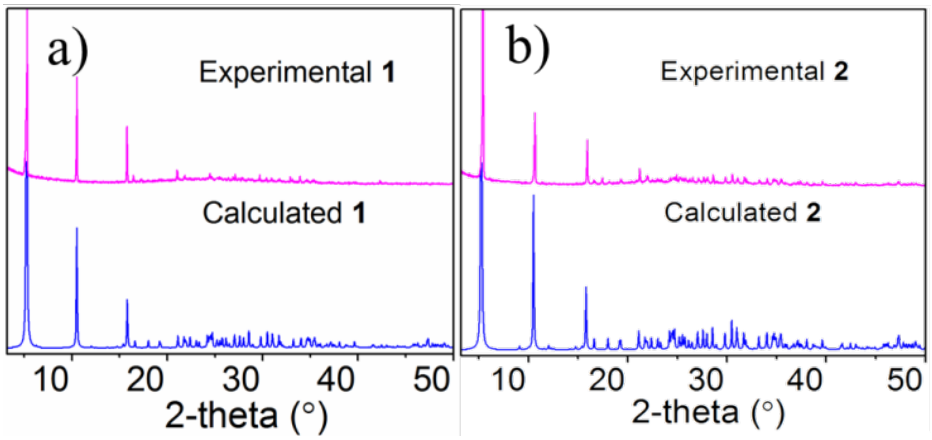

Figure S4 The experimental and calculated PXRD of **1** and **2**.

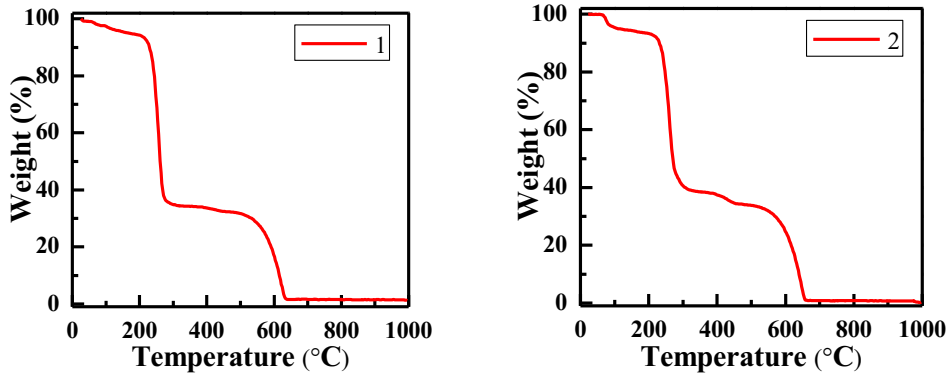

Figure S5 The TGA curves of compounds **1** and **2**.

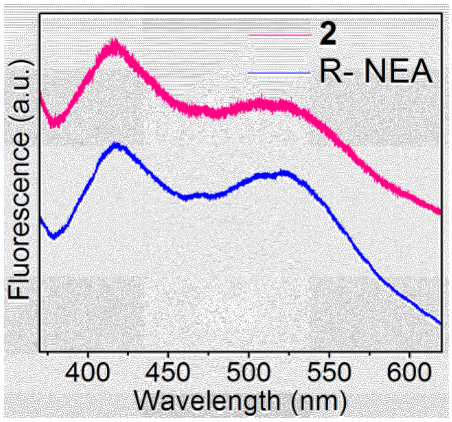

Figure S6 The photoluminescence spectra of **2** and R-NEA. The layers in the plot have been shifted along the y axis.

Table S1 Summary of the crystal data and structure refinements for **1** and **2**.

Compound name	**1**	**2**
Empirical formula	$C_{30}H_{42}Cl_{10}N_4O_2Pb_4$	$C_{30}H_{42}Cl_{10}N_4O_2Pb_4$
Formula weight	1673.98	1673.98
Crystal size (mm)	0.22×0.15×0.06	0.22×0.13×0.05
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
T/K	296	296
λ/ Å	0.71073	0.71073
a/ Å	16.3182(3)	16.3288(4)
b/ Å	8.1686(1)	8.1696 (2)
c/ Å	18.0061(4)	18.0090(4)
α/°	90	90
β/°	110.944(1)	110.918(1)
γ/°	90	90
V/ Å^3	2241.58(7)	2244.06(9)
Z	2	2
D_c/ g·cm^{-3}	2.480	2.477
μ/mm^{-1}	15.605	15.587
F(000)	1528.0	1528.0
2θ for data collection (°)	5.658-50.054	5.656-50.052
Measured refls.	43650	27803
Independent refls.	7893	7906
Observed reflection(I>2σ(I))	7246	6265
Peak and hole/ e Å^{-3}	1.44/-0.53	0.82/-0.54
R_{int}	0.0348	0.0457
No. of parameters	459	459
GOF	0.993	0.879
[a]R_1, wR_2 [$I > 2\sigma(I)$]	0.0223, 0.0551	0.0298, 0.0651
R_1, wR_2(all data)	0.0265, 0.0575	0.0464, 0.0723
Flack parameter	0.011(4)	-0.016(8)

[a]$R_1 = \sum||Fo|-|Fc||/\sum|Fo|$, w$R_2 = \{\sum w[(Fo)^2-(Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$.

Table S2 Atomic coordinates (×10^4) and equivalent displacement parameters (Å^2×10^3) of non−hydrogen atoms for **1**.

Atoms	x	y	z	Ueq
Pb(1)	10350.7(2)	3271.4(3)	-61.5(2)	30.81(10)
Pb(2)	7901.1(2)	1650.5(4)	32.7(2)	33.04(9)
Pb(3)	7188.9(2)	6713.2(4)	236.3(2)	34.27(10)
Pb(4)	4633.1(2)	8214.0(3)	71.8(2)	29.84(9)
Cl(1)	9960.3(12)	1591(3)	1084.7(11)	34.3(4)
Cl(2)	9050.9(13)	1441(3)	-1107.9(13)	35.1(5)
Cl(3)	8747.3(13)	4963(3)	22.0(14)	34.0(4)
Cl(4)	7443.8(13)	3502(2)	1118.7(12)	32.7(5)
Cl(5)	6533.1(13)	3060(3)	-1095.0(13)	36.8(5)
Cl(6)	8607.6(13)	8321(3)	1280.2(12)	38.4(5)
Cl(7)	7526.8(13)	8515(2)	-932.9(12)	31.5(5)
Cl(8)	6315.7(13)	9930(3)	223.0(13)	34.9(5)
Cl(9)	5309.0(12)	6454(3)	-955.0(12)	31.1(4)
Cl(10)	5833.5(14)	6391(3)	1190.2(13)	38.2(5)
N(1)	9791(5)	5033(10)	2138(4)	45.5(19)
C(1)	9358(7)	3037(11)	2940(6)	50(2)
C(2)	9277(6)	4810(11)	2669(5)	36(2)
C(3)	9573(6)	6015(9)	3357(5)	34(2)
C(4)	10394(6)	6667(13)	3625(5)	48(2)
C(5)	10666(7)	7730(12)	4292(6)	53(3)

C(6)	10128(7)	8065(12)	4685(6)	55(3)
C(7)	9281(6)	7402(10)	4442(5)	40(2)
C(8)	8716(8)	7712(12)	4871(6)	55(3)
C(9)	7906(8)	7051(14)	4638(7)	63(3)
C(10)	7602(7)	6054(11)	3966(7)	57(3)
C(11)	8123(6)	5725(10)	3536(6)	45(2)
C(12)	8991(6)	6359(10)	3770(5)	35(2)
N(2)	4549(5)	4623(9)	2035(4)	38.8(17)
C(13)	4372(7)	3257(12)	3156(6)	50(2)
C(14)	4188(6)	4800(10)	2685(5)	33.2(19)
C(15)	4545(5)	6357(10)	3169(5)	33.9(19)
C(16)	5263(6)	7139(11)	3123(6)	49(3)
C(17)	5599 (7)	8565(14)	3592(8)	70(3)
C(18)	5236(7)	9133(13)	4101(7)	63(3)
C(19)	4496(6)	8351(12)	4170(5)	51(2)
C(20)	4095(9)	8898(14)	4699(7)	67(3)
C(21)	3386(9)	8134(18)	4768(7)	81(4)
C(22)	3018(7)	6818(17)	4290(6)	63(3)
C(23)	3380(6)	6230(12)	3769(6)	45(2)
C(24)	4145(5)	6915(10)	3701(5)	36(2)
O(2)	6240(4)	3304(9)	2847(4)	58.5(18)
N(4)	7196(5)	1212(9)	2948(5)	42.4(19)
C(29)	7480(8)	-82(13)	2554(7)	62(3)
C(28)	7598(7)	1369(12)	3805(5)	58(3)
C(30)	6548(6)	2240(12)	2560(6)	44(2)
O(1)	11427(5)	3613(10)	2978(5)	66(2)
N(3)	11907(6)	1150(11)	2722(6)	54(2)
C(27)	12332(8)	219(14)	2296(7)	64(3)
C(26)	11805(7)	2739(12)	2642(7)	50(3)
C(25)	11427(10)	224(18)	3128(10)	104(6)

Table S3 Bond lengths (Å) and bond angles (o) for **1**.

Pb(1)-Cl(1)#1	3.215(2)	Pb(4)-Cl(9)#6	3.072(2)	C(8)-C(9)	1.348(14)
Pb(1)-Cl(1)	2.737(2)	Pb(4)-Cl(9)	2.8565(19)	C(9)-C(10)	1.394(15)
Pb(1)-Cl(2)#1	3.259(2)	Pb(4)-Cl(10)#6	3.353(2)	C(10)-C(11)	1.365(13)
Pb(1)-Cl(2)	2.725(2)	Pb(4)-Cl(10)	2.700(2)	C(11)-C(12)	1.423(12)
Pb(1)-Cl(3)	3.010(2)	Cl(1)-Pb(1)2	3.215(2)	N(2)-C(14)	1.494(10)
Pb(1)-Cl(3)#2	3.066(2)	Cl(2)-Pb(1)2	3.259(2)	C(13)-C(14)	1.488(12)
Pb(1)-Cl(6)#2	3.221(2)	Cl(3)-Pb(1)#1	3.066(2)	C(14)-C(15)	1.534(12)
Pb(1)-Cl(7)#2	3.287(2)	Cl(4)-Pb(4)#4	3.308(2)	C(15)-C(16)	1.362(11)
Pb(2)-Cl(1)	3.2143(19)	Cl(5)-Pb(4)#4	3.088(2)	C(15)-C(24)	1.414(11)
Pb(2)-Cl(2)	3.244(2)	Cl(6)-Pb(1)#1	3.221(2)	C(16)-C(17)	1.428(13)
Pb(2)-Cl(3)	3.041(2)	Cl(6)-Pb(2)#5	3.452(2)	C(17)-C(18)	1.340(14)
Pb(2)-Cl(4)	2.7768(19)	Cl(7)-Pb(1)#1	3.287(2)	C(18)-C(19)	1.410(14)
Pb(2)-Cl(5)	2.682(2)	Cl(7)-Pb(2)#5	3.033(2)	C(19)-C(20)	1.407(14)
Pb(2)-Cl(6)#3	3.453(2)	Cl(8)-Pb(2)#5	3.0690(19)	C(19)-C(24)	1.439(12)
Pb(2)-Cl(7)#3	3.033(2)	Cl(8)-Pb(4)#6	3.048(2)	C(20)-C(21)	1.358(17)
Pb(2)-Cl(8)#3	3.0691(19)	Cl(9)-Pb(4)#4	3.072(2)	C(21)-C(22)	1.374(18)
Pb(3)-Cl(3)	3.060(2)	Cl(10)-Pb(4)#4	3.353(2)	C(22)-C(23)	1.363(12)
Pb(3)-Cl(4)	3.018(2)	N(1)-C(2)	1.492(10)	C(23)-C(24)	1.412(12)
Pb(3)-Cl(6)	2.740(2)	C(1)-C(2)	1.518(12)	O(2)-C(30)	1.210(11)
Pb(3)-Cl(7)	2.781(2)	C(2)-C(3)	1.519(11)	N(4)-C(29)	1.439(12)
Pb(3)-Cl(8)	2.985(2)	C(3)-C(4)	1.360(12)	N(4)-C(28)	1.451(11)
Pb(3)-Cl(9)	3.058(2)	C(3)-C(12)	1.427(12)	N(4)-C(30)	1.335(12)
Pb(3)-Cl(10)	3.260(2)	C(4)-C(5)	1.419(12)	O(1)-C(26)	1.234(12)
Pb(4)-Cl(4)#6	3.308(2)	C(5)-C(6)	1.338(13)	N(3)C(27)	1.425(13)
Pb(4)-Cl(5)#6	3.088(2)	C(6)-C(7)	1.401(13)	N(3)-C(26)	1.310(13)
Pb(4)-Cl(8)	3.007(2)	C(7)-C(8)	1.421(12)	N(3)-C(25)	1.459(14)

Pb(4)-Cl(8)#4	3.048(2)	C(7)-C(12)	1.417(12)		
Cl(1)-Pb(1)-Cl(1)#2	145.44(6)		Cl(9)-Pb(4)-Cl(8)	75.05(6)	
Cl(1)-Pb(1)-Cl(2)#2	90.45(6)		Cl(9)-Pb(4)-Cl(9)#6	145.21(5)	
Cl(1)#2-Pb(1)-Cl(2)#2	69.49(6)		Cl(9)-Pb(4)-Cl(10)#6	89.86(5)	
Cl(1)-Pb(1)-Cl(3)	75.63(7)		Cl(9)#6-Pb(4)-Cl(10)#6	68.99(5)	
Cl(1)-Pb(1)-Cl(3)#1	77.27(6)		Cl(10)-Pb(4)-Cl(4)#6	145.55(6)	
Cl(1)-Pb(1)-Cl(6)#1	147.35(7)		Cl(10)-Pb(4)-Cl(5)#6	88.28(6)	
Cl(1)#2-Pb(1)-Cl(6)#1	67.21(5)		Cl(10)-Pb(4)-Cl(8)	78.12(6)	
Cl(1)-Pb(1)-Cl(7)#1	95.94(5)		Cl(10)-Pb(4)-Cl(8)#4	80.35(7)	
Cl(1)#2-Pb(1)-Cl(7)#1	100.42(5)		Cl(10)-Pb(4)-Cl(9)	81.96(6)	
Cl(2)-Pb(1)-Cl(1)	84.99(7)		Cl(10)-Pb(4)-Cl(9)#6	102.08(6)	
Cl(2)-Pb(1)-Cl(1)#2	98.18(6)		Cl(10)-Pb(4)-Cl(10)#6	149.42(4)	
Cl(2)-Pb(1)-Cl(2)#2	149.54(4)		Pb(1)-Cl(1)-Pb(1)#1	91.29(5)	
Cl(2)-Pb(1)-Cl(3)	79.10(6)		Pb(1)-Cl(1)-Pb(2)	91.38(6)	
Cl(2)-Pb(1)-Cl(3)#1	77.35(6)		Pb(2)-Cl(1)-Pb(1)#1	75.96(5)	
Cl(2)-Pb(1)-Cl(6)#1	90.33(6)		Cl(10)-Pb(4)-Cl(5)#6	88.28(6)	
Cl(2)#2-Pb(1)-Cl(7)#1	65.55(5)		Cl(10)-Pb(4)-Cl(8)	78.12(6)	
Cl(2)-Pb(1)-Cl(7)#1	144.86(6)		Cl(10)-Pb(4)-Cl(8)#4	80.35(7)	
Cl(3)#1-Pb(1)-Cl(1)#2	137.13(5)		Cl(10)-Pb(4)-Cl(9)	81.96(6)	
Cl(3)-Pb(1)-Cl(1)#2	71.29(6)		Cl(10)-Pb(4)-Cl(9)#6	102.08(6)	
Cl(3)-Pb(1)-Cl(2)#2	70.61(6)		Cl(10)-Pb(4)-Cl(10)#6	149.42(4)	
Cl(3)#1-Pb(1)-Cl(2)#2	130.90(6)		Pb(1)-Cl(1)-Pb(1)#1	91.29(5)	
Cl(3)-Pb(1)-Cl(3)#1	145.31(6)		Pb(1)-Cl(1)-Pb(2)	91.38(6)	
Cl(3)#1-Pb(1)-Cl(6)#1	70.19(6)		Pb(2)-Cl(1)-Pb(1)#1	75.96(5)	
Cl(3)-Pb(1)-Cl(6)#1	135.08(6)		Pb(1)-Cl(2)-Pb(1)#1	90.56(6)	
Cl(3)#1-Pb(1)-Cl(7)#1	68.72(5)		Pb(1)-Cl(2)-Pb(2)	90.95(6)	
Cl(3) -Pb(1)-Cl(7)#1	135.69(6)		Pb(2)-Cl(2)-Pb(1)#1	74.95(5)	
Cl(6) #1 -Pb(1)-Cl(2)#2	108.73(6)		Pb(1)-Cl(3)-Pb(1)#2	89.27(5)	
Cl(6) #1 -Pb(1)-Cl(7)#2	70.15(5)		Pb(1)-Cl(3)-Pb(2)	89.80(6)	
Cl(1)-Pb(2)-Cl(2)	69.69(5)		Pb(1)-Cl(3)-Pb(3)	175.85(9)	
Cl(1)-Pb(2)-Cl(6)#3	64.47(5)		Pb(2)-Cl(3)-Pb(1)#2	178.12(9)	
Cl(2)-Pb(2)-Cl(6)#3	103.65(5)		Pb(2)-Cl(3)-Pb(3)	90.86(5)	
Cl(3)-Pb(1)-Cl(2)#2	70.61(6)		Pb(3)-Cl(3)-Pb(1)#2	89.95(6)	
Cl(3)#1-Pb(1)-Cl(2)#2	130.90(6)		Pb(2)-Cl(4)-Pb(3)	97.11(6)	
Cl(3)-Pb(1)-Cl(3)#1	145.31(6)		Pb(2)-Cl(4)-Pb(4)#4	88.62(5)	
Cl(3)#1-Pb(1)-Cl(6)#1	70.19(6)		Pb(3)-Cl(4)-Pb(4)#4	78.70(5)	
Cl(3)-Pb(1)-Cl(6)#1	135.08(6)		Pb(2)-Cl(5)-Pb(4)#4	95.13(6)	
Cl(3)#1-Pb(1)-Cl(7)#1	68.72(5)		Pb(1)#2-Cl(6)-Pb(2)#5	72.63(4)	
Cl(3)#1-Pb(1)-Cl(1)#2	137.13(5)		Pb(3)-Cl(6)-Pb(1)#2	92.80(6)	
Cl(3)-Pb(1)-Cl(1)#2	71.29(6)		Pb(3)-Cl(6)-Pb(1)#2	92.80(6)	
Cl(3)-Pb(1)-Cl(2)#2	70.61(6)		Pb(3)-Cl(6)-Pb(2)#5	85.84(6)	
Cl(4)-Pb(2)-Cl(1)	94.63(6)		Pb(2)#5-Cl(7)-Pb(1)#2	77.40(5)	
Cl(4)-Pb(2)-Cl(2)	146.77(6)		Pb(3)-Cl(7)-Pb(1)#2	90.64(6)	
Cl(4)-Pb-2Cl(3)	75.93(6)		Pb(3)-Cl(7)-Pb(2)#5	93.82(6)	
Cl(4)-Pb(2)-Cl(6)#3	94.71(5)		Pb(3)-Cl(8)-Pb(2)#5	89.14(5)	
Cl(4)-Pb(2)-Cl(7)#3	144.48(5)		Pb(3)-Cl(8)-Pb(4)	90.47(6)	
Cl(4)-Pb(2)-Cl(8)#3	73.82(6)		Pb(3)-Cl(8)-Pb(4)#6	170.95(8)	
Cl(5)-Pb(2)-Cl(1)	149.84(7)		Pb(4)-Cl(8)-Pb(2)#5	169.16(8)	
Cl(5)-Pb(2)-Cl(2)	93.25(6)		Pb(4)#6-Cl(8)-Pb(2)#5	88.48(6)	
Cl(5)-Pb(2)-Cl(3)	82.53(7)		Pb(4)-Cl(8)-Pb(4)#6	90.23(5)	
Cl(5)-Pb(2)-Cl(4)	86.50(6)		Pb(3)-Cl(9)-Pb(4)#4	81.89(5)	
Cl(5)-Pb(2)-Cl(6)#3	145.57(6)		Pb(4)-Cl(9)-Pb(3)	91.93(6)	
Cl(5)-Pb(2)-Cl(7)#3	89.20(6)		Pb(4)-Cl(9)-Pb(4)#4	92.64(5)	
Cl(5)-Pb(2)-Cl(8)#3	76.96(6)		Pb(3)-Cl(10)-Pb(4)#4	74.80(5)	
Cl(7)#3-Pb(2)-Cl(1)	106.20(6)		Pb(4)-Cl(10)-Pb(3)	90.60(6)	
Cl(7)#3-Pb(2)-Cl(2)	68.65(5)		Pb(4)-Cl(10)-Pb(4)#4	89.60(6)	
Cl(7)#3-Pb(2)-Cl(3)	138.31(5)		N(1)-C(2)-C(1)	108.5(8)	
Cl(7)#3-Pb(2)-Cl(6)#3	70.10(6)		N(1)-C(2)-C(3)	110.8(7)	
Cl(7)#3-Pb(2)-Cl(8)#3	70.86(5)		C(1)-C(2)-C(3)	113.0(7)	
Cl(8)#3-Pb(2)-Cl(1)	132.27(6)		C(4)-C(3)-C(2)	121.9(8)	
Cl(8)#3-Pb(2)-Cl(2)	138.41(6)		C(4)-C(3)-C(12)	119.5(8)	

Cl(8)#3-Pb(2)-Cl(6)#3	70.45(5)	C(12)-C(3)-C(2)	118.4(8)
Cl(3)-Pb(3)-Cl(10)	141.25(6)	C(3)-C(4)-C(5)	120.7(9)
Cl(4)-Pb(3)-Cl(3)	72.30(6)	C(6)-C(5)-C(4)	120.4(9)
Cl(4)-Pb(3)-Cl(9)	102.95(6)	C(5)-C(6)-C(7)	121.2(9)
Cl(4)-Pb(3)-Cl(10)	69.16(6)	C(6)-C(7)-C(8)	121.5(9)
Cl(6)-Pb(3)-Cl(3)	76.93(6)	C(6)-C(7)-C(12)	119.3(8)
Cl(6)-Pb(3)-Cl(4)	97.58(6)	C(12)-C(7)-C(8)	119.2(9)
Cl(6)-Pb(3)-Cl(7)	85.30(6)	C(9)-C(8)-C(7)	120.9(10)
Cl(6)-Pb(3)-Cl(8)	82.38(7)	C(8)-C(9)-C(10)	120.6(10)
Cl(6)-Pb(3)-Cl(9)	154.71(7)	C(11)-C(10)-C(9)	120.5(10)
Cl(6)-Pb(3)-Cl(10)	104.08(6)	C(10)-C(11)-C(12)	121.1(9)
Cl(7)-Pb(3)-Cl(3)	75.70(6)	C(7)-C(12)-C(3)	118.8(8)
Cl(7)-Pb(3)-Cl(4)	146.24(5)	C(7)-C(12)-C(11)	117.7(8)
Cl(7)-Pb(3)-Cl(8)	75.60(5)	C(11)-C(12)-C(3)	123.5(8)
Cl(7)-Pb(3)-Cl(9)	85.77(5)	N(2)-C(14)-C(15)	110.4(7)
Cl(7)-Pb(3)-Cl(10)	142.86(6)	C(13)-C(14)-N(2)	108.0(7)
Cl(8)-Pb(3)-Cl(3)	145.70(6)	C(13)-C(14)-C(15)	114.9(7)
Cl(8)-Pb(3)-Cl(4)	138.16(5)	C(16)-C(15)-C(14)	121.0(7)
Cl(8)-Pb(3)-Cl(9)	72.49(6)	C(16)-C(15)-C(24)	120.3(8)
Cl(8)-Pb(3)-Cl(10)	70.34(6)	C(24)-C(15)-C(14)	118.6(7)
Cl(8)-Pb(3)-Cl(3)	145.70(6)	C(15)-C(16)-C(17)	120.3(9)
Cl(8)-Pb(3)-Cl(3)	145.70(6)	C(18)-C(1)-C(16)	121.1(9)
Cl(8)-Pb(3)-Cl(4)	138.16(5)	C(17)-C(18)-C(19)	120.4(9)
Cl(8)-Pb(3)-Cl(9)	72.49(6)	C(18)-C(19)-C(24)	119.4(8)
Cl(8)-Pb(3)-Cl(10)	70.34(6)	C(20)-C(19)-C(18)	122.4(10)
Cl(9)-Pb(3)-Cl(9)	123.35(6)	C(20)-C(19)-C(24)	118.1(10)
Cl(9)-Pb(3)-Cl(10)	70.40(5)	C(21)-C(20)-C(19)	122.3(11)
Cl(4) #6-Pb(3)-Cl(10)#6	64.78(5)	C(20)-C(21)-C(22)	119.8(11)
Cl(5)#6-Pb(4)-Cl(4)#6	71.48(5)	C(23)-C(22)-C(21)	120.5(11)
Cl(5)#6-Pb(4)-Cl(10)#6	113.37(6)	C(22)-C(23)-C(24)	122.3(10)
Cl(8)#4-Pb(4)-Cl(4)#6	67.09(5)	C(15)-C(24)-C(19)	118.5(8)
Cl(8) -Pb(4)-Cl(4)#6	135.75(5)	C(23)-C(24)-C(15)	124.6(8)
Cl(8)-Pb(4)-Cl(8)#4	144.75(6)	C(23)-C(24)-C(19)	116.8(8)
Cl(8) -Pb(4)-Cl(9)#6	71.4(5)	C(29)-N(4)-C(28)	119.1(8)
Cl(8)-Pb(4)-Cl(9)#6	140.20(5)	C(30)-N(4)-C(29)	122.6(9)
Cl(8) -Pb(4)-Cl(10)#6	71.30(6)	C(30)-N(4)-C(28)	118.3(8)
Cl(8) #4-Pb(4)-Cl(10)#6	125.81(6)	O(2)-C(30)-N(4)	126.9(9)
Cl(9) #6-Pb(4)-Cl(4)#6	96.26(5)	C(27)-N(3)-C(25)	116.5(10)
Cl(9) -Pb(4)-Cl(4)#6	99.18(5)	C(26)-N(3)-C(27)	122.5(10)
Cl(9) -Pb(4)-Cl(5)#6	145.94(6)	C(26)-N(3)-C(25)	119.9(11)
Cl(9) #6 -Pb(4)-Cl(5)#6	68.76(5)	O(1)-C(26)-N(3)	125.9(11)
Cl(9)-Pb(4)-Cl(8)#4	74.56(6)		

Symmetry transformations used to generate equivalent atoms: #1 2-X, 1/2+Y, -Z; #2 2-X, -1/2+Y, -Z; #3 +X, -1+Y, +Z; #4 1-X, -1/2+Y, -Z; #5 +X, 1+Y, +Z; # 6 1-X, 1/2+Y, -Z

Table S4 Hydrogen bonds for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)-H(1A)...Cl(1)	0.89	2.74	3.458(8)	138.8
N(1)-H(1A)...Cl(3)	0.89	2.88	3.576(8)	136.0
N(1)-H(1B)...O(1)	0.89	1.93	2.805(12)	166.1
N(1)-H(1C)...Cl(6)	0.89	2.62	3.346(9)	139.5
C(2)-H(2)...Cl(4)	0.98	2.70	3.451(9)	133.6
N(2)-H(2A)...Cl(7)#1	0.89	2.73	3.380(7)	130.5
N(2)-H(2A)...Cl(9)#1	0.89	2.62	3.295(7)	133.3
N(2)-H(2B)...O(2)	0.89	1.96	2.833(10)	166.5
N(2)-H(2C)...Cl(5)#2	0.89	2.65	3.425(8)	145.5
N(2)-H(2C)...Cl(10)	0.89	2.81	3.327(7)	118.2
C(13)-H(13A)...O(2)	0.96	2.56	3.287(12)	133.1
C(14)-H(14)...Cl(7)#1	0.98	2.89	3.546(9)	125.5

C(30)-H(30)...Cl(9)#1	0.93	2.70	3.418(10)	134.7
C(27)-H(27C)...Cl(7)#3	0.96	2.79	3.705(12)	160.6
C(26)-H(26)...Cl(7)#3	0.93	2.81	3.670(11)	154.7

Symmetry transformations used to generate equivalent atoms:# 1 1-X, -1/2+Y, -Z; #2 1-X, 1/2+Y, -Z; #3 2-X, -1/2+Y, -Z

Table S5 Atomic coordinates ($\times 10^4$) and equivalent displacement parameters ($Å^2 \times 10^3$) of non−hydrogen atoms for **2**.

Atoms	*x*	*y*	*z*	*Ueq*
Pb(1)	-350.8(3)	6728.6(6)	10061.3(3)	31.37(14)
Pb(2)	2099.3(3)	8350.0(7)	9967.8(3)	33.59(14)
Pb(3)	2810.6(3)	3288.2(7)	9764.1(3)	35.03(15)
Pb(4)	5367.1(3)	1785.8(5)	9928.3(3)	30.52(14)
Cl(1)	39(2)	8400(5)	8911.0(16)	35.1(8)
Cl(2)	948(2)	8554(5)	11108.7(18)	37.1(9)
Cl(3)	1254(2)	5037(5)	9976(2)	33.9(7)
Cl(4)	2552(2)	6495(4)	8879.3(17)	33.1(8)
Cl(5)	3466(2)	6925(5)	11096.4(18)	39.1(9)
Cl(6)	1394(2)	1669(5)	8721.4(17)	39.1(8)
Cl(7)	2472(2)	1490(4)	10932.2(17)	32.4(8)
Cl(8)	3685(2)	72(5)	9777.2(18)	36.1(8)
Cl(9)	4692(2)	3549(5)	10954.9(16)	31.0(8)
Cl(10)	4170(2)	3607(5)	8809.5(18)	39.1(9)
N(1)	197(8)	4971(15)	7864(6)	48(3)
C(1)	634(10)	6931(18)	7071(7)	48(4)
C(2)	722(9)	5181(17)	7332(7)	34(3)
C(3)	431(8)	3960(15)	6639(7)	31(3)
C(4)	-407(8)	3316(19)	6375(6)	47(4)
C(5)	-664(10)	2269(17)	5712(7)	51(4)
C(6)	-115(10)	1895(19)	5313(8)	55(4)
C(7)	722(9)	2578(15)	5559(7)	40(4)
C(8)	1275(10)	2261(17)	5140(8)	53(4)
C(9)	2107(11)	2940(20)	5358(9)	65(5)
C(10)	2398(11)	3925(17)	6038(9)	59(5)
C(11)	1869(9)	4257(17)	6464(8)	44(4)
C(12)	1013(8)	3617(16)	6234(7)	35(3)
N(2)	5459(7)	5363(14)	7974(5)	36(3)
C(13)	5622(10)	6720(20)	6842(8)	56(4)
C(14)	5812(9)	5175(16)	7323(7)	33(3)
C(15)	5465(8)	3636(17)	6831(6)	34(3)
C(16)	4733(9)	2863(17)	6878(8)	52(4)
C(17)	4405(11)	1440(20)	6426(10)	72(6)
C(18)	4782(11)	880(19)	5891(9)	60(5)
C(19)	5514(9)	1682(16)	5836(7)	43(4)
C(20)	5912(11)	1110(20)	5308(9)	66(5)
C(21)	6632(12)	1880(20)	5246(9)	75(6)
C(22)	6998(11)	3230(20)	5707(8)	67(5)
C(23)	6621(9)	3779(19)	6231(8)	50(4)
C(24)	5861(8)	3091(17)	6297(6)	38(3)
O(2)	3765(7)	6700(15)	7148(6)	59(3)
N(4)	2807(8)	8768(14)	7051(6)	41(3)
C(29)	2521(11)	10080(20)	7437(9)	62(5)
C(28)	2397(10)	8660(20)	6191(8)	61(5)
C(30)	3442(10)	7750(20)	7438(9)	51(5)
O(1)	-1429(8)	6392(16)	7023(6)	65(3)
N(3)	-1911(10)	8847(19)	7280(8)	56(4)
C(27)	-2343(12)	9810(20)	7701(9)	63(5)
C(26)	-1804(12)	7290(20)	7359(10)	54(5)
C(25)	-1455(17)	9820(30)	6852(13)	109(9)

Table S6 Bond lengths (Å) and bond angles (o) for **2**.

Pb(1)-Cl(1)#1	3.226(4)	Pb(4)-Cl(9)	2.857(3)	C(8)-C(9)	1.388(15)
Pb(1)-Cl(1)	2.739(3)	Pb(4)-Cl(9)#6	3.070(4)	C(9)-C(10)	1.399(15)
Pb(1)-Cl(2)#1	3.264(4)	Pb(4)-Cl(10)#6	3.355(4)	C(10)-C(11)	1.372(14)
Pb(1)-Cl(2)	2.724(4)	Pb(4)-Cl(10)	2.698(3)	C(11)-C(12)	1.409(14)
Pb(1)-Cl(3)#2	3.068(4)	Cl(1)-Pb(1)#2	3.226(4)	N(2)-C(14)	1.486(15)
Pb(1)-Cl(3)	3.015(4)	Cl(2)-Pb(1)#2	3.264(4)	C(13)-C(14)	1.498(19)
Pb(1)-Cl(6)#2	3.222(3)	Cl(3)-Pb(1)#1	3.068(4)	C(14)-C(15)	1.527(17)
Pb(1)-Cl(7)#2	3.288(3)	Cl(4)-Pb(4)#4	3.317(3)	C(15)-C(16)	1.380(14)
Pb(2)-Cl(1)	3.220(3)	Cl(5)-Pb(4)#4	3.092(3)	C(15)-C(24)	1.409(13)
Pb(2)-Cl(2)	3.247(3)	Cl(6)-Pb(1)#1	3.222(3)	C(16)-C(17)	1.409(14)
Pb(2)-Cl(3)	3.041(4)	Cl(6)-Pb(2)#5	3.445(4)	C(17)-C(18)	1.393(15)
Pb(2)-Cl(4)	2.779(3)	Cl(7)-Pb(1)#1	3.288(3)	C(18)-C(19)	1.399(14)
Pb(2)-Cl(5)	2.688(3)	Cl(7)-Pb(2)#5	3.035(3)	C(19)-C(20)	1.409(14)
Pb(2)-Cl(6)#3	3.445(4)	Cl(8)-Pb(2)#5	3.072(3)	C(19)-C(24)	1.415(14)
Pb(2)-Cl(7)#3	3.035(3)	Cl(8)-Pb(4)#6	3.049(4)	C(20)-C(21)	1.373(16)
Pb(2)-Cl(8)#3	3.072(4)	Cl(9)-Pb(4)#4	3.070(4)	C(21)-C(22)	1.381(16)
Pb(3)-Cl(3)	3.056(4)	Cl(10)-Pb(4)#4	3.355(4)	C(22)-C(23)	1.373(14)
Pb(3)-Cl(4)	3.017(3)	N(1)-C(2)	1.506(16)	C(23)-C(24)	1.404(14)
Pb(3)-Cl(6)	2.743(3)	C(1)-C(2)	1.495(18)	O(2)-C(30)	1.218(18)
Pb(3)-Cl(7)	2.778(3)	C(2)-C(3)	1.535(17)	N(4)-C(29)	1.444(18)
Pb(3)-Cl(8)	2.987(4)	C(3)-C(4)	1.382(13)	N(4)-C(28)	1.454(15)
Pb(3)-Cl(9)	3.062(3)	C(3)-C(12)	1.417(13)	N(4)-C(30)	1.317(18)
Pb(3)-Cl(10)	3.267(3)	C(4)-C(5)	1.407(13)	O(1)-C(26)	1.243(19)
Pb(4)-Cl(4)#6	3.317(3)	C(5)-C(6)	1.369(14)	N(3)-C(27)	1.44(2)
Pb(4)-Cl(5)#6	3.092(3)	C(6)-C(7)	1.395(14)	N(3)-C(26)	1.284(19)
Pb(4)-Cl(8)#4	3.049(4)	C(7)-C(8)	1.391(14)	N(3)-C(25)	1.48(2)
Pb(4)-Cl(8)	3.007(4)	C(7)-C(12)	1.419(13)		

Cl(1)-Pb(1)-Cl(1)#2	145.34(10)	Cl(9)#6-Pb(4)-Cl(5)#6	68.56(10)
Cl(1)-Pb(1)-Cl(2)#2	90.26(10)	Cl(9)-Pb(4)-Cl(8)	75.07(10)
Cl(1)#2-Pb(1)-Cl(2)#2	69.52(9)	Cl(9)-Pb(4)-Cl(8)#4	74.50(10)
Cl(1)-Pb(1)-Cl(3)#1	77.51(11)	Cl(9)-Pb(4)-Cl(9)#6	145.24(9)
Cl(1)-Pb(1)-Cl(3)	75.49(11)	Cl(9)#6-Pb(4)-Cl(10)#6	69.02(8)
Cl(1)-Pb(1)-Cl(6)#1	147.60(12)	Cl(9)-Pb(4)-Cl(10)#6	89.86(9)
Cl(1)-Pb(1)-Cl(7)#1	95.86(8)	Cl(10)-Pb(4)-Cl(4)#6	145.53(10)
Cl(1)#2-Pb(1)-Cl(7)#1	100.49(8)	Cl(10)-Pb(4)-Cl(5)#6	88.31(10)
Cl(2)-Pb(1)-Cl(1)#2	98.03(10)	Cl(10)-Pb(4)-Cl(8)	78.14(11)
Cl(2)-Pb(1)-Cl(1)	85.25(11)	Cl(10)-Pb(4)-Cl(8)#4	80.32(11)
Cl(2)-Pb(1)-Cl(2)#2	149.46(8)	Cl(10)-Pb(4)-Cl(9)#6	101.99(10)
Cl(2)-Pb(1)-Cl(3)	79.06(11)	Cl(10)-Pb(4)-Cl(9)	82.03(10)
Cl(2)-Pb(1)-Cl(3)#1	77.43(11)	Cl(10)-Pb(4)-Cl(10)#6	149.38(7)
Cl(2)-Pb(1)-Cl(6)#1	90.41(10)	Pb(1)-Cl(1)-Pb(1)#1	91.04(8)
Cl(2)#2-Pb(1)-Cl(7)#1	65.66(8)	Pb(1)-Cl(1)-Pb(2)	91.29(8)
Cl(2)-Pb(1)-Cl(7)#1	144.84(10)	Pb(2)-Cl(1)-Pb(1)#1	75.76(7)
Cl(3)#1-Pb(1)-Cl(1)#2	137.00(9)	Pb(1)-Cl(2)-Pb(1)#1	90.50(9)
Cl(3)-Pb(1)-Cl(1)#2	71.37(10)	Pb(1)-Cl(2)-Pb(2)	90.98(9)
Cl(3)-Pb(1)-Cl(2)#2	70.59(9)	Pb(2)-Cl(2)-Pb(1)#1	74.88(8)
Cl(3)#1-Pb(1)-Cl(2)#2	130.95(9)	Pb(1)-Cl(3)-Pb(1)#2	89.15(10)
Cl(3)-Pb(1)-Cl(3)#1	145.34(12)	Pb(1)-Cl(3)-Pb(2)	89.80(11)
Cl(3)-Pb(1)-Cl(6)#1	135.08(9)	Pb(1)-Cl(3)-Pb(3)	175.93(13)
Cl(3)#1-Pb(1)-Cl(6)#1	70.22(10)	Pb(2)-Cl(3)-Pb(1)#2	178.16(14)
Cl(3)-Pb-Cl(7)#1	135.33(9)	Pb(2)-Cl(3)-Pb(3)	90.93(10)
Cl(3)#1-Pb(1)-Cl(7)#1	68.62(9)	Pb(3)-Cl(3)-Pb(1)#2	90.01(11)
Cl(6)#1-Pb(1)-Cl(1)#2	67.06(9)	Pb(2)-Cl(4)-Pb(3)	97.08(9)
Cl(6)#1-Pb(1)-Cl(2)#2	108.57(10)	Pb(2)-Cl(4)-Pb(4)#4	88.48(8)
Cl(6)#1-Pb(1)-Cl(7)#1	70.06(8)	Pb(3)-Cl(4)-Pb(4)#4	78.61(7)
Cl(1)-Pb(2)-Cl(2)	69.79(7)	Pb(2)-Cl(5)-Pb(4)#4	94.98(9)
Cl(1)-Pb(2)-Cl(6)#3	64.49(9)	Pb(1)#2Cl(6)-Pb(2)#5	72.76(7)

Cl(2)-Pb(2)-Cl(6)#3	103.75(9)	Pb(3)-Cl(6)-Pb(1)#2	92.77(9)
Cl(3)-Pb(2)-Cl(1)	68.54(11)	Pb(3)-Cl(6)-Pb(2)#5	85.97(9)
Cl(3)-Pb(2)-Cl(2)	71.10(10)	Pb(2)#5-Cl(7)-Pb(1)#2	77.39(7)
Cl(3)-Pb(2)-Cl(6)#3	131.08(9)	Pb(3)-Cl(7)-Pb(1)#2	90.71(8)
Cl(3)-Pb(2)-Cl(8)#3	144.13(11)	Pb(3)-Cl(7)-Pb(2)#5	93.84(8)
Cl(4)-Pb(2)-Cl(1)	94.31(9)	Pb(3)-Cl(8)-Pb(2)#5	89.08(9)
Cl(4)-Pb(2)-Cl(2)	146.56(11)	Pb(3)-Cl(8)-Pb(4)	90.55(10)
Cl(4)-Pb(2)-Cl(3)	75.74(10)	Pb(3)-Cl(8)-Pb(4)#6	170.94(12)
Cl(4)-Pb(2)-Cl(6)#3	94.63(9)	Pb(4)-Cl(8)-Pb(2)#5	169.15(12)
Cl(4)-Pb(2)-Cl(7)#3	144.59(10)	Pb(4)#6-Cl(8)-Pb(2)#5	88.47(10)
Cl(4)-Pb(2)-Cl(8)#3	73.95(10)	Pb(4)-Cl(8)-Pb(4)#6	90.22(9)
Cl(5)-Pb(2)-Cl(1)	149.58(12)	Pb(3)-Cl(9)-Pb(4)#4	81.89(8)
Cl(5)-Pb(2)-Cl(2)	93.19(9)	Pb(4)-Cl(9)-Pb(3)	91.96(8)
Cl(5)-Pb(2)-Cl(3)	82.32(12)	Pb(4)-Cl(9)-Pb(4)#4	92.69(8)
Cl(5)-Pb(2)-Cl(4)	86.51(10)	Pb(3)-Cl(10)-Pb(4)#4	74.71(7)
Cl(5)-Pb(2)-Cl(6)#3	145.84(11)	Pb(4)-Cl(10)-Pb(3)	90.59(9)
Cl(5)-Pb(2)-Cl(7)#3	89.46(10)	Pb(4)-Cl(10)-Pb(4)#4	89.59(9)
Cl(5)-Pb(2)-Cl(8)#3	77.14(10)	N(1)-C(2)-C(3)	111.2(11)
Cl(7)#3-Pb(2)-Cl(1)	106.33(10)	C(1)-C(2)-N(1)	107.2(11)
Cl(7)#3-Pb(2)-Cl(2)	68.76(9)	C(1)-C(2)-C(3)	113.5(10)
Cl(7)#3-Pb(2)-Cl(3)	138.42(9)	C(4)-C(3)-C(2)	120.5(12)
Cl(7)#3-Pb(2)-Cl(6)#3	70.11(8)	C(4)-C(3)-C(12)	120.7(12)
Cl(7)#3-Pb(2)-Cl(8)#3	70.86(9)	C(12)-C(3)-C(2)	118.5(10)
Cl(8)#3-Pb(2)-Cl(1)	132.27(9)	C(3)-C(4)-C(5)	118.8(13)
Cl(8)#3-Pb(2)-Cl(2)	138.50(9)	C(6)-C(5)-C(4)	121.9(13)
Cl(8)#3-Pb(2)-Cl(6)#3	70.48(9)	C(5)-C(6)-C(7)	119.7(12)
Cl(3)-Pb(3)-Cl(9)	123.43(9)	C(6)-C(7)-C(12)	120.1(12)
Cl(3)-Pb(3)-Cl(10)	141.27(10)	C(8)-C(7)-C(6)	120.4(12)
Cl(4)-Pb(3)-Cl(3)	72.20(10)	C(8)-C(7)-C(12)	119.5(13)
Cl(4)-Pb(3)-Cl(9)	103.05(9)	C(9)-C(8)-C(7)	122.1(14)
Cl(4)-Pb(3)-Cl(10)	69.28(9)	C(8)-C(9)-C(10)	117.9(15)
Cl(4)-Pb(3)-Cl(3)	72.20(10)	C(11)-C(10)-C(9)	121.3(15)
Cl(6)-Pb(3)-Cl(3)	77.03(11)	C(10)-C(11)-C(12)	121.3(13)
Cl(6)-Pb(3)-Cl(4)	97.62(10)	C(3)-C(12)-C(7)	118.6(11)
Cl(6)-Pb(3)-Cl(7)	85.19(10)	C(11)-C(12)-C(3)	123.6(11)
Cl(6)-Pb(3)-Cl(8)	82.24(11)	C(11)-C(12)-C(7)	117.8(12)
Cl(6)-Pb(3)-Cl(9)	154.52(12)	N(2)-C(14)-C(13)	108.1(11)
Cl(6)-Pb(3)-Cl(10)	104.09(9)	N(2)-C(14)-C(15)	112.1(10)
Cl(7)-Pb(3)-Cl(3)	75.71(10)	C(13)-C(14)-C(15)	113.6(10)
Cl(7)-Pb(3)-Cl(4)	146.19(9)	C(16)-C(15)-C(14)	119.4(11)
Cl(7)-Pb(3)-Cl(8)	75.68(9)	C(16)-C(15)-C(24)	121.0(12)
Cl(7)-Pb(3)-Cl(9)	85.84(9)	C(24)-C(15)-C(14)	119.4(11)
Cl(7)-Pb(3)-Cl(10)	142.82(9)	C(15)-C(16)-C(17)	120.1(13)
Cl(8)-Pb(3)-Cl(3)	145.78(11)	C(18)-C(17)-C(16)	120.0(14)
Cl(8)-Pb(3)Cl(4)	138.13(9)	C(17)-C(18)-C(19)	119.7(13)
Cl(8)-Pb(3)-Cl(9)	72.45(9)	C(18)-C(19)-C(20)	120.3(13)
Cl(8)-Pb(3)-Cl(10)	70.21(10)	C(18)-C(19)-C(24)	120.8(12)
Cl(9)-Pb(3)-Cl(10)	70.30(8)	C(24)-C(19)-C(20)	118.9(13)
Cl(4)#6-Pb(4)-Cl(10)#6	64.85(8)	C(21)-C(20)-C(19)	121.0(14)
Cl(5)#6-Pb(4)-Cl(4)#6	71.45(8)	C(20)-C(21)-C(22)	121.1(14)
Cl(5)#6-Pb(4)-Cl(10)#6	113.26(10)	C(23)-C(22)-C(21)	118.1(15)
Cl(8)-Pb(4)-Cl(4)#6	135.77(9)	C(22)-C(23)-C(24)	123.6(14)
Cl(8)#4-Pb(4)-Cl(4)#6	67.13(9)	C(15)-C(24)-C(19)	118.2(11)
Cl(8)#4-Pb(4)-Cl(5)#6	71.86(10)	C(23)-C(24)-C(15)	124.4(12)
Cl(8)-Pb(4)-Cl(5)#6	134.48(9)	C(23)-C(24)-C(19)	117.2(12)
Cl(8)-Pb(4)-Cl(8)#4	144.70(10)	C(29)-N(4)-C(28)	117.0(12)
Cl(8)-Pb(4)-Cl(9)#6	72.14(9)	C(30)-N(4)-C(29)	122.9(13)
Cl(8)#4-Pb(4)-Cl(9)#6	140.23(9)	C(30)-N(4)-C(28)	119.9(13)
Cl(8)#4-Pb(4)-Cl(10)#6	125.88(9)	O(2)-C(30)-N(4)	126.7(15)
Cl(8)-Pb(4)-Cl(10)#6	71.24(9)	C(27)-N(3)-C(25)	114.4(16)
Cl(9)#6-Pb(4)-Cl(4)#6	96.26(9)	C(26)-N(3)-C(27)	123.9(17)
Cl(9)-Pb(4)-Cl(4)#6	99.20(8)	C(26)-N(3)-C(25)	120.9(18)

Cl(9)-Pb(4)-Cl(5)#6	146.10(11)	OC(26)-N(3)	127.0(19)

Symmetry transformations used to generate equivalent atoms: #1 -X, 1/2+Y, 2-Z; #2 -X, -1/2+Y, 2-Z; # 3 +X, 1+Y, +Z; # 4 1-X, 1/2+Y, 2-Z; #5 +X, -1+Y, +Z; #6 1-X, -1/2+Y, 2-Z

Table S7 Hydrogen bonds for **2**.

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)-H(1A)...Cl(1)	0.89	2.75	3.438(13)	135.5
N(1)-H(1A)...Cl(3)	0.89	2.85	3.573(10)	139.1
N(1)-H(1B)...Cl(6)	0.89	2.67	3.366(14)	135.6
N(1)-H(1C)...O(1)	0.89	1.92	2.796(17)	170.0
C(1)-H(1E)...O(1)	0.96	2.63	3.37(2)	133.5
C(2)-H(2)...Cl(4)	0.98	2.69	3.450(13)	134.3
N(2)-H(2A)...Cl(7)#1	0.89	2.75	3.375(11)	128.0
N(2)-H(2A)...Cl(9)#1	0.89	2.61	3.301(10)	135.3
N(2)-H(2B)...Cl(5)#2	0.89	2.63	3.417(12)	148.4
N(2)-H(2B)...Cl(10)	0.89	2.83	3.319(11)	115.9
N(2)-H(2C)...O(2)	0.89	1.99	2.850(15)	162.3
C(13)-H(13A)...O(2)	0.96	2.54	3.27(2)	133.4
C(14)-H(14)...Cl(7)#1	0.98	2.89	3.548(13)	125.5
C(30)-H(30)...Cl(9)#1	0.93	2.74	3.434(15)	132.5
C(27)-H(27B)...Cl(7)#3	0.96	2.83	3.721(17)	154.6
C(26)-H(26)...Cl(7)#3	0.93	2.80	3.672(18)	155.9
N(1)-H(1A)...Cl(1)	0.89	2.75	3.438(13)	135.5
N(1)-H(1A)...Cl(3)	0.89	2.85	3.573(10)	139.1

Symmetry transformations used to generate equivalent atoms: #1 1-X, 1/2+Y, 2-Z; #2 1-X, -1/2+Y, 2-Z; # 3 -X, 1/2+Y, 2-Z