

## *catena*-Poly[[lead(II)-bis( $\mu_2$ -quinolin-8-olato)- $\kappa^3$ N,O:O; $\kappa^3$ O:N,O] N,N-dimethylformamide hemisolvate]

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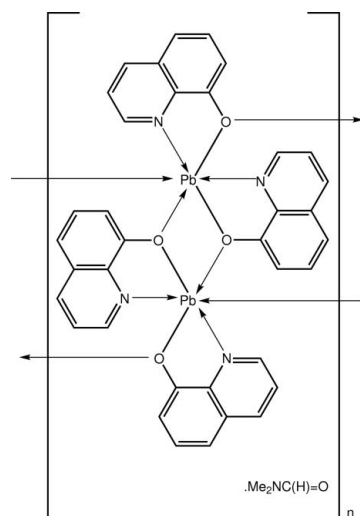
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å; disorder in solvent or counterion;  $R$  factor = 0.021;  $wR$  factor = 0.049; data-to-parameter ratio = 14.2.

The asymmetric unit of the title compound,  $\{[\text{Pb}(\text{C}_9\text{H}_6\text{NO})_2] \cdot 0.5\text{C}_3\text{H}_7\text{NO}\}_n$ , comprises  $\text{Pb}(\text{quinolate})_2$  and half a dimethylformamide molecule (which is disordered about a centre of inversion). The quinolate ligands  $N,O$ -chelate to a  $\text{Pb}^{\text{II}}$  ion and simultaneously bridge a neighbouring  $\text{Pb}^{\text{II}}$  ion to form a polymeric chain along  $[100]$  comprising  $\text{Pb}$ -linked  $\text{Pb}_2\text{O}_2$  distorted rhombi. These chains pack to form a square grid, with the channels thus defined occupied by the disordered solvent molecules.

### Related literature

For a recent  $\text{Pb}^{\text{II}}$  mixed quinolate carboxylate structure, see: Ghaemi *et al.* (2012). For the structure of the solvent-free  $\text{Pb}^{\text{II}}$  quinolate, see: Zhu *et al.* (2005).



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### Experimental

#### Crystal data

$[\text{Pb}(\text{C}_9\text{H}_6\text{NO})_2] \cdot 0.5\text{C}_3\text{H}_7\text{NO}$   
 $M_r = 532.04$   
 Triclinic,  $P\bar{1}$   
 $a = 8.1841(2)$  Å  
 $b = 9.6606(3)$  Å  
 $c = 10.8619(3)$  Å  
 $\alpha = 96.683(3)^\circ$   
 $\beta = 98.277(2)^\circ$

$\gamma = 94.225(3)^\circ$   
 $V = 840.48(4)$  Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 10.06$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.30 \times 0.08 \times 0.04$  mm

#### Data collection

Agilent SuperNova Dual diffractometer with Atlas detector  
 Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)  
 $T_{\text{min}} = 0.152$ ,  $T_{\text{max}} = 0.689$

13299 measured reflections  
 3866 independent reflections  
 3613 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.036$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.049$   
 $S = 1.01$   
 3866 reflections  
 272 parameters

36 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.71$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

|       |           |                     |           |
|-------|-----------|---------------------|-----------|
| Pb—O2 | 2.408 (2) | Pb—N1               | 2.566 (3) |
| Pb—O1 | 2.468 (2) | Pb—O1 <sup>i</sup>  | 2.618 (2) |
| Pb—N2 | 2.470 (3) | Pb—O2 <sup>ii</sup> | 2.812 (2) |

Symmetry codes: (i)  $-x + 2, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5166).

### References

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**supplementary materials**

*Acta Cryst.* (2012). E68, m210 [ doi:10.1107/S1600536812002796 ]

***catena*-Poly[[lead(II)-bis( $\mu_2$ -quinolin-8-olato)- $\kappa^3 N,O:O;\kappa^3 O:N,O$ ] hemisolvate] *N,N*-dimethylformamide**

**A. Ghaemi, Z. Dadkhah, S. W. Ng and E. R. T. Tiekink**

### Comment

During the course of recent studies into the structural chemistry of mixed  $Pb^{II}$  quinolate carboxylates (Ghaemi *et al.*, 2012), the title binary  $Pb^{II}$  quinolate was isolated as a DMF hemi-solvate, (I), from an attempted reaction with maleic acid. The crystal structure of the solvent free and polymeric  $Pb(\text{quinolate})_2$  has been described (Zhu *et al.*, 2005).

The asymmetric unit of (I) comprises  $Pb(\text{quinolate})_2$  and half a solvent DMF molecule (this is disordered over a centre of inversion), Fig. 1. Each quinolate anion *N,O*-chelates a  $Pb^{II}$  atom and at the same time bridges a neighbouring  $Pb^{II}$  atom *via* the carbonyl-O atom. The result is a polymeric chain comprising alternating  $Pb_2O_2$  rhombi, Fig. 2. The degree in asymmetry in the  $Pb-O$  bridges varies, Table 1. The coordination geometry of the  $Pb^{II}$  atom is based on a distorted pentagonal bipyramid with one N atom occupying an axial site. The lone pair of electrons occupies the second axial position. It is noted that the O3 and O3' atoms (each with a 0.25 site occupancy factor) of disordered DMF molecule approach the  $Pb^{II}$  at distances 2.903 (12) and 2.977 (12) Å, respectively. These are not *trans* to the axial N atom forming angles of approximately 140°. If one of the DMF-O atoms is included as part of the coordination sphere, the coordination geometry would be described as  $\psi$ -dodecahedral.

In the crystal packing, the polymeric chains pack into a square grid which defines channels in which reside the disordered solvent molecules, Fig. 3. The aforementioned weak  $Pb \cdots O(\text{DMF})$  interactions serve to connect the polymeric chains into a layer in the *ab* plane.

### Experimental

The title complex was obtained by the following method. 8-Hydroxyquinoline (0.036 g, 0.25 mmol) was added to an aqueous solution (5 ml) of  $Pb(\text{NO}_3)_2$  (0.082 g, 0.25 mmol). The mixture was stirred for 15 min. Then to this solution, a DMF solution (5 ml) of maleic acid (0.029 g, 0.25 mmol) which with triethylamine neutralized was added slowly at room temperature. This mixture was filtered. After keeping the filtrate in air, crystals were formed at the bottom of the vessel on slow evaporation of the solvents at room temperature. M.p. 590 K. Yield: 65%.

### Refinement

Carbon-bound H atoms were placed in calculated positions [ $C-H$  0.95–0.98 Å,  $U_{\text{iso}}(\text{H})$  1.2–1.5 $U_{\text{eq}}(\text{C})$ ] and were included in the refinement in the riding model approximation.

The DMF molecule is disordered over two sites over a centre of inversion. The  $C-O$  distances were restrained to 1.25 (1) Å, the  $C_{\text{carbonyl}}-N$  distances to 1.35 (1) Å and the  $C_{\text{methyl}}-N$  distances to 1.45 (1) Å. Each component was restrained

## supplementary materials

to lie on a plane; the anisotropic displacement parameters of the primed atoms were set to those of the unprimed ones, and they were tightly restrained to be nearly isotropic.

The final difference Fourier map had a peak of  $1.23 \text{ \AA}^{-3}$  at  $1.10 \text{ \AA}$  from the Pb atom.

### Figures

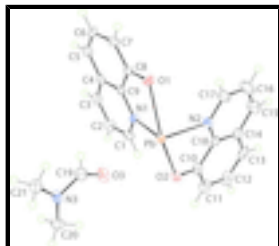


Fig. 1. The asymmetric unit of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

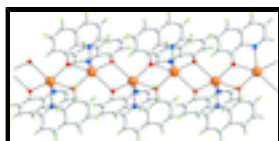


Fig. 2. A view of the polymeric chain along [100] in (I).

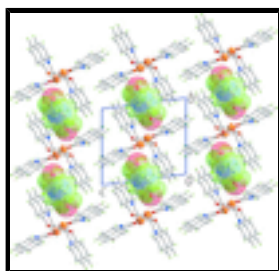


Fig. 3. A view in projection down the  $a$  axis of the unit-cell contents of (I) highlighting the square grid defined by the polymeric chains and the inclusion of the solvent molecules (shown in space-filling mode) in the channels.

### **catena-Poly[[lead(II)-bis( $\mu_2$ -quinolin-8-olato)- $\kappa^3 N,O:O;\kappa^3 O:N,O$ ] $N,N$ -dimethylformamide hemisolvate]**

#### *Crystal data*

$[\text{Pb}(\text{C}_9\text{H}_6\text{NO})_2] \cdot 0.5\text{C}_3\text{H}_7\text{NO}$

$M_r = 532.04$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 8.1841 (2) \text{ \AA}$

$b = 9.6606 (3) \text{ \AA}$

$c = 10.8619 (3) \text{ \AA}$

$\alpha = 96.683 (3)^\circ$

$\beta = 98.277 (2)^\circ$

$\gamma = 94.225 (3)^\circ$

$V = 840.48 (4) \text{ \AA}^3$

$Z = 2$

$F(000) = 504$

$D_x = 2.102 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8798 reflections

$\theta = 2.5\text{--}27.5^\circ$

$\mu = 10.06 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, yellow

$0.30 \times 0.08 \times 0.04 \text{ mm}$

#### *Data collection*

Agilent SuperNova Dual

3866 independent reflections

diffractometer with Atlas detector  
 Radiation source: SuperNova (Mo) X-ray Source 3613 reflections with  $I > 2\sigma(I)$   
 Mirror  $R_{\text{int}} = 0.036$   
 Detector resolution: 10.4041 pixels  $\text{mm}^{-1}$   $\theta_{\text{max}} = 27.6^\circ$ ,  $\theta_{\text{min}} = 2.5^\circ$   
 $\omega$  scans  $h = -10 \rightarrow 10$   
 Absorption correction: multi-scan  
 (CrysAlis PRO; Agilent, 2010)  $k = -12 \rightarrow 12$   
 $T_{\text{min}} = 0.152$ ,  $T_{\text{max}} = 0.689$   $l = -14 \rightarrow 14$   
 13299 measured reflections

### Refinement

Refinement on  $F^2$  Primary atom site location: structure-invariant direct methods  
 Least-squares matrix: full Secondary atom site location: difference Fourier map  
 $R[F^2 > 2\sigma(F^2)] = 0.021$  Hydrogen site location: inferred from neighbouring sites  
 $wR(F^2) = 0.049$  H-atom parameters constrained  
 $S = 1.01$   $w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 0.0115P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 3866 reflections  $(\Delta/\sigma)_{\text{max}} = 0.002$   
 272 parameters  $\Delta\rho_{\text{max}} = 1.23 \text{ e } \text{\AA}^{-3}$   
 36 restraints  $\Delta\rho_{\text{min}} = -0.71 \text{ e } \text{\AA}^{-3}$

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|    | $x$           | $y$           | $z$           | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|----|---------------|---------------|---------------|----------------------------------|-----------|
| Pb | 0.758370 (14) | 0.465630 (13) | 0.543410 (11) | 0.01554 (5)                      |           |
| O1 | 1.0552 (3)    | 0.4449 (3)    | 0.6130 (2)    | 0.0232 (6)                       |           |
| O2 | 0.5307 (3)    | 0.5563 (3)    | 0.6350 (2)    | 0.0180 (5)                       |           |
| N1 | 0.8296 (3)    | 0.4221 (3)    | 0.7727 (3)    | 0.0162 (6)                       |           |
| N2 | 0.8215 (4)    | 0.7122 (3)    | 0.6385 (3)    | 0.0249 (7)                       |           |
| C1 | 0.7215 (4)    | 0.4163 (4)    | 0.8528 (3)    | 0.0206 (8)                       |           |
| H1 | 0.6154        | 0.4481        | 0.8308        | 0.025*                           |           |
| C2 | 0.7575 (5)    | 0.3651 (4)    | 0.9686 (3)    | 0.0248 (8)                       |           |
| H2 | 0.6775        | 0.3630        | 1.0238        | 0.030*                           |           |

## supplementary materials

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|      |             |             |             |             |      |
|------|-------------|-------------|-------------|-------------|------|
| C3   | 0.9089 (5)  | 0.3184 (4)  | 1.0005 (3)  | 0.0247 (8)  |      |
| H3   | 0.9344      | 0.2833      | 1.0784      | 0.030*      |      |
| C4   | 1.0284 (4)  | 0.3217 (4)  | 0.9190 (3)  | 0.0204 (8)  |      |
| C5   | 1.1862 (5)  | 0.2725 (4)  | 0.9433 (4)  | 0.0259 (8)  |      |
| H5   | 1.2177      | 0.2343      | 1.0190      | 0.031*      |      |
| C6   | 1.2937 (5)  | 0.2792 (4)  | 0.8591 (4)  | 0.0296 (9)  |      |
| H6   | 1.3985      | 0.2434      | 0.8756      | 0.036*      |      |
| C7   | 1.2512 (4)  | 0.3389 (4)  | 0.7477 (4)  | 0.0253 (8)  |      |
| H7   | 1.3301      | 0.3448      | 0.6920      | 0.030*      |      |
| C8   | 1.0982 (4)  | 0.3891 (4)  | 0.7165 (3)  | 0.0193 (7)  |      |
| C9   | 0.9830 (4)  | 0.3776 (4)  | 0.8040 (3)  | 0.0178 (7)  |      |
| C10  | 0.9624 (5)  | 0.7881 (5)  | 0.6391 (6)  | 0.0462 (14) |      |
| H10  | 1.0427      | 0.7492      | 0.5938      | 0.055*      |      |
| C11  | 0.9986 (6)  | 0.9237 (5)  | 0.7038 (7)  | 0.071 (2)   |      |
| H11  | 1.1016      | 0.9753      | 0.7023      | 0.086*      |      |
| C12  | 0.8836 (6)  | 0.9807 (5)  | 0.7689 (6)  | 0.0586 (17) |      |
| H12  | 0.9070      | 1.0722      | 0.8134      | 0.070*      |      |
| C13  | 0.7312 (5)  | 0.9046 (4)  | 0.7703 (4)  | 0.0306 (9)  |      |
| C14  | 0.6057 (5)  | 0.9570 (4)  | 0.8344 (4)  | 0.0311 (9)  |      |
| H14  | 0.6214      | 1.0486      | 0.8795      | 0.037*      |      |
| C15  | 0.4614 (5)  | 0.8749 (4)  | 0.8309 (4)  | 0.0299 (9)  |      |
| H15  | 0.3775      | 0.9103      | 0.8744      | 0.036*      |      |
| C16  | 0.4342 (5)  | 0.7391 (4)  | 0.7644 (4)  | 0.0263 (9)  |      |
| H16  | 0.3319      | 0.6856      | 0.7640      | 0.032*      |      |
| C17  | 0.5523 (4)  | 0.6806 (4)  | 0.6993 (3)  | 0.0188 (7)  |      |
| C18  | 0.7048 (4)  | 0.7676 (4)  | 0.7030 (3)  | 0.0199 (7)  |      |
| O3   | 0.5643 (14) | 0.2137 (13) | 0.5793 (11) | 0.0316 (18) | 0.25 |
| N3   | 0.476 (2)   | -0.011 (2)  | 0.4938 (14) | 0.0236 (17) | 0.25 |
| C19  | 0.588 (2)   | 0.1025 (17) | 0.5172 (12) | 0.031 (4)   | 0.25 |
| H19  | 0.6900      | 0.0971      | 0.4850      | 0.037*      | 0.25 |
| C20  | 0.319 (3)   | -0.009 (3)  | 0.540 (2)   | 0.026 (4)   | 0.25 |
| H20A | 0.3237      | -0.0606     | 0.6134      | 0.039*      | 0.25 |
| H20B | 0.2305      | -0.0539     | 0.4745      | 0.039*      | 0.25 |
| H20C | 0.2977      | 0.0877      | 0.5650      | 0.039*      | 0.25 |
| C21  | 0.557 (2)   | -0.112 (2)  | 0.4205 (18) | 0.026 (4)   | 0.25 |
| H21A | 0.4848      | -0.1461     | 0.3412      | 0.039*      | 0.25 |
| H21B | 0.5803      | -0.1910     | 0.4675      | 0.039*      | 0.25 |
| H21C | 0.6618      | -0.0679     | 0.4030      | 0.039*      | 0.25 |
| O3'  | 0.7253 (14) | 0.1552 (12) | 0.5310 (11) | 0.0316 (18) | 0.25 |
| N3'  | 0.492 (3)   | 0.0002 (19) | 0.4949 (14) | 0.0236 (17) | 0.25 |
| C19' | 0.5783 (18) | 0.124 (2)   | 0.5450 (16) | 0.031 (4)   | 0.25 |
| H19' | 0.5247      | 0.1905      | 0.5929      | 0.037*      | 0.25 |
| C20' | 0.511 (3)   | -0.130 (2)  | 0.4189 (19) | 0.026 (4)   | 0.25 |
| H20D | 0.4190      | -0.1498     | 0.3493      | 0.039*      | 0.25 |
| H20E | 0.5115      | -0.2068     | 0.4708      | 0.039*      | 0.25 |
| H20F | 0.6162      | -0.1220     | 0.3856      | 0.039*      | 0.25 |
| C21' | 0.323 (3)   | -0.023 (3)  | 0.518 (2)   | 0.026 (4)   | 0.25 |
| H21D | 0.3170      | -0.0921     | 0.5772      | 0.039*      | 0.25 |
| H21E | 0.2505      | -0.0590     | 0.4388      | 0.039*      | 0.25 |

H21F                    0.2859                    0.0649                    0.5533                    0.039\*                    0.25

*Atomic displacement parameters (Å<sup>2</sup>)*

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| Pb   | 0.01436 (7) | 0.01590 (8) | 0.01590 (8) | 0.00224 (5)  | 0.00048 (5)  | 0.00189 (5)  |
| O1   | 0.0172 (12) | 0.0320 (15) | 0.0241 (14) | 0.0070 (11)  | 0.0044 (10)  | 0.0146 (12)  |
| O2   | 0.0180 (12) | 0.0203 (13) | 0.0154 (13) | 0.0008 (10)  | 0.0042 (10)  | -0.0007 (10) |
| N1   | 0.0178 (14) | 0.0164 (15) | 0.0138 (15) | 0.0004 (11)  | 0.0001 (11)  | 0.0032 (12)  |
| N2   | 0.0189 (16) | 0.0168 (16) | 0.040 (2)   | 0.0027 (12)  | 0.0041 (14)  | 0.0068 (15)  |
| C1   | 0.0215 (18) | 0.0200 (19) | 0.0199 (19) | -0.0006 (14) | 0.0047 (14)  | -0.0002 (15) |
| C2   | 0.034 (2)   | 0.024 (2)   | 0.0167 (19) | -0.0017 (16) | 0.0065 (16)  | 0.0016 (16)  |
| C3   | 0.039 (2)   | 0.0175 (19) | 0.0156 (18) | 0.0003 (16)  | -0.0020 (16) | 0.0022 (15)  |
| C4   | 0.0273 (19) | 0.0124 (17) | 0.0176 (18) | -0.0047 (14) | -0.0054 (14) | 0.0012 (14)  |
| C5   | 0.028 (2)   | 0.021 (2)   | 0.025 (2)   | -0.0033 (15) | -0.0080 (16) | 0.0071 (16)  |
| C6   | 0.0201 (19) | 0.022 (2)   | 0.047 (3)   | 0.0030 (15)  | -0.0066 (17) | 0.0151 (19)  |
| C7   | 0.0186 (18) | 0.025 (2)   | 0.034 (2)   | 0.0006 (15)  | 0.0031 (16)  | 0.0136 (18)  |
| C8   | 0.0185 (17) | 0.0180 (18) | 0.0213 (19) | -0.0001 (14) | -0.0001 (14) | 0.0072 (15)  |
| C9   | 0.0184 (17) | 0.0130 (17) | 0.0195 (18) | -0.0032 (13) | -0.0028 (13) | 0.0019 (14)  |
| C10  | 0.021 (2)   | 0.024 (2)   | 0.095 (4)   | 0.0009 (17)  | 0.013 (2)    | 0.005 (3)    |
| C11  | 0.031 (3)   | 0.021 (2)   | 0.158 (7)   | -0.003 (2)   | 0.015 (3)    | -0.003 (3)   |
| C12  | 0.041 (3)   | 0.014 (2)   | 0.113 (5)   | -0.0008 (19) | -0.002 (3)   | -0.007 (3)   |
| C13  | 0.035 (2)   | 0.0173 (19) | 0.036 (2)   | 0.0053 (16)  | -0.0092 (18) | 0.0034 (18)  |
| C14  | 0.048 (3)   | 0.019 (2)   | 0.024 (2)   | 0.0141 (18)  | -0.0063 (18) | -0.0012 (17) |
| C15  | 0.049 (3)   | 0.031 (2)   | 0.0136 (19) | 0.0164 (19)  | 0.0081 (17)  | 0.0035 (17)  |
| C16  | 0.034 (2)   | 0.029 (2)   | 0.0175 (19) | 0.0051 (17)  | 0.0097 (16)  | 0.0032 (17)  |
| C17  | 0.0270 (19) | 0.0208 (18) | 0.0089 (16) | 0.0056 (15)  | 0.0017 (14)  | 0.0023 (14)  |
| C18  | 0.0213 (18) | 0.0189 (18) | 0.0193 (19) | 0.0062 (14)  | -0.0017 (14) | 0.0044 (15)  |
| O3   | 0.036 (4)   | 0.026 (3)   | 0.031 (4)   | -0.003 (3)   | 0.005 (3)    | 0.003 (3)    |
| N3   | 0.025 (4)   | 0.023 (3)   | 0.025 (3)   | -0.001 (3)   | 0.012 (2)    | 0.007 (2)    |
| C19  | 0.029 (5)   | 0.031 (8)   | 0.035 (8)   | 0.001 (5)    | 0.006 (5)    | 0.017 (7)    |
| C20  | 0.024 (5)   | 0.031 (6)   | 0.025 (5)   | 0.000 (4)    | 0.007 (4)    | 0.007 (4)    |
| C21  | 0.029 (5)   | 0.026 (6)   | 0.026 (6)   | 0.005 (4)    | 0.012 (4)    | 0.003 (4)    |
| O3'  | 0.036 (4)   | 0.026 (3)   | 0.031 (4)   | -0.003 (3)   | 0.005 (3)    | 0.003 (3)    |
| N3'  | 0.025 (4)   | 0.023 (3)   | 0.025 (3)   | -0.001 (3)   | 0.012 (2)    | 0.007 (2)    |
| C19' | 0.029 (5)   | 0.031 (8)   | 0.035 (8)   | 0.001 (5)    | 0.006 (5)    | 0.017 (7)    |
| C20' | 0.024 (5)   | 0.031 (6)   | 0.025 (5)   | 0.000 (4)    | 0.007 (4)    | 0.007 (4)    |
| C21' | 0.029 (5)   | 0.026 (6)   | 0.026 (6)   | 0.005 (4)    | 0.012 (4)    | 0.003 (4)    |

*Geometric parameters (Å, °)*

|                     |            |         |           |
|---------------------|------------|---------|-----------|
| Pb—O2               | 2.408 (2)  | C12—C13 | 1.403 (6) |
| Pb—O1               | 2.468 (2)  | C12—H12 | 0.9500    |
| Pb—N2               | 2.470 (3)  | C13—C14 | 1.413 (6) |
| Pb—N1               | 2.566 (3)  | C13—C18 | 1.421 (5) |
| Pb—O1 <sup>i</sup>  | 2.618 (2)  | C14—C15 | 1.366 (6) |
| Pb—O2 <sup>ii</sup> | 2.812 (2)  | C14—H14 | 0.9500    |
| Pb—O3               | 2.903 (12) | C15—C16 | 1.408 (6) |

## supplementary materials

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|                       |            |             |            |
|-----------------------|------------|-------------|------------|
| Pb—O3'                | 2.977 (12) | C15—H15     | 0.9500     |
| O1—C8                 | 1.317 (4)  | C16—C17     | 1.392 (5)  |
| O1—Pb <sup>i</sup>    | 2.618 (2)  | C16—H16     | 0.9500     |
| O2—C17                | 1.304 (4)  | C17—C18     | 1.445 (5)  |
| N1—C1                 | 1.330 (4)  | O3—C19      | 1.244 (10) |
| N1—C9                 | 1.367 (4)  | N3—C19      | 1.350 (10) |
| N2—C10                | 1.319 (5)  | N3—C20      | 1.449 (10) |
| N2—C18                | 1.367 (5)  | N3—C21      | 1.448 (10) |
| C1—C2                 | 1.405 (5)  | C19—H19     | 0.9500     |
| C1—H1                 | 0.9500     | C20—H20A    | 0.9800     |
| C2—C3                 | 1.361 (5)  | C20—H20B    | 0.9800     |
| C2—H2                 | 0.9500     | C20—H20C    | 0.9800     |
| C3—C4                 | 1.412 (5)  | C21—H21A    | 0.9800     |
| C3—H3                 | 0.9500     | C21—H21B    | 0.9800     |
| C4—C5                 | 1.409 (5)  | C21—H21C    | 0.9800     |
| C4—C9                 | 1.429 (5)  | O3'—C19'    | 1.254 (10) |
| C5—C6                 | 1.361 (6)  | N3'—C19'    | 1.357 (10) |
| C5—H5                 | 0.9500     | N3'—C21'    | 1.453 (10) |
| C6—C7                 | 1.410 (5)  | N3'—C20'    | 1.455 (10) |
| C6—H6                 | 0.9500     | C19'—H19'   | 0.9500     |
| C7—C8                 | 1.387 (5)  | C20'—H20D   | 0.9800     |
| C7—H7                 | 0.9500     | C20'—H20E   | 0.9800     |
| C8—C9                 | 1.439 (5)  | C20'—H20F   | 0.9800     |
| C10—C11               | 1.402 (7)  | C21'—H21D   | 0.9800     |
| C10—H10               | 0.9500     | C21'—H21E   | 0.9800     |
| C11—C12               | 1.366 (8)  | C21'—H21F   | 0.9800     |
| C11—H11               | 0.9500     |             |            |
| O2—Pb—O1              | 136.81 (8) | C11—C10—H10 | 118.6      |
| O2—Pb—N2              | 67.61 (9)  | C12—C11—C10 | 119.0 (4)  |
| O1—Pb—N2              | 84.94 (9)  | C12—C11—H11 | 120.5      |
| O2—Pb—N1              | 77.78 (8)  | C10—C11—H11 | 120.5      |
| O1—Pb—N1              | 65.49 (8)  | C11—C12—C13 | 120.4 (5)  |
| N2—Pb—N1              | 82.06 (10) | C11—C12—H12 | 119.8      |
| O2—Pb—O1 <sup>i</sup> | 133.72 (8) | C13—C12—H12 | 119.8      |
| O1—Pb—O1 <sup>i</sup> | 67.90 (9)  | C12—C13—C14 | 123.6 (4)  |
| N2—Pb—O1 <sup>i</sup> | 80.59 (10) | C12—C13—C18 | 117.0 (4)  |
| N1—Pb—O1 <sup>i</sup> | 131.30 (8) | C14—C13—C18 | 119.4 (4)  |
| C8—O1—Pb              | 118.6 (2)  | C15—C14—C13 | 119.4 (4)  |
| C8—O1—Pb <sup>i</sup> | 129.3 (2)  | C15—C14—H14 | 120.3      |
| Pb—O1—Pb <sup>i</sup> | 112.10 (9) | C13—C14—H14 | 120.3      |
| C17—O2—Pb             | 119.0 (2)  | C14—C15—C16 | 121.6 (4)  |
| C1—N1—C9              | 119.1 (3)  | C14—C15—H15 | 119.2      |
| C1—N1—Pb              | 124.9 (2)  | C16—C15—H15 | 119.2      |
| C9—N1—Pb              | 114.9 (2)  | C17—C16—C15 | 122.2 (4)  |
| C10—N2—C18            | 119.0 (4)  | C17—C16—H16 | 118.9      |
| C10—N2—Pb             | 124.8 (3)  | C15—C16—H16 | 118.9      |
| C18—N2—Pb             | 116.1 (2)  | O2—C17—C16  | 124.0 (3)  |



|  |              |   |            |
|--|--------------|---|------------|
| N1—C1—C2                               | 122.8 (3)    | O2—C17—C18  | 119.8 (3)  |
| N1—C1—H1                               | 118.6        | C16—C17—C18   | 116.2 (3)  |
| C2—C1—H1                               | 118.6        | N2—C18—C13  | 121.8 (3)  |
| C3—C2—C1                               | 118.9 (3)    | N2—C18—C17  | 117.0 (3)  |
| C3—C2—H2                               | 120.5        | C13—C18—C17   | 121.3 (3)  |
| C1—C2—H2                               | 120.5        | C19—N3—C20  | 121.2 (19) |
| C2—C3—C4                               | 120.7 (3)    | C19—N3—C21  | 103.1 (15) |
| C2—C3—H3                               | 119.6        | C20—N3—C21  | 135.6 (19) |
| C4—C3—H3                               | 119.6        | O3—C19—N3   | 122.8 (18) |
| C3—C4—C5                               | 124.4 (3)    | O3—C19—H19  | 118.6      |
| C3—C4—C9                               | 116.8 (3)    | N3—C19—H19  | 118.6      |
| C5—C4—C9                               | 118.8 (3)    | C19 <sup>i</sup> —N3 <sup>i</sup> —C21 <sup>i</sup> | 118 (2)    |
| C6—C5—C4                               | 120.5 (4)    | C19 <sup>i</sup> —N3 <sup>i</sup> —C20 <sup>i</sup> | 141 (2)    |
| C6—C5—H5                               | 119.8        | C21 <sup>i</sup> —N3 <sup>i</sup> —C20 <sup>i</sup> | 101.4 (16) |
| C4—C5—H5                               | 119.8        | O3 <sup>i</sup> —C19 <sup>i</sup> —N3 <sup>i</sup>  | 123 (2)    |
| C5—C6—C7                               | 120.7 (3)    | O3 <sup>i</sup> —C19 <sup>i</sup> —H19 <sup>i</sup> | 118.6      |
| C5—C6—H6                               | 119.6        | N3 <sup>i</sup> —C19 <sup>i</sup> —H19 <sup>i</sup> | 118.6      |
| C7—C6—H6                               | 119.6        | N3 <sup>i</sup> —C20 <sup>i</sup> —H20D             | 109.5      |
| C8—C7—C6                               | 122.4 (3)    | N3 <sup>i</sup> —C20 <sup>i</sup> —H20E             | 109.5      |
| C8—C7—H7                               | 118.8        | H20D—C20 <sup>i</sup> —H20E                         | 109.5      |
| C6—C7—H7                               | 118.8        | N3 <sup>i</sup> —C20 <sup>i</sup> —H20F             | 109.5      |
| O1—C8—C7                               | 123.6 (3)    | H20D—C20 <sup>i</sup> —H20F                         | 109.5      |
| O1—C8—C9                               | 119.8 (3)    | H20E—C20 <sup>i</sup> —H20F                         | 109.5      |
| C7—C8—C9                               | 116.6 (3)    | N3 <sup>i</sup> —C21 <sup>i</sup> —H21D             | 109.5      |
| N1—C9—C4                               | 121.6 (3)    | N3 <sup>i</sup> —C21 <sup>i</sup> —H21E             | 109.5      |
| N1—C9—C8                               | 117.4 (3)    | H21D—C21 <sup>i</sup> —H21E                         | 109.5      |
| C4—C9—C8                               | 120.9 (3)    | N3 <sup>i</sup> —C21 <sup>i</sup> —H21F             | 109.5      |
| N2—C10—C11                             | 122.8 (4)    | H21D—C21 <sup>i</sup> —H21F                         | 109.5      |
| N2—C10—H10                             | 118.6        | H21E—C21 <sup>i</sup> —H21F                         | 109.5      |
| O2—Pb—O1—C8                            | 50.9 (3)     | C6—C7—C8—C9   | 0.0 (6)    |
| N2—Pb—O1—C8                            | 100.2 (3)    | C1—N1—C9—C4   | 1.6 (5)    |
| N1—Pb—O1—C8                            | 16.6 (2)     | Pb—N1—C9—C4   | -167.0 (3) |
| O1 <sup>i</sup> —Pb—O1—C8              | -178.0 (3)   | C1—N1—C9—C8   | -178.3 (3) |
| O2—Pb—O1—Pb <sup>i</sup>               | -131.10 (11) | Pb—N1—C9—C8   | 13.1 (4)   |
| N2—Pb—O1—Pb <sup>i</sup>               | -81.88 (12)  | C3—C4—C9—N1   | -1.8 (5)   |
| N1—Pb—O1—Pb <sup>i</sup>               | -165.45 (14) | C5—C4—C9—N1   | 177.5 (3)  |
| O1 <sup>i</sup> —Pb—O1—Pb <sup>i</sup> | 0.0          | C3—C4—C9—C8   | 178.2 (3)  |
| O1—Pb—O2—C17                           | 48.0 (3)     | C5—C4—C9—C8   | -2.6 (5)   |
| N2—Pb—O2—C17                           | -6.7 (2)     | O1—C8—C9—N1   | 2.0 (5)    |
| N1—Pb—O2—C17                           | 79.7 (2)     | C7—C8—C9—N1   | -177.8 (3) |
| O1 <sup>i</sup> —Pb—O2—C17             | -57.0 (3)    | O1—C8—C9—C4   | -177.9 (3) |
| O2—Pb—N1—C1                            | 20.5 (3)     | C7—C8—C9—C4   | 2.3 (5)    |
| O1—Pb—N1—C1                            | 177.2 (3)    | C18—N2—C10—C11                                      | 0.3 (8)    |
| N2—Pb—N1—C1                            | 89.2 (3)     | Pb—N2—C10—C11                                       | -174.2 (5) |
| O1 <sup>i</sup> —Pb—N1—C1              | 159.2 (2)    | N2—C10—C11—C12                                      | -0.2 (10)  |
| O2—Pb—N1—C9                            | -171.7 (2)   | C10—C11—C12—C13                                     | -0.4 (10)  |
| O1—Pb—N1—C9                            | -14.9 (2)    | C11—C12—C13—C14                                     | -179.3 (5) |

## supplementary materials

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|                            |            |                   |            |
|----------------------------|------------|-------------------|------------|
| N2—Pb—N1—C9                | -103.0 (2) | C11—C12—C13—C18   | 0.7 (8)    |
| O1 <sup>i</sup> —Pb—N1—C9  | -33.0 (3)  | C12—C13—C14—C15   | -179.7 (5) |
| O2—Pb—N2—C10               | -179.4 (4) | C18—C13—C14—C15   | 0.3 (6)    |
| O1—Pb—N2—C10               | 34.7 (4)   | C13—C14—C15—C16   | -0.3 (6)   |
| N1—Pb—N2—C10               | 100.6 (4)  | C14—C15—C16—C17   | 0.3 (6)    |
| O1 <sup>i</sup> —Pb—N2—C10 | -33.7 (4)  | Pb—O2—C17—C16     | -174.8 (3) |
| O2—Pb—N2—C18               | 6.0 (2)    | Pb—O2—C17—C18     | 6.8 (4)    |
| O1—Pb—N2—C18               | -139.9 (3) | C15—C16—C17—O2    | -178.8 (3) |
| N1—Pb—N2—C18               | -74.0 (3)  | C15—C16—C17—C18   | -0.4 (5)   |
| O1 <sup>i</sup> —Pb—N2—C18 | 151.7 (3)  | C10—N2—C18—C13    | 0.0 (6)    |
| C9—N1—C1—C2                | -0.5 (5)   | Pb—N2—C18—C13     | 175.1 (3)  |
| Pb—N1—C1—C2                | 166.9 (3)  | C10—N2—C18—C17    | 179.9 (4)  |
| N1—C1—C2—C3                | -0.4 (6)   | Pb—N2—C18—C17     | -5.1 (4)   |
| C1—C2—C3—C4                | 0.2 (6)    | C12—C13—C18—N2    | -0.5 (6)   |
| C2—C3—C4—C5                | -178.4 (4) | C14—C13—C18—N2    | 179.5 (3)  |
| C2—C3—C4—C9                | 0.8 (5)    | C12—C13—C18—C17   | 179.6 (4)  |
| C3—C4—C5—C6                | 179.7 (4)  | C14—C13—C18—C17   | -0.3 (6)   |
| C9—C4—C5—C6                | 0.5 (5)    | O2—C17—C18—N2     | -0.9 (5)   |
| C4—C5—C6—C7                | 1.7 (6)    | C16—C17—C18—N2    | -179.4 (3) |
| C5—C6—C7—C8                | -2.0 (6)   | O2—C17—C18—C13    | 178.9 (3)  |
| Pb—O1—C8—C7                | 162.6 (3)  | C16—C17—C18—C13   | 0.4 (5)    |
| Pb <sup>i</sup> —O1—C8—C7  | -14.9 (5)  | C20—N3—C19—O3     | 0.0 (3)    |
| Pb—O1—C8—C9                | -17.2 (4)  | C21—N3—C19—O3     | -179.9 (3) |
| Pb <sup>i</sup> —O1—C8—C9  | 165.3 (2)  | C21'—N3'—C19'—O3' | 179.9 (3)  |
| C6—C7—C8—O1                | -179.8 (4) | C20'—N3'—C19'—O3' | 0.0 (5)    |

Symmetry codes: (i)  $-x+2, -y+1, -z+1$ ; (ii)  $-x+1, -y+1, -z+1$ .

Fig. 1

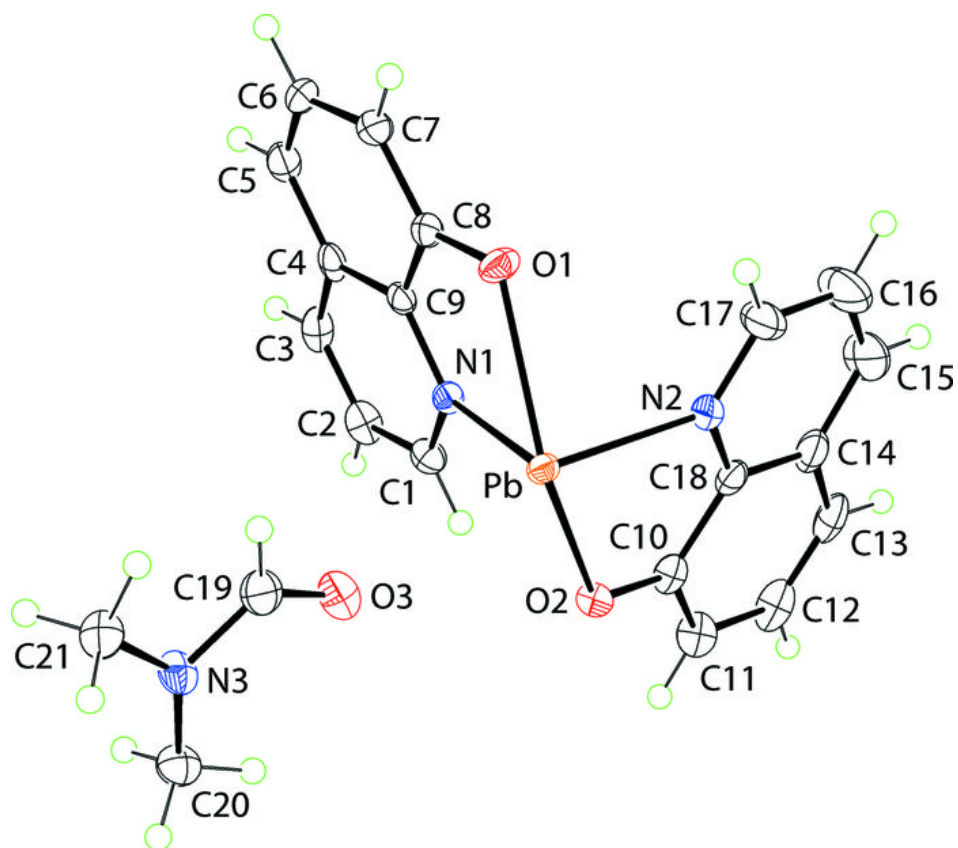


Fig. 2

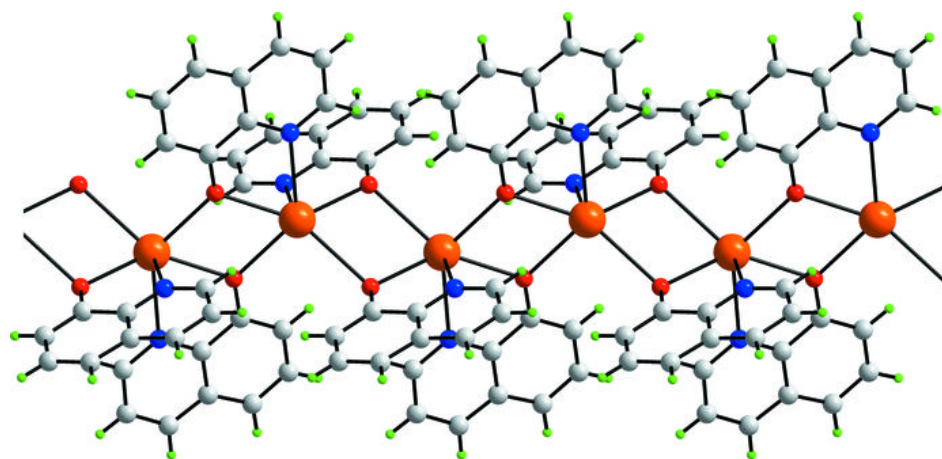


Fig. 3

