

## A new polymorph of poly[bis( $\mu_2$ -perchlorato- $\kappa^2$ O:O')(2,2':6',2''-terpyridine- $\kappa^3$ N,N',N'')lead(II)] with a greatly extended chain repeat distance

Alexander J. Blake,<sup>a\*</sup> Claudia Caltagirone,<sup>b</sup> Vito Lippolis<sup>b</sup> and Mojtaba Shamsipur<sup>c</sup>

<sup>a</sup>School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, England, <sup>b</sup>Dipartimento di Chimica Inorganica ed Analitica, Università degli Studi di Cagliari, Complesso Universitario di Monserrato, S.S. 554 Bivio per Sestu, 09042 Monserrato (CA), Italy, and <sup>c</sup>Department of Chemistry, Razi University, Kermanshah, Iran  
Correspondence e-mail: a.j.blake@nottingham.ac.uk

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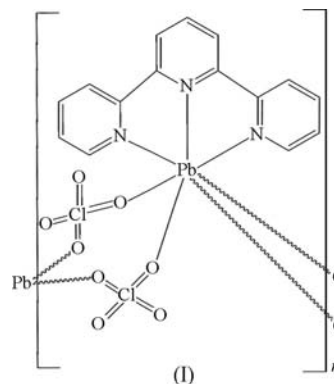
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In the title compound,  $[\text{Pb}(\text{ClO}_4)_2(\text{C}_{15}\text{H}_{11}\text{N}_3)]_n$ , two molecules occupy general positions while the third lies on a crystallographic twofold axis, giving a total of two and a half molecules per asymmetric unit. Each metal centre is coordinated equatorially by three 2,2':6',2''-terpyridine (terpy) N-donor atoms and axially by two perchlorate O-donor atoms. The distorted pentagonal bipyramidal geometry is completed by two equatorial O-donor atoms from two perchlorate anions which bridge to two different adjacent metal centres. The coordination about each metal centre is very similar to that seen at the unique  $\text{Pb}^{\text{II}}$  centre in the previously published polymorph [Engelhardt, Harrowfield, Miyamae, Patrick, Skelton, Soudi & White (1996). *Aust. J. Chem.* **49**, 1135–1146], but the new polymorph differs from it by the insertion on each side of an existing [bis(perchlorato)(terpy)lead(II)] molecule of two additional such units. Pairs of asymmetrically bridging perchlorate anions link irregularly spaced  $\text{Pb}^{\text{II}}$  centres into undulating chains parallel to [201] which exhibit a repeat distance of 26.280 (4) Å. The significance of this new polymorph lies in the fact that, while it is chemically identical to the known polymorph, it is structurally distinct from it.

### Comment

Polydentate analogues of the pyridine molecule have played an important role in the development of coordination chemistry and continue to be of considerable interest, in particular the metal complexes of  $N,N'$ -bidentate aromatic ligands such as 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and the tridentate analogue 2,2':6',2''-terpyridine (terpy). This interest stems not only from the similarity of these ligands to biologically important nitrogen-containing heterocyclic ligands

such as porphyrins and purines, but also from their use as building blocks in the construction of supramolecular systems, macromolecules, metallo-oligomers and polymers exhibiting a wide variety of chromophoric, electrochemical, luminescent and magnetic properties (Sauvage *et al.*, 1994; Kaes *et al.*, 2000; Chelucci & Thummel, 2002; Hofmeier & Schubert, 2004; Baronoff *et al.*, 2004; Eryazici *et al.*, 2008; Glasson *et al.*, 2008; Constable, 2007, 2008). In particular, terpy is a ligand with a very extensive coordination chemistry. In principle, it can exhibit a variety of coordination modes towards metals, *i.e.* monodentate, bidentate, terdentate and bridging, but, in practice, it almost invariably acts as a planar tridentate ligand forming 1:1 and 1:2 (metal-to-ligand) five- or six-coordinate complexes with divalent transition and post-transition metal ions (Brandt *et al.*, 1954; Cargill Thompson, 1997). Particularly interesting from a structural point of view are the 1:1 complexes in which the coordination sphere of the metal ion is completed by solvent or adventitious oxygenated ligands which can also function as bridging ligands, resulting in extended polynuclear architectures of different dimensionalities. In this paper, we report the crystal structure of a new polymorph of  $[\text{Pb}(\text{ClO}_4)_2(\text{terpy})]$  obtained by reacting a 1:1 molar ratio of  $\text{Pb}(\text{ClO}_4)_2$  and terpy in acetonitrile.

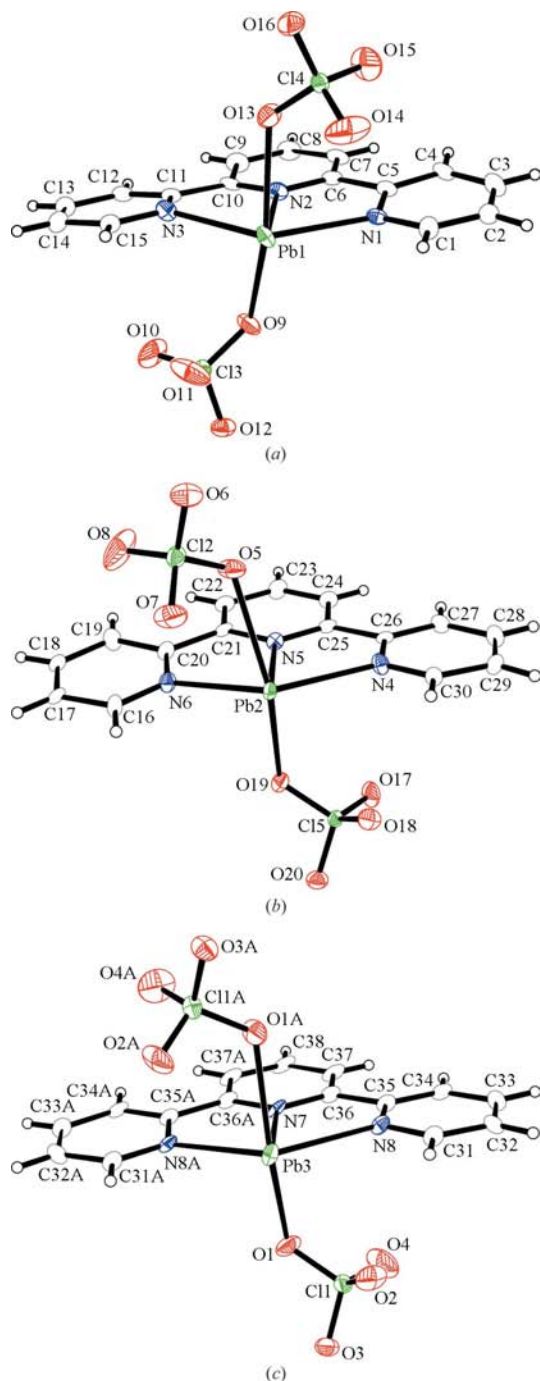


In the title compound, (I), the molecules containing atoms Pb1 (Fig. 1) and Pb2 occupy general positions while Pb3 lies on a crystallographic twofold axis that also passes through the middle of the central pyridyl ring (atoms N7, C38 and H38). Each metal centre is coordinated by all three pyridyl N-donor atoms from the terpy ligand [ $\text{Pb}-\text{N} = 2.494$  (8)– $2.540$  (9) Å; Table 1] in the equatorial plane and by two axial perchlorate O-donor atoms at distances in the range 2.532 (10)– $2.626$  (10) Å. Considering only these linkages, the anions may be regarded as monodentate with respect to any one metal centre; an alternative description as strongly asymmetrically bidentate (see below) would involve the consideration of a wide range of much longer  $\text{Pb}-\text{O}$  distances in the range 3.151 (12)– $3.404$  (14) Å. The seven coordination at each of the three metal centres in (I) is completed by two equatorial O atoms [ $\text{Pb}-\text{O} = 2.969$  (11)– $3.024$  (11) Å; Table 1] from two anions bridging to two different adjacent metal centres (Fig. 2). The significant deviations of these O-donor atoms in opposing directions out of the equatorial plane represent the principal

# metal-organic compounds

distortion from pentagonal bipyramidal geometry at each metal centre.

Other notable features of the coordination geometry are the markedly nonlinear O(axial)—Pb—O(axial) angles



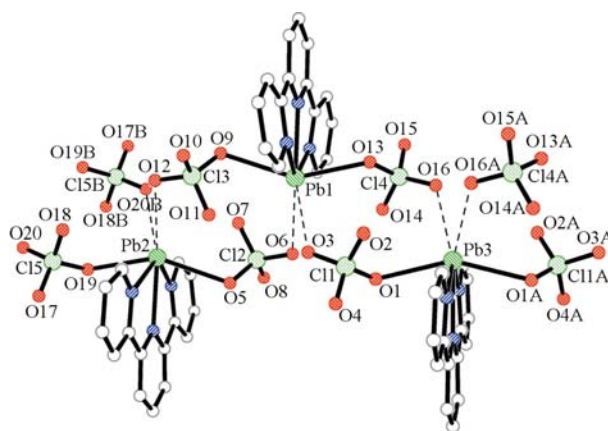
**Figure 1**

Views of the two and a half independent molecules of the title compound in each asymmetric unit, showing the atom-numbering scheme and with displacement ellipsoids drawn at the 30% probability level. For clarity, coordination of Pb by anions primarily bonded to other Pb<sup>II</sup> centres is not shown. The molecules containing Pb1 (a) and Pb2 (b) occupy general positions while Pb3 (c) lies on a crystallographic twofold axis which also bisects the central ring of the ligand. Atoms whose labels include the suffix 'A' are related to their unsuffixed equivalents by the symmetry operation  $(1 - x, y, \frac{1}{2} - z)$ .

(Table 1) which have values of around  $150^\circ$ , and the dihedral angles between the terminal pyridyl rings of the terpy ligand in each molecule which adopt similar values of  $11.8$  (5),  $6.9$  (4) and  $4.0$  (4) $^\circ$  for the ligand coordinated to Pb1, Pb2 and Pb3, respectively.

The pairs of asymmetrically bridging perchlorate anions described above lead to an extended structure wherein the Pb<sup>II</sup> centres are linked into undulating chains which run parallel to the [201] direction (Fig. 3a) and which are significantly interdigitated. The spacing of the Pb<sup>II</sup> centres is irregular [Pb1...Pb2 =  $5.5835$  (10) Å, Pb2...Pb2 =  $6.2364$  (11) Å and Pb1...Pb3 =  $6.0004$  (10) Å] and this can be traced to variations in the Pb—O—Cl angles associated with the perchlorate bridges: for the shortest Pb1...Pb2 distance, these range between  $110.1$  (6) and  $116.9$  (6) $^\circ$ , averaging  $114^\circ$ ; for the longest Pb2...Pb2 distance, the angles are much wider [ $121.4$  (4) and  $134.7$  (5) $^\circ$ , average  $128^\circ$ ]; while for the intermediate Pb1...Pb3 distance, the angles [ $118.8$  (5)– $129.4$  (6) $^\circ$ , average  $124^\circ$ ] are correspondingly intermediate. In the literature, the main distribution of  $M$ —O—Cl angles in perchlorate bridges covers a wide range ( $115$ – $140^\circ$ , with a few examples extending this range to between  $105$  and  $150^\circ$ ; Allen, 2002). We believe that this flexibility in the coordination geometry of the perchlorate anion is the prime factor that allows different polymorphs to exist. We have every reason to suspect the existence of other polymorphs based on different proportions of perchlorate geometries. Fig. 3(b) shows alternating regions of hydrophilic perchlorate and hydrophobic terpy units along the  $b$  axis.

Crystals of the previously published polymorph were prepared by a different synthetic route (*cf. Experimental*): hot equimolar solutions of  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  in water and terpy in MeOH were combined and the mixture boiled before being allowed to cool overnight (Engelhardt *et al.*, 1996). The resulting structure is considerably simpler, with a single independent Pb<sup>II</sup> centre: this lies on a crystallographic twofold



**Figure 2**

A view of the asymmetric unit, extended to complete the coordination sphere around Pb2 and Pb3, and showing the distorted  $\text{N}_3\text{O}_4$  coordination at each metal centre. The unlabelled N atoms (shown as blue circles in the electronic version of the paper) are shaded bottom left to top right. Atoms whose labels include the suffixes 'A' and 'B' are related to their unsuffixed equivalents by the symmetry operations  $(1 - x, y, \frac{1}{2} - z)$  and  $(-x, 1 - y, -z)$ , respectively.

axis, with pairs of symmetry-related perchlorate anions linking successive Pb<sup>II</sup> centres into a one-dimensional polymeric chain. The authors characterize each perchlorate as a highly asymmetric *O,O'*-bidentate ligand [Pb—O = 2.554 (5) and 3.258 (9) Å] to one metal centre while another O atom forms one of the links to the adjacent metal. The same paper reports very similar chain structures for complexes with other small oxoanions (nitrate and nitrite). The structure of the current polymorph may be formally converted into that of the original polymorph by removal of the [bis(perchlorato)(terpy)-lead(II)] units centred on Pb1 and Pb2 and linking Pb3-centred units directly *via* pairwise perchlorate bridges. The unique repeat distance along the chain in the original polymorph is 6.0670 (6) Å, while in the current structure the

Pb3···Pb3 distance is 26.280 (4) Å. Because of the irregularity of the Pb···Pb distances (see above), this considerably longer distance must be regarded as the fundamental repeat distance along the chain. Interestingly, similar undulating chains of doubly-bridged [(terpy)lead(II)] units are observed in the extended structures of [Pb(NO<sub>3</sub>)<sub>2</sub>(C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>)]<sub>∞</sub> (Engelhardt *et al.*, 1996) and [Pb(SCN)<sub>2</sub>(C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>)]<sub>∞</sub> (Engelhardt *et al.*, 1989), with Pb···Pb repeat distances of 6.892 (3) and 6.018 (4) Å, respectively.

## Experimental

The title salt was prepared by reaction of Pb(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (5 mg, 0.0215 mmol) and terpyridine (9.9 mg, 0.0215 mmol) in MeCN (5 ml). Crystals were grown by diffusion of diethyl ether into the reaction mixture. Analysis found (calculated for C<sub>15</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>8</sub>Pb): C 28.10 (28.18), H 1.80 (1.73), N 6.55% (6.57%).

### Crystal data

[Pb(ClO <sub>4</sub> ) <sub>2</sub> (C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> )]	<i>V</i> = 9002 (4) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 639.36	<i>Z</i> = 20
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 25.440 (4) Å	<i>μ</i> = 9.72 mm <sup>-1</sup>
<i>b</i> = 16.333 (3) Å	<i>T</i> = 150 (2) K
<i>c</i> = 21.916 (4) Å	0.25 × 0.08 × 0.05 mm
<i>β</i> = 98.671 (2)°	

### Data collection

Bruker SMART APEX CCD	27358 measured reflections
area-detector diffractometer	8832 independent reflections
Absorption correction: multi-scan	4705 reflections with <i>I</i> > 2σ( <i>I</i> )
( <i>SADABS</i> ; Sheldrick, 1996)	<i>R</i> <sub>int</sub> = 0.052
<i>T</i> <sub>min</sub> = 0.514, <i>T</i> <sub>max</sub> = 1.000	
(expected range = 0.316–0.615)	

### Refinement

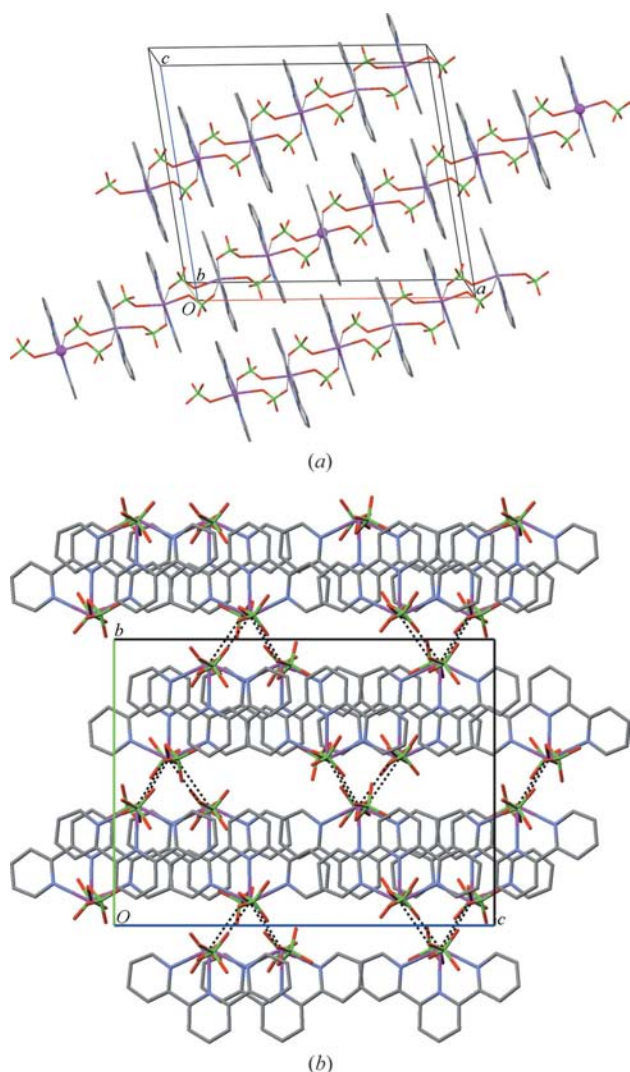
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.045	220 restraints
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.126	H-atom parameters constrained
<i>S</i> = 1.03	Δ <i>ρ</i> <sub>max</sub> = 2.07 e Å <sup>-3</sup>
8832 reflections	Δ <i>ρ</i> <sub>min</sub> = -2.43 e Å <sup>-3</sup>
655 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Pb1—O3	2.980 (11)	Pb2—O19	2.547 (8)
Pb1—O6	2.987 (11)	Pb2—O20 <sup>i</sup>	2.975 (9)
Pb1—O9	2.598 (10)	Pb2—N4	2.540 (9)
Pb1—O13	2.532 (10)	Pb2—N5	2.502 (11)
Pb1—N1	2.511 (9)	Pb2—N6	2.501 (9)
Pb1—N2	2.494 (8)	Pb3—O1	2.548 (10)
Pb1—N3	2.506 (10)	Pb3—O16	2.969 (11)
Pb2—O5	2.626 (10)	Pb3—N7	2.499 (15)
Pb2—O12	3.024 (11)	Pb3—N8	2.519 (9)
O9—Pb1—O13	148.8 (4)	Pb1—O9—Cl3	116.9 (6)
O5—Pb2—O19	148.1 (3)	Pb2—O12—Cl3	110.1 (6)
O1—Pb3—O1 <sup>ii</sup>	152.7 (4)	Pb1—O13—Cl4	122.0 (5)
Pb3—O1—Cl1	118.8 (5)	Pb3—O16—Cl4	125.7 (6)
Pb1—O3—Cl1	129.4 (6)	Pb2—O19—Cl5	121.4 (4)
Pb2—O5—Cl2	114.7 (5)	Pb2—O20 <sup>i</sup> —Cl5 <sup>i</sup>	134.7 (5)
Pb1—O6—Cl2	114.0 (6)		

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



**Figure 3**

(a) A view, approximately along the *b* axis, showing chains of molecules running along the [201] direction. The atoms shown as spheres in the central chain are Pb3 and two of its symmetry equivalents. The shortest Pb3···Pb3 separation along the chain is 26.280 (4) Å and represents the fundamental repeat distance. (b) An orthogonal view, showing the alternation of hydrophilic (perchlorate) and hydrophobic (terpy) regions along the *b* axis.

H atoms were placed geometrically and refined riding at a distance of 0.95 Å from their parent C atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Rigid bond restraints were applied to all anisotropic displacement parameters.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE* and *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2003) and *pubCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3072). Services for accessing these data are described at the back of the journal.

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