

# Poly[ $\{\mu_{10}-[(\text{phosphonomethyl})\text{imino-dimethylene}]diphosphonato\}$ -dithallium(I)]

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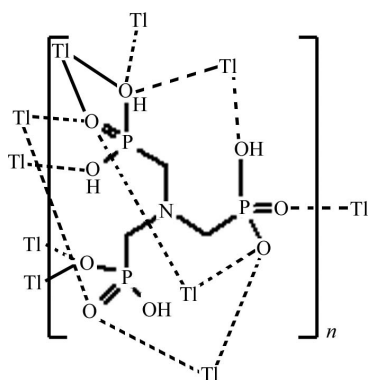
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{N}-\text{C}) = 0.008$  Å;  $R$  factor = 0.025;  $wR$  factor = 0.055; data-to-parameter ratio = 16.8.

The title compound,  $[\text{Tl}_2(\text{C}_3\text{H}_{10}\text{NO}_9\text{P}_3)]_n$ , a  $\text{Tl}^{\text{I}}$  organic-inorganic hybrid complex, was synthesized by the reaction of nitrilotris(methylenephosphonic acid) with thallium(I) nitrate. There are two types of  $\text{Tl}^+$  ions in the complex, with coordination numbers of eight and seven and with stereochemically active and inactive lone-pair electrons, respectively. In the crystal, the doubly deprotonated ligands form two-dimensional hydrogen-bonded layers through  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. The  $\text{NH}$  group is involved in a trifurcated intramolecular hydrogen bond. Coordination of the phosphonate ligands to the  $\text{Tl}^+$  ions creates a three-dimensional structure.

## Related literature

For related metal phosphonate complexes of the same ligand, see: Sharma *et al.* (2001).



## Experimental

### Crystal data

$[\text{Tl}_2(\text{C}_3\text{H}_{10}\text{NO}_9\text{P}_3)]$	$\gamma = 68.085 (1)^\circ$
$M_r = 705.77$	$V = 635.06 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.9236 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.0932 (6) \text{ \AA}$	$\mu = 25.76 \text{ mm}^{-1}$
$c = 10.9136 (8) \text{ \AA}$	$T = 100 \text{ K}$
$\alpha = 81.422 (1)^\circ$	$0.16 \times 0.14 \times 0.10 \text{ mm}$
$\beta = 79.023 (1)^\circ$	

### Data collection

Bruker APEXII CCD area-detector diffractometer	6627 measured reflections
Absorption correction: numerical ( <i>XPREP</i> ; Bruker, 2007)	2744 independent reflections
$T_{\text{min}} = 0.104$ , $T_{\text{max}} = 0.183$	2437 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	12 restraints
$wR(F^2) = 0.055$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.72 \text{ e \AA}^{-3}$
2744 reflections	$\Delta\rho_{\text{min}} = -1.83 \text{ e \AA}^{-3}$
163 parameters	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O3}$	0.87	2.39	2.882 (5)	116
$\text{N1}-\text{H1N}\cdots\text{O5}$	0.87	2.53	2.957 (6)	111
$\text{N1}-\text{H1N}\cdots\text{O8}$	0.87	2.19	2.837 (7)	131
$\text{O1}-\text{H1O}\cdots\text{O1}^{\text{i}}$	0.82	1.78	2.504 (8)	147
$\text{O2}-\text{H2O}\cdots\text{O2}^{\text{ii}}$	0.82	1.68	2.497 (7)	171
$\text{O6}-\text{H6O}\cdots\text{O9}^{\text{iii}}$	0.82	1.67	2.484 (6)	171
$\text{O7}-\text{H7O}\cdots\text{O4}^{\text{iv}}$	0.82	1.70	2.521 (6)	180

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Support of this investigation by Tarbiat Modares University Research Council is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2128).

## References

- Bruker (2007). *APEX2*, *SAINT* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sharma, C. V. K., Clearfield, A., Cabeza, A., Aranda, M. A. G. & Bruque, S. (2001). *J. Am. Chem. Soc.* **123**, 2885–2886.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

**supplementary materials**

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## Poly[ $\{\mu_{10}$ -[(phosphonomethyl)iminodimethylene]diphosphonato}dithallium(I)]

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### Comment

Metal phosphonate complexes of the ligand nitrilotris(methylenephosphonic acid (H6L), giving two different types of 1:1 (M/L) metal phosphonate complexes,  $M[\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]$  ( $M = \text{Mn, Co, Ni, Cu, Zn, Cd}$ ), with two-dimensional hydrogen-bonded layered structures, have been prepared previously by (Sharma *et al.*, 2001).

In the structure of the title compound, synthesized by the reaction of the same ligand with thallium(I) nitrate, the nitrilotris(methylenephosphonate) ( $\text{H}_4\text{L}^{2-}$ ) group is doubly deprotonated and two different environments for the Thallium atoms are observed, as shown in Figs. 1 and 2. Eight O-atoms of five  $\text{H}_4\text{L}^{2-}$  phosphonate ligands are coordinated to the Tl1 ion (Fig. 1), while seven oxygen atoms of five  $\text{H}_4\text{L}^{2-}$  phosphonate ligands are coordinated to the Tl2 ion (Fig. 2).

The conformation of the doubly deprotonated nitrilotris(methylenephosphonate) ligand is illustrated in Fig. 3. The hydrogen atoms on atoms O1 and O2 are positionally disordered with relative occupancies of 0.5:0.5. Each  $\text{H}_4\text{L}^{2-}$  dianion links to five Tl1 and five Tl2 ions (Fig. 4).

The doubly deprotonated  $\text{H}_4\text{L}^{2-}$  ligand forms two-dimensional hydrogen bonded layers *via* O—H $\cdots$ O hydrogen bonds involving hydroxyl groups O1, O2, O6 and O7 (Table 1 and Fig. 5). Atoms O3, O5 and O8 do not contribute in this type of hydrogen bond, rather they coordinate only to the  $\text{Tl}^+$  ions. The NH group is involved in a 4-centre trifurcated intramolecular hydrogen bond with O-atoms O3, O5 and O8 (Table 1). Coordination of the ligand to the metal ions in the interlayer space creates a three-dimensional structure (Fig. 6).

### Experimental

Thallium(I)nitrate (0.133 g, 0.5 mmol) was added in several portions to a solution of nitrilotris(methylenephosphonicacid) (H6L) (0.104 g, 0.35 mmol) in 12 ml of a deionized water-ethanol mixture (3:5). The solution was stirred for seven days and a white precipitate was obtained. This was filtered off and recrystallized from deionized water at rt. Colorless prism-like crystals of the title compound were obtained in 68% yield (based on the Tl atom). Elemental analysis for  $\text{Tl}_2(\text{H}_4\text{L})$ ,  $\text{C}_3\text{H}_{10}\text{NO}_9\text{P}_3\text{Tl}_2$ : C, 5.06; H, 1.36; N, 2.03%. Calc.: C, 5.10; H, 1.41; N, 1.98%.

### Refinement

The NH and OH H-atoms were located in a difference electron-density map and were refined with distance restraints: O—H = 0.82 (2) and N—H = 0.86 (2) Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$ . The C-bound H atoms were positioned geometrically and refined using a riding model: C—H = 0.99 Å, with  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$ .

## Figures

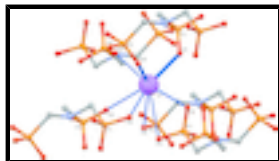


Fig. 1. Environment of the Tl1 atom.

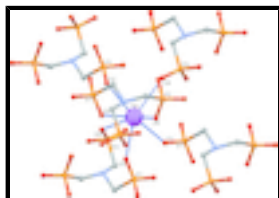


Fig. 2. Environment of the Tl2 atom.

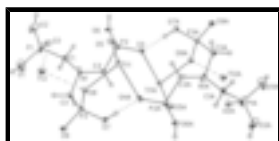


Fig. 3. The conformation of the doubly deprotonated nitrilotris(methylenephosphonate) ligand.

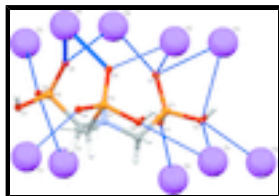


Fig. 4. Each H4L<sup>2-</sup> dianion links to five Tl1 and five Tl2 ions.

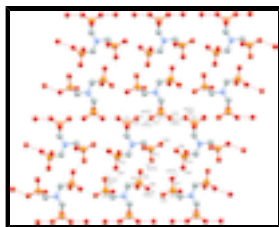


Fig. 5. Two-dimensional hydrogen-bonded layers formed *via* O—H...O hydrogen bonds involving hydroxyl groups.

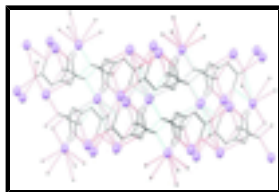


Fig. 6. The three-dimensional structure resulting from the coordination of the ligand to the metal ions in the interlayer space.



Fig. 7. Reaction scheme.

## Poly[ $\{\mu\text{-}[(\text{phosphonomethyl})\text{iminodimethylene}]\text{diphosphonato}\}$ dithallium(I)]

### Crystal data

[Tl<sub>2</sub>(C<sub>3</sub>H<sub>10</sub>NO<sub>9</sub>P<sub>3</sub>)]

$M_r = 705.77$

Triclinic,  $P\bar{1}$

$Z = 2$

$F(000) = 628$

$D_x = 3.691 \text{ Mg m}^{-3}$

Hall symbol: -P 1  
 $a = 7.9236$  (6) Å  
 $b = 8.0932$  (6) Å  
 $c = 10.9136$  (8) Å  
 $\alpha = 81.422$  (1)°  
 $\beta = 79.023$  (1)°  
 $\gamma = 68.085$  (1)°  
 $V = 635.06$  (8) Å<sup>3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 266 reflections  
 $\theta = 3\text{--}26^\circ$   
 $\mu = 25.76$  mm<sup>-1</sup>  
 $T = 100$  K  
 Prism, colorless  
 $0.16 \times 0.14 \times 0.10$  mm

### Data collection

Bruker APEXII CCD area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 graphite  
 $\omega$  scans  
 Absorption correction: numerical  
 (XPREP; Bruker, 2007)  
 $T_{\min} = 0.104$ ,  $T_{\max} = 0.183$   
 6627 measured reflections

2744 independent reflections  
 2437 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$   
 $\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 1.9^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -10 \rightarrow 10$   
 $l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.055$   
 $S = 1.05$   
 2744 reflections  
 163 parameters  
 12 restraints

Primary atom site location: structure-invariant direct  
 methods  
 Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring  
 sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 1.104P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 1.72$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.83$  e Å<sup>-3</sup>

### 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.

## supplementary materials

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Tl1	0.29076 (3)	-0.05875 (3)	0.25484 (2)	0.01064 (7)	
Tl2	0.23248 (3)	0.24843 (3)	0.54672 (2)	0.01703 (8)	
P1	0.7521 (3)	0.2462 (3)	0.42352 (16)	0.0201 (4)	
P2	0.7554 (2)	-0.0669 (2)	0.10302 (14)	0.0090 (3)	
P3	0.2557 (2)	0.4329 (2)	0.20298 (14)	0.0091 (3)	
O1	0.6684 (8)	0.4387 (7)	0.4597 (5)	0.0331 (13)	
H1O	0.5753	0.4894	0.5072	0.040*	0.50
O2	0.9424 (7)	0.1622 (8)	0.4631 (5)	0.0311 (12)	
H2O	0.9828	0.0586	0.4936	0.037*	0.50
O3	0.6291 (6)	0.1391 (5)	0.4655 (4)	0.0119 (9)	
O4	0.7469 (6)	-0.1263 (6)	-0.0199 (4)	0.0148 (9)	
O5	0.6365 (6)	-0.1126 (6)	0.2173 (4)	0.0151 (9)	
O6	0.9564 (6)	-0.1194 (5)	0.1274 (4)	0.0129 (9)	
H6O	1.0047	-0.2157	0.1660	0.015*	
O7	0.2360 (6)	0.4303 (6)	0.0624 (4)	0.0145 (9)	
H7O	0.2418	0.3313	0.0485	0.017*	
O8	0.2641 (6)	0.2594 (5)	0.2794 (4)	0.0108 (8)	
O9	0.1203 (6)	0.6039 (6)	0.2530 (4)	0.0141 (9)	
N1	0.6274 (7)	0.2583 (6)	0.2032 (4)	0.0086 (10)	
H1N	0.5590	0.2094	0.2560	0.010*	
C1	0.7944 (8)	0.2553 (8)	0.2523 (6)	0.0116 (12)	
H1A	0.8225	0.3638	0.2177	0.014*	
H1B	0.9018	0.1497	0.2251	0.014*	
C2	0.6768 (8)	0.1763 (8)	0.0791 (5)	0.0089 (11)	
H2A	0.7749	0.2130	0.0257	0.011*	
H2B	0.5677	0.2209	0.0351	0.011*	
C3	0.4836 (8)	0.4433 (8)	0.1986 (6)	0.0111 (12)	
H3A	0.5140	0.5133	0.1209	0.013*	
H3B	0.4828	0.5047	0.2708	0.013*	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Tl1	0.00946 (12)	0.01138 (12)	0.01117 (12)	-0.00463 (9)	-0.00049 (9)	-0.00006 (9)
Tl2	0.01643 (14)	0.01862 (14)	0.00967 (13)	-0.00101 (10)	0.00066 (10)	0.00088 (10)
P1	0.0291 (10)	0.0340 (10)	0.0090 (8)	-0.0260 (9)	-0.0018 (7)	0.0005 (7)
P2	0.0088 (7)	0.0092 (7)	0.0072 (7)	-0.0023 (6)	0.0003 (6)	0.0001 (6)
P3	0.0081 (7)	0.0095 (7)	0.0080 (7)	-0.0021 (6)	0.0001 (6)	0.0003 (6)
O1	0.048 (3)	0.031 (2)	0.028 (2)	-0.026 (2)	0.006 (2)	-0.0084 (19)
O2	0.023 (2)	0.051 (3)	0.027 (2)	-0.0233 (19)	-0.0095 (18)	0.0074 (19)
O3	0.011 (2)	0.012 (2)	0.013 (2)	-0.0062 (17)	-0.0001 (18)	0.0018 (17)
O4	0.023 (2)	0.010 (2)	0.011 (2)	-0.0034 (18)	-0.0045 (19)	-0.0010 (17)
O5	0.010 (2)	0.020 (2)	0.011 (2)	-0.0038 (18)	0.0011 (18)	0.0028 (18)
O6	0.010 (2)	0.010 (2)	0.015 (2)	-0.0028 (17)	-0.0031 (18)	0.0090 (17)

O7	0.020 (2)	0.012 (2)	0.011 (2)	-0.0045 (19)	-0.0062 (19)	0.0013 (17)
O8	0.010 (2)	0.009 (2)	0.012 (2)	-0.0033 (17)	0.0013 (17)	-0.0001 (16)
O9	0.011 (2)	0.013 (2)	0.014 (2)	0.0010 (18)	-0.0017 (18)	-0.0027 (18)
N1	0.009 (2)	0.011 (2)	0.007 (2)	-0.005 (2)	0.0031 (19)	-0.0031 (19)
C1	0.009 (3)	0.016 (3)	0.014 (3)	-0.007 (2)	-0.001 (2)	-0.004 (2)
C2	0.006 (3)	0.011 (3)	0.007 (3)	-0.001 (2)	0.002 (2)	-0.001 (2)
C3	0.010 (3)	0.012 (3)	0.009 (3)	-0.003 (2)	0.004 (2)	-0.006 (2)

*Geometric parameters (Å, °)*

Tl1—O8	2.555 (4)	P3—C3	1.830 (6)
Tl1—O5	2.569 (4)	O1—Tl2 <sup>iii</sup>	2.906 (5)
Tl1—O4 <sup>i</sup>	2.778 (4)	O1—H1O	0.8200
Tl1—O3 <sup>ii</sup>	3.159 (4)	O2—Tl2 <sup>vi</sup>	2.965 (5)
Tl2—O5 <sup>ii</sup>	2.870 (4)	O2—H2O	0.8201
Tl2—O8	2.871 (4)	O3—Tl2 <sup>ii</sup>	2.926 (4)
Tl2—O1 <sup>iii</sup>	2.906 (5)	O3—Tl1 <sup>ii</sup>	3.159 (4)
Tl2—O3	2.922 (4)	O4—Tl1 <sup>i</sup>	2.778 (4)
Tl2—O3 <sup>ii</sup>	2.926 (4)	O5—Tl2 <sup>ii</sup>	2.870 (4)
Tl2—O2 <sup>iv</sup>	2.965 (5)	O6—H6O	0.8200
Tl2—O9 <sup>v</sup>	3.159 (4)	O7—H7O	0.8201
P1—O3	1.501 (4)	O9—Tl2 <sup>v</sup>	3.159 (4)
P1—O2	1.522 (5)	N1—C3	1.506 (7)
P1—O1	1.529 (6)	N1—C1	1.510 (7)
P1—C1	1.829 (6)	N1—C2	1.517 (7)
P2—O5	1.502 (5)	N1—H1N	0.8699
P2—O4	1.512 (4)	C1—H1A	0.9900
P2—O6	1.552 (4)	C1—H1B	0.9900
P2—C2	1.823 (6)	C2—H2A	0.9900
P3—O9	1.503 (4)	C2—H2B	0.9900
P3—O8	1.507 (4)	C3—H3A	0.9900
P3—O7	1.576 (4)	C3—H3B	0.9900
O8—Tl1—O5	82.65 (14)	O9—P3—O7	109.6 (2)
O8—Tl1—O4 <sup>i</sup>	73.72 (13)	O8—P3—O7	112.4 (2)
O5—Tl1—O4 <sup>i</sup>	90.64 (13)	O9—P3—C3	105.9 (3)
O8—Tl1—O3 <sup>ii</sup>	84.83 (12)	O8—P3—C3	104.2 (3)
O5—Tl1—O3 <sup>ii</sup>	80.14 (12)	O7—P3—C3	105.6 (3)
O4 <sup>i</sup> —Tl1—O3 <sup>ii</sup>	157.62 (11)	P1—O1—Tl2 <sup>iii</sup>	140.5 (3)
O8—Tl1—Tl2	42.43 (9)	P1—O1—H1O	131.2
O5—Tl1—Tl2	88.38 (10)	Tl2 <sup>iii</sup> —O1—H1O	87.0
O4 <sup>i</sup> —Tl1—Tl2	115.70 (8)	P1—O2—Tl2 <sup>vi</sup>	142.9 (3)
O3 <sup>ii</sup> —Tl1—Tl2	44.31 (7)	P1—O2—H2O	122.8
O5 <sup>ii</sup> —Tl2—O8	153.26 (12)	Tl2 <sup>vi</sup> —O2—H2O	91.4
O5 <sup>ii</sup> —Tl2—O1 <sup>iii</sup>	90.93 (14)	P1—O3—Tl2	131.5 (2)

## supplementary materials

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O8—T12—O1 <sup>iii</sup>	94.48 (13)	P1—O3—T12 <sup>ii</sup>	121.5 (2)
O5 <sup>ii</sup> —T12—O3	79.76 (12)	T12—O3—T12 <sup>ii</sup>	106.77 (13)
O8—T12—O3	76.90 (12)	P1—O3—T11 <sup>ii</sup>	95.14 (19)
O1 <sup>iii</sup> —T12—O3	72.87 (14)	T12—O3—T11 <sup>ii</sup>	91.85 (11)
O5 <sup>ii</sup> —T12—O3 <sup>ii</sup>	76.88 (12)	T12 <sup>ii</sup> —O3—T11 <sup>ii</sup>	86.74 (11)
O8—T12—O3 <sup>ii</sup>	84.01 (11)	P2—O4—T11 <sup>i</sup>	130.9 (2)
O1 <sup>iii</sup> —T12—O3 <sup>ii</sup>	145.49 (14)	P2—O5—T11	130.2 (2)
O3—T12—O3 <sup>ii</sup>	73.23 (13)	P2—O5—T12 <sup>ii</sup>	122.6 (2)
O5 <sup>ii</sup> —T12—O2 <sup>iv</sup>	123.69 (14)	T11—O5—T12 <sup>ii</sup>	106.85 (15)
O8—T12—O2 <sup>iv</sup>	66.41 (13)	P2—O6—H6O	119.1
O1 <sup>iii</sup> —T12—O2 <sup>iv</sup>	137.28 (16)	P3—O7—H7O	111.0
O3—T12—O2 <sup>iv</sup>	132.04 (14)	P3—O8—T11	141.1 (2)
O3 <sup>ii</sup> —T12—O2 <sup>iv</sup>	73.22 (14)	P3—O8—T12	118.2 (2)
O5 <sup>ii</sup> —T12—O9 <sup>v</sup>	76.06 (12)	T11—O8—T12	100.67 (13)
O8—T12—O9 <sup>v</sup>	129.64 (11)	P3—O9—T12 <sup>v</sup>	141.9 (3)
O1 <sup>iii</sup> —T12—O9 <sup>v</sup>	92.73 (14)	C3—N1—C1	111.4 (4)
O3—T12—O9 <sup>v</sup>	151.59 (11)	C3—N1—C2	112.6 (4)
O3 <sup>ii</sup> —T12—O9 <sup>v</sup>	114.72 (11)	C1—N1—C2	112.4 (4)
O2 <sup>iv</sup> —T12—O9 <sup>v</sup>	74.91 (13)	C3—N1—H1N	95.5
O5 <sup>ii</sup> —T12—T11	125.55 (9)	C1—N1—H1N	113.9
O8—T12—T11	36.90 (8)	C2—N1—H1N	109.9
O1 <sup>iii</sup> —T12—T11	129.09 (10)	N1—C1—P1	110.2 (4)
O3—T12—T11	79.78 (8)	N1—C1—H1A	109.6
O3 <sup>ii</sup> —T12—T11	48.95 (8)	P1—C1—H1A	109.6
O2 <sup>iv</sup> —T12—T11	52.33 (11)	N1—C1—H1B	109.6
O9 <sup>v</sup> —T12—T11	126.82 (8)	P1—C1—H1B	109.6
O3—P1—O2	115.2 (3)	H1A—C1—H1B	108.1
O3—P1—O1	114.5 (3)	N1—C2—P2	110.9 (4)
O2—P1—O1	108.2 (3)	N1—C2—H2A	109.5
O3—P1—C1	106.0 (3)	P2—C2—H2A	109.5
O2—P1—C1	104.8 (3)	N1—C2—H2B	109.5
O1—P1—C1	107.4 (3)	P2—C2—H2B	109.5
O5—P2—O4	117.4 (3)	H2A—C2—H2B	108.1
O5—P2—O6	111.2 (2)	N1—C3—P3	110.7 (4)
O4—P2—O6	112.0 (3)	N1—C3—H3A	109.5
O5—P2—C2	106.8 (3)	P3—C3—H3A	109.5
O4—P2—C2	104.8 (3)	N1—C3—H3B	109.5
O6—P2—C2	103.2 (3)	P3—C3—H3B	109.5
O9—P3—O8	118.1 (3)	H3A—C3—H3B	108.1
O8—T11—T12—O5 <sup>ii</sup>	-151.22 (18)	O5—P2—O4—T11 <sup>i</sup>	132.5 (3)
O5—T11—T12—O5 <sup>ii</sup>	-70.36 (17)	O6—P2—O4—T11 <sup>i</sup>	-97.0 (3)
O4 <sup>i</sup> —T11—T12—O5 <sup>ii</sup>	-160.29 (15)	C2—P2—O4—T11 <sup>i</sup>	14.2 (4)
O3 <sup>ii</sup> —T11—T12—O5 <sup>ii</sup>	7.15 (15)	O4—P2—O5—T11	-51.5 (4)



O5—T11—T12—O8	80.86 (17)	O6—P2—O5—T11	177.6 (3)
O4 <sup>i</sup> —T11—T12—O8	-9.07 (17)	C2—P2—O5—T11	65.7 (4)
O3 <sup>ii</sup> —T11—T12—O8	158.37 (18)	O4—P2—O5—T12 <sup>ii</sup>	136.2 (3)
O8—T11—T12—O1 <sup>iii</sup>	-23.9 (2)	O6—P2—O5—T12 <sup>ii</sup>	5.3 (3)
O5—T11—T12—O1 <sup>iii</sup>	56.95 (18)	C2—P2—O5—T12 <sup>ii</sup>	-106.6 (3)
O4 <sup>i</sup> —T11—T12—O1 <sup>iii</sup>	-32.99 (19)	O8—T11—O5—P2	-77.8 (3)
O3 <sup>ii</sup> —T11—T12—O1 <sup>iii</sup>	134.46 (19)	O4 <sup>i</sup> —T11—O5—P2	-4.3 (3)
O8—T11—T12—O3	-81.77 (16)	O3 <sup>ii</sup> —T11—O5—P2	-163.8 (3)
O5—T11—T12—O3	-0.90 (12)	T12—T11—O5—P2	-120.0 (3)
O4 <sup>i</sup> —T11—T12—O3	-90.84 (13)	O8—T11—O5—T12 <sup>ii</sup>	95.39 (16)
O3 <sup>ii</sup> —T11—T12—O3	76.60 (15)	O4 <sup>i</sup> —T11—O5—T12 <sup>ii</sup>	168.88 (15)
O8—T11—T12—O3 <sup>ii</sup>	-158.37 (18)	O3 <sup>ii</sup> —T11—O5—T12 <sup>ii</sup>	9.39 (13)
O5—T11—T12—O3 <sup>ii</sup>	-77.51 (15)	T12—T11—O5—T12 <sup>ii</sup>	53.19 (12)
O4 <sup>i</sup> —T11—T12—O3 <sup>ii</sup>	-167.44 (15)	O9—P3—O8—T11	137.8 (3)
O8—T11—T12—O2 <sup>iv</sup>	100.75 (19)	O7—P3—O8—T11	8.7 (5)
O5—T11—T12—O2 <sup>iv</sup>	-178.39 (16)	C3—P3—O8—T11	-105.1 (4)
O4 <sup>i</sup> —T11—T12—O2 <sup>iv</sup>	91.67 (17)	O9—P3—O8—T12	-39.7 (3)
O3 <sup>ii</sup> —T11—T12—O2 <sup>iv</sup>	-100.88 (17)	O7—P3—O8—T12	-168.8 (2)
O8—T11—T12—O9 <sup>v</sup>	109.29 (17)	C3—P3—O8—T12	77.3 (3)
O5—T11—T12—O9 <sup>v</sup>	-169.85 (14)	O5—T11—O8—P3	86.5 (4)
O4 <sup>i</sup> —T11—T12—O9 <sup>v</sup>	100.22 (15)	O4 <sup>i</sup> —T11—O8—P3	-6.3 (4)
O3 <sup>ii</sup> —T11—T12—O9 <sup>v</sup>	-92.34 (15)	O3 <sup>ii</sup> —T11—O8—P3	167.2 (4)
O3—P1—O1—T12 <sup>iii</sup>	173.5 (4)	T12—T11—O8—P3	-177.8 (5)
O2—P1—O1—T12 <sup>iii</sup>	43.6 (5)	O5—T11—O8—T12	-95.68 (14)
C1—P1—O1—T12 <sup>iii</sup>	-69.0 (5)	O4 <sup>i</sup> —T11—O8—T12	171.49 (16)
O3—P1—O2—T12 <sup>vi</sup>	-143.4 (4)	O3 <sup>ii</sup> —T11—O8—T12	-14.98 (12)
O1—P1—O2—T12 <sup>vi</sup>	-13.9 (6)	O5 <sup>ii</sup> —T12—O8—P3	-121.0 (3)
C1—P1—O2—T12 <sup>vi</sup>	100.4 (5)	O1 <sup>iii</sup> —T12—O8—P3	-20.0 (3)
O2—P1—O3—T12	144.1 (3)	O3—T12—O8—P3	-91.2 (2)
O1—P1—O3—T12	17.7 (4)	O3 <sup>ii</sup> —T12—O8—P3	-165.3 (3)
C1—P1—O3—T12	-100.5 (3)	O2 <sup>iv</sup> —T12—O8—P3	120.4 (3)
O2—P1—O3—T12 <sup>ii</sup>	-42.3 (4)	O9 <sup>v</sup> —T12—O8—P3	77.3 (3)
O1—P1—O3—T12 <sup>ii</sup>	-168.6 (3)	T11—T12—O8—P3	178.4 (3)
C1—P1—O3—T12 <sup>ii</sup>	73.1 (3)	O5 <sup>ii</sup> —T12—O8—T11	60.5 (3)
O2—P1—O3—T11 <sup>ii</sup>	47.0 (3)	O1 <sup>iii</sup> —T12—O8—T11	161.60 (16)
O1—P1—O3—T11 <sup>ii</sup>	-79.3 (3)	O3—T12—O8—T11	90.36 (14)
C1—P1—O3—T11 <sup>ii</sup>	162.5 (2)	O3 <sup>ii</sup> —T12—O8—T11	16.23 (13)
O5 <sup>ii</sup> —T12—O3—P1	-106.4 (3)	O2 <sup>iv</sup> —T12—O8—T11	-58.05 (16)
O8—T12—O3—P1	86.7 (3)	O9 <sup>v</sup> —T12—O8—T11	-101.10 (16)
O1 <sup>iii</sup> —T12—O3—P1	-12.2 (3)	O8—P3—O9—T12 <sup>v</sup>	-15.8 (5)
O3 <sup>ii</sup> —T12—O3—P1	174.3 (4)	O7—P3—O9—T12 <sup>v</sup>	114.7 (4)

## supplementary materials

O2 <sup>iv</sup> —Tl2—O3—P1	127.0 (3)	C3—P3—O9—Tl2 <sup>v</sup>	-131.9 (4)
O9 <sup>v</sup> —Tl2—O3—P1	-74.5 (4)	C3—N1—C1—P1	80.8 (5)
Tl1—Tl2—O3—P1	124.3 (3)	C2—N1—C1—P1	-151.7 (4)
O5 <sup>ii</sup> —Tl2—O3—Tl2 <sup>ii</sup>	79.25 (14)	O3—P1—C1—N1	33.2 (5)
O8—Tl2—O3—Tl2 <sup>ii</sup>	-87.61 (13)	O2—P1—C1—N1	155.5 (4)
O1 <sup>iii</sup> —Tl2—O3—Tl2 <sup>ii</sup>	173.44 (17)	O1—P1—C1—N1	-89.7 (5)
O3 <sup>ii</sup> —Tl2—O3—Tl2 <sup>ii</sup>	0.0	C3—N1—C2—P2	-152.4 (4)
O2 <sup>iv</sup> —Tl2—O3—Tl2 <sup>ii</sup>	-47.3 (2)	C1—N1—C2—P2	80.8 (5)
O9 <sup>v</sup> —Tl2—O3—Tl2 <sup>ii</sup>	111.2 (2)	O5—P2—C2—N1	39.1 (4)
Tl1—Tl2—O3—Tl2 <sup>ii</sup>	-50.01 (10)	O4—P2—C2—N1	164.3 (4)
O5 <sup>ii</sup> —Tl2—O3—Tl1 <sup>ii</sup>	-7.90 (11)	O6—P2—C2—N1	-78.3 (4)
O8—Tl2—O3—Tl1 <sup>ii</sup>	-174.76 (12)	C1—N1—C3—P3	-156.6 (4)
O1 <sup>iii</sup> —Tl2—O3—Tl1 <sup>ii</sup>	86.28 (14)	C2—N1—C3—P3	76.0 (5)
O3 <sup>ii</sup> —Tl2—O3—Tl1 <sup>ii</sup>	-87.15 (13)	O9—P3—C3—N1	156.2 (4)
O2 <sup>iv</sup> —Tl2—O3—Tl1 <sup>ii</sup>	-134.49 (15)	O8—P3—C3—N1	31.0 (4)
O9 <sup>v</sup> —Tl2—O3—Tl1 <sup>ii</sup>	24.0 (3)	O7—P3—C3—N1	-87.6 (4)
Tl1—Tl2—O3—Tl1 <sup>ii</sup>	-137.17 (9)		

Symmetry codes: (i)  $-x+1, -y, -z$ ; (ii)  $-x+1, -y, -z+1$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $x-1, y, z$ ; (v)  $-x, -y+1, -z+1$ ; (vi)  $x+1, y, z$ .

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ O3	0.87	2.39	2.882 (5)	116
N1—H1N $\cdots$ O5	0.87	2.53	2.957 (6)	111
N1—H1N $\cdots$ O8	0.87	2.19	2.837 (7)	131
O1—H1O $\cdots$ O1 <sup>iii</sup>	0.82	1.78	2.504 (8)	147
O2—H2O $\cdots$ O2 <sup>vii</sup>	0.82	1.68	2.497 (7)	171
O6—H6O $\cdots$ O9 <sup>viii</sup>	0.82	1.67	2.484 (6)	171
O7—H7O $\cdots$ O4 <sup>i</sup>	0.82	1.70	2.521 (6)	180

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

Fig. 1

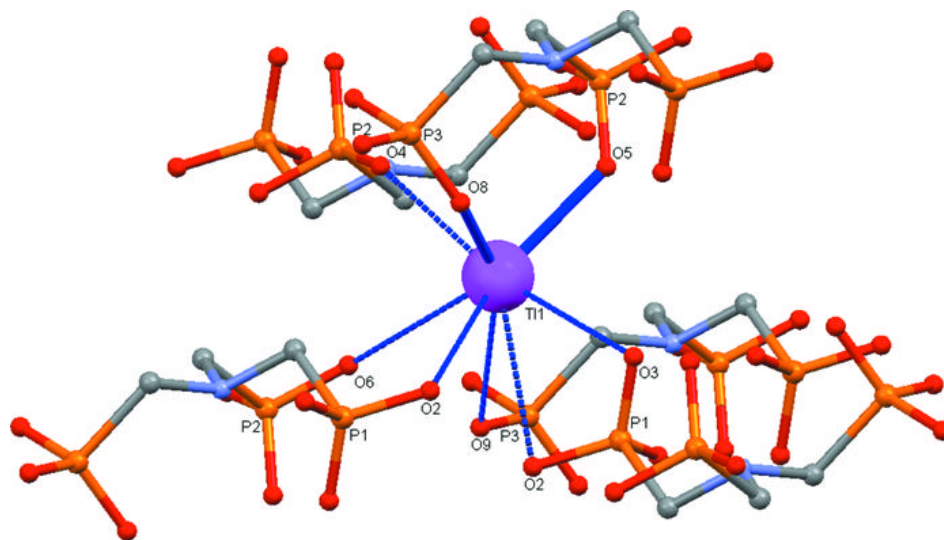


Fig. 2

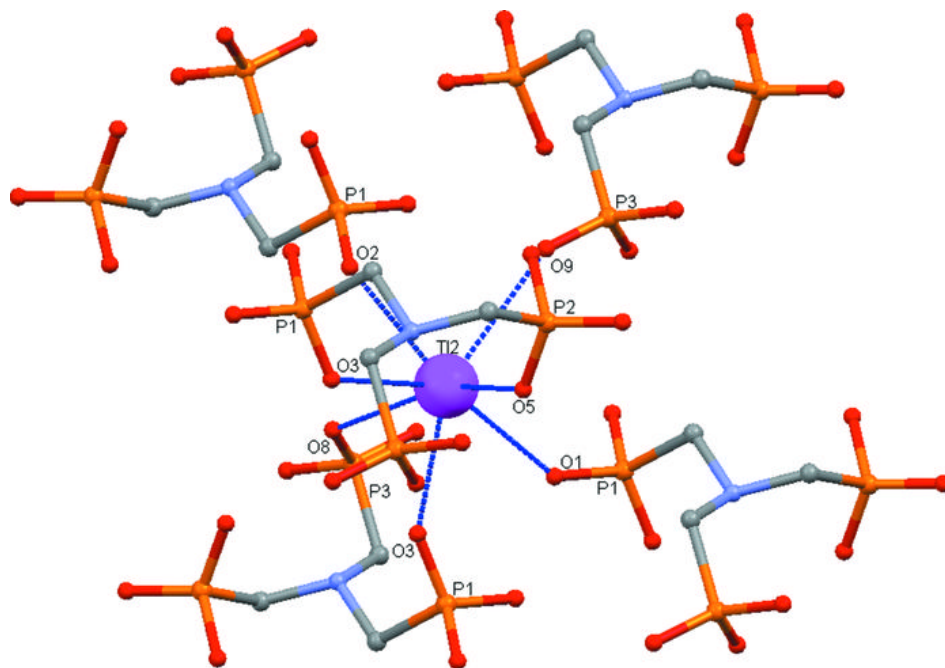


Fig. 3

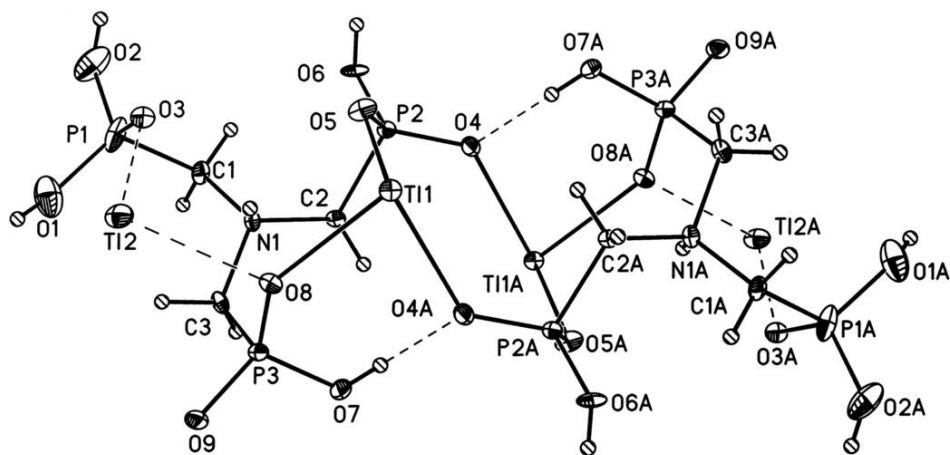


Fig. 4

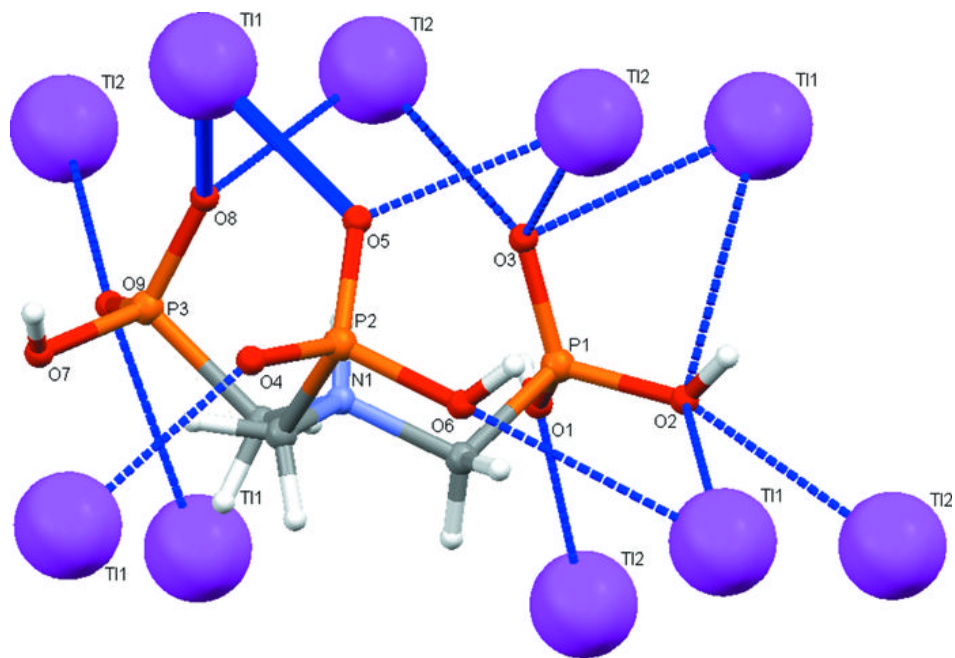


Fig. 5

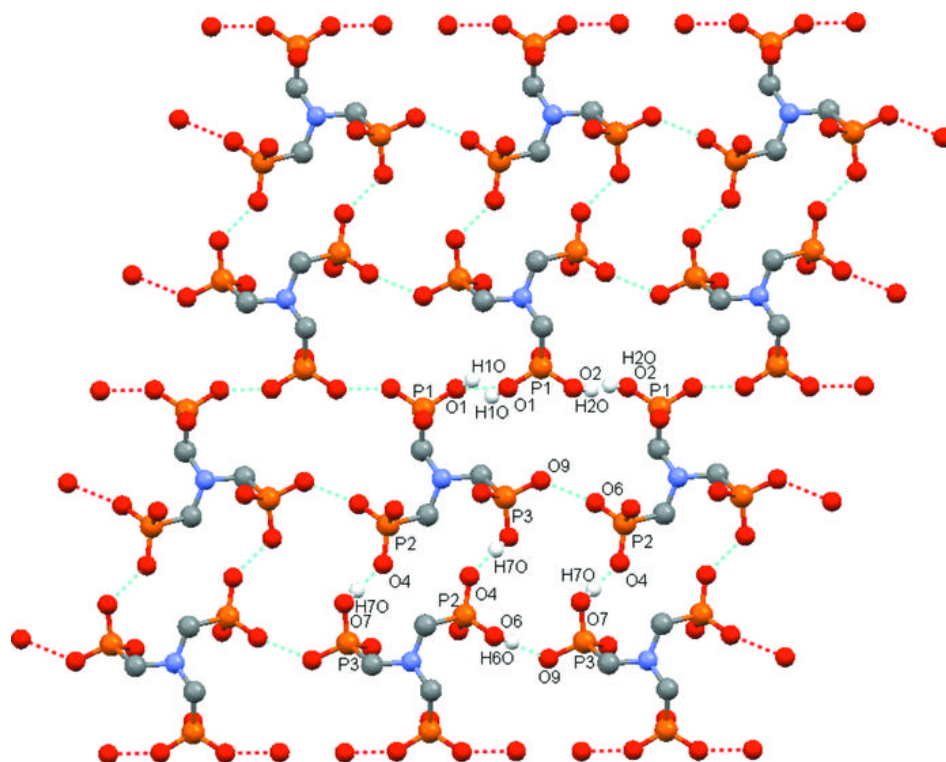


Fig. 6

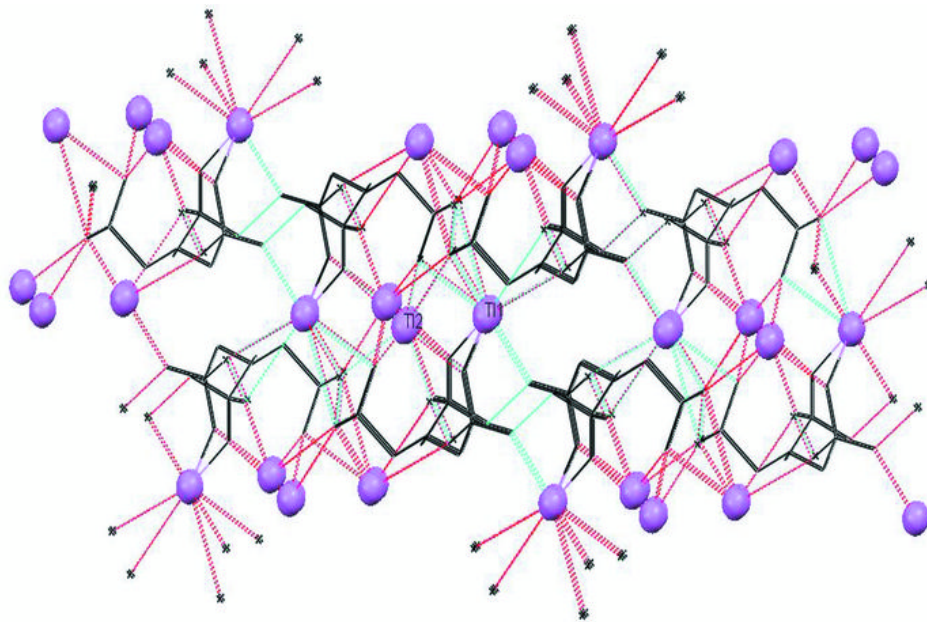




Fig. 7

