

## Tetramethyllead(IV) at 150 K

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## Key indicators

Single-crystal X-ray study

$T = 150\text{ K}$

Mean  $\sigma(\text{Pb}-\text{C}) = 0.008\text{ \AA}$

$R$  factor = 0.033

$wR$  factor = 0.105

Data-to-parameter ratio = 33.9

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

Tetramethyllead,  $[\text{Pb}(\text{CH}_3)_4]$ , crystallizes in the cubic space group  $P\bar{a}3$ , with the Pb atom and one C atom on a crystallographic threefold axis. The average Pb—C distance is 2.211 (11) Å. The crystal structure is isostructural with that of the Sn analogue, and adopts the  $\text{SnI}_4$ -type structure.

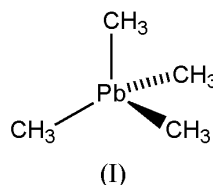
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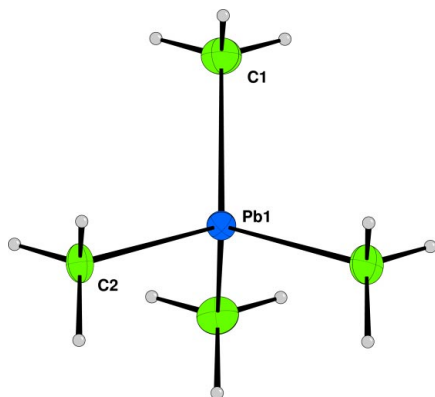
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## Comment

Tetramethyl lead, (I), is a compound that has been widely used in the past as an 'anti-knock' additive in gasoline (Salooja, 1967), and as a precursor for the preparation of lead chalcogenides by chemical vapour deposition (Manasevit *et al.*, 1986). It exists under normal conditions as a volatile liquid (m.p. 243 K) with a normal boiling point of approximately 383 K. An electron-diffraction study has shown that, in the gas phase, the molecule is tetrahedral with a Pb—C bond length of 2.24 (2) Å (Oyamada *et al.*, 1971). Inelastic neutron scattering studies of the solid assumed the same space group ( $P\bar{a}3$ ) and number of molecules within the unit cell as for  $\text{Sn}(\text{CH}_3)_4$ , and showed that, on the basis of tunnelling spectra, one of the methyl groups is hindered by a higher rotational barrier, suggesting that the molecule is compressed along a threefold axis (Prager & Müller-Warmuth, 1984*a,b*).



In agreement with the inelastic neutron scattering study,  $\text{Pb}(\text{CH}_3)_4$  crystallizes in the cubic crystal system, space group  $P\bar{a}3$ , with  $Z = 8$ , and is isomorphous with  $\text{Sn}(\text{CH}_3)_4$  (Krebs *et al.*, 1989). As pointed out previously by Krebs, the structure is of the  $\text{SnI}_4$  type, with the Pb atom residing on a crystallographic threefold axis. The structure shows isolated regular tetrahedral molecules, with an average Pb—C bond length of 2.211 (11) Å (Fig. 1). A riding correction for librational motion (*XP*; Sheldrick, 1997) increases this average to 2.24 Å, in excellent agreement with that found for the molecule in the gas phase and typical of Pb—C distances found for other organolead compounds, *e.g.*  $\text{PbPh}_4$  (Preut & Huber, 1993),  $\text{Pb}(o\text{-tolyl})_4$  (Schneider & Dräger, 1991),  $\text{Pb}(m\text{-tolyl})_4$  (Schneider-Koglin *et al.*, 1994) and  $\text{Pb}(p\text{-tolyl})_4$  (Schneider-Koglin *et al.*, 1993). Unlike  $\text{Pb}(\text{CH}_3)_4$ , however, several of these compounds show a distortion from regular tetrahedral geometry, such that they are compressed along a molecular  $S_4$



**Figure 1**  
The structure of  $\text{Pb}(\text{CH}_3)_4$  in the crystal. Ellipsoids are drawn at the 50% probability level.

axis, e.g. the two sets of C—Pb—C angles in  $\text{Pb}(p\text{-tolyl})_4$  are 115.4 (3) and 106.6 (1)° (Schneider-Koglin *et al.*, 1993). This is presumably a consequence of the anisotropy of the steric effects of these substituents. The present study illustrates the value of studying the crystal structures of very simple molecules where steric influences are small or, at least, more isotropic.

In  $\text{Sn}(\text{CH}_3)_4$  there is a small but significant difference between the two unique Sn—C bond lengths, with Sn—C1 measuring 2.102 (8) Å and Sn—C2 2.138 (6) Å, which is consistent with the inelastic neutron-scattering results. In  $\text{Pb}(\text{CH}_3)_4$ , Pb1—C1 is also shorter than Pb1—C2, but here the difference is not statistically significant.

## Experimental

Tetramethyllead was prepared by the method of Gilman & Jones (1950) and its purity checked by reference to its  $^1\text{H}$  NMR spectrum. A single crystal was grown in a Pyrex capillary mounted on a Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems low-temperature device. After establishing a solid-liquid equilibrium at 243 K, the sample was cooled to 235 K at a rate of 120 K  $\text{h}^{-1}$ . This caused the sample to crystallize into one continuous crystalline column of length 3 mm and outer diameter 0.4 mm. The crystal was therefore much larger than the diameter of the X-ray beam (0.5 mm). This is frequently an issue in *in situ* crystallization experiments on low-melting compounds, where there is little experimental control over the length of a crystal. Görbitz (1999) has shown that multi-scan absorption correction procedures are quite efficient for large crystals, although the subject of that work was a modestly absorbing ‘organic’ crystal. The refinement statistics presented here suggest, however, that an effective correction has been made for absorption in the case of the data set collected for  $\text{PbMe}_4$  (it was, anyway, not possible to measure the faces of the sample, making a numerical absorption unfeasible). It is possible that the efficiency of the procedure relied here on the smooth variation of transmission factors of the inclined cylindrical sample (the  $\chi$  angle is held at a constant value of 54.78° on most SMART diffractometers) as a function of  $\omega$  and the very high data redundancy obtained for this cubic crystal.

## Crystal data

$[\text{Pb}(\text{CH}_3)_4]$   
 $M_r = 267.34$   
Cubic,  $P\bar{a}3$   
 $a = 11.1725$  (6) Å  
 $V = 1394.60$  (13) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 2.546$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation

Cell parameters from 3546 reflections  
 $\theta = 3\text{--}28.5^\circ$   
 $\mu = 24.07$  mm<sup>-1</sup>  
 $T = 150$  K  
Cylinder, colourless  
3.0 mm (length)  $\times$  0.20 mm (radius)

## Data collection

Bruker SMART APEX CCD diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan [SADABS (Sheldrick, 2002), based on the method of Blessing (1995)]  
 $T_{\text{min}} = 0.111$ ,  $T_{\text{max}} = 1.000$

7703 measured reflections  
586 independent reflections  
375 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.062$   
 $\theta_{\text{max}} = 28.6^\circ$   
 $h = -13 \rightarrow 14$   
 $k = -14 \rightarrow 14$   
 $l = -7 \rightarrow 14$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.105$   
 $S = 1.07$   
577 reflections  
17 parameters  
H-atom parameters not refined

Weighting scheme: see text  
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.55$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.84$  e Å<sup>-3</sup>  
Extinction correction: Larson (1970), equation 22  
Extinction coefficient: 139 (12)

**Table 1**

Selected geometric parameters (Å, °).

Pb1—C1	2.194 (15)	Pb1—C2	2.216 (7)
C2—Pb1—C1	108.96 (16)	C2—Pb1—C2 <sup>i</sup>	109.98 (16)

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

A Tukey & Prince (Carruthers & Watkin, 1979) weighting scheme was used, with weight =  $w[1 - \{\Delta F/6\sigma(F)\}^2]$ , where  $w$  is given by a five-term Chebychev polynomial with coefficients: 96.4, 162.0, 107.0, 51.2 and 13.7. H atoms were placed geometrically and constrained, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The final difference map extremes were within 1 Å of the Pb atom.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: CRYSTALS (Watkin *et al.*, 2001); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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