Lead(IV) chloride at 150 K

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Key indicators

Single-crystal X-ray study

$T = 150$ K

Mean σ(Pb–Cl) = 0.003 Å

R factor = 0.019

wR factor = 0.057

Data-to-parameter ratio = 21.4

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

Lead(IV) chloride, $PbCl_4$, is a volatile air-sensitive liquid under ambient conditions. The crystal structure consists of tetrahedral molecules residing on crystallographic twofold axes, with no intermolecular interactions within the sum of van der Waals radii. Unlike the lighter Group 14 analogues, which are based on hexagonal close packing of Cl atoms, the Cl atoms in $PbCl_4$ form a cubic close-packed array.

Comment

Lead(IV) chloride exists under ambient conditions as a volatile air-sensitive liquid, with a melting point of 258 K (Biltz & Meinecke, 1923). The compound is thermally fragile and decomposes readily under ambient conditions to give lead(II) chloride and chlorine. A gas electron-diffraction study of the vapour has shown the presence of tetrahedral molecules with a Pb—Cl bond length of 2.373 (3) Å (Haaland *et al.*, 1992). Vibrational spectra of the liquid and solid also suggest a structure composed of essentially isolated tetrahedral molecules (Clark & Willis, 1971; Clark & Hunter, 1971), in contrast to the pseudo-octahedral geometries found for lead in PbF_4 (Bork & Hoppe, 1996).

(I)
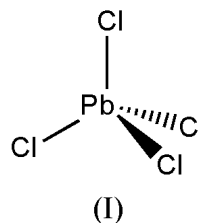
The crystal structures of the Group 14 tetrachlorides, MCl_4, have been reported for M = C (Piermarini, 1973), Si (Zakharov *et al.*, 1986), Ge (Merz & Driess, 2002) and Sn (Reuter & Pawlak, 2000). They form an isostructural series, being monoclinic, $P2_1/c$, with cell dimensions in the ranges a = 9.07–9.86, b = 5.76–6.68 and c = 9.20–9.94 Å, which all increase as the group is descended from carbon to tin. All structures have values of β in the range 103–105°. The structures consist of isolated tetrahedral MCl_4 molecules.

The structure of lead(IV) chloride also consists of essentially isolated tetrahedral molecules of $PbCl_4$ (Fig. 1). However, though the crystal system is monoclinic, the lattice type is centred (*I*-centred in the setting given here) rather than primitive, and it is clear that this compound does not follow the trend established by the lighter members of Group 14. The molecule resides on a crystallographic twofold axis at (3/4, y, 0), where y is very close to 1/4. This introduces a pseudo-*C*-centring operation into the lead positions, with the
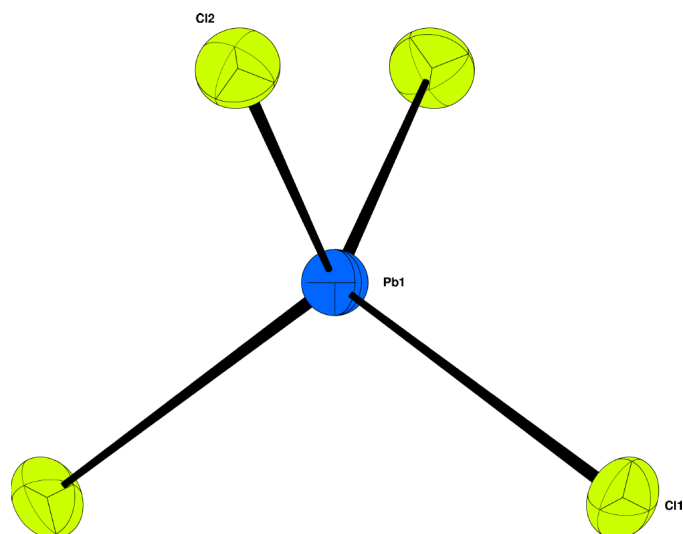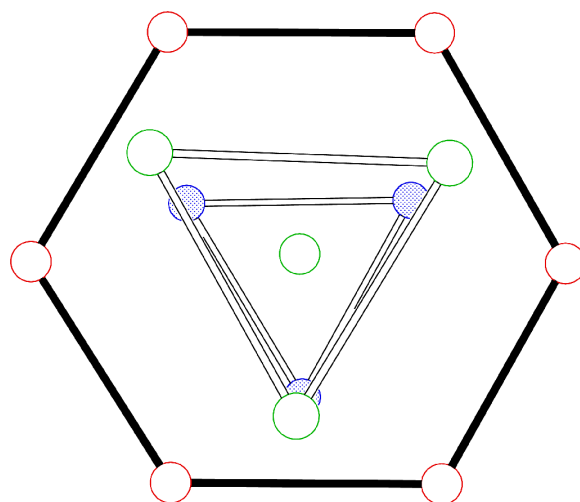
Figure 1
The structure of $PbCl_4$ in the crystal. The view is along the b axis, and the ellipsoids enclose 50% probability surfaces.
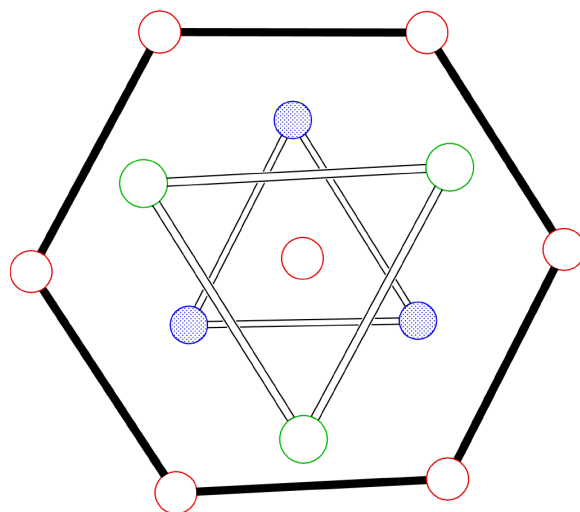

Figure 2
The hexagonal close packing of the Cl atoms in $SnCl_4$. The geometry around atom Cl1 is shown.

Figure 3
The cubic close packing of the Cl atoms in $PbCl_4$. The geometry around atom Cl1 is shown.

result that, though the mean I/σ for the data set as a whole is 27.1, that for data with $h + k \neq 2n$ is only 5.4. There is also pseudosymmetry in the Cl positions, and this is discussed in more detail below. The Pb—Cl bond lengths are 2.360 (2) and 2.363 (2) Å, which correspond to exactly one bond-valence unit (Brown, 2002).

The shortest Cl$\cdots$Cl contact observed in this structure is 3.661 (5) Å, which is slightly larger than twice the van der Waals radius of chlorine (3.5 Å; Bondi, 1964). The Pb$\cdots$Cl contacts are well outside the sum of the van der Waals radii of Pb and Cl (4.09 Å). There are concentric shells of Cl atoms around the lead atom, the first of them consisting of 12 Cl atoms at a distance of 4.340–4.455 (2) Å. The shortest Pb$\cdots$Pb distance is 5.359 (1) Å. As in the structures of the lighter analogues, therefore, there are no intermolecular contacts of any significance.

The structures of carbon, silicon, germanium and tin tetrachlorides can all be considered to be based on hexagonal close packing (h.c.p.) of Cl atoms (Reuter & Pawlak, 2000). Fig. 2 is taken from the structure of $SnCl_4$ and shows the ABA layers characteristic of h.c.p. arrays. By contrast the Cl atoms in $PbCl_4$ form a cubic close-packed (c.c.p.) array; Fig. 3 shows the characteristic ABC layering sequence. Deviations from ideal symmetry may be gauged using the continuous symmetry measure (CSM) parameter described by Pinsky & Avnir (1998). The collection of 13 atoms shown in Fig. 3 has a CSM of 0.044% relative to perfect c.c.p.; the corresponding figure for the geometry about Cl2 is 0.037%. For comparison, the CSM values for the four independent Cl atoms in $SnCl_4$ versus perfect h.c.p. are 0.103, 0.070, 0.073 and 0.081% for Cl1 to Cl4, respectively. The agreement with perfect close packing is excellent in both cases; the slightly larger deviations for perfect h.c.p. are to be expected, because the layer separation in h.c.p. is not restricted by symmetry.

Experimental

The sample of $PbCl_4$ was prepared by the reaction between pyridinium hexachloroplumbate(IV) and sulfuric acid according to the method of Kauffman et al. (1983).

Crystal data

$PbCl_4$	Mo $K\alpha$ radiation
$M_r = 349.01$	Cell parameters from 88
Monoclinic, $I2/a$	reflections
$a = 10.542 (8)$ Å	$\theta = 13–21°$
$b = 5.359 (3)$ Å	$\mu = 29.35$ mm^{-1}
$c = 11.958 (5)$ Å	$T = 150$ K
$\beta = 115.83 (2)°$	Cylinder, colourless
$V = 608.0 (6)$ Å^3	1.00 mm (length) $\times$ 0.20 mm
$Z = 4$	(diameter)
$D_x = 3.812$ Mg m^{-3}	

Data collection

Stoe Stadi-4 diffractometer	$R_{int} = 0.07$
ω/θ scans	$\theta_{max} = 25.0°$
Absorption correction: empirical	$h = -11 \rightarrow 12$
via ψ scans [XPREP (Sheldrick	$k = -6 \rightarrow 6$
(2001) based on method of North	$l = -14 \rightarrow 2$
et al. (1968)]	3 standard reflections
$T_{min} = 0.001$, $T_{max} = 0.002$	every 0 reflections
2322 measured reflections	frequency: 60 min
536 independent reflections	intensity decay: none
363 reflections with $I > 4\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$\Delta\rho_{max} = 1.64$ e Å^{-3}
$wR(F^2) = 0.057$	$\Delta\rho_{min} = -0.71$ e Å^{-3}
$S = 0.94$	Extinction correction: Larson
534 reflections	(1970), equation 22
25 parameters	Extinction coefficient: 51 (3)
Weighting scheme: see below	

Table 1
Selected geometric parameters (Å, °).

Pb1—Cl1	2.360 (2)	Pb1—Cl2	2.363 (2)
Cl1—Pb1—Cl1^i	110.01 (12)	Cl1—Pb1—Cl2^i	110.35 (8)
Cl1—Pb1—Cl2	107.86 (8)	Cl2—Pb1—Cl2^i	110.41 (12)

Symmetry code: (i) $\frac{3}{2} - x, y, -z$.

A stable solid–liquid equilibrium was established at 262 K in a sample of lead(IV) chloride held in a capillary mounted on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device. A crystal was then obtained by cooling the sample at a rate of 10 K h^{-1}. Data were collected at 150 K, a previous experiment having shown that the sample decomposed in the X-ray beam during data collection at 220 K.

The length of a crystal is difficult to control when growing a crystal of a low-melting compound in a capillary. It was almost certainly larger than the 0.8 mm collimator used. The value of μ is high, and a numerical absorption correction would normally be required. However, the cylindrical symmetry of the axially mounted sample meant that absorption anisotropy was low. A cylindrical absorption correction was attempted, and the results were satisfactory [$R(F) = 2.3\%$, $\Delta\rho_{max} = +1.8$ e Å^{-3}]. However, slightly better results were obtained by applying ψ scans, and these are the results presented here.

The highest difference Fourier peak was 0.935 Å from Pb1. A Tukey & Prince (Carruthers & Watkin, 1979) weighting scheme was used, with $w = [\text{weight}][1-(\Delta F/6\sigma F)^2]^2$, where [weight] is given by a four-term Chebychev polynomial with coefficients 43.7, 56.2, 32.6 and 13.2.

Continuous symmetry measures were calculated using a locally written program based on the procedure given by Pinsky & Avnir (1998).

The data for calculating bond valences were taken from http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/bond_valence_parm/.

Data collection: DIF4 (Stoe & Cie, 1990); cell refinement: DIF4; data reduction: REDU4 (Stoe & Cie, 1990); program(s) used to solve structure: DIRDIF96 (Beurskens et al., 1996); program(s) used to refine structure: CRYSTALS (Watkin et al., 2001); molecular graphics: CAMERON (Watkin et al., 1996) and XP (Sheldrick, 2001); software used to prepare material for publication: CRYSTALS.

References

Beurskens, P. T., Beurskens, G., Bosman, W. P., de Gelder, R., Garcia Granda, S., Gould, R. O., Israel, R. & Smits J. M. M. (1996). DIRDIF96. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Biltz, W. & Meinecke, E. (1923). Z. Anorg. Allg. Chem. 131, 1–21.
Bondi, A. (1964). J. Phys. Chem. 68, 441–451.
Bork, M. & Hoppe, R. (1996). Z. Anorg. Allg. Chem. 622, 1557–1563.
Brown, I. D. (2002). The Chemical Bond in Inorganic Chemistry: The Bond Valence Method. IUCr Monographs on Crystallography, Oxford University Press, Oxford, England.
Carruthers, J. R. & Watkin, D. J. (1979). Acta Cryst. A35, 698–699.
Clark, R. J. H. & Hunter, B. K. (1971). J. Chem. Soc. A, pp. 2999–3006.
Clark, R. J. H. & Willis, C. J. (1971). Inorg. Chem. 10, 1118–1126.
Haaland, A., Hammel, A., Martinsen, K.-G., Tremmel, J. & Volden, H.-V. (1992). J. Chem. Soc. Dalton Trans. pp. 2209–2214.
Kauffman, G. B., Kim, L. & Marino, D. F. (1983). Inorg. Synth. 22, 149–150.
Larson, A. C. (1970). Crystallogr. Comput. Proc. Int. Summer Sch., Meeting Date 1969, pp. 291–294.
Merz, K. & Driess, M. (2002). Acta Cryst. C58, i101–i102.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). Acta Cryst. A24, 351–359.
Piermarini, G. J. (1973). J. Chem. Phys. 58, 1974–1982.
Pinsky, M. & Avnir, D. (1998). Inorg. Chem. 37, 5575–5582.
Reuter, H. & Pawlak, R. (2000). Z. Anorg. Allg. Chem. 626, 925–929.
Sheldrick, G. M. (2001). XPREP and XP. University of Göttingen, Germany, and Bruker-Nonius, Madison, Wisconsin, USA.
Stoe & Cie (1990). DIF4 and REDU4. Stoe & Cie, Darmstadt, Germany.
Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper, R. I. (2001). CRYSTALS. Issue 11. Chemical Crystallography Laboratory, Oxford, England.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). CAMERON. Chemical Crystallography Laboratory, Oxford, England.
Zakharov, L. N., Antipin, M. Yu., Struchkov, Yu. T., Gusev, A. V., Gibin, A. M. & Zhernenkov, N. V. (1986). Kristallografiya, 31, 171–172.