

## Lead tartrate from X-ray powder diffraction data

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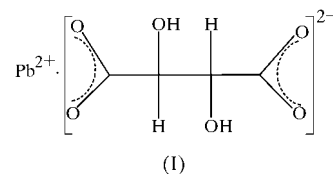
The structure of lead tartrate,  $\text{Pb}^{2+} \cdot \text{C}_4\text{H}_4\text{O}_6^{2-}$ , has been solved from X-ray powder diffraction data. The cation exhibits ninefold coordination and the tartrate groups are linked through  $\text{Pb} \cdots \text{O}$  contacts to form a three-dimensional network.

### Comment

The structure determination presented in this paper is part of a series of attempts to determine crystal structures from powder diffraction data (e.g. Goubitz *et al.*, 2001; Dova *et al.*, 2001). Crystal structure determination from single-crystal data has become a standard procedure in the last few decades, providing it is possible to grow suitable crystals. If only a powder is available, then structure determination is by no means a standard procedure. In the last ten years, a number of research groups have attempted to tackle this problem and a couple of program packages now exist, e.g. *POWSIM* (Jansen *et al.*, 1992*a,b*, 1993) and *SIRPOW* (Altomare *et al.*, 1994, 1995). These programs apply direct methods to solve the structure.

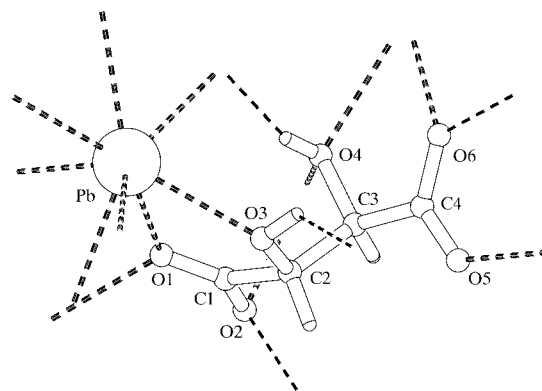
Recently, Harris *et al.* (2001) discussed the contemporary advances achieved using Monte Carlo, simulated annealing, grid search and genetic algorithm search methods as the basis of direct-space techniques for powder structure solution. The main problem in structure determination is the number of reflections with reliable intensity that can be extracted from a powder diffractogram. Particularly for lower symmetries (up to orthorhombic) and larger structures, the overlap of reflections often prevents the extraction of reliable intensities, especially at higher  $\theta$  values. The grid search technique (Chernyshev & Schenk, 1998) used here can overcome this problem for molecules with known conformation. Only the lower angle part of the diffractogram, where overlap of reflections is less severe, is needed to obtain a reliable estimate of the position and orientation of the molecule within the asymmetric unit. Such a solution can be used to refine the structure in a Rietveld refinement procedure.

The title compound, (I), is used as an additive in petroleum to prevent 'knocking' or 'pinging' in internal combustion engines. It is very toxic and is dangerous for the environment.



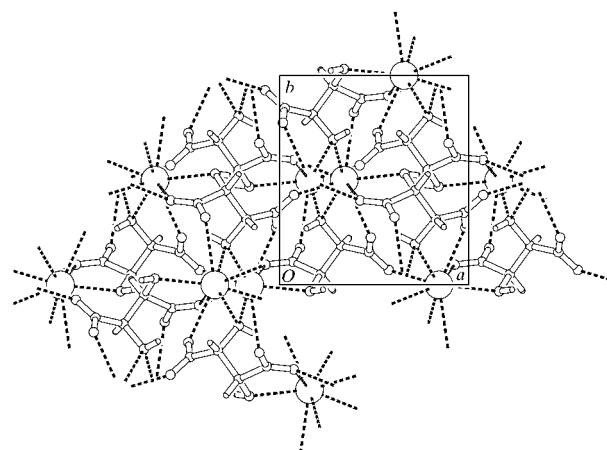
Compound (I) turned out to be isomorphous with barium tartrate (González-Silgo *et al.*, 1999). Bond lengths and angles in the tartrate anion of (I) are normal and do not deviate significantly from those of other reported tartrates with divalent cations, *i.e.*  $\text{Ca}^{2+}$  (Hawthorne *et al.*, 1982; Ambady, 1968),  $\text{Mn}^{2+}$  (Ruiz-Pérez *et al.*, 1996),  $\text{Ni}^{2+}$  (Bostelaar *et al.*, 1984),  $\text{Zn}^{2+}$  (Templeton *et al.*, 1985),  $\text{Sr}^{2+}$  (Ambady, 1968) and  $\text{Ba}^{2+}$  (González-Silgo *et al.*, 1999) (Table 1).

The C1/O1/O2/C2/O3 and C4/O5/O6/C3/O4 planes in (I) (Fig. 1) are flat [maximum deviation 0.08 (2) Å for atom C3], and the angle between these planes is 67.6 (6)°, which is close to the value of ~60° usually found in tartrates. The four C atoms assume a typical zigzag planar conformation [C1–C2–C3–C4 = –180 (1)°].



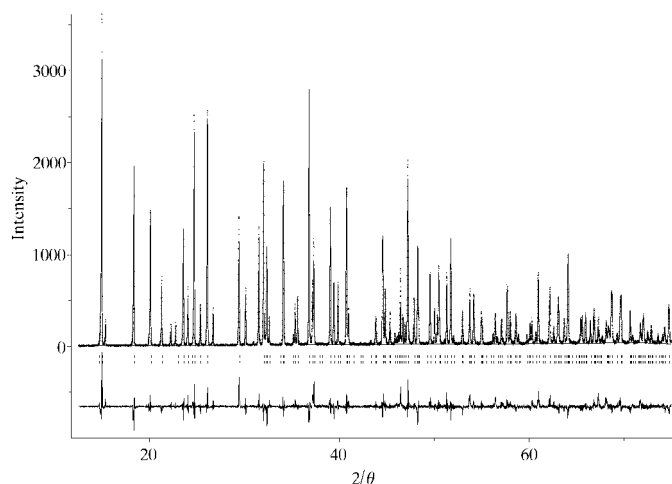
**Figure 1**

A molecular diagram of the tartrate anion and  $\text{Pb}^{2+}$  cation in (I), showing the atom-numbering scheme.



**Figure 2**

A packing diagram for (I), viewed along the *c* axis.



**Figure 3**  
A Rietveld plot for (I), showing the observed and difference profiles. The reflection positions are shown at the bottom.

The molecular packing of (I) is shown in Fig. 2. The  $\text{Pb}^{2+}$  cation is surrounded by six tartrate groups and is linked to nine O atoms (Table 2); the average  $\text{Pb}\cdots\text{O}$  distance is 2.780 (11) Å. In general, the  $\text{Pb}^{2+}$  cation has a coordination number of eight or ten (see, for example, the overview given by Rogers *et al.*, 1996); a coordination number of nine is also found in  $[\text{Pb}(18\text{-crown-6})(\text{CH}_3\text{CN})_3]$  (von Arnim *et al.*, 1993), in the lead(II) bromide complex with heptaethyleneglycol (Rogers *et al.*, 1996) and in  $[\text{Pb}_9\{\text{calix}[4]\text{diquinone diacid}\}_3(\text{ClO}_4)_6(\text{OH})_6]$  (Beer *et al.*, 2000). In the series of reported tartrates with divalent cations, ninefold coordination is also observed for  $\text{Ba}^{2+}$  (González-Silgo *et al.*, 1999), and eightfold coordination is found for  $\text{Ca}^{2+}$  (Hawthorne *et al.*, 1982; Ambady, 1968) and  $\text{Sr}^{2+}$  (Ambady, 1968), whereas  $\text{Mn}^{2+}$  (Ruiz-Pérez *et al.*, 1996),  $\text{Ni}^{2+}$  (Bostelaar *et al.*, 1984) and  $\text{Zn}^{2+}$  (Templeton *et al.*, 1985) are sixfold coordinated.

## Experimental

Lead tartrate was obtained from Fluka (purity  $\geq 98\%$ ) and used without further purification.

### Crystal data

$\text{Pb}^{2+}\cdot\text{C}_4\text{H}_4\text{O}_6^{2-}$   
 $M_r = 355.27$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 7.99482$  (3) Å  
 $b = 8.84525$  (4) Å  
 $c = 8.35318$  (4) Å  
 $V = 590.705$  (4) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 3.983$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation  
 $\mu = 55.35$  mm<sup>-1</sup>  
 $T = 295$  K  
 Specimen shape: flat sheet  
 20 mm (diameter)  $\times$  0.05 mm  
 (maximum thickness)  
 Particle morphology: no specific  
 habit, white

### Data collection

XPRT PRO Alpha-1  
 diffractometer  
 Specimen mounting: sprinkled as a  
 thin layer on the specimen  
 holder  
 Specimen mounted in reflection  
 mode

Absorption correction: *GSAS*  
 (Larson & Von Dreele, 1994)  
 absorption/surface roughness  
 correction: function number 3  
 $T_{\min} = 0.532$ ,  $T_{\max} = 0.913$   
 $h = 0 \rightarrow 6$   
 $k = 0 \rightarrow 7$   
 $l = 0 \rightarrow 7$   
 $2\theta_{\min} = 12.003$ ,  $2\theta_{\max} = 81.998^\circ$   
 Increment in  $2\theta = 0.005^\circ$

### Refinement

$R_p = 0.114$   
 $R_{\text{wp}} = 0.152$   
 $R_{\text{exp}} = 0.091$   
 $S = 1.69$   
 $2\theta_{\min} = 12.438$ ,  $2\theta_{\max} = 74.933^\circ$   
 Increment in  $2\theta = 0.005^\circ$   
 Excluded region(s): none  
 210 reflections  
 43 parameters

Profile function: profile function  
 number 3 with 19 terms, pseudo-  
 Voigt profile coefficients as para-  
 meterized in Thompson *et al.*  
 (1987); asymmetry correction  
 according to Finger *et al.* (1994)  
 H-atom parameters constrained  
 $(\Delta/\sigma)_{\max} = 0.13$   
 Preferred orientation correction:  
 spherical harmonic ODF (*GSAS*;  
 Von Dreele, 1997)

**Table 1**

Average geometric values (Å, °) for the tartrate ligand.

C—C	1.476 (12)	C—O(carboxyl)	1.268 (12)
C—O(hydroxyl)	1.433 (16)		
C—C—C	116.1 (13)	C—C—O(carboxyl)	123.6 (13)
C—C—O(hydroxyl)	110.1 (11)	O—C—O	109.3 (13)

**Table 2**

Short-contact distances (Å).

$\text{Pb}\cdots\text{O1}$	2.754 (12)	$\text{Pb}\cdots\text{O4}^{\text{iii}}$	2.847 (12)
$\text{Pb}\cdots\text{O1}^{\text{i}}$	2.859 (12)	$\text{Pb}\cdots\text{O5}^{\text{iv}}$	2.398 (11)
$\text{Pb}\cdots\text{O2}^{\text{ii}}$	2.975 (13)	$\text{Pb}\cdots\text{O5}^{\text{v}}$	3.330 (10)
$\text{Pb}\cdots\text{O3}^{\text{i}}$	2.637 (9)	$\text{Pb}\cdots\text{O6}^{\text{iii}}$	2.575 (12)
$\text{Pb}\cdots\text{O4}^{\text{ii}}$	2.649 (11)	$\text{Pb}\cdots\text{Pb}^{\text{v}}$	4.4258 (10)

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

The specimen was mounted in reflection mode (Bragg–Brantano geometry) and spun during measurement. The counting time was 12 s per step. The measurement was performed with a variable divergence slit to irradiate a constant length of 10 mm. The peaks were located with the program *PROFIT* (Philips, 1996). The orthorhombic cell dimensions were determined using *ITO* (Visser, 1969) and refined to  $M_{20} = 150$  and  $F = 280$  using the first 70 peak positions. To obtain reflection intensities, a full-pattern decomposition (FPD) procedure using the program *MRIA* (Zlokazov & Chernyshev, 1992) was performed; the powder diffraction pattern was fitted employing a split-type pseudo-Voigt peak profile function (Toraya, 1986). The initial molecular model was built from barium L-tartrate obtained from the Cambridge Structural Database (Allen & Kennard, 1993), entry HIXZOD (González-Silgo *et al.*, 1999), replacing Ba with Pb.

To position the molecule in the asymmetric part of the unit cell, the initial model was used in the grid-search procedure (Chernyshev & Schenk, 1998) performed by the program *MRIA*, using 75 low-angle  $X_{\text{obs}}$  values [ $X_{\text{obs}}$  and  $R(X)$  are defined in expressions (1) and (2) of Chernyshev & Schenk (1998)] extracted from the pattern after the FPD procedure. The model was translated and rotated through the asymmetric unit, with grid increments of  $\sim 0.17$  Å for molecule translations along **a**, **b** and **c**, and  $15^\circ$  for the three rotations around  $\varphi$ ,  $\psi$  and  $\kappa$  angles, resulting in an  $R(X)$  value of 32.8%.

Bond- and angle-restrained Rietveld refinement (RR) was performed with *GSAS* (Larson & Von Dreele, 1994). The multi-term Simpson's rule integration of the pseudo-Voigt profile function (Howard, 1982) was used and its first 19 coefficients were refined. The preferred orientation was corrected using the spherical-harmonics

function implemented in *GSAS* (Von Dreele, 1997). A cylindrical sample symmetry was chosen and a maximum harmonic order of  $L = 12$  was considered. The weight factors ( $f_d$  and  $f_a$ ), weighting the effect of distance and angle restraints on the minimization function, were gradually reduced (from 5000 to 1) in subsequent refinement cycles. During RR, the  $U_{\text{iso}}$  values of all atoms were kept fixed at  $0.01 \text{ \AA}^2$ . Two powder absorption factors were taken into account for the surface roughness effect, with coefficients  $A_{B1} = 0.38408$  and  $A_{B2} = 0.27990$  (Suortti, 1972). The X-ray diffraction profile and the difference between the measured and calculated profiles after the RR are shown in Fig. 3.

Data collection: XPERT data collection software; data reduction: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to solve structure: grid-search procedure (Chernyshev & Schenk, 1998) with *MRIA*; program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1994); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *GSAS*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1119). Services for accessing these data are described at the back of the journal.

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