

**Discussion.** Details of the tartrate molecule are shown in Fig. 1. The bond lengths and angles observed are conformable with those reported for (+)-tartaric acid (Okaya, Stemple & Kay, 1966). Calcium is surrounded by eight oxygens at distances between 2.377 (3) and

2.518 (3) Å, arranged in a distorted Siamese dodecahedron (Johnson, 1966).

The intermolecular linkages are shown in Fig. 2. Calcium links the tartrate molecules into infinite chains parallel to the *c* axis, with one Ca—O bond per tartrate molecule linking adjacent chains in the *a* direction. Most interchain linkage is provided by the network of hydrogen bonds formed by the additional water molecules. Calcium bonds directly to O(7) and O(8), each of which hydrogen bonds to an adjacent tartrate group. The water molecules O(9) and O(10) only participate in intermolecular linkage through hydrogen bonding.

Intensity data were collected at the Materials Research Institute, McMaster University, Hamilton. Financial support was provided by the National Science and Engineering Research Council, in the form of a fellowship (to FCH) and grants (FCH and RBF).

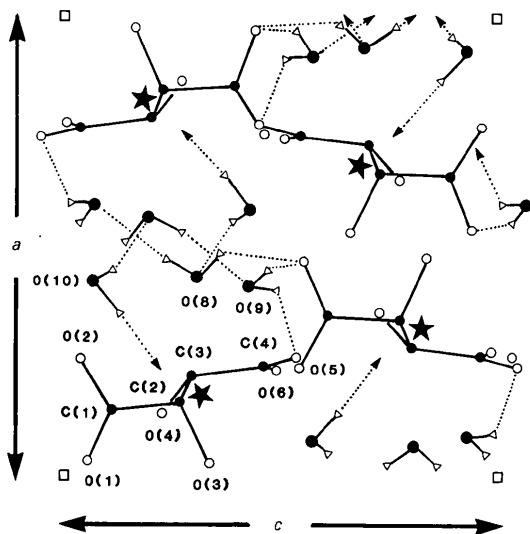


Fig. 2. A projection of the calcium tartrate tetrahydrate structure down the *b* axis. Ca—O and intramolecular hydrogen bonds have been omitted for clarity. The O(7) water molecule is almost occluded by Ca in this view and is also omitted: hydrogen bonds to O(7) are shown by arrowheads. Ca is represented by stars, C by small filled circles, O by hollow circles, H by hollow triangles and water oxygen atoms by large filled circles.

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*Acta Cryst.* (1982). **B38**, 2463–2465

### *cis*-Dichlorobis[dibenzyl(phenyl)phosphine]platinum(II)

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(Received 19 January 1982; accepted 19 April 1982)

**Abstract.** [Pt(C<sub>20</sub>H<sub>19</sub>P)<sub>2</sub>Cl<sub>2</sub>], C<sub>40</sub>H<sub>38</sub>Cl<sub>2</sub>P<sub>2</sub>Pt, monoclinic; at 289 K: *C*2/*c*, *a* = 20.017 (5), *b* = 13.772 (5), *c* = 15.306 (4) Å, β = 114.47 (2)°, *V* = 2840 (2) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.51, *D*<sub>x</sub> = 1.47 g cm<sup>-3</sup>, μ(Mo Kα) = 39.37 cm<sup>-1</sup>. *R* = 0.038 for 3170 observed reflections. Distances around Pt are normal [Pt—Cl 2.355 (4), Pt—P 2.246 (4) Å] but some angles indicate a significant degree of overcrowding [P—Pt—P 103.0 (1)°, one P—C(CH<sub>2</sub>)—C(aromatic) 120.2 (4)°].

**Introduction.** The title compound was prepared in the course of investigations into Pt—SnCl<sub>3</sub> compounds (Nelson, MacDougall, Holt, Alcock & Mathey, 1981). Its structure is of interest in relation to other *cis*-square-planar complexes for the degree of overcrowding around the heavy-metal atom (Alcock, Kemp & Wimmer, 1981). Chunky crystals were isolated by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of *trans*-(Bz<sub>2</sub>PPh)<sub>2</sub>Pt(SnCl<sub>3</sub>)Cl (Bz = benzyl). Although <sup>31</sup>P

and  $^{195}\text{Pt}$  NMR show that the only species in solution is *trans*- $L_2\text{Pt}(\text{SnCl}_3)\text{Cl}$ , it is *cis*- $L_2\text{PtCl}_2$  that crystallizes out. NMR data for the complex *trans*-( $\text{Bz}_2\text{PPh}$ ) $_2\text{Pt}(\text{SnCl}_3)\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  at 223 K are:  $\delta^{31}\text{P}$  9.3 p.p.m. relative to 85%  $\text{H}_3\text{PO}_4$ ,  $\delta^{195}\text{Pt} = -6743$  p.p.m. relative to  $\text{H}_2\text{PtCl}_6$ ,  $^1J_{\text{PtP}} = 2266$  Hz,  $^2J_{\text{SnP}} = 152$  Hz,  $^1J_{\text{Pt}^{119}\text{Sn}} = 28203$  Hz,  $^1J_{\text{Pt}^{117}\text{Sn}} = 27686$  Hz. The NMR data for *cis*-( $\text{Bz}_2\text{PPh}$ ) $_2\text{PtCl}_2$  have been given elsewhere (MacDougall, Nelson & Mathey, 1982).

Data were collected with a Syntex  $P2_1$  four-circle diffractometer. Maximum  $2\theta$  was  $50^\circ$ , with scan range  $\pm 0.9^\circ$  ( $2\theta$ ) around the  $K\alpha_1$ - $K\alpha_2$  angles, scan speed  $2$ - $29^\circ \text{ min}^{-1}$ , depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The crystal was held at 153 K with the Syntex LT-1 attachment. Three standard reflections were monitored every 200 reflections, and showed slight decreases during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 3170 observed reflections [ $I/\sigma(I) > 3.0$ ] were used in refinement, and corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970); maximum and minimum transmission factors were 0.462 and 0.381. The crystal dimensions were  $0.38 \times 0.30 \times 0.38$  mm. Systematic absences  $hkl$ ,  $h + k = 2n + 1$ ,  $h0l$ ,  $l = 2n + 1$ , indicated space group *Cc* or *C2/c*. The latter was initially selected and shown to be satisfactory in the final refinement. The heavy atom was located by Patterson

Table 1. Atomic coordinates ( $\times 10^4$ ) with standard deviations in parentheses and average isotropic  $U$  values ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Pt	0	1059.0 (5)	2500	20
Cl	814 (2)	-171 (2)	2490 (3)	31
P(1)	834 (2)	2074 (2)	2375 (3)	22
C(111)	604 (6)	3372 (8)	2077 (9)	32
C(112)	1080 (6)	3877 (8)	1669 (9)	32
C(113)	1763 (7)	4251 (8)	2266 (10)	37
C(114)	2223 (7)	4636 (9)	1882 (12)	50
C(115)	1999 (8)	4664 (10)	909 (13)	62
C(116)	1313 (10)	4336 (11)	304 (12)	63
C(117)	853 (7)	3942 (10)	682 (10)	42
C(121)	1682 (6)	2075 (8)	3477 (8)	28
C(122)	1560 (6)	2076 (8)	4379 (8)	28
C(123)	1534 (6)	1197 (9)	4816 (9)	32
C(124)	1439 (7)	1162 (10)	5658 (9)	38
C(125)	1349 (7)	2021 (10)	6075 (9)	42
C(126)	1357 (8)	2901 (10)	5643 (10)	43
C(127)	1467 (7)	2926 (9)	4799 (9)	34
C(131)	1100 (6)	1719 (8)	1421 (8)	28
C(132)	1818 (6)	1847 (9)	1501 (9)	33
C(133)	1973 (7)	1683 (9)	711 (10)	44
C(134)	1434 (8)	1397 (9)	-150 (10)	44
C(135)	722 (8)	1254 (10)	-231 (9)	41
C(136)	556 (7)	1413 (9)	547 (9)	34

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Pt-Cl	2.355 (4)	Cl-Pt-Cl	87.9 (1)
Pt-P	2.246 (4)	Cl-Pt-P	84.6 (1)
		Cl-Pt-P	171.6 (1)
		P-Pt-P	103.0 (1)
P-C(111)	1.86 (1)	C(111)-P-Pt	120.2 (4)
P-C(121)	1.83 (1)	C(121)-P-Pt	111.1 (5)
P-C(131)	1.82 (1)	C(131)-P-Pt	112.1 (4)
		C(111) P C(121)	105.5 (5)
		C(111) P C(131)	100.8 (6)
		C(121) P C(131)	105.8 (6)
C(111)-C(112)	1.51 (2)	C(112)-C(111)-P	114.2 (9)
C(121)-C(122)	1.50 (2)	C(122)-C(111)-P	113.9 (8)

C-C (aromatic) 1.386 (5, avg.), C-C-C (aromatic) 120.0 (4, avg.). Individual distances, e.s.d. 0.02-0.03  $\text{\AA}$ , and angles, e.s.d. 1.2-1.5 $^\circ$ , do not deviate by more than one standard deviation from these averages.

techniques and the light atoms were then found on successive Fourier syntheses. H atoms were inserted at calculated positions with fixed isotropic temperature factors,  $B = 5.0 \text{\AA}^2$ , and were not refined. Final refinement was by least-squares methods, in large blocks. Unit weights were used and were shown to be satisfactory by a weight analysis. The final  $R$  value was 0.038. Computing was with the XRAY 76 system (Stewart, 1976), on a Burroughs B6700 and a CDC7600 computer. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1 and bond lengths and angles in Table 2.\*

**Discussion.** The compound is monomeric, with crystallographic twofold symmetry (Fig. 1). The Pt-Cl distance [2.355 (4)  $\text{\AA}$ ] is slightly but significantly shorter than those in the related compounds [ $(\text{Me}_2\text{Ph})\text{P}$ ] $_2\text{PtCl}_2$  (Baker, Braithwaite & Nyholm, 1972), and [ $\text{Me}_3\text{P}$ ] $_2\text{PtCl}_2$  (Messmer, Amma & Ibers, 1967) [average over four Pt-Cl distances, 2.374 (3)  $\text{\AA}$ ]; the Pt-P distances are the same to within experimental error. Kaduk & Ibers (1977) have compared Pt-Cl and Pt-P distances in a number of complexes and found that Pt-Cl ranges from 2.291 (2) to 2.454 (4)  $\text{\AA}$  and Pt-P ranges from 2.268 (4) to 2.328 (2)  $\text{\AA}$ . Thus, the Pt-Cl distance in *cis*-( $\text{Bz}_2\text{PPh}$ ) $_2\text{PtCl}_2$  is in the mid-point of this range but the Pt-P distance is short.  $\text{Bz}_3\text{P}$  is easily *ortho*-metallated and the complex [ $\text{Bz}_2\text{PCH}_2\text{C}_6\text{H}_4$ ] $_2\text{Pt}$  shows Pt-P 2.277 (2)  $\text{\AA}$  (average), with Pt-C of 2.067 (7)  $\text{\AA}$  (average) (Porzio, 1980). The dihedral angles of the P-C bonds in the present compound are such that the

\* Lists of structure factors, hydrogen atom parameters, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36910 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

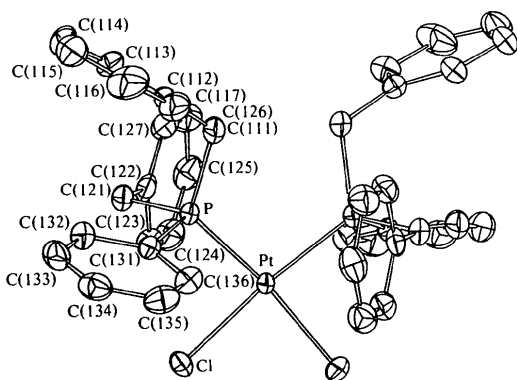


Fig. 1. The molecule of  $[(C_6H_5CH_2)_2(C_6H_5)P]_2PtCl_2$ , showing the atomic numbering.

closest Pt—C(*o*) approach is 3.61 (1) Å, to C(123), too long to indicate incipient *ortho*-metallation. The title compound appears to be significantly more crowded than either of the parallels cited above, from its P—Pt—P angle [103.0 (1) *vs* 94.5 and 96.2°]. It also shows the single large C—P—M angle [here 120.2 (4)°] similar to those of 120.7 and 121.5° found in the notably overcrowded  $\{(C_3H_7)_3P\}PdCl_2$  (Alcock, Kemp & Wimmer, 1981). However, the conformation around Pt shows only slight deviations from planarity with Cl and P atoms alternately up and down by  $\pm 0.07$  Å. This is probably better viewed as a twist between the

P—Pt—P plane and the Cl—Pt—Cl plane, of 5.1 (2)°. The title compound is also more crowded than the *ortho*-metallated compound for which the PPtP angle is 106.0° and the twist angle is 1.5°.

We thank SRC for assistance in the purchase of X-ray equipment.

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*Acta Cryst.* (1982). **B38**, 2465–2468

## Tetrakis(4-ethylpyridinium) Decavanadate

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(Received 23 December 1980; accepted 8 April 1982)

**Abstract.**  $[NHC_7H_9]_4[V_{10}H_2O_{28}]$ , monoclinic,  $P2_1/n$ ,  $a = 19.473$  (2),  $b = 9.938$  (1),  $c = 11.965$  (4) Å,  $\beta = 92.26$  (1)°,  $V = 2314.8$  Å<sup>3</sup>,  $\mu(Mo K\alpha) = 17.35$  mm<sup>-1</sup>,  $D_m$  (pycnometric method) =  $D_x = 2.00$  Mg m<sup>-3</sup> for

$Z = 2$ . The structure was solved by direct methods and refined to a final  $R$  value of 0.08 for 2842 observed reflexions. The 4-ethylpyridinium groups are bonded to the oxygens of the decavanadate anion by an intermolecular hydrogen bond between the pyridine nitrogen and the most basic oxygens of the decavanadate group. This group consists of ten distorted  $VO_6$  octahedra that

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