

Bis(propylammonium) Tetrachloropalladate(II)

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Abstract. $(C_3H_7NH_3)_2PdCl_4$ [PA_2PdCl_4], monoclinic, $P2_1/c$, $a = 12.42$ (1), $b = 8.038$ (4), $c = 7.404$ (3) Å, $\beta = 109.20$ (2)°. The salt contains discrete $PdCl_4^{2-}$ anions (average Pd–Cl = 2.313 Å) which pack together to form a two-dimensional palladium chloride layer. The interionic Pd–Cl distance is 3.2 Å. Through hydrogen bonding, the $C_3H_7NH_3^+$ ions form a two-dimensional sandwich around each Pd–Cl layer. These organic cations are disordered.

Introduction. The preparation of the analogous ethylammonium salt, $(C_2H_5NH_3)_2PdCl_4$, has been reported by Daoud (1976), who gave orthorhombic lattice constants of $a = 7.44$, $b = 20.51$, $c = 8.02$ Å from powder diffraction measurements. The crystals of PA_2PdCl_4 were prepared by refluxing equimolar mixtures of $PdCl_2$ and PA_3 in acetone for several days and allowing the resulting solution to slowly evaporate. Flat, red–orange, monoclinic crystals are obtained. The crystals, like the analogous Mn salt (Peterson & Willett, 1972), are very fragile and difficult to handle, the slightest pressure causing the crystal to warp. A small crystal ($0.10 \times 0.33 \times 0.35$ mm) was mounted for data collection. Systematic extinctions were $l = 2n + 1$ for $h0l$ reflections, and $k = 2n + 1$ for $0k0$ reflections, indicating the unique space group $P2_1/c$. An automated Picker diffractometer was used for data collection with Zr-filtered Mo $K\alpha$ radiation. A θ – 2θ step scan was employed with 20 steps/degree and a scan rate of 3.5 s/step with background measured for 17.5 s before and after each peak. Because of the large mosaic spread of the crystal, it was necessary to use a scan width of 2.5°. 645 independent reflections were examined in the range $2\theta < 40^\circ$. The standard deviation in intensity was calculated by $\sigma^2(I) = TC + 2.5BC + (0.04)^2 I_o^2$, where TC = total count, BC = background count, and $I_o = TC - 5BC$. Three standards monitored every 40 reflections showed no systematic variation from counting statistics. Absorption corrections ($\mu = 19.13$ cm⁻¹) were made with transmission factors ranging from 0.68 to 0.93.

Pd and Cl positions were determined from a Patterson function, and the general locations of the N and C atoms were obtained from subsequent electron density and difference electron density maps. These showed definite evidence of disordering of the PA ions. The two sites appear to be related by a 180° rotation about (roughly) the N–C(3) axis, where C(3) is the terminal

C in the propyl chain. Thus C(1) and C(2) are disordered. On the basis of the electron density maps, the relative occupancy of the two sites was approximately 70/30. Full-matrix refinement proceeded relatively straightforwardly to a final conventional R value of 0.095 and a weighted R value of 0.108 [$\omega_{hkl} = 1/\sigma^2(F)$]. The refinement was carried out on the 475 reflections with $F \geq 3\sigma(F)$. Because of the interdependence of parameters, the thermal parameters of the disordered atoms were retained in isotropic form, and no attempt was made to vary the positional parameters of C(1') and C(2') (the sites with 30% occupancy). The standard error of an observation of unit weight was 1.51. The unusually large R values are a direct consequence of the poor quality of the crystal and the small crystal size. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final positional parameters are given in Table 1 and pertinent distances and angles in Table 2.* Computer programs used were part of a local library (Anderson, 1971; Caputo, 1975). An illustration of the structure is given in Fig. 1.

Discussion. The structure consists of discrete, planar $PdCl_4^{2-}$ ions with Pd–Cl distances of 2.308 (8) and 2.317 (7) Å. These anions pack together to form a

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32453 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional parameters ($\times 10^4$) for $(C_3H_7NH_3)_2PdCl_4$

Standard deviations in the least significant figures are given in parentheses.

	Occupancy factor	x	y	z
Pd	0.5	0	0	0
Cl(1)	1.0	281 (8)	2079 (8)	2279 (10)
Cl(2)	1.0	1931 (7)	–534 (8)	900 (10)
N	1.0	1578 (19)	5423 (17)	891 (30)
C(3)	1.0	4694 (27)	3725 (40)	2212 (50)
C(1)	0.7	2753 (55)	5110 (90)	1209 (77)
C(2)	0.7	3390 (61)	3764 (91)	1689 (92)
C(1')	0.3	2424	3852	1639
C(2')	0.3	3425	4531	2344

layer structure in which the closest interionic contact is a Pd...Cl distance of 3.190 (8) Å. The pseudo four-fold symmetry axis of the PdCl₄²⁻ ion lies approximately in the *bc* plane, but the bridging Pd—Cl...Pd angle is decidedly non-linear at 165.4 (4)°. This causes the layer to be puckered. The packing of the PdCl₄²⁻ ions is basically the same as the packing of the CuCl₄²⁻ ions in (RNH₃)₂CuCl₄ salts, except that the interionic *M*...Cl distance is 0.2 Å longer for the Pd salt (Willett & Steadman, 1970; Barendregt & Schenk, 1970). This results in the *b* axis being approximately 8.0 Å, rather than the normal 7.3–7.5 Å found in the Cu salts.

The NH₃⁺ moieties of the PA⁺ ions hydrogen bond down into the Pd—Cl network, inducing the puckering

Table 2. *Interatomic distances (Å) and angles (°)*

Standard deviations in the least significant figures are given in parentheses.

Pd—Cl(1)	2.317 (7)	Cl(1)—Pd—Cl(2)	91.5 (3)
Pd—Cl(1')	3.190 (8)	Cl(1)—Pd—Cl(1')	95.4 (1)
Pd—Cl(2)	2.308 (8)	Pd—Cl(1)—Pd	165.4 (4)
N—C(1)	1.42 (7)	N—C(1)—C(2)	133 (6)
C(1)—C(2)	1.32 (8)	C(1)—C(2)—C(3)	125 (6)
C(2)—C(3)	1.54 (9)		
N—C(1')	1.62	N—C(1')—C(2')	104
C(1')—C(2')	1.30	C(1')—C(2')—C(3)	126
C(2')—C(3)	1.74		
N—Cl(I ⁱⁱ)	3.31 (2)	C(1)—N—Cl(I ⁱⁱ)	103 (3)
N—Cl(I ⁱⁱⁱ)	3.33 (3)	C(1)—N—Cl(I ⁱⁱⁱ)	145 (3)
N—Cl(I ^{iv})	3.37 (2)	C(1)—N—Cl(I ^{iv})	131 (3)
N—Cl(1)	3.45 (2)	C(1)—N—Cl(1)	111 (3)
N—Cl(2)	3.28 (2)	C(1)—N—Cl(2')	93 (3)
N—Cl(2)	3.59 (2)	C(1)—N—Cl(2)	94 (2)

Symmetry code

- | | | | |
|-------|---|------|-----------------|
| (i) | $x, \frac{1}{2} - y, -\frac{1}{2} + z$ | (iv) | $-x, 1 - y, -z$ |
| (ii) | $x, \frac{1}{2} - y, \frac{1}{2} + z$ | (v) | $x, -1 + y, z$ |
| (iii) | $-x, -\frac{1}{2} + y, \frac{1}{2} - z$ | | |

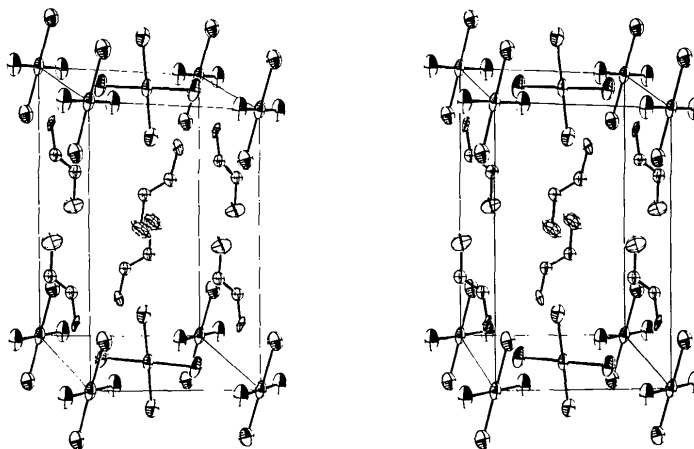
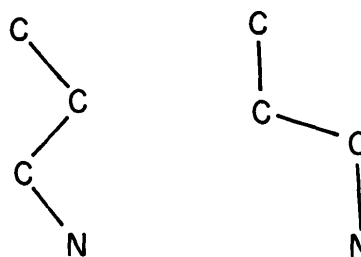


Fig. 1. Stereoscopic view of the crystal structure of (C₃H₇NH₃)₂PdCl₄.

that is so typical of these salts. In other metal salts of the type (RNH₃)₂MCl₄ which have been studied, the orientation of the RNH₃⁺ ion with respect to the plane of the layer is as illustrated in Fig. 2(a). In this compound, however, the two observed configurations of these ions are a superposition of those depicted in Fig. 2(a) and (b), with the predominate contribution coming from the second configuration. These two configurations are simply related by a 180° rotation about the N—C(terminal) axis. Thus, both the N and C(3) positions represent weighted averages and the observed thermal parameters merely represent a best attempt to match that electron density. The details of which configuration is more stable probably involve both the relative hydrogen-bonding strengths of the two configurations and the steric packing effects. By analogy with other structures of the (RNH₃)₂MCl₄ salts, it seems likely that the disorder is of a dynamic nature, rather than static (Willett & Riedel, 1975). The disorder may be a prototype of the β phase of (C_{*n*}H_{2*n*+1}NH₃)MnCl₄ salts (*n* ≥ 10) recently reported.



(a)

(b)

Fig. 2. Configurations of the propylammonium ions. The *c* axis is vertical.

The observed lengthening of the b axis is interesting. It could be due either to the length of the interionic Pd...Cl bond or to the steric forces caused by the disorder of the PA⁺ ions. The same lengthening is observed in (C₂H₅NH₃)₂PdCl₄ which indicates that it may be a characteristic of the Pd-Cl framework, rather than the organic cation. If this is true, it is interesting to speculate on the nature of the long Pd...Cl interaction. Based on simple close-packing arguments, a M...Cl distance of 2.8 Å is predicted on the assumption of van der Waals contacts between Cl atoms on adjacent ions. This is the minimum value observed for the Cu salts, and is taken as evidence for a basic 'non-bonded' Cu...Cl interaction. Hence, if 3.2 Å represents the normal Pd...Cl distance, there must be significant repulsive interactions between the Pd and Cl. In both the CuCl₄²⁻ and the PdCl₄²⁻ salts, it is noted that the bridging M-Cl distance is longer than the terminal M-Cl distance. The greater involvement of the bridging halide ion in N-H...Cl hydrogen bonds as compared to the terminal halide ion is probably as significant in accounting for this lengthening as the long M...Cl interactions.

Finally, it should be noted that this lattice will be an ideal host lattice for studying the EPR spectrum of the planar CuCl₄²⁻ in an environment very little perturbed from that found in (RNH₃)₂CuCl₄ salts.

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Propylenediammonium Tetrachlorocadmate(II)

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Abstract. (C₃H₆N₂H₆)CdCl₄ [PDACdCl₄], orthorhombic, $Pnam$, $a = 7.373$ (5), $b = 7.523$ (5), $c = 19.111$ (8) Å; $\rho_{\text{calc}} = 2.07$, $\rho_{\text{obs}} = 2.10$ g cm⁻³, $Z = 4$. The salt is layered, with two-dimensional arrays of corner-shared CdCl₆ octahedra sandwiched between layers of the propylenediammonium ions. Cd-Cl = 2.58 (terminal) and 2.67 Å (bridging). The bridging Cd-Cl-Cd angle is 160.8°. The organic cation is ordered and essentially planar.

Introduction. Colorless, flat platelets of PDACdCl₄ with {110}, {110} and {001} faces developed were prepared by slow evaporation of a stoichiometric alcoholic or aqueous solution. A small crystal (0.20 × 0.20 × 0.09 mm) was mounted with the c axis of the crystal approximately parallel to the θ axis of the full-circle orienter. Systematic absences were $k + l = 2n + 1$ for Ok reflections, and $h = 2n + 1$ for hOl reflections. Intensity data were collected on an automated Picker

diffractometer with Zr-filtered Mo $K\alpha$ radiation. A θ - 2θ step scan was used, with scans of 1.8°, 20 steps/degree and 2.5 s/step. Background measurements of 25 s were made before and after each scan. The standard deviation in intensity was calculated by $\sigma^2(I_o) = TC + 1.8BC + (0.03)^2 I_o^2$, where TC = total count, BC = background count, and $I_o = TC - BC$. 929 independent reflections were collected in the range $2\theta \leq 50^\circ$. Refinement was carried out on the 674 reflections with $F_o > 3\sigma(F)$. Three standards monitored every 100 reflections showed no systematic deviations from normal counting statistics. Absorption corrections ($\mu = 29.8$ cm⁻¹) were made with transmission factors ranging from 0.57 to 0.80.

Cd and Cl positions were assumed from the structure of the analogous Mn and Fe salts (Willett & Riedel, 1975). C and N positions were found on the electron density maps based on the heavy-atom positions. Full-matrix refinement proceeded smoothly in $Pnam$ to