

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<sup>+</sup> ions. The same lengthening is observed in (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>PdCl<sub>4</sub> 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 CuCl<sub>4</sub><sup>2-</sup> and the PdCl<sub>4</sub><sup>2-</sup> 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 CuCl<sub>4</sub><sup>2-</sup> in an environment very little perturbed from that found in (RNH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> salts.

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## Propylenediammonium Tetrachlorocadmate(II)

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**Abstract.** (C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>H<sub>6</sub>)CdCl<sub>4</sub> [PDACdCl<sub>4</sub>], 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<sup>-3</sup>,  $Z = 4$ . The salt is layered, with two-dimensional arrays of corner-shared CdCl<sub>6</sub> 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 PDACdCl<sub>4</sub> 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  $\theta$  axis of the full-circle orienter. Systematic absences were  $k + l = 2n + 1$  for  $Ok$  reflections, and  $h = 2n + 1$  for  $h0l$  reflections. Intensity data were collected on an automated Picker

diffractometer with Zr-filtered Mo  $K\alpha$  radiation. A  $\theta$ - $2\theta$  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<sup>-1</sup>) 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

a final conventional  $R$  value of 0.049, and a weighted  $R$  value of 0.045 [ $\omega_{hkl} = 1/\sigma^2(F)$ ]. The standard error of an observation of unit weight was 1.31. Four reflections thought to be suffering from extinction were omitted from the final least-squares cycle. Atomic

Table 1. Final positional parameters for PDACdCl<sub>4</sub>

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

	$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^5)$
Cd	0	0	0
Cl(1)	2231 (2)	2777 (2)	1773 (9)
Cl(2)	188 (3)	-525 (2)	13327 (9)
N	-349 (8)	5231 (8)	38087 (30)
C(1)	376 (10)	4305 (12)	31500 (35)
C(2)	-454 (16)	5289 (14)	25000

Table 2. Bond distances (Å) and angles (°) in PDACdCl<sub>4</sub>

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

Cd-Cl(1)	2.680 (2)	Cl(1)-Cd-Cl(1 <sup>b</sup> )	92.01 (1)
Cd-Cl(1 <sup>b</sup> )	2.661 (2)	Cl(1)-Cd-Cl(2)	87.80 (6)
Cd-Cl(2)	2.581 (2)	Cd-Cl(1)-Cd	160.84 (7)
N-C(1)	1.535 (8)	N-C(1)-C(2)	107.4 (6)
C(1)-C(2)	1.570 (9)	C(1)-C(2)-C(1 <sup>b</sup> )	104.6 (8)
N-Cl(1 <sup>ii</sup> )	3.318 (6)	C(1)-N-Cl(1 <sup>ii</sup> )	175.6 (4)
N-Cl(1 <sup>iii</sup> )	3.284 (6)	C(1)-N-Cl(1 <sup>iii</sup> )	91.6 (4)
N-Cl(1 <sup>iv</sup> )	3.473 (6)	C(1)-N-Cl(1 <sup>iv</sup> )	109.9 (4)
N-Cl(2 <sup>v</sup> )	3.228 (6)	C(1)-N-Cl(2 <sup>v</sup> )	109.7 (4)
N-Cl(2 <sup>vi</sup> )	3.309 (6)	C(1)-N-Cl(2 <sup>vi</sup> )	108.0 (4)

Symmetry code

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

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.\* No attempt was made to locate H atoms and the final difference map showed no unusual features. Computer programs used were part of a local program library (Anderson, 1971; Caputo, 1975). The structure is illustrated in Fig. 1.

**Discussion.** The structure of the title salt is closely related to the analogous Mn and Fe salts. Both contain the typical puckered metal-halogen layer characteristic of octahedrally coordinated  $(RNH_3)_2MX_4$  or  $(NH_3RNH_3)MX_4$  salts. The  $MX_6$  octahedra share corners to form the two-dimensional network and the ammonium ions occupy holes between the octahedra, stabilizing the structure through hydrogen bonding. However, in the Mn and Fe salts (space group *Imma*), the PDA ion is disordered, while no evidence of disorder is apparent in the present compound. The difference in the two types of structure is the absence of a mirror plane perpendicular to the  $a$  axis in the Cd salt. It should be noted that the PDA ion is not disordered in the analogous Cu salt, PDACuCl<sub>4</sub> (Phelps, Bloese, Hatfield & Hodgson, 1976).

The coordination geometry around the Cd ion shows the typical axial compression of the octahedral geometry, with the bridging Cd-Cl distances longer than the terminal Cd-Cl distances. As anticipated on the basis of ionic radii, the Cd-Cl distances are 0.09 Å longer than the corresponding Mn-Cl distances in PDAMnCl<sub>4</sub>. For these two electronically spherical

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32454 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

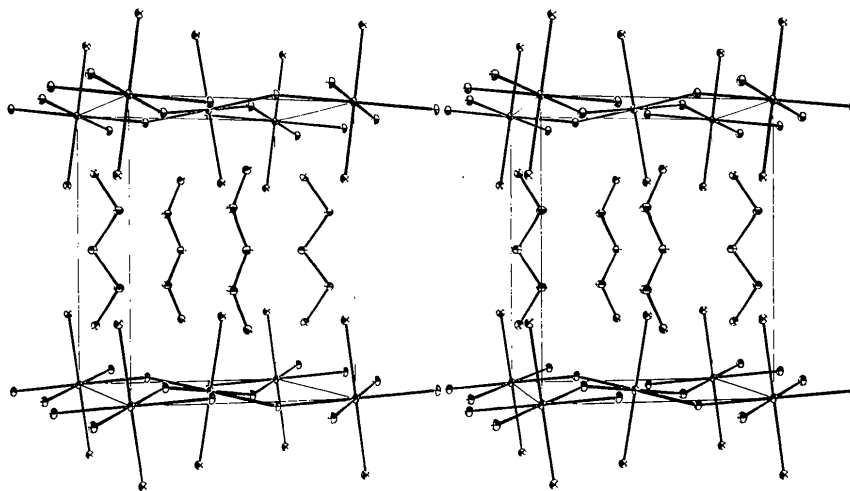


Fig. 1. Stereoscopic drawing of the structure of  $(C_3H_6N_2H_6)CdCl_4$ .

ions, the difference between  $M\text{-Cl}_{\text{axial}}$  and  $M\text{-Cl}_{\text{eq}}$  is exactly the same, 0.09 Å. Thus, this should be a near ideal lattice for EPR studies on  $\text{Mn}^{2+}$  doped into a diamagnetic lattice.

The PDA ion is nearly planar, with the plane of the ion sitting athwart the crystallographic  $bc$  plane. This presumably allows the  $\text{-NH}_3^+$  groups to hydrogen bond to the Cd-Cl layers in a manner analogous to that in the Mn and Fe salts, the disorder being absent. The C(1)-N and C(1)-C(2) distances are slightly longer than normal, 1.534 (8) and 1.570 (9) Å respectively, probably because of neglect of the H scattering. Those determined for the Mn, Fe and Cu salts are normal (1.47-1.48 Å, 1.49-1.50 Å).

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## 1,4,9,12-Tetraoxadispiro[4.2.4.2]tetradecane

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**Abstract.**  $\text{C}_{10}\text{H}_{16}\text{O}_4$ ,  $M_r = 200.12$ , monoclinic,  $P2_1/c$ ,  $a = 5.767$  (5),  $b = 8.566$  (8),  $c = 10.635$  (10) Å,  $\beta = 109.02$  (2)°,  $Z = 2$ ,  $D_x = 1.34$  g cm $^{-3}$ . The cyclohexane ring has the usual chair conformation, and the ketal rings have an intermediate conformation between twist and envelope. Axial and equatorial C-O lengths (uncorrected for libration) are 1.424 (3) and 1.431 (3) Å, equal within experimental error. The corrected values are both 1.437 Å.

**Introduction.** Our main aim in this study was to find out whether axial and equatorial C-O bonds on a cyclohexane ring differ in length. Crystals (m.p. 79-80°C), obtained by slow cooling of a saturated *n*-hexane solution, were kindly provided by Dr K. Müller. They were sealed in capillaries for X-ray analysis.

Intensities from a crystal, 0.3 mm in edge, were collected on an automated Hilger & Watts Y290 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å,  $\mu = 1.10$  cm $^{-1}$ ); 871 reflexions ( $2\theta < 50^\circ$ ), 833 with  $I \geq 3\sigma(I)$ . The structure (Fig. 1) was solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1970) and refined by full-matrix least squares (XRAY system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with experimental weights. At an intermediate stage, all H atoms were located from a difference map (sin  $\theta/\lambda$  limit 0.45 Å $^{-1}$ ) and subsequently included. The final  $R$  was 0.055,

including extinction corrections. Final positional parameters and isotropic thermal parameters (for H) are

Table 1. Atomic coordinates (*e.s.d.*'s in parentheses) for non-hydrogen atoms ( $\times 10^4$ ) (asymmetric unit only)

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	4450 (3)	3046 (2)	3987 (2)
C(2)	2264 (4)	3931 (3)	3706 (3)
C(3)	731 (5)	3024 (3)	4334 (3)
O(4)	1522 (3)	1468 (2)	4320 (2)
C(5)	4058 (4)	1534 (3)	4453 (2)
C(6)	4588 (4)	287 (3)	3594 (2)
C(14)	5654 (4)	1342 (3)	5889 (2)

Table 2. Atomic coordinates and isotropic  $U$  values for hydrogen atoms (all  $\times 10^3$ ) (asymmetric unit only)

	<i>x</i>	<i>y</i>	<i>z</i>	$U$ (Å $^2$ )
H(1)C(2)	152 (10)	401 (7)	271 (5)	101 (18)
H(2)C(2)	269 (11)	503 (7)	404 (6)	128 (21)
H(1)C(3)	104 (11)	338 (7)	536 (6)	147 (22)
H(2)C(3)	-104 (10)	305 (6)	379 (5)	93 (18)
H(1)C(6)	345 (8)	44 (6)	263 (4)	61 (14)
H(2)C(6)	630 (8)	46 (5)	358 (4)	61 (14)
H(1)C(14)	739 (8)	156 (5)	596 (4)	58 (14)
H(2)C(14)	520 (8)	213 (5)	642 (4)	58 (14)