

Crystal Structure of Ethylenediammonium Tetrachloropalladate(II)

ROLF W. BERG and INGER SØTOFTE

Chemistry Departments A and B, The Technical University of Denmark, DK-2800 Lyngby, Denmark

The ethylenediammonium cation (abbreviated enH_2^+) is structurally interesting because of its possibility in the solid state to adopt different conformations *via* C—C bond rotation. Depending on the type of anion with which the crystal is formed both the *planar* centrosymmetric *trans*-conformation and the C_2 -symmetric *gauche*-conformation of the ethylenediammonium ion have been found; *trans* in $[\text{enH}_2]\text{Cl}_2$,¹ $[\text{enH}_2]\text{Br}_2$,² and $[\text{enH}_2][\text{Au}(\text{SO}_3)_2\text{en}]^3$ and *gauche* in $[\text{enH}_2][\text{SO}_4]$.⁴ In a recent investigation⁵ X-ray and infrared data seemed to indicate that $[\text{enH}_2][\text{PdCl}_4]$ contains $[\text{enH}_2]^{2+}$ ions of *trans*-conformation. This work was undertaken to establish the complete structure of $[\text{enH}_2][\text{PdCl}_4]$ and to see if the structural deductions based on polarized single crystal infrared spectra⁵ agree with this structure. Also, it was found of interest to investigate the hydrogen bonding scheme and to see if $[\text{PdCl}_4]^{2-}$, one of the typical ions of D_{4h} symmetry in inorganic chemistry, remains square planar in the crystal.

Experimental. Three-dimensional X-ray data were measured at room temperature from a cleaved crystal of size $0.4 \times 0.2 \times 0.05$ mm, obtained as described in Ref. 5 and mounted with its [010] axis as rotation axis. A Stoe & Cie semiautomatic equinclination diffractometer with ω -scan technique and graphite monochromated $\text{MoK}\alpha$ radiation was used. Harmonics were excluded by means of a pulse height discriminator. Reflections between a cylinder of radius $r = 5.4^\circ$ and a hemisphere with $\sin \theta/\lambda \leq 0.7 \text{ \AA}^{-1}$ were measured ($0 \leq k \leq 10$) giving 1304 independent reflections of which 1224 had $I > 2\sigma(I)$, where $\sigma(I) = [(1 + 0.04^2)\text{PC} + \text{BC}]$ (PC = peak count and BC = background count). The diffractometer output was processed by the programme used in Ref. 2 prior to subsequent calculations performed on an IBM 370/165 computer using the X-RAY system⁶ and ORTEP.⁷ The atomic scattering factors for C, N, Cl⁻, and Pd²⁺ were those of Cromer and Mann.⁸ No correction was made for X-ray absorption. All symmetry related reflections were averaged and hydrogen atoms were neglected.

Crystal data. Preliminary results⁵ were confirmed. $(\text{CH}_2\text{NH}_3)_2\text{PdCl}_4$. $M = 310.33$ g/mol. Monoclinic. $a = 7.34(2) \text{ \AA}$, $b = 7.66(2) \text{ \AA}$, $c = 7.91(2) \text{ \AA}$, $\beta = 91.90(1)^\circ$. $V = 444.49 \text{ \AA}^3$. $Z = 2$. $D_c = 2.318$, $D_o = 2.33$ g/cm³ (floatation). $F(000) = 300$. $\mu(\text{MoK}\alpha) = 32.2$ cm⁻¹. Systematic absences: $h0l$ when h odd and $0k0$ for k odd. Space group: $P2_1/a$ (No. 14).

Structure determination. Starting phases were calculated from the scattering of the palladium atom which is in the special position (0,0,0) and which accounts for 31% of the charge density. Subsequent Fourier maps revealed the chlorine, nitrogen, and carbon atoms and the structure was refined by full matrix least square minimisation of $\sum w(|F_o| - |F_c|)^2$. With anisotropic temperature factors, omission of one reflection, (001), nearest to the beam and the use of the weighting scheme $w^{-1} = 2.53 + 0.833|\sigma(F)|^2 - 0.0522|F|^2 + 0.0052|F|^4 - 3.49 \sin \theta/\lambda$ the refinement resulted in $R = 0.050$ ($R_w = 0.067$). The correctness of the resulting structure was checked by a difference Fourier map. A listing of observed and calculated structure factors may be obtained from the authors upon request.

Description of the structure. The structure is shown in Fig. 1. Both anions and cations are situated at sites of inversion. This implies that the $[\text{PdCl}_4]^{2-}$ anions are planar. The anions are nearly regularly square, having Pd—Cl bond lengths near the normal value 2.31(1) Å found for $(\text{NH}_4)_2\text{PdCl}_4$ and K_2PdCl_4 .⁹⁻¹¹ The angles Cl—Pd—Cl are essentially right, 89.77(7) and 90.23(7)°, and hence the deviation from the regular square planar coordination is dominated by the presence of long [2.323(6) Å] and short [2.300(5) Å] Pd—Cl bonds.

Due to the inversion center the $[\text{enH}_2]^{2+}$ cation has a planar N—C—C—N skeleton, and *trans*-conformation. The C—C and C—N bond lengths have the values 1.510(9) and 1.479(8) Å, respectively. These lengths agree well (within 0.02 Å) with previously reported values for other crystals containing *trans*- $[\text{enH}_2]^{2+}$.¹⁻³ The C—C—N angle of 111.8(5)° observed is slightly larger than the tetrahedral angle (found in the chloride salt¹) and this feature has also been observed for the bromide² and the *bis*-[*cis*-ethylenediaminedisulfato]urate(III)³ salts of $[\text{enH}_2]^{2+}$, which display C—C—N angles of 112.7(9) and 110.5(7)°, respectively.

The structure found can conveniently be viewed as consisting of essentially square planar $[\text{PdCl}_4]^{2-}$ anions stacked in "stripes" along [001], the stripes being mutually twisted in opposite directions due to Cl—Cl repulsions and the formation of N—H...Cl hydrogen bonds. The structure is kept together *via* interleaving $[\text{enH}_2]^{2+}$ ions. The shortest N—Cl distances are 3.22(1), 3.27(1), 3.39(1), 3.42(2), and 3.44(2) Å of which the three first ones should be short enough to allow considerable hydrogen bonding. A typical N—H...Cl hydrogen bond is 3.3 Å¹² and Pimentel and McClellan¹³ list N—H...Cl hydrogen bonded distances ranging from 2.91 to 3.41 Å. It turns out that the three shortest N—Cl contacts (shown as thin lines in Fig. 1) go from one N to three Cl in different $[\text{PdCl}_4]^{2-}$ ions. These N—Cl contacts form approximately tetra-

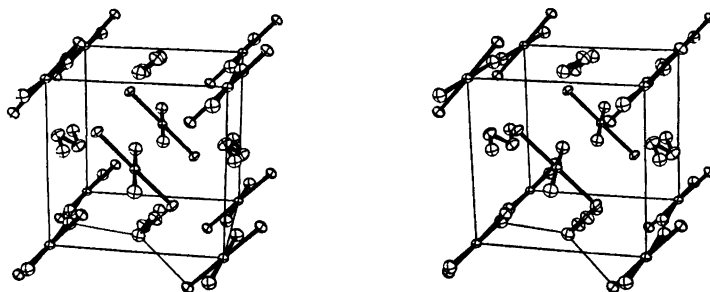


Fig. 1. Stereoscopic view of the structure of ethylenediammonium tetrachloropalladate(II) along the c axis. The horizontal axis is a and the vertical b . Thermal ellipsoids of 50 % charge density are shown. Hydrogen bonds around one N are shown as thin lines.

Table 1. Positional and thermal parameters (U_{ij} in units of 10^{-4} \AA^2) with estimated standard deviations. The form of the temperature factor expression is $\exp[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}]$.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.0	0.0	0.0	133(2)	201(3)	230(3)	-4(1)	0(1)	0(1)
Cl1	0.0345(2)	0.0487(2)	0.2892(1)	348(5)	379(6)	211(4)	2(4)	-14(3)	-21(4)
Cl2	0.2217(1)	0.2048(1)	-0.0473(1)	195(4)	262(4)	436(5)	-77(3)	39(3)	22(3)
N	0.5014(7)	0.0268(7)	0.2620(5)	344(21)	333(15)	227(16)	11(17)	-3(14)	34(14)
C	0.4505(7)	0.0461(8)	0.5693(6)	335(20)	414(22)	257(17)	109(19)	37(14)	17(16)

hedral angles with each other and with the C-N bond. Therefore it can be assumed that a 3-dimensional network of hydrogen bonds exists in the crystal.

Discussion. The presence of hydrogen bonds is in accordance with the infrared results,⁵ which also predicted that the $[\text{PdCl}_4]^{2-}$ square plane was neither parallel nor perpendicular to the b axis and that the N-C-C-N plane was not perpendicular to b . During the optical examination⁵ a contact twinning on (110) (with the present axes) was observed. From Fig. 1 the twinning can be explained predominantly as a $\approx 90^\circ$ rotation of only the $[\text{enH}_2]^{2+}$ ions around c followed by very small adjustments in the Cl parameters. From Fig. 1 it seems quite reasonable that the barrier to the c -rotation of $[\text{enH}_2]^{2+}$ ions is small and this is also reflected in the shape of the carbon thermal ellipsoids. The marked cleavage⁵ along the form (010) is understandable noting that the shortest N-H...Cl contact connects ions along b .

- Ashida, T. and Hirokawa, S. *Bull. Chem. Soc. Jpn.* 36 (1963) 704; Koo, C. H., Kim, M. I. and Yoo, C. S. *J. Korean Chem. Soc.* 7 (1963) 293.
- Søtofte, I. *Acta Chem. Scand. A* 30 (1976) 309.

- Dunand, A. and Gerdil, R. *Acta Crystallogr. B* 31 (1975) 370.
- Sakurai, K. *J. Phys. Soc. Jpn.* 16 (1961) 1205.
- Berg, R. W. *Spectrochim. Acta A* 32 (1976). *In press.*
- Stewart, J. M., Kundell, F. A. and Baldwin, J. C. *The X-Ray System, Version 1972*, Chemistry Department, Univ. of Maryland, U.S.A.
- Johnson, C. K. *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.
- Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
- Bell, J. D., Hall, D. and Waters, T. N. *Acta Crystallogr.* 21 (1966) 440.
- Mais, R. H. B., Owston, P. G. and Wood, A. M. *Acta Crystallogr. B* 28 (1972) 393.
- Larsen, F. K. and Berg, R. W. *In preparation.*
- Hamilton, W. C. and Ibers, J. A. *Hydrogen Bonding in Solids*, Benjamin, New York 1968, p. 184.
- Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*, Freeman & Co., London 1960, p. 290.

Received September 23, 1976.