

Jan Fábry,<sup>a\*</sup> Radmila Krupková,<sup>a</sup>  
Přemysl Vaněk,<sup>a</sup> Michal Dušek<sup>a</sup>  
and Ivan Němec<sup>b</sup><sup>a</sup>Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czech Republic, and <sup>b</sup>Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 43 Praha 2, Czech Republic

Correspondence e-mail: fabry@fzu.cz

## Key indicators

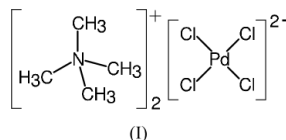
Single-crystal X-ray study  
 $T = 292$  K  
Mean  $\sigma(\text{C-N}) = 0.002$  Å  
 $R$  factor = 0.022  
 $wR$  factor = 0.075  
Data-to-parameter ratio = 40.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Bis(tetramethylammonium) tetrachloropalladate(II)

The structure of a room-temperature phase of bis(tetramethylammonium) tetrachloropalladate(II),  $(\text{C}_4\text{H}_{12}\text{N})_2[\text{PdCl}_4]$ , is reported. All the H atoms were observed in a Fourier map. The presence of  $\text{C-H}\cdots\text{Cl}$  hydrogen bonds, with  $\text{H}\cdots\text{Cl}$  distances as short as 2.92 Å, was confirmed by vibrational spectroscopy. The symmetry of the cation and anion are  $\bar{4}$  and  $mmm$ , respectively.

## Comment

The present study was undertaken because of the absence of structural data for the title compound, (I).



In the title compound, a phase transition was detected by Vaněk *et al.* (1993) by differential scanning calorimetry and optical observation at 473 K. Sato *et al.* (1987) found no anomaly by DTA between 125 and 450 K. The structure of (I) is reported for the first time in this study, although it has been suggested that it is tetragonal at room temperature (Sato *et al.*, 1987; Vaněk *et al.*, 1993). Sato *et al.* (1987) found that the phase transition temperatures in isomorphous (*ibid.*)  $[\text{N}(\text{CH}_3)_4][\text{PdBr}_4]$  and  $[\text{N}(\text{CH}_3)_4][\text{PtBr}_4]$  are sensitive to moisture and that the phase transitions in these Br complexes are influenced by previous heating of the samples. Their structures are probably also unknown in detail because they are not mentioned in the Cambridge Structural Database (CSD; Version as525be with addenda up to April 2004; Allen, 2002).

The title compound is chemically related to an interesting compound bis(ammonium) tetrachloropalladate,  $(\text{NH}_4)_2[\text{PdCl}_4]$  (Adams & Berg, 1976; Krebs Larsen & Berg, 1977; Asai & Kiriya, 1979; Prager & Badurek, 1986; Vaněk & Havránková, 1992; Gesi, 2001). Both compounds contain the  $[\text{PdCl}_4]^{2-}$  anion.

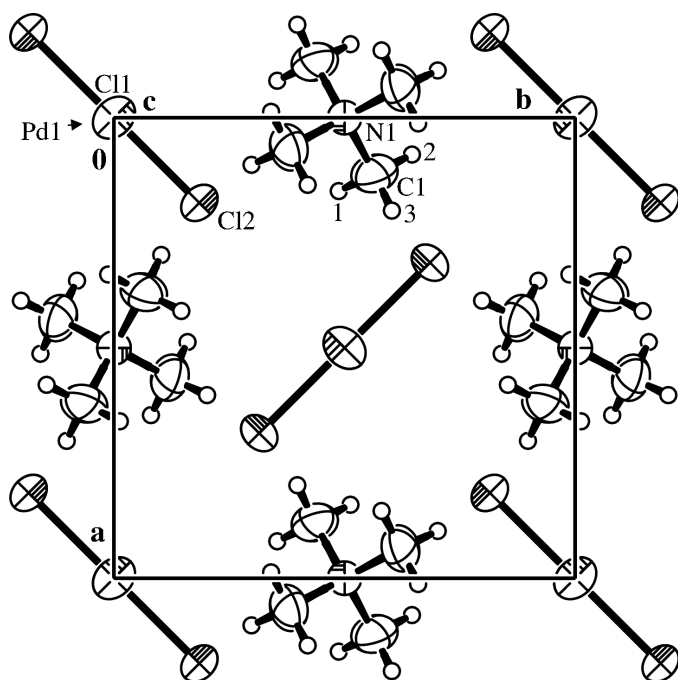
The Pd–Cl distances in the title structure (Table 1) correspond well to the distances in the  $[\text{PdCl}_4]^{2-}$  anion reported in the CSD; for 39 hits, the mean Pd–Cl distance is 2.304 (4) Å. (Two other hits were excluded because of an improbably large deviation of the Pd–Cl distance from the mean value or because of a high  $R$  factor.) The C–N values are also normal.

The shortest C–H $\cdots$ Cl distances (Table 2) are about the values of the N–H $\cdots$ Cl hydrogen bonds for Cl bonded to a transition metal (Desiraju & Steiner, 1999; Aullón *et al.*, 1998).

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**Figure 1**  
Crystal packing of the title compound, viewed down the *c* axis. The atomic displacement ellipsoids are drawn at the 50% probability level.

On the other hand, they are somewhat longer than  $C_{\text{methylene}}-\text{H}\cdots\text{Cl}$  in bis(tetra-*n*-ethylammonium) tetrachloropalladate(II), *n*-( $\text{Et}_4\text{N}$ )<sub>2</sub>[PdCl<sub>4</sub>] (Fábry *et al.*, 2004), which are as short as  $\sim 2.85$  Å for the room-temperature phase. The vibrational spectroscopic data can serve as criteria (James *et al.*, 1996) for deciding whether a hydrogen bond is really present, because of a decrease of a pertinent frequency of a donor hydrogen bond. In addition, according to Koller *et al.* (1992), a red shift of tetramethylammonium C–H stretching vibrations, especially of antisymmetric ones, is considered as evidence of C–H $\cdots$ X hydrogen bonds, where X is a halogen or another electronegative element.

In order to confirm the presence of C–H $\cdots$ Cl hydrogen bonds, IR and Raman spectra were recorded. Six bands were recorded in the IR spectrum within the C–H stretching vibrations region, *viz.* a medium intensity band at  $3024\text{ cm}^{-1}$  ( $\nu_{\text{as}}\text{CH}_3$ ) with a shoulder at  $3018\text{ cm}^{-1}$ , a weak band at  $2960\text{ cm}^{-1}$  ( $\nu_{\text{s}}\text{CH}_3$ ), and three weak bands at 2925, 2875 and  $2829\text{ cm}^{-1}$ . The complementary Raman spectrum exhibits six bands at  $3022$  (*vs*),  $3016$  (*sh*),  $2976$  (*m*),  $2960$  (*m*),  $2926$  (*s*) and  $2827$  (*m*)  $\text{cm}^{-1}$ . The bands at  $3022$  and  $2960\text{ cm}^{-1}$  can be assigned to fundamental antisymmetric and symmetric stretching CH<sub>3</sub> vibrations, respectively. The remaining bands in both spectra are regarded (Ohe, 1975; Zeegers-Huyskens & Bator, 1996) as higher-order vibrational bands enhanced by Fermi resonance.

If our spectroscopic results are compared with other tetramethylammonium compounds (Harmon *et al.*, 1974; Ohe, 1975; Wilson *et al.*, 1989; Koller *et al.*, 1992; Zeegers-Huyskens & Bator, 1996; Ouasri *et al.*, 2002), the positions of  $\nu\text{CH}_3$  bands in the title compound spectra clearly indicate the existence of C–H $\cdots$ Cl hydrogen bonds. For example, the wavenumber of

the antisymmetric CH<sub>3</sub> stretching vibration is lower by  $12\text{--}28\text{ cm}^{-1}$  than that of the chlorine-containing tetramethylammonium salts  $[\text{N}(\text{CH}_3)_4]\text{Cl}$ ,  $[\text{N}(\text{CH}_3)_4]_2[\text{SnCl}_6]$  or  $[\text{N}(\text{CH}_3)_4]_2[\text{UCl}_6]$  (Harmon *et al.*, 1974; Ohe, 1975). Another piece of evidence for the presence of the C–H $\cdots$ Cl hydrogen bonds is the characteristic band shape (Harmon *et al.*, 1974; Ouasri *et al.*, 2002) of the IR spectrum, *i.e.* the presence of several weaker bands located on the lower-frequency side of the CH stretching region.

## Experimental

Crystals of (I) were grown from an aqueous stoichiometric solution containing PdCl<sub>2</sub> (Merck, for synthesis) and  $[\text{N}(\text{CH}_3)_4]\text{Cl}$  (Merck, pure). The sample was prepared about 10 years ago.

### Crystal data

(C<sub>4</sub>H<sub>12</sub>N)<sub>2</sub>[PdCl<sub>4</sub>]  
 $M_r = 396.49$   
 Tetragonal,  $P4_2/mmm$   
 $a = 8.8281(10)\text{ \AA}$   
 $c = 11.4206(10)\text{ \AA}$   
 $V = 890.07(16)\text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.479\text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 46 reflections  
 $\theta = 10.4\text{--}14.0^\circ$   
 $\mu = 1.62\text{ mm}^{-1}$   
 $T = 292(2)\text{ K}$   
 Plate, red  
 $0.61 \times 0.41 \times 0.12\text{ mm}$

### Data collection

Kuma XCalibur diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: Gaussian  
 (JANA2000; Petříček & Dušek, 2000)  
 $T_{\text{min}} = 0.553$ ,  $T_{\text{max}} = 0.814$   
 5577 measured reflections  
 962 independent reflections  
 639 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$   
 $\theta_{\text{max}} = 40.5^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -16 \rightarrow 16$   
 $l = 0 \rightarrow 15$   
 3 standard reflections  
 every 100 reflections  
 intensity decay: 4.2%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.075$   
 $S = 1.12$   
 962 reflections  
 24 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.0815P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.58\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.70\text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å).

Pd1—Cl1	2.2971 (13)	N1—C1	1.489 (2)
Pd1—Cl2	2.3110 (9)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C1—H1 $\cdots$ Cl2	0.96	3.03	3.939 (3)	160
C1—H2 $\cdots$ Cl2 <sup>i</sup>	0.96	3.14	4.019 (3)	153
C1—H3 $\cdots$ Cl1 <sup>ii</sup>	0.96	2.92	3.679 (3)	137

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

All H atoms were located in a difference Fourier map and were then treated as riding [ $\text{C—H} = 0.96\text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C1})$ ]. PLATON (Spek, 2003) indicated voids in Wyckoff site 2a. The size of these voids ( $48\text{ \AA}^3$ ) does not preclude the possibility that a water molecule could be present in the structure. The maximal residual

electron density is located at (0.07, 0.07, 0), *i.e.* close to Wyckoff site 2a. The low value of the residual density means that, if water is present in this void, the molecule is not ordered.

Data collection: *KM4B8* (Gałdecki *et al.*, 1997); cell refinement: *KM4B8*; data reduction: *JANA2000* (Petříček & Dušek, 2000); program(s) used to solve structure: *SIR97* (Cascarano *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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