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## Bis(diethylenetriammonium) Tetrachloroplatinate(II) Tetrachloride

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**Abstract.** [C<sub>4</sub>H<sub>16</sub>N<sub>3</sub>]<sub>2</sub>[PtCl<sub>4</sub>]Cl<sub>4</sub>, 2C<sub>4</sub>H<sub>16</sub>N<sub>3</sub><sup>3+</sup>·4Cl<sup>-</sup>·Cl<sub>4</sub>Pt<sup>2-</sup>, monoclinic, *C*2/*c*, *Z* = 4, *a* = 21·496 (3), *b* = 6·841 (1), *c* = 15·820 (4) Å, β = 104·14 (2)°, *V* = 2256·0 (7) Å<sup>3</sup>, *D*<sub>calc</sub> = 2·03, *D*<sub>obs</sub> = 2·02 Mg m<sup>-3</sup>. The structure was determined by Patterson and electron density difference methods and refined by full-matrix least squares to *R* = 0·034, *R*<sub>w</sub> = 0·050. The structure comprises discrete diethylenetriammonium, chloride and tetrachloroplatinate(II) ions. Bond distances are normal and NH–Cl hydrogen bonds are involved in crystal packing.

**Introduction.** The title compound was prepared by a modification of the method of Watt & Cude (1968). Potassium tetrachloroplatinate(II) (0·26 g) was refluxed with diethylenetriamine (0·13 g) in 1 *M* HCl (50 ml) for 4–5 hours. The solution was allowed to stand for 18 hours, when the title compound separated as red-orange crystals. (Analysis: calculated: C, 13·9; H, 4·7; N, 12·2; Cl, 41·0%; found: C, 14·0; H, 4·8; N, 12·1; Cl, 41·2%.)

A crystal, homogeneous under the polarizing microscope, was cut and ground to a cylinder of radius 0·157 mm and length 0·506 mm. Precession photographs showed the systematic absences of the space groups *C*2/*c* and *C*c. *C*2/*c* was chosen as the correct space group (see below). The cell parameters were determined by the least-squares fit of 15 well centred reflections (17° < 2θ < 25°) on a Syntex *P*2<sub>1</sub> diffractometer and the density was determined by flotation in a diiodomethane–carbon tetrachloride mixture, yielding *Z* = 4 for the title formula. Intensities were measured up to 2θ = 55° using a computer-controlled Syntex *P*2<sub>1</sub> diffractometer operated in a

2θ(counter)–θ(crystal) scan mode with a crystal monochromator and Mo *K*α radiation.

After averaging and removal of systematically absent reflections, 2374 reflections were considered significant [*I* > 3σ(*I*)] and were used for structure determination: 211 were considered unobserved and were given no weight in the structure determination unless *F*<sub>c</sub> > *F*<sub>o</sub>. The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). Correction was made both for absorption (μ = 7·49 mm<sup>-1</sup>; *A*\* varied from 4·618 to 6·764) and secondary extinction (Larson, 1967; *g* = 1·353 × 10<sup>-7</sup>). The stability of the experimental system was monitored by measuring two standard reflections after every 48 reflections (512, 11, 1, 2); these showed e.s.d.'s of 1·9 and 2·3% with no time variation.

The space group *C*2/*c* was chosen after obvious symmetry correlations in a Patterson map computed in *C*c and is justified by the successful solution of the structure. The chloride ions were located from an electron density difference synthesis and in further full-matrix least-squares refinement, minimizing ∑w(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>, the temperature factors of the Pt and Cl atoms were made anisotropic. Statistical tests (Hamilton, 1965) showed that this was significant but that the use of anisotropic temperature factors for the C and N atoms was not. Convergence was obtained with 71 variables at *R* = 0·032 (0·034) and *R*<sub>w</sub> = 0·050 (0·050) for the observed (all) reflections. The weighting scheme applied was 1/*w* = σ<sub>F</sub><sup>2</sup> + (0·03*F*<sub>o</sub>)<sup>2</sup>; the standard deviation of an observation of unit weight was 1·286. Scattering factors were taken from Cromer & Waber (1974) and correction for anomalous scattering

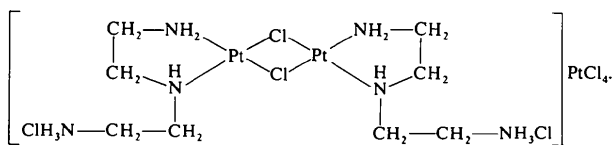
Table 1. Positional parameters and isotropic temperature factors ( $U_{iso}$  or  $U_{eq}$ ) for [NH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[PtCl<sub>4</sub>]Cl<sub>4</sub> ( $\times 10^4$ )

	x	y	z	$U_{eq}^*$ or $U_{iso}$
Pt	0	741.0 (4)	2500	235 (2)*
Cl(1)	200.7 (7)	3095 (2)	3575.6 (9)	331 (7)*
Cl(2)	156.2 (7)	-1613 (2)	3562.8 (9)	335 (7)*
Cl(3)	1946.7 (8)	-642 (2)	2704 (1)	363 (7)*
Cl(4)	1979.7 (7)	5254 (2)	4556.6 (9)	358 (7)*
N(1)	3935 (2)	775 (6)	2382 (3)	320 (10)
C(1)	3601 (3)	-954 (7)	2627 (3)	280 (10)
C(2)	3514 (3)	-642 (7)	3548 (4)	300 (10)
N(2)	3295 (2)	-2553 (7)	3866 (3)	300 (10)
C(3)	3846 (3)	-3795 (9)	4321 (4)	350 (10)
C(4)	3644 (3)	-5729 (8)	4621 (4)	370 (10)
N(3)	3429 (3)	-5602 (7)	5452 (4)	360 (10)

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

was applied to Pt and Cl (Cromer, 1974). H atoms were not detected. In the last cycle of refinement, no parameter shifted by more than 0.02 of its error; the average was 0.003. A final difference map was essentially featureless, the maximum being 2.84 e Å<sup>-3</sup> and the minimum -1.51 e Å<sup>-3</sup>, both near Pt.\* Positional parameters and  $U_{iso}$  or  $U_{eq}$  are given in Table 1.

**Discussion.** Attempts to prepare [Pt{NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH-(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>}OH<sub>2</sub>]<sup>2+</sup> as part of our structural studies on Pt<sup>II</sup>-OH<sub>2</sub> and Pt<sup>II</sup>-OH complexes (Faggiani, Lippert, Lock & Rosenberg, 1977a,b, 1978; Lippert, Lock, Rosenberg & Zvagulis, 1978) involved the preparation of various halide-containing precursors (Watt & Cude, 1968) and we have attempted to prepare a material claimed to be



The product we obtained clearly differed from the above, as shown by differences in the infrared spectra (Fig. 1 and Watt & Cude, 1968), even though it was prepared by a similar procedure. The compound we isolated was the title compound.

The structure comprises discrete diethylenetriammonium [N(1)C(1)C(2)N(2)C(3)C(4)N(3)], chloride [Cl(3), Cl(4)] and tetrachloroplatinate(II) [Pt-Cl(1)Cl(2)] ions. Bond distances and angles within

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34752 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

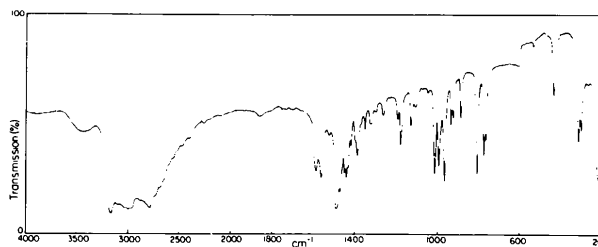


Fig. 1. Infrared spectrum (KBr disc) of [NH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[PtCl<sub>4</sub>]Cl<sub>4</sub>. The drop in absorption at 600 cm<sup>-1</sup> is caused by a grating change. (Recorded on a Perkin-Elmer 283.)

Table 2. Selected interatomic distances (Å) and angles (°) for [NH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[PtCl<sub>4</sub>]Cl<sub>4</sub>

(a) Bonded	(b) Non-bonded or hydrogen bonded
Pt-Cl(1)	N(1)-Cl(3) <sup>a</sup>
Pt-Cl(2)	N(1)-Cl(4) <sup>b</sup>
N(1)-C(1)	N(1)-Cl(1) <sup>b</sup>
C(1)-C(2)	N(1)-Cl(2) <sup>a</sup>
C(2)-N(2)	N(1)-Cl(2) <sup>d</sup>
N(2)-C(3)	N(1)-Cl(1) <sup>c</sup>
C(3)-C(4)	N(2)-Cl(4) <sup>e</sup>
C(4)-N(3)	N(2)-Cl(3) <sup>b</sup>
Cl(1)-Pt-Cl(1)	N(2)-Cl(3)
Cl(1)-Pt-Cl(2)	N(2)-Cl(4) <sup>f</sup>
Cl(1)-Pt-Cl(2)	N(3)-Cl(4) <sup>f</sup>
Cl(2)-Pt-Cl(2)	N(3)-Cl(4) <sup>g</sup>
N(1)-C(1)-C(2)	N(3)-Cl(3) <sup>g</sup>
C(1)-C(2)-N(2)	N(3)-Cl(2) <sup>g</sup>
C(2)-N(2)-C(3)	N(3)-Cl(1) <sup>g</sup>
N(2)-C(3)-C(4)	
C(3)-C(4)-N(3)	

Atoms with superscripts are related to the atoms in Table 1 by the transformations: (a)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (b)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (c)  $\frac{1}{2} + x, y - \frac{1}{2}, z$ ; (d)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (e)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (f)  $x, y - 1, z$ ; (g)  $\frac{1}{2} - x, -y - \frac{1}{2}, 1 - z$ ; (h)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (i)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (j)  $x, 1 + y, z$ .

the tetrachloroplatinate(II) ion are normal (Purnell & Hodgson, 1976). Distances and angles (see Table 2) within the diethylenetriammonium ion are similar to those observed in diethylenetriammonium tetrachlorocuprate(II) chloride (Greenough & Ladd, 1977), but there are some differences in the two halves of the cation in our compound and between cations in the two compounds. Equivalent bond distances do not differ significantly except that C(2)-N(2) is significantly longer than the equivalent distance in the Cu complex (3.7σ).\* Differences in angles are much more marked. In the Cu complex, the angles N(terminal)-C-C [112.0 (2)°] differed by 15.2σ from C-C-N(middle) [107.7 (2)°]. In our compound there are insignificant differences in these angles in a given half [113.6 (5),

\* σ used for comparison is given by  $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$ .

113.4 (5) and 108.5 (4), 108.4 (4)°], but clearly the two halves differ markedly (7.89σ). The normal conformations of an N—C—C—N system are *trans* where the dihedral angle between the two N—C—C planes is close to 180° and *cis* where the dihedral angle is about 70°. The former arrangement is observed for the title compound in the half where the N—C—C angles are close to the tetrahedral angle (dihedral angle 169.0°), but larger N—C—C angles are found in the half with the *cis* arrangement (dihedral angle 79.9°). This arrangement brings the N atoms fairly close together [3.22 (1) Å] and apparently induces sufficient strain to enlarge the N—C—C angles. In the Cu complex both halves have the *trans* arrangement. The central C—N—C angle is different in the two compounds, being 6.93σ smaller for our compound.

Hydrogen bonding is clearly important in holding the crystal together but, because we were unable to locate the H atoms, there are ambiguities as to which atoms are hydrogen bonded and these cannot be resolved by considering interatomic distances and angles (see Table 2). The arrangement of the three N atoms about Cl(1) and Cl(2) is interesting because it is essentially the same for both atoms. The three N atoms form the apices of a T with the junction at Cl, the T being oriented such that the Pt—Cl—N angles are all close to 90°.

The packing within the unit cell is shown in Fig. 2. It is interesting that although the Pt and Cu complexes

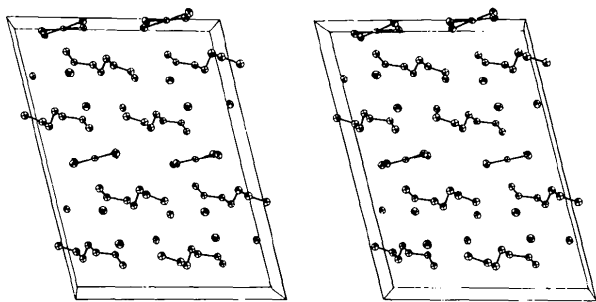


Fig. 2. Stereoscopic view of the contents of the unit cell of [NH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[PtCl<sub>4</sub>]Cl<sub>4</sub>.

are made up of similarly shaped and charged ions, the stoichiometries are different and thus so are the crystal structures. The structure of the title compound is essentially a series of layers parallel to the *bc* plane. Core layers of PtCl<sub>4</sub><sup>2-</sup> ions lie at *x* = 0 and  $\frac{1}{2}$  and these are sandwiched between and hydrogen-bonded to layers of diethylenetriammonium ions displaced roughly  $\pm 0.15$  along *a*. These cation layers are in turn separated and cross hydrogen-bonded to irregular layers of Cl(3) and Cl(4) ions centred at *x* =  $\frac{1}{4}$  and  $\frac{3}{4}$ . Packing within the *bc* planes shows no peculiarities and is determined by the hydrogen-bonding requirements.

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