anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). A difference synthesis calculated at this stage showed a large negative peak in the neighbourhood of the F atoms and slightly smaller positive peaks in the positions expected for the methyl H atoms. The H atoms were therefore included in a further calculation in which the positional and temperature coordinates of the H and methyl C atoms were varied. The agreement index dropped to $R_1 = 0{\cdot}026$ and $R_w = 0{\cdot}026$. The average shift/error for this refinement was 0·4 [max. = 1·5 for $U$ of H(3)]. The final value of $[\sum w(|F_c| - |F_o|)^2]/$(number of reflections − number of variables) = 2·2. The final positional coordinates are given in Table 1.*

**Discussion.** Bond lengths and angles are given in Table 2 and the structure is illustrated in Fig. 1. The dimer is essentially identical to that of $\{[(C_4H_9)_2Sn(O_2CCCl_3)]_2O\}_2$ (Graziani *et al.* 1977) although the packing of the molecules, and consequently the crystal cell and space group, are quite different. $\{[(CH_3)_2Sn(O_2CCH_3)]_2O\}_2$ crystallizes with a cell similar to the trifluoroacetate and presumably has the same structural topology (Zvonkova, Povet'eva, Vozžennikov, Gluškova, Jakovenko & Khvatkina, 1966) although the space group is different ($P2_1/a$ in the setting used here). In the trifluoroacetate all atoms, except the methyl groups and two thirds of the F atoms, lie in the mirror plane. Each dimer contains four Sn atoms of which two are crystallographically distinct. Both have trigonal bipyramidal coordination with the two methyl groups (Sn—C = 2·11 Å) and the bridging oxygen (Sn—O = 2·040 Å) in the equatorial plane. The axial Sn—O bonds are slightly longer (2·24 Å average). In addition each Sn has one or two further O neighbours (Sn—O ~ 2·8 Å) lying between the two methyl groups.

Although the Sn atoms have similar environments, the trifluoroacetate (tfa) ions are quite different. One forms a symmetrical bridge between Sn(1) and Sn(2). The other is strongly bonded only to Sn(2) making the ion very asymmetric. The other oxygen atom, O(3), forms a weak bond to Sn(2) in the adjacent dimer linking the molecules into chains running along the $c$ axis. The chains are bonded to each other only through weak C—H···F interactions between the F atoms of one chain and the methyl groups of the chains related by the $C$-centring operation.

The model successfully refined with each $-CF_3$ group replaced by two half $-CF_3$ groups rotated by 60° about the tfa C—C axis. The temperature factors of the F atoms are elongated in such a way as to suggest that the $CF_3$ groups might be rotating but a hindered rotation or even static disorder cannot be ruled out. All other atoms show their largest thermal vibrations perpendicular to the molecular plane.

We wish to thank the National Research Council of Canada for operating grants.

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# Trichloro($\eta$-*N*-methyl-4-pentenylammonium)platinum(II)

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**Abstract.** $C_6H_{14}Cl_3NPt$, orthorhombic, $Pna2_1$, $a = 18{\cdot}623\,(7)$, $b = 8{\cdot}385\,(2)$, $c = 7{\cdot}261\,(2)$ Å, $D_m = 2{\cdot}31\,(1)$, $Z = 4$, $D_c = 2{\cdot}338$ g cm$^{-3}$. Cell parameters were determined by a least-squares refinement of the setting angles of 15 reflections. The zwitterionic complex was prepared by method (1) of Denning & Venanzi [*J. Chem. Soc.* (1963), pp. 3241–3247]. *N*-Methyl-4-pentenylamine was provided by J. Ambühl [Dis-

sertation ETH (1977), No. 6022] who prepared it by the method of Perie, Laval, Rousse & Lattes [*Tetrahedron* (1972), **28**, 675–699].

**Introduction.** In the solid state, zwitterionic complexes of the type [$PtCl_3(L)$], where $L$ is an unsaturated ammonium cation bound to platinum(II) through the olefinic double bond, take part in packing dominated by a hydrogen-bond network (Mura, Spagna & Zambonelli, 1977; and references therein). In fact, considering the number of N···Cl contacts shorter than the sum of the ionic radii, it can be stated that all the H atoms of the $-NH_3^+$ group take part in N—H···Cl hydrogen bonds, some of which are bifurcated (Hamilton & Ibers, 1968).

It seemed interesting to define the role that the hydrogen bonds play in the structure and to test how the geometry of the molecule and its packing could be affected by a decrease in the number of hydrogen bonds. For this investigation, therefore, a series of three complexes was needed in which the possibility of hydrogen bonding is gradually reduced by substitution of H atoms of the $-NH_3^+$ group with alkyl groups. The three complexes [$PtCl_3(L)$] with $L$ = *N*-methyl-, *N*,*N*-dimethyl- and *N*,*N*,*N*-trimethyl-4-pentenylammonium, which were also interesting for a study of the platinum-promoted cyclization of 4-pentenylamine (Ambühl, Pregosin, Venanzi, Ughetto & Zambonelli, 1975), were considered relevant to this study. Unfortunately only the complex with *N*-methyl-4-pentenylammonium gave crystals suitable for X-ray analysis; therefore only its structure is reported here.

A crystal 0·07 × 0·12 × 0·20 mm was used for data collection on a Syntex $P2_1$ automatic diffractometer (graphite-monochromatized Mo $K\alpha$ radiation).

The unique set collected ($\theta$ range 1·5–28°, $\theta$–$2\theta$ scan, scan range 1·60°, scan speed 2·0–29·3° min$^{-1}$) contained 911 reflections with $I > 3\sigma(I)$. These reflections were corrected for Lorentz and polarization effects, and for the shape anisotropy of the crystal used [$\mu$(Mo $K\alpha$) = 131·7 cm$^{-1}$].

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations. The H atoms were positioned geometrically and their fixed contribution was included in the last cycles of anisotropic refinement, with their positions adjusted after each cycle.

The final $R$ is 0·038 ($R_w$ = 0·056). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 4F_o^2/\sigma(F_o^2)$.

Atomic scattering factors and anomalous dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). The calculations were performed, using local programs, on the Univac 1110 computer of the University of Rome and on the HP 21MX minicomputer of the CNR Research Area.

The final atomic parameters are given in Table 1.* Interatomic distances and bond angles are reported in Table 2.

**Discussion.** Fig. 1. shows a perspective view of the molecule and Fig. 2 illustrates the packing of the molecules.

Pt is four-coordinated, in a square-planar configuration, by the three Cl atoms and the olefinic double bond of the unsaturated ammonium cation. Pt and the three Cl are almost exactly coplanar; the best plane through them makes a dihedral angle of 84·6° with the plane defined by Pt, C(4) and C(5) and makes exactly the same angle with the direction of the olefinic double bond. The midpoint of the double bond is 0·1 Å out of the coordination plane.

The geometric features of the molecule of $PtCl_3$(η-*N*-methyl-4-pentenylammonium) compare with those found in other analogous complexes (Mura *et al.*, 1977;

Table 1. *Positional parameters* (×10$^4$)

Estimated standard deviations are given in parentheses.

| | *x* | *y* | *z* |
|---|---|---|---|
| Pt | 3947 (0) | 6017 (1) | 5000 (0) |
| Cl(1) | 4501 (4) | 8275 (8) | 3961 (11) |
| Cl(2) | 3190 (4) | 5975 (9) | 2566 (12) |
| Cl(3) | 3414 (5) | 3727 (8) | 6222 (14) |
| N | 3241 (16) | 9943 (27) | 11369 (37) |
| C(1) | 3561 (18) | 10437 (34) | 9657 (24) |
| C(2) | 3668 (21) | 8991 (55) | 8395 (61) |
| C(3) | 4382 (14) | 7997 (45) | 8538 (43) |
| C(4) | 4308 (17) | 6410 (29) | 7904 (39) |
| C(5) | 4838 (18) | 5597 (37) | 6894 (50) |
| C(6) | 3164 (26) | 11229 (35) | 12755 (54) |

Table 2. *Bond lengths and angles*

Estimated standard deviations are given in parentheses; *M* defines the midpoint of the olefinic double bond.

| | | | |
|---|---|---|---|
| Pt—Cl(1) | 2·285 (7) Å | Cl(1)—Pt—Cl(2) | 92·1 (3)° |
| Pt—Cl(2) | 2·261 (9) | Cl(1)—Pt—Cl(3) | 176·7 (3) |
| Pt—Cl(3) | 2·336 (8) | Cl(1)—Pt—*M* | 91·5 |
| Pt—C(4) | 2·24 (3) | Cl(2)—Pt—Cl(3) | 91·1 (3) |
| Pt—C(5) | 2·19 (4) | Cl(2)—Pt—*M* | 175·1 |
| Pt—*M* | 2·10 | Cl(3)—Pt—*M* | 85·2 |
| N—C(1) | 1·44 (4) | C(4)—Pt—C(5) | 37 (1) |
| C(1)—C(2) | 1·53 (5) | N—C(1)—C(2) | 110 (3) |
| C(2)—C(3) | 1·57 (5) | C(1)—C(2)—C(3) | 119 (3) |
| C(3)—C(4) | 1·42 (4) | C(2)—C(3)—C(4) | 113 (3) |
| C(4)—C(5) | 1·41 (5) | C(3)—C(4)—C(5) | 124 (3) |
| N—C(6) | 1·48 (4) | C(1)—N—C(6) | 115 (2) |

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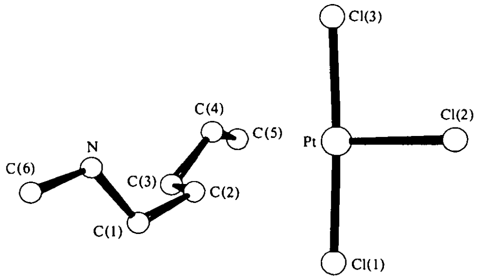

Fig. 1. Perspective view of the zwitterionic [$PtCl_3$($\eta$-*N*-methyl-4-pentenylammonium)] complex in its C(4)*R* configuration.

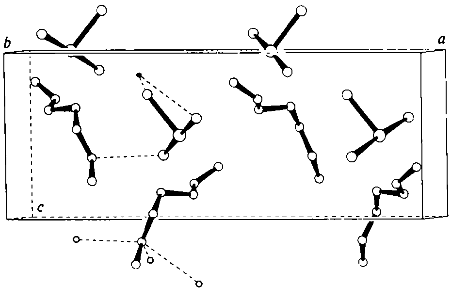

Fig. 2. Packing of the molecules: the hydrogen-bond network of the unit at *xyz* is shown by broken lines. Small filled and open circles indicate respectively N and Cl atoms of neighbouring units.

and references therein) except for the three Pt—Cl bonds. In fact, in the present structure one of the Pt—Cl bonds, in the *cis* position with respect to the coordinated double bond, is longer than the others (~8$\sigma$) while in general the Pt—Cl bond *trans* to the double bond is the longer one.

In Table 3 the torsion angles (Klyne & Prelog, 1960) of the *N*-methyl-4-pentenylammonium cation are reported. Apart from the *N*-methyl group, the conformation of the chain resembles that of the 4-pentenylammonium cation in its [$PtCl_3$(*L*)] complex, as found in the so-called 'yellow form' (Spagna & Zambonelli, 1972).

The optically active complex (Paiaro & Panunzi, 1964) is present in the crystal in the racemic form, the C(4)*R* and C(4)*S* configurations (Cahn, Ingold & Prelog, 1956) being related by the glide plane; Fig. 1 and the tables refer to the molecule with C(4)*R* configuration.

All the N···Cl contacts, which are shorter than the sum of the ionic radii (3·62 Å) and suggest N—H···Cl hydrogen bonds, are reported in Table 4. As expected, short N···Cl contacts are less numerous than in the cases where the —$NH_3^+$ groups are not substituted, but on the whole this structure does not present substantial differences from the complexes with unsubstituted ammonium cations.

Table 3. *Some relevant internal rotation angles*

Estimated standard deviations are given in parentheses.

| | |
|---|---|
| C(6)—N—C(1)—C(2) | 176 (3)° |
| N—C(1)—C(2)—C(3) | −88 (4) |
| C(1)—C(2)—C(3)—C(4) | 156 (3) |
| C(2)—C(3)—C(4)—C(5) | 141 (3) |

Table 4. *Intermolecular contacts shorter than the sum of the ionic radii* (3·62 Å)

| | |
|---|---|
| N···Cl($3^i$) | 3·25 (3) Å |
| N···Cl($1^{ii}$) | 3·32 (3) |
| N···Cl($2^{ii}$) | 3·44 (3) |

Symmetry code

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

This investigation is not conclusive since the most significant complexes, in particular that with *L* = *N*,*N*,*N*-trimethyl-4-pentenylammonium, could not be studied.

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