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Trichloro-(π-*cis*-pent-3-enylammonium)platinum(II)

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Abstract. $PtCl_3(C_5H_{12}N)$, monoclinic, $P2_1/c$, $a=8{\cdot}521$ (5), $b=7{\cdot}569$ (8), $c=15{\cdot}073$ (16) Å, $\beta=102{\cdot}45$ (7)°, $D_m=2{\cdot}71$ (1), $Z=4$, $D_c=2{\cdot}702$ g cm^{-3}. The zwitterionic complex was prepared by method (1) of Denning & Venanzi [*J. Chem. Soc.* (1963), pp. 3241–3247]. The ligand *cis*-pent-3-enylammine hydrochloride was prepared from 1-chloro-3-pentyne by the Gabriel phthalimide method [Sheenan & Bolhofer, *J. Amer. Chem. Soc.* (1950), **72**, 2786–2788] through the Lindlar hydrogenation of 3-pentyne-1-phthalimide.

Introduction. Cell parameters were determined by a least-squares refinement of the setting angles of 15 reflexions centred on a Syntex $P2_1$ automatic diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite crystal. Systematic absences were $h0l$ with l odd and $0k0$ with k odd. The intensities were obtained from a crystal ($0{\cdot}15\times0{\cdot}15\times0{\cdot}24$ mm) mounted on the diffractometer (Mo $K\alpha$ monochromatized, θ–2θ scan). 3611 independent reflexions were measured up to $2\theta=60°$; 2554 of these, with $F_o>3\sigma(F_o)$, were used for the analysis. A correction for the shape anisotropy [μ(Mo $K\alpha$) = 162·5 cm^{-1}] was applied (Furnas, 1975; North, Phillips & Matthews, 1968) with a procedure similar to that previously described (Spagna & Zambonelli, 1971). For this correction the variation in intensity of the conveniently intense reflexions (320, 632, 732 and 842) with χ angles near to 90 or 270° was measured as a function of φ. Lorentz and polarization corrections were applied. The structure was solved by Patterson and Fourier methods. The full-matrix least-squares refinement converged at $R=0{\cdot}065$ and $R=0{\cdot}045$ with isotropic and anisotropic temperature factors respectively. At this stage H atoms were positioned geometrically and included in the structure-factor calculations, being readjusted after each cycle. The final R is 0·044 ($R_w=0{\cdot}044$). The function minimized was $\sum w(|F_o|-|F_c|)^2$ with weights $w=4F_o^2/\sigma(F_o^2)$.

Atomic form factors given by Cromer & Mann (1968) for Pt, Cl, N and C, and by Hanson, Herman, Lea & Skillman (1964) for H were used. The effects of anomalous dispersion were included: the values of $\Delta f'$ and $\Delta f''$ for Pt and Cl were those computed by Cromer (1965). In Table 1 the positional and thermal parameters for the non-hydrogen atoms are reported; the idealized positions of the H atoms are given in Table 2. Bond lengths and angles are given in Table 3.*

Discussion. Fig. 1 shows a perspective view of the molecule of the zwitterionic platinum–olefin complex. Pt is four-coordinated, in a square-planar configuration, by the three Cl atoms and the olefinic double bond of the pentenylammonium cation. The best plane ($-4{\cdot}900x+5{\cdot}880y+5{\cdot}648z-1{\cdot}433=0$, in terms of monoclinic coordinates) was calculated through the Pt and the Cl atoms. The midpoint of the olefinic double bond is 0·30 Å out of this principal plane, and the double bond makes an angle of 81·9° with it. The

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31785 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters* ($\times10^4$) *for the non-hydrogen atoms*

Estimated standard deviations are given in parentheses. Coefficients b_{ij} are defined by the expression

$$T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)].$$

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pt	2049 (0)	2246 (0)	1897 (0)	60 (0)	10 (1)	16 (0)	48 (1)	−2 (1)	19 (0)
Cl(1)	−379 (3)	999 (3)	1208 (2)	89 (3)	−54 (6)	21 (3)	105 (4)	−33 (4)	34 (1)
Cl(2)	1844 (3)	848 (3)	3253 (2)	112 (4)	15 (7)	35 (3)	105 (4)	21 (3)	25 (1)
Cl(3)	4378 (3)	3575 (3)	2654 (2)	65 (3)	1 (6)	−6 (3)	101 (4)	2 (3)	35 (1)
N	2006 (10)	7038 (11)	2143 (5)	86 (11)	12 (22)	43 (11)	92 (16)	−9 (12)	33 (4)
C(1)	1935 (11)	7216 (13)	1144 (6)	82 (13)	23 (26)	24 (12)	81 (15)	17 (14)	30 (4)
C(2)	2751 (11)	5709 (12)	769 (6)	79 (13)	8 (23)	31 (12)	67 (16)	5 (13)	29 (4)
C(3)	1881 (10)	3970 (12)	727 (6)	64 (12)	6 (22)	18 (11)	73 (16)	11 (12)	21 (4)
C(4)	2604 (14)	2385 (13)	550 (6)	196 (22)	−10 (32)	57 (15)	70 (18)	9 (13)	22 (4)
C(5)	4341 (15)	2152 (16)	509 (8)	154 (19)	70 (36)	86 (16)	138 (22)	15 (19)	39 (5)

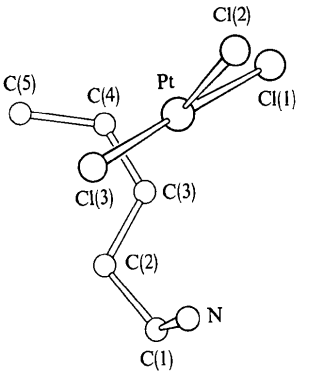

Fig. 1. Trichloro-(π-*cis*-pent-3-enylammonium)platinum(II). A perspective view of the molecule.

Table 2. *Idealized coordinates* (×10³) *for the hydrogen atoms*

The isotropic temperature factor was 3·0 Å² for all the hydrogens.

	x	*y*	*z*
H(1)N	145	807	236
H(2)N	315	701	248
H(3)N	146	592	226
H(4)C(1)	247	835	104
H(5)C(1)	78	725	82
H(6)C(2)	385	556	116
H(7)C(2)	285	603	14
H(8)C(3)	76	395	83
H(9)C(4)	190	131	44
H(10)C(5)	454	89	37
H(11)C(5)	504	248	111
H(12)C(5)	460	293	2

Table 3. *Bond lengths and angles in trichloro-(cis-pent-3-enylammonium)platinum*(II)

Estimated standard deviations are given in parentheses. MP defines the midpoint of the olefinic double bond.

Pt—Cl(1)	2·307 (2) Å	Cl(1)–Pt—Cl(2)	88·8 (1)°
Pt—Cl(2)	2·341 (2)	Cl(1)–Pt—Cl(3)	176·1 (1)
Pt—Cl(3)	2·297 (2)	Cl(1)–Pt—MP	88·2
Pt—MP	2·063	Cl(2)–Pt—Cl(3)	89·0 (1)
Pt—C(3)	2·173 (9)	Cl(2)–Pt—MP	173·1
Pt—C(4)	2·185 (11)	Cl(3)–Pt—MP	94·3
N—C(1)	1·500 (13)	C(3)–Pt—C(4)	37·5 (4)
C(1)–C(2)	1·508 (14)	N—C(1)–C(2)	112·7 (8)
C(2)–C(3)	1·505 (13)	C(1)–C(2)–C(3)	114·5 (8)
C(3)–C(4)	1·400 (14)	C(2)–C(3)–C(4)	121·6 (9)
C(4)–C(5)	1·504 (18)	C(3)–C(4)–C(5)	125·8 (10)

plane through Pt, C(3) and C(4) makes an angle of 85·4° with the principal plane.

The Pt–Cl bond *trans* to the coordinated olefinic double bond is significantly longer (20σ) than those in the *cis* positions, which are almost equivalent. In the present case the *trans* bond-lengthening is rather pronounced.

The *cis*-pentenylammonium cation, coordinated through its double bond to the Pt, has lost its pure *cis* configuration; in Table 4 the internal rotation angles of the ligand are reported (Klyne & Prelog, 1960). The optically active complex (Paiaro & Panuzzi, 1964) is present in the crystal in the racemic form, the C(3)*R*:C(4)*S* and C(3)*S*:C(4)*R* configurations (Cahn, Ingold & Prelog, 1956) being related by the glide plane; Fig. 1 and the coordinates in the tables refer to the molecule with C(3)*S*:C(4)*R* configuration.

Table 4. *Internal rotation angles of the cis-pent-3-enylammonium cation coordinated to the platinum*(II)

The convention of Klyne & Prelog (1960) is adopted. Estimated standard deviations are given in parentheses.

N—C(1)–C(2)–C(3)	70·3 (9)°
C(1)–C(2)–C(3)–C(4)	−168·6 (8)
C(2)–C(3)–C(4)–C(5)	8·9 (14)

Probably the H atoms of the $-NH_3^+$ group take part in a N–H···Cl hydrogen-bond network: short contacts between the N and Cl atoms are observed (Table 5). For the structure of other platinum(II)–olefin complexes see Spagna, Ughetto & Zambonelli (1973) and references quoted therein.

Table 5. *Intermolecular contacts between nitrogen and chlorine atoms shorter than the sum of the ionic radii* (3·62 Å)

N···Cl(1^{i})	3·19 Å	N···Cl(3)	3·30 Å
N···Cl(2^{ii})	3·35	N···Cl(3^{iii})	3·25
N···Cl(2^{i})	3·33		

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

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