The preparation and X-ray crystal structure of the $[PtCl_5(PEt_3)]^-$ anion: the *trans*-influence in platinum(IV) compounds

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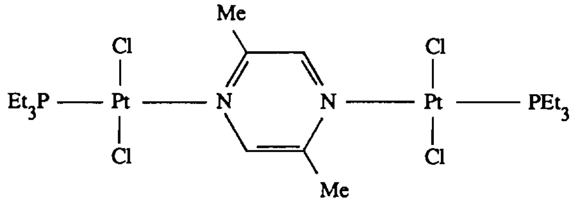
Abstract

The X-ray crystal structure of $[pppzH][PtCl_5(PEt_3)]$ (ppz = 2,5-dimethylpyrazine) was determined. It was found that the Pt–Cl distance for Cl *trans* to P is longer than the corresponding distance in $[PtCl_3(PEt_3)]^-$ showing that the *trans*-influence of a P-donor is greater in Pt(IV) than in Pt(II). Crystal data: $C_{12}H_{24}Cl_5N_2PPt$, triclinic, space group $P\bar{1}$, $a = 9.459(3)$, $b = 12.979(2)$, $c = 17.568(3)$ Å, $\alpha = 72.34(1)°$, $\beta = 86.86(2)°$, $\gamma = 83.72(2)°$, $V = 2042.2$, $Z = 4$ and $R = 0.035$ for 5371 observed reflections.

Introduction

A recent publication from our group described the preparation and characterization of complexes of the type *trans*-$[LCl_2Pt(\mu\text{-}1,4\text{-diazine})PtCl_2L]$ ($L = PR_3$ or C_2H_4) [1]. During this work attempts were made to obtain the corresponding platinum(IV) complexes by chlorine oxidation. It was found that when *trans*-$[(PEt_3)Cl_2Pt(\mu\text{-ppz})PtCl_2(PEt_3)]$ (ppz = 2,5-dimethylpyrazine) (**1**) was used, this reaction gave a mixture of compounds (see 'Experimental') from which greenish-yellow crystals of $[ppzH]^+[PtCl_5(PEt_3)]$ (**2**) were obtained. The structure of this compound was determined by X-ray diffraction.



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Results and discussion

An ORTEP view of one of the two independent molecules in the unit cell of $[ppzH][PtCl_5(PEt_3)]$, with the atomic numbering scheme, is shown in Fig. 1 while a selection of bond lengths and angles is

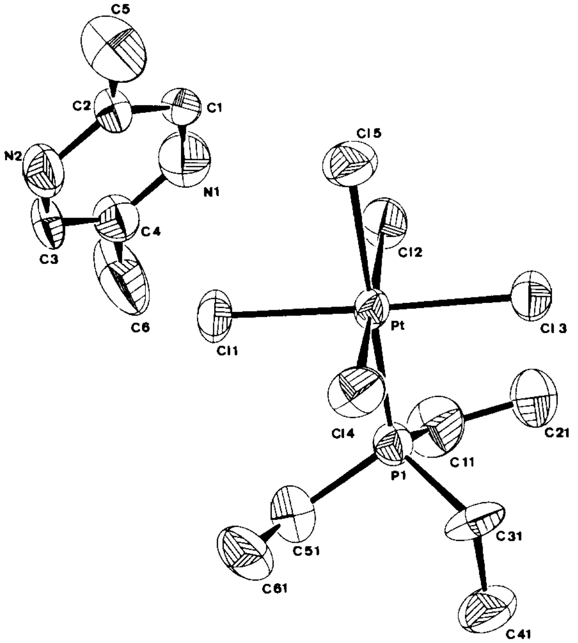

Fig. 1. An ORTEP view of one of the independent molecules of $[ppzH][PtCl_5(PEt_3)]$.

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TABLE 1. Relevant bond lengths (Å) and angles (°) for $[pppzH][PtCl_5(PEt_3)]$

	Molecule 1	Molecule 2
Pt–Cl(1)	2.321(3)	2.313(3)
Pt–Cl(2)	2.319(4)	2.313(3)
Pt–Cl(3)	2.317(3)	2.320(3)
Pt–Cl(4)	2.311(4)	2.314(3)
Pt–Cl(5)	2.425(3)	2.424(4)
Pt–P	2.314(3)	2.302(4)
Cl(1)–Pt–Cl(3)	176.8(1)	177.1(1)
Cl(2)–Pt–Cl(4)	177.3(1)	177.1(1)
Cl(1)–Pt–Cl(5)	88.9(1)	90.0(1)
Cl(2)–Pt–Cl(5)	89.1(1)	88.3(1)
Cl(3)–Pt–Cl(5)	88.0(1)	87.6(1)
Cl(4)–Pt–Cl(5)	89.9(1)	89.5(1)
Cl(1)–Pt–Cl(2)	90.3(1)	90.8(1)
Cl(2)–Pt–Cl(3)	89.8(1)	90.6(1)
Cl(3)–Pt–Cl(4)	87.6(1)	87.3(1)
Cl(1)–Pt–Cl(4)	92.2(1)	91.1(1)
P–Pt–Cl(1)	89.7(1)	88.7(1)
P–Pt–Cl(2)	90.3(1)	89.0(1)
Pt–Pt–Cl(3)	93.4(1)	93.8(1)
P–Pt–Cl(4)	90.7(1)	93.2(1)
P–Pt–Cl(5)	178.5(2)	176.9(1)

given in Table 1. The structure consists of monoprotonated 2,5-dimethylpyrazine cations, $[pzH]^+$ and octahedral $[PtCl_5(PEt_3)]^-$ anions.

The major feature of the structure is the difference in Pt–Cl bond lengths, i.e. $Pt–Cl_{trans} = 2.424(1)$ Å (av.) versus $Pt–Cl_{cis} = 2.316(4)$ Å (av.). While such differences have been observed before in platinum complexes, that reported above is, to our knowledge, the largest observed to date.

A discussion of the differences in Pt–Cl and Pt–P bond distances in $[PtCl_3(PEt_3)]^-$ is best preceded by a consideration of the changes in structural parameters between corresponding platinum(II) and platinum(IV) complexes. Some of these data are summarized in Table 2. As can be seen there, the change in the Pt–Cl distance between $[PtCl_4]^{2-}$ (2.310(1) Å) and $[PtCl_6]^{2-}$ (2.314(1) Å) is only very slight. In this context it is worth noting that the 'ionic radii' for Pt^{2+} (square planar) and Pt^{4+} (octahedral) as tabulated by Shannon [13], have been assigned the values 0.60 and 0.625 Å, respectively. It can be presumed that the decrease in radius, which normally occurs when the oxidation state of the metal center increases, in the case of platinum(II) and platinum(IV), is compensated by the increase in radius which accompanies an increase in coordination number.

The changes in Pt–Cl distances in complexes also containing other donor atoms are more subtle and are dominated by the well-known *trans*-influence [14]. As shown in Table 2, the Pt–Cl distances in $[PtCl_3(NH_3)]^-$ (entry no. 3) are significantly different: that *trans* to ammonia (2.317(7) Å) is longer than that *trans* to chlorine (2.285(7) Å), i.e. the former being practically equal to the Pt–Cl distance in $[PtCl_4]^{2-}$ (2.310 Å).

The replacement of NH_3 by PEt_3 (entry no. 4) leaves the Pt–Cl distances for the Cl atoms *trans* to Cl practically unchanged (2.300(2) Å av.) while that *trans* to PEt_3 is considerably longer (2.382(4) Å) in accordance with the higher *trans*-influence of the PR_3 ligand.

A comparison of $[PtCl_3(PEt_3)]^-$ with $[PtCl_5(PEt_3)]^-$ (entry nos. 4 and 5, respectively, in Table 2) shows that the increase in oxidation state is accompanied by a lengthening of the Pt–Cl bond

TABLE 2. Some Pt–Cl, Pt–N and Pt–P bond distances (Å) in related platinum(II) and platinum(IV) complexes

Entry no.	Compound	Pt–Cl (*trans* to L)	Pt–Cl (*trans* to Cl)	Pt–L (*trans* to L)	Pt–L (*trans* to Cl)	Reference
1.	$[PtCl_4]^{2-}$	2.310(1)				2
2.	$[PtCl_6]^{2-}$	2.314(1)				3
3.	$[PtCl_3(NH_3)]^-$	2.317(7)[a]	2.285(7) (av.)		2.04(2)	4
4.	$[PtCl_3(PEt_3)]^-$	2.382(4)	2.300(2) (av.)		2.215(4)	5
5.	$[PtCl_5(PEt_3)]^-$	2.424(1) (av.)	2.316(4) (av.)		2.308(8) (av.)	this work
6.	*trans*-$[PtCl_2(NH_3)_2]$		2.32(1)	2.05(4)		6
7.	*cis*-$[PtCl_2(NH_3)_2]$	2.330(3) (av.)			2.00(7)	6
8.	*trans*-$[PtCl_4(NH_3)_2]$		2.30[b]	2.00[b]		7
9.	*trans*-$[PtCl_2(PEt_3)_2]$		2.294(9)	2.298(18)		8
10.	*cis*-$[PtCl_2(PMe_3)_2]$	2.376(17) (av.)			2.247(12) (av.)	9
11.	*cis*-$[PtCl_2(PMe_2Ph)_2]$	2.357(3) (av.)			2.243(2) (av.)	10
12.	*trans*-$[PtCl_4(PEt_3)_2]$		2.332(5)	2.393(5)		11
13.	*cis*-$[PtCl_4(PEt_3)_2]$	2.394(3)	2.321(3)		2.335(3)	12

[a] Values obtained from the refinement in the space group $Cmc2_1$. [b] No standard deviations are given.

TABLE 3. Experimental data for the X-ray diffraction study of [ppzH][$PtCl_5(PEt_3)$]

Formula	$C_{12}H_{24}Cl_5N_2PPt$
M	599.67
Crystal size (mm)	0.20 × 0.20 × 0.30
Data collection T (°C)	21
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.459(3)
b (Å)	12.979(2)
c (Å)	17.568(3)
α (°)	72.34(1)
β (°)	86.86(2)
γ (°)	83.72(2)
V (Å^3)	2042.2
Z	4
D (g cm^{-1})	1.947
μ (cm^{-1})	74.76
Radiation	Mo $K\bar{\alpha}$ graphite monochromated ($\lambda = 0.71069$ Å)
Measured reflections	$\pm h$, $\pm k + 1$
θ range (°)	$2.2 \leqslant 2\theta \leqslant 25.0$
Scan type	$\omega/2\theta$
Scan width (°)	$1.10 + 0.35\tan\theta$
Maximum counting time (s)	60
Background time (s)	0.5 × scan-time
Maximum scan speed (° min^{-1})	10.2
Prescan rejection limit	0.65 (1.54σ)
Prescan acceptance limit	0.025 (40σ)
Horizontal receiving slit (mm)	$1.80 + \tan\theta$
Vertical receiving slit (mm)	4.00
No. unique data collected	7168
No. observed reflections (n_v) ($F_o \geqslant 2.0\sigma(F)$]	5371
No. parameters refined (n_p)	378
R	0.035
R_w	0.042

$R = \Sigma \| F_o | - 1/k | F_c \| / \Sigma | F_o |$. $R_w = [\Sigma w(| F_o | - 1/k | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$.

in *trans*-position to PEt_3 (2.382(4) versus 2.424(1) Å). However, although there is a slight numerical incresae in the Pt–Cl bond in *trans*-position to Cl (2.300(2) versus 2.316(4) Å) this is of limited significance given the magnitude of the standard deviations. Thus, the latter differences follow the pattern found for $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$.

Another significant feature in the structure of $[PtCl_5(PEt_3)]^-$ is the Pt–P distance (2.308(8) Å), which is longer than in $[PtCl_3(PEt_3)]^-$ (2.215(4) Å). Thus one can state that the static *trans*-influence of PEt_3 in the platinum(IV) complex is higher than that in the platinum(II) complex although the Pt–P bond in the platinum(IV) complex is also longer.

In this context it is worth re-examining the bond distances in *cis*-$[PtCl_2(PR_3)_2]$ and in *cis*-$[PtCl_4(PR_3)_2]$ (entry nos. 10, 11 and 13) and in *trans*-$[PtCl_2(PR_3)_2]$ and *trans*-$[PtCl_4(PR_3)_2]$ (entry nos. 9 and 12). This comparison shows that the difference between each set of Pt(II)/Pt(IV) compounds is constant, i.e. *c.* 0.04 Å for Pt–Cl in *trans*-position to PR_3 and 0.09 Å for Pt–P in *trans*-position to a chlorine atom. The new data presented here also show that this lengthening is *not* observed for chlorine atoms in mutually *trans*-positions.

It is regrettable that the paucity and quality of the corresponding data for the NH_3 complexes (particularly for entry nos. 6–8) cannot be used to establish whether similar effects are operative in the ammine complexes. However, it must now be taken into account that, contrary to expectations, the *trans*-influence of a complex in a higher oxidation state can be greater than in the corresponding species in the lower oxidation state.

Finally, mention should be made that the preparation and spectroscopic characterization (IR and NMR) of $[PtCl_5(PMe_3)]^-$ has been previously reported [15] and that the NMR data for this anion are very similar to those found for $[PtCl_5(PEt_3)]^-$ (see 'Experimental').

The differences in bonding parameters between the two independent molecules in the unit cell are

TABLE 4. Final atomic coordinated and equivalent thermal parameters (Å^2) for [pppzH][PtCl$_5$(PEt$_3$)] with e.s.d.s. in parentheses

	x/a	y/b	z/c	B_{eq}
Pt	0.21423(4)	0.25348(3)	0.01632(3)	2.97(1)
Cl1	0.4089(3)	0.1859(3)	−0.0465(2)	4.6(2)
Cl2	0.0614(3)	0.1954(2)	−0.0575(2)	4.1(1)
Cl3	0.0205(3)	0.3301(3)	0.0736(2)	4.5(2)
Cl4	0.3579(3)	0.3172(3)	0.0908(2)	5.3(3)
Cl5	0.2140(4)	0.4246(3)	0.0894(2)	4.8(2)
P1	0.2176(3)	0.0879(2)	−0.1150(2)	3.3(2)
Pt′	0.3119(4)	0.2153(3)	0.56593(3)	2.69(1)
Cl1′	0.1056(3)	0.3213(3)	0.5157(2)	4.2(2)
Cl2′	0.4485(3)	0.3384(2)	0.4778(2)	4.0(2)
Cl3′	0.5149(3)	0.1019(3)	0.6144(2)	4.4(3)
Cl4′	0.1819(3)	0.0852(2)	0.6521(2)	4.1(2)
Cl5′	0.3076(4)	0.1226(5)	0.4654(2)	4.3(1)
P1′	0.3174(3)	0.3119(3)	0.6559(2)	3.7(2)
N1	0.1202(13)	0.4947(11)	0.1719(8)	5.6(7)
N2	0.3805(13)	0.5530(12)	0.1409(10)	5.1(8)
C1	0.1513(13)	0.5573(8)	0.1005(6)	2.5(5)
C2	0.2808(12)	0.5867(10)	0.0809(7)	3.7(5)
C3	0.3507(11)	0.4907(10)	0.2124(6)	3.4(8)
C4	0.2239(14)	0.4603(11)	0.2297(8)	3.5(4)
C5	0.3136(18)	0.6542(16)	−0.0044(10)	6.6(8)
C6	0.1881(22)	0.3879(21)	0.3116(11)	6.9(9)
N1′	0.3602(15)	−0.1724(12)	0.6319(9)	6.6(7)
N2′	0.0895(15)	−0.1825(12)	0.6076(9)	4.1(6)
C1′	0.3118(12)	−0.1361(9)	0.5581(7)	3.4(5)
C2′	0.1781(13)	−0.1398(9)	0.5427(8)	4.1(5)
C3′	0.1350(11)	−0.2208(10)	0.6830(7)	3.3(5)
C4′	0.2706(14)	−0.2182(9)	0.6944(8)	3.9(5)
C5′	0.1285(17)	−0.1015(12)	0.4578(10)	5.6(8)
C6′	0.3175(18)	−0.2680(12)	0.7820(9)	5.4(8)
C11	0.0535(17)	0.0716(13)	0.1801(10)	5.9(7)
C21	−0.0775(15)	0.0557(13)	0.1376(9)	5.3(7)
C31	0.3561(18)	0.0559(14)	0.1894(11)	6.7(8)
C41	0.5107(15)	0.0480(13)	0.1527(11)	5.8(6)
C51	0.2402(15)	−0.0269(9)	0.0727(9)	4.5(7)
C61	0.2487(18)	−0.1364(11)	0.1348(12)	6.2(10)
C11′	0.4804(17)	0.2867(14)	0.7115(9)	5.9(7)
C21′	0.6144(19)	0.3343(15)	0.6580(12)	7.3(9)
C31′	0.1897(15)	0.2754(13)	0.7398(8)	5.0(8)
C41′	0.0301(19)	0.3103(17)	0.7169(11)	7.5(10)
C51′	0.2878(17)	0.4579(10)	0.6070(9)	5.0(7)
C61′	0.2850(22)	0.5245(13)	0.6665(12)	8.2(8)

Anisotropically refined atoms are given as isotropic equivalent displacement parameters defined as $1/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\ \gamma)B(1,2)+ac(\cos\ \beta)B(1,3)+bc(\cos\ \alpha)B(2,3)]$. Primed atoms refer to those of the second independent molecule in the asymmetric unit (molecule 2).

within the standard deviations with very few exceptions. These are likely to be due to packing forces.

Comparison of the bond lengths and angles between the 2,5-dimethylpyrazinium cation and the parent heterocycle are small and as they fall within the standard deviations, will not be commented upon.

Experimental

Instrumentation and starting materials.

These were described elsewhere [1].

Preparation of [2,5-dimethyl-1,4-dimethylpyrazinium][PtCl$_5$(PEt$_3$)]

Solid [Pt$_2$Cl$_4$(PEt$_3$)$_2$] (200 mg, 0.26 mmol) was added to a solution of the pyrazine (30 μl, 0.27 mmol) in 50 ml CCl$_4$. The suspension was refluxed for 30 min, the resulting orange–yellow solution was cooled down to room temperature and a solution of Cl$_2$ (6 equiv.) in CCl$_4$ was added. A sticky yellow precipitate formed. This was allowed to solidify for *c.* 2 h and collected by filtration. The solid was redissolved in pyrazine (25 μl, 0.23 mmol) and an n-hexane layer placed over the solution. After a few days greenish yellow crystals of the product and some greenish precipitate had formed. The former were separated mechanically. Yield 30%. Decomp. > 147 °C. *Anal.* Calc. for $C_{12}H_{24}Cl_5N_2PPt$: C, 24.02; H, 4.00; N, 4.67; Cl, 29.56. Found: C, 23.93; H, 3.78; N, 4.60; Cl, 29.31%. ^{1}H NMR (CDCl$_3$): 15.07 (s, br, 1H, H$^+$N); 8.98 (s, br, arom-H, 2H) 2.91 (s, br, 6H, –CH$_3$), 2.43 (dq, 6H, P–CH$_2$–, ^2J(P,H) = 12.3 Hz, ^3J(H,H) = 7.6 Hz), 1.31 (dt, 9H, P–CH$_2$C*H*$_3$, ^3J(H,H) = 7.6 Hz, ^3J(P,H) = 19.0 Hz. ^{31}P NMR (CDCl$_3$): 28.78 (^1J(Pt,P) = 2160 Hz). ^{195}Pt NMR (CDCl$_3$): -1462 (d, ^1J(Pt,P) = 2153 Hz).

Crystallography

The crystals used for X-ray diffraction were those obtained as described above and are air stable.

A prismatic crystal was mounted on a glass fiber at a random orientation on an Enraf-Nonius CAD4 diffractometer for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by least-squares fit of the 2θ values of 25 high order reflections ($10.0 < \theta < 17.0°$) using the CAD4 centering routines. A list of structural and data collection parameters is given in Table 3.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every hour; no significant variation was detected. The orientation of the crystal was checked by measuring three reflections every 300. Data have been corrected for Lorentz and polarization factors and for decay, using the data reduction programs of the CAD4-SDP package [16]. An empirical adsorption correction was applied by using azimuthal (Ψ) scans of three 'high χ' angle reflections ($\chi > 87°$). Transmission factors were in the range 0.81–1.00. A total of 5371 intensities was considered as observed having $|F_o| > 2.0\sigma|F|$, and used for the solution and refinement of the structure. The value $F_o = 0.0$ was given to those reflections having negative net intensities.

The structure was solved by a combination of Patterson and Fourier methods and refined by block-diagonal least-squares [17] (the function minimized was $[\Sigma w(F_o - {}^1/k\, F_c)^2]$) using a Cruickshank weighting scheme [18] by demanding that no systematic trend be present in the weights with $|F_o|$ or $(\sin\theta/\lambda)$. No extinction correction was applied. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion were taken from ref. 19. Anisotropic temperature factors were used for all atoms. Upon convergence (no parameter shift $> 0.2\sigma\ (p)$) the Fourier difference map showed no significant feature. Final atomic coordinates and equivalent isotropic thermal displacements are given in Table 4.

Supplementary material

The anisotropic thermal displacements, an extended list of bond lengths and angles, and a list of observed and calculated structure factors are available from the authors upon request.

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