

BOND LENGTHS IN PLATINUM(II) AND PLATINUM(IV) COMPLEXES. CRYSTAL AND MOLECULAR STRUCTURE OF cis-TETRACHLOROBIS(TRIETHYLPHOSPHINE) PLATINUM(IV) *

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SUMMARY

The crystal and molecular structure of cis-[PtCl₄(PEt₃)₂] has been determined. Crystals are monoclinic, space group C2/c, a = 8.791(2), b = 12.501(2), c = 17.899(3) Å, $\beta = 91.92(2)^\circ$, Z = 4. Intensities were measured by diffractometer and the structure solved by the heavy atom method and refined to R = 0.053. The crystal comprises discrete molecules with a C₂ axis of symmetry with bond lengths (in Å) Pt-P 2.335(3), Pt-Cl 2.321(3) (trans to Cl) and 2.394(3) (trans to P). Steric interactions, principally between the phosphine ligands (\angle P-Pt-P' 98.1°), cause some deviations from regular octahedral co-ordination. Bond lengths in platinum(IV) complexes depend on the nature of the trans ligand, and available results are used to determine the trans influence orders: Cl << carbene < phosphine < carbonionic ligand (with respect to Pt(IV)-Cl lengths) and Cl << phosphine < alkyl (with respect to Pt(IV)-P lengths). It is shown that differences in metal-ligand vibrational frequencies between platinum(IV) complexes are not simply related to the changes in the bond lengths.

INTRODUCTION

The oxidative addition and reductive elimination cycles of several reactions that are homogeneously catalysed by transition metal complexes involve the interconversion of square planar complexes of lower oxidation states (such as Rh^I or Pt^{II}) and octahedral complexes of higher oxidation states (Rh^{III} or Pt^{IV}). In

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recent years accurate structural information has been obtained for many square planar complexes, especially those of platinum(II), but the higher oxidation states such as platinum(IV) have been comparatively neglected. Whilst there is spectroscopic evidence that platinum(IV)-ligand bond strengths depend on the nature of the trans ligand in a way that is qualitatively similar to that of platinum(II)-ligand bonds [1], the available structural information for platinum(IV) complexes suggests that the relative strengths of Pt-P and Pt-Cl bonds (as indicated by the bond lengths) may be substantially different in these two oxidation states. We now report the crystal and molecular structure of cis-[PtCl₄(PEt₃)₂]; the bond lengths in this complex provide a number of significant points of comparison with results for platinum(II) and platinum(IV) complexes from the literature.

EXPERIMENTAL

Crystals of cis-[PtCl₄(PEt₃)₂] were obtained by treatment of cis-[PtCl₂(PEt₃)₂] in benzene-dichloromethane with chlorine followed by recrystallisation from dichloromethane-ether.

Crystal Data

C₁₂H₃₀Cl₄P₂Pt, M, 573.3, Monoclinic, a = 8.791(2), b = 12.501(2), c = 17.899(3) Å, β = 91.92(2)^o, U = 1965.9 Å³, Z = 4, D_m = 2.17 (floatation), D_c = 1.94 g cm⁻³, F(000) = 1112. Mo-K α radiation, μ = 81.8 cm⁻¹, space group C2/c from systematic absences of h k l for (h + k) odd and h 0 l for l odd.

Crystallographic Measurements

A crystal of size 0.85 x 0.36 x 0.18 mm was mounted along the needle axis and used for data collection on a Hilger and Watts Y290 four circle diffractometer (graphite crystal monochromator). Preliminary photographic data had indicated a triclinic cell and accurate cell dimensions in this assignment were calculated from the setting angles of 12 reflections [λ (Mo-K α ₁) = 0.70926 Å] on the diffractometer to give a = 17.899(3), b = 7.644(1), c = 7.638(2) Å, α = 70.23(2), β = 88.92(2), γ = 91.13^o. Intensity data for unique reflections with 2 < θ < 25^o were collected by an $\epsilon/2\theta$ step scan. After the structure had been solved, the high molecular two-fold symmetry prompted a re-examination of the unit cell, and it was found that the crystal needle axis was in fact a face diagonal of the

monoclinic cell shown in the crystal data. The intensity data was re-indexed on the basis of the monoclinic cell using the matrix $(0 \ -1 \ 1/0 \ 1 \ 1/1 \ 0 \ 0)$.

Lorentz and polarization corrections were applied and the data corrected for absorption with the program ABSCOR[2]. Symmetry equivalent reflections were averaged to give 1653 independent reflections with $I > 3\sigma(I)$.

Structure Determination

All non-hydrogen atoms were located by heavy atom procedures with the molecule lying on the crystallographic two fold axis. Least squares refinement with anisotropic temperature factors converged at $R = 0.058$. Hydrogen atoms

TABLE 1

FRACTIONAL ATOMIC CO-ORDINATES ($\times 10^4$) WITH STANDARD DEVIATIONS

Atom	x	y	z
Pt	0	1039.5(4)	2500
Cl(1)	2405(3)	1005(2)	3076(2)
Cl(2)	-816(4)	-356(2)	3311(2)
P(1)	699(3)	2264(2)	1588(2)
C(1)	-584(14)	3395(9)	1495(7)
C(2)	-296(19)	4153(11)	857(9)
C(3)	2593(13)	2804(9)	1750(7)
C(4)	3897(14)	2077(12)	1508(9)
C(5)	757(16)	1720(10)	648(6)
C(6)	-729(19)	1352(13)	284(9)
H(11)	-502(14)	3847(19)	2009(7)
H(12)	-1726(14)	3086(9)	1417(7)
H(21)	-1190(19)	4724(11)	956(9)
H(22)	-565(19)	3713(11)	351(9)
H(23)	769(19)	4571(11)	801(9)
H(31)	2750(13)	2959(9)	2341(7)
H(32)	2666(13)	3547(9)	1445(7)
H(41)	5091(14)	2206(12)	1639(9)
H(42)	3718(14)	2016(12)	910(9)
H(43)	3532(14)	1345(12)	1769(9)
H(51)	1515(16)	1040(10)	669(6)
H(52)	1220(16)	2332(10)	296(6)
H(61)	-617(19)	919(13)	-233(9)
H(62)	-1458(19)	2037(13)	189(9)
H(63)	-1222(19)	834(13)	694(9)

were introduced at idealised positions [$d(\text{C-H}) 1.08 \text{ \AA}$]. Methyl groups were refined as rigid bodies with a common hydrogen isotropic temperature factor, and methylene hydrogen atoms were constrained to ride on the corresponding carbon atom, again with a common isotropic temperature factor. Refinement converged at $R 0.053$, $R_w = 0.070$ with a maximum shift to error for positional parameters of 0.08. The weighting scheme was defined empirically as $w = 102/(1 + 0.000025 F_o^2)$. Scattering factors for neutral atoms and dispersion corrections were taken from ref. 3. Final atomic co-ordinates are given in Table 1, and anisotropic thermal parameters are given in Table 2.*

RESULTS AND DISCUSSION

The crystals are composed of discrete units separated by normal van der Waals contacts. Bond lengths and angles are given in Table 3, and a diagram of the molecular structure with the numbering scheme for the atoms is given in Figure 1. The molecule has a C_2 axis of symmetry and shows some distortions from regular octahedral co-ordination. A least-squares plane defined by Pt, P(1), P(1'), Cl(2), and Cl(2') passes above P(1) and Cl(2), and below P(1') and Cl(2'); distances from the plane are 0.080 \AA (P) and 0.086 \AA (Cl), which are somewhat smaller than the deviations from planarity found for *cis*-[PtCl₂(PMe₂)₂] [4]. The angle P(1)-Pt-P(1') (98.1°) is similar to the corresponding angle in *cis*-[PtCl₂(PMe₂)₂] [$96.2(4)^\circ$] and is enlarged from above 90° due to H...H contacts between methylene hydrogen atoms of the triethylphosphine ligands. Several distances H...Cl, obtained from the idealised co-ordinates of the hydrogen atoms, are between 2.47 \AA and the van der Waals contact distance (2.90 \AA), and some compression of the PtCl₄ moiety is evident from the bond angles Cl(1)-Pt-Cl(2') (88.2°), Cl(2)-Pt-Cl(2') (86.5°), and Cl(1)-Pt-Cl(1') (177.8°). The angle Cl(1)-Pt-Cl(2) (90.2°) appears to be free from compression because a hydrogen atom on C(6') [H(6'3')] lies between these two chlorine atoms (H...Cl distances 2.47 and 2.89 \AA).

The length of the Pt-Cl(1) bond *trans* to chlorine [$2.321(3) \text{ \AA}$] is similar to those in *trans*-[PtCl₄(PEt₂)₂] [$2.332(5) \text{ \AA}$] [5] and tetrachloro(pyridinium propylidene)pyridineplatinum(IV) [mean value $2.316(11) \text{ \AA}$] [6], and is not significantly different from that in [PtCl₂(C₇H₅N)₂C₃H₉] [mean value $2.290(16) \text{ \AA}$] [7]. The bond lengths in

* Structural factor tables are available from the authors.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) OF THE FORM: $\exp[-2\pi^2 - U_{11}h^2a^{*2} + U_{22}l^2b^{*2} + U_{33}k^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$ WITH STANDARD DEVIATIONS IN PARENTHESIS

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	341(3)	282(3)	594(4)	0	-35(2)	0
Cl(1)	435(15)	614(19)	856(21)	-2(11)	-103(14)	98(14)
Cl(2)	659(17)	370(13)	808(19)	-76(11)	80(14)	92(12)
P(1)	431(13)	342(13)	612(16)	22(11)	-13(11)	28(10)
C(1)	689(70)	427(57)	669(68)	145(51)	61(55)	132(50)
C(2)	853(99)	545(70)	825(91)	144(64)	116(75)	201(64)
C(3)	499(59)	423(55)	836(80)	-77(46)	79(55)	26(53)
C(4)	475(64)	723(85)	1076(108)	75(60)	-45(65)	75(77)
C(5)	782(81)	571(68)	494(59)	4(58)	17(55)	-37(49)
C(6)	964(112)	763(88)	727(86)	29(82)	-151(78)	-251(74)

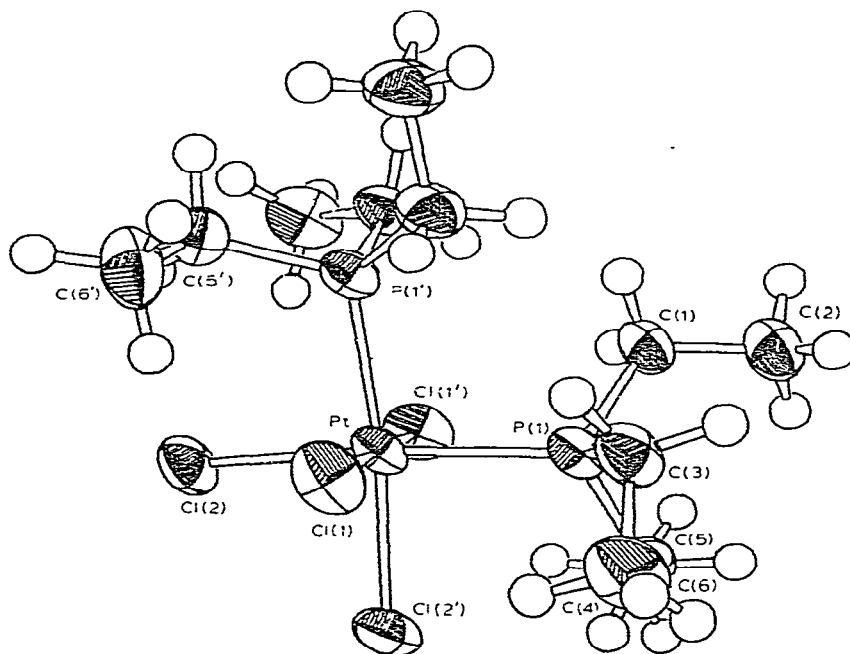


Fig. 1. A view of the molecular structure; thermal ellipsoids enclose 50% of probability. The molecule has a two fold axis of symmetry.

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH
STANDARD DEVIATIONS

Bond lengths			
Pt-Cl(1)	2.321(3)	P(1)-C(5)	1.816(11)
Pt-Cl(2)	2.394(3)	C(1)-C(2)	1.512(17)
Pt-P(1)	2.335(3)	C(3)-C(4)	1.536(17)
P(1)-C(1)	1.813(11)	C(5)-C(6)	1.512(19)

Bond angles			
P(1)-Pt-P(1')	98.1(1)	Pt-P(1)-C(1)	113.4(4)
P(1)-Pt-Cl(1)	93.8(1)	Pt-P(1)-C(3)	113.3(4)
P(1)-Pt-Cl(1')	87.6(1)	Pt-P(1)-C(5)	114.7(4)
P(1)-Pt-Cl(2')	87.9(1)	C(1)-P(1)-C(3)	106.8(6)
Cl(1)-Pt-Cl(2)	90.2(1)	C(1)-P(1)-C(5)	104.1(6)
Cl(1)-Pt-Cl(2')	88.2(1)	C(3)-P(1)-C(5)	103.5(6)
Cl(2)-Pt-Cl(2')	86.5(1)	P(1)-C(1)-C(2)	116.0(9)
P(1)-Pt-Cl(2)	172.9(1)	P(1)-C(3)-C(4)	115.1(9)
C-(1)-Pt-Cl(1')	177.8(1)	P(1)-C(5)-C(6)	117.5(10)

TABLE 4

MEAN BOND LENGTHS (Å) IN cis AND trans ISOMERS OF [PtCl₂(PET₃)₂] AND
[PtCl₄(PET₃)₂]

Bond	Configuration	Pt(II)	Pt(IV)
Pt-P(<u>trans</u> to Cl)	<u>cis</u>	2.258(4) ^a	2.335(3) ^b
Pt-Cl(<u>trans</u> to P)	<u>cis</u>	2.361(5)	2.394(3)
Pt-P(<u>trans</u> to P)	<u>trans</u>	2.314 ^c	2.393(5) ^d
Pt-Cl(<u>trans</u> to Cl)	<u>trans</u>	2.301(5)	2.332(5)

^a ref. 12. ^b this work. ^c estimated values - see text. ^d ref. 5.

the trans P-Pt-P moieties of trans-[PtCl₄(PEt₃)₂] [2.393(5) Å] [5] and of [PtCl₂{C-(Cl.C₆H₃NH)(NHMe)}₂(PEt₃)₂]ClO₄ [mean value 2.388(4)] [8] are also closely similar, so the available results suggest that the bond lengths in platinum(IV) complexes are not significantly dependent on the nature of ligands in cis relationship. Both the Pt-Cl and the Pt-P lengths in platinum(IV) complexes depend significantly on the nature of the trans ligand. The Pt-Cl lengths (in Å) associated with the various trans ligands are 2.321(3) and 2.332(5) trans to Cl (this work and ref. 5), 2.372(3) trans to a carbene ligand [8], 2.394(3) trans to triethylphosphine (this work), and 2.415(4) trans to a carbanionic ligand [8]. The Pt-P lengths vary in a similar manner: 2.335(3) trans to chloride (this work), 2.388(4) and 2.393(5) trans to triethylphosphine [8, 5], and 2.418(3) Å trans to a carbanionic ligand [9]. For platinum(II) complexes Pt-Cl distances (in Å) trans to various ligands are: 2.304(4) trans to Cl [10], 2.362 trans to a carbene ligand [11], 2.361(5) trans to triethylphosphine in cis-[PtCl₂(PEt₃)₂] [12], and 2.398(4)–2.415(4) [13] trans to carbanionic ligands. There is a satisfactory correlation between the Pt-Cl distances in the platinum(IV) and platinum(II) complexes, indicating that at least for these ligands the mechanism of trans influence is similar in the two oxidation states. These results are analogous to those of Clark et al. [1] who showed that there was a good correlation between values of ¹J(Pt-C) for platinum(IV) and platinum(II) methyl complexes containing various ligands trans to the methyl group.

Bond lengths have been determined for both cis and trans isomers of the platinum(II) and platinum(IV) complexes [PtCl₂(PEt₃)₂] [12, 14] and [PtCl₄(PEt₃)₂] (this work and ref. 5), but the results for trans-[PtCl₂(PEt₃)₂] were obtained from two-dimensional data and so are of low precision. More accurate values of the bond lengths in trans-[PtCl₂(PEt₃)₂] can be estimated from the results for related complexes, since the bond lengths in platinum(II) complexes depend mainly on the nature of the trans group. The Pt-Cl distance is estimated at 2.301(5) Å from the value obtained for [PtCl₃(PEt₃)⁻] [10] and other complexes containing a trans Cl-Pt-Cl moiety [15], and the Pt-P distance of 2.314(5) Å can be inferred from the values 2.314(8) and 2.315(4) Å found for trans-[PtBr₂(PEt₃)₂] [14] and trans-[PtI₂(PMe₃)₂] [16]. The results (Table 4) show that on oxidation of platinum(II) to platinum(IV) the Pt-Cl distances increase by 0.03 Å and the Pt-P distances increase by 0.08 Å, and that these increments are not significantly dependent on the nature of the trans ligand. Comparison of bond lengths in the square planar

rhodium(II) complex $[\text{RhCl}(\text{PPh}_3)_2]$ [7] with those in the octahedral rhodium(III) complex $\text{mer-}[\text{RhCl}_3(\text{PBu}_3)_2 \text{P}(\text{OMe})_2]$ [18] shows that in the higher oxidation state the Rh-Cl bond (trans to P) is 0.03 \AA longer and the Rh-P bond (trans to P) is 0.065 \AA longer. Although this comparison is less precise than that for the platinum complexes because of the variation in the phosphorus ligands, the similarity of the results suggests that the trends noted for the platinum complexes may be general for oxidation of square planar d^8 complexes to octahedral d^6 complexes.

The oxidation from platinum(II) to platinum(IV) involves a change of coordination number as well as a change of electronic structure. The results contrast somewhat with those of Mason *et al.* [5] who studied the changes in M-P and M-Cl lengths in the M(III) and M(IV) complexes $\text{mer-}[\text{MCl}_3(\text{PMe}_2\text{Ph})_2]$ and $\text{trans-}[\text{MCl}_4(\text{PMe}_2\text{Ph})_2]$ [M = Re, Os, and Ir], for which there is no variation in coordination number with oxidation state. They found that on oxidation from M(III) to M(IV) the M-Cl bonds (trans to Cl) shorten by $0.025(3)$ (Re), $0.028(6)$ (Os), and $0.037(6) \text{ \AA}$ (Ir), and the M-P bonds (trans to P) lengthen by $0.047(6)$ (Re), 0.040 (Os) and $0.029(6) \text{ \AA}$ (Ir). The lengthening of the M-P bonds on oxidation appears to be analogous to that observed for the platinum complexes, but the changes in the M-Cl lengths are in the opposite sense to those found for platinum. A number of uncertainties precludes a more detailed analysis at present. The oxidation of the octahedral complexes involves removal of electrons of (idealised) t_{2g} symmetry, whereas the d_{z^2} electrons are involved in the oxidation of platinum(II) to platinum(IV). Also, Mason *et al.* [5] noted a discontinuity between the results for iridium(IV) and those for platinum(IV), in a graph of M-P length against electron configuration, so there would be a possibility of error in attempting to extrapolate their results to provide a more quantitative explanation of the bond length changes in the platinum complexes.

The bond lengths in Table 4 can be compared with other physical parameters of these complexes. A detailed study of the platinum-ligand vibrations has been made for trimethylphosphine analogues of the complexes in Table 4 [19]. The mean wavenumber changes on oxidation from platinum(II) to platinum(IV) are $+9 \text{ cm}^{-1}$ for Cl-Pt-Cl vibrations, -9 cm^{-1} for Pt-Cl vibrations (trans to P), -19 cm^{-1} for Pt-P vibrations trans to Cl, and -9 cm^{-1} for P-Pt-P vibrations. The

differences in vibrational frequencies between octahedral iridium(III) and platinum (IV) complexes were also studied, and they appear to correlate reasonably well with the bond length changes found by Mason *et al.*, [5]. However, the changes in vibrational frequencies on oxidation of platinum(II) to platinum(IV) are clearly not simply related to the bond length changes (Table 4), so the direct comparison of vibrational frequencies in square planar and octahedral complexes may not be a valid method of estimating relative bond strengths. The n.m.r. coupling constant $^1J(\text{Pt-P})$ for *trans*-[PtCl₄(PMe₃)₂] is a factor of 0.664 smaller than that for the corresponding platinum(II) complex, and the similar factor for the *cis* complexes is 0.646 [19]. Since the coupling constants are related to the s-characters of the orbitals forming the Pt-P bonds, a factor of 0.667 would be expected for the idealised dsp² and d²sp³ hybridization states of platinum [20]. Although there are some significant assumptions involved in the interpretation of the coupling constants [20], it is now clear that the similar values of the factors for the *cis* and *trans* complexes and the implied similarity in the changes in the Pt-P bonds are consistent with the observed changes in length of the Pt-P bonds (Table 4). For platinum(II) complexes there is a fair correlation between the coupling constants and the Pt-P bond lengths [21], which implies that bonds with a higher s-orbital component are also shorter. Although the s-components of the bonds are not expected to be necessarily closely related to the values obtained from simple hybridization theory, the smaller coupling constants for the platinum(IV) complexes are now shown to be associated with relatively long Pt-P bonds, and the results are not inconsistent with the possibility that the correlation between $^1J(\text{Pt-P})$ and the Pt-P lengths applies to both platinum(II) and platinum(IV) complexes.

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