*Journal of Organometallic Chemistry*, 104 (1976) 387—392

# THE CRYSTAL STRUCTURE OF TETRABUTYLAMMONIUM TRICHLOROCARBONYLPLATINATE(II)

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(Received July 17th, 1975)

## Summary

Crystals of $[C_{16}H_{36}N]^+[Cl_3COPt]^-$ are monoclinic, space group $P2_1/n$, with $a$ 14.949(8), $b$ 8.892(7), $c$ 18.232(10) Å, $\beta$ 105.5(3)°, $Z$ 4. The structure has been refined by least-squares to a final $R$ of 0.042 for 2358 counter intensities. The Pt—Cl bond lengths in the square-planar anion are not significantly different (mean value 2.291 Å) and the Pt—C (carbonyl) bond length is 1.82 Å.

Conclusions are drawn on the factors affecting the *trans* influence in this complex and a number of related square planar $Pt^{II}$ chloro-complexes.

## Introduction

We were interested in the factors that determine the *trans*-influence of a ligand and, in common with others [1], concluded that the general type of grouping $Pt^{II}L_3L'$ is most suited to a study of *cis*- and *trans*-influence as ligand L′ is varied. We report here the structure of the tetra-*n*-butylammonium salt of the anion with $L = Cl^-$ and $L' = CO$.

## Experimental

The pale yellow crystals are plates on $\{101\}$ with the forms $\{010\}$ and $\{10\bar{1}\}$ commonly developed. The cell dimensions were determined from precession photographs [$\lambda$(Mo-$K_\alpha$) 0.7107 Å]. The intensities of reflexions with $\theta < 30°$ were measured in ten layers $h0l$ through $h9l$ with monochromatic Mo-$K_\alpha$ radiation and a $\omega$-scan technique. A crystal of approximate dimensions 0.056 × 0.020 × 0.009 cm was used. The 2358 reflexions with significant intensity $[I < 3\sigma(I)]$ and $\sin\theta/\lambda > 0.1$ Å$^{-1}$ were corrected for Lorentz, polarization and absorption [2,3] effects* [$\mu$(Mo-$K_\alpha$) 67.5 cm$^{-1}$].

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* The importance of an absorption correction may be gauged by the fact that prior to application refinement converged with $R$ 0.129 and bond lengths in the anion of Pt—Cl(1) 2.28(1), Pt—Cl(2) 2.29(1) Pt—Cl(3) 2.25(1) Å.

TABLE I

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

| | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|
| Pt | 0.00241(3) | 0.12669(6) | 0.22083(3) | $a$ |
| Cl(1) | −0.0460(4) | −0.0408(6) | 0.2980(3) | $a$ |
| Cl(2) | 0.0528(3) | 0.2980(5) | 0.1470(2) | $a$ |
| Cl(3) | −0.1396(2) | 0.1140(5) | 0.1337(2) | $a$ |
| C(1) | 0.1167(10) | 0.1335(19) | 0.2889(8) | 6.8(3) |
| O(1) | 0.1878(9) | 0.1346(17) | 0.3289(7) | 10.5(3) |
| N(1) | 0.6963(5) | 0.1239(11) | 0.4392(4) | 3.6(1) |
| C(11) | 0.6972(7) | 0.1484(13) | 0.3571(6) | 4.3(2) |
| C(12) | 0.6430(9) | 0.0355(15) | 0.3016(7) | 5.2(2) |
| C(13) | 0.6588(10) | 0.0604(18) | 0.2229(8) | 6.6(3) |
| C(14) | 0.6086(10) | −0.0531(19) | 0.1641(8) | 6.9(3) |
| C(21) | 0.5980(7) | 0.1239(14) | 0.4473(5) | 4.0(2) |
| C(22) | 0.5405(8) | 0.2577(15) | 0.4198(7) | 5.1(2) |
| C(23) | 0.4420(9) | 0.2373(15) | 0.4298(7) | 5.2(2) |
| C(24) | 0.3798(10) | 0.3769(20) | 0.4082(8) | 7.4(3) |
| C(31) | 0.7358(7) | −0.0303(13) | 0.4676(6) | 4.2(2) |
| C(32) | 0.8364(9) | −0.0557(15) | 0.4692(7) | 5.3(2) |
| C(33) | 0.8625(9) | −0.2193(16) | 0.4896(7) | 5.7(3) |
| C(34) | 0.9639(11) | −0.2507(19) | 0.4955(9) | 7.4(4) |
| C(41) | 0.7540(7) | 0.2489(13) | 0.4844(6) | 4.2(2) |
| C(42) | 0.7664(9) | 0.2464(15) | 0.5689(7) | 5.4(3) |
| C(43) | 0.8297(9) | 0.3744(18) | 0.6071(7) | 6.4(3) |
| C(44) | 0.8445(12) | 0.3768(24) | 0.6939(10) | 9.1(4) |

$^a$ Temperature factors in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$ where:

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Pt | 5.54(2) | 4.24(2) | 4.10(2) | 0.02(2) | 1.54(1) | 0.34(2) |
| Cl(1) | 11.1(3) | 8.3(3) | 9.2(3) | 3.1(2) | 4.3(2) | −0.8(2) |
| Cl(2) | 6.8(2) | 7.1(2) | 6.1(2) | 1.9(2) | 2.6(1) | 0.8(2) |
| Cl(3) | 5.6(2) | 5.6(2) | 8.5(2) | −0.7(2) | 0.7(1) | 0.5(2) |

Scattering factors were taken from ref. 4. The positions of the platinum and chlorine atoms were deduced from a Patterson synthesis and the remaining non-hydrogen atoms from a difference synthesis. Block-diagonal least-squares refinement reduced $R$ to 0.042 [$R_w = \Sigma w(|F_o| - |F_c|) |\Sigma w |F_o| = 0.044$ where $w = (3.32 - 0.097|F_o| + 0.0017|F_o|^2)^{-1}$]. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, the weighting scheme introduced in order that $w(|F_o| - |F_c|)^2$ be approximately independent of $|F_o|$. Anisotropic thermal parameters for the platinum and chloride atoms were refined. Methylene hydrogen atoms, at positions calculated from the molecular geometry assuming a C—H bond length of 1.0 Å, were included in the structure factor calculations with a temperature factor of $B$ 5.0 Å [2]. A correction to the structure factors for the anomalous dispersion [5] of Pt and Cl was applied. The maximum shift in the final cycle was 0.2 $\sigma$. The final atomic parameters are listed in Table 1* and the atomic numbering is shown in Figs. 1 and 2.

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* A list of observed and calculated structure factors, hydrogen atomic coordinates, a list of bond lengths and angles in the cation and the shorter interionic contacts may be obtained from the authors.

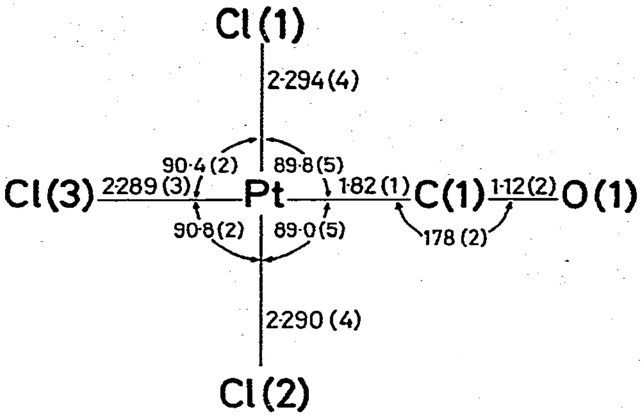


Fig. 1. Bond lengths and angles with estimated standard deviations (in parentheses) in the anion.

## Discussion

Bond lengths and angles in the anion are shown in Fig. 1. Cationic bond lengths and angles are unexceptional (a list may be obtained from the authors on request). The molecular packing (illustrated in Fig. 2) produces no exceptionally short interionic contacts (the shorter contacts have been deposited with the structure factor table) and we therefore assume the anion to be essentially undistorted by crystal packing forces. The anion is virtually planar with deviations from the mean plane of —0.01, —0.03, —0.03, 0.04, —0.01 and 0.04 Å for Pt, Cl(1), Cl(2), Cl(3), C(1) and O(1) respectively.

In Table 2 we have compared the bond lengths in the anion with bond lengths in related compounds [1,6—19]. The conclusions we draw from this tabulation are as follows:

*(i)*. With the exception of the acetylene complex the mean Pt—Cl bond length of mutually *trans* chlorine atoms is constant (mean value of 2.299 Å with a standard deviation of 0.009 Å) and does not depend on the *cis* ligands.

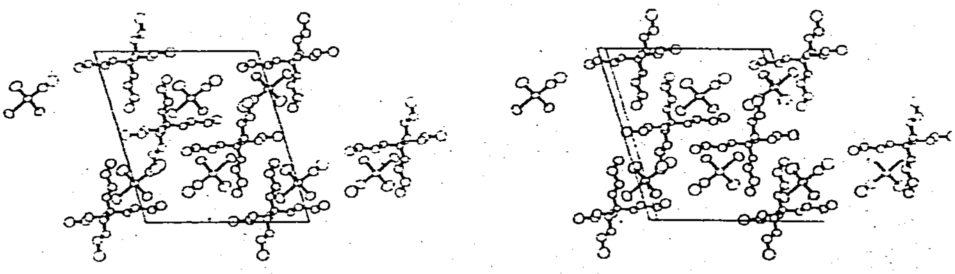
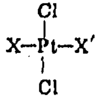
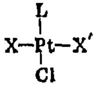
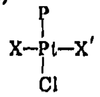


Fig. 2. Stereoscopic ORTEP drawing of the unit cell contents viewed approximately along *b*.

TABLE 2

A COMPARISON OF Pt—Cl BOND LENGTHS IN $Pt^{II}$ COMPLEXES

| (i)  | | | (ii)  | | | | (iii)  | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| X | X′ | Pt—Cl(mean) | X | X′ | L | Pt—Cl | X | X′ | Pt—Cl | Pt—P |
| $Cl^-$ | $Cl^-$ | 2.308(2)[a] | $Cl^-$ | $Cl^-$ | $Cl^-$ | 2.308(2)[a] | $Cl^-$ | CO | 2.342(3)[o] | 2.279(3)[j] |
| $Cl^-$ | $NH_3$ | 2.284(20)[b] | $PEt_3$ | $PEt_3$ | $Cl^-$ | 2.294(9)[g] | $Cl^-$ | $PMe_3$ | 2.376(8) | 2.248(8)[k] |
| $Cl^-$ | $PEt_3$ | 2.301(4)[c] | $Cl^-$ | $Cl^-$ | CO | 2.289(3)[f] | $Cl^-$ | Carbene | 2.387(3) | 2.234(3)[m] |
| $Cl^-$ | Olefin[p] | 2.300(4)[d] | $PEt_3$ | $PEt_3$ | CO | 2.30[i] | Cl | $Cl^-$ | 2.382(4) | 2.215(4)[c] |
| $Cl^-$ | Acetylene | 2.336(6)[e] | $Cl^-$ | $PPh_3$ | CO | 2.277(3)[j] | | | | |
| $Cl^-$ | CO | 2.292(4)[f] | $Cl^-$ | $Cl^-$ | Acetylene | 2.287(6)[e] | | | | |
| $PEt_3$ | $PEt_3$ | 2.294(9)[g] | $Cl^-$ | $Cl^-$ | $NH_3$ | 2.317(7)[b] | | | | |
| $PEt_3$ | Carbene | 2.311(6)[h] | $Cl^-$ | $Cl^-$ | Olefin[p] | 2.323(8)[d] | | | | |
| | | | $Cl^-$ | CO | $PPh_3$ | 2.342(3)[j] | | | | |
| | | | $Cl^-$ | $Cl^-$ | $PEt_3$ | 2.382(4)[c] | | | | |
| | | | $Cl^-$ | $PMe_3$ | $PMe_3$ | 2.376(8)[k] | | | | |
| | | | $PPh_3$ | $PPh_3$ | H | 2.422(9)[l] | | | | |

[a] $K_2[PtCl_4]$, ref. 6. [b] $K[PtCl_3NH_3]$ ref. 7. [c] $[NEt_4][PtCl_3PEt_3]$ ref. 1. [d] Refs. 14—18. [e] $K[PtCl_3Et_2(OH)CC{\equiv}CC(OH)Et_2]$, ref. 8. [f] This work. [g] *trans*-$PtCl_2(PEt_3)_2$, ref. 10. [h] *trans*-$PtCl_2PEt_3[C(NPhCH_2)_2]$, ref. 13. [i] *trans*-$Pt(PEt_3)_2ClCO$, ref. 12. [j] *cis*-$PtCl_2CO(PPh)_3$, ref. 9. [k] *cis*-$PtCl_2(PMe_3)_2$, ref. 11. [l] *trans*-$Pt(PPh_3)_2HCl$, ref. 19. [m] *cis*-$PtCl_2PEt_3[C(NPhCH_2)_2]$. [p] Mean of five determinations with standard deviation of the mean. [o] *trans* to $PPh_3$, Other Pt—Cl bonds in this column are *trans* to trialkylphosphines.

*(ii)*. The Pt—Cl bond *trans* to a ligand L depends only on the ligand L and is independent of the *cis* ligands. The increase in Pt—Cl bond length indicates the increasing *trans* influence of ligand L and follows the trends in Pt—Cl stretching frequencies in $[PtCl_3L]^-$ anions [20]. We note that the ordering of Pt—Cl bond lengths implies that triarylphosphine ligands have a smaller *trans* influence than trialkylphosphine ligands in keeping with the poorer $\sigma$-donor properties of the former.

The first two observations are in agreement with the $\sigma$-bond theory of the *trans* influence originally proposed by Syrkin [21] which would predict a bond lengthening *trans* to, and at most a second order effect *cis* to, any ligand L which is strongly $\sigma$-bonded to the metal.

*(iii)*. The Pt—P bond varies in length as the *cis* ligands are varied. We believe this is due to competition between $\pi$-acceptor ligands. Thus we expect that as the ligands X and X′ improve in $\pi$-acid properties the Pt—P bond will lengthen. We regard this competitive effect as being essentially isotropic, i.e. it will effect *cis* and *trans* bonds equally but will *only* affect bonds to other $\pi$-acid ligands. A striking example is the lengthening of the mean Rh—P bond and the constancy of the Rh—Cl bond in the complexes *trans*-$Rh(PPh_3)_2ClL$ [22] as L changes from $PPh_3$ to $C_2F_4$ (the better $\pi$-acceptor).

These latter observations indicate that phosphines *do* act to a significant extent as $\pi$-acceptors. Venanzi [23] observed that trends in bond lengths for *cis* and *trans* phosphine complexes may be explained on $\sigma$-bonding theories alone and therefore cast doubt on the importance of $\pi$-bonding in Pt—P bonds. We would rationalise this observation with the above arguments by noting that for complexes containing the same type and number of $\pi$-acid ligands, effects due to $\pi$-acceptor competition are constant and only the effects due to $\sigma$-bonding would be apparent.

Recently a series of $Pt^{II}$ complexes in which Cl is *trans* to a C-bonded ligand have been studied [24]. A shortening of the Pt—Cl bonds with increasing $\pi$-acidity of the *trans* ligand was reported. Although a shortening of the Pt—C bond along the series may be attributed to an increase in Pt—C multiple bonding we regard the shortening of the *trans*-Pt—Cl bond as being due to a decrease in $\sigma$-donation from the *trans* ligand rather than an increase in its $\pi$-acidity.

## Acknowledgements

We thank Dr. P. Goggin for providing us with crystals and the University of Leicester Computer Laboratory for the use of its facilities.

## References

1 G.W. Bushnell, A. Pidcock and M.A.R. Smith, J. Chem. Soc., Dalton Trans., (1975) 572.
2 J. de Meulenaer and H. Tompa, Acta Crystallogr., 19 (1965) 1014.
3 N.W. Alcock, Acta Crystallogr., Sect. A, 25 (1969) 518.
4 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
5 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
6 R.H.B. Mais, P.G. Owston and A.M. Wood, Acta Crystallogr., Sect. B, 28 (1972) 393.
7 Y.P. Jeannin and D.R. Russell, Inorg. Chem., 9 (1969) 778.
8 A.L. Beauchamp, F.D. Rochon and T. Theophanides, J. Can. Chem., 51 (1973) 126.
9 R. Walker, L. Manojlovic-Muir and K.W. Muir, J. Organometal. Chem., 66 (1974) C21.

10 G.G. Messmer and E.L. Amma, Inorg. Chem., 5 (1966) 1775.
11 G.G. Messmer, E.L. Amma and J.A. Ibers, Inorg. Chem., 6 (1967) 725.
12 H.C. Clark, P.W.R. Corfield, K.R. Dixon and J.A. Ibers, J. Amer. Chem. Soc., 89 (1967) 3360.
13 D.J. Cardin, B. Cetinkaya, E. Cetinkaya, M.F. Lappert, L. Manojlovic-Muir and K.W. Muir, J. Organometal. Chem., 44 (1972) C59.
14 J.A.J. Jarvis, B.T. Kilbourn and P.G. Owston, Acta Crystallogr. Sect. B, 27 (1971) 366.
15 M. Colapietro and L. Zambonelli, Acta Crystallogr., Sect. B, 27 (1971) 734.
16 R. Spagna and L. Zambonelli, J. Chem. Soc. A, (1971) 2544.
17 R. Spagna, L.M. Venanzi and L. Zambonelli, Inorg. Chim. Acta, 4 (1970) 283.
18 R. Spagna, L.M. Venanzi and L. Zambonelli, Inorg. Chim. Acta, 4 (1970) 475.
19 R. Eisenberg and J.A. Ibers, Inorg. Chem., 4 (1965) 773.
20 R. Goodfellow, P. Goggin and D.A. Duddel, J. Chem. Soc. A, (1968) 504.
21 Y.K. Syrkin, Bull. Acad. Sci., USSR, Cl. Sci. Chim., (1948) 69.
22 P.B. Hitchcock, M. McPartlin and R. Mason, Chem. Commun., (1969) 1367.
23 L.M. Venanzi, Chem. Brit., 4 (1968) 162.
24 L. Manojlovic-Muir and K.W. Muir, Inorg. Chim. Acta, 10 (1974) 47.