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Crystal and molecular structure of cis-Dichlorobis(triphenylphosphite) Platinum(II)

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Abstract: The single crystal structure of cis-dichlorobis(triphenyphosphite) platinum(II), $[PtCl_2(P(OPh)_3)_2]$ has been determined. This complex crystallises in the orthorhombic space group, $P2_12_12_1$ with cell constant, a=10.4135(13), b=14.0635(16), c=23.505(3) Å and v=3448.3(7) Å ^{3}. The Pt-Cl_1 and Pt-Cl_2 distances are 2.3390(10) Å and 2.3256 Å, which are longer than Pt-P_1 and Pt-P_2 with 2.1985(12) Å and 2.1998(10) Å respectively. These data together with bond angles suggest a distorted square planar geometry for this complex with two chlorine ligands in a cis configuration.

Keywords: Crystal structure, Molecular structure, Triphenylphosphite ligands, Platinum complex

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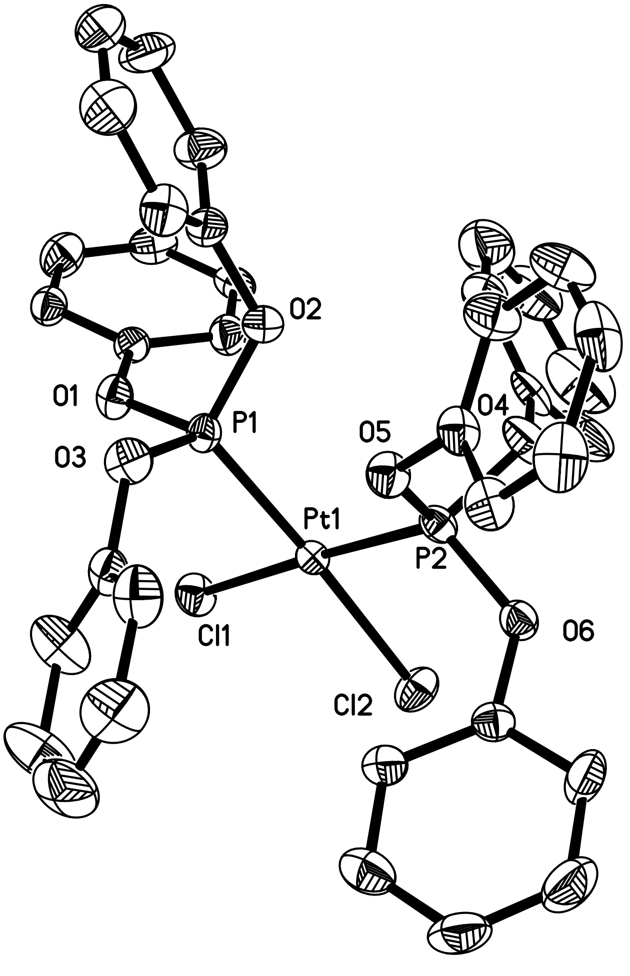
Introduction

In spite of the extensive structural studies on platinum and palladium complexes containing a variety of P-donor ligands [1,2], X-ray structure analyses of platinum derivatives containing triphenylphosphite derivatives are scarce. To the best of our knowledge no such determinations of the title compound have been reported so far. We have recently reported a new procedure for the synthesis of a palladium complex [3] and herein we describe the synthesis and structure determination of an analogous platinum complex.

Results and discussion

Cis-dichlorobis(triphenylphophite)platinum, [$PtCl_2(P(OPh)_3)_2$], (**1**) has been studied in solution This complex was synthesised using a new method but the IR and NMR data are in excellent agreement with an earlier conclusion [1]. However, relatively little work has been done on structural determinations of this type of complex and this lack of information is probably due to difficulty experienced in crystallising the compound from the ethanol reaction solution [4,5]. This work describes the new method of the preparation and characterisation of (**1**). The structure of (**1**) is shown in Figure 1.

Figure1. Molecular structure of [$PtCl_2(P(OPh)_3)_2$] showing the atom numbering scheme used.



Crystal data, structural refinement are summarised in Table 1.

Table 1. Crystal data and structure refinement

Identification code	jsa1
Empirical formula	$C_{36}H_{30}Cl_2O_6P_2Pt$
Formula weight	886.59
Temperature	213(2) K
Wavelength	0.71073 A°
Crystal system, space group	orthorhombic, P 2_1 2_1 2_1
Unit cell dimensions	a = 10.4315 (13) Å alpha = 90 deg.
	b = 14.0635 (16) Å beta = 90 deg.
	c = 23.505 (3) Å gamma = 90 deg.
Volume	3448.3 (7) Å^3
Z, calculated density	4, 1.708 Mg/m^3
Absorption coefficient	4.164 mm^{-1}
F (000)	1744
Crystal size	0.68 × 0.20 × 0.16 mm
Theta range for data collection	1.73 to 24.26 deg.
Index ranges	-11<=h<11, -16<=k<=16, -26<=1<=26
Reflections collected / unique	22003/5449 [R(int)=0.0534]
Completeness to 2theta = 24.26	98.0%
Max. and min. transmission	0.5554 and 0.1640
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	5449 / 0 /424
Goodness-of-fit on F^2	0.943
Final r indices [I>2sigma(I)]	R_1 = 0.0203, WR_2 = 0.0410
R indices (all data)	R_1 = 0.0280, WR_2 = 0.0425
Absolute structure parameter	-0.018(5)
Largest diff. peak and hole	0.559 and -0.783 e.A^{-3}
Absorption correction	numerical (X-SHAPE : Stoe, 1997)
	T_{min} =0.1640, T_{max} =0.5554
	22003 measured reflections
	5449 independent reflections
	4677 reflections with> 2sigma(I
	R_{int} = 0.0534

The more important bond lengths and angles together with references are presented in Table 2.

Table 2. Selected distances and angles for $[PtCl_2(P(OPh)_3)_2]$.

Distances (Å)			
O_1-P_1	1.579(3)	O_6-P_2	1.577(3)
O_2-P_2	1.589(3)	P_1-Pt_1	2.1985(2)
O_3-P_1	1.484(3)	P_2-Pt_1	2.1998(10)
O_4-P_2	1.570(3)	Cl_1-Pt_1	2.3390(10)
O_5-P_2	1.589(3)	Cl_2-Pt_1	2.3256(11)
Angles (°)			
O_1-P_1-O_2	104.69(17)	O_4-P_2-Pt_1	117.27(14)
O_1-P_1-O_3	98.42(19)	O_5-P_2-Pt_1	111.30(13)
O_2-P_1-O_3	103.42(17)	O_6-P_2-Pt_1	119.44(13)
O_1-P_1-Pt_1	118.46(12)	P_1-Pt_1-P_2	93.56(4)
O_2-P_1-Pt_1	113.57(12)	P_1-Pt_1-Cl_2	177.20(4)
O_3-P_1-Pt_1	116.12(14)	P_1-Pt_1Cl_1	89.38(4)
O_4-P_2-O_5	104.7(2)	P_2-Pt_1-Cl_2	88.58(4)
O_4-P_2-O_6	96.90(18)	P_2-Pt_1-Cl_1	176.93(4)
O_5-P_2-O_6	105.27(18)	P_1 -Pt_1 -Cl_2	88.51(4)

Data collection: EXPOSE [5]. Cell refinement: CELL [6]. Data reduction: INTEGRATE [7]. Program(s) used to solve structure: [8]. Program(s) used to refine structure: SHELXL97 [9]. Molecular graphic: ORTEP3 (Farrugia, 1997).

Atomic coordinates are given in Table 3.

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	X	Y	Z	U(eq)
C(1)	-2590(4)	790(3)	676(2)	23(1)
C(2)	-3845(4)	792(3)	527(2)	27(1)
C(3)	-4399(5)	1648(4)	360(2)	38(1)
C(4)	-3686(5)	2466(4)	354(2)	33(1)
C(5)	-2407(5)	2449(3)	506(2)	29(1)
C(6)	-1838(4)	1607(3)	666(2)	29(1)
C(7)	-1961(4)	353(3)	2097(2)	29(1)

C(8)	-2141 (4)	-373(3)	2478(2)	33(1)
C(9)	-3208(6)	-338(4)	2833(2)	43(2)
C(10)	-4054(6)	411(4)	2806(3)	50(2)
C(11)	-3837(6)	1135(4)	2425(3)	45(2)
C(12)	-2744(5)	1116(4)	2075(2)	37(1)
C(13)	-363(4)	-2130(3)	1175(2)	27(1)
C(14)	-472(6)	-2386(4)	629(3)	43(2)
C(15)	169(7)	-3192(4)	440(3)	59(2)
C(16)	863(8)	-3722(4)	806(3)	59(2)
C(17)	940(9)	-3467(4)	1371(3)	51(2)
C(18)	327(6)	-2650(4)	1571(3)	37(2)
C(19)	1955(5)	1924(3)	1511(2)	29(1)
C(20)	2633(7)	2444(4)	1139(3)	60(2)
C(21)	2063(9)	3343(5)	949(3)	68(2)
C(22)	900(10)	3581(5)	1160(4)	59(2)
C(23)	272(8)	3078(5)	1545(4)	60(2)
C(24)	793(6)	2243(4)	1729(3)	45(2)
C(25)	2115(5)	-548(3)	2526(2)	26(1)
C(26)	1685(4)	120(5)	2905(2)	36(1)
C(27)	2154(5)	107(5)	3455(2)	41(1)
C(28)	3020(5)	-574(4)	3614(2)	39(1)
C(29)	3433(5)	-1243(4)	3231(2)	37(1)
C(30)	2986(5)	-1238(3)	2681(2)	30(1)
C(31)	4158(4)	-1167(3)	1316(2)	24(1)
C(32)	5391(5)	-1294(4)	1486(3)	38(1)
C(33)	5971(6)	-2158(4)	1380(3)	51(2)
C(34)	5323(5)	-2877(4)	1112(3)	43(2)
C(35)	4070(6)	-2743(3)	951(2)	38(1)
C(36)	3466(5)	-1882(4)	1050(2)	32(1)
O(1)	-2095(3)	-105(3)	865(1)	26(1)
O(2)	-868(3)	348(2)	1741(1)	26(1)
O(3)	-1010(3)	-1320(2)	1391(1)	30(1)
O(4)	2427(3)	1063(2)	1730(2)	36(1)
O(5)	1607(3)	-558(2)	1966(1)	28(1)
O(6)	3653(3)	-252(2)	1432(1)	24(1)
P(1)	-772(1)	-267(1)	1176(1)	22(1)
P(2)	2200(1)	53(1)	1446(1)	22(1)

Cl(1)	-175(1)	-72(1)	-151(1)	30(1)
Cl(2)	2851(1)	175(1)	153(1)	32(1)
Pt(1)	1005(1)	-26(1)	694(1)	18(1)

The structural analysis proved a cis-distorted square planar arrangement for **1**, and different interatomic distances and bond angles in comparison with $[PtCl_4]^{2-}$ (**2**) was observed. The Pt-P and Pt-Cl bonds are approximately within the same range of other phosphine complexes [1,2], but the Pt-Cl distances are significantly shorter than Pt-P (see Table 3). This causes a big distortion which leads to asymmetric structure and is much bigger than what we observed in cis-$[PdCl_2(P(OPh)_3)_2]$ (**3**) structure [3]. Evidently the small difference between Cl_2-Pt_1-P_1 [177.20° (4)] and Cl_1-Pt_1-P_2 [176.93°(4)] angles also confirms the distorted square planar geometry of **1**. This is in contrast with what has been observed in solution [5]. Discussion of bond-length in **1** [in comparison with **2** containing a C_2 axis] in relation to the above configuration is quite interesting. We noticed that **1** with the different P_1-Pt_1-P_2 [93.56° (4)], P_1-Pt_1-Cl_1 [89.38° (4)], P_2-Pt_1-Cl_2 [88.58° (4)] and Cl_1Pt_1-Cl_2 [88.51° (4)] angles is completely asymmetrical. Not only it changes from D_{4h} and C_{2v} symmetry from **2** and **3** respectively but it is also consistent with C_1 symmetry structure. These can be taken probably as a structural confirmation of the effect of different metal atoms in **1** and **3** or a larger proportion of σ -donor character in the Pt-P bonds for **1** in comparison with the Pd-P bonds of **3,** which results in a greater strict effect of the phosphite ligands. All the bond lengths (Table 2) are approximately within the normal range compared with other phosphine complexes [1,2]. Finally as one can see the P_1-Pt_1-Cl_2 angle [88.51°(4)] is narrower than the P_1-Pt_1-P_2 [93.56°(4)] angle and this is apparently due to the steric effect of phosphite ligands.

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Experimental

Refluxing $PtCl_2$ and $POPh_3$ at 60 ºC in a molar ratio of 1:2 in toluene for 6 h. gave a yellowish precipitate, which was extracted from the obtained suspension. Colourless crystals suitable for X-ray diffraction analysis were obtained by slow addition of methanol to a chloroform solution containing the compound. Crystallographic data was recorded on a Stoe IPDS diffractometer using graphite monochromated Mokα-radiation ($\lambda = 0.71073$ Å), T = 200 K. Structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data. Supplementary material, comprising crystallographic experimental details, positional parameters for all atoms, bond distances and angles, anisotropic thermal parameters and hydrogen atoms coordinates has been deposited with the Cambridge Crystallographic Database. The deposition code is CCDC144750.

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