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The Crystal Structure of *cis*-Dibromotriphenylphosphite Platinum(II)

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The X-ray crystal structure of *cis*-dibromotriphenylphosphite platinum(II), $[PtBr_2(POPh_3)_2]$ has been determined. This complex crystallises in the space group monoclinic, $P2_1/C$, with cell constants a = 14.115(4), b = 10.6648(15), c = 23.254(4) Å and v = 3468.2(12) $Å^3$. The Pt-Br_1 and Pt-Br_2 distances are 2.4739(5) Å and 2.4702 (5) Å which are longer than Pt-P_1 and Pt-P_2 with 2.2049(11) and 2.2051(11)Å respectively. These data together with bond angles suggest a distorted square-planar geometry for this complex.

INTRODUCTION

A variety of complexes of the type $[MX_2PR_3]$ (M = Pt, Pd; X = Cl, Br; R = phosphine, phosphite) have been prepared and characterised[1, 2]. Surprisingly, there appear to be no reports of the X-ray characterisation of *cis*-dibromotriphenylphosphite platinum *cis*-$[PtBr_2(POPh_3)_2]$ (**1**). Although **1** has been prepared and characterised by spectroscopic methods, but we noticed a considerable difference on comparing its X-ray structure with that of the solution. In this report, we describe the new method of preparation of this complex, as well as its single crystal X-ray structure.

EXPERIMENTAL

Preparation: Refluxing $PtBr_2$ and $POPh_3$ at 60°C in a molar ratio of 1 : 2 in toluene for 6 h gives a yellowish precipitate which was extracted from the obtained suspension. Colourless crystals suitable for X-ray diffraction analysis were obtained by slow addition of the methanol to a solution containing the compound in chloroform.

Structure analysis: The crystal structure was determined at room temperature. Crystallographic data were recorded on stoe IPDS diffractometer using graphite monochromated Mo_{ka} radiation (λ = 0.71073 Å), T = 213 K. Structure was solved by direct methods and refined by full matrix least squares F^2 using all data† (Table-1)[3].

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†Supplementary material, comprising crystallographic experimental details, positional parameters for all atoms, bond distances and angles, isotropic, thermal parameters and hydrogen atom coordinates, has been deposited with the Cambridge crystallographic Data Base. The deposition code is: CCDC 144751.

TABLE-1
SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[PtBr_2(POPh_3)_2]$

O_1-P_1	1.579(3)	O_6-P_2	1.581(13)
O_2-P_1	1.592(3)	P_1-Pt_1	2.2049(11)
O_3-P_1	1.592(3)	P_2-Pt_1	2.2051(11)
O_4-P_2	1.584(3)	Br_1-Pt_1	2.4739(5)
O_5-P_2	1.588(3)	Br_2-Pt_1	2.4702(5)
O_1-P_1-O_2	94.69(16)	O_4-P_2-Pt_1	117.81(12)
O_1-P_1-O_3	103.55(16)	O_5-P_2-Pt_1	110.27(11)
O_2-P_1-O_3	107.49(17)	O_6-P_2-Pt_1	119.61(12)
O_1-P_1-Pt_1	121.32(12)	P_1-Pt_1-P_2	95.39(4)
O_2-P_1-Pt_1	114.25(12)	P_1-Pt_1-Br_2	175.92(3)
O_3-P_1-Pt_1	113.33(12)	P_1-Pt_1-Br_1	86.10(3)
O_4-P_2-O_5	106.55(16)	P_2-Pt_1-Br_2	88.53(3)
O_4-P_2-O_6	96.46(16)	P_2-Pt_1-Br_1	178.01(3)
O_5-P_2-O_6	104.38(15)	Br_1-Pt_1-Br_2	89.96(19)

RESULTS AND DISCUSSION

The X-ray structure of (1) is shown in Fig. 1 and important bond distances and angles are given in Table-1. Crystal data and atomic coordinates are given in Tables 2 and 3. The geometry obtained from X-ray structure analysis of (**1**) is differnt from assigned earlier based on NMR and IR data[4, 5]. Although a rather complex far IR spectrum for (**1**) has been obtained[6], but based on ^{31}P NMR spectrum at room temperature with single ^{31}P resonance, a square-planar geometry has been assigned[5, 6]. Our structural results clearly suggest the only *cis* isomer existing in solid state.

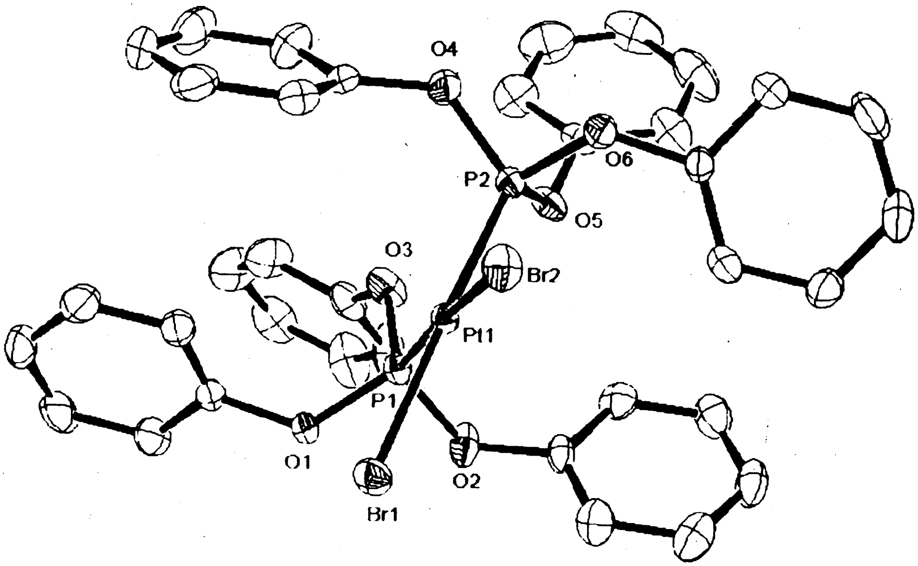

Fig. 1 Molecular structure of $[PtBr_2(POPh_3)_2]$ showing the atom numbering scheme used. Ellipsoids are drawn at the 30% probability level. H atoms have been excluded for clarity.

Comparison of Pt-Br [2.4720] and Pt-P [2.2050] Å average distances and Br_2-Pt-Br_1 [89.96 (19)] and P_1-Pt-P_2 [95.93 (4)] angles in **(1)** shows a significant difference between these two bond lengths and angles. By now it is clear that the distorted square-planar is the dominant geometry for **(1)**.

The Pt-Br bond distance of 2.4739(5) Å and 2.4702(5.) Å are similar to those found in other complexes of platinum (II) and paladium (II) such as *cis*-$[Pt(NH_3)_2Cl_2]$, $K[Pt(NH_3)Cl_3]H_2O$, *cis*-$[PtCl_2(POPh_3)_2]$, *cis*-$[PdCl_2(POPh_3)_2]$ and $[PtCl_4]^{2-}$ for which Pt-Cl distances of 2.328(9) and 2.333(9)[7], 2.300–2.311[8], 2.3256–2.3390[9], 2.3253(9)–2.3445 Å[10] and 2.281–2.309 Å[11] respectively have been reported. The Pt-P bond distances of 2.1985(2) and 2.3390(10) Å obtained for **(1)** are similar to those previously observed for platinum(II)-phosphine bonds[1, 2]. The slightly shorter distance being due to the fact that the oxygen in present complex is part of chelate rings, which causes contraction of the metal-nitrogen bond distance.

TABLE-2
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $[PtBr_2(POPh_3)_2]$

Empirical formula	$C_{36}H_{30}Br_2O_6P_2Pt$	
Formula weight	975.51	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system, Space group	Monoclinic, P2/c	
Unit cell dimensions	a = 14.115(4) Å	α = 90 deg.
	b = 10.6648(15) Å	β = 97.62(3) deg.
	c = 23.245(4) Å	γ = 90 deg.
Volume	3468.2(12) $Å^3$	
Z, calculated density	4, 1.868 mg/m^3	
Absorption coefficent	6.260 mm^{-1}	
F(000)	1888	
Crystal size	0.56 × 0.24 × 0.20 mm	
θ range for data collection	1.77 to 24.19 deg.	
Index range	$-16 \le h \le 16, -12 \le k \le 12, -26 \le l \le 26$	
Reflection collected/unique	21571/5484 [R(int) = 0.0608]	
Completeness to $2\theta = 24.19$	92.6%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5484/0/424	
Goodness-of-fit on F^2	0.886	
Final R indices [I > 2 sigma (I)]	$R_1 = 0.0224$, $wR_2 = 0.0448$	
R indices (all data)	$R_1 = 0.0326$, wR = 0.467	
Largest diff. peak and hole	0.573 and –0.628 e Å	

TABLE-3

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTOPIC DISPLACEMENT PARAMETERS ($A^2 \times 10^3$)

[U(eq) Is Defined as One-third of the Trace of the Orthogonalized u_{ij} Tensor]

	X	Y	Z	U(eq.)
C(1)	1523(3)	5488(4)	6136(2)	20(1)
C(2)	1460(3)	6602(4)	6424(2)	29(1)
C(3)	578(4)	7169(4)	6382(2)	42(1)
C(4)	–210(4)	6630(5)	6061(2)	40(1)
C(5)	–114(3)	5515(5)	5782(2)	35(1)
C(6)	763(3)	4931(4)	5818(2)	27(1)
C(7)	4623(3)	3007(4)	6321(2)	24(1)
C(8)	5123(3)	3211(4)	5865(4)	32(1)
C(9)	5914(3)	2479(5)	5819(2)	41(1)
C(10)	6188(3)	1560(5)	6224(2)	37(1)
C(11)	5670(3)	1349(5)	6673(2)	36(1)
C(12)	4872(3)	2072(4)	6725(2)	29(1)
C(13)	2273(4)	3750(4)	7259(2)	31(1)
C(14)	3978(4)	4055(5)	7614(2)	45(1)
C(15)	2991(4)	4740(50)	8115(2)	50(2)
C(16)	2110(4)	5079(5)	8240(2)	45(1)
C(17)	1305(4)	4752(5)	7874(2)	49(1)
C(18)	1379(4)	4072(5)	7372(2)	41(1)
C(19)	389(3)	1083(4)	5908(2)	24(1)
C(20)	–99(3)	1338(5)	6364(2)	36(1)
C(21)	–940(3)	2026(5)	6264(2)	46(1)
C(22)	–1270(3)	2455(5)	5721(2)	43(1)
C(23)	–762(3)	2180(5)	5266(2)	41(1)
C(24)	64(3)	1479(4)	5357(2)	28(1)
C(25)	2852(3)	–194(4)	6999(2)	27(1)
C(26)	2190(4)	29(5)	7367(2)	38(1)
C(27)	2201(4)	–736(6)	7846(2)	50(2)
C(28)	2864(5)	–1675(5)	7961(2)	52(2)
C(29)	3527(4)	–1859(5)	7586(2)	50(2)
C(30)	3539(4)	–1107(4)	7096(2)	37(1)
C(31)	3399(4)	–1224(4)	5644(2)	21(1)
C(32)	3434(4)	–2504(4)	5684(2)	30(1)
C(33)	4310(4)	–3089(5)	5710(2)	41(1)
C(34)	5132(3)	–2405(5)	5689(2)	36(1)
C(35)	5068(3)	–1119(4)	5632(2)	31(1)

	X	Y	Z	U(eq.)
C(36)	4203(3)	–515(4)	5612(2)	28(1)
O(1)	2473(2)	4992(2)	6176(1)	23(1)
O(2)	3870(2)	3828(3)	6410(1)	30(1)
O(3)	2313(2)	3039(3)	6744(1)	30(1)
O(4)	1206(2)	316(3)	6024(1)	31(1)
O(5)	2898(2)	645(3)	5629(1)	26(1)
O(6)	2480(2)	–693(3)	5648(1)	24(1)
P(1)	2769(1)	3562(1)	6201(1)	19(1)
P(2)	2264(1)	626(1)	5912(1)	19(1)
Br(1)	2791(1)	4244(1)	4862(1)	26(1)
Br(2)	2244(1)	112(1)	4522(1)	28(1)
Pt(1)	2497(1)	2351(1)	5427(1)	16(1)

Considering the difference between Br_2-Pt_1-P_1 [175.92(3)] and Br_1-Pt_1-P_2 [178.01(3)] angles shows that Pt atom is slightly out of the plane of the molecule. This is in contrast with what was found in solution based on NMR measurements[6]. Different P_1-Pt_1-P_2 [95.34(4)], P_1-Pt_1-Br_1 [86.10(3)], P_2-Pt_1-Br_2 [88.53(3)] and Br_1-Pt_1-Br_2 [89.96(19)] angles make (1) to lose D_4h symmetry. Finally the narrower Br_1-Pt_1-Br_2 [89.96(19)] angle in comparison with P_1-Pt_1-P_2 [95.39(4)] angle is due to steric effect of phosphite ligands.

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