Journal of Organometallic Chemistry, 479 (1994) 87–91

Synthesis and characterization of chloro/pyrazolato bridged binuclear organoplatinum(II) complexes: Single crystal structure of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$

Anshu Singhal, Vimal K. Jain and Rajan P. Patel

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 (India)

Anima Vyas and Rakesh Bohra

Department of Chemistry, University of Rajasthan, Jaipur 302004 (India)

(Received October 6, 1993; in revised form December 29, 1993)

Abstract

Chloro/pyrazolato-bridged binuclear organoplatinum(II) complexes of the type $[Pt_2Ar_2(\mu\text{-}Cl)(\mu\text{-}NN)(PR_3)_2]$ (Ar = Ph or C_6H_4OMe-4; NNH = pyrazole (pzH), 3,5-dimethylpyrazole (dmpzH) or 3,4,5-tri-methylpyrazole (tmpzH); $PR_3 = PBu_3$, PMe_2Ph or $PMePh_2$) have been synthesized. These complexes exist exclusively in the *cis* form in which the phosphine ligands are *trans* to the bridging pyrazolate group. The crystal structure of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$ is reported.

Key words: Platinum; Crystal structure

1. Introduction

Pyrazolato-bridged complexes of types $M(\mu\text{-}NN)_2M$ and $M(\mu\text{-}X)(\mu\text{-}NN)M$ of platinum group metals are currently of much interest owing to their rich reaction chemistry and interesting structural features [1–7]. In continuation of our work on pyrazolato-bridged binuclear palladium and platinum complexes [4–7], we now report the synthesis and characterization of binuclear organoplatinum complexes containing both chloro and pyrazolato bridges.

2. Results and discussion

The reaction of $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ with one mole equivalent of pyrazole (pzH), 3,5-dimethylpyrazole (dmpzH) or 3,4,5-trimethylpyrazole (tmpzH) in the presence of sodium hydroxide afforded colourless crystalline complexes of the type $[Pt_2Ar_2(\mu\text{-}Cl)(\mu\text{-}NN)(PR_3)_2]$ (Ar = Ph or C_6H_4OMe-4; NN = pz, dmpz or tmpz; $PR_3 = PBu_3$, PMe_2Ph or $PMePh_2$). Although, this reaction in 1:2 stoichiometry under similar conditions readily gives $[Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2]$ for $PR_3 = PBu_3$, $PMePh_2$, in the case of $[Pt_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with pyrazole (pzH), a mixture of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$ and $[Pt_2Ph_2(\mu\text{-}pz)(PMe_2Ph)_2]$ complexes was formed. The latter complex could be isolated in the pure form when the reaction was carried out in 1:3 stoichiometry.

The chloro/pyrazolato-bridged complexes were characterized by elemental analyses and NMR spectroscopy (Table 1). These complexes exist only in one isomeric form as their ^{31}P NMR spectra displayed a single resonance with platinum satellites. It is noteworthy that both the chloro-bridged precursors, $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ [8] and the bis(pyrazolato)-bridged complexes $[Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2]$ [6] exist as a mixture of *cis* and *trans* isomers. The complexes, $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}NN)(PR_3)_2]$ (X = Cl, SR, SePh, TeR) [4,10] have a *cis* configuration with the phosphine *trans* to the bridging X and exhibit $^3J(^{195}Pt\text{-}^{31}P)$ of the order of 40 Hz. However, such a coupling was not observed in the present case. The absence of ^3J(Pt–P) and the

---

Correspondence to: Dr. R.P. Patel

0022-328X/94/$7.00
SSDI 0022-328X(94)24420-N

TABLE 1. Analytical and NMR (^{1}H and ^{31}P) data for [$Pt_2Ar_2(\mu$-X)(μ-NN)($PR_3)_2$] (X = Cl or NN)

Complex [a]	m.p. °C	Found (required) (%)			^{31}P NMR data		^{1}H NMR data [b]
		C	H	N	δ in ppm	^{1}J(Pt–P) in Hz	
[$Pt_2Ph_2(\mu$-Cl)(μ-pz)($PBu_3)_2$]	135–137	44.9(44.5)	6.5(6.4)	2.4(2.7)	−7.4	3784	0.93(t, 7 Hz), 1.38(br, m), 1.57(br) [PBu]; 5.72 (s, 1H, H-4 pz); 6.75 (br, s, 2H, H-3,5 pz); 6.88–6.93(m), 7.44(m) [10H, Ph]
[$Pt_2(C_6H_4OMe$-4$)_2(\mu$-Cl)(μ-pz)($PBu_3)_2$]	114–117	44.4(44.3)	6.4(6.4)	2.5(2.5)	−7.4	3776	0.93(t, 7 Hz), 1.39(br, m,) 1.57(br) [PBu]; 3.75(s, 6H, OMe); 5.74(s, 1H, H-4 pz), 6.61 (d, 7.5 Hz, 4H, C_6H_4); 6.76(s, 2H, H-3, 5 pz); 7.31 (d, 7.5 Hz, 4H, C_6H_4)
[$Pt_2Ph_2(\mu$-Cl)(μ-pz)($PMe_2Ph)_2$]	162–165 [c]	40.4(40.3)	3.9(3.8)	3.1(3.0)	−19.4	3876	1.52(d, 10.6 Hz, 12H, PMe); 5.78 (s, 1H, H-4 pz); 6.82(s, 2H, H-3,5 pz); 6.88(br), 7.29–7.43 (m), 7.80(m) [20H, Ph]
[$Pt_2Ph_2(\mu$-Cl)(μ-dmpz)($PMePh_2)_2$]	193–195^{3}	48.5(48.0)	4.1(4.0)	3.0(2.6)	−5.5	3958	1.48(d, 10.5 Hz, 6H, PMe); 1.61 (s, 6H, Me-3,5 pz); 5.58(s, 1H, H-4 pz); 6.66–6.73(m), 7.13–7.55(m) [30H, Ph]
[$Pt_2Ph_2(\mu$-Cl)(μ-tmpz)($PMePh_2)_2$]	164–168 [c]	48.2(48.5)	4.1(4.2)	2.5(2.6)	−5.4	3940	1.47(d, 10.2 Hz, 6H, PMe), 1.57 (s, 6H, Me-3,5 pz); 1.62(s, 3H, Me-4 pz); 6.73–6.65(m) 7.13–7.56(m) [30H, Ph]
[$Pt_2(C_6H_4OMe$-4$)_2(\mu$-Cl)(μ-pz)($PMePh_2)_2$]	182–185 [c]	45.9(46.6)	4.0(3.9)	2.4(2.5)	−5.0	3953	1.51(d, 10.5 Hz, 6H, PMe); 3.69(s, 6H, OMe); 5.79(s, 1H, H-4 pz); 6.45(d, 8.5 Hz, 4H, C_6H_4); 6.87(s, 2H, H-3, 5 pz); 7.11(d, 8.5 Hz, 4H, C_6H_4); 7.26–7.34(m); 7.57 (m) [20H, Ph]
[$Pt_2Ph_2(\mu$-pz$)_2(PMe_2Ph)_2$]	212–216 [c]	42.3(42.7)	3.9(4.0)	5.1(5.8)	−18.4 [d] −18.5 [e]	3942 3942	1.36(d), 1.43(d) [each 10.4 Hz, 12H, PMe] [d], 5.88(d, 1.6 Hz, H-4 pz) [d]; 1.42(d), 1.39(d) [each 10.4 Hz, 12H, PMe] [e]; 5.85(s, 1H, H-4 pz) [e]; 6.02(t, 1.9 Hz, 1H, H-4 pz [e] 6.79–8.17(m, 24H, Ph + H-3,5 pz)

---

[a] Complexes were recrystallized from dichloromethane-hexane mixture in 47–60% yield.

[b] s = singlet; d = doublet; t = triplet, m = multiplet; br = broad.

[c] Decomposed.

[d] For *trans* isomer.

[e] For *cis* isomer.

magnitude of ^1J(Pt–P) which is comparable to the corresponding bis(pyrazolato)-bridged complexes [6] indicates that these complexes have a *cis* configuration with the phosphine ligands *trans* to the bridging pyrazolato group. The ^{1}H NMR spectra of the chloro/pyrazolato-bridged complexes displayed two resonances attributable to the substituents at the 3,5-positions and the 4 position of the bridging pyrazolate group. The complex $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$ exhibited one doublet for the PMe_2 protons, whereas two such doublets for each isomer (*cis* and *trans*) were observed for $[Pt_2Ph_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$.

2.1. Structure of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$

The molecular structure of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$ following ORTEP [11] is shown in Fig. 1. Table 2 lists the fractional coordinates of the non-hydrogen atoms while, in Table 3 selected intra-molecular bond lengths and angles are presented. The geometry around the two platinum atoms is essentially square-planar since the atoms defining the respective metal-coordination planes are all coplanar within 0.02 Å. However, the bond angles around the two platinums suggest a marginally higher distortion from square-planar geometry at Pt(1) relative to that at Pt(2). The deviation of the two metal atoms from the mean plane of the pyrazolato ring (Pt(1) = 0.16 and Pt(2) = 0.05 Å) also supports this observation. The Pt–P distances (2.218(3) Å) are normal and fall within the range of values reported [13,14] in complexes with PMe_2Ph ligands.

TABLE 2. Positional parameters with e.s.d.'s for $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$

Atom	*x*	*y*	*z*	*B* (Å^2)
Pt(1)	0.16867(2)	1.04775(2)	0.12981(2)	2.224(6)
Pt(2)	0.44263(2)	0.99725(2)	0.15242(2)	2.361(7)
Cl	0.2832(2)	0.9238(2)	0.1401(2)	3.48(5)
P(1)	0.0756(2)	0.9754(2)	0.1919(1)	2.64(5)
P(2)	0.5396(2)	0.8865(2)	0.2317(2)	3.31(6)
N(1)	0.2535(5)	1.1202(5)	0.0717(4)	2.4(1)
N(2)	0.3520(5)	1.1011(5)	0.0785(4)	2.6(1)
C(1)	0.3766(7)	1.1581(6)	0.0262(6)	3.0(2)
C(2)	0.2943(7)	1.2153(7)	−0.0140(6)	3.6(2)
C(3)	0.2194(6)	1.1906(6)	0.0169(6)	3.0(2)
C(4)	0.0743(6)	1.1540(6)	0.1154(5)	2.7(2)
C(5)	0.1071(7)	1.2258(6)	0.1741(6)	3.7(2)
C(6)	0.0504(7)	1.3031(7)	0.1582(6)	4.5(2)
C(7)	−0.0466(8)	1.3094(8)	0.0842(7)	4.9(3)
C(8)	−0.0812(7)	1.2388(8)	0.0295(7)	4.4(2)
C(9)	−0.0218(7)	1.1604(7)	0.0450(6)	3.7(2)
C(10)	0.5728(6)	1.0611(6)	0.1628(6)	3.0(2)
C(11)	0.6173(6)	1.0477(7)	0.0983(6)	3.3(2)
C(12)	0.769(7)	1.0990(8)	0.1048(6)	4.3(2)
C(13)	0.7514(7)	1.1586(8)	0.1712(7)	4.7(3)
C(14)	0.7096(8)	1.1700(8)	0.2371(7)	4.6(3)
C(15)	0.6205(7)	1.1247(7)	0.2302(6)	3.8(2)
C(16)	−0.0636(7)	0.9725(9)	0.1290(7)	4.6(3)
C(17)	0.1066(8)	0.8561(6)	0.2118(6)	4.3(2)
C(18)	0.0935(7)	1.0158(7)	0.3017(6)	3.4(2)
C(19)	0.0156(9)	1.0536(9)	0.3210(7)	6.0(3)
C(20)	0.028(1)	1.083(1)	0.4037(8)	7.1(4)
C(21)	0.125(1)	1.077(1)	0.4705(8)	7.3(4)
C(22)	0.208(1)	1.040(1)	0.4532(9)	8.0(4)
C(23)	0.1940(8)	1.0096(9)	0.3694(7)	5.7(3)
C(24)	0.6823(8)	0.9033(9)	0.2836(9)	6.4(4)
C(25)	0.5064(9)	0.8581(9)	0.3288(6)	5.6(3)
C(26)	0.5255(6)	0.7823(6)	0.1728(5)	3.0(2)
C(27)	0.5918(7)	0.7101(7)	0.2132(7)	4.3(2)
C(28)	0.5795(8)	0.6301(7)	0.1657(7)	4.8(2)
C(29)	0.5068(9)	0.6226(8)	0.0796(7)	5.5(3)
C(30)	0.4421(9)	0.6956(8)	0.0387(7)	5.3(3)
C(31)	0.4519(7)	0.7747(7)	0.0867(6)	3.7(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3[a^{*2} \times B(1,1) + b^{*2} \times B(2,2) + c^{*2} \times B(3,3) + ab(\cos \gamma^*) \times B(1,2) + ac(\cos B^*) \times B(1,3) + bc(\cos \alpha^*) \times B(2,3)]$.

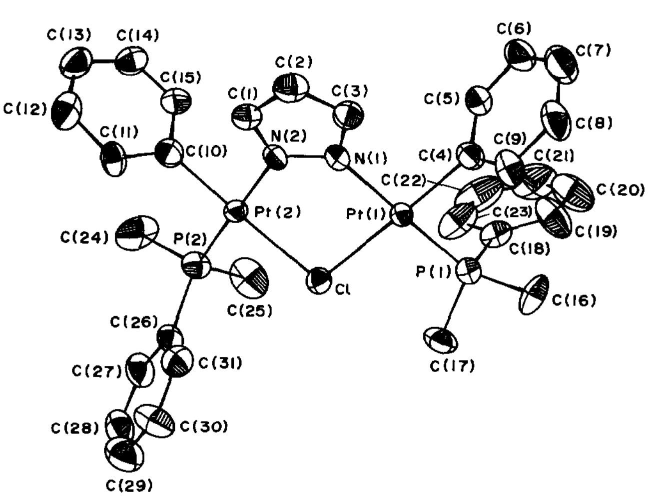

Fig. 1. ORTEP view of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$.

The Pt–N bond distance (2.081(7) Å) and the Pt–Cl bond distance (2.412(2) Å) found here are marginally higher than those reported by Deese et al. [12] for the complex $[Pt_2(\mu\text{-}Cl)(\mu\text{-}pz)(C_2H_4)_2Cl_2]$ the corresponding values being (2.04(1) Å) and (2.296(6) Å) respectively. These authors were the first to characterize a bridged binuclear complex having a single bridging pyrazolato group. Contrary to expectation they found the central five membered [Pt(1), N(1), N(2), Pt(2), Cl(2)] ring to be distinctly planar. All previously reported structures with two bridging pyrazolato groups exhibited a puckered (usually boat form) conformation for the central five-membered ring. They found the inter-planar angle between the two respective metal coordination planes to be 7.5° and attributed this planarity to two reasons *viz.* (i) weak Van der Waals dimerization and (ii) π-back bonding of the pyrazolato

TABLE 3. Selected bond lengths (Å) and bond angles (°) for $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$ with e.s.d.'s in parentheses

Pt(1)–Pt(2)	3.752(3)	P(1)–C(17)	1.85(1)
Pt(1)–Cl	2.414(2)	P(1)–C(18)	1.82(2)
Pt(1)–P(1)	2.218(3)	P(2)–C(24)	1.84(2)
Pt(1)–C(4)	2.022(9)	P(2)–C(25)	1.87(1)
Pt(1)–N(1)	2.088(8)	P(2)–C(26)	1.81(1)
Pt(2)–Cl	2.411(2)	N(1)–N(2)	1.36(1)
Pt(2)–P(2)	2.218(2)	N(1)–C(3)	1.35(2)
Pt(2)–C(10)	1.994(9)	N(2)–C(1)	1.35(1)
Pt(2)–N(2)	2.075(6)	C(1)–C(2)	1.38(1)
P(1)–C(16)	1.80(1)	C(2)–C(3)	1.37(2)
N(1)–Pt(1)–C(4)	89.3(3)	C(16)–P(1)–C(17)	101.7(5)
C(4)–Pt(1)–P(1)	88.6(3)	C(16)–P(1)–C(18)	106.0(5)
P(1)–Pt(1)–Cl	94.2(1)	C(17)–P(1)–C(18)	102.6(5)
N(1)–Pt(1)–Cl	87.9(2)	Pt(2)–P(2)–C(24)	117.7(5)
Pt(1)–Cl–Pt(2)	102.1(1)	Pt(2)–P(2)–C(25)	112.1(4)
Pt(1)–N(1)–N(2)	125.5(5)	Pt(2)–P(2)–C(26)	115.1(3)
N(2)–Pt(2)–Cl	88.2(2)	C(24)–P(2)–C(25)	102.4(6)
N(2)–Pt(2)–C(10)	90.5(4)	C(24)–P(2)–C(26)	103.8(5)
C(10)–Pt(2)–P(2)	89.4(2)	C(25)–P(2)–C(26)	104.2(5)
P(2)–Pt(2)–Cl	91.8(1)	N(1)–N(2)–C(1)	108.1(6)
Pt(1)–P(1)–C(16)	115.9(4)	N(2)–C(1)–C(2)	109.6(9)
Pt(1)–P(1)–C(17)	114.9(5)	C(1)–C(2)–C(3)	105.0(9)
Pt(1)–P(1)–C(18)	114.2(3)	C(2)–C(3)–N(1)	109.8(8)
Pt(2)–N(2)–N(1)	124.7(5)	C(3)–N(1)–N(2)	107.5(7)

group to Pt, although for the second reason no significant bond shortening was observed. In the present case, the inter-planar angle between the two metal-coordination planes is 35.7° which suggests that the central five membered ring is not planar but is substantially puckered. The reason for this appears to be the size and nature of the other terminal auxiliary ligands. In the earlier case these happen to be chlorine and C_2H_4, whereas in the present case they are phenyl and PMe_2Ph which are substantially bulky in comparison. Consequently, in order to minimize the short contacts between the protons of pyrazolato group and those of the phenyl group, the central five-membered ring adopts a puckered conformation. This also accounts for the preference of the pz group to be *cis* to the phenyl rings rather than the sterically crowded PMe_2Ph ligands thereby resulting in an overall symmetrical *cis* configuration for this hetero bridged binuclear complex. The bridging chlorine angle [102.1(1)°] is significantly shorter than reported [108.1(2)°] for the olefinic derivative by Deese *et al.* [12]. The reason for this is not apparent. However, the Pt–Pt distance [3.75 Å here and 3.72 Å (Deese *et al.*)] is comparable in both complexes and rules out the possibility of any metal–metal interaction.

A second feature that is regularly seen in these bridged complexes is that the terminal PMe_2Ph ligands adopt different conformations. One of the methyl carbons [C(16)] attached to P(1) lies very nearly in the plane of the phenyl ring attached to P(1) [torsion angle C16–P1–C18–C19 = −13.0°], whereas those attached to P(2) in the other PMe_2Ph ligand are considerably away from the respective phenyl ring plane [torsion angle C24–P2–C26–C27 = 42.4° and C25–P2–C26–C27 = −64.1°]. Exactly similar conformations have been observed for this ligand in other chloro, mercaptoethyl bridged binuclear complexes reported [13,14] by us earlier. The C–C bond distances (C–C = 1.40(2) Å) and bond angles (120.0°) in the four phenyl rings are normal. The pyrazolato ring is planar with the atoms defining the plane all being coplanar within 0.01 Å. The P–C bond length (1.83(2) Å) is also normal. The Pt–P–C bond angles in the two PMe_2Ph ligands are significantly higher (range 112°–117°) than the corresponding C–P–C angles (range 102°–106°). This appears to be due to the larger ionic radius of the Pt atom relative to the C-atom.

3. Experimental details

The complexes $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$, *cis*-$[PtCl_2(CH_2{=}CH_2)(PR_3)]$, $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ [8] and Me_3SnAr [6] (Ar = Ph or C_6H_4OMe-4) were prepared according to the literature methods. The pyrazoles and the tertiary phosphines were obtained from commercial sources. All the preparations were carried out under nitrogen atmosphere. Elemental analysis for C, H and N were carried out in the Analytical Chemistry Division of this Research Centre. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX-500 spectrometer in 5 mm tubes and the chemical shifts were referenced to internal chloroform peak (δ 7.26 ppm) for proton and external 85% H_3PO_4 for ^{31}P.

3.1. Preparation of $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-}pz)(PMe_2Ph)_2]$

To a methanol suspension (25 ml) of $[Pt_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (156 mg, 0.176 mmol) was added a solution of pyrazole (12 mg, 0.176 mmol) in methanolic sodium hydroxide [0.33 ml (0.532 N) 0.176 mmol] with vigorous stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h. The solvent was evaporated *in vacuo* and the residue was extracted with dichloromethane (3 × 5 ml). After reducing the volume (2 ml), hexane (5 ml) was added and the solution cooled in the freezer for 24 h to yield colourless crystals of the title complex (94 mg, 58%). Other complexes were prepared similarly. The same reaction in 1:3 stoichiometry afforded $[Pt_2Ph_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$ which was subsequently crystallized from dichloromethane-ethanol mixture in 78% yield. Pertinent data are given in Table 1.

TABLE 4. Crystal data and refinement details of $C_{31}H_{38}N_2P_2ClPt_2$

Formula	$C_{31}H_{38}N_2P_2ClPt_2$
Molecular weight	926.2
Crystal habit	Colourless plates
Crystal size(mm)	$0.25 \times 0.25 \times 0.20$
Crystal system	Monoclinic
Space group	$P2_{1/c}$
a(Å)	13.877(1)
b(Å)	15.058(2)
c(Å)	16.386(3)
β(deg)	112.95(1)
V(Å^3)	3153.2
Z	4
D_{calc}(g cm^{-3})	1.951
F(000)	1764
μ(cm^{-1})	91.65
T(K)	295
θ limits (deg)	$3 < \theta < 25$
No. of data collected	6056
No. of unique data	5766
No. of unique reflections used with $I > 3\sigma(I)$	4174
R	0.035
R_w	0.045
Residual ρ_{max}e Å^{-3}	1.41 (near platinum)
$(\Delta/\sigma)_{max}$	0.92

3.2. Crystallography

All diffraction measurements were performed at room temperature (295 K) on an Enraf Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation, $\lambda = 0.7107$ Å employing $\omega : 2\theta$ scan technique. The unit cell was determined from 25 randomly selected reflections by using the automatic search, index, and least-square routines. Table 4 lists the relevant crystal data together with details of the intensity measurements. All the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data by measuring the intensities of four reflections with χ near 90° for different ψ values ($0° < \psi < 360°$ every 10°) and using the EAC program, from the Enraf Nonius Package. The maximum and minimum transmission factors were 0.99 and 0.84. Two standard reflections (5 −4 −5 and 5 1 −7) measured every 1800 s showed no intensity variation. The structure was solved by routine heavy atom methods and refined by full matrix least squares with non-hydrogen atoms anisotropic. Hydrogen atoms were omitted.

The weighting scheme employed was $w = 1/\sigma^2(F_o)$ and the final residuals were $R = 0.035$ and $R_w = 0.045$. A final difference map had maximum density of 1.41 e Å^{-3} near platinum atoms. Programs from the Enraf Nonius SDP Plus Package [9] were run on a PDP 11/73 computer. Other crystallographic details comprising thermal parameters, all bond distances and angles, torsion angles, least square plane fits and F_o/F_c tables are deposited.

Acknowledgments

We thank Dr J.P. Mittal for his support and encouragement for this work. We are grateful to TIFR for providing the ^1H NMR spectra on their 500 MHz National facility and Head, Analytical Chemistry Division for microanalyses. RB thanks UGC for providing the CAD-4 facility at the university of Rajasthan.

References

1 S. Trofimenko, *Prog. Inorg. Chem., 34* (1986) 115.

2 A.W. Coleman, D.T. Eadie, S.R. Stobart, M.J. Zaworotko and J.L. Alwood, *J. Am. Chem. Soc., 104* (1982) 922; F. Barcelo, P. Lahureta, M.A. Ubeda, C. Foces-Foces, F.H. Cano and M. Martinez Ripoll, *Organometallics, 7* (1988) 584; G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J. Casabo, E. Molins and C. Miravitlles, *Inorg. Chem., 30* (1991) 2605.

3 A. Tiripicchio and M.T. Camellini, *J. Chem. Soc., Dalton Trans.*, (1990) 989; M.T. Pinillos, A. Elduque, J.A. Lopez, F.J. Lahoz and L.A. Oro, *J. Chem. Soc., Dalton Trans.*, (1991) 1391; A. Eduque, L.A. Oro, M.T. Pinillos, C. Tejel, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, (1991) 2807.

4 V.K. Jain and S. Kannan, *Polyhedron, 11* (1992) 27; V.K. Jain and S. Kannan, *J. Chem. Res. (S),* (1992) 278; A. Singhal and V.K. Jain, *J. Chem. Soc., Dalton Trans.*, (1993) 1515.

5 V.K. Jain and S. Kannan and E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.*, (1992) 2231.

6 A. Singhal, V.K. Jain and S. Kannan, *J. Organomet. Chem., 447* (1993) 317.

7 V.K. Jain and S. Kannan and E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.*, in press.

8 C. Eaborn, K.J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, (1978) 1288.

9 Enraf Nonius Structure Determination Package, Enraf Nonius, Delft, Netherlands, 1983.

10 F. Bonati, H.C. Clark and C.S. Wang, *Can. J. Chem., 58* (1980) 1435.

11 C.K. Johnson, ORTEP II Report ORNL-5138, Oak Ridge National Laboratory, TN, USA, 1976.

12 W.C. Deese, D.A. Johnson and A.W. Cordes, *Inorg. Chem., 20* (1981) 1519.

13 V.K. Jain, R.P. Patel, K.V. Muralidharan and R. Bohra, *Polyhedron, 8* (1989) 2151.

14 V.K. Jain, R.P. Patel and K. Venkatasubramanian, *Polyhedron, 10* (1991) 851.