Crystal Structure of Bis(2-methoxy-6-((Z)-(p-tolylimino)methyl)phenoxy)palladium

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The structure of bis(2-methoxy-6-((Z)-(p-tolylimino)methyl)phenoxy)palladium crystallized in a monoclinic system and was characterized thus: $P2_1/c$, $a = 13.0221(14)$, $b = 11.6615(13)$, $c = 8.4898(9)$ Å, $\beta = 97.327(4)^\circ$, $Z = 2$, $V = 1278.7(2)$ Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0349$ [$I > 2\sigma(I)$] and $wR2 = 0.0824$. The molecules have two-fold symmetry about the centre Pd1 atom. Two ligands were coordinated to the Pd1 atom via oxygen and nitrogen atoms in a bidentate manner to form a square-planar geometrical structure.

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Schiff-base complexes are being continuously studied concerning catalyst,¹⁻³ biomedical^{4,5} and material applications for their structural fundamental and theoretical understanding. Pd(II) Schiff-base complexes have remarkable properties, such as high selectivity and activity by manipulating the ligand environment.⁶ The complex $C_{30}H_{28}N_2O_4Pd$ was synthesized according to previous studies⁷ with slight modification. A 0.2-mmol (Z)-2-methoxy-6-((p-tolylimino)methyl)phenol was added to a stirred solution of 0.1 mmol of palladium(II) acetate in 5 mL of ethanol. The solution was refluxed for 6 h, and cooled to the room temperature.

The precipitate was filtered off and air-dried. The product was recrystallized in ethanol:chloroform (1:1) through a slow evaporation method to produce an orange crystal. Yield, 62.0%; m.p. 558 – 561 K. *Anal.* Calc. for $C_{30}H_{28}N_2O_4Pd$: C, 61.8; H, 4.4; N, 10.3%; Found: C, 61.6; H, 4.5; N, 10.7%. The IR spectrum was obtained as a KBr disc on a Perkin Elmer Spectrum One FTIR Spectrometer from 450 – 4000 cm⁻¹. The peaks at 1596, 1327, 1258, 1542, 580 and 449 cm⁻¹ were assigned to $\nu(C=N)$, $\nu(C-N)$, $\nu(C-O)$, $\nu(C=C \text{ aromatic})$, $\nu(Pd-O)$ and $\nu(Pd-N)$, respectively. The infrared data obtained are nearly similar based on a previous study reported.⁸ The NMR spectrum was obtained as a CDCl₃ solution on Jeol 400 MHz spectrometer. The ¹H NMR chemical shifts, δ , observed are (ppm): 2.42 (s, 3H, CH₃), 3.36 (s, 3H, OCH₃), 6.39 – 7.29 (m, 7H, aromatic, $J_{HH} = 1 - 3$ and 6 – 9 Hz), 7.66 (s, 1H, HC=N). The coupling constant indicates the presence of *meta* and *ortho* aromatic protons.

The crystal and structure-refinement data are summarized in Table 1 and selected bond distances and angles in Table 2. H atoms were positioned geometrically and allowed to ride on the parent C atom, with C-H = 0.95 – 0.98 Å, and with $U_{iso}(H) = 1.2$ (1.5 for methyl groups) times $U_{eq}(C)$. Figure 1 represents the

chemical diagram whereas Fig. 2 shows the ORTEP structure of the title compound. In this centrosymmetric complex, the two ligands are symmetrically related to each other and have the same bond angles and distances. The ligand was coordinated to the metal center through *ONNO* atoms, forming a square-planar complex, yielding two six-membered rings surrounding the metal center.

Table 1 Crystal and experimental data

Chemical formula: $C_{30}H_{28}N_2O_4Pd$	
Molecular weight: 586.94	
$T = 273(2)$ K	
Crystal system: monoclinic	
Space group: $P2_1/c$	
$a = 13.0221(14)$ Å	
$b = 11.6615(13)$ Å	$\beta = 97.327(4)^\circ$
$c = 8.4898(9)$ Å	
$V = 1278.7(2)$ Å ³	
$Z = 2$	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$)	
$\mu(\text{Mo } K\alpha) = 0.765$	
$F(0\ 0\ 0) = 600$	
Crystal size = 0.600 × 0.590 × 0.160 mm	
No. of reflections collected = 24990	
No. of independent reflections = 3186	
θ range for data collection: 2.984 to 28.365°	
Data/Restraints/Parameters = 3186/0/169	
Goodness-of-fit on $F^2 = 1.185$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0349$, $wR2 = 0.0742$	
R indices (all data): $R1 = 0.0472$, $wR2 = 0.0824$	
Measurement: Bruker SMART CCD	
Program system: SHELXTL-2008, SADABS	
Structure determination: SHELXS-2008	
CCDC deposition number: 1885447	

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Table 2 Selected geometric parameters, bond length (Å) and angles (°)

Bond	Bond length/Å	Bond	Bond angle/°
Pd1-O2	1.9636(19)	O2-Pd1-O2A	180.0
Pd1-N1	2.021(2)	O2-Pd1-N1A	90.71(8)
N1-C8	1.292(3)	N1-Pd1-N1A	180.0
N1-C9	1.440(3)	O2-Pd1-N1	89.29(8)

Fig. 1 Chemical structure of bis(2-methoxy-6-((Z)-(p-tolylimino)-methyl)phenoxy)palladium.

Two rings (Pd1/O2/C6/C1/C8/N1) are approximately planar, with a maximum deviation of 0.191 Å for atom Pd1. The bond lengths [Pd1-N1, 2.021(2)Å], [Pd1-O2, 1.9636(19)Å] and angles [89.29(8) to 180.0°] (Table 2) of the metal environments are comparable to the structures reported previously. The central complex, (Pd1/N1/O2) phenyl rings (C1-C6) and (C9-C14) are slightly planar with a maximum deviation of 0.016 Å for the C6 atom from the mean plane. The dihedral angles between the central complex (Pd1/N1/O2), phenyl rings [(C1-C6) and (C9-C14)] are 22.19 and 63.04°, respectively. The inclination angle for the phenyl rings is 41.15°. In the crystal packing, each of the molecule is stabilized by an intermolecular C-H...O hydrogen bond forming dimers. The bond length of the weak interaction is given in Table 3.

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Fig. 2 ORTEP structure of bis(2-methoxy-6-((Z)-(p-tolylimino)-methyl)phenoxy)palladium, showing 50% probability ellipsoids.

Table 3 Hydrogen-bond geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
C13-H13A...O2 ⁱ	0.93	2.45	3.236(4)	143

Symmetry codes: (i) $x, 1/2-y, 1/2+z$.

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