Crystal Structure of (4-Vinylpyridine)[2-[2-acetyl-2-(ethoxycarbonyl)ethyl]-8-quinolinol-*C,N,O*]palladium(II)

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The crystal structure of (4-vinylpyridine)[2-[2-acetyl-2-(ethoxycarbonyl)ethyl]-8-quinolinol-*C,N,O*]palladium(II) was determined by X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.274(4)\text{\AA}$, $b = 19.087(9)\text{\AA}$, $c = 13.084(6)\text{\AA}$, $\beta = 94.335(5)^\circ$, $V = 2060(1)\text{\AA}^3$, and $Z = 4$. The final R value is 0.075. The crystal structure reveals that the complex has a 5,5-chelate ring system, that the geometry around Pd(II) is described as a distorted square-planar, and that the pyridine ring is almost perpendicular to the quinoline ring.

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It is well known that 8-quinolinol functions as a bidentate ligand and forms stable chelates with a variety of metal ions. The high stability of the complexes can be ascribed to the fixed planar ligand structure containing a phenolic oxygen and a heteroaromatic nitrogen atom. On the other hand, we reported a series of stable cyclometalated Pd(II) complexes that contain both 2-substituted-8-quinolinol with $C(\text{sp}^3)$, *N,O*-donor atoms and amine with an *N*-donor atom as ligands. Such cyclometalated complexes have a 5,5- or 5,6-chelate ring system.¹ These complexes are expected to show not only antibacterial action, but also an electroluminescent characteristic. Because of our interests in the properties of polymer complexes possessing *C,N,O*-cyclometalated Pd(II), we sought the synthesis of a new complex that can polymerize. Therefore we carried out the introduction of 4-vinylpyridine, which has a vinyl group that can polymerize as an amine ligand into the above-mentioned cyclometalated Pd(II) complex. We report here on the crystal structure of the title compound.

The title compound was prepared by a ligand-exchange reaction with 4-vinylpyridine, as described in a previous paper.² Single crystals were grown from a chloroform solution. Since the title compound has an asymmetric atom of the carbon attached to Pd(II), the crystal contains two racemic compounds. The crystal and experimental data are given in Table 1.

Fig. 1 Chemical structure of the title compound.

Diffraction data were collected by a Rigaku/MSM Mercury CCD diffractometer at 296 K with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71070\text{\AA}$). The structure was solved by direct methods.³ The non-hydrogen atoms were refined anisotropically by full-matrix least-squares. The positions of hydrogen atoms were calculated geometrically. All of the calculations were performed using the teXsan program package.⁴ The final positional parameters are given in Table 2, and selected bond lengths, bond angles, and torsion angles are listed in Table 3.

An ORTEP drawing of the title compound with the atomic-labeling scheme is shown in Fig. 2. The crystal structure reveals that the complex has a 5,5-chelate ring system and that the Pd atom is coordinated to two nitrogen atoms of quinoline

Table 1 Crystal and experimental data

Formula:	$\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_4\text{Pd}$
Formula weight	= 496.84
Crystal color, habit:	yellow, needle
Crystal size:	$0.25 \times 0.08 \times 0.05\text{ mm}$
Crystal system:	monoclinic
Space group:	$P2_1/n$ $Z = 4$
T :	296 K
a :	$8.274(4)\text{\AA}$
b :	$19.087(9)\text{\AA}$
c :	$13.084(6)\text{\AA}$
β :	$94.335(5)^\circ$
V :	$2060(1)\text{\AA}^3$
D_{calc} :	1.327 g/cm^3
No. of reflections used	= 4697 ($I > 2.00\sigma(I)$)
$2\theta_{\text{max}}$:	55.0° with Mo K_α ($0.71070\text{\AA}$)
R :	0.075
R_w :	0.158
$(\Delta/\sigma)_{\text{max}}$:	0.229
$(\Delta\rho)_{\text{max}}$:	$1.25\text{ e}\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$:	$-0.99\text{ e}\text{\AA}^{-3}$
Measurement:	Rigaku/MSM Mercury CCD
Program system:	teXsan
Structure determination:	direct method (SIR97)
Refinement:	full-matrix least-squares

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Table 2 Atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
Pd(1)	0.07158(5)	0.32798(2)	0.53938(3)	3.64(1)
O(1)	0.2324(4)	0.4056(2)	0.5958(3)	4.12(9)
O(2)	-0.1811(6)	0.2495(3)	0.3258(4)	6.4(1)
O(3)	-0.0435(6)	0.1694(2)	0.4189(3)	5.5(1)
O(4)	-0.2385(5)	0.2479(3)	0.6663(3)	6.2(1)
N(1)	-0.0868(5)	0.3971(2)	0.5716(3)	3.6(1)
N(2)	0.2483(5)	0.2592(2)	0.5044(3)	3.8(1)
C(1)	-0.2448(6)	0.3883(3)	0.5507(4)	3.7(1)
C(2)	-0.3523(7)	0.4409(4)	0.5760(5)	4.5(1)
C(3)	-0.2938(7)	0.5016(3)	0.6201(4)	4.4(1)
C(4)	-0.1250(7)	0.5119(3)	0.6418(4)	3.8(1)
C(5)	-0.0506(8)	0.5720(3)	0.6868(5)	4.7(2)
C(6)	0.1158(8)	0.5736(3)	0.7019(5)	4.8(2)
C(7)	0.2153(6)	0.5198(3)	0.6722(5)	4.5(1)
C(8)	0.1483(7)	0.4595(3)	0.6274(4)	3.9(1)
C(9)	-0.0239(6)	0.4577(3)	0.6146(4)	3.7(1)
C(10)	-0.2816(7)	0.3212(3)	0.4944(5)	4.7(2)
C(11)	-0.1421(6)	0.2674(3)	0.5055(4)	3.9(1)
C(12)	-0.1271(8)	0.2291(3)	0.4075(5)	4.3(1)
C(13)	-0.0186(9)	0.1285(4)	0.3270(5)	5.9(2)
C(14)	0.063(1)	0.0623(5)	0.3629(7)	7.9(3)
C(15)	-0.1465(7)	0.2284(3)	0.6051(5)	4.5(1)
C(16)	-0.0418(9)	0.1677(4)	0.6340(6)	6.1(2)
C(17)	0.3372(8)	0.2246(4)	0.5788(5)	4.6(1)
C(18)	0.4451(7)	0.1732(4)	0.5571(6)	5.0(2)
C(19)	0.4690(7)	0.1559(3)	0.4569(6)	4.9(2)
C(20)	0.3854(7)	0.1946(4)	0.3822(5)	4.8(2)
C(21)	0.2771(7)	0.2451(3)	0.4073(4)	4.1(1)
C(22)	0.5750(10)	0.0976(5)	0.4253(10)	9.1(3)
C(23)	0.636(2)	0.0540(7)	0.463(2)	16.6(6)

$$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha).$$

Table 3 Selected bond lengths ($\text{\AA}$), bond angles ($^\circ$) and torsion angles ($^\circ$)

Atom	Atom	Distance	Atom	Atom	Distance
Pd(1)	O(1)	2.089(4)	Pd(1)	N(1)	1.928(4)
Pd(1)	N(2)	2.042(4)	Pd(1)	C(11)	2.131(5)
O(1)	C(8)	1.325(7)	N(1)	C(1)	1.326(6)
N(1)	C(9)	1.372(7)	C(1)	C(10)	1.497(8)
C(8)	C(9)	1.423(7)	C(10)	C(11)	1.543(9)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(1)	Pd(1)	N(1)	82.1(2)	O(1)	Pd(1)	N(2)	95.0(2)
O(1)	Pd(1)	C(11)	162.7(2)	N(1)	Pd(1)	N(2)	176.8(2)
N(1)	Pd(1)	C(11)	81.3(2)	N(2)	Pd(1)	C(11)	101.6(2)
Pd(1)	O(1)	C(8)	109.0(3)	Pd(1)	N(1)	C(1)	123.0(4)
Pd(1)	N(1)	C(9)	115.0(3)	Pd(1)	N(2)	C(17)	121.0(4)
C(1)	N(1)	C(9)	121.9(5)	Pd(1)	N(2)	C(21)	121.6(4)
C(17)	N(2)	C(21)	117.4(5)	N(1)	C(1)	C(2)	119.7(5)
N(1)	C(1)	C(10)	111.7(5)	N(1)	C(9)	C(4)	120.9(5)
N(1)	C(9)	C(8)	114.5(5)	C(1)	C(10)	C(11)	113.6(5)
Pd(1)	C(11)	C(10)	105.2(4)	Pd(1)	C(11)	C(12)	108.9(4)

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
Pd(1)	O(1)	C(8)	C(9)	-2.8(6)	Pd(1)	N(1)	C(1)	C(10)	-3.4(7)
Pd(1)	N(1)	C(9)	C(8)	0.4(6)	Pd(1)	C(11)	C(10)	C(1)	-24.4(6)
O(1)	Pd(1)	N(2)	C(17)	73.0(5)					

and pyridine, one phenolate oxygen atom, and one carbon atom of the substituent of 8-quinolinol. The bond lengths of Pd(1)–O(1), Pd(1)–N(1), Pd(1)–N(2), and Pd(1)–C(11) are 2.089(4), 1.928(4), 2.042(4), and 2.131(5) $\text{\AA}$, respectively, showing that the values are quite similar to those for the Pd(II)

Fig. 2 ORTEP drawing of the title compound with atom labeling. The thermal ellipsoids are drawn at the 50% probability level. The spheres of the hydrogen atoms are drawn in an arbitrary scale.

complex associated with the pyridine ligand.² The geometry around Pd(II) is described as a distorted square-planar [O(1)–Pd(1)–N(1) = 82.1(2) $^\circ$, O(1)–Pd(1)–N(2) = 95.0(2) $^\circ$, N(1)–Pd(1)–C(11) = 81.3(2) $^\circ$, N(2)–Pd(1)–C(11) = 101.6(2) $^\circ$]. The Pd atom lies on the line defined by two nitrogen atoms [N(1)–Pd(1)–N(2) = 176.8(2) $^\circ$]. The deviation for Pd(1) from the plane composed of the quinoline ring is 0.020(6) $\text{\AA}$. Two carbon atoms of C(10) and C(11) do not lie in the corresponding plane. The maximum deviations are –0.127(8) $\text{\AA}$ for C(10) and 0.289(9) $\text{\AA}$ for C(11). Further, the torsion angle Pd(1)–C(11)–C(10)–C(1) of –24.4(6) $^\circ$ shows that the five-membered ring composed of Pd(1), N(1), C(1), C(10) and C(11) is distorted, in contrast to the planarity of another five-membered ring composed of Pd(1), N(1), C(9), C(8) and O(1). The pyridine ring is almost perpendicular to the quinoline ring, and thus the dihedral angle between them is 110.3(2) $^\circ$. Although the final convergence was achieved with $R = 0.075$, $(\Delta/\sigma)_{\max}$ is 0.229. Such a value is ascribed to the structural disorder of the vinyl group containing C(22) and C(23).

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