

Structures of {Diethyl 2-[(8-Hydroxy- κ O-2-quinolyl- κ N)methyl]malonato(2-)- κ C²}(pyridine)palladium(II) and the Analogous Ethyl Complex

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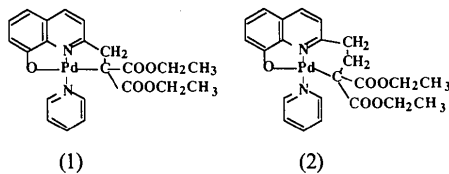
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Abstract. {Diethyl 2-[(8-hydroxy- κ O-2-quinolyl- κ N)methyl]malonato(2-)- κ C}(pyridine)palladium(II) dihydrate, [Pd(C₁₇H₁₇NO₅)(C₅H₅N)]·2H₂O (1), M_r = 536.82, triclinic, $P\bar{1}$, a = 11.674 (1), b = 11.740 (3), c = 10.863 (3) Å, α = 128.34 (2), β = 91.93 (1), γ = 97.18 (2)°, V = 1146.7 (8) Å³, Z = 2, D_m = 1.441, D_x = 1.555 g cm⁻³, λ (Mo $K\alpha$) = 0.7107 Å, μ = 8.4 cm⁻¹, $F(000)$ = 548, T = 295 K, final R = 0.033 for 4922 independent reflections having $|F_o| > \sigma(F_o)$. {Diethyl 2-[(8-hydroxy- κ O-2-quinolyl- κ N)ethyl]malonato(2-)- κ C}(pyridine)palladium(II), [Pd(C₁₈H₁₉NO₅)(C₅H₅N)] (2), M_r = 514.85, monoclinic, $P2_1/n$, a = 19.349 (2), b = 7.544 (2), c = 14.826 (2) Å, β = 94.11 (1)°, V = 2158.6 (5) Å³, Z = 4, D_m = 1.624, D_x = 1.585 g cm⁻³, λ (Mo $K\alpha$) = 0.7107 Å, μ = 8.8 cm⁻¹, $F(000)$ = 1048, T = 295 K, final R = 0.034 for 4459 independent reflections having $|F_o| > \sigma(F_o)$. The structures of the two molecules are characterized by 5,5- and 5,6-bicyclic chelating systems originating from novel quinolinol ligands containing three donor sites (C, N and O atoms). Some distortions are observed in the square-planar coordination geometry and are assumed to be due to the bicyclic chelating systems. Pd—N(pyridine) bond lengths are practically identical [2.049 (3) and 2.053 (3) Å], whereas other Pd—N lengths are significantly different [1.938 (3) and 2.032 (3) Å]. It is confirmed that the radical C(15) atom in the 2-substituted group acts as a donor and constructs a stable Pd—C(sp^3) σ bond.

Introduction. Previously, we prepared the novel 2-substituted 8-quinolinols containing C, N and O donor sites in the same molecule and synthesized Pd complexes having a Pd—C(sp^3) σ bond in the pres-

ence of a pyridine ligand (Yoneda, Newkome & Theriot, 1991). The Pd complexes exhibit 5,5- or 5,6-bicyclic chelating systems and have great stability; however, the asymmetric square-planar Pd units are much distorted compared with other reported Pd^{II} complexes possessing a Pd—C σ bond (Okeya, Kawaguchi, Yasuoka, Kai & Kasai, 1976; Newkome, Kawato, Kohli, Puckett, Olivier, Chiari, Fronczek & Deutsch, 1981; Newkome, Kohli & Fronczek, 1982; Newkome, Theriot, Cheskin, Evans & Baker, 1990; DeGraaf, Boersma, Smeets, Spek & Koten, 1989). Here we report the crystal structures of two Pd complexes and illustrate the differences between the two structures.



Experimental. The title complexes were prepared by the method described in a previous paper (Yoneda, Newkome & Theriot, 1991). Yellow needle-like parallelepiped crystals were obtained by recrystallization from a dichloromethane–hexane solution. The crystals of (1) and (2) used in the intensity measurements had approximate dimensions of 0.1 × 0.1 × 0.3 mm and 0.1 × 0.1 × 0.8 mm, respectively. The intensity data were collected on a Rigaku automated four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation from a Rigaku RU-300 rotating-anode X-ray generator operated at 50 kV, 300 mA. Respective lattice parameters were determined by the least-squares method from 2θ values for 20 carefully measured reflections ($29 < 2\theta$

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses
$$B_{\text{eq}} = \frac{1}{3}(\beta_1^2 a^2 + \beta_2^2 b^2 + \beta_3^2 c^2).$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
(1)				
Pd(1)	0.77346 (2)	0.27025 (2)	0.14394 (3)	3.5
O(1)	0.9106 (2)	0.1852 (2)	0.1749 (2)	4.3
O(2)	0.4889 (2)	0.2475 (3)	0.2125 (3)	7.3
O(3)	0.4873 (2)	0.1882 (3)	-0.0265 (3)	6.8
O(4)	0.6977 (3)	0.5802 (3)	0.1688 (3)	8.0
O(5)	0.6227 (2)	0.3574 (3)	-0.0558 (3)	6.7
N(1)	0.7644 (2)	0.1413 (3)	-0.0976 (3)	4.3
N(2)	0.7881 (2)	0.3876 (3)	0.3723 (3)	3.7
C(1)	0.9354 (3)	0.2511 (3)	0.3295 (4)	4.1
C(2)	1.0197 (3)	0.2207 (4)	0.3932 (4)	5.9
C(3)	1.0392 (3)	0.2971 (5)	0.5585 (5)	7.1
C(4)	0.9769 (3)	0.4023 (4)	0.6614 (4)	6.2
C(5)	0.8898 (3)	0.4372 (3)	0.6029 (4)	4.5
C(6)	0.8712 (3)	0.3600 (3)	0.4378 (3)	4.0
C(7)	0.8184 (3)	0.5441 (4)	0.6935 (4)	4.9
C(8)	0.7377 (3)	0.5700 (4)	0.6238 (4)	4.9
C(9)	0.7228 (3)	0.4885 (3)	0.4577 (4)	4.4
C(10)	0.6871 (3)	0.0147 (4)	-0.1939 (4)	5.0
C(11)	0.6811 (4)	-0.0749 (4)	-0.3558 (4)	5.9
C(12)	0.7564 (4)	-0.0348 (5)	-0.4221 (4)	7.3
C(13)	0.8370 (4)	0.0933 (6)	-0.3246 (5)	8.9
C(14)	0.8394 (3)	0.1797 (5)	-0.1625 (4)	6.6
C(15)	0.6360 (3)	0.3852 (3)	0.1821 (4)	4.6
C(16)	0.6549 (3)	0.4513 (4)	0.0995 (4)	5.5
C(17)	0.6399 (4)	0.4136 (5)	-0.1429 (5)	8.4
C(18)	0.5808 (4)	0.2952 (6)	-0.3074 (6)	9.4
C(19)	0.5307 (3)	0.2684 (4)	0.1256 (4)	5.2
C(20)	0.3836 (3)	0.0758 (5)	-0.0858 (5)	7.6
C(21)	0.3449 (5)	0.0161 (7)	-0.2506 (7)	12.5
C(22)	0.6463 (3)	0.5099 (4)	0.3640 (4)	5.2
O(101)	0.9031 (3)	0.8788 (3)	0.0109 (3)	6.9
O(102)	0.8920 (4)	0.7196 (6)	0.1276 (6)	18.2
(2)				
Pd(1)	0.82607 (1)	0.33668 (3)	0.07018 (2)	2.8
O(1)	0.8836 (1)	0.4330 (3)	0.1827 (2)	3.8
O(2)	0.7368 (2)	0.3388 (4)	-0.1902 (2)	5.7
O(3)	0.7336 (1)	0.5209 (3)	-0.0732 (1)	3.7
O(4)	0.7180 (2)	-0.0140 (3)	0.0320 (2)	5.3
O(5)	0.6528 (1)	0.2145 (3)	-0.0193 (2)	4.5
N(1)	0.7379 (1)	0.4072 (4)	0.1306 (2)	3.1
N(2)	0.9213 (1)	0.2822 (4)	0.0276 (2)	3.3
C(1)	0.9499 (2)	0.3997 (5)	0.1761 (2)	3.7
C(2)	1.0006 (2)	0.4325 (6)	0.2455 (3)	4.9
C(3)	1.0709 (2)	0.3992 (6)	0.2335 (3)	5.8
C(4)	1.0926 (2)	0.3416 (6)	0.1532 (3)	5.5
C(5)	1.0437 (2)	0.3047 (5)	0.0810 (3)	4.3
C(6)	0.9724 (2)	0.3274 (4)	0.0942 (2)	3.5
C(7)	1.0602 (2)	0.2462 (5)	-0.0056 (3)	5.1
C(8)	1.0093 (2)	0.2050 (5)	-0.0691 (3)	4.5
C(9)	0.9385 (2)	0.2199 (4)	-0.0510 (2)	3.7
C(10)	0.7134 (2)	0.5728 (4)	0.1235 (2)	3.5
C(11)	0.6593 (2)	0.6305 (5)	0.1722 (3)	4.5
C(12)	0.6301 (2)	0.5148 (6)	0.2298 (3)	4.9
C(13)	0.6540 (2)	0.3428 (6)	0.2366 (3)	4.8
C(14)	0.7083 (2)	0.2943 (5)	0.1861 (2)	3.8
C(15)	0.7724 (2)	0.2263 (4)	-0.0422 (2)	3.1
C(16)	0.7133 (2)	0.1277 (4)	-0.0055 (2)	3.8
C(17)	0.5926 (2)	0.1287 (7)	0.0142 (4)	6.5
C(18)	0.5355 (2)	0.2592 (8)	0.0042 (5)	8.6
C(19)	0.7458 (2)	0.3647 (4)	-0.1104 (2)	3.2
C(20)	0.6985 (2)	0.6535 (5)	-0.1315 (2)	4.9
C(21)	0.6225 (3)	0.6316 (8)	-0.1312 (3)	7.2
C(22)	0.8834 (2)	0.1668 (5)	-0.1226 (2)	4.2
C(23)	0.8178 (2)	0.0917 (5)	-0.0876 (2)	3.9

< 32°). Data collections were carried out in the 2θ range 3.5–55° for (1), and 2.1–55° for (2); θ -scan mode, scan speed 8° min⁻¹ (θ), scan width (2.0 + 0.35tan θ)° for (1) and (1.2 + 0.35tan θ)° for (2), background counts for 3 s before and after each scan. Three standard reflections monitored every 100 reflections showed no significant change. In (1), 4720 reflections were measured having $|F| \geq \sigma(F)$, and

Table 2. Selected bond lengths (\AA) and angles (°) with *e.s.d.*'s in parentheses

	(1)	(2)	(1)	(2)	
Pd(1)—O(1)	2.111 (3)	2.070 (3)	C(2)—C(3)	1.416 (7)	1.406 (7)
Pd(1)—N(1)	2.049 (3)	2.053 (3)	C(3)—C(4)	1.368 (7)	1.362 (7)
Pd(1)—N(2)	1.938 (3)	2.032 (3)	C(4)—C(5)	1.412 (6)	1.405 (6)
Pd(1)—C(15)	2.112 (4)	2.074 (3)	C(5)—C(6)	1.412 (5)	1.417 (5)
N(1)—C(10)	1.338 (6)	1.337 (4)	C(5)—C(7)	1.422 (6)	1.415 (6)
N(1)—C(14)	1.342 (6)	1.341 (4)	C(7)—C(8)	1.364 (6)	1.349 (6)
N(2)—C(6)	1.368 (5)	1.389 (4)	C(8)—C(9)	1.413 (6)	1.418 (5)
N(2)—C(9)	1.324 (5)	1.321 (4)	C(9)—C(22)	1.486 (6)	1.504 (5)
O(1)—C(1)	1.342 (5)	1.319 (4)	C(10)—C(11)	1.372 (7)	1.383 (5)
O(2)—C(19)	1.216 (6)	1.200 (5)	C(11)—C(12)	1.369 (8)	1.371 (6)
O(3)—C(19)	1.329 (6)	1.330 (4)	C(12)—C(13)	1.369 (9)	1.379 (6)
O(3)—C(20)	1.455 (7)	1.457 (5)	C(13)—C(14)	1.380 (9)	1.382 (6)
O(4)—C(16)	1.216 (6)	1.205 (5)	C(15)—C(16)	1.513 (6)	1.498 (5)
O(5)—C(16)	1.323 (6)	1.346 (5)	C(15)—C(19)	1.500 (6)	1.517 (4)
O(5)—C(17)	1.458 (7)	1.450 (6)	C(15)—C(22)	1.554 (6)	—
C(1)—C(2)	1.386 (6)	1.392 (6)	C(15)—C(13)	—	1.530 (5)
C(1)—C(6)	1.419 (5)	1.428 (5)	C(17)—C(18)	1.482 (9)	1.480 (9)
			C(20)—C(21)	1.49 (1)	1.480 (7)
			C(22)—C(23)	—	1.514 (5)
O(1)—Pd(1)—N(1)	95.5 (1)	88.5 (1)	O(3)—C(20)—C(21)	106.6 (5)	110.0 (4)
N(1)—Pd(1)—N(2)	177.2 (1)	171.2 (1)	O(3)—C(19)—C(15)	115.4 (4)	113.3 (3)
Pd(1)—N(1)—C(14)	120.4 (3)	120.5 (2)	O(5)—C(16)—O(4)	121.9 (4)	122.5 (3)
Pd(1)—N(2)—C(9)	121.8 (3)	129.6 (2)	O(4)—C(16)—C(15)	123.2 (4)	125.1 (3)
Pd(1)—C(15)—C(19)	101.8 (3)	112.7 (2)	O(5)—C(17)—C(18)	107.1 (5)	106.3 (5)
O(1)—Pd(1)—N(2)	81.7 (1)	82.8 (1)	O(5)—C(16)—C(15)	114.8 (4)	112.4 (3)
Pd(1)—O(1)—C(1)	109.0 (2)	110.1 (2)	C(16)—O(5)—C(17)	117.6 (4)	116.2 (3)
Pd(1)—N(1)—C(10)	121.1 (3)	120.6 (2)	C(1)—C(2)—C(3)	120.5 (4)	120.7 (4)
Pd(1)—N(2)—C(6)	115.2 (2)	110.2 (2)	C(1)—C(6)—C(5)	123.6 (4)	121.5 (3)
Pd(1)—C(15)—C(16)	107.1 (3)	105.0 (2)	C(6)—C(1)—C(2)	116.7 (4)	117.1 (3)
N(1)—Pd(1)—C(15)	100.7 (1)	94.1 (1)	C(4)—C(3)—C(2)	122.2 (5)	122.0 (5)
O(1)—Pd(1)—C(15)	163.7 (1)	176.4 (1)	C(5)—C(4)—C(3)	119.7 (5)	119.8 (4)
N(2)—Pd(1)—C(15)	82.1 (1)	94.7 (1)	C(6)—C(5)—C(4)	117.4 (4)	118.7 (4)
Pd(1)—C(15)—C(22)	106.8 (3)	—	C(4)—C(5)—C(7)	126.7 (4)	124.7 (4)
Pd(1)—C(15)—C(23)	—	110.4 (2)	C(8)—C(7)—C(5)	121.5 (4)	120.2 (4)
N(1)—C(14)—C(13)	121.7 (5)	122.6 (3)	C(6)—C(5)—C(7)	115.9 (4)	116.7 (4)
N(1)—C(10)—C(11)	122.1 (4)	122.0 (3)	C(9)—C(8)—C(7)	119.9 (4)	121.1 (4)
C(14)—N(1)—C(10)	118.5 (4)	118.5 (3)	C(8)—C(9)—C(22)	127.1 (4)	119.4 (3)
N(2)—C(9)—C(8)	118.9 (4)	120.2 (3)	C(10)—C(11)—C(12)	119.4 (5)	119.1 (4)
N(2)—C(6)—C(1)	115.6 (3)	117.0 (3)	C(19)—C(15)—C(16)	119.8 (4)	110.7 (3)
N(2)—C(9)—C(22)	113.8 (4)	120.4 (3)	C(14)—C(13)—C(12)	119.4 (7)	118.3 (4)
N(2)—C(6)—C(5)	120.8 (3)	121.5 (3)	C(13)—C(12)—C(11)	118.9 (6)	119.6 (4)
C(9)—N(2)—C(6)	122.9 (3)	120.1 (3)	C(16)—C(15)—C(23)	—	107.9 (3)
O(1)—C(1)—C(6)	118.5 (3)	119.6 (3)	C(16)—C(15)—C(22)	110.2 (4)	—
O(1)—C(1)—C(2)	124.9 (4)	123.3 (3)	C(19)—C(15)—C(23)	—	110.0 (3)
O(3)—C(19)—O(2)	122.3 (4)	122.4 (3)	C(19)—C(15)—C(22)	110.1 (3)	—
O(2)—C(19)—C(15)	122.3 (4)	124.3 (3)	C(9)—C(22)—C(23)	—	115.3 (3)
			C(9)—C(22)—C(15)	113.3 (4)	—

202 reflections with $|F| \leq \sigma(F)$ were recorded as zero ($-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $0 \leq l \leq 14$); in (2), 4172 reflections with $|F| \geq \sigma(F)$ were observed and 287 reflections had $|F| \leq \sigma(F)$ ($-25 \leq h \leq 25$, $0 \leq k \leq 9$, $0 \leq l \leq 19$). Lorentz-polarization corrections were carried out, but no absorption correction was applied to the intensity data. Both structures were solved by direct methods based on *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The positions of the H atoms were checked in a difference Fourier map and two solvent molecules were also found in complex (1). Positional and thermal parameters and scale factors were refined by the method of block-diagonal least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1.00$, with the program *HBLS* (Ashida, 1973) using 4922 reflections for (1) and 4459 for (2). Refinement of 32 (1), 31 (2) anisotropic non-H atoms and 26 (1), 24 (2) isotropic H atoms [393 (1), 376 (2) variables] was performed. After a few cycles, the refinement converged with $R = 0.033$, $wR = 0.035$, $S = 0.8936$

for (1) and $R = 0.034$, $wR = 0.034$, $S = 1.6487$ for (2). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). In the final least-squares cycle, $(\Delta/\sigma)_{\max}$ was 0.1060 for (1) and 0.4452 for (2). Max. and min. peaks in the difference Fourier map were 0.88 and $-0.50 \text{ e } \text{Å}^{-3}$ for (1), and 0.39 and -0.33 for (2). All calculations were carried out on a PC98/Vm microcomputer (NEC Co. Ltd) and a Titan graphics workstation (Kubota Inc.) at the Himeji Institute of Technology.

Discussion. Positional and thermal parameters for non-H atoms are given in Table 1.* Selected bond distances and angles for (1) and (2) are listed in Table 2. ORTEP (Johnson, 1976) drawings with

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55728 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0558]

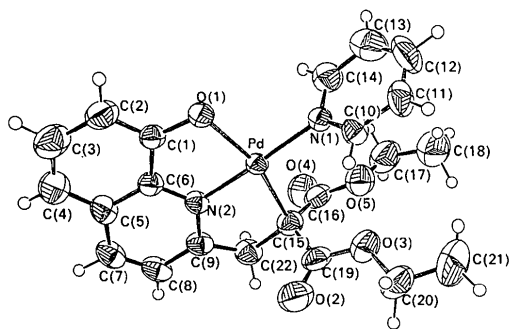


Fig. 1. An ORTEP drawing of (1) with anisotropic thermal ellipsoids.

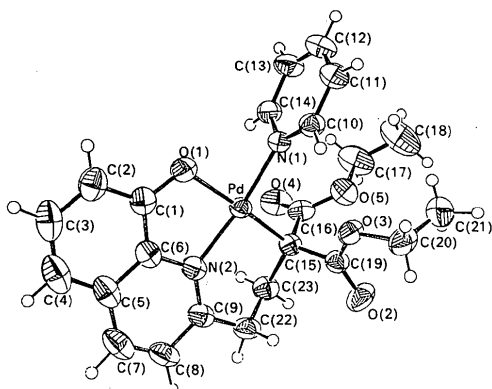


Fig. 2. An ORTEP drawing of (2) with anisotropic thermal ellipsoids.

anisotropic thermal ellipsoids are presented in Figs. 1 and 2.

Inspection of the two coordination geometries demonstrates the difference between the orientation and configuration of the functional groups in both complexes. The N(2)—Pd—O(1) angles are almost identical, whereas the N(2)—Pd—C(15) angle is larger in (2) than in (1) because of the presence of an additional atom [C(23)]. The Pd—C(15) distances [2.112 (4) for (1) and 2.074 (3) Å for (2)], are typical of Pd^{II}—C(*sp*³) bonds (Okeya *et al.*, 1976; Newkome *et al.*, 1981, 1982; DeGraaf *et al.*, 1989). Other bond lengths such as C—C, C—N, C—O in the pyridine, quinoline ring and ethoxycarbonyl groups agree well with those found in previous reports (Okeya *et al.*, 1976; Newkome *et al.*, 1981, 1982, 1990). Both (1) and (2) form planes composed of Pd, N(1), N(2), O(1) and C(15), each having very small deviations (0.06 Å). The plane composed of Pd, N(2), C(9), C(22), C(23) and C(15) was distorted with a maximum deviation of 0.42 (1) Å for C(23); the deviation of the corresponding plane in (1) was 0.13 (1) Å for the C(22) atom. This was caused by the presence of the additional C(23) atom, resulting in an increased N(2)—Pd—C(15)—C(23) dihedral angle in (2) of 22.7 (3)°, compared with the corresponding N(2)—Pd—C(15)—C(22) dihedral angle in (1) of 10.6 (2)°. Two solvent molecules were also found in (1), their intermolecular distances being 2.830 (8) and 2.841 (8) Å for O(101)⋯O(102) and O(102)⋯O(4), respectively. Their interactions can be considered as hydrogen bonds. In contrast, there are no solvent molecules associated with (2).

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