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An organopalladium(II) compound including enolate oxygen- and sp^3-carbon-bound 1,3-dimethylbarbiturate ligands: (1,2-diaminoethane)bis(1,3-dimethylbarbiturato)palladium(II) 5.5-hydrate

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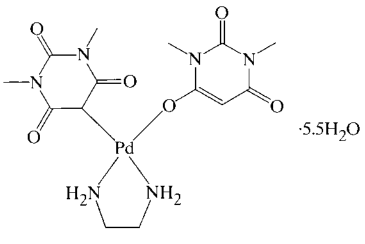
In the title compound, $[Pd(C_6H_7N_2O_3)_2(C_2H_8N_2)]\cdot 5.5H_2O$, the Pd atom is coordinated by two 1,3-dimethylbarbiturate anions through a deprotonated tetrahedral carbon and the enolate oxygen. The Pd—N bond length of 2.078 (2) Å *trans* to the C atom is shorter than the Pt—N distance of 2.098 (3) Å in the Pt analog.

Comment

By using a cyclic β-diketone, cyclohexane-1,3-dione (Hchdo) and 1,3-dimethylbarbituric acid (Hdmbarb), we have recently synthesized new organoplatinum(II) compounds. Among them, two linkage isomers of Pt(en)(dmbarb-*C*)(dmbarb-*O*)], (I′), and $[Pt(en)(dmbarb\text{-}C)_2]\cdot 2H_2O$, (II′), (en = 1,2-diaminoethane) have been found (Noguchi *et al.*, 2000); in aqueous solution, the monoalkyl (I′) has gradually rearranged to the dialkyl (II′). The palladium(II) compounds in the same group as the platinum(II) generally react much more rapidly. From an aqueous solution containing Hdmbarb and $[Pd(en)(OH)_2]$, replacing Pt^{II} with Pd^{II}, we have obtained only monoalkylpalladium(II) compound [Pt(en)(dmbarb-*C*)(dmbarb-*O*)]$\cdot 5.5H_2O$, (I).



(I)

The molecular structure of [Pd(en)(dmbarb–C)(dmbarb–O)] in (I) is similar to that of [Pt(en)(dmbarb-*C*)(dmbarb-*O*)] in (I′); the two independent dmbarb$^-$ anions as monodentate ligands coordinate to the Pd atom at the tetrahedral C15 atom and the enolate O24 atom. In spite of difference between Pd and Pt, the bond lengths and angles about the coordination centers in (I) and (I′) almost correspond with each other within their s.u.'s except for Pd—N1 and Pt—N1. The shorter Pd—N1 bond length of 2.078 (2) Å in (I) may be influenced more weakly by the tetrahedral C15 atom at the *trans* position, compared with the Pt—N1 of 2.098 (3) Å in (I'). In the palladium(II) barbiturate complex $[Pd(en)(\mu\text{-barb-}C,N)]_2\cdot 4H_2O$, (III), where barb is a barbiturate dianion, the Pd—N bond length of 2.070 (3) Å at the *trans* position of the C atom is quite comparable (Sinn *et al.*, 1978). The Pd—N1 in (I) and the Pt—N1 in (I′) are apparently longer than the Pd—N2 and Pt—N2 distances of 2.016 (2) and 2.015 (3) Å, respectively.

Both dmbarb$^-$ ligands are approximately planar within 0.027 Å, except the tetrahedral C15 atom with the deviation of 0.213 (4) Å from the least-squares plane of N11, C12, N13, C14 and C16. The moleuclar planes of the two dmbarb$^-$ ligands except C15, are almost parallel with the dihedral angle of 7.2 (1)° different from the Pt-analog (I′) with 40.7 (2)°, and are perpendicular to the Pd coordination plane with the dihedral angles of 89.44 (8) and 87.00 (7)° for the β-diketonato and the enolato dmbarb$^-$, respectively. The Pt—O24—C24=C25 torsion angle is 8.8 (4)°.

The water molecules included in (I) seem to make a remarkable difference between the structures of (I) and (I″). Water molecules in (I) occupy the intermolecular space to form a close hydrogen-bonded lattice together with the carbonyl O12, O14, O22 and O26 of the dmbarb$^-$ ligands and the amino N1 and N2 of the en (Table 2). The hydrogen bonds between the adjacent Pd complexes are found only between N2 and O16 in (I), while a two-dimensional hydrogen-bond network is formed between the adjacent Pt complexes in (I′). The water molecules seem to determine the orientations of the O-bonded enolato dmbarb$^-$.

Experimental

Hdmbarb (0.313 g, 2.00 mmol) dissolved in water (50 ml) was added to a 20 ml solution of $[Pd(en)(OH)_2]$, prepared by passing an aqueous solution of $[Pd(en)(ONO_2)_2]$ (0.291 g, 1.00 mmol) through a column packed with anion-exchange resin. The solution is evaporated to *ca* 40 ml keeping at *ca* 303 K. After standing for 4 d in the dark at 278 K, yellow needles crystallized (0.151 g, 26% yield). Analysis found: C 29.19, H 5.52, N 14.58%; calculated for $C_{14}H_{33}N_6O_{11.5}Pd$: C 29.20, H 5.78, N, 14.59%.

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Crystal data

$[Pd(C_6H_7N_2O_3)_2(C_2H_8N_2)]\cdot 5.5H_2O$
$M_r = 575.86$
Monoclinic, $C2/c$
$a = 24.225\ (3)$ Å
$b = 8.307\ (3)$ Å
$c = 25.396\ (2)$ Å
$\beta = 113.505\ (5)^\circ$
$V = 4686.4\ (15)$ Å^3
$Z = 8$
$D_x = 1.632$ Mg m^{-3}
$D_m = 1.67$ Mg m^{-3}
D_m measured by flotation in $CCl_4/CHBr_3$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 16.77–17.47^\circ$
$\mu = 0.859$ mm^{-1}
$T = 296\ (2)$ K
Needle, yellow
0.25 × 0.12 × 0.06 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6982 measured reflections
6837 independent reflections
4810 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\rm max} = 30.0^\circ$
$h = 0 \rightarrow 34$
$k = 0 \rightarrow 11$
$l = -35 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.080$
$S = 1.016$
6837 reflections
327 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 1.9140P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.46$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—N1	2.078 (2)	O14—C14	1.229 (3)
Pd—N2	2.016 (2)	O16—C16	1.219 (3)
Pd—C15	2.115 (3)	C24—C25	1.374 (4)
Pd—O24	2.042 (2)	C25—C26	1.402 (4)
C14—C15	1.457 (4)	O22—C22	1.229 (3)
C15—C16	1.461 (4)	O24—C24	1.275 (3)
O12—C12	1.218 (3)	O26—C26	1.246 (3)
N1—Pd—N2	83.91 (9)	Pd—O24—C24	120.8 (2)
N1—Pd—C15	174.09 (10)	O14—C14—C15	124.0 (3)
N1—Pd—O24	92.20 (9)	C14—C15—C16	118.0 (2)
N2—Pd—C15	90.31 (10)	O16—C16—C15	123.9 (2)
N2—Pd—O24	174.85 (8)	O24—C24—C25	126.7 (2)
C15—Pd—O24	93.65 (9)	C24—C25—C26	122.4 (2)
Pd—C15—C14	104.0 (2)	O26—C26—C25	125.3 (3)
Pd—C15—C16	105.6 (2)		
Pd—O24—C24—C25	8.8 (4)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O22$^{\rm i}$	0.79 (2)	2.01 (2)	2.793 (3)	172 (4)
O1—H12···O2	0.78 (2)	2.02 (3)	2.760 (4)	160 (4)
O2—H21···O26$^{\rm ii}$	0.81 (2)	1.95 (3)	2.727 (3)	159 (4)
O2—H22···O4$^{\rm iii}$	0.84 (2)	1.91 (2)	2.738 (4)	175 (4)
O3—H31···O2	0.88 (3)	1.88 (3)	2.758 (5)	177 (6)
O3—H32···O12$^{\rm iv}$	0.82 (3)	1.96 (3)	2.765 (3)	169 (6)
O4—H41···O3	0.85 (2)	1.78 (3)	2.628 (5)	173 (4)
O4—H42···O1$^{\rm v}$	0.80 (2)	1.94 (3)	2.727 (4)	169 (4)
O5—H51···O4	0.84 (2)	1.98 (3)	2.776 (4)	157 (4)
O5—H52···O14	0.81 (2)	2.01 (3)	2.810 (4)	169 (4)
O6—H61···O26	0.85 (2)	2.18 (3)	2.907 (3)	143 (4)
N1—H1···O1	0.90	2.24	3.065 (4)	152
N1—H2···O5$^{\rm vi}$	0.90	2.19	3.030 (4)	155
N2—H7···O16$^{\rm vii}$	0.90	2.11	2.863 (3)	141
N2—H8···O5	0.90	2.14	3.038 (4)	175

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $x, y-1, z$; (vi) $x, 1+y, z$; (vii) $1-x, y, \frac{3}{2}-z$.

All H atoms other than those on H_2O were included as riding models and the positions of the H atoms on H_2O were refined with O—H constrained at 0.82 (3) Å; $U_{\rm iso}(H) = 1.2U_{\rm eq}$(parent atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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