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Linkage isomerism of organoplatinum(II) compounds coordinated by two 1,3-dimethylbarbiturate anions

Kishie Noguchi, Takashi Tamura, Hidetaka Yuge* and Takeshi Ken Miyamoto

Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228-8555, Japan
Correspondence e-mail: yuge@kitasato-u.ac.jp

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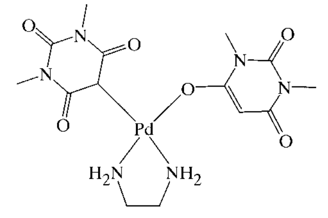
In two linkage isomers, bis[1,3-dimethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrionato]-C^5,O^4-(ethylenediamine-*N*,*N*′)platinum(II), $[Pt(C_6H_7N_2O_3)_2(C_2H_8N_2)]$, (I), and bis[1,3-dimethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrionato-C^5](ethylenediamine-*N*,*N*′)platinum(II) dihydrate, $[Pt(C_6H_7N_2O_3)_2(C_2H_8N_2)]\cdot 2H_2O$, (II), crystallized from the same aqueous solution containing $[Pt(en)(OH)_2]$ and 1,3-dimethylbarbituric acid (Hdmbarb) in a 1:2 molar ratio, a pair of monodentate dmbarb$^-$ anions coordinate to the Pt atom at tetrahedral C atoms for (II), while one dmbarb$^-$ anion coordinates at the carbon and the other at a deprotonated enol oxygen for (I). The Pt—C distances in (I) and (II) are comparable: 2.112 (4) Å for (I), and 2.114 (4) and 2.117 (4) Å for (II).

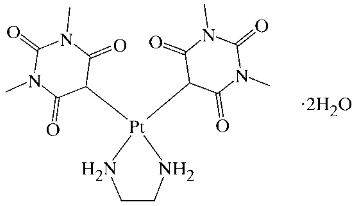
Comment

Some water-soluble palladium(II) and platinum(II) complexes involved with ambidentate *β*-diketonate are known as organometallic compounds, *e.g.* K[PtCl(acac-*C*)(acac-*O,O*′)] (Hacac = 2,4-pentanedione) (Mason *et al.*, 1969). By using a cyclic *β*-diketone, 1,3-cyclohexanedione (Hchdo), in place of ambidentate Hacac, we have recently reported the monoalkylplatinum(II) compound [Pt(en)(chdo-*C*)(chdo-*O*)]$\cdot 3H_2O$, (III) (en = 1,2-diaminoethane), crystallized from a solution containing a 1:2 molar ratio of $[Pt(en)(OH)_2]$ and Hchdo (Yuge & Miyamoto, 1999); two monodentate chdo$^-$ ligands are bound to the Pt coordination centre at a Csp^3 atom and at an enolate oxygen. No other compounds, such as the dialkyl, were obtained from the solution. The water-soluble dialkylplatinum(II) compound [Pt(en)(dmbarb-*C*)$_2$]$\cdot 2H_2O$, (II), was isolated *via* [Pt(en)(dmbarb-*C*)(dmbarb-*O*)], (I), replacing Hchdo with 1,3-dimethylbarbituric acid (Hdmbarb) as another potential monodentate ligand.

As shown in Figs. 1 and 2, the Pt complexes of (I) and (II) are found to be linkage isomers; two crystallographically independent dmbarb$^-$ anions coordinate to the Pt atom as monodentate ligands. In (I), one of the dmbarb$^-$ anions is bound at C15 and the other at O24 of the deprotonated enol, similar to the chdo$^-$ anions in (III). On the contrary, in (II), both dmbarb$^-$ anions coordinate to the Pt atom at C15 and C25. The C-bound *β*-diketonate and O-bound enolate forms of the dmba$^-$ anions were confirmed by the bond lengths and angles. The angles about the donor C atoms are almost



(I)



(II)

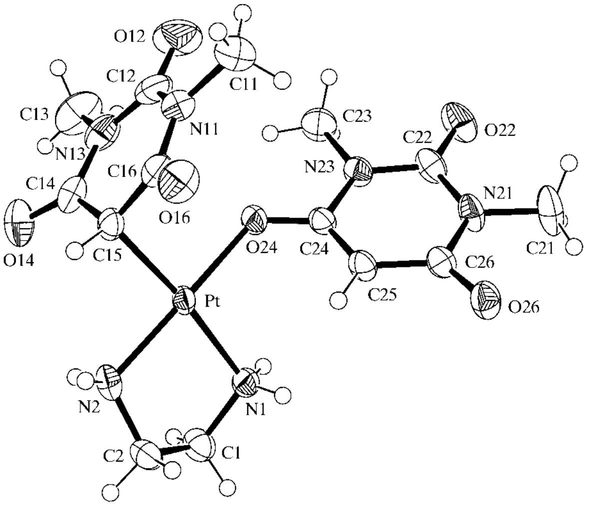


Figure 1
The asymmetric unit of [Pt(en)(dmbarb-*C*)(dmbarb-*O*)], (I), showing displacement ellipsoids at the 50% probability level.

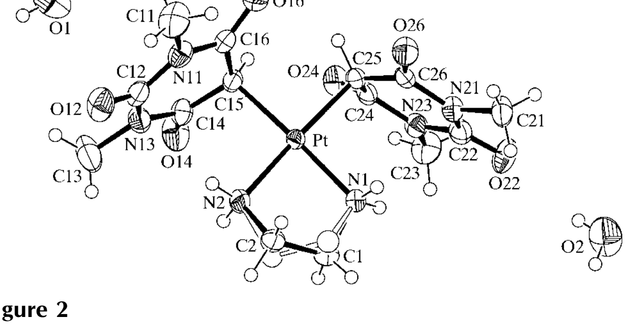


Figure 2
The asymmetric unit of [Pt(en)(dmbarb-*C*)$_2$]$\cdot 2H_2O$, (II), showing displacement ellipsoids at the 50% probability level. One disordered conformer of the en ligand is drawn with open circles and bonds.

tetrahedral: 103.4 (3), 107.2 (3) and 117.1 (4)° for C15 in (I); 109.5 (3), 105.3 (3) and 115.9 (4)° for C15 in (II); and 104.8 (3), 109.9 (3) and 116.8 (4)° for C25 in (II). In (I), the enol O24—C24 bond length of 1.275 (5) Å is apparently longer than the carbonyl bond lengths O22=C22 of 1.231 (5) Å and O26=C26 of 1.245 (5) Å. The Pt—C bond lengths, 2.112 (4) Å for (I), and 2.114 (4) and 2.117 (4) Å for (II), are comparable with that of 2.123 (4) Å in (III). Due to the *trans* influence of the Csp^3 atoms, the Pt—N bond lengths *trans* to Pt—C, 2.098 (3) Å for (I), and 2.087 (3) and 2.098 (3) Å for (II), are longer than that *trans* to Pt—O in (I), 2.015 (3) Å, as observed in (III) [2.070 (3) and 2.025 (3) Å]. The dmbarb$^-$ ligands in both compounds are approximately planar within 0.04 Å, except for the Csp^3 atoms, C15 in (I) and C15 and C25 in (II), with respective deviations of 0.288 (6), 0.309 (6) and 0.242 (6) Å from the least-square planes. Ignoring the Csp^3 atoms from the molecular planes of the dmbarb$^-$ ligands, the C-bound ligands are almost perpendicular to the Pt coordination planes with dihedral angles of 88.8 (1)° for (I), and 85.5 (1) and 84.9 (1)° for (II); the angle for the O-bound ligand in (I), is 59.5 (1)°. In (I), the two-dimensional hydrogen-bond network is formed along the *bc* plane by the amino N1 and N2 atoms of the en chelate and the carbonyl O16, O22 and O26 atoms of the dmbarb$^-$ ligands (Table 2), while the closer three-dimensional framework in (II) is built up by the amino groups, the carbonyl groups and water molecules (Table 4).

The ^{1}H and ^{13}C NMR spectra of (I) and (II) in D_2O solutions show that the molecular structures are consistent with those in the solid state, and that (I) changes into (II) after two weeks at room temperature. No changes were found in the spectrum of (II) for up to a month afterwards. Accordingly, the dialkylplatinum(II) compound (II) should be a thermodynamically stable species in aqueous solution compared with the monoalkyl compound (I).

Experimental

Each isomer was isolated by the following procedure: an aqueous solution of Hdmbarb (0.937 g, 6.001 mmol) was added to the yellow eluate containing [Pt(en)$(OH)_2$], prepared from [Pt(en)$(ONO_2)_2$] (1.135 g, 2.993 mmol). After rotoevaporation to 30 ml the solution was allowed to stand at 278 K for 2 d to form pale-yellow crystals of (I) (0.600 g, 35% yield). Analysis found: C 29.34, H 4.00, N 14.82%; calculated for $C_{14}H_{22}N_6O_6Pt$: C 29.74, H 3.92, N 14.86%. ^{1}H NMR (0.01 mol dm^{-3} in D_2O, 300 MHz, p.p.m.): δ 5.66 (*s*, 1H, CH), 4.40 (*s*, 1H, CH), 3.08 (*s*, 3H, CH_3), 2.99 (*s*, 3H, CH_3), 2.92 (*s*, 6H, CH_3), 2.49 (*m*, 4H, CH_2); ^{13}C{^{1}H} NMR (75.5 MHz, p.p.m.): δ 176.33 (C14, C16), 167.12 (C26), 165.73 (C24), 153.96, 153.23 (C12, C22), 80.07 (C25), 49.39, 45.49 (C1, C2), 47.20 (C15), 27.67, 27.63, 27.53, 26.34 (C11, C13, C21, C23). Another aqueous solution of [Pt(en)$(OH)_2$] prepared from [Pt(en)$(ONO_2)_2$] (0.379 g, 0.999 mmol) was rotoevaporated to 10 ml, and was added to 10 ml of an aqueous solution of Hdmbarb (0.312 g, 1.998 mmol). After standing at room temperature for 14 d, yellow crystals of (II) were obtained (0.336 g, 56% yield). Analysis found: C 27.84, H 4.34, N 14.04%; calculated for $C_{14}H_{26}N_6O_8Pt$: C 27.96, H 4.36, N 13.97%. ^{1}H NMR (0.01 mol dm^{-3} in D_2O, 300 MHz, p.p.m.): δ 4.13 (*s*, 2H, CH), 3.07 (*s*, 12H, CH_3), 2.43 (*s*, 4H, CH_2); ^{13}C{^{1}H} NMR (75.5 MHz, p.p.m.): δ 176.80 (C14, C16, C24, C26), 154.17 (C12, C22), 47.21 (C1, C2, C15, C25), 27.69 (C11, C13, C21, C23).

Compound (I) is more soluble in H_2O than (II): up to 0.015 mol dm^{-3} for (I) and less than 0.01 mol dm^{-3} for (II) at room temperature. Both compounds were air stable in the solid state, but (I) dissolved in H_2O changed into (II) over a period of two weeks. It was difficult to recrystallize (I) from H_2O because of the contamination of (II), while (II) could be recrystallized from H_2O.

Compound (I)

Crystal data

$[Pt(C_6H_7N_2O_3)_2(C_2H_8N_2)]$
M_r = 565.47
Triclinic, $P\overline{1}$
a = 9.505 (2) Å
b = 11.2518 (9) Å
c = 9.464 (2) Å
α = 103.10 (1)°
β = 110.52 (1)°
γ = 87.93 (1)°
V = 922.2 (2) Å^3
Z = 2
D_x = 2.036 Mg m^{-3}
D_m = 2.04 Mg m^{-3}
D_m measured by flotation in CCl_4/$CHBr_3$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 16.91–17.50°
μ = 7.653 mm^{-1}
T = 296 (2) K
Thin plate, pale yellow
0.20 × 0.10 × 0.07 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.294, $T_{\rm max}$ = 0.585
5685 measured reflections
5383 independent reflections
4663 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.029
$\theta_{\rm max}$ = 30°
$h = -13 \rightarrow 0$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.061
S = 1.028
5383 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.5877P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 1.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.14 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 2.3 (2) × 10^{-3}

Table 1

Selected geometric parameters (Å, °) for (I).

Pt—N1	2.098 (3)	O14—C14	1.222 (5)
Pt—N2	2.015 (3)	O16—C16	1.227 (5)
Pt—C15	2.112 (4)	C24—C25	1.368 (5)
Pt—O24	2.041 (3)	C25—C26	1.413 (5)
C14—C15	1.464 (6)	O22—C22	1.231 (5)
C15—C16	1.460 (6)	O24—C24	1.275 (5)
O12—C12	1.212 (6)	O26—C26	1.245 (5)
N1—Pt—N2	83.2 (1)	Pt—O24—C24	125.1 (3)
N1—Pt—C15	173.2 (1)	O14—C14—C15	124.0 (5)
N1—Pt—O24	94.8 (1)	C14—C15—C16	117.1 (4)
N2—Pt—C15	90.4 (1)	O16—C16—C15	123.2 (4)
N2—Pt—O24	172.6 (1)	O24—C24—C25	127.1 (4)
C15—Pt—O24	91.9 (1)	C24—C25—C26	121.7 (4)
Pt—C15—C14	103.4 (3)	O26—C26—C25	125.8 (4)
Pt—C15—C16	107.2 (3)		
Pt—O24—C24—C25	−16.4 (6)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O22^{i}	0.90	2.06	2.958 (5)	172
N1—H2$\cdots$O16^{ii}	0.90	2.17	2.939 (5)	142
N2—H7$\cdots$O26^{ii}	0.90	2.11	2.998 (5)	167
N2—H8$\cdots$O26^{iii}	0.90	2.02	2.893 (4)	163

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, z-1$.

Compound (II)

Crystal data

$[Pt(C_6H_7N_2O_3)_2(C_2H_8N_2)]\cdot 2H_2O$
$M_r = 601.50$
Monoclinic, $P2_1/c$
$a = 12.840$ (2) Å
$b = 10.7834$ (9) Å
$c = 14.727$ (2) Å
$\beta = 107.051$ (9)°
$V = 1949.5$ (4) Å^3
$Z = 4$
$D_x = 2.049$ Mg m^{-3}
$D_m = 2.04$ Mg m^{-3}

D_m measured by flotation in $CCl_4/CHBr_3$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 19.09$–$19.90°$
$\mu = 7.254$ mm^{-1}
$T = 296$ (2) K
Prism, yellow
0.16 × 0.16 × 0.07 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.390$, $T_{max} = 0.631$
5892 measured reflections
5664 independent reflections
4415 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$
$\theta_{max} = 30°$
$h = 0 \rightarrow 18$
$k = -15 \rightarrow 0$
$l = -20 \rightarrow 19$
3 standard reflections every 150 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.065$
$S = 1.016$
5664 reflections
284 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.6000P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 9.2 (9) × 10^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Pt—N1	2.087 (3)	O14—C14	1.225 (5)
Pt—N2	2.098 (3)	O16—C16	1.230 (5)
Pt—C15	2.114 (4)	C24—C25	1.467 (6)
Pt—C25	2.117 (4)	C25—C26	1.460 (6)
C14—C15	1.462 (6)	O22—C22	1.212 (5)
C15—C16	1.470 (6)	O24—C24	1.226 (5)
O12—C12	1.214 (5)	O26—C26	1.232 (5)
N1—Pt—N2	81.7 (1)	Pt—C25—C24	104.8 (3)
N1—Pt—C15	177.0 (1)	Pt—C25—C26	109.9 (3)
N1—Pt—C25	95.2 (1)	O14—C14—C15	124.1 (4)
N2—Pt—C15	96.9 (1)	C14—C15—C16	115.9 (4)
N2—Pt—C25	175.6 (1)	O16—C16—C15	124.3 (4)
C15—Pt—C25	86.4 (2)	O24—C24—C25	124.0 (4)
Pt—C15—C14	109.5 (3)	C24—C25—C26	116.8 (4)
Pt—C15—C16	105.3 (3)	O26—C26—C25	123.3 (4)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O16^{i}	0.90	2.29	3.005 (5)	136
N1—H2$\cdots$O26^{ii}	0.90	2.08	2.969 (5)	169
N2—H7$\cdots$O12^{iii}	0.90	2.20	2.915 (5)	136
N2—H8$\cdots$O1^{i}	0.90	2.11	2.923 (6)	149
O1—H11$\cdots$O2^{iv}	0.83 (3)	2.06 (4)	2.837 (7)	154 (7)
O1—H12$\cdots$O14^{v}	0.83 (3)	2.03 (3)	2.840 (6)	165 (7)
O2—H21$\cdots$O22	0.82 (3)	2.31 (5)	3.040 (6)	149 (7)
O2—H22$\cdots$O24^{vi}	0.84 (3)	1.99 (3)	2.819 (5)	171 (7)

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

For both compounds, H atoms other than those on H_2O were included as riding models and the positions of the H atoms on H_2O in (II) were refined with O—H restrained at 0.82 (3) Å; $U_{iso}(H) = 1.2U_{eq}$(parent atom). The site-occupancy parameters of the disordered ethylene chains in (II) were refined to 0.84 (1) for C1 and C2, and 0.16 (1) for C10 and C20.

For both compounds, 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); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1096). Services for accessing these data are described at the back of the journal.

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