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Bis(cyclohexane-1,3-dionato)-C^2,O^1-(ethylenediamine-N,N')platinum(II) trihydrate and bis(cyclohexane-1,3-dionato)-C^2,O^1-(N,N-dimethylethylenediamine-N,N')-platinum(II)

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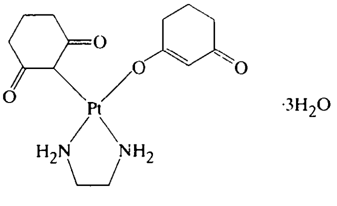
Abstract

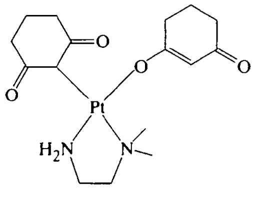
In each of the title organoplatinum(II) compounds, $[Pt(C_6H_7O_2)_2(C_2H_8N_2)]\cdot 3H_2O$, (1), and $[Pt(C_6H_7O_2)_2(C_4H_{12}N_2)]$, (2), one 1,3-cyclohexanedionate monoanion is bound to the Pt atom at the Csp^3 atom and the other is bound at the enolate O atom. The Pt—C bond lengths in (1) and (2) are 2.123 (4) and 2.108 (5) Å, respectively. The shorter Pt—C distance in (2) may be due to a *trans* influence of the NMe_2 moiety of the *N*,*N*-dimethylethylenediamine ligand.

Comment

The reactions of bis(acetylacetonato)platinum(II) compounds with certain bases in organic solvents have been investigated previously. By means of vibrational and NMR spectroscopy, the acetylacetonate anions in the products were found to be an *O*,*O'*-bonded chelate or a central-*C*-bonded form (Ito *et al.*, 1976). We have recently reported the structure of [Pt(*trans*-1*R*,2*R*-dach)(acac-*O*,*O'*)](acac) (dach is diaminocyclohexane and Hacac is acetylacetone), crystallized from an aqueous solution containing a 1:2 ratio of [Pt(*trans*-1*R*,2*R*-dach)$(OH)_2$] and Hacac (Yuge & Miyamoto, 1997). By using 1,3-cyclohexanedione (Hchdo) in place of Hacac to be a potential monodentate ligand, the title compounds, (1) and (2), have been synthesized and their crystal structures are reported here.



(1)



(2)

In (1) and (2), two independent chdo$^-$ anions behave as monodentate ligands in different ways (Figs. 1 and 2); one coordinates to the Pt atom at the 2-C atom and the other is bound at the O atom as an enolate with a *Z* conformation. The donor C atoms of the former appear to be sp^3 hydridized because of their nearly tetrahedral environment. In the latter, the enolate O21—C21 bond lengths of 1.290 (4) Å in (1) and 1.290 (6) Å in (2) are apparently longer than the carbonyl O23=C23 of 1.256 (5) Å in (1) and 1.243 (7) Å in (2). The Pt—O21—C21=C22 torsion angles and the dihedral angles between the enolate ligands and the square planes about the Pt atoms are −10.2 (6) and 63.3 (2)° in (1), and −6.2 (8) and 88.2 (3)° in (2).

The coordination geometry about the Pt atom is similar to that of [Pt*L*(asc-C^2,O^5)]$\cdot 3H_2O$, (3) and (4) (*L* is *cis*- and *trans*-1*R*,2*R*-dach, and asc^{2-} is the L-ascorbate dianion; Hollis *et al.*, 1985; Yuge & Miyamoto, 1996), where the Pt atom is coordinated by a chelating diamine and by the asc^{2-} anion at the O and C atoms. The

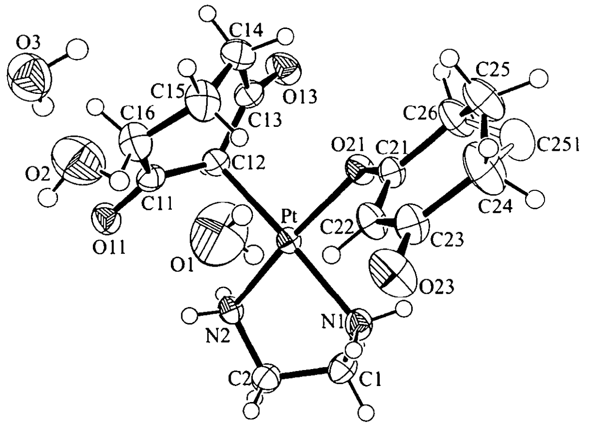


Fig. 1. The asymmetric unit of (1), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. One disordered conformer of the enolate chdo$^-$ ligand is drawn with an open ellipsoid and bonds. H atoms are shown as spheres of arbitrary radii.

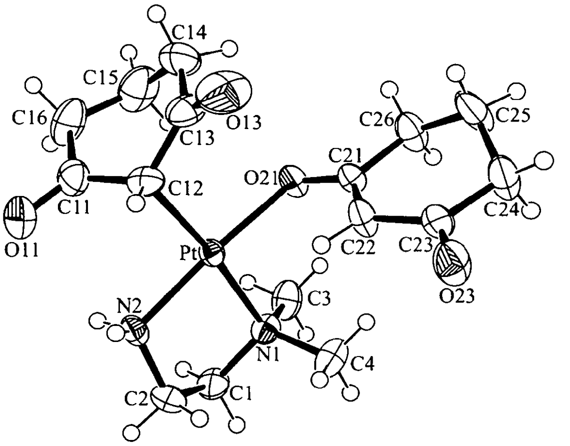


Fig. 2. The molecule of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

bond lengths about the Pt atoms in the four complexes are also comparable. In (1) and (2), the fact that the Pt—N1 bond lengths are longer than the Pt—N2 bond lengths suggests the influence of the C12 atoms at the *trans* positions, as observed in (3) and (4); the Pt—N1 and Pt—N2 bond lengths are 2.070 (3) and 2.025 (3) Å in (1), 2.124 (5) and 2.019 (5) Å in (2), 2.100 (6) and 2.047 (8) Å in (3), and 2.093 (5) and 2.033 (5) Å in (4), respectively. The steric repulsion of the methyl groups of the dmen ligand (dmen is *N*,*N*-dimethylethylenediamine) in (2) may give rise to the slightly longer Pt—N1 [2.124 (5) Å] and the shorter Pt—C12 [2.108 (5) Å] distances.

In (1), the [Pt(en)(chdo)$_2$] molecule is surrounded by three crystallographically independent water molecules (Fig. 3), which form a two-dimensional hydrogen-bond network with the carbonyl O11, O13 and O23 atoms of the chdo$^-$ anions and with the amino N1 and N2 atoms of the en ligand (en is ethylenediamine) (Table 2), while a one-dimensional hydrogen-bonding chain is formed with the carbonyl O23 and amino N2 atoms along the *c* axis in (2) (Table 4).

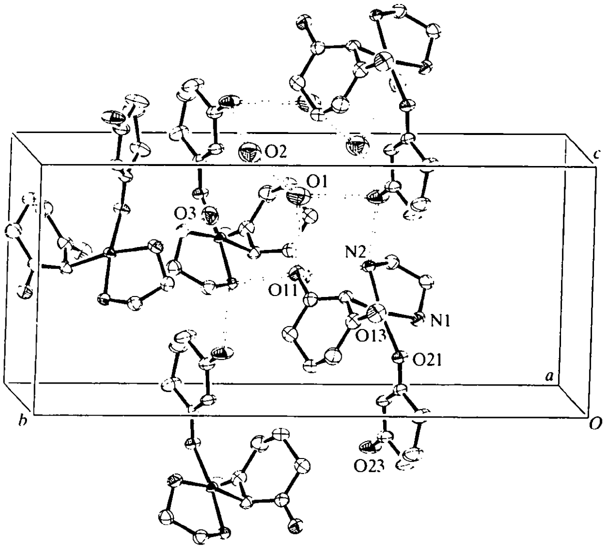


Fig. 3. The packing diagram of (1), showing the hydrogen-bond network with dashed lines. H and disordered C atoms have been omitted for clarity.

The ^1H and ^{13}C NMR spectra of (1) in D_2O are consistent with the molecular structure in the crystalline state. The spectra of (2) in D_2O are very similar to those of (1), aside from signals due to the methyl groups of the dmen ligand. Any signals of other possible isomers were not found in the spectra of the mother solutions of (1) and (2). Accordingly, no compounds involving two or more Pt—C bonds would be formed, and the Pt—C bond in (2) would be selectively formed at the *trans* position of the dimethylamino group.

Experimental

For (1), Hchdo (0.225 g, 2.01 mmol) dissolved in water (10 ml) was added to a solution (100 ml) of [Pt(en)(OH)$_2$], prepared by passing an aqueous solution of [Pt(en)(ONO$_2$)$_2$] (0.381 g, 1.00 mmol) through a column packed with anion-exchange resin. After standing overnight at room temperature, rotary evaporation to *ca* 5 ml followed by addition of acetone (20 ml) gave a pale-yellow precipitate of (1) (0.339 g, 64% yield). Analysis found: C 31.39, H 5.21, N 5.23%; calculated for $C_{14}H_{28}N_2O_7Pt$: C 31.64, H 5.31, N 5.27%; ^1H NMR (D_2O, 300 MHz, δ p.p.m.): 4.21, 6.00 (2*s*, 2H, CH), 1.7–2.6 (*m*, 16H, CH$_2$); $^{13}C\{^1H\}$ NMR (D_2O, 75.5 MHz, δ p.p.m.): 217.2 (2C, C═O), 202.8 (C═O), 196.0 (C—O), 104.7 (CH), 49.5, 48.8 [2C, CH_2(en)], 46.3 (CH), 36.6 [2C, CH_2(chdo$^-$)], 34.7, 33.9, 21.2, 18.1 [4C, CH_2(chdo$^-$)]. For (2), an aqueous solution (5 ml) containing Hchdo (0.228 g, 2.03 mmol) and [Pt(dmen)(ONO_2)$_2$] (0.407 g, 1.00 mmol) was treated with a 1,4-dioxane/acetonitrile (1:1 *v*/*v*) mixture (20 ml) to obtain (2) (0.192 g, 38% yield). Analysis found: C 37.70, H 5.11, N 5.55%; calculated for $C_{16}H_{26}N_2O_4Pt$: C 38.02, H 5.18, N 5.54%; ^{1}H NMR (D_2O, 300 MHz, δ p.p.m.): 4.21, 6.00 (2*s*, 2H, CH), 1.7–2.6 (*m*, 16H, CH_2); $^{13}C\{^1H\}$ NMR (D_2O, 75.5 MHz, δ p.p.m.): 217.7 (2C, C=O), 202.8 (C=O), 194.7 (C—O), 105.7 (CH), 66.1 (2C, CH_3) 50.7, 45.0 [2C, CH_2(en)], 46.1 (CH), 36.7 [2C, CH_2(chdo$^-$)], 34.7, 33.9, 21.1, 18.3 [4C, CH_2(chdo$^-$)]. Both compounds were recrystallized from water. In the solid state, the isolated compounds were fairly stable for months, even in air, and no changes in the NMR spectra of either compound were observed over a period of at least a week, whereas the yellow aqueous solutions turned brown in a few months.

Compound (1)

Crystal data

[Pt($C_6H_7O_2$)$_2$($C_2H_8N_2$)]·3H_2O
$M_r = 531.47$
Monoclinic
$P2_1/a$
$a = 9.152\,(1)$ Å
$b = 20.886\,(1)$ Å
$c = 9.555\,(1)$ Å
$\beta = 97.57\,(1)^\circ$
$V = 1810.4\,(4)$ Å^3
$Z = 4$
$D_x = 1.950$ Mg m^{-3}
$D_m = 1.96$ Mg m^{-3}
D_m measured by flotation in CCl_4/$CHBr_3$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 16.7$–18.6°
$\mu = 7.787$ mm^{-1}
$T = 296\,(2)$ K
Rhombic plate
0.32 × 0.14 × 0.10 mm
Pale yellow

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.171$, $T_{\max} = 0.459$
5587 measured reflections
5285 independent reflections
4283 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\max} = 30^\circ$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 29$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.058$
$S = 1.037$
5285 reflections
246 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -1.07$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0015 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Pt—N1	2.070 (3)	C11—C12	1.470 (5)
Pt—N2	2.025 (3)	C12—C13	1.474 (5)
Pt—C12	2.123 (4)	O21—C21	1.290 (4)
Pt—O21	2.034 (3)	O23—C23	1.256 (5)
O11—C11	1.240 (4)	C21—C22	1.374 (5)
O13—C13	1.235 (5)	C22—C23	1.407 (5)
C12—Pt—N1	171.2 (1)	Pt—O21—C21	125.0 (2)
C12—Pt—N2	90.0 (1)	O11—C11—C12	122.0 (4)
C12—Pt—O21	93.5 (1)	O13—C13—C12	120.7 (4)
O21—Pt—N1	92.7 (1)	C11—C12—C13	117.1 (3)
O21—Pt—N2	173.3 (1)	O21—C21—C22	125.4 (3)
N1—Pt—N2	83.2 (1)	O23—C23—C22	123.8 (4)
Pt—C12—C11	104.5 (2)	C21—C22—C23	123.2 (4)
Pt—C12—C13	107.1 (2)		
Pt—O21—C21—C22	−10.2 (6)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3$^{\rm i}$	0.90	2.13	3.014 (5)	169
N1—H2···O3$^{\rm ii}$	0.90	2.25	3.042 (5)	147
N2—H7···O11$^{\rm iii}$	0.90	2.10	2.940 (4)	154
N2—H8···O23$^{\rm iv}$	0.90	2.02	2.899 (4)	165
O2—H26···O1	0.81 (3)	1.99 (3)	2.800 (7)	176 (7)
O3—H27···O2	0.82 (3)	1.94 (3)	2.756 (6)	175 (5)
O1—H23···O23	0.81 (3)	2.29 (5)	2.996 (6)	145 (7)
O1—H24···O11$^{\rm v}$	0.81 (3)	2.07 (3)	2.872 (5)	170 (8)
O2—H25···O23$^{\rm ii}$	0.81 (3)	2.02 (3)	2.817 (5)	170 (7)
O3—H28···O13$^{\rm vi}$	0.81 (3)	1.98 (3)	2.786 (5)	170 (6)

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

Compound (2)

Crystal data

[Pt($C_6H_7O_2$)$_2$($C_4H_{12}N_2$)]
$M_r = 505.48$
Orthorhombic
$P2_12_12_1$
$a = 12.630\,(3)$ Å
$b = 14.938\,(3)$ Å
$c = 9.276\,(1)$ Å
$V = 1750.0\,(5)$ Å^3
$Z = 4$
$D_x = 1.919$ Mg m^{-3}
$D_m = 1.91$ Mg m^{-3}
D_m measured by flotation in CCl_4/$CHBr_3$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.6$–19.2°
$\mu = 8.039$ mm^{-1}
$T = 296\,(2)$ K
Rhombic plate
0.25 × 0.10 × 0.10 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.213$, $T_{\max} = 0.448$
5478 measured reflections
2884 independent reflections (plus 2220 Friedel-related reflections)

4715 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 30^\circ$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 21$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.068$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}

$S = 1.021$
5104 reflections
208 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 0.0057P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.040 (12)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Pt—N1	2.124 (5)	C11—C12	1.487 (10)
Pt—N2	2.019 (5)	C12—C13	1.467 (9)
Pt—C12	2.108 (5)	O21—C21	1.290 (6)
Pt—O21	2.058 (4)	O23—C23	1.243 (7)
O11—C11	1.222 (8)	C21—C22	1.375 (8)
O13—C13	1.220 (8)	C22—C23	1.436 (8)
C12—Pt—N1	173.7 (2)	Pt—O21—C21	120.5 (3)
C12—Pt—N2	89.8 (2)	O11—C11—C12	122.5 (7)
C12—Pt—O21	94.6 (2)	O13—C13—C12	122.3 (7)
O21—Pt—N1	91.5 (2)	C11—C12—C13	115.1 (6)
O21—Pt—N2	175.4 (2)	O21—C21—C22	124.2 (5)
N1—Pt—N2	84.1 (2)	O23—C23—C22	123.1 (6)
Pt—C12—C13	109.5 (4)	C21—C22—C23	123.2 (6)
Pt—C12—C11	104.5 (4)		
Pt—O21—C21—C22	−6.2 (8)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H5···O23^{i}	0.90	2.16	2.985 (7)	152
N2—H6···O23^{ii}	0.90	2.20	3.046 (7)	157

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

For both compounds, all H atoms other than those of water were included as riding and the positions of the water H atoms in (1) were refined with O—H constrained to 0.82 (3) Å; $U_{iso}(H) = 1.2U_{eq}$(parent atom). A disordered conformation was observed in (1) for the enolate chdo$^-$ and the site-occupancy factors of C25 and C251 were refined to 0.65 (2) and 0.35 (2), respectively. Each member of the Friedel pairs in (2) was treated as an independent observation in the least-squares refinement.

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* (Molecular Structure Corporation, 1993*b*); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

The authors thank Mr Takahiro Kishi for his help in the preparative work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1013). Services for accessing these data are described at the back of the journal.

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Sodium hydrogen *trans*-glutaconate and ammonium hydrogen *trans*-glutaconate

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Abstract

Sodium hydrogen *trans*-glutaconate (sodium hydrogen *trans*-pent-2-ene-1,5-dioate, $Na^+\cdot C_5H_5O_4^-$), (I), crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, and ammonium hydrogen *trans*-glutaconate (ammonium hydrogen *trans*-pent-2-ene-1,5-dioate, $NH_4^+\cdot C_5H_5O_4^-$), (II), crystallizes in the orthorhombic space group *Ibam* with $Z = 8$. In both crystals, a non-centrosymmetric O—H···O hydrogen bond is formed between the carboxyl and carboxylate groups of neighboring anions. The Na^+ cation in (I) is coordinated by six O atoms. There are two symmetry-independent NH_4^+ cations in (II). The number of hydrogen bonds around each NH_4^+ cation is four.

Comment

The crystal structures of the title compounds, sodium hydrogen *trans*-glutaconate, (I), and ammonium hydrogen *trans*-glutaconate, (II), have been determined as part of a detailed investigation of H-atom bonding behavior in short asymmetric O—H···O hydrogen bonds in

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