Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

cis-Bis(3,6-dihydro-2*H*-1,2-oxazine-*N*)diiodoplatinum(II) and *cis*-bis(3,4,5,6-tetrahydro-2*H*-1,2-oxazine-*N*)diiodoplatinum(II)

Jennifer A. Saltmarsh *et al.*

Electronic paper
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Jennifer A. Saltmarsh, Bob A. Howell and Philip J. Squattrito*

Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA
Correspondence e-mail: p.squattrito@cmich.edu

Received 19 June 2000
Accepted 10 July 2000

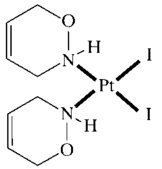
Data validation number: IUC0000191

The title complexes, [Pt($C_4H_7NO)_2I_2$], (I), and [Pt($C_4H_9NO)_2I_2$], (II), possess similar square-planar coordination geometries with modest distortions from ideality. For (I), the *cis*-*L*—Pt—*L* angles are in the range 87.0 (4)–94.2 (3)°, while the *trans* angles are 174.4 (3) and 176.4 (3)°. For (II), *cis*-*L*—Pt—*L* are 86.1 (8)–94.2 (6)° and *trans*-*L*—Pt—*L* are 174.4 (6) and 177.4 (5)°. One 3,6-dihydro-2*H*-1,2-oxazine ligand in (I) is rotated so that the N—O bond is out of the square plane by approximately 70°, while the N—C bond is only *ca* 20° out of the plane. The other oxazine ligand is rotated so that the N—C bond is about 80° out of the plane, while the N—O bond is out of the plane by approximately 24°. In (II), the 3,4,5,6-tetrahydro-2*H*-1,2-oxazine ligands are also positioned with one having the N—O bond further out of the plane and the other having the N—C bond positioned in that fashion. Both ligands, however, are rotated approximately 90° compared with their positions in (I). In both complexes, this results in an unsymmetrical distortion of the I—Pt—N bond angles in which one is expanded and the other contracted. These features are compared to those of reported *cis*-diaminediiodoplatinum(II) complexes.

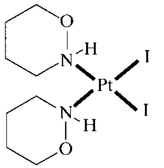
Comment

As part of a continuing study of potential chemotherapeutic alternatives to cisplatin and carboplatin (Lippard, 1982; Rosenberg, 1985), we have been examining the use of 1,2-oxazines as the *cis*-amine ligands in these platinum complexes (Dyksterhouse *et al.*, 2000). Compounds (I) and (II) were obtained as intermediate products in an as yet unsuccessful effort to prepare *cis*-bis(1,2-oxazine)-1,1-cyclobutanedicarboxylatoplatinum(II). They are part of a small family of *cis*-diaminediiodoplatinum(II) complexes that have been structurally characterized. The Pt coordination geometry (Table 1) shows modest distortions from the square-planar ideal. All *cis* angles are within 4° of 90°, while the *trans* angles differ by 6 and 4° from 180°. The mean deviation from the PtI_2N_2 least-squares plane is 0.028 (5) Å, though only N2 is displaced by more than two s.u.'s, −0.17 (1) Å. The Pt—I and Pt—N distances are consistent with those seen in similar complexes (Raudaschl-Sieber *et al.*, 1986; Oksanen *et al.*, 1989; Zimmerman *et al.*, 1999). The 3,6-dihydro-2*H*-1,2-oxazine ligands in (I) are bulkier than those found in the reported complexes, leading to an irregular distortion in the ligand bond angles not seen in the others. In *cis*-diamminediiodoplatinum(II) (*N*,*N*-dimethylacetamide solvate) (Raudaschl-Sieber *et al.*, 1986), the I—Pt—I angle is approximately 93°, while the I—Pt—N and N—Pt—N angles are all about 89°, which is attributed to the large size of the I atoms. An essentially identical pattern is found in *cis*-diiodobis(2-hydroxyethylamine)platinum(II) (Zimmerman *et al.*, 1999). In *cis*-bis(cyclopropylamine)diiodoplatinum(II) (Oksanen *et al.*, 1989), the I—Pt—I angle is about 94°, the I—Pt—N angles are 86 and 88°, and the N—Pt—N angle is nearly 93°. The opening of the N—Pt—N angle and closing of the I—Pt—N angles occurs presumably to avoid non-bonded contacts between the cyclopropyl groups. In (I), the expansion and contraction of the bond angles is lopsided: N2—Pt—I1 is 87.6 (3)°, while N1—Pt—I2 is 94.0 (3)°, and N1—Pt—N2 is actually smaller [87.2 (4)°] than in any of the other *cis*-amine complexes. This distortion is consistent with the rotations of the oxazine groups with respect to the ligand plane. The N2 ring is twisted so that C8 is nearly perpendicular to the plane [torsion angle I1—Pt—N2—C8 −83.1 (8)°], thus minimizing contacts with I1, allowing for a smaller bond angle. To avoid unfavorable contacts with the N2 ring, the N1 ring is rotated so that O1 is out of the plane [torsion angle I2—Pt—N1—O1 107.9 (6)°] and C4 is directed away from the other ring. This conformation, however, places C4 in closer contact with I2 [torsion angle I2—Pt—N1—C4 −20.8 (9)°] which apparently results in the larger I—Pt—N angle. Both oxazine rings are in cyclohexene-like conformations with normal bond distances and angles. The absolute configurations at N are opposite for the two rings. The coordination environment for (II) (Table 2) is similar to that in (I). The average deviation from the PtI_2N_2 least-squares plane is 0.030 (8) Å with both N atoms displaced above the plane by significant amounts [0.089 (19) Å for N1 and 0.058 (17) Å for N2]. As in (I), the *trans* bond angles differ from 180° by roughly 6 and 4°. Also, the *cis* bond angles show the same type of unsymmetrical distortion in which one I—Pt—N angle is opened and the other is contracted. In this case, the N1 ring is rotated so that the N1—C4 bond is approximately perpendicular to the ligand plane [torsion angle I2—Pt—N1—C4 78 (2)°] allowing for closer contact with the neighboring I atom. Since O1 is then directed towards the N2 ring, the latter twists away so that O2 is out of the plane and C8 is directed towards I1 [torsion angles I1—Pt—N2—O2 −108 (1)°; I1—Pt—N2—C8 17 (2)°], resulting in a larger N2—Pt—I1 angle. Both oxazine ligands possess a chair conformation with bond distances and angles similar to those in reported saturated oxazine derivatives (Riddell *et al.*, 1974; Holzapfel *et al.*, 1987). As is the case for the 3,6-dihydro-2*H*-

1,2-oxazine ligands in (I), the 3,4,5,6-tetrahydro-2*H*-1,2-oxazine ligands in (II) have opposite absolute configurations at N.



(I)



(II)

Experimental

Preparation of (I): to a solution of potassium tetrachloroplatinate (2.09 g, 5.04 mmol) in water (50 ml) was added a solution of potassium iodide (8.34 g, 50.2 mmol) in water (5 ml), followed by 3,6-dihydro-2*H*-1,2-oxazine (0.876 g, (10.3 mmol). The mixture was stirred for 45 min and the yellow powder that formed was isolated by filtration (yield 3.12 g). Recrystallization from a mixture of dimethylformamide and water yielded small orange crystals of (I). Preparation of (II): to a solution of potassium tetrachloroplatinate (1.66 g, 4.00 mmol) in water (35 ml) was added a solution of potassium iodide (6.64 g, 40.0 mmol) in water (5 ml), followed by a solution of 3,4,5,6-tetrahydro-2*H*-1,2-oxazine hydrochloride (0.988 g, 8.00 mmol) and potassium hydroxide (0.5 g, 9 mmol) in water (15 ml). The resulting mixture was stirred for 50 min and the orange powder that formed (2.17 g) was filtered. Crystals of (II) were obtained by recrystallization from a dimethylformamide/water solution.

Compound (**I**)

Crystal data

$[Pt(C_4H_7NO)_2I_2]$
$M_r = 619.11$
Monoclinic, $P2_1/n$
$a = 10.146\ (4)$ Å
$b = 9.003\ (7)$ Å
$c = 15.035\ (2)$ Å
$\beta = 92.28\ (2)°$
$V = 1372\ (1)$ Å^3
$Z = 4$

$D_x = 2.996$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 23 reflections
$\theta = 9.2–13.4°$
$\mu = 14.8$ mm^{-1}
$T = 296$ K
Flat needle, yellow–orange
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.039$, $T_{max} = 0.052$
2718 measured reflections
2387 independent reflections
1544 reflections with $I > 3\sigma(I)$

$R_{int} = 0.022$
$\theta_{max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 11$
$l = -18 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: 3.5%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.028$
$S = 1.48$
1544 reflections
136 parameters

H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 1.49$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

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

Pt—I1	2.593 (1)	O1—C1	1.45 (1)
Pt—I2	2.582 (1)	O2—N2	1.45 (1)
Pt—N1	2.103 (9)	O2—C5	1.47 (1)
Pt—N2	2.085 (10)	N1—C4	1.47 (1)
O1—N1	1.47 (1)	N2—C8	1.50 (2)
I1—Pt—I2	91.31 (4)	O2—N2—C8	108.6 (9)
I1—Pt—N1	174.4 (3)	N1—C4—C3	110 (1)
I1—Pt—N2	87.5 (3)	C1—C2—C3	121 (1)
I2—Pt—N1	94.2 (3)	C2—C3—C4	121 (1)
I2—Pt—N2	176.4 (3)	O1—C1—C2	114 (1)
N1—Pt—N2	87.0 (4)	N2—C8—C7	110 (1)
N1—O1—C1	106.4 (9)	C5—C6—C7	123 (1)
N2—O2—C5	111.2 (9)	C6—C7—C8	122 (1)
O1—N1—C4	107.7 (9)	O2—C5—C6	110 (1)

Compound (**II**)

Crystal data

$[Pt(C_4H_9NO)_2I_2]$
$M_r = 623.14$
Triclinic, $P\overline{1}$
$a = 9.379\ (5)$ Å
$b = 9.537\ (4)$ Å
$c = 8.950\ (4)$ Å
$\alpha = 91.10\ (4)°$
$\beta = 98.37\ (4)°$
$\gamma = 66.98\ (4)°$
$V = 728.3\ (7)$ Å^3

$Z = 2$
$D_x = 2.841$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 21 reflections
$\theta = 11.8–16.1°$
$\mu = 13.9$ mm^{-1}
$T = 296$ K
Slab, orange
0.30 × 0.15 × 0.15 mm

Data collection

Rigaku AFC-6*S* diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.076$, $T_{max} = 0.124$
2734 measured reflections
2561 independent reflections
1673 reflections with $I > 3\sigma(I)$

$R_{int} = 0.079$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: 7.0%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.058$
$S = 2.70$
1673 reflections
136 parameters

H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 2.35$ e Å^{-3}
$\Delta\rho_{min} = -3.17$ e Å^{-3}

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

Pt—I1	2.583 (3)	O1—C1	1.43 (3)
Pt—I2	2.604 (2)	O2—N2	1.43 (2)
Pt—N1	2.05 (2)	O2—C5	1.44 (3)
Pt—N2	2.05 (2)	N1—C4	1.47 (3)
O1—N1	1.45 (2)	N2—C8	1.48 (3)
I1—Pt—I2	91.11 (8)	N1—Pt—N2	86.1 (8)
I1—Pt—N1	177.4 (5)	N1—O1—C1	111 (1)
I1—Pt—N2	94.2 (6)	N2—O2—C5	110 (1)
I2—Pt—N1	88.5 (6)	O1—N1—C4	111 (1)
I2—Pt—N2	174.4 (6)	O2—N2—C8	105 (1)

For (I), the minimum and maximum points on the final difference electron-density map were 0.86 Å from I1 and 1.12 Å from Pt,

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respectively. For (II), the minimum peak in the final difference electron-density map was 1.12 Å from Pt, approximately perpendicular to the square plane, while the maximum peak was 1.26 Å from Pt along the Pt—I1 bond.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software;* data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*; program(s) used to solve structure: *MITHRIL* (Gilmore, 1983) for (I) and *SIR* (Burla *et al.*, 1989) for (II).

Partial support of this work by the Elsa U. Pardee Foundation and the Michigan Research Excellence Fund is gratefully acknowledged. The Herbert H. and Grace A. Dow Foundation and The Dow Chemical Company Foundation provided funding for the establishment of the CMU X-ray Crystallography Facility.

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