metal-organic compounds

trans,cis-Dibromido[diethyl (ethane-1,2-diyldiimino)diacetate-$\kappa^2 N$,N']dimethyl-platinum(IV)

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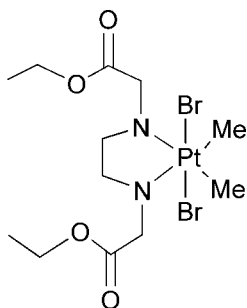Correspondence e-mail: goran.kaluderovic@chemie.uni-halle.de

The title complex, $[PtBr_2(CH_3)_2(C_{10}H_{20}N_2O_4)]$, has a slightly distorted octahedral coordination geometry as reflected in the bond lengths and angles around the Pt^{IV} atom. A crystallographic C_2 rotation axis bisects the C—C bond of the central ethylene group and passes through the Pt atom.

Related literature

For background information, see: Kaluderović, Đinović et al. (2005); Kaluderović, Miljković et al. (2005); Kaluderović, Schmidt, Schwieger et al. (2007); Kaluderović, Schmidt, Wagner et al. (2007). For related literature, see: Contreras et al. (2001); Hindmarsh et al. (1997); Hughes et al. (2001); Rostovtsev et al. (2002).

Experimental

Crystal data

$[PtBr_2(CH_3)_2(C_{10}H_{20}N_2O_4)]$	b = 8.1405 (12) Å
M_r = 617.26	c = 12.153 (2) Å
Monoclinic, $C2/c$	β = 118.75 (3)°
a = 21.419 (4) Å	V = 1857.9 (6) Å^3

Z = 4	T = 220 (2) K
Mo $K\alpha$ radiation	$0.25 \times 0.22 \times 0.18$ mm
μ = 11.87 mm^{-1}	

Data collection

Stoe IPDS diffractometer	5983 measured reflections
Absorption correction: numerical	1754 independent reflections
(*IPDS Software*; Stoe & Cie, 1999)	1644 reflections with $I > 2\sigma(I)$
T_{min} = 0.086, T_{max} = 0.186	R_{int} = 0.088

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	98 parameters
$wR(F^2)$ = 0.116	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 3.61 e Å^{-3}
1754 reflections	$\Delta\rho_{min}$ = −3.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—Pt	2.052 (8)	Br—Pt	2.4431 (10)
N—Pt	2.234 (6)		
C1^i—Pt—C1	87.1 (5)	N—Pt—Br	91.01 (15)
C1—Pt—N	96.0 (3)	C1—Pt—Br^i	88.8 (2)
C1—Pt—N^i	176.8 (3)	N—Pt—Br^i	89.58 (15)
N—Pt—N^i	80.8 (3)	Br—Pt—Br^i	179.23 (4)
C1—Pt—Br	90.7 (2)		

Symmetry code: (i) $-x-1, y, -z-\frac{3}{2}$.

Data collection: *IPDS Software* (Stoe & Cie, 1999); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2429).

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supplementary materials

trans,cis-Dibromido[diethyl (ethane-1,2-diyldiimino)diacetate-*κ²N,N'*]dimethylplatinum(IV)

G. N. Kaluderovic, H. Schmidt, C. Wagner and **D. Steinborn**

Comment

In this paper, we report the structure of *trans,cis*-dibromodimethyl(*O,O'*-diethyl-ethylenediamine- *N,N'*-diacetate)platinum(IV) (configuration index: *OC*-6–13) *trans,cis*-[PtBr$_2$Me$_2$(Et$_2$edda)], prepared as part of our investigation on basic coordination modes and antitumoral activity of platinum(IV) complexes with esters of H$_2$edda-type (ethylenediamine-*N,N'*-diacetatic acid) ligands (Kaluđerović, Đinović *et al.*, 2005; Kaluđerović, Miljković *et al.*, 2005; Kaluđerović, Schmidt, Schwieger *et al.*, 2007).

The title compound crystallizes in the space group *C*2/*c* as isolated molecules and exhibits a crystallographically imposed C_2 symmetry axis bisecting the C2—C2^i bond and passing through the Pt atom. The Pt atom adopts a [Br$_2$C$_2$N$_2$] distorted octahedral coordination; the Pt, C, N atoms lie in a plane with meaningless deviation from the mean plane: 0.004 (6) Å and 0.005 (9) Å for N and C1 atoms, respectively. Due to the C_2 symmetry, the five-membered ring PtNC2C2^{i}N^i exibits an ideal half twisted conformation with a twist around the C2—C2^i bond. Because of an inversion center within the unit cell the compound crystallized as a mixture of molecules with $λ$ and $δ$ oriented five-membered cycles in 1:1 ratio. Fig. 1 illustrates the $λ$ oriented complex.

Almost all angles in the coordination polyhedron are very close to the ideal value of 90° (87.1 (5) − 91.0 (2)°), with the exception of angles N—Pt—N^i = 80.8 (3)° and C1—Pt—N = 96.0 (3)°, due to the constraints of the chelate binding Et$_2$edda ligand. The angle N—Pt—N^i is smaller than in structures [PtCl$_4$(R_2edda)] (*R* = Me, 83.1 (6)°; Et, 84.0 (3)°, (I); Kaluđerović, Schmidt, Schwieger *et al.*, 2007), [PtBr$_4$(en)] (83.1 (9)°; Hindmarsh *et al.*, 1997), [PdCl$_2$(R_4edta)] (*R* = Me, 85.9 (2)°; Et, 85.6 (3)°; Kaluđerović, Schmidt, Wagner *et al.*, 2007) and in [PtMe$_2$I$_2$(tmeda)], (II), [PtMe$_2$I(*n*-C$_3$F$_7$)(tmeda)], (III), and [PtMeI$_2$(*n*-C$_3$F$_7$)(tmeda)], (IV), (tmeda = tetramethyl-*N,N,N',N'*-ethylenediamine; 82.3 (2) − 82.8 (5)°; Hughes *et al.*, 2001).

The Pt—C1 bond length of 2.052 (8) Å is comparable to the Pt—C distances found in *trans*-[PtBr$_2$Me$_2${o-Ph$_2$P(S)C$_6$H$_4$SMe- $κ^2S,S$}], 2.065 (6)/2.106 (5) Å (Contreras *et al.*, 2001) and in [Pt(X)(OMe)(Me)$_2$(tmeda)] structures (X = OH, OOH), 2.007 (8) − 2.07 (2) Å (Rostovtsev *et al.*, 2002). The Pt—Br bond lengths (2.443 (1) Å) are similar to those found in (I) (2.447 (1)/2.460 (1) Å), [PtBr$_4$(*L*)] (*L* = ethylenediamine, 2.461 (2)/2.448 (2) Å; 1,3-propylenediamine, 2.452 (4)/2.455 (4) Å; Hindmarsh *et al.*, 1997). In accordance with the high *trans* influence of the Me ligand the Pt—N bond (2.234 (6) Å) is relatively long although comparable with structures (II), (III) and (IV) (2.226 (5) − 2.312 (7) Å; Hughes *et al.*, 2001), in which the Me ligand is also *trans* to N atom. The Pt—N bonds with Cl ((I): 2.110 (6) Å) or Br ([PtBr$_4$(*L*)]; *L* = ethylenediamine, 2.05 (2) Å; *L* = 1,3-propylenediamine, 2.04 (3) Å; Hindmarsh *et al.*, 1997) *trans* to a N atom are shorter relative to corresponding bond length in the title compound. Weak intramolecular H-bond (C5—H···O1) may stabilize the structure (distance C5···O1 = 2.70 (1) Å).

supplementary materials

Besides *trans*-[PtBr$_2$Me$_2${*o*-Ph$_2$P(S)C$_6$H$_4$SMe-κ^2*S,S*}] (Contreras *et al.*, 2001), the title complex is the only other mono-nuclear dibromodimethylplatinum(IV) complex that has been structurally characterized to date.

Experimental

[{PtBr$_2$Me$_2$}$_n$] (0.3 mmol) and Et$_2$edda·2HCl (0.3 mmol) were suspended in methanol-chloroform solution (10 ml, 1:1 *v/v*). The mixture was stirred under reflux for 2 h. From the resulting yellow solution the title complex crystallized as well shaped crystals within one week at room temperature.

Refinement

H atoms were included in calculated positions [C—H = 0.97–0.98 Å; N—H = 0.92 Å] and included in the refinement in a riding-model approximation with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H6) = 0.023 Å^3.
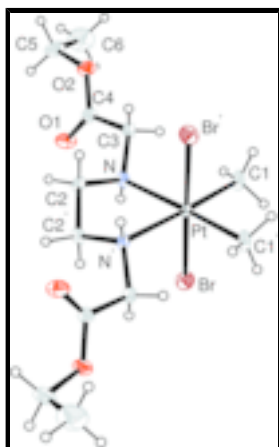
Figures

Fig. 1. Molecular structure of the λ oriented complex. Displacement ellipsoids are plotted at the 30% probability level and H atoms are shown as small spheres of arbitrary radii [Symmetry code: (i) −*x* − 1, *y*, −*z* + 5/2].

***trans,cis*-Dibromido[diethyl (ethane-1,2-diyldiimino)diacetate- κ^2*N,N*']dimethylplatinum(IV)**

Crystal data

[PtBr$_2$(C$_1$H$_3$)$_2$(C$_{10}$H$_{20}$N$_2$O$_4$)]	F_{000} = 1168
M_r = 617.26	D_x = 2.207 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 8000 reflections
a = 21.419 (4) Å	θ = 4.2–51.7°
b = 8.1405 (12) Å	μ = 11.87 mm^{-1}
c = 12.153 (2) Å	*T* = 220 (2) K
β = 118.75 (3)°	Block, yellow
V = 1857.9 (6) Å^3	0.25 × 0.22 × 0.18 mm
Z = 4	

Data collection

Stoe IPDS diffractometer	1754 independent reflections
Radiation source: fine-focus sealed tube	1644 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.088$
$T = 220(2)$ K	$\theta_{max} = 25.9°$
area detector scans	$\theta_{min} = 3.6°$
Absorption correction: numerical (IPDS Software; Stoe & Cie, 1999)	$h = -26 \rightarrow 26$
$T_{min} = 0.086$, $T_{max} = 0.186$	$k = -9 \rightarrow 9$
5983 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 23.535P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 3.61$ e Å^{-3}
1754 reflections	$\Delta\rho_{min} = -3.25$ e Å^{-3}
98 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0019 (4)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	−0.5342 (5)	−0.3798 (9)	−0.8827 (8)	0.0342 (17)
H2	−0.4982	−0.2945	−0.8564	0.041*
H1	−0.5782	−0.3334	−0.8921	0.041*

H3	−0.5423	−0.4251	−0.9623	0.041*
C2	−0.5342 (4)	−0.9177 (9)	−0.8120 (7)	0.0253 (15)
H4	−0.5372	−1.0180	−0.8589	0.030*
H5	−0.5753	−0.9149	−0.7970	0.030*
C3	−0.6049 (4)	−0.7510 (9)	−0.9974 (7)	0.0277 (15)
H7	−0.6055	−0.6461	−1.0376	0.033*
H8	−0.6416	−0.7462	−0.9715	0.033*
C4	−0.6227 (4)	−0.8873 (10)	−1.0917 (7)	0.0281 (15)
C5	−0.7193 (5)	−1.0109 (14)	−1.2714 (10)	0.051 (3)
H10	−0.7643	−1.0599	−1.2853	0.061*
H9	−0.6848	−1.0997	−1.2529	0.061*
C6	−0.7306 (8)	−0.9233 (19)	−1.3865 (12)	0.079 (4)
H11	−0.7488	−0.9995	−1.4565	0.095*
H12	−0.6857	−0.8779	−1.3738	0.095*
H13	−0.7646	−0.8351	−1.4046	0.095*
N	−0.5353 (3)	−0.7714 (7)	−0.8859 (5)	0.0218 (12)
H6	−0.5018	−0.7864	−0.9118	0.023*
O1	−0.5801 (3)	−0.9721 (9)	−1.1044 (6)	0.0436 (16)
O2	−0.6931 (3)	−0.8978 (8)	−1.1645 (6)	0.0406 (15)
Br	−0.61452 (5)	−0.56041 (10)	−0.75172 (9)	0.0390 (3)
Pt	−0.5000	−0.56242 (4)	−0.7500	0.02106 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.055 (5)	0.018 (4)	0.027 (4)	−0.003 (3)	0.018 (4)	0.003 (3)
C2	0.037 (4)	0.022 (3)	0.012 (3)	−0.005 (3)	0.008 (3)	−0.001 (3)
C3	0.033 (3)	0.024 (3)	0.020 (4)	0.003 (3)	0.008 (3)	−0.001 (3)
C4	0.031 (3)	0.027 (4)	0.023 (4)	−0.002 (3)	0.010 (3)	−0.001 (3)
C5	0.034 (4)	0.057 (6)	0.052 (6)	−0.010 (4)	0.012 (4)	−0.030 (5)
C6	0.082 (8)	0.102 (11)	0.035 (7)	−0.002 (7)	0.014 (6)	−0.019 (7)
N	0.033 (3)	0.017 (3)	0.015 (3)	0.001 (2)	0.012 (2)	0.001 (2)
O1	0.031 (3)	0.060 (4)	0.035 (4)	0.005 (3)	0.012 (3)	−0.020 (3)
O2	0.029 (3)	0.043 (3)	0.039 (4)	−0.001 (2)	0.008 (3)	−0.018 (3)
Br	0.0423 (5)	0.0406 (5)	0.0378 (5)	0.0055 (3)	0.0222 (4)	−0.0027 (3)
Pt	0.0311 (3)	0.0134 (2)	0.0187 (3)	0.000	0.01205 (19)	0.000

Geometric parameters (Å, °)

C1—Pt	2.052 (8)	C5—O2	1.466 (11)
C1—H2	0.9700	C5—C6	1.483 (19)
C1—H1	0.9700	C5—H10	0.9800
C1—H3	0.9700	C5—H9	0.9800
C2—N	1.485 (9)	C6—H11	0.9700
C2—C2^i	1.515 (14)	C6—H12	0.9700
C2—H4	0.9800	C6—H13	0.9700
C2—H5	0.9800	N—Pt	2.234 (6)
C3—N	1.464 (9)	N—H6	0.9200

C3—C4	1.506 (11)	Br—Pt	2.4431 (10)
C3—H7	0.9800	Pt—C1[i]	2.052 (8)
C3—H8	0.9800	Pt—N[i]	2.234 (6)
C4—O1	1.213 (10)	Pt—Br[i]	2.4431 (10)
C4—O2	1.334 (9)		
Pt—C1—H2	109.5	C5—C6—H12	109.5
Pt—C1—H1	109.5	H11—C6—H12	109.5
H2—C1—H1	109.5	C5—C6—H13	109.5
Pt—C1—H3	109.5	H11—C6—H13	109.5
H2—C1—H3	109.5	H12—C6—H13	109.5
H1—C1—H3	109.5	C3—N—C2	111.3 (5)
N—C2—C2[i]	109.1 (5)	C3—N—Pt	115.5 (4)
N—C2—H4	109.9	C2—N—Pt	105.2 (4)
C2[i]—C2—H4	109.9	C3—N—H6	108.2
N—C2—H5	109.9	C2—N—H6	108.2
C2[i]—C2—H5	109.9	Pt—N—H6	108.2
H4—C2—H5	108.3	C4—O2—C5	117.2 (6)
N—C3—C4	113.2 (6)	C1[i]—Pt—C1	87.1 (5)
N—C3—H7	108.9	C1[i]—Pt—N	176.8 (3)
C4—C3—H7	108.9	C1—Pt—N	96.0 (3)
N—C3—H8	108.9	C1[i]—Pt—N[i]	96.0 (3)
C4—C3—H8	108.9	C1—Pt—N[i]	176.8 (3)
H7—C3—H8	107.8	N—Pt—N[i]	80.8 (3)
O1—C4—O2	124.0 (7)	C1[i]—Pt—Br	88.8 (2)
O1—C4—C3	125.8 (7)	C1—Pt—Br	90.7 (2)
O2—C4—C3	110.2 (6)	N—Pt—Br	91.01 (15)
O2—C5—C6	110.7 (10)	N[i]—Pt—Br	89.58 (15)
O2—C5—H10	109.5	C1[i]—Pt—Br[i]	90.7 (2)
C6—C5—H10	109.5	C1—Pt—Br[i]	88.8 (2)
O2—C5—H9	109.5	N—Pt—Br[i]	89.58 (15)
C6—C5—H9	109.5	N[i]—Pt—Br[i]	91.01 (15)
H10—C5—H9	108.1	Br—Pt—Br[i]	179.23 (4)
C5—C6—H11	109.5		
N—C3—C4—O1	−25.8 (12)	C3—N—Pt—C1	−41.3 (5)
N—C3—C4—O2	156.9 (7)	C2—N—Pt—C1	−164.5 (5)
C4—C3—N—C2	−65.9 (8)	C3—N—Pt—N[i]	138.8 (6)
C4—C3—N—Pt	174.2 (5)	C2—N—Pt—N[i]	15.7 (3)
C2[i]—C2—N—C3	−170.9 (7)	C3—N—Pt—Br	49.4 (5)
C2[i]—C2—N—Pt	−45.2 (7)	C2—N—Pt—Br	−73.7 (4)
O1—C4—O2—C5	−4.6 (13)	C3—N—Pt—Br[i]	−130.1 (5)
C3—C4—O2—C5	172.7 (8)	C2—N—Pt—Br[i]	106.8 (4)
C6—C5—O2—C4	−93.6 (11)		

Symmetry codes: (i) −*x*−1, *y*, −*z*−3/2.

Fig. 1