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cis-(3-Hydroxycyclobutane-1,1-dicarboxylato-κ^2O,O')bis(2-methylpyridine-κN)-platinum(II)

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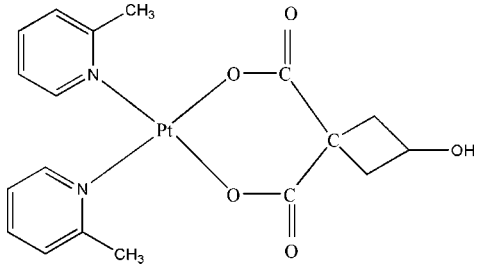
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.022 Å; R factor = 0.053; wR factor = 0.150; data-to-parameter ratio = 19.0.

In the crystal structure of the title compound, $[Pt(C_6H_6O_4)(C_6H_7N)_2]$, the platinum(II) ion is tetracoordinated in a square-planar coordination. The structure involves intramolecular C—H···O hydrogen bonds.

Related literature

For related literature, see: Ali *et al.* (2002); Jakuper *et al.* (2003); Tu *et al.* (2004); Zhang *et al.* (2002).



Experimental

Crystal data

$[Pt(C_6H_6O_4)(C_6H_7N)_2]$
M_r = 539.45
Orthorhombic, $P2_12_12_1$
a = 9.5157 (7) Å
b = 13.1417 (9) Å
c = 15.2884 (11) Å
V = 1911.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 7.37 mm^{-1}
T = 298 (2) K
0.24 × 0.22 × 0.17 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2004)
T_{min} = 0.271, T_{max} = 0.367
16189 measured reflections
4511 independent reflections
3991 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.151
S = 1.10
4511 reflections
238 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 4.96 e Å^{-3}
$\Delta\rho_{min}$ = −2.22 e Å^{-3}
Absolute structure: Flack (1983), with 1810 Friedel pairs
Flack parameter: 0.03 (2)

Table 1
Selected geometric parameters (Å, °).

Pt1—O1	1.992 (8)	Pt1—N1	2.005 (10)
Pt1—O2	2.001 (8)	Pt1—N2	2.008 (9)
O1—Pt1—O2	91.4 (4)	O1—Pt1—N2	177.7 (4)
O1—Pt1—N1	86.3 (4)	O2—Pt1—N2	87.1 (4)
O2—Pt1—N1	177.0 (5)	N1—Pt1—N2	95.3 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15B···O3	0.97	2.48	2.826 (16)	101
C12—H12A···O2	0.96	2.58	3.170 (16)	120

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2138).

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supplementary materials

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cis-(3-Hydroxycyclobutane-1,1-dicarboxylato-κ^2O,O')bis(2-methylpyridine-κN)platinum(II)

M.-J. Xie, Y. Yu, W.-P. Liu, S.-Q. Hou and X. Chen

Comment

In an attempt to overcome drawbacks of cisplatin, numerous analogues have been prepared and evaluated in a search for an alternativeactive agent. Among them, *cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II) (Carboplatin) is commonly used for the treatment of testicular and ovarian cancer as well as cervical, bladder and head and neck tumors. It has proven to be the only second-generation platinum complex commercially available worldwide at present (Jakuper *et al.*, 2003). But the application of Carboplatin in therapy is limited by the dose-dependent nephrotoxicity and other side effects. Therefore, the search for the new potent platinum complexes possessing high antitumor activity and lack of cross-resistance is needed. The title compound is a new soluble carboplatin analogue containing an asymmetric chelating malonate anion as its carrier and anticancer tests are presently being carried out.

The title complex consists of discrete monomeric units where the Pt(II) is coordinated by two crystallographically independent 2-methylpyridine ligands and 3-hydroxy-1,1-cyclobutanedicarboxylate anions with a square planar geometry (Table 1, Fig. 1) The 1,1-cyclobutanedicarboxylate ligand displays similar features to those described in the literature (Tu *et al.*, 2004; Zhang *et al.*, 2002; Ali *et al.*, 2002). The six-membered chelate ring built up of the Pt(II) atom and the 3-hydroxy-1,1-cyclobutanedicarboxylate anion adopts a boat conformation and the two 2-methylpyridine liagnds are oriented perpendicular to each other.

Experimental

Potassium tetrachloroplatinate(II) (5 g, 12 mmol) was dissolved in water (50 ml) and treated with KI (12 g, 72 mmol). After left in a dark for 30 min at room temperature, a solution of 2-methylpyridine (1.08 g, 12 mmol in 50 ml water) was added dropwise. The mixture was stirred for 4 h and the yellow precipitate was filtrated off. Then to a suspension of di(2-methylpyridine)PtI_2 (2.5 g, 0.044 mmol) in 75 ml water was added (1.36 g, 3.65 mmol) disilver 3-hydroxy-1,1-cyclobutanedicarboxylate, and the reaction mixture was stirred at 323 K for 72 h. Then the AgI formed was filtrated off and the filtrate was condensed at 313 K under reduced pressure to 5 ml, and a colourless crystalline product was precipitated. The compound was recrystallized from water to obtain crystals suitable for X-ray structure analysis.

Refinement

All H atoms were initially located in a difference Fourier map but were positioned with idealized geometry and refined isotropic with U_{iso}(H) = 1.2U_{eq}(C) (1.5 for methyl H atoms) using a riding model with C—H = 0.93 and 0.97 Å).

Figures

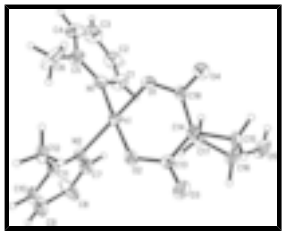


Fig. 1. Molecular structure of (I) with the atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level.

cis-(3-Hydroxycyclobutane-1,1-dicarboxylato-κ^2*O*,*O*^{1})bis(2-methylpyridine- κ*N*)platinum(II)

Crystal data

$[Pt(C_6H_6O_4)(C_6H_7N)_2]$	F_{000} = 1040
M_r = 539.45	D_x = 1.874 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P2ac2ab	Cell parameters from 4511 reflections
a = 9.5157 (7) Å	θ = 2.0–28.3º
b = 13.1417 (9) Å	μ = 7.37 mm^{-1}
c = 15.2884 (11) Å	*T* = 298 (2) K
V = 1911.9 (2) Å^3	Block, colourless
Z = 4	0.24 × 0.22 × 0.17 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	4511 independent reflections
Radiation source: fine-focus sealed tube	3991 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.054
T = 298(2) K	θ_{max} = 28.3º
φ and ω scans	θ_{min} = 2.0º
Absorption correction: numerical (APEX2; Bruker, 2004)	*h* = −12→12
T_{min} = 0.271, T_{max} = 0.367	*k* = −17→16
16189 measured reflections	*l* = −20→20

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.053	$w = 1/[\sigma^2(F_o^2) + (0.1024P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.151	$(\Delta/\sigma)_{max}$ = 0.002
S = 1.10	$\Delta\rho_{max}$ = 4.96 e Å^{-3}

4511 reflections	$\Delta\rho_{min} = -2.22$ e Å^{-3}
238 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with how many Friedel pairs?
Secondary atom site location: difference Fourier map	Flack parameter: 0.03 (2)

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}
Pt1	0.11187 (4)	0.91536 (3)	0.94090 (2)	0.03526 (14)
N1	0.2783 (10)	0.9230 (10)	0.8607 (6)	0.048 (2)
N2	0.2200 (10)	0.8622 (7)	1.0440 (6)	0.0370 (19)
O1	−0.0012 (9)	0.9638 (7)	0.8395 (5)	0.0448 (19)
O2	−0.0581 (9)	0.9143 (8)	1.0179 (6)	0.0482 (19)
O3	−0.2424 (12)	1.0008 (9)	1.0680 (8)	0.073 (3)
O4	−0.1914 (11)	1.0397 (9)	0.7953 (6)	0.063 (3)
O5	−0.1137 (19)	1.3303 (7)	0.9751 (9)	0.086 (4)
H5	−0.1290	1.3371	0.9226	0.104*
C1	0.3516 (16)	1.0153 (14)	0.8581 (11)	0.066 (4)
H1	0.3235	1.0688	0.8939	0.079*
C2	0.4629 (17)	1.0274 (15)	0.8039 (12)	0.073 (5)
H2	0.5208	1.0841	0.8092	0.087*
C3	0.4895 (19)	0.9557 (18)	0.7413 (14)	0.085 (6)
H3	0.5567	0.9695	0.6988	0.103*
C4	0.4248 (17)	0.8695 (16)	0.7389 (10)	0.073 (5)
H4	0.4459	0.8217	0.6960	0.088*
C5	0.3196 (16)	0.8488 (11)	0.8039 (9)	0.057 (3)
C6	0.249 (2)	0.7510 (17)	0.8104 (16)	0.123 (10)
H6A	0.2251	0.7379	0.8704	0.185*
H6B	0.3105	0.6983	0.7895	0.185*
H6C	0.1651	0.7520	0.7757	0.185*
C7	0.3179 (18)	0.9235 (11)	1.0828 (10)	0.064 (4)
H7	0.3370	0.9855	1.0560	0.077*
C8	0.388 (2)	0.9018 (15)	1.1558 (13)	0.093 (7)
H8	0.4519	0.9479	1.1795	0.111*
C9	0.3624 (18)	0.8037 (12)	1.1973 (13)	0.077 (5)
H9	0.4081	0.7839	1.2483	0.092*

C10	0.2683 (16)	0.7436 (11)	1.1568 (10)	0.061 (3)
H10	0.2503	0.6800	1.1810	0.073*
C11	0.1944 (12)	0.7709 (8)	1.0794 (7)	0.039 (2)
C12	0.0894 (18)	0.6987 (9)	1.0333 (10)	0.065 (4)
H12A	−0.0046	0.7235	1.0416	0.098*
H12B	0.0974	0.6317	1.0578	0.098*
H12C	0.1101	0.6962	0.9719	0.098*
C13	−0.1430 (12)	0.9925 (10)	1.0153 (7)	0.042 (3)
C14	−0.1268 (10)	1.0706 (7)	0.9431 (7)	0.036 (2)
C15	−0.2338 (13)	1.1622 (9)	0.9461 (9)	0.047 (3)
H15A	−0.2537	1.1920	0.8893	0.057*
H15B	−0.3198	1.1475	0.9777	0.057*
C16	−0.1254 (17)	1.2203 (9)	0.9991 (10)	0.059 (4)
H16	−0.1411	1.2118	1.0621	0.070*
C17	−0.0093 (13)	1.1523 (8)	0.9672 (9)	0.044 (3)
H17A	0.0549	1.1303	1.0127	0.053*
H17B	0.0412	1.1789	0.9170	0.053*
C18	−0.1097 (14)	1.0224 (8)	0.8538 (7)	0.039 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.0451 (2)	0.02367 (19)	0.0370 (2)	0.00148 (15)	0.00061 (16)	−0.00037 (16)
N1	0.045 (5)	0.059 (7)	0.041 (5)	0.008 (5)	0.002 (4)	0.006 (6)
N2	0.041 (5)	0.027 (4)	0.043 (5)	−0.001 (3)	−0.004 (4)	0.001 (4)
O1	0.052 (5)	0.052 (5)	0.030 (4)	0.010 (4)	−0.003 (3)	−0.004 (3)
O2	0.049 (4)	0.042 (4)	0.053 (5)	0.006 (4)	0.011 (4)	0.016 (5)
O3	0.075 (6)	0.060 (6)	0.085 (7)	0.011 (5)	0.044 (6)	0.015 (6)
O4	0.072 (7)	0.065 (6)	0.052 (5)	0.014 (5)	−0.012 (5)	−0.002 (5)
O5	0.131 (11)	0.029 (5)	0.099 (8)	0.010 (6)	0.038 (9)	−0.013 (5)
C1	0.061 (9)	0.069 (10)	0.068 (9)	−0.014 (7)	0.006 (7)	−0.009 (8)
C2	0.057 (9)	0.078 (11)	0.083 (12)	−0.016 (8)	0.007 (8)	0.006 (9)
C3	0.055 (9)	0.110 (15)	0.091 (13)	−0.001 (10)	0.033 (9)	0.028 (11)
C4	0.067 (10)	0.100 (13)	0.052 (8)	−0.010 (9)	0.011 (7)	−0.011 (8)
C5	0.066 (8)	0.050 (8)	0.055 (7)	−0.006 (6)	−0.002 (6)	−0.014 (6)
C6	0.134 (18)	0.085 (14)	0.15 (2)	−0.036 (14)	0.093 (17)	−0.066 (15)
C7	0.098 (11)	0.034 (7)	0.061 (8)	0.002 (7)	−0.016 (7)	0.002 (6)
C8	0.097 (13)	0.086 (13)	0.096 (13)	−0.040 (11)	−0.057 (11)	0.042 (10)
C9	0.087 (12)	0.045 (8)	0.099 (12)	−0.009 (7)	−0.029 (10)	0.016 (8)
C10	0.086 (9)	0.026 (6)	0.070 (9)	0.010 (6)	−0.003 (7)	0.007 (6)
C11	0.055 (7)	0.024 (5)	0.036 (5)	0.005 (4)	−0.002 (4)	0.005 (4)
C12	0.101 (12)	0.018 (5)	0.077 (9)	−0.003 (6)	0.000 (8)	0.005 (5)
C13	0.045 (7)	0.043 (6)	0.037 (6)	0.004 (5)	0.005 (5)	0.005 (5)
C14	0.038 (5)	0.026 (5)	0.042 (5)	0.001 (4)	0.007 (4)	−0.003 (4)
C15	0.048 (6)	0.039 (6)	0.055 (7)	0.013 (5)	0.000 (6)	0.011 (6)
C16	0.083 (11)	0.034 (7)	0.059 (7)	0.005 (6)	0.014 (8)	−0.009 (6)
C17	0.049 (6)	0.021 (5)	0.063 (8)	−0.013 (4)	0.007 (5)	0.003 (5)
C18	0.050 (6)	0.028 (5)	0.040 (5)	−0.001 (5)	−0.006 (5)	0.002 (4)

Geometric parameters (Å, °)

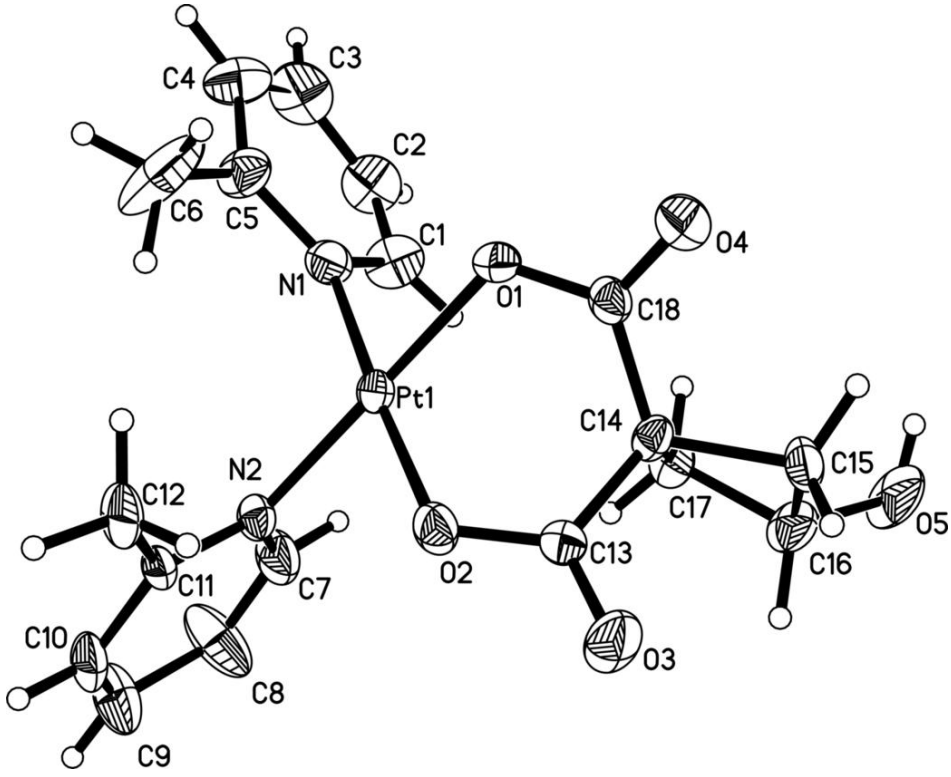
Pt1—O1	1.992 (8)	C6—H6C	0.9600
Pt1—O2	2.001 (8)	C7—C8	1.33 (2)
Pt1—N1	2.005 (10)	C7—H7	0.9300
Pt1—N2	2.008 (9)	C8—C9	1.46 (2)
N1—C5	1.364 (17)	C8—H8	0.9300
N1—C1	1.40 (2)	C9—C10	1.34 (2)
N2—C11	1.338 (13)	C9—H9	0.9300
N2—C7	1.368 (18)	C10—C11	1.422 (18)
O1—C18	1.306 (15)	C10—H10	0.9300
O2—C13	1.307 (15)	C11—C12	1.548 (19)
O3—C13	1.248 (15)	C12—H12A	0.9600
O4—C18	1.207 (15)	C12—H12B	0.9600
O5—C16	1.495 (18)	C12—H12C	0.9600
O5—H5	0.8200	C13—C14	1.515 (15)
C1—C2	1.35 (2)	C14—C18	1.513 (15)
C1—H1	0.9300	C14—C15	1.577 (14)
C2—C3	1.37 (3)	C14—C17	1.593 (14)
C2—H2	0.9300	C15—C16	1.52 (2)
C3—C4	1.29 (3)	C15—H15A	0.9700
C3—H3	0.9300	C15—H15B	0.9700
C4—C5	1.44 (2)	C16—C17	1.502 (18)
C4—H4	0.9300	C16—H16	0.9800
C5—C6	1.45 (2)	C17—H17A	0.9700
C6—H6A	0.9600	C17—H17B	0.9700
C6—H6B	0.9600		
O1—Pt1—O2	91.4 (4)	C8—C9—H9	122.2
O1—Pt1—N1	86.3 (4)	C9—C10—C11	124.3 (13)
O2—Pt1—N1	177.0 (5)	C9—C10—H10	117.9
O1—Pt1—N2	177.7 (4)	C11—C10—H10	117.9
O2—Pt1—N2	87.1 (4)	N2—C11—C10	118.2 (11)
N1—Pt1—N2	95.3 (4)	N2—C11—C12	118.8 (10)
C5—N1—C1	117.3 (12)	C10—C11—C12	122.9 (11)
C5—N1—Pt1	125.5 (10)	C11—C12—H12A	109.5
C1—N1—Pt1	117.0 (10)	C11—C12—H12B	109.5
C11—N2—C7	118.4 (10)	H12A—C12—H12B	109.5
C11—N2—Pt1	122.5 (8)	C11—C12—H12C	109.5
C7—N2—Pt1	119.0 (8)	H12A—C12—H12C	109.5
C18—O1—Pt1	119.0 (7)	H12B—C12—H12C	109.5
C13—O2—Pt1	118.4 (7)	O3—C13—O2	121.1 (11)
C16—O5—H5	109.5	O3—C13—C14	119.2 (11)
C2—C1—N1	120.6 (16)	O2—C13—C14	119.5 (9)
C2—C1—H1	119.7	C18—C14—C13	112.6 (9)
N1—C1—H1	119.7	C18—C14—C15	114.5 (9)
C1—C2—C3	119.5 (17)	C13—C14—C15	115.5 (9)
C1—C2—H2	120.3	C18—C14—C17	114.5 (9)
C3—C2—H2	120.3	C13—C14—C17	111.1 (9)

C4—C3—C2	122.5 (16)	C15—C14—C17	86.1 (8)
C4—C3—H3	118.8	C16—C15—C14	87.7 (9)
C2—C3—H3	118.8	C16—C15—H15A	114.0
C3—C4—C5	118.6 (16)	C14—C15—H15A	114.0
C3—C4—H4	120.7	C16—C15—H15B	114.0
C5—C4—H4	120.7	C14—C15—H15B	114.0
N1—C5—C4	120.4 (14)	H15A—C15—H15B	111.2
N1—C5—C6	117.1 (13)	O5—C16—C17	116.1 (12)
C4—C5—C6	122.4 (14)	O5—C16—C15	113.9 (13)
C5—C6—H6A	109.5	C17—C16—C15	91.5 (9)
C5—C6—H6B	109.5	O5—C16—H16	111.3
H6A—C6—H6B	109.5	C17—C16—H16	111.3
C5—C6—H6C	109.5	C15—C16—H16	111.3
H6A—C6—H6C	109.5	C16—C17—C14	87.7 (9)
H6B—C6—H6C	109.5	C16—C17—H17A	114.0
C8—C7—N2	125.5 (14)	C14—C17—H17A	114.0
C8—C7—H7	117.3	C16—C17—H17B	114.0
N2—C7—H7	117.3	C14—C17—H17B	114.0
C7—C8—C9	117.9 (16)	H17A—C17—H17B	111.2
C7—C8—H8	121.0	O4—C18—O1	119.6 (11)
C9—C8—H8	121.0	O4—C18—C14	121.4 (11)
C10—C9—C8	115.6 (15)	O1—C18—C14	118.9 (10)
C10—C9—H9	122.2		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15B···O3	0.97	2.48	2.826 (16)	101
C12—H12A···O2	0.96	2.58	3.170 (16)	120

Fig. 1


C4
C3
C2
C6
C5
C1
O4
N1
O1
C18
Pt1
C14
C15
N2
C12
C17
O5
O2
C13
C16
C11
C7
C10
O3
C8
C9