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cis-Tetrachloridobis(1*H*-imidazole-κN^3)-platinum(IV)

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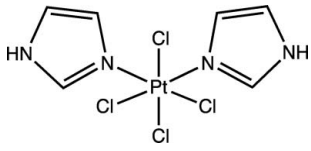
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.005 Å; R factor = 0.019; wR factor = 0.037; data-to-parameter ratio = 19.5.

In the title complex, *cis*-$[PtCl_4(C_3H_4N_2)_2]$, the Pt^{IV} ion lies on a twofold rotation axis and is coordinated in a slightly distorted octahedral geometry. The dihedral angle between the imidazole rings is 69.9 (2)°. In the crystal, molecules are linked by N—H···Cl hydrogen bonds, forming a three-dimensional network.

Related literature

For applications of platinum species bearing N-bonded heterocycles, see: Ravera *et al.* (2011); Esmaeilbeig *et al.* (2011); Al-Shuneigat *et al.* (2010); Wheate *et al.* (2007); van Zutphen *et al.* (2006); Fritsky *et al.* (2000); Krämer & Fritsky (2000). For the synthesis of platinum complexes with *N*-heterocyclic ligands, see: Bokach, Kuznetsov *et al.* (2011); Kritchenkov *et al.* (2011); Bokach, Balova *et al.* (2011); Tskhovrebov *et al.* (2009); Luzyanin *et al.* (2009); Bokach *et al.* (2009). For related structures, see: Khripun *et al.* (2006, 2007); Korte *et al.* (1981); Kuduk-Jaworska *et al.* (1988); Bayon *et al.* (1987); Yip *et al.* (1993); Chen *et al.* (2006); Gao *et al.* (2004); Garcia *et al.* (2000); Hao & Yu (2007); Huo *et al.* (2004). For bond-length data, see: Orpen *et al.* (1989).



Experimental

Crystal data

$[PtCl_4(C_3H_4N_2)_2]$
M_r = 473.05
Monoclinic, $C2/c$
a = 7.7264 (4) Å
b = 11.8757 (6) Å
c = 12.9471 (5) Å
β = 93.332 (3)°
V = 1185.97 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 12.70 mm^{-1}
T = 120 K
0.15 × 0.13 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.193, T_{max} = 0.411
7759 measured reflections
1362 independent reflections
1275 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.037
S = 1.05
1362 reflections
70 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.73 e Å^{-3}

Table 1
Selected bond lengths (Å).

Pt1—N1	2.046 (3)	Pt1—Cl1	2.3193 (8)
Pt1—Cl2	2.3141 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···Cl1^{ii}	0.98	2.66	3.355 (3)	128
N2—H2*N*···Cl2^{ii}	0.98	2.70	3.320 (3)	122
N2—H2*N*···Cl1^{iii}	0.98	2.82	3.368 (3)	116

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5433).

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supplementary materials

Acta Cryst. (2012). E**68**, m547–m548 [doi:10.1107/S1600536812013323]

cis-Tetrachloridobis(1*H*-imidazole-κN^3)platinum(IV)

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Comment

Platinum species, bearing *N*-bonded heterocycles (including, in particular, imidazoles) have drawn attention as efficient antitumor agents (Ravera *et al.*, 2011; Esmaeilbeig *et al.*, 2011; Al-Shuneigat *et al.*, 2010; Wheate *et al.*, 2007; van Zutphen *et al.*, 2006). Within the framework of our projects the focus is on the synthesis of platinum complexes with *N*-heterocyclic ligands (Bokach, Kuznetsov *et al.*, 2011; Kritchenkov *et al.*, 2011; Bokach, Balova *et al.*, 2011; Tskhovrebov *et al.*, 2009; Luzyanin *et al.*, 2009; Bokach *et al.*, 2009; Krämer *et al.*, 2000; Fritsky *et al.*, 2000), the title compound (**I**) was synthesized and characterized by single-crystal X-ray diffraction.

In (**I**) the Pt^{IV} ion is in a slightly distorted octahedral coordination geometry formed by two N and four Cl atoms. Two imidazole ligands are in a *cis* orientation. The Pt—Cl bond distances are similar, within 3σ, to other Pt—Cl bond lengths [2.323 (38) Å] in platinum(IV) complexes (Orpen *et al.*, 1989). The Pt—N distances are usual for platinum complexes bearing two *cis*-coordinated *N*-bonded heterocycles, *e.g.* 2.044 (3)–2.055 (5) Å in platinum(IV) complexes (Khripun *et al.*, 2007; Khripun *et al.*, 2006).

The title compound (**1**) represents the first example of the structurally characterized platinum complex having the neutral unsubstituted imidazole ligand and the second example of an imidazole Pt(IV) complex (Kuduk-Jaworska *et al.*, 1988). The dihedral angle between the imidazole rings is 69.9 (2)°. The bond distances and angles in the heterocyclic ligands are in good agreement with those previously observed for imidazole ligands at platinum (Korte *et al.*, 1981; Kuduk-Jaworska *et al.*, 1988; Bayon *et al.*, 1987; Yip *et al.*, 1993) and other transition metal centers (for recent examples see Huo *et al.*, 2004; Chen *et al.*, 2006; Garcia *et al.*, 2000; Hao *et al.*, 2007; Gao *et al.*, 2004). In the crystal, molecules are linked bt N—H···.Cl hydrogen bonds to form a three-dimensional network (Table 2).

Experimental

Complex (**1**) was synthesized by the reaction of *cis*-$[PtCl_4(EtCN)_2]$ with 2 equivs of imidazole in CH_2Cl_2 solution at room temperature. The crystals suitable for X-ray crystallography were obtained from an acetone/toluene solution by a slow evaporation of the solvent at room temperature.

Refinement

The NH hydrogen was initially located in difference Fourier maps but was included in a calculated position as riding with U_{iso} = 1.5 U_{eq}(N). Other H atoms were positioned geometrically and also allowed to ride on their parent atoms, with C—H = 0.95 Å, and U_{iso} = 1.2 U_{eq}(C). The highest peak is located 0.85 Å from atom Pt1 and the deepest hole is located 0.89 Å from atom Pt1.

Computing details

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

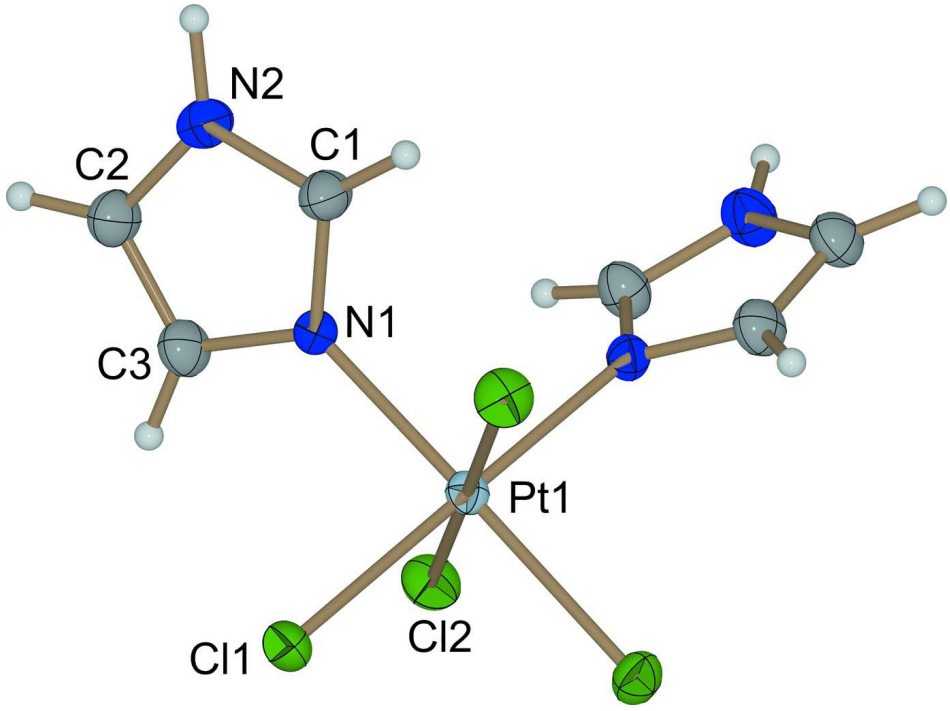

Figure 1

The molecular structure of (**I**), with displacement ellipsoids drawn at the 40% probability level. Unlabled atoms are related by the symmetry operator (-x, y, -z+1/2).

cis-Tetrachloridobis(1*H*-imidazole-κN^3)platinum(IV)

Crystal data

$[PtCl_4(C_3H_4N_2)_2]$
$M_r = 473.05$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 7.7264$ (4) Å
$b = 11.8757$ (6) Å
$c = 12.9471$ (5) Å
$\beta = 93.332$ (3)°
$V = 1185.97$ (10) Å^3
$Z = 4$
$F(000) = 872$
$D_x = 2.649$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4469 reflections
$\theta = 1.0$–$27.5°$
$\mu = 12.70$ mm^{-1}
$T = 120$ K
Plate, yellow
0.15 × 0.13 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Horizontally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
φ scans and ω scans with κ offset
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)

T_{min} = 0.193, T_{max} = 0.411
7759 measured reflections
1362 independent reflections
1275 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

θ_{max} = 27.5°, θ_{min} = 3.2°
h = −9→10
k = −15→15
l = −16→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.037
S = 1.05
1362 reflections
70 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0108P)^2 + 3.3813P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.73 e Å^{-3}

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Pt1	0.0000	0.132240 (14)	0.2500	0.01672 (7)
Cl1	0.07166 (12)	−0.00761 (7)	0.37001 (7)	0.02527 (19)
Cl2	−0.28465 (11)	0.13451 (7)	0.29654 (7)	0.02696 (19)
N1	0.0594 (4)	0.2545 (2)	0.3576 (2)	0.0184 (6)
N2	0.1812 (4)	0.3987 (3)	0.4316 (2)	0.0292 (7)
H2N	0.2549	0.4662	0.4359	0.044*
C1	0.1675 (5)	0.3389 (3)	0.3449 (3)	0.0265 (8)
H1	0.2259	0.3543	0.2838	0.032*
C2	0.0790 (5)	0.3503 (3)	0.5026 (3)	0.0274 (8)
H2	0.0644	0.3754	0.5712	0.033*
C3	0.0036 (5)	0.2603 (3)	0.4555 (3)	0.0266 (8)
H3	−0.0747	0.2097	0.4852	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.01632 (10)	0.01756 (10)	0.01655 (10)	0.000	0.00311 (7)	0.000
Cl1	0.0301 (5)	0.0228 (4)	0.0226 (4)	−0.0022 (3)	−0.0010 (4)	0.0041 (3)
Cl2	0.0199 (4)	0.0313 (5)	0.0303 (5)	−0.0019 (3)	0.0074 (3)	0.0022 (4)
N1	0.0200 (15)	0.0182 (14)	0.0168 (14)	−0.0014 (11)	0.0002 (11)	−0.0001 (11)
N2	0.0340 (18)	0.0251 (15)	0.0287 (17)	−0.0063 (13)	0.0030 (14)	−0.0034 (13)

C1	0.028 (2)	0.0261 (18)	0.025 (2)	−0.0052 (15)	0.0041 (16)	−0.0030 (14)
C2	0.030 (2)	0.0280 (19)	0.0248 (19)	0.0004 (15)	0.0060 (16)	−0.0032 (15)
C3	0.028 (2)	0.0293 (19)	0.0236 (19)	0.0000 (15)	0.0072 (15)	−0.0002 (15)

Geometric parameters (Å, º)

Pt1—N1^{i}	2.046 (3)	N2—C1	1.327 (5)
Pt1—N1	2.046 (3)	N2—C2	1.372 (5)
Pt1—Cl2^{i}	2.3141 (8)	N2—H2N	0.9830
Pt1—Cl2	2.3141 (8)	C1—H1	0.9500
Pt1—Cl1	2.3193 (8)	C2—C3	1.347 (5)
Pt1—Cl1^{i}	2.3193 (8)	C2—H2	0.9500
N1—C1	1.321 (4)	C3—H3	0.9500
N1—C3	1.364 (4)		
N1^{i}—Pt1—N1	89.55 (15)	C1—N1—C3	108.3 (3)
N1^{i}—Pt1—Cl2^{i}	89.63 (8)	C1—N1—Pt1	124.9 (2)
N1—Pt1—Cl2^{i}	89.43 (8)	C3—N1—Pt1	126.7 (2)
N1^{i}—Pt1—Cl2	89.43 (8)	C1—N2—C2	108.8 (3)
N1—Pt1—Cl2	89.63 (8)	C1—N2—H2N	120.1
Cl2^{i}—Pt1—Cl2	178.67 (4)	C2—N2—H2N	131.1
N1^{i}—Pt1—Cl1	178.88 (8)	N1—C1—N2	108.7 (3)
N1—Pt1—Cl1	90.97 (8)	N1—C1—H1	125.7
Cl2^{i}—Pt1—Cl1	89.38 (3)	N2—C1—H1	125.7
Cl2—Pt1—Cl1	91.57 (3)	C3—C2—N2	106.3 (3)
N1^{i}—Pt1—Cl1^{i}	90.97 (8)	C3—C2—H2	126.9
N1—Pt1—Cl1^{i}	178.88 (8)	N2—C2—H2	126.9
Cl2^{i}—Pt1—Cl1^{i}	91.57 (3)	C2—C3—N1	108.0 (3)
Cl2—Pt1—Cl1^{i}	89.38 (3)	C2—C3—H3	126.0
Cl1—Pt1—Cl1^{i}	88.54 (4)	N1—C3—H3	126.0

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···Cl1^{ii}	0.98	2.66	3.355 (3)	128
N2—H2*N*···Cl2^{ii}	0.98	2.70	3.320 (3)	122
N2—H2*N*···Cl1^{iii}	0.98	2.82	3.368 (3)	116

Symmetry codes: (ii) *x*+1/2, *y*+1/2, *z*; (iii) −*x*+1/2, −*y*+1/2, −*z*+1.