

3,3'-{Ethane-1,2-diylbis[carbonyl-bis(azanediyl)]}dipyridinium tetrachloridoplatinate(II)

N. N. Adarsh,^a D. Krishna Kumar^b and Parthasarathi Dastidar^{a*}

^aDepartment of Organic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S C Mullick Road, Jadavpur, Kolkata 700 032, India, and ^bPresent address: Department of Chemistry, Imperial College, London SW7 2AZ, England
Correspondence e-mail: parthod123@rediffmail.com

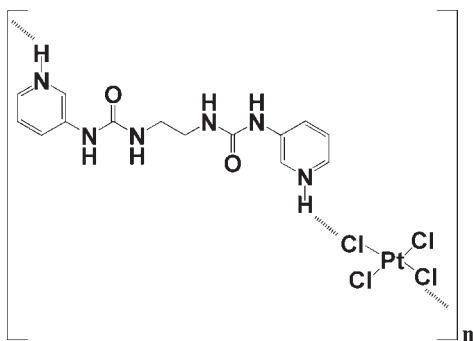
Received 16 January 2010; accepted 3 February 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in main residue; R factor = 0.025; wR factor = 0.064; data-to-parameter ratio = 14.2.

In the crystal structure of the title compound, $(\text{C}_{14}\text{H}_{18}\text{N}_6\text{O}_2)\text{-}[\text{PtCl}_4]$, the cation and square-planar anion are located on special positions (on a twofold axis and an inversion centre, respectively). In the crystal structure, $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds lead to a staircase-like motif. The central ethane backbone of the cation is disordered over two positions of equal occupancy.

Related literature

For organic-inorganic hybrid compounds displaying $\text{N}-\text{H}\cdots\text{Cl}$ -metal hydrogen bonds, see: Adams *et al.* (2007); Deifela & Cahill (2009). Orpen *et al.* (2004); Krishna Kumar *et al.* (2005, 2006).



Experimental

Crystal data

$(\text{C}_{14}\text{H}_{18}\text{N}_6\text{O}_2)[\text{PtCl}_4]$

$M_r = 639.23$

Monoclinic, $C2/c$
 $a = 17.8126$ (13) Å
 $b = 7.0799$ (5) Å
 $c = 15.5765$ (12) Å
 $\beta = 103.332$ (1)°
 $V = 1911.4$ (2) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 7.92$ mm⁻¹
 $T = 100$ K
 $0.22 \times 0.14 \times 0.05$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2006)
 $T_{\min} = 0.275$, $T_{\max} = 0.693$

7045 measured reflections
1877 independent reflections
1693 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.064$
 $S = 0.97$
1877 reflections
132 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.89$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl2}^i$	0.76 (5)	2.55 (5)	3.259 (4)	156 (5)

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

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2 and SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97, publCIF (Westrip, 2010) and PLATON (Spek, 2009).

We thank the Department of Science and Technology (DST), New Delhi, India, for financial support. NNA thanks IACS for research fellowships.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5171).

References

- Adams, C. J., Colquhoun, H. M., Crawford, P. C., Lusi, M. & Orpen, A. G. (2007). *Angew. Chem. Int. Ed.* **46**, 1124–1128.
Bruker (2006). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Deifela, N. P. & Cahill, C. L. (2009). *CrystEngComm*, **11**, 2739–2744.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Krishna Kumar, D., Ballabh, A., Jose, D. A., Dastidar, P. & Das, A. (2005). *Cryst. Growth Des.* **5**, 651–660.
Krishna Kumar, D., Das, A. & Dastidar, P. (2006). *Cryst. Growth Des.* **6**, 216–223.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Orpen, A. G., Podesta, T. J. & Shore, B. J. (2004). *Chem. Eur. J.* **10**, 3783–3791.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Westrip, S. P. (2010). *publCIF*. In preparation.

supplementary materials

Acta Cryst. (2010). E66, m270 [doi:10.1107/S1600536810004253]

3,3'-{Ethane-1,2-diylbis[carbonylbis(azanediy)]}dipyridinium tetrachloridoplatinate(II)

N. N. Adarsh, D. Krishna Kumar and P. Dastidar

Comment

Suitable single crystals of the title compound were obtained by the resultant reaction of **BPEBU** and $[K_2(PtCl_4)]$ in acidic medium (see experimental). The asymmetric unit consists of half of $(PtCl_4)$ and one half molecule of bis-protonated **BPEBU**. The ORTEP diagram with 50% probability is given in Fig. 1. The metal center Pt(II) displayed a slight distorted square planar geometry [$Cl-Pt-Cl = 89.91(4)-90.09(4)^\circ$]. In the crystal structure, the bis-protonated ligand **BPEBU** displays *syn-anti-syn* conformation (scheme 1). $N-H\cdots Cl$ hydrogen bonds lead to a staircase like structure (Fig. 2).

Experimental

Synthesis: The title compound was synthesized by layering a methanolic solution of BPEBU (30 mg, 0.1 mmol) containing HCl (MeOH : HCl = 8 ml : 2 ml) over an aqueous solution of $[K_2(PtCl_4)]$ (41.5 mg, 0.1 mmol) containing HCl ($H_2O : HCl = 8 ml : 2 ml$). After a period of two weeks, X-ray quality single crystals were obtained (yield = 30 mg, 47%). FT-IR (KBr, cm^{-1}): 3325 (b, O—H, N—H stretch), 3082 (b, aromatic C—H stretch), 2965 (b, aliphatic C—H), 1686 (s, urea C=O stretch), 1612 (s, urea N—H bend), 1580, 1520, 1480, 1422, 1331, 1264, 1238, 1191, 1111, 1024, 989, 864, 800, 694.

Refinement

H-atoms bonded to C were refined using a riding model with C—H ranging from 0.95 Å to 0.99 Å and $U(H) = 1.2U_{eq}(C)$. The coordinates of the H atoms bonded to N were refined with $U(H) = 1.2U_{eq}(N)$. The central C—C bond in the cation (located on the 2 fold axis) is disordered over two equally occupied positions.

Figures

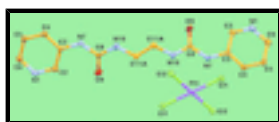


Fig. 1. Ortep diagram of title compound with anisotropic displacement ellipsoids drawn at the 50% probability level. H atoms omitted for clarity.



Fig. 2. Staircase like hydrogen bonded network via $N-H\cdots Cl$ interactions

3,3'-{Ethane-1,2-diylbis[carbonylbis(azanediy)]}dipyridinium tetrachloridoplatinate(II)

Crystal data

(C ₁₄ H ₁₈ N ₆ O ₂)[PtCl ₄]	$F(000) = 1224$
$M_r = 639.23$	$D_x = 2.221 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 17.8126 (13) \text{ \AA}$	Cell parameters from 566 reflections
$b = 7.0799 (5) \text{ \AA}$	$\theta = 2.4\text{--}27.8^\circ$
$c = 15.5765 (12) \text{ \AA}$	$\mu = 7.92 \text{ mm}^{-1}$
$\beta = 103.332 (1)^\circ$	$T = 100 \text{ K}$
$V = 1911.4 (2) \text{ \AA}^3$	Plate, yellow
$Z = 4$	$0.22 \times 0.14 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer	1877 independent reflections
Radiation source: fine-focus sealed tube graphite	1693 reflections with $I > 2\sigma(I)$
φ - ω scan	$R_{\text{int}} = 0.044$
Absorption correction: multi-scan (SADABS; Bruker, 2006)	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$
$T_{\text{min}} = 0.275$, $T_{\text{max}} = 0.693$	$h = -21 \rightarrow 21$
7045 measured reflections	$k = -8 \rightarrow 8$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.025$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.064$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.97$	$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 6.3133P]$
1877 reflections	where $P = (F_o^2 + 2F_c^2)/3$
132 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 1.51 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.89 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pt1	0.5000	0.5000	0.0000	0.01584 (10)	
Cl1	0.39171 (5)	0.65021 (15)	-0.07921 (6)	0.0228 (2)	
Cl2	0.50224 (6)	0.69911 (14)	0.11747 (7)	0.0226 (2)	
N1	0.1742 (2)	-0.0639 (6)	-0.1087 (3)	0.0250 (8)	
H1	0.139 (3)	-0.108 (7)	-0.096 (3)	0.030*	
C2	0.2331 (3)	-0.0133 (5)	-0.0434 (3)	0.0193 (9)	
H2	0.2297	-0.0254	0.0163	0.023*	
C3	0.3001 (2)	0.0577 (6)	-0.0639 (2)	0.0160 (8)	
C4	0.3007 (2)	0.0717 (7)	-0.1528 (3)	0.0223 (8)	
H4	0.3455	0.1183	-0.1690	0.027*	
C5	0.2379 (3)	0.0195 (6)	-0.2176 (3)	0.0305 (12)	
H5	0.2391	0.0310	-0.2781	0.037*	
C6	0.1730 (3)	-0.0497 (7)	-0.1941 (3)	0.0304 (10)	
H6	0.1288	-0.0861	-0.2378	0.036*	
N7	0.36384 (19)	0.1145 (5)	-0.0011 (2)	0.0176 (7)	
C8	0.3757 (2)	0.0918 (6)	0.0896 (3)	0.0214 (9)	
O9	0.3290 (2)	0.0132 (4)	0.1240 (3)	0.0367 (10)	
N10	0.4417 (2)	0.1661 (6)	0.1358 (2)	0.0275 (9)	
C11A	0.4643 (5)	0.2153 (13)	0.2283 (5)	0.0202 (16)*	0.50
H11A	0.4227	0.1819	0.2582	0.024*	0.50
H11B	0.4740	0.3528	0.2351	0.024*	0.50
C11B	0.4631 (5)	0.1063 (12)	0.2315 (5)	0.0185 (16)*	0.50
H11C	0.4728	-0.0314	0.2365	0.022*	0.50
H11D	0.4213	0.1381	0.2614	0.022*	0.50
H7	0.400 (3)	0.164 (6)	-0.020 (3)	0.022*	
H10	0.467 (3)	0.219 (7)	0.116 (3)	0.032*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.01344 (14)	0.01733 (15)	0.01748 (14)	-0.00161 (7)	0.00507 (9)	-0.00225 (7)
Cl1	0.0172 (5)	0.0302 (5)	0.0211 (5)	0.0044 (4)	0.0046 (4)	0.0037 (4)
Cl2	0.0192 (5)	0.0254 (5)	0.0239 (5)	-0.0025 (4)	0.0062 (4)	-0.0096 (4)
N1	0.0220 (19)	0.0246 (19)	0.030 (2)	-0.0071 (16)	0.0105 (16)	-0.0072 (17)
C2	0.019 (2)	0.019 (2)	0.021 (2)	-0.0005 (14)	0.0066 (19)	-0.0024 (15)
C3	0.020 (2)	0.0134 (17)	0.0147 (19)	0.0009 (16)	0.0045 (16)	-0.0006 (16)
C4	0.020 (2)	0.030 (2)	0.018 (2)	-0.0010 (18)	0.0067 (17)	-0.0012 (18)
C5	0.023 (3)	0.050 (3)	0.018 (2)	0.0020 (19)	0.004 (2)	-0.0089 (18)
C6	0.023 (2)	0.040 (2)	0.026 (3)	-0.002 (2)	0.003 (2)	-0.017 (2)

supplementary materials

N7	0.0184 (17)	0.0221 (18)	0.0135 (16)	-0.0055 (13)	0.0064 (14)	0.0016 (13)
C8	0.019 (2)	0.033 (2)	0.0128 (19)	0.0068 (17)	0.0043 (16)	0.0044 (17)
O9	0.028 (2)	0.063 (3)	0.0219 (18)	-0.0011 (14)	0.0108 (16)	0.0151 (14)
N10	0.022 (2)	0.046 (2)	0.0143 (18)	-0.0013 (16)	0.0037 (15)	-0.0045 (16)

Geometric parameters (\AA , $^\circ$)

Pt1—C11 ⁱ	2.2971 (9)	C6—H6	0.9500
Pt1—C11	2.2971 (9)	N7—C8	1.389 (5)
Pt1—C12 ⁱ	2.3028 (9)	N7—H7	0.83 (5)
Pt1—C12	2.3028 (9)	C8—O9	1.223 (5)
N1—C6	1.330 (6)	C8—N10	1.337 (6)
N1—C2	1.331 (6)	N10—C11A	1.447 (8)
N1—H1	0.76 (5)	N10—C11B	1.511 (9)
C2—C3	1.397 (6)	N10—H10	0.71 (5)
C2—H2	0.9500	C11A—C11B ⁱⁱ	1.513 (10)
C3—N7	1.377 (5)	C11A—H11A	0.9900
C3—C4	1.392 (5)	C11A—H11B	0.9900
C4—C5	1.374 (7)	C11B—C11A ⁱⁱ	1.513 (10)
C4—H4	0.9500	C11B—H11C	0.9900
C5—C6	1.380 (7)	C11B—H11D	0.9900
C5—H5	0.9500		
C11 ⁱ —Pt1—C11	180.0	C3—N7—C8	126.6 (3)
C11 ⁱ —Pt1—C12 ⁱ	90.11 (4)	C3—N7—H7	116 (3)
C11—Pt1—C12 ⁱ	89.89 (4)	C8—N7—H7	117 (3)
C11 ⁱ —Pt1—C12	89.89 (4)	O9—C8—N10	123.1 (4)
C11—Pt1—C12	90.11 (4)	O9—C8—N7	122.6 (4)
C12 ⁱ —Pt1—C12	180.0	N10—C8—N7	114.3 (4)
C6—N1—C2	124.9 (4)	C8—N10—C11A	129.8 (5)
C6—N1—H1	118 (4)	C8—N10—C11B	114.3 (4)
C2—N1—H1	117 (4)	C11A—N10—C11B	30.3 (4)
N1—C2—C3	119.0 (4)	C8—N10—H10	122 (4)
N1—C2—H2	120.5	C11A—N10—H10	105 (4)
C3—C2—H2	120.5	C11B—N10—H10	123 (4)
N7—C3—C4	119.4 (4)	N10—C11A—C11B ⁱⁱ	107.6 (6)
N7—C3—C2	123.4 (4)	N10—C11A—H11A	110.2
C4—C3—C2	117.2 (4)	C11B ⁱⁱ —C11A—H11A	110.2
C5—C4—C3	121.3 (4)	N10—C11A—H11B	110.2
C5—C4—H4	119.3	C11B ⁱⁱ —C11A—H11B	110.2
C3—C4—H4	119.3	H11A—C11A—H11B	108.5
C4—C5—C6	119.4 (5)	N10—C11B—C11A ⁱⁱ	105.2 (5)
C4—C5—H5	120.3	N10—C11B—H11C	110.7
C6—C5—H5	120.3	C11A ⁱⁱ —C11B—H11C	110.7
N1—C6—C5	118.1 (4)	N10—C11B—H11D	110.7
N1—C6—H6	121.0	C11A ⁱⁱ —C11B—H11D	110.7
C5—C6—H6	121.0	H11C—C11B—H11D	108.8

C6—N1—C2—C3	-1.1 (7)	C3—N7—C8—O9	1.0 (7)
N1—C2—C3—N7	179.7 (4)	C3—N7—C8—N10	-177.7 (4)
N1—C2—C3—C4	0.2 (6)	O9—C8—N10—C11A	-17.3 (8)
N7—C3—C4—C5	-178.9 (4)	N7—C8—N10—C11A	161.5 (6)
C2—C3—C4—C5	0.6 (6)	O9—C8—N10—C11B	13.7 (7)
C3—C4—C5—C6	-0.5 (7)	N7—C8—N10—C11B	-167.5 (5)
C2—N1—C6—C5	1.2 (7)	C8—N10—C11A—C11B ⁱⁱ	122.2 (6)
C4—C5—C6—N1	-0.3 (7)	C11B—N10—C11A—C11B ⁱⁱ	53.4 (10)
C4—C3—N7—C8	-172.8 (4)	C8—N10—C11B—C11A ⁱⁱ	-176.5 (5)
C2—C3—N7—C8	7.7 (6)	C11A—N10—C11B—C11A ⁱⁱ	-48.3 (10)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots C12 ⁱⁱⁱ	0.76 (5)	2.55 (5)	3.259 (4)	156 (5)

Symmetry codes: (iii) $-x+1/2, -y+1/2, -z$.

Fig. 1

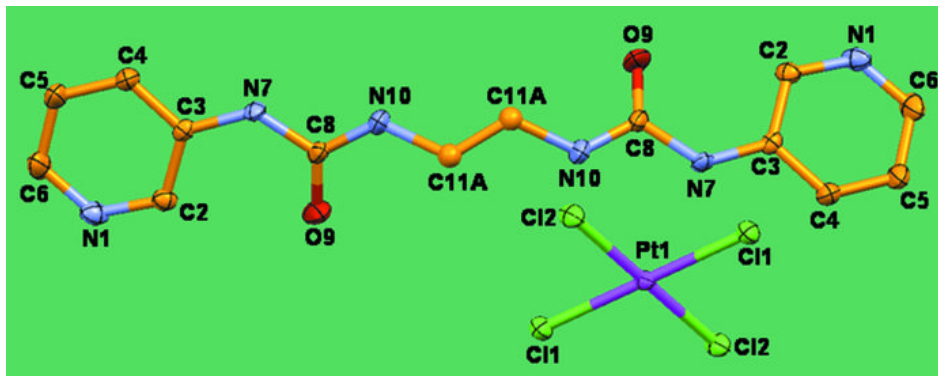


Fig. 2

