Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Redetermination of *catena*-poly[[[bis(ethylenediamine)platinum(II)]-μ-chloro-[bis(ethylenediamine)platinum(IV)]-μ-chloro] tetrakis(hexafluorophosphate)]

Nobuyuki Matsushita

Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Meguro, 153-8902 Tokyo, Japan

Correspondence e-mail:
cnmatsu@mail.ecc.u-tokyo.ac.jp

Received 26 May 2005
Accepted 6 June 2005
Online 10 June 2005

The structure of the title compound, $\{[\mathrm{Pt^{II/IV}Cl}(\mathrm{C_2H_8N_2})_2](\mathrm{PF_6})_2\}_n$ or $[\mathrm{Pt^{II}}(\mathrm{C_2H_8N_2})_2][\mathrm{Pt^{IV}Cl_2}(\mathrm{C_2H_8N_2})_2](\mathrm{PF_6})_4$, has been redetermined [Matsushita (1993). *Synth. Met.* **56**, 3401–3406] from image-plate data. No superstructure was observed, in contrast to the situation in related compounds. The linear chain structure consists of square-planar $[\mathrm{Pt(en)_2}]^{2+}$ and elongated octahedral *trans*-$[\mathrm{PtCl_2(en)_2}]^{2+}$ cations (en is ethylenediamine) stacked alternately, bridged by the Cl atoms, along the *b* axis. The Pt atom is located on an inversion centre and the Cl atom (site symmetry 2) is disordered over two sites, resulting in $\mathrm{Pt^{IV}}$–Cl and $\mathrm{Pt^{II}}\cdots$Cl bond distances of 2.327 (4) and 3.191 (4) Å, respectively. The δ structural parameter, indicating the mixed-valence state of the Pt atoms, is 0.729.

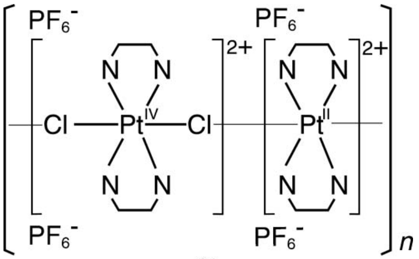
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(P–F) = 0.007 Å
Disorder in main residue
R factor = 0.030
wR factor = 0.087
Data-to-parameter ratio = 20.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, $[\mathrm{Pt(en)_2}][\mathrm{PtCl_2(en)_2}](\mathrm{PF_6})_4$ (en is ethylenediamine), (I), is a member of the class of one-dimensional halogen-bridged mixed-valence metal complexes, formulated as $[M^{\rm II}(AA)_2][M^{\rm IV}X_2(AA)_2]Y_4$ [$M^{\rm II}/M^{\rm IV}$ = $\mathrm{Pt^{II}/Pt^{IV}}$, $\mathrm{Pd^{II}/Pd^{IV}}$, $\mathrm{Ni^{II}/Ni^{IV}}$, $\mathrm{Pd^{II}/Pt^{IV}}$ and $\mathrm{Ni^{II}/Pt^{IV}}$; X = Cl, Br and I; AA = $\mathrm{NH_2(CH_2)_2NH_2}$ *etc.*; Y = $\mathrm{ClO_4}^-$, $\mathrm{HSO_4}^-$, X^- *etc.*], hereafter abbreviated as *MX*-chain compounds, which are typical mixed-valence compounds belonging to class II in the classification of Robin & Day (1967). The present X-ray crystallographic analysis of (I) was performed in order to gather further structural information on these *MX*-chain compounds. We have already reported the crystal data of (I) and some of the bond distances (Matsushita, 1993). As the unit-cell volume of (I) measured in 1993 was a quarter of the volume of typical *MX*-chain compounds, we have remeasured intensity data using an image-plate diffractometer for the purpose of searching for weak reflections indicating a doubling or other superstructure of the unit cell. However, no superstructure reflections were observed.



(I)

We report here the full structure determination of (I) using the new data set with consequent improvement in precision for the geometric parameters. In particular, the Pt–Cl chain

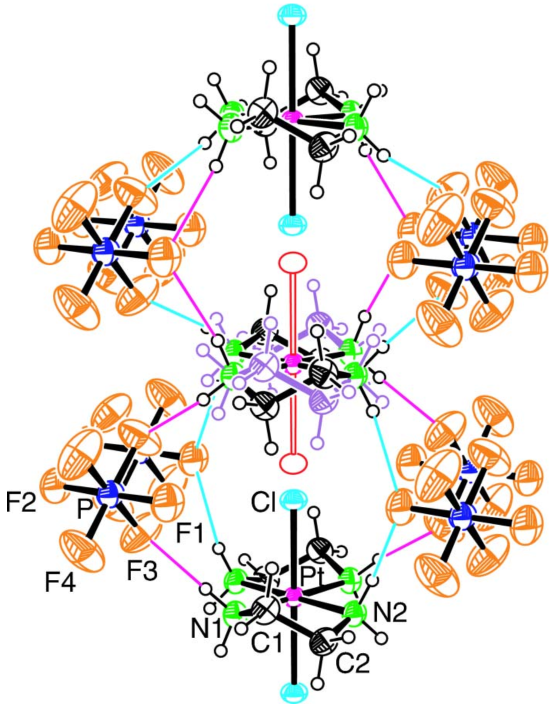


Figure 1
A view of the columnar structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level for non-H atoms. Red ellipsoids and bonds represent the disordered structure of the Pt–Cl chain. For the central Pt complex, the other conformation of the disordered chelate ring is represented by purple ellipsoids and bonds. Magenta and cyan lines represent the N1···F and N2···F hydrogen bonds, respectively.

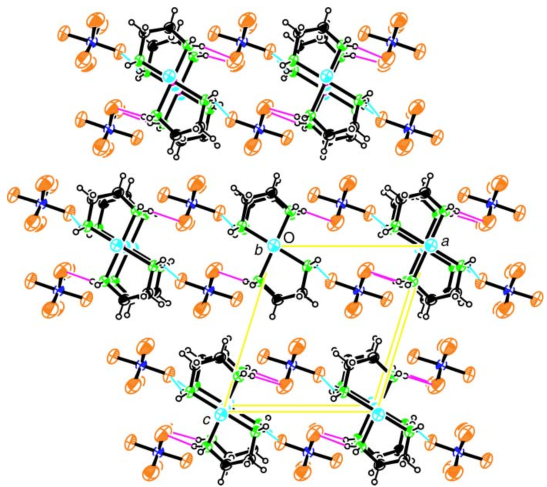


Figure 2
The crystal packing of the title compound viewed along the *b* axis. The minor disorder component has been omitted for clarity. Magenta and cyan lines indicate the N···F hydrogen bonds.

structure and the crystal packing of (I) are reported in detail. As shown in Fig. 1, the structure of (I) is built up from columns composed of square-planar $[Pt(en)_2]^{2+}$ and elongated octahedral *trans*-$[PtCl_2(en)_2]^{2+}$ cations stacked alternately, bridged by the Cl^- ions, along the *b* axis. In each column, an infinite $\cdots Cl–Pt^{IV}—Cl\cdots Pt^{II}\cdots$ chain is present. The Pt and Cl atoms lie on the twofold axis and form a straight chain. The Cl atoms are not located at the exact mid-point between the adjacent Pt atoms at the inversion centre at $(0, \frac{1}{2}, 0)$ and equivalent positions, but are disordered over two sites close to the mid-point. An ethylene grouping of the chelate ring of the $[Pt(en)_2]$ group is also disordered over two conformations as a result of the Pt complex being located on a site of crystallographic symmetry $2/m$.

Each Pt site is occupied by a disordered combination of Pt^{II} and Pt^{IV}. The valence ordering of the Pt site in (I) belongs to one of three different classes of the order-disorder problem pointed out by Keller (1982); the structure of (I) can be regarded as being of the one-dimensionally ordered structure type, with the other two directions being in a disordered state. The structural order–disorder situation of the Pt site in (I) has been observed in a number of other *MX*-chain compounds (Beauchamp *et al.*, 1982; Yamashita *et al.*, 1985; Toriumi *et al.*, 1986; Matsushita *et al.*, 1992; Toriumi *et al.*, 1993; Huckett *et al.*, 1993; Matsushita, 2003, 2005).

With respect to the two sites for the disordered Cl atom, the shorter Pt—Cl distance [2.327 (4) Å] is assigned to $Pt^{IV}—Cl$ and the longer one [3.191 (4) Å] to $Pt^{II}\cdots Cl$. The structural parameter indicating the mixed-valence state of the Pt atom, expressed by $\delta = (Pt^{IV}—Cl)/(Pt^{II}\cdots Cl)$, is 0.729. This value is smaller than those of $[Pt(en)_2][PtCl_2(en)_2]Y_4$ [0.739 for $Y = HSO_4$ (Matsushita, 2003), 0.750 for $Y = ClO_4$ (Huckett *et al.*, 1993) and 0.760 for $Y = BF_4$ (Matsushita, 2005)]. A similar relation between values of the δ parameter of palladium complexes belonging to *MX*-chain compounds, $[Pd^{II}L]$-$[Pd^{IV}Cl_2L]Y_4$ (*L* is 1,4,8,11-tetraazacyclotetradecane) [0.66 for $Y = PF_6$ and 0.72 for $Y = ClO_4$; Toriumi *et al.*, 1986), has been reported. The δ parameter, which correlates well with the energy position of the inter-valence charge transfer absorption band (Matsushita, 1993), depends on the radius of the counter-anion, as described previously (Matsushita *et al.*, 1995).

Table 2 lists the N—H··· F hydrogen bonds which stabilize the columnar structure composed only of cationic complexes (Fig. 1). A $[Pt^{II/IV}(en)_2]$ group is bound to an adjacent Pt complex in the column by the hydrogen-bond linkage, NH···counter-anion···HN. Its number between the complex units depends on the conformational disorder of the chelate ring in (I), and the maximum number is 4. A similar system of four hydrogen-bond linkages has been also observed in $[Pt(en)_2][PtCl_2(en)_2]Y_4$ [$Y = HSO_4$ (Matsushita, 2003) and BF_4 (Matsushita, 2005)]. In (I), there are two kinds of binding relation between the adjacent Pt complex units in respect of the hydrogen-bond linkage; one relation is composed of two N1—H1*A*···F3—P—F3···H1*A*—N1 linkages and two N2—H2*B*···F2···H2*B*—N2 linkages, and the other is composed of two N1—H1*B*···F1···H1*B*—N1 linkages and two N2—H2*A*···F3—P—F3···H2*A*—N2 linkages. An N1—H1*A*···F3—P—F1···H1*B*—N1 hydrogen-bond linkage is also possible, depending on the conformational disorder of the chelate ring. The crystal packing is further stabilized by intercolumnar hydrogen-bond linkages, as shown in Fig. 2. The network of the intercolumnar hydrogen-bond linkage of (I) is two-dimensional, while that of $[Pt(en)_2][PtCl_2(en)_2]Y_4$ ($Y = HSO_4$ and BF_4) is three-dimensional. Seven columns have been drawn viewed along the column in Fig. 2 in order to compare easily with the column packing of $[Pt(en)_2][PtCl_2(en)_2]Y_4$ (Y = HSO_4 and BF_4) in the published drawing (Matsushita, 2003, 2005).

Experimental

Compound (I) was prepared using the published procedure (Matsushita, 1993). Orange prismatic crystals were obtained by recrystallization from an aqueous solution on slow evaporation.

Crystal data

$[PtCl(C_2H_8N_2)_2](PF_6)_2$
M_r = 640.69
Monoclinic, $P2/m$
a = 8.193 (3) Å
b = 5.518 (2) Å
c = 9.233 (4) Å
β = 107.33 (3)°
V = 398.5 (3) Å^3
Z = 1

D_x = 2.67 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10346 reflections
θ = 3.7–32.6°
μ = 9.30 mm^{-1}
T = 296 K
Prism, orange
0.17 × 0.15 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.184, T_{max} = 0.248
10579 measured reflections

1547 independent reflections
1547 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 32.6°
$h = -12 \rightarrow 12$
$k = -7 \rightarrow 8$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.087
S = 1.19
1547 reflections
77 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.7131P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.49 e Å^{-3}
$\Delta\rho_{min}$ = −2.87 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.031 (3)

Table 1
Selected geometric parameters (Å, °).

Pt—Cl	2.327 (4)	P—F1	1.596 (6)
Pt—Cl^i	3.191 (4)	P—F2	1.605 (6)
Pt—N1	2.047 (6)	P—F3	1.593 (6)
Pt—N2	2.048 (6)	P—F4	1.554 (6)
N1—Pt—N2	83.1 (3)	F2—P—F3	88.9 (3)
C1—N1—Pt	108.8 (5)	F2—P—F4	91.4 (3)
C2—N2—Pt	109.2 (5)	F3—P—F4	90.0 (4)
F1—P—F2	178.0 (4)	F3—P—F3^{ii}	89.2 (6)
F1—P—F3	89.7 (3)	F3—P—F4^{ii}	179.1 (5)
F1—P—F4	90.0 (3)	F4—P—F4^{ii}	90.8 (7)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···F3^{iii}	0.90	2.13	2.996 (8)	162
N1—H1B···F1^{iv}	0.90	2.30	3.186 (5)	171
N2—H2A···F3^{v}	0.90	2.47	3.258 (8)	146
N2—H2B···F2	0.90	2.32	3.149 (4)	154

Symmetry codes: (iii) $x-1, y, z$; (iv) $x-1, y-1, z$; (v) $-x+1, -y, -z$.

The H atoms were placed in geometrically calculated positions and refined as riding (C—H = 0.97 Å and N—H = 0.90 Å), with the constraint $U_{iso}(H) = 1.5U_{eq}(C,N)$. The largest electron density peak and hole lie within 0.68 Å of the Pt atom.

Data collection: *RAPID-AUTO* (Rigaku, 2002); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This work was partly supported by a Grant-in-Aid for Scientific Research (A) Project No. 12354008 from the Japan Society for the Promotion of Science.

References

Beauchamp, A. L., Layek, D. & Theophanides, T. (1982). *Acta Cryst.* B**38**, 1158–1164.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Huckett, S. C., Scott, B., Love, S. P., Donohoe, R. J., Burns, C. J., Grcia, E., Frankcom, T. & Swanson B. I. (1993). *Inorg. Chem.* **32**, 2137–2144.
Keller, H. J. (1982). *Extended Linear Chain Compounds*, edited by J. S. Miller, pp. 357–407. New York: Plenum.
Matsushita, N. (1993). *Synth. Met.* **56**, 3401–3406.
Matsushita, N. (2003). *Acta Cryst.* E**59**, m26–m28.
Matsushita, N. (2005). *Acta Cryst.* E**61**, m514–m516.
Matsushita, N., Kitagawa, H. & Mitani, T. (1995). *Synth. Met.* **71**, 1933–1934.
Matsushita, N., Taga, T. & Tsujikawa, I. (1992). *Acta Cryst.* C**48**, 1936–1939.
Rigaku (2002). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Robin, M. B. & Day, P. (1967). *Advances in Inorganic Chemistry and Radiochemistry,* edited by H. J. Emeléus & A. G. Sharpe, Vol. 10, pp. 247–422. New York: Academic Press.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Toriumi, K., Yamashita, M., Ito, H. & Ito, T. (1986). *Acta Cryst.* C**42**, 963–968.
Toriumi, K., Yamashita, M., Kurita, S., Murase, I. & Ito, T. (1993). *Acta Cryst.* B**49**, 497–506.
Yamashita, M., Toriumi, K. & Ito, T. (1985). *Acta Cryst.* C**41**, 876–878.