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A one-dimensional Cl-bridged Pt^{II}/Pt^{IV} mixed-valence complex, *catena*-poly[[[bis(ethylenediamine)-platinum(II)]-μ-chloro-[bis(ethylenediamine)-platinum(IV)]-μ-chloro] tetrakis(tetrafluoroborate)]

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

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The title compound, $\{[Pt_2Cl_2(C_2H_8N_2)_4](BF_4)_4\}_n$ or $[Pt^{II}(C_2H_8N_2)_2][Pt^{IV}Cl_2(C_2H_8N_2)_2](BF_4)_4$, has a linear chain structure composed of square-planar $[Pt(en)_2]^{2+}$ and elongated octahedral *trans*-$[PtCl_2(en)_2]^{2+}$ cations (en is ethylenediamine) stacked alternately, bridged by the Cl atoms, along the *c* axis. The Cl atom bridging the adjacent Pt atoms is disordered over two sites along the $\cdots Cl—Pt^{IV}—Cl\cdots Pt^{II}\cdots$ chain, which lies on a twofold axis. The $Pt^{IV}—Cl$ and $Pt^{II}\cdots Cl$ bond distances are 2.319 (3) and 3.052 (3) Å, respectively. A structural parameter indicating the mixed-valence state of the Pt atom, expressed by $\delta = (Pt^{IV}—Cl)/(Pt^{II}\cdots Cl)$, is 0.760.

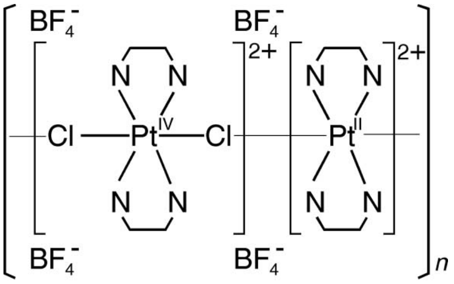
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.011 Å
Disorder in main residue
R factor = 0.026
wR factor = 0.068
Data-to-parameter ratio = 19.6

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

Comment

The title compound, (I), is a member of the class of one-dimensional halogen-bridged mixed-valence metal complexes, formulated as $[M^{II}(AA)_2][M^{IV}X_2(AA)_2]Y_4$ [where $M^{II}—M^{IV}$ = $Pt^{II}—Pt^{IV}$, $Pd^{II}—Pd^{IV}$, $Ni^{II}—Ni^{IV}$, $Pd^{II}—Pt^{IV}$, $Ni^{II}—Pt^{IV}$; X = Cl^-, Br^-, I^-; $AA = NH_2(CH_2)_2NH_2$, *etc.*; $Y = ClO_4^-$, HSO_4^-, X^-, *etc.*], hereinafter abbreviated as *MX*-chain compounds, which are typical mixed-valence compounds belonging to Class II in the classification of mixed-valence compounds of Robin & Day (1967). *MX*-chain compounds have attracted much interest, as a result of their one-dimensional mixed-valence electron systems. Unusual physical properties, such as a remarkably dichroic intense absorption band attributed to an intervalence charge-transfer (IVCT) transition from M^{II} to M^{IV} in the mixed-valence state, progressive Raman scattering in resonance with the IVCT band, and photoinduced mid-gap absorption bands due to soliton and polaron formation, are characteristics of the one-dimensional mixed-valence system. The metal–halogen distances in crystals of *MX*-chain compounds structurally characterize these physical properties based on the mixed-valence state.



(I)

The present X-ray crystallographic analysis of the title compound, (I), $[Pt(en)_2][PtCl_2(en)_2](BF_4)_4$ (en is ethylenediamine), was performed in order to gather further structural

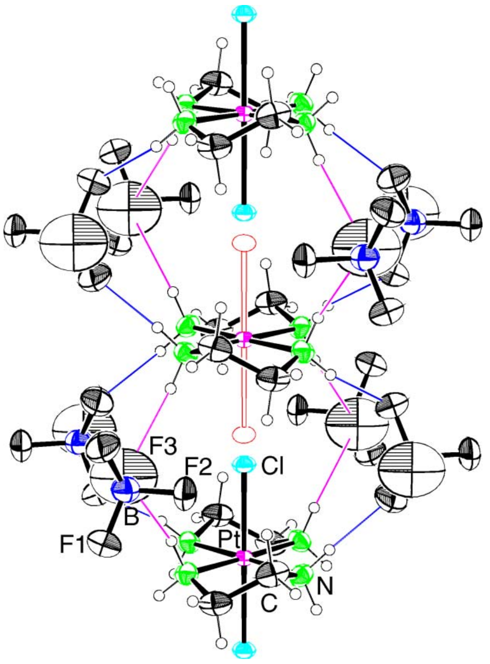


Figure 1
A view of the columnar structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Red ellipsoids and bonds represent the disordered structure of the Pt—Cl chain. The major orientation of the disordered BF_4^- ion is shown, while the minor one has been omitted for clarity. Blue and magenta lines represent N$\cdots$F1 and N$\cdots$F3 hydrogen bonds, respectively.

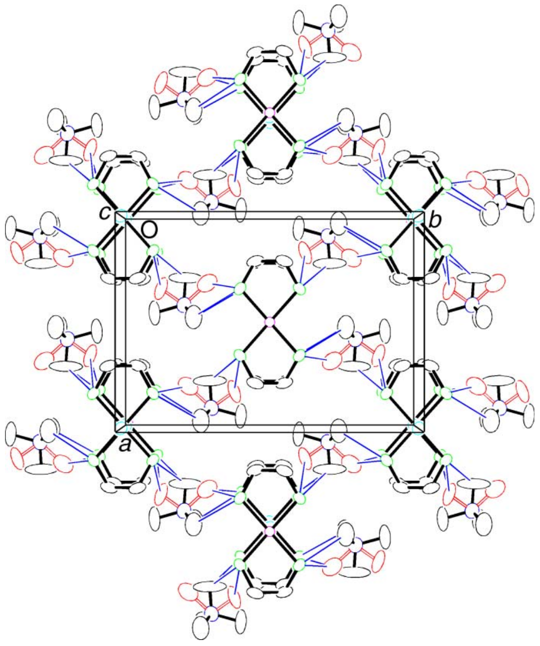


Figure 2
The crystal packing of (I), viewed along the *c* axis. Disordered F atoms of the BF_4^- are represented by red ellipsoids and bonds. H atoms have been omitted for clarity. Blue lines indicate the N$\cdots$F hydrogen bonds.

information on these *MX*-chain compounds. We have already reported the crystal data of (I) and some of the bond distances (Matsushita *et al.*, 1995). Here, we report the full structure determination of (I) based on refinement against F^2, rather than F as in the previous study, with consequent improvement in precision for the geometrical parameters. In particular, the Pt–Cl chain 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 comprising 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 *c* axis. In the column, an infinite $\cdots Cl—Pt^{IV}—Cl\cdots Pt^{II}\cdots$ chain is present along the *c* axis. The Pt and Cl atoms lie on the same twofold axis and form a straight chain. The Cl atoms are not located at the exact midpoint between adjacent Pt atoms and are disordered over two sites close to the midpoint. Thus, 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, 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 which crystallize in the same space group as (I) (Beauchamp *et al.*, 1982; Yamashita *et al.*, 1985; Matsushita *et al.*, 1992; Toriumi *et al.*, 1993; Huckett *et al.*, 1993; Matsushita, 2003).

Corresponding to the two sites for the disordered Cl atoms, the shorter Pt—Cl distance [2.319 (3) Å] is assigned to $Pt^{IV}—Cl$ and the longer one [3.052 (3) 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 0.760. The δ parameter, which correlates well with the position of the IVCT 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$\cdots$F hydrogen bonds [N$\cdots$F1 2.973 (8) Å and N$\cdots$F3 3.252 (16) Å] which stabilize the columnar structure composed only of cationic complexes, as shown in Fig. 1. A $[Pt^{II/IV}(en)_2]$ moiety is bound to an adjacent Pt-complex moiety in the column by four hydrogen-bond linkages. Two of these are N—H2$\cdots$F1—B—F1$\cdots$H2—N, represented with blue lines in Fig. 1, and the others are N—H1$\cdots$F3$\cdots$H1—N, represented with magenta lines. Intercolumnar hydrogen-bond linkages stabilize the crystal packing, as shown in Fig. 2.

The BF_4^- counter-anion is disordered over two orientations. Atoms F2 and F3 of the BF_4^- ion have two possible positions, the major one with 60% occupancy. The orientational disorder of the counter-anion is also observed in the corresponding *MX*-chain compounds having ClO_4^- (Toriumi *et al.*, 1993; Huckett *et al.*, 1993) and HSO_4^- (Matsushita, 2003) as the counter-anion. The orientation of the disordered BF_4^- ion is the same as that of the ClO_4^- ion, but is different from that of the HSO_4^- ion.

Experimental

Compound (I) was prepared using the published procedure of Matsushita *et al.* (1989). Intense-red elongated block-like crystals were obtained by recrystallization from an aqueous solution on slow evaporation.

Crystal data

$[Pt_2Cl_2(C_2H_8N_2)_4](BF_4)_4$
$M_r = 1048.74$
Orthorhombic, *Ibam*
$a = 9.580$ (2) Å
$b = 13.416$ (2) Å
$c = 10.743$ (2) Å
$V = 1380.7$ (4) Å^3
$Z = 2$
$D_x = 2.523$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.5$–$14.8°$
$\mu = 10.44$ mm^{-1}
$T = 295$ K
Block, intense red
0.33 × 0.30 × 0.15 mm

Data collection

Rigaku AFC-5S diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (Coppens *et al.*, 1965)
$T_{min} = 0.077$, $T_{max} = 0.255$
3523 measured reflections
1311 independent reflections
821 reflections with $F^2 > 2\sigma(F^2)$

$R_{int} = 0.023$
$\theta_{max} = 32.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 16$
3 standard reflections
every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.068$
$S = 1.07$
1311 reflections
67 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.52$ e Å^{-3}
$\Delta\rho_{min} = -1.33$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0063 (3)

Table 1

Selected geometric parameters (Å, °).

Pt—N	2.049 (4)	Cl—Pt^i	3.052 (3)
Pt—Cl	2.319 (3)		
N—Pt—N^{ii}	83.1 (2)	N—Pt—Cl	89.43 (12)

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N—H2···F1	0.90	2.12	2.973 (8)	158
N—H1···F3	0.90	2.41	3.252 (16)	157
N—H2···F3′	0.90	2.35	3.134 (15)	146
N—H1···F2′	0.90	2.45	3.172 (17)	137

Refinement based on an ordered model of the BF_4^- ion gave elongated anisotropic displacement parameters (ADPs) for atoms F2 and F3, which suggested two separate positions. A disordered model of atoms F2 (F2′) and F3 (F3′), equally occupied, still gave large ADPs for F2′ and F3′. Refinement of the occupancy of atoms F2 (F2′) and F3 (F3′) converged to 60% (40%) and gave improved ADPs. In the final refinement, their occupancies were fixed. The H atoms were located at 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 0.97 Å of the Pt atom.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1987); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: local program; program(s) used to solve structure: *UNICS3* (Sakurai & Kobayashi, 1979); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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