metal-organic papers

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

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The title compound, [PtCl$_2$(C$_2$H$_8$N$_2$)$_4$](HSO$_4$)$_4$ or [Pt(C$_2$H$_8$N$_2$)$_2$][Pt$_2$Cl$_2$(C$_2$H$_8$N$_2$)$_2$](HSO$_4$)$_4$, 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 lengths are 2.323 (2) and 3.142 (2) Å, respectively. A structural parameter $\delta = (Pt^{IV}—Cl)/(Pt^{II}\cdots Cl)$, indicating the mixed-valence state of the Pt atom ($\delta = 0.739$), shows a good correlation with the data of the intervalence charge-transfer (IVCT) absorption band.

Comment

The title compound, (I), is a member of the one-dimensional halogen-bridged mixed-valence metal complexes, formulated as [M^{II}(AA)$_2$][$M^{IV}X_2$(AA)$_2$]Y_4 [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$_2$)$_2$NH$_2$ *etc.*; Y = ClO$_4^-$, BF$_4^-$, X^- *etc.*], hereafter 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 been attracting much interest as a result of the one-dimensional mixed-valence

(I)
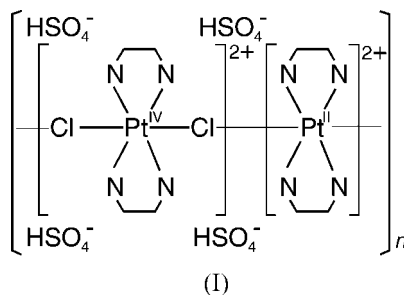
electron system. In MX-chain compounds, a remarkably dichroic intense absorption band attributed to an intervalence charge-transfer (IVCT) transition from 'M^{II}' to 'M^{IV}' in the mixed-valence state, progressive Raman scattering in resonace with the IVCT band, photoinduced mid-gap absorption bands due to soliton and polaron, and so on, are characteristics of the one-dimensional mixed-valence system. The metal–halogen distances in crystals of the MX-chain compounds structurally characterize these physical properties based on the mixed-valence state. X-ray crystallography of the title compound, (I), [Pt(en)$_2$][PtCl$_2$(en)$_2$](HSO$_4$)$_4$ (en = ethylenediamine), was performed to collect structural information for the MX-chain compounds. We have already reported the crystal data of (I)
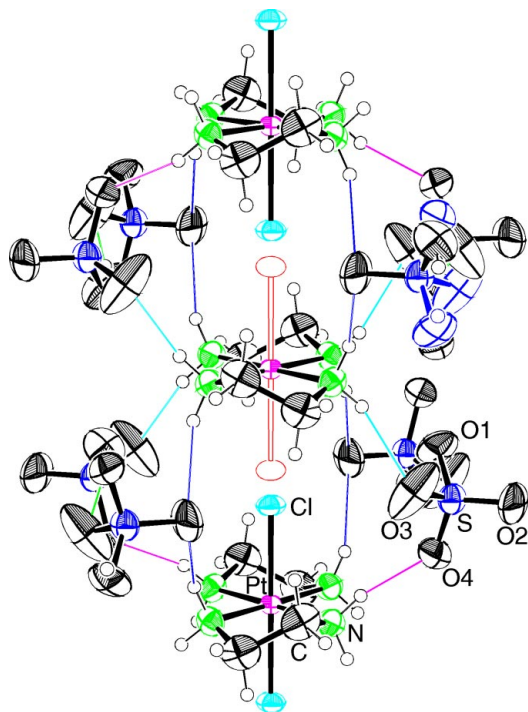
Figure 1
A view of the columnar structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. The red ellipsoids and bonds represent the disordered structure of the Pt—Cl chain. Another orientation of the disordered HSO_4^- ion is represented by blue ellipsoids and bonds for one of eight sites of the HSO_4^- ions drawn here; the other orientation of the disordered HSO_4^- ions at the other sites has been omitted for clarity. Blue, cyan, magenta and green lines represent $N\cdots O2$, $N\cdots O3$, $N\cdots O4$ and $O1\cdots O3$ hydrogen bonds, respectively.

Figure 2
The crystal packing of the title compound viewed along the c axis. H atoms and one orientation of the disordered HSO_4^- ion have been omitted for clarity. Blue and green lines indicate the $N\cdots O$ and $O\cdots O$ hydrogen bonds, respectively.

and some of the bond distances (Matsushita, Toriumi & Kojima, 1992; Matsushita, 1993). This paper is the full report of the crystal structure of (I). Although the refinements were performed on F in the previous reports, the refinement was performed on F^2 in the present study. This change gives an improved R factor, and the s.u. values for the bond distances and angles decrease. Also, the geometry of the counter-ion, HSO_4^- and its disordered structure have been elucidated. 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 of 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 atoms, along the c axis. In the column, an infinite chain of $\cdots Cl-Pt^{IV}-Cl\cdots Pt^{II}\cdots$ 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 the adjacent two Pt atoms and are disordered over two sites close to the midpoint. Thus, each Pt site is occupied by Pt^{II} and Pt^{IV} in a disordered state. The valence order of the Pt site in this structure belongs to one of three different classes of the order–disorder problem pointed out by
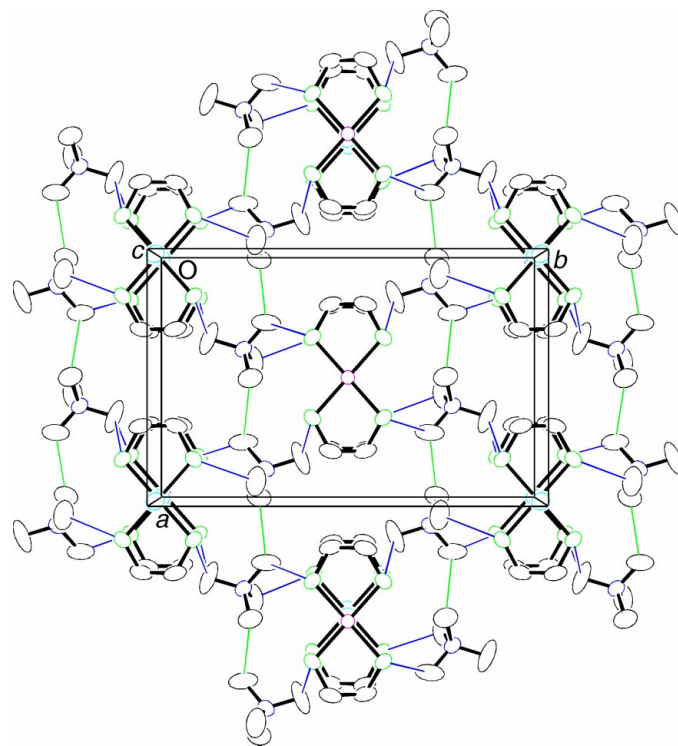
Keller (1982); namely, the structure can be regarded as the one-dimensionally ordered structure with the two other directions in a disordered state. The structural order–disorder situation of the Pt site in (I) is the same as one reported in some MX-chain compounds which crystallize in the same space group as the title compound (Beauchamp *et al.*, 1982; Yamashita *et al.*, 1985; Matsushita, Taga & Tsujikawa, 1992; Toriumi *et al.*, 1993; Huckett *et al.*, 1993).

Corresponding to the two sites for the disordered Cl atoms, the shorter Pt—Cl distance [2.323 (2) Å] is assigned to Pt^{IV}—Cl and the longer one [3.142 (2) Å] to $Pt^{II}\cdots$Cl. A structural parameter indicating the mixed-valence state of the Pt atom, expressed by $\delta = (Pt^{IV}-Cl)/(Pt^{II}\cdots Cl)$, is 0.739. This value correlates well with the data of the IVCT absorption band (Matsushita, 1993).

Hydrogen bonds [$N\cdots O4 = 2.860\,(11)$ Å, $N\cdots O3 = 3.002\,(12)$ Å and $N\cdots O2 = 3.182\,(5)$ Å] stabilize the columnar structure composed of only 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 linkages of the hydrogen bonds. Two linkages are $N-H1N\cdots O2\cdots H1N-N$, represented with two blue lines in Fig. 1, and the others are $N-H2N\cdots O3-S-O4\cdots H2N-N$, represented with a cyan line and a magenta line. Intercolumnar linkages of the hydrogen bonds and another hydrogen bond [$O1\cdots O3 =$

2.848 (14) Å] between the counter-anions stabilize the crystal packing, as shown in Fig. 2.

The counter-anion, HSO_4^-, is disordered over two orientation. Atoms O1, O3 and O4 of the HSO_4^- ion have two possible positions, equally occupied. Similar disorder of the counter-anion is also observed in the corresponding MX-chain compounds having ClO_4^- as the counter-anion (Toriumi *et al.*, 1993; Huckett *et al.*, 1993). The disordered structure of the HSO_4^- ion naturally induces a disordered structure of the hydrogen-bonding network, *viz.* N—H2N···O3—S—O4···H2N—N and N—H2N···O4—S—O3···H2N—N. The network of the O1···O3 hydrogen bond between the counter-anions is also disordered. In Fig. 2, only one orientation of the disordered HSO_4^- ion at each site is represented.

Although the perchlorates exhibit phase transitions from orthorhombic to monoclinic on cooling (Toriumi *et al.*, 1993; Huckett *et al.*, 1993), (I) does not exhibit such a phase transition over the range from room temperature down to 180 K; this was confirmed by X-ray crystallography. In the perchlorates, such a hydrogen bond as O1···O3 between the counter-anions is absent. This allows us to speculate that the O1···O3 hydrogen bond contributes to the stabilization of the orthorhombic phase of (I). This may be related to no observation of such a phase transition down to 180 K in (I).

Experimental

The title compound was prepared as described previously (Matsushita *et al.*, 1989). Intense red needle-like crystals were obtained by recrystallization from a dilute sulfuric acid solution on cooling.

Crystal data

$[Pt_2Cl_2(C_2H_8N_2)_4](HSO_4)_4$	Mo $K\alpha$ radiation
$M_r = 1089.77$	Cell parameters from 50
Orthorhombic, *Ibam*	reflections
$a = 9.261\ (1)$ Å	$\theta = 10.0–14.6°$
$b = 14.422\ (2)$ Å	$\mu = 10.12$ mm^{-1}
$c = 10.929\ (1)$ Å	$T = 295$ K
$V = 1459.7\ (3)$ Å^3	Needle, intense red
$Z = 2$	$0.28 \times 0.16 \times 0.12$ mm
$D_x = 2.48$ Mg m^{-3}	

Data collection

Rigaku AFC-5*S* diffractometer	$R_{int} = 0.029$
$\theta/2\theta$ scans	$\theta_{max} = 32.5°$
Absorption correction: Gaussian	$h = 0 \rightarrow 14$
(Coppens *et al.*, 1965)	$k = 0 \rightarrow 21$
$T_{min} = 0.187$, $T_{max} = 0.702$	$l = -16 \rightarrow 16$
3059 measured reflections	3 standard reflections
1387 independent reflections	every 50 reflections
975 reflections with $F > 3\sigma(F)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2]$
$R[F > 3\sigma(F)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.048$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.14$	$\Delta\rho_{max} = 1.51$ e Å^{-3}
975 reflections	$\Delta\rho_{min} = -1.19$ e Å^{-3}
68 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0054 (2)

Table 1
Selected geometric parameters (Å, °).

Pt—Cl	2.323 (2)	S—O3	1.420 (8)
Pt—Cl^i	3.142 (2)	S—O4	1.480 (11)
Pt—N	2.041 (3)	N—C	1.483 (7)
S—O1	1.494 (10)	C—C^{ii}	1.491 (12)
S—O2	1.400 (5)		
N—Pt—N^{ii}	82.7 (2)	O2—S—O3	113.1 (5)
N—Pt—Cl	89.50 (11)	O2—S—O4	108.6 (5)
O1—S—O2	113.8 (6)	O3—S—O4	110.2 (8)
O1—S—O3	103.5 (6)	C—N—Pt	109.1 (3)
O1—S—O4	107.5 (8)	N—C—C^{ii}	107.1 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H2N···O4^{iii}	0.90	1.99	2.860 (11)	162
N—H2N···O3^{iv}	0.90	2.22	3.002 (12)	146
N—H1N···O2	0.90	2.43	3.182 (5)	142
O1—H1O···O3^{v}	0.82	2.04	2.848 (14)	168

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

H atoms were placed at geometrically calculated positions and refined with a riding model. C—H, N—H and O—H bond distances were constrained to be 0.97, 0.90 and 0.82 Å, respectively. H-atom isotropic displacement parameters were set to be $1.5U_{eq}$ of the parent atoms. The maximum and minimum electron-density peaks lie within 0.82 Å of the Pt atom.

Data collection: *AFC Diffractometer Control Software* (Rigaku, 1987); cell refinement: *AFC Diffractometer Control Software*; data reduction: local program; program(s) used to solve structure: *UNICS*3 (Sakurai & Kobayashi, 1979); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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