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Structure of a One-Dimensional Br-Bridged Pt^{II}–Pt^{IV} Mixed-Valence Complex, *catena*-Poly[bis(ethylenediamine)platinum(II,IV)-μ-bromo bis(hydrogensulfate)]

BY NOBUYUKI MATSUSHITA

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba Meguro-ku, Tokyo 153, Japan

TOORU TAGA

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, Japan

AND IKUJI TSUJIKAWA*

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Abstract. $[Pt^{II}(C_2H_8N_2)_2][Pt^{IV}Br_2(C_2H_8N_2)_2](HSO_4)_4$, $M_r = 1178.65$, orthorhombic, *Ibam*, $a = 9.263$ (2), $b = 14.317$ (3), $c = 11.036$ (5) Å, $V = 1463.6$ (8) Å^3, $Z = 2$, $D_x = 2.67$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 12.64$ mm^{-1}, $F(000) = 1116$, $T = 296$ K, $R = 0.049$, $wR = 0.079$ for 773 observed reflections [$|F_o| > 3\sigma(|F_o|)$]. The crystal contains columns composed of square-planar $[Pt(en)_2]^{2+}$ and elongated octahedral *trans*-$[PtBr_2(en)_2]^{2+}$ units (en = ethylenediamine) stacked alternately along the *c* axis. The Br ions bridging the adjacent Pt ions are disordered over two sites along the ···Br—Pt^{IV}—Br···Pt^{II}··· linear chain. The Pt^{IV}—Br and Pt^{II}···Br bonds are 2.474 (3) and 3.044 (4) Å, respectively. The structural parameter $\delta = (Pt^{IV}—Br)/(Pt^{II}···Br)$ bears a good correlation with the data of the intervalence charge-transfer (IVCT) absorption edge ($\delta = 0.813$). The hydrogen bonds along the column [N···O = 3.06 (3) and 3.24 (2) Å] and the intercolumn hydrogen bonds [O···O = 3.13 (3) Å] stabilize the structure.

Introduction. The title compound is a one-dimensional halogen-bridged M^{II}–M^{IV} mixed-valence complex analogous to Wolffram's Red Salt, $[Pt(C_2H_5NH_2)_4][PtCl_2(C_2H_5NH_2)_4]Cl_4.4H_2O$. The compound exhibits an absorption band corresponding to intervalence charge-transfer (IVCT) transition from Pt^{II} to Pt^{IV}. The IVCT absorption edge depending on the mixed-valence state of the Pt ions has a strong relation to the hydrogen-bond network between amines and counter ions (Matsushita, Kojima, Ban & Tsujikawa, 1989*a*,*b*), and the energy of the IVCT absorption edge in the title compound is larger than

* Present address: Hyuga 32, Momoyama-cho, Hushimi-ku, Kyoto 612, Japan.

that in the analogous perchlorate Br-bridged complex. As reported previously, the existence of mid-gap absorption bands in the energy region below the IVCT absorption band also seems to depend on the hydrogen-bond network (Matsushita *et al.*, 1989*a*). One of the main aims of this work is therefore to understand the hydrogen-bond network in the crystal structure of the title compound in relation to the absorption bands.

Experimental. The title compound was prepared as described previously (Matsushita *et al.*, 1989*a*). Single crystals were obtained by recrystallization from a dilute sulfuric acid solution on cooling. A metallic lustrous green needle-like crystal with dimensions $0.15 \times 0.15 \times 0.23$ mm was used to collect intensity data with a Rigaku AFC-5RU automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation and θ–2θ scans. Lattice parameters were determined by least-squares fit of 20 reflections ($25 < 2\theta < 35°$). 2151 intensities were measured in the range $2\theta \le 60°$; $0 \le h \le 13$, $0 \le k \le 20$, $0 \le l \le 15$. Three standard reflections, 022, 130 and 040, monitored every 56 measurements, showed no significant variation: 0.955–1.056 for 022; 0.963–1.057 for 130; 0.953–1.050 for 040. The number of observed reflections $[|F_o| > 3\sigma(|F_o|)]$ was 773. The intensity data were corrected for Lorentz–polarization effects and empirical absorption factors based on ψ scans. For the latter, minimum and maximum transmission factors (on F) were 0.827 and 1.174. The structure was solved by conventional heavy-atom methods and refined on $w(|F_o| - |F_c|)^2$ by full-matrix least-squares methods with anisotropic thermal parameters for non-H atoms. All H atoms were located at geometrically calculated positions with isotropic thermal parameters, but were not refined. The structure was solved successfully in the centrosymmetric space group *Ibam* (No. 72). The refinement with 54 parameters converged to $R = 0.049$, $wR = 0.079$, $S = 1.68$, $(\Delta/\sigma)_{max} = 0.13$; weighting scheme $w = (\sigma^2_{count} + 0.0004|F_o|^2)^{-1}$. The minimum and maximum peaks in the final $\Delta\rho$ map were -2.57 and 2.44 e Å^{-3}, respectively, near Pt. Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs used were *KPPXRAY* (Taga, Higashi & Iizuka, 1985), on a FACOM M382 at the Data Processing Center of Kyoto University, *SHELX*76 (Sheldrick, 1976), on a HITAC M-880/310 at the Computer Center of the University of Tokyo, and *ORTEP*II (Johnson, 1976), on a personal computer (Toyoda, 1990).

Discussion. Positional parameters and equivalent isotropic thermal parameters for non-H atoms are given

Table 1. *Positional parameters and equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt	0.0	0.0	0.25	0.0348 (4)
Br	0.0	0.0	0.0258 (3)	0.051 (2)
S	0.3842 (6)	0.2168 (4)	0.0	0.053 (3)
O(1)	0.467 (3)	0.2440 (16)	0.1052 (16)	0.17 (2)
O(2)	0.344 (3)	0.1229 (13)	0.0	0.11 (2)
O(3)	0.278 (3)	0.281 (2)	0.0	0.20 (3)
N	0.1618 (15)	0.0954 (10)	0.2478 (9)	0.058 (7)
C	0.3001 (17)	0.0463 (14)	0.2865 (17)	0.072 (11)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and hydrogen-bond contacts* (Å) *with e.s.d.'s in parentheses*

$[Pt(en)_2]^{2+}/[PtBr_2(en)_2]^{2+}$

Pt^{IV}—Br	2.474 (3)	Br—Pt—N	89.3 (3)
Pt^{II}···Br^i	3.044 (3)	Br—Pt—N^{ii}	90.7 (3)
Pt—N	2.03 (1)	N—Pt—N^{ii}	84.7 (6)
N—C	1.52 (2)	N—Pt—N^{iii}	95.3 (6)
C—C^{ii}	1.55 (3)	Pt—N—C	108 (1)
		N—C—C^{ii}	104 (1)

HSO_4^-

S—O(1)	1.45 (2)	O(1)—S—O(2)	114 (1)
S—O(2)	1.39 (2)	O(1)—S—O(3)	102 (1)
S—O(3)	1.35 (3)	O(2)—S—O(3)	118 (2)
		O(1)—S—O(1^i)	107 (1)

Hydrogen-bond contacts
N···O(1^{iv})	3.06 (3)
N···O(2)	3.24 (2)
O(1)···O(3^v)	3.13 (3)

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

in Table 1.* Selected bond lengths, bond angles and hydrogen-bond distances are given in Table 2.

Fig. 1 shows the crystal structure viewed along the c axis. The structure is built up of columns composed of square-planar $[Pt(en)_2]^{2+}$ and elongated octahedral *trans*-$[PtBr_2(en)_2]^{2+}$ units stacked alternately along the c axis. Fig. 2 shows a view of the infinite chain of ···Br—Pt^{IV}—Br···Pt^{II}··· along the c axis. The Pt and Br atoms lie on the same twofold axis, and form a linear chain. The Br atoms are not at the exact midpoint between the 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} with different valences in a disordered state. 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 which is disordered in two other directions. The Pt sites in one Pt chain are distinguishable for the valences in an ordered state. On the other hand, the Pt sites in the crystal containing many chains are not distinguishable in the disordered state because the Pt sites are averaged in the two other directions, as reported previously (Beauchamp, Layek & Theophanides, 1982; Matsumoto, Yamashita, Kida & Ueda, 1979). In a structure of this category, the repeating distance of the crystal axis along the Pt chain is usually equal
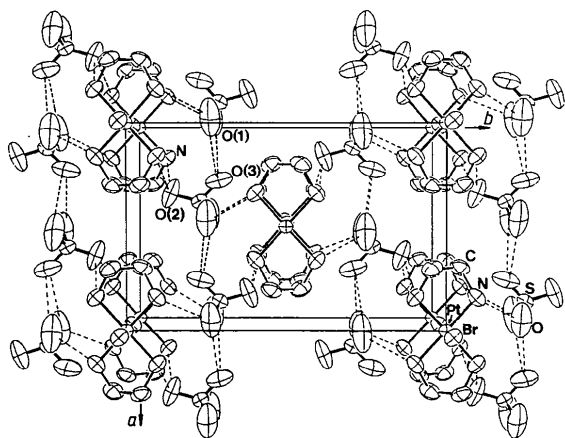
Fig. 1. View of the crystal structure along the c axis. The hydrogen bonds between N of ethylenediamines and O of hydrogensulfate ions and between O(1) and O(3) of different hydrogensulfate ions are partially shown by the dashed lines.
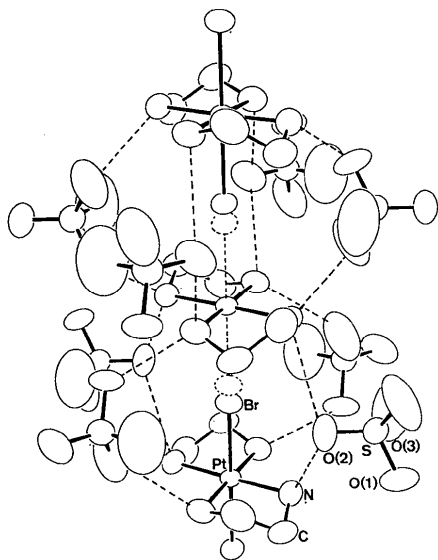
to the adjacent Pt···Pt distance. But, in the present case, the repeating distance of the c axis (chain axis) is two times that of the Pt···Pt distance although the Pt atoms have the same averaged valence.

Corresponding to the two sites for the disordered Br atoms, the Pt^{IV}—Br distance is 2.474 (3) Å and the Pt^{II}···Br distance is 3.044 (4) Å. The structural parameter of the mixed-valence state, expressed by δ = (Pt^{IV}—Br)/(Pt^{II}···Br), is 0.813. As shown in Fig. 3, plots of the IVCT absorption edge as a function of the δ parameters for the complexes [Pt(en)$_2$][PtBr$_2$-(en)$_2$]Y_4 [Y = ClO$_4^-$, HSO$_4^-$, $\frac{1}{2}$(SO$_4^{2-}$.3H$_2$O)] show considerably good correlation. This linear relation indicates that the energy difference in d_{z^2} orbitals between the Pt^{II} and the Pt^{IV} of the title complex is smaller than that of the SO$_4^{2-}$ complex but larger than that of the ClO$_4^-$ complex. A similar relation has been reported for the substitution of the bridging halogen in [Pt(en)$_2$][PtX$_2$(en)$_2$](ClO$_4$)$_4$ (X = Cl, Br, I) (Wada, Mitani, Yamashita & Koda, 1985). The structure is isomorphous with those of [M(en)$_2$]-[MX_2(en)$_2$](ClO$_4$)$_4$ (M = Pd, Pt; X = Cl, Br) in a high-temperature phase (Beauchamp et al., 1982; Yamashita, Toriumi & Ito, 1985; Toriumi, Yamashita, Kurita, Murase & Ito, 1992). Although these perchlorate complexes have phase transitions between a monoclinic form in a low-temperature phase and an orthorhombic form in a high-temperature phase (Toriumi et al., 1992), the title compound does not exhibit such a phase transition over the range from room temperature to liquid-helium temperature.
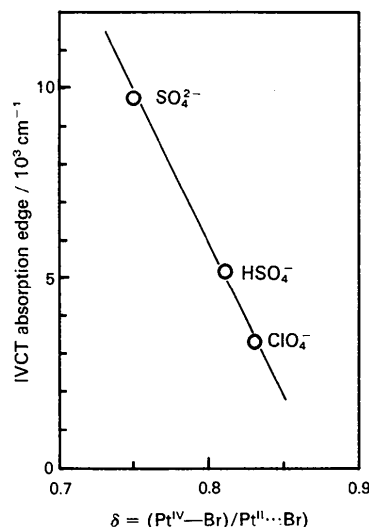

Fig. 2. View of the infinite chain of ···Br—Pt^{IV}—Br···Pt^{II}··· along the c axis. The dashed ellipsoids of Br and the dashed bonds between Pt and Br represent the disordered positions of the Pt—Br bonds. The dashed bonds between N and O represent the hydrogen bonds.

Fig. 3. The energy of the IVCT absorption edges as a function of the δ parameters, (Pt^{IV}—Br)/(Pt^{II}···Br), for [Pt(en)$_2$][PtBr$_2$-(en)$_2$]Y_4 [Y = ClO$_4^-$ (Toriumi et al., 1992; Matsushita et al., 1989b), HSO$_4^-$ (this work; Matsushita et al., 1989a), $\frac{1}{2}$(SO$_4^{2-}$.3H$_2$O) (Matsushita et al. to be published; Matsushita et al., 1989a)].

As shown in Fig. 2, there are four hydrogensulfate ions between two adjacent $[Pt^{II/IV}(en)_2]$ moieties along the Pt chain, and one moiety is surrounded by eight hydrogensulfate ions. All the eight H(N) atoms of the ethylenediamines in one moiety make hydrogen bonds with the hydrogensulfate ions [3.06 (3), 3.24 (2) Å]. The adjacent $[Pt^{II/IV}(en)_2]$ moieties along the Pt chain are connected by four linkages consisting of hydrogen bonds. In addition to the N···O hydrogen bonds, the hydrogensulfate ions arranged along the a axis are linked by the O(1)···O(3) hydrogen bonds [3.13 (3) Å]. The orientation of the hydrogensulfate ion is fixed by the O(1)···O(3) hydrogen bond. The intercolumnar hydrogen bonds stabilize the crystal structure, and this hydrogen-bond system explains why a phase transition was not observed for this complex. The O(1)···O(3) hydrogen bond may weaken the linkage of the N···O(1) hydrogen bond when compared to a complex without the O···O hydrogen bond. Therefore, it can be interpreted that the energy difference of d_{z^2} orbitals between Pt^{II} and Pt^{IV} of the title complex is larger than that in the ClO_4^- complex without the O···O hydrogen bond.

In recent years, it has been reported that some of the Pt^{II}–Pt^{IV} mixed-valence complexes exhibit mid-gap absorption bands in the energy region below the IVCT absorption edge, and that the mid-gap absorption bands are related to the mismatch of the valence alternation in the one-dimensional electron system (Matsushita, Kojima, Ban & Tsujikawa, 1987; Kuroda, Sakai, Nishina, Tanaka & Kurita, 1987; Kurita, Haruki & Miyagawa, 1988; Donohoe, Ekberg, Tait & Swanson, 1989; Matsushita, Kojima, Watanabe & Ban, 1989). The title complex exhibits no mid-gap absorption bands (Matsushita et al., 1989a). This fact suggests that the Pt^{II}–Pt^{IV} alternate arrangement is complete for a long region in one Pt chain; namely, very few mismatches of the valence alternation exist. On the other hand, each Pt site in the crystal is not distinguishable by valence and is in a disordered state. This is explained by the fact that the Pt^{II}–Pt^{IV} arrangements are not correlative and that each Pt site is averaged for the valences in the interchain directions. In this complex, the alternately

stacked $[Pt^{II/IV}(en)_2]$ moieties are strongly connected by the four hydrogen-bond linkages through the hydrogensulfate ions, while in the SO_4^{2-} complexes exhibiting the mid-gap absorption bands, only two hydrogen-bond linkages exist. This strong hydrogen-bond network may prevent the mismatch of the valence alternation in the one-dimensional electron system.

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