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DESIGN OF HYDROGEN BOND NETWORK IN HALOGEN-BRIDGED MIXED-VALENCE PLATINUM COMPLEXES BY SUBSTITUTION OF COUNTER ION

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Abstract Sulfates in one-dimensional halogen-bridged mixed-valence platinum complexes were synthesized in order to elucidate contributions of hydrogen bonds between in-plane ligand amines and counter ions to the mixed-valence state. Their intervalence charge-transfer bands measured by using the single crystals and their structures determined by single crystal X-ray diffraction analyses show that the energy difference of d_{z^2} orbitals between the Pt^{II} and the Pt^{IV} becomes larger with decreasing linkages between the Pt units by the hydrogen bonds, comparing with perchlorates and hydrogensulfates.

INTRODUCTION

One-dimensional halogen-bridged mixed-valence platinum complexes have a structure built up of columns composed of square-planar $[Pt(en)_2]^{2+}$ units and elongated octahedral *trans*-$[PtX_2(en)_2]^{2+}$ (X=Cl, Br, I) units alternately stacked, and the columns are surrounded with counter anions. The cation column structure is supported by hydrogen bond linkages connecting the adjacent Pt units, Pt–NH$\cdots Y\cdots$HN–Pt, where NH denotes a in-plane ligand amine and Y denotes a counter ion. If the mixed-valence state depends on the hydrogen bond linkage, it is possible that the electronic state of the mixed-valence compounds is controlled by design of the hydrogen bond network. In order to elucidate the contribution of the hydrogen bond linkage to the

mixed-valence state, we synthesized sulfates by substituting the counter ion from the perchlorate ion or the hydrogensulfate ion to the sulfate ion. The purpose of the substitution of the counter ion is that the number of the hydrogen bond linkages is varied. In this paper, we discuss the relation between the mixed-valence state and the hydrogen bond linkage from the intervalence charge-transfer (IVCT) bands and the crystal structures.

EXPERIMENTAL

The mixed-valence complexes were synthesized by methods described in previous papers.[1-4] Single crystals of the sulfates were obtained by recrystallization from aqueous solution on slowly evaporating. Those of the hydrogensulfates were obtained from sulfuric acid solution on cooling. The absorption and reflection spectra of single crystals were measured at room temperature with a Jasco CT-100 spectrometer using a tungsten lamp for the light source. A Glan-Taylor prism was used for polarising light in the absorption spectra measurement. A half-mirror was used for the angle 0° of incidence in the reflection spectra measurement. A lock-in system working with HTV R376 and R316 photomultipliers and a PbS photoconductive cell was used for detection. The spectra were measured by irradiating the sample with monochromatic light. The X-ray diffraction data were measured at room temperature on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo *Ka* (λ=0.71069Å) radiation.

RESULTS AND DISCUSSION

Table I shows Pt-Pt separation distances and two bond distances between the Pt atom and the bridging halogen atom with their differences and two kind mixed-valence parameters, $\delta=(Pt^{IV}-X)/(Pt^{II}\cdots X)$ and $\Delta=\{(Pt^{II}\cdots X)-(Pt^{IV}-X)\}/(Pt-Pt)$, for $[Pt(en)_2][PtX_2(en)_2]Y_4$. The former parameter becomes 1 and the latter becomes 0 when the Pt sites are equivalent. The two kind mixed-valence parameters are well correlative to each other. The distances of $Pt^{II}\cdots X$ are widely varied by the substitution of the counter ion and well correlative to the mixed-valence parameters. On the other hand, the distances of $Pt^{IV}-X$ are little varied. The Pt-Pt separation distances are also

TABLE I Selected bond lengths (Å) and mixed-valence parameters

X	Y	Pt–Pt	Pt^{IV}–X	$Pt^{II}\cdots X$	δ [a]	Δ [b]	ref.
Cl	SO_4^{2-}	5.749	2.320(4)	3.460(4)	0.671	0.198	5
Cl	PF_6^-	5.506	2.320(4)	3.186(4)	0.728	0.157	6
Cl	HSO_4^-	5.465	2.311(6)	3.154(6)	0.733	0.154	7
Cl	ClO_4^-	5.404	2.318(7)	3.085(7)	0.751	0.142	8[c]
Br	SO_4^{2-}	5.747	2.476(1)	3.299(1)	0.751	0.143	5
Br	HSO_4^-	5.518	2.474(3)	3.044(3)	0.813	0.103	9
Br	ClO_4^-	5.470	2.473(1)	2.997(1)	0.825	0.096	10[c]
Br	ClO_4^-	5.487	2.487(1)	3.006(1)	0.827	0.095	10[d]
I	HSO_4^-	5.954	2.711(2)	3.243(2)	0.836	0.089	11
I	SO_4^{2-}	5.831	2.719(1)	3.143(1)	0.864	0.073	5
I	ClO_4^-	5.827	2.791(8)	3.036(8)	0.919	0.042	12

a $\delta=(Pt^{IV}\text{–}X)/(Pt^{II}\cdots X)$,
b $\Delta=\{(Pt^{II}\cdots X)-(Pt^{IV}\text{–}X)\}/(Pt\text{–}Pt)$
c high temperature phase, orthorhombic
d low temperature phase, monoclinic

widely varied by the substitution of the counter ion and well correlative to the mixed-valence parameters in the chloro and bromo bridged complexes, but they are not much varied in the iodo bridged complexes. Figure 1 shows plots of the IVCT absorption edges and reflection peaks as the function of the δ parameters for $[Pt(en)_2][PtX_2(en)_2]$-Y_4. The energy of the IVCT band is the energy difference of d_{z^2} orbitals between the Pt^{II} and the Pt^{IV}, and directly shows the mixed-valence state. The IVCT bands and the δ parameters are well correlative to each other. The both IVCT and δ mixed-valence parameters show that the substitution effect of the counter ion from a monovalent anion, ClO_4^- or HSO_4^- to a divalent anion, SO_4^{2-} is comparable to the substitution effect of the bridging halogen for the mixed-valence state. The number of the counter ions per a Pt unit is important for the control of the mixed-valence state.

Views of the infinite chain of $\cdots X\text{–}Pt^{IV}\text{–}X\cdots Pt^{II}\cdots$ with hydrogen bonds for $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ and $[Pt(en)_2][PtCl_2(en)_2](SO_4)_2\cdot 6H_2O$ are shown in Figur 2. As shown in Figure 2 (a), in $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$, there are four hydro-

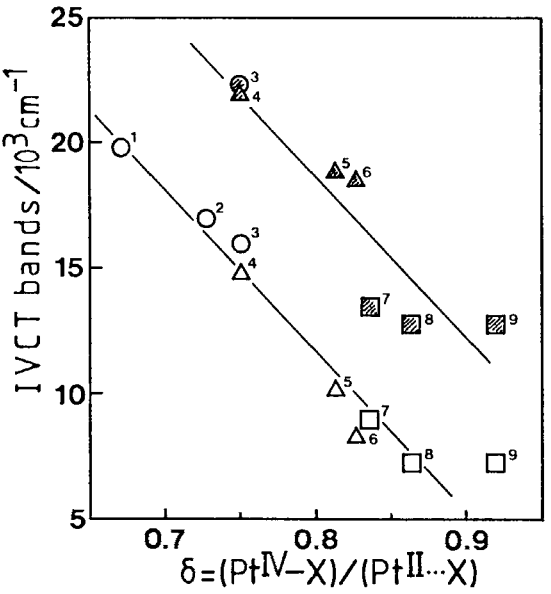

FIGURE 1 Plots of IVCT bands as a function of δ parameters. Circles, triangles and rectangulars denote Cl-, Br- and I- bridged complexes, respectively. Shaded marks and non-shaded marks denote reflection peaks and absorption edges, respectively. Lines are guides for your eyes. The number denotes the complexes; 1,(X=Cl, Y=SO_4^{2-})[4,5]; 2,(Cl,PF_6^-)[6,*]; 3,(Cl, ClO_4^-)[8,13,14]; 4,(Br, SO_4^{2-})[4,5,*]; 5,(Br,HSO_4^-)[4,9,*]; 6,(Br,ClO_4^-)[4,10,13]; 7,(I,HSO_4^-)[4,11,*]; 8(I,SO_4^{2-})[4,5,*]; 9,(I,ClO_4^-)[12,13,14]. * denotes this work.

gensulfate ions between two adjacent [$Pt^{II/IV}(en)_2$] moieties along the Pt chain, and the one moiety is surrounded by the eight hydrogensulfate ions. All eight N–H of the ethylenediamines in the one moiety contribute to hydrogen bonds between N of the ethylenediamines and O of the hydrogensulfate ions. The adjacent [$Pt^{II/IV}(en)_2$] moieties along the Pt chain are linked by four linkages of the hydrogen bonds. On the other hand, as shown in Figure 2 (b), in $[Pt(en)_2][PtCl_2(en)_2](SO_4)_2\cdot 6H_2O$, there are two sulfate ions between two adjacent [$Pt^{II/IV}(en)_2$] moieties along the Pt chain, and the two sulfate ions are not in the relation of an axial symmetry. The one moiety is surrounded by the four sulfate ions, two of which are in one side of the PtN_4 plane and in one side of two ethylendiamines, and the others are in the opposite side. Six of all eight N–H of the ethylenediamines in the one moiety contribute to hydrogen bonds between N of the ethylenediamines and O of the sulfate ions. The

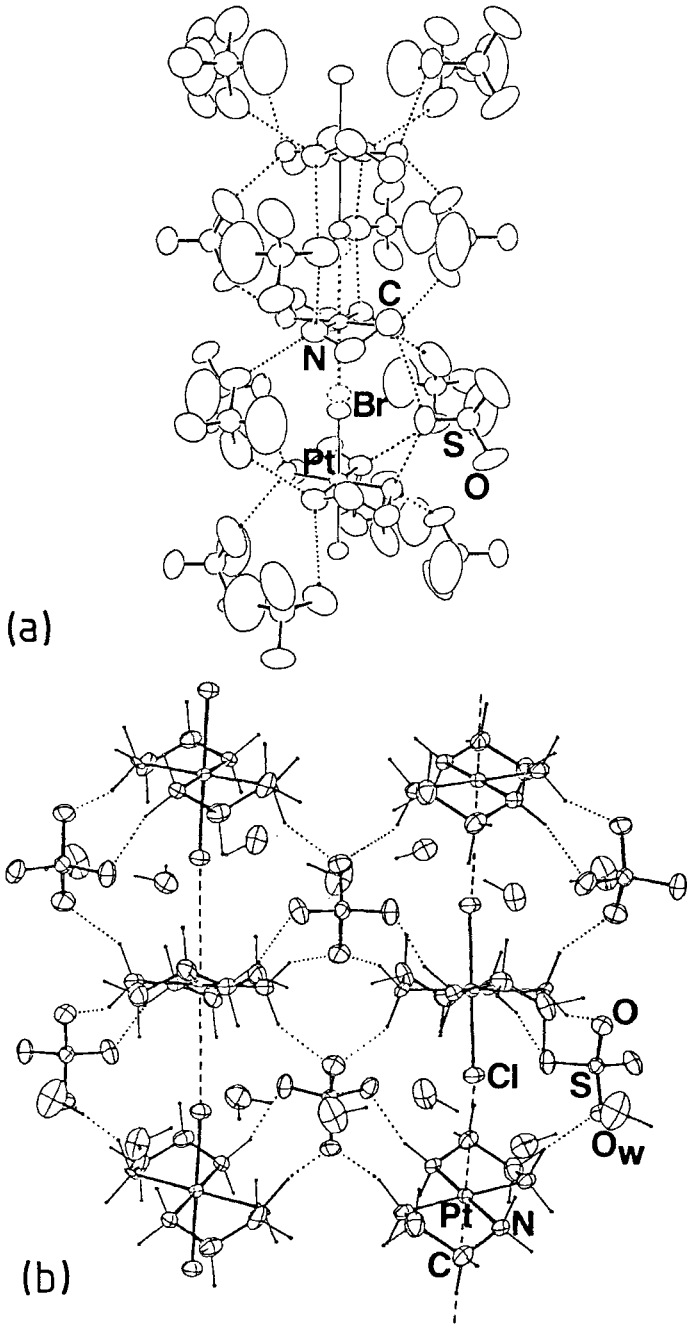

FIGURE 2 Views of the infinite chain of $\cdots X\text{-}Pt^{IV}\text{-}X\cdots Pt^{II}\cdots$ with hydrogen bonds for (a) $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ and (b) $[Pt(en)_2][PtCl_2(en)_2](SO_4)_2 \cdot 6H_2O$. Hydrogen bonds are indicated by the dotted lines. Thermal ellipsoids are 50% probability surfaces.

adjacent $[Pt^{II/IV}(en)_2]$ moieties along the Pt chain are linked by two linkages of the hydrogen bonds, and the linkage is a branching type. $[Pt(en)_2][PtX_2(en)_2]Y_4$ (X=Cl, Br, Y=ClO_4^-, HSO_4^-) are isomorphous to each other, and $[Pt(en)_2][PtX_2(en)_2](SO_4)_2 \cdot 6H_2O$ (X=Cl, Br, I) are also isomorphous to each other. The hydrogen bond linkages in the perchlorates and the hydrogensulfates are more than those in the sulfates, and the energy difference of d_z2 orbitals between the Pt^{II} and the Pt^{IV} in the formers is smaller than that in the latters. This result shows that the number of the hydrogen bond linkages influence the energy difference of the electronic state between the Pt^{II} and Pt^{IV}, namely, the mixed-valence state.

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