Comparison between Optical Properties of Sulfates and Hydrogensulfates in Halogen-Bridged Mixed-Valence Platinum(II, IV) Complexes

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Syntheses and optical properties of some new halogen-bridged mixed-valence platinum complexes analogous to Wolffram's Red Salt, $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ (PBHS), $[Pt(en)_2][PtI_2(en)_2](HSO_4)_4\cdot 4H_2O$ (PIHS), and $[Pt(en)_2][PtX_2(en)_2](SO_4)_2\cdot 6H_2O$ {X=Br(PBSW), I(PISW)}, are reported. The powder X-ray diffraction pattern shows that PBHS is isomorphous with $[Pt(en)_2][PtCl_2(en)_2](HSO_4)_4$ (PCHS), and that PBSW and PISW are isomorphous. The hydrogensulfates PBHS and PIHS crystallize from an aqueous sulfuric acid solution, whereas the sulfates PBSW and PISW crystallize from an aqueous solution. The single crystal absorption spectra of PBHS, PIHS, PBSW, and PISW have been investigated at 4.2 K. The intense optical absorption due to intervalence charge-transfer transition from Pt(II) to Pt(IV) has been observed for the light polarized parallel to the Pt chain axis (*E*//chain). From the comparison of the energy of the intervalence charge-transfer absorption edges in PBHS, PBSW, and PISW, one can conclude that the influence of the substitution of the counterions HSO_4^- with SO_4^{2-} on the Pt(II)-Pt(IV) mixed-valence state is no less better than that of the substitution of the bridging halogen. The role of the counterion on the mixed-valence state is explained by the hydrogen bond network (Pt-NH···counterion···HN-Pt) on individual chains.

In recent years,[1-3] one-dimensional halogen-bridged mixed-valence complexes analogous to Wolffram's Red Salt (WRS) $[Pt(C_2H_5NH_2)_4][PtCl_2(C_2H_5NH_2)_4]Cl_4\cdot 4H_2O$ have been investigated from viewpoints of physics and chemistry as a model of one-dimensional mixed-valence compounds. Many Wolffram's Red Salt Analogues (WRA) have ever been synthesized and studied, through the substitution of the in-plane ligand amines, bridging halogen and counterions. They comprise elongated octahedral $[Pt^{IV}X_2(AA)_2]^{2+}$ and square-planar $[Pt^{II}(AA)_2]^{2+}$ units alternately stacked along an axis, and counterions supporting the platinum complex columns, where AA denotes a bidentate amine or two monodentate amines etc., and X denotes a bridging halogen. Consequently, they comprise infinite platinum chains $(\cdots Pt^{II}\cdots X\text{-}Pt^{IV}\text{-}X\cdots)$ bridged by halogens which are not at the middle point between Pt(II) and Pt(IV), but closer to Pt(IV) than Pt(II). There is a charge-transfer interaction between an electronic state of Pt(II) and that of Pt(IV) through the bridging halogen.[4] The XPS measurement[5] suggests that the electronic state of Pt is not strictly divalence or tetravalence, and approaches that of Pt(III) by the medium of this interaction.

In WRS[4,6] and WRA,[6] the intervalence charge-transfer transition from an electronic state containing mainly d_{z^2} orbitals of Pt(II) to a state containing mainly d_{z^2} orbitals of Pt(IV) causes an intense optical absorption. This absorption appears in the spectral region from the visible to near-infrared, for light polarized parallel to the Pt chain axis (*E*//chain). Therefore, the single crystal spectrum for *E*//chain is a good probe of the Pt(II)-Pt(IV) mixed-valence state attributed to the charge-transfer interaction. Theoretical and experimental analyses of the above mentioned phenomena have been carried out on the basis of the extended Peierls-Hubbard model.[7,8]

The solid state properties in WRS and WRA have been investigated, mainly through the substitution of the metal atom (Pt, Pd, Ni) and the bridging halogen (Cl, Br, I).[8] Clark and Kurmoo[9] suggest that the hydrogen bond between a counterion and an in-plane ligand amine affects both the Pt(II)-Pt(IV) distances and the intervalence charge-transfer transition energies. Nevertheless, the influence of the hydrogen bond on the Pt mixed-valence state has not been investigated in detail by means of the substitution of the counterion. In order to elucidate the influence of the hydrogen bond on the Pt mixed-valence state we have investigated the WRA mixed-valence complexes comprising SO_4^{2-} and HSO_4^- as the counterions. Since the composition ratio of counterions for a platinum atom in the hydrogensulfate is twice as much as that in the sulfate, we can expect that the mixed-valence state of the complexes comprising SO_4^{2-} is clearly different from that of the complexes comprising HSO_4^-.

Layek and Papavassiliou[10] also reported the syntheses and Raman spectra of single crystals in WRA comprising SO_4^{2-} and HSO_4^-, $[Pt(en)_2][PtCl_2(en)_2](HSO_4)_4$ and $[Pt(en)_2][PtX_2(en)_2](SO_4)_2$ (X=Br, I), where en denotes ethylenediamine. We were able to prepare similar mixed-valence complexes, $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ (PBHS), $[Pt(en)_2][PtI_2(en)_2](HSO_4)_4\cdot 4H_2O$ (PIHS), and $[Pt(en)_2][PtX_2(en)_2](SO_4)_2\cdot 6H_2O$ {X=Br (PBSW), I (PISW)} which have different counterion composition and contain water of crystallization. In this paper, we report the syntheses and the optical properties of single crystals in PBHS, PIHS, PBSW, and PISW, and discuss the influence of the hydrogen bond on the Pt mixed-valence state.

Experimental

Preparation of the Constituent Complexes. The Pt(II) constituent complex $[Pt(en)_2]Cl_2$ was prepared by the procedure of Basolo et al.[11] The Pt(IV) constituent complexes $[PtBr_2(en)_2]Cl_2$ and $[PtI_2(en)_2]Cl_2$ were obtained by oxidation of $[Pt(en)_2]Cl_2$ in ethanol-water with Br_2 and I_2, respectively.

Preparation of the Mixed-Valence Complexes. The Pt(II)–Pt(IV) mixed-valence complexes were prepared by a procedure similar to that of Bekaroglu et al.[12] for $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ (X=Br, I).

$[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ (PBHS): $[Pt(en)_2]Cl_2$ (1.2 g) was dissolved in water (ca. 40 mL). This solution was divided into two equal parts. Water (ca. 100 mL) and ethanol (ca. 20 mL) were added into one of them, and Br_2 (ca. 0.1 mL) was dissolved in this solution with stirring. The color of the solution became pale yellow. The volume slowly reduced to ca. 70 mL on a hot plate. The solution, which had no odor of bromine, was then cooled and mixed with the other part of $[Pt(en)_2]Cl_2$ solution. A 62% aqueous sulfuric acid (ca. 3 mL) was then added. This solution was concentrated to ca. 10 mL on a water bath (ca. 40 °C) and then cooled. Green metallic lustrous needle-like crystals were obtained. They were filtered off and washed with diethyl ether; yield 1.6 g (87%). The single crystals were obtained by recrystallization from a dilute sulfuric acid solution. Found: C, 8.10; H, 3.00; N, 9.49; O, 21.96; S, 10.98; Br, 13.48%. Calcd for $C_8H_{36}Br_2N_8O_{16}Pt_2S_4$: C, 8.15; H, 3.08; N, 9.51; O, 21.72; S, 10.88; Br, 13.56%.

$[Pt(en)_2][PtI_2(en)_2](HSO_4)_4\cdot 4H_2O$ (PIHS): $[Pt(en)_2]Cl_2$ (2.01 g) was dissolved in water (ca. 100 mL). This solution divided into two equal parts. An ethanol solution of I_2 (1.06 g/50 mL) was added to one of them. This solution was stirred overnight and evaporated to dryness by rotary evaporator to remove excess I_2. The residue was dissolved in water. This solution of Pt(IV) complex was added to the other part of $[Pt(en)_2]Cl_2$ solution, and the mixture was concentrated to ca. 40 mL on a hot plate. A 62% aqueous sulfuric acid (15 mL) was gradually added to the concentrated solution with stirring on an ice bath. Then, golden fine powdery solids were rapidly formed. This powder was filtered off, washed successively with a diethyl ether and sulfuric acid mixture (2:1, v/v), diethyl ether, and etanol; yield 2.59 g (74.2%). Plate-like single crystals were obtained by recrystallization from a dilute sulfuric acid solution. Found: C, 7.15; H, 3.06; N, 8.07; O, 23.87; I, 17.96%. Calcd for $C_8H_{44}I_2N_8O_{20}Pt_2S_4$: C, 7.15; H, 3.30; N, 8.33; O, 23.80; I, 18.87%.

$[Pt(en)_2][PtBr_2(en)_2](SO_4)_2\cdot 6H_2O$ (PBSW): A solution, which contains a mixture of $[Pt(en)_2]Cl_2$ and $[PtBr_2(en)_2]Cl_2$, was prepared by the same procedure employed for the preparation of PBHS, using $[Pt(en)_2]Cl_2$ (3.66 g) and Br_2 (ca. 0.3 mL). An aqueous solution of Na_2SO_4 (2.0 g/20 mL) was added to the Pt(II)–Pt(IV) solution. This was concentrated on a steam bath to ca. 120 mL and then cooled. Reddish-brown plate-like crystals were obtained. They were filtered off and washed with ethanol; yield 4.41 g (85.4%). Single crystals were obtained by recrystallization from an aqueous solution. Found: C, 8.93; H, 4.10; N, 10.35; O, 20.44; S, 5.93; Br, 14.63%. Calcd for $C_8H_{44}Br_2N_8O_{14}Pt_2S_2$: C, 8.81; H, 4.07; N, 10.27; O, 20.54; S, 5.88; Br, 14.65%.

$[Pt(en)_2][PtI_2(en)_2](SO_4)_2\cdot 6H_2O$ (PISW): A solution of $[Pt(en)_2]Cl_2$ and $[PtI_2(en)_2]Cl_2$ was prepared by the same procedure employed for the preparation of PIHS, using $[Pt(en)_2]Cl_2$ (3.17 g) and I_2 (2.0 g). To this solution, an aqueous solution of $NaHSO_4$ (1.9 g/10 mL) was added, and the mixture solution was concentrated on a steam bath to ca. 75 mL and then cooled. Golden lustrous plate-like crystals were obtained. They were filtered off and washed with a small amount of water; yield 3.13 g (64.4%). Single crystals were obtained by recrystallization from an aqueous solution. Found: C, 8.15; H, 3.70; N, 9.44; O, 18.77; I, 21.12%. Calcd for $C_8H_{44}I_2N_8O_{14}Pt_2S_2$: C, 8.11; H, 3.74; N, 9.46; O, 18.91; I, 21.43%.

$[Pt(en)_2][PtCl_2(en)_2](HSO_4)_4$ (PCHS): $[PtCl_2(en)_2]Cl_2$ (327 mg), which was obtained by oxidation of $[Pt(en)_2]Cl_2$ with an aqueous hydrogen peroxide solution, and $[Pt(en)_2]Cl_2$ (285 mg) were dissolved in water (ca. 20 mL). To this solution a 30% aqueous surfuric acid (ca. 2 mL) was added. This solution was slowly concentrated to a few milliliters at ca. 30 °C on a water bath. Red needle-like crystals obtained, were filtered off and dried in a desiccator containing silica gel. Yield 0.39 g (48%). Found: C, 8.78; H, 3.29; N, 9.82; O, 24.17; S, 11.77; Cl, 6.53%. Calcd for $C_8H_{36}Cl_2N_8O_{16}Pt_2S_4$: C, 8.82; H, 3.33; N, 10.28; O, 23.49; S, 11.77; Cl, 6.51%.

Elemental analysis was carried out by "The Laboratory for Organic Elemental Microanalysis" of Kyoto University.

Instrumental Measurements. Powder X-ray diffraction patterns were recorded at room temperature on a Rigaku diffractometer using the θ-2θ scan technique and graphite-monochromated Cu $K\alpha$ radiation (λ=1.5418 Å). For PBHS, PBSW, and PISW, lattice constants were obtained on a Rigaku four-circle diffractometer.

The TGA was performed on a Rigaku TG DTA 8112S apparatus in the temperature region from room temperature to 200 °C.

The absorption spectra of single crystals were measured at 4.2 K with a Jasco CT-100 spectrometer using a tungsten lamp for the light source and a Glan-Taylar prism for polarizing light. A lock-in system working with HTV R376 and R316 photomultipliers and a PbS photoconductive cell was used for detection. The sample was placed in glass Dewar's vessel and immersed in liquid helium to cool. The typical sizes of measured samples are $2\times1\times0.2$ (mm^3) for PBHS, $3\times2\times0.06$ (mm^3) for PIHS, $3\times2\times0.4$ (mm^3) for PBSW, and $4\times3\times0.04$ (mm^3) for PISW.

The absorption spectra of solutions were measured at room temperature with a Hitachi model 356 Double Beam Spectrophotometer.

Results and Discussion

Compounds. The complexes PBHS and PIHS are recrystallized from an aqueous sulfuric acid solution, and the PBSW and PISW are recrystallized from an aqueous solution. The result shows that the concentration of SO_4^{2-} and HSO_4^-, namely, the pH of the crystallizing solution dominates whether the hydrogensulfate or the sulfate crystallizes.

Table 1 shows the appearance of the single crystals of PCHS, PBHS, PIHS, PBSW, and PISW. Both the iodo-bridged mixed-valence complexes, PIHS and PISW, are golden in color. However, the bromo-

Table 1. Crystal Appearance of Mixed-Valence Complexes

Complex		Color		Shape
		Crystal	Powder	
$[Pt(en)_2][PtCl_2(en)_2](HSO_4)_4$	PCHS	Dull red	Red	Needle
$[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$	PBHS	Metallic green	Green	Needle
$[Pt(en)_2][PtI_2(en)_2](HSO_4)_4 \cdot 4H_2O$	PIHS	Golden	Black	Plate
$[Pt(en)_2][PtBr_2(en)_2](SO_4)_2 \cdot 6H_2O$	PBSW	Reddish brown	Orange	Plate
$[Pt(en)_2][PtI_2(en)_2](SO_4)_2 \cdot 6H_2O$	PISW	Golden	Black	Plate

Table 2. Lattice Constants of PCHS, PBHS, PBSW, and PISW

Complex	a/Å	b/Å	c/Å	β/°
PCHS[a)]	9.27	14.43	10.94[c)]	—
PBHS[a)]	9.263(1)	14.317(3)	11.036(5)[c)]	—
PBSW[b)]	14.012(2)	11.494(2)[c)]	9.217(1)	102.08(1)
PISW[b)]	14.044(2)	11.662(1)[c)]	9.292(1)	103.16(1)

a) Orthorhombic. b) Monoclinic. c) Pt chain axis.

Table 3. Results of TGA in the Temperature Range from Room Temperature to 200 °C

Complex	Exp.		Calcd wt(%)[a)]
	Wt loss (%)	Temp range (°C)	
PIHS	1.4	24—48	
	3.1	60—84	
	1.1	90—122	
	5.6	(Total)	5.4
PBSW	9.8	87—148	9.9
PISW	9.0	86—178	9.1

a) Weight percentages of water of crystallization in chemical formulas estimated from the elemental analysis.

bridged complexes, PBHS and PBSW, are different in color. Although PBHS and other bromo-bridged mixed-valence platinum complexes analogous to WRS are all metallic lustrous green in color, PBSW is similar to chloro-bridged complexes in color.

The powder X-ray diffraction pattern shows that PCHS and PBHS are isomorphous, and that PBSW and PISW are isomorphous. The X-ray pattern of PIHS is different from that of PCHS, PBHS, PBSW, and PISW. These results are consistent with the results of the elemental analysis.

Table 2 shows the lattice constants of PCHS,[13)] PBHS,[14)] PBSW,[15)] and PISW.[15)] The distance between Pt atoms on the chain can be preliminary estimated from the lattice constant of the Pt chain axis. The Pt-Pt distances of PCHS and PBHS are as long as that of other chloro- and bromo-bridged complexes with a univalence counterion.[16—18)] On the other hand, the Pt-Pt distance of PBSW (5.747(2) Å) is longer than that of PBHS (5.518(5) Å), and that of PISW (5.831(1) Å) are also slightly longer than that of the iodo-bridged complexes with a univalence counterion and a bidentate amine.[18—20)] The results show that the Pt-Pt distance of the complexes with a bivalence counterion is longer than that of the complexes with a univalence counterion.

For the WRA halogen-bridged mixed-valence complexes of which the structures were known, the chloro- and bromo-bridged complexes[16—18,21—25)] are isomorphous each other, but are different from the corresponding iodo-bridged complex[19,20,26)] in structure. The structures of the hydrogensulfates are classified into two groups in structure as same as above mentioned, namely the group of the chloro- and bromo-bridged complexes and the group of the iodo-bridged complex. For the sulfates, however, the bromo- and iodo-bridged complexes are isomorphous. It is the first example of the corresponding bromo- and iodo-bridged complexes belonging to the same group in structure, according to our knowledge.

Table 3 shows the results of TGA obtained from room temperature to 200 °C. The weight loss on heating of PIHS, PBSW, and PISW is consistent with the weight percentage of the water of crystallization in chemical formulas estimated from the elemental analysis. Thus, the complexes PIHS, PBSW, and PISW contain water of crystallization. In the hydrogensulfates PCHS, PBHS, and PIHS, only the iodo-bridged complex PIHS contains water of crystallization, which can be explained by the following considerations. The Pt-Pt distance of the iodo-bridged complexes is longer than that of the chloro- and bromo-bridged complexes, because iodide ion is the largest among the halide ions, (Cl^-, Br^-, and I^-). Thus, in the case that the framework of the halogen-bridged Pt complex column are only retained in the crystal structure of the halogen-bridged mixed-valence complexes, the cavity size between the halogen-bridged Pt chains of PIHS is larger than that of PCHS and PBHS. The water of crystallization of PIHS, therefore, is needed to occupy a free space which the counterions cannot occupy in the cavity between the Pt chains. Since the complexes PCHS and PBHS will not have the free space, they don't contain the water of crystallization. Similar mixed-valence complexes, $[Pt(NH_3)_4][PtX_2(NH_3)_4](HSO_4)_4$ (X=Cl,[16)] Br[22,23)]) and $[Pt(NH_3)_4][PtI_2(NH_3)_4](HSO_4)_4 \cdot 2H_2O$[26)] were previously reported. For the hydrogensulfates of the ammonia complexes, equally, only the iodo-bridged complex contains the water of crystallization. For the water of crystallization in the sulfates PBSW and PISW, the same explanation is given. Because the sulfates contain one-half of the counterions in the hydrogensulfates, the free space which the counterions don't occupy in the cavity between the Pt chains of the sulfates is larger than that of the hydrogensulfates. The sulfates PBSW and PISW, therefore, contain six molecules of water of crystallization per a chemical formula. We consider that whether or not the WRA mixed-valence complexes contain water of crystallization depends on the free space, namely, the relation between the volume of the counterion and the cavity between the Pt chains.

Similar WRA, $[Pt(en)_2][PtCl_2(en)_2](HSO_4)_4$, and $[Pt(en)_2][PtX_2(en)_2](SO_4)_2$ (X=Br, I) were previously reported by Layek and Papavassiliou.[10] Our chloro-bridged complex PCHS is the same as their chloro-bridged complex from the elemental analysis, whereas our bromo-bridged complexes PBHS and PBSW, and our iodo-bridged complexes PIHS and PISW are different from their bromo- and iodo-bridged complexes, respectively. Thus, our complexes PBHS, PIHS, PBSW, and PISW are new WRA halogen-bridged mixed-valence platinum complexes.

Spectra. Figures 1, 2, 3, and 4 show the absorption spectra of the single crystal in PBHS, PIHS, PBSW and PISW at 4.2 K and the corresponding spectra of aqueous solutions at room temperature, respectively.

The solution spectrum of PBHS is the same as that of PBSW, and that of PIHS is the same as that of PISW. In the solution, thus, an electronic state of the platinum complex in the hydrogensulfate is the same as that in the sulfate. This is consistent with the fact that the recrystallization of the hydrogensulfate and the sulfate depends on the pH of the recrystallizing solution as above mentioned.

The single crystal absorption spectra of the WRA mixed-valence complexes with univalence anions have been reported.[4,6,27] The single crystal absorption spectra of the WRA mixed-valence complexes with bivalence anions, however, have not yet been reported, except for our previous paper.[28] The absorption spectra of the single crystal in PBSW and PISW are reported for the first time in the WRA mixed-valence complexes with bivalence counterions.

Single crystals of PBHS, PIHS, PBSW, and PISW showed the strong absorption spectra in the region from visible to near-infrared. These spectra are attributed to the intervalence charge-transfer transition from Pt(II) to Pt(IV), which is a common feature of the WRA mixed-valence complexes, namely the class II mixed-valence compounds.[29] The single crystal spectra in this region showed a remarkable dichroism.

The strong absorption spectra for *E*//chain are due to the charge-transfer transition from the d_{z^2} of Pt(II) to the d_{z^2} of Pt(IV),[4,27] which is only allowed by selection rule for the light polarized parallel to the Pt chain axis. Absorption coefficients of the strong

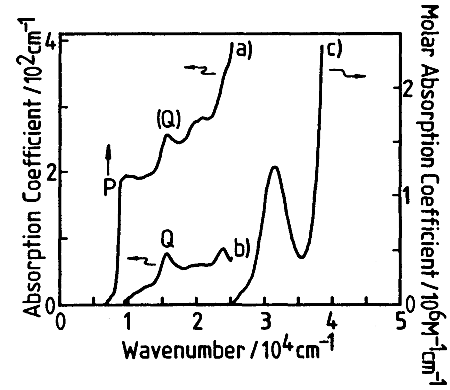

Fig. 1. Single crystal absorption spectra at 4.2 K and solution absorption spectrum at room temperature (R.T.) of $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ (PBHS). Curve a) is single crystal spectrum for the light polarized parallel to the Pt chain axis (*E*//chain). Curve b) is single crystal spectrum for the light polarized perpendicular to the Pt chain axis (*E*⊥chain). Curve c) is solution spectrum.

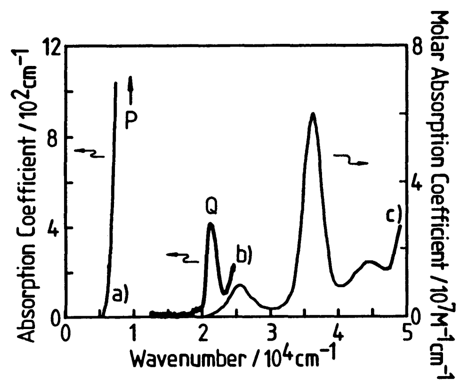

Fig. 2. Single crystal absorption spectra at 4.2 K and solution absorption spectrum at R.T. of $[Pt(en)_2][PtI_2(en)_2](HSO_4)_4 \cdot 4H_2O$ (PIHS). Curve a) is single crystal spectrum for *E*//chain. Curve b) is single crystal spectrum for *E*⊥ chain. Curve c) is solution spectrum.

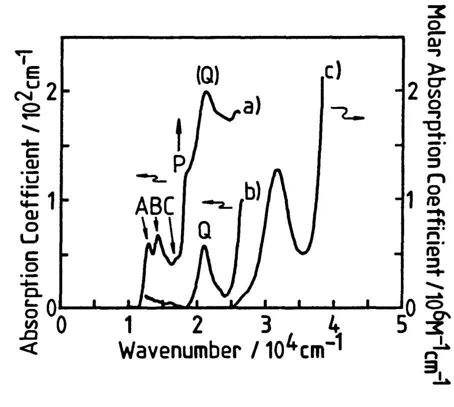

Fig. 3. Single crystal absorption spectra at 4.2 K and solution absorption spectrum at R.T. in $[Pt(en)_2][PtBr_2(en)_2](SO_4)_2 \cdot 6H_2O$ (PBSW). Curve a) is single crystal spectrum for *E*//chain. Curve b) is single crystal spectrum for *E*⊥chain. Curve c) is solution spectrum.

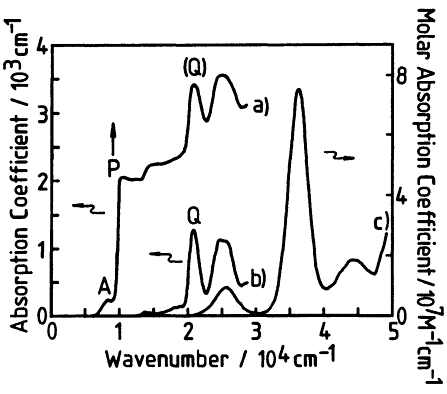

Fig. 4. Single crystal absorption spectra at 4.2 K and solution absorption spectrum at R.T. in $[Pt(en)_2][PtI_2(en)_2](SO_4)_2\cdot 6H_2O$ (PISW). Curve a) is single crystal spectrum for *E*//chain. Curve b) is single crystal spectrum for *E*⊥chain. Curve c) is solution spectrum.

absorption region in these single crystal spectra are saturated. The notation P in Figs. 1—4 shows the absorption edge of the low energy side of the absorption band due to the charge-transfer transition from the d_{z^2} of Pt(II) to the d_{z^2} of Pt(IV). The absorption band Q is due to the charge-transfer transition from an electronic state consisting mainly of d_{xz} and d_{yz} orbitals of Pt(II) to a state consisting mainly of d_{z^2} of Pt(IV).27) This is allowed only for the light polarized perpendicular to the Pt chain axis (*E*⊥chain). However, this absorption band Q appears also in the spectrum with *E*//chain. We consider that the structure in the region of the saturated absorption coefficient for *E*//chain is attributed to a leakage of the spectrum for *E*⊥chain by a slight optical inhomogeneity, as previously reported.8) Table 4 shows the energy of the absorption edges P and the bands Q of PBHS, PIHS, PBSW, and PISW. In the case of hydrogensulfates whose counterion is univalence, the energy of P of PBHS is higher than that of PIHS. Equally, in the case of sulfates whose counterion is bivalence, the energy of P of PBSW is higher than that of PISW. In both univalence and bivalence salts the energy of P of the bromo-bridged complex is higher than that of the iodo-bridged complex.

Comparison between PBHS and PBSW, and comparison between PBSW and PISW show that the energy shift of P by substituting counterion (i.e. PBSW → PBHS) is comparable to that by substituting bridging halogen (i.e. PBSW → PISW). Namely, the energy of the absorption edge of the iodo-bridged sulfate PISW with the bivalence counterion is as much as that of the bromo-bridged hydrogensulfate PBHS with the univalence counterion. Thus, one can conclude that an influence of the substitution of the univalence counterion HSO_4^- with the bivalence counterion SO_4^{2-} on the Pt(II)-Pt(IV) mixed-valence state is comparable to that of the substitution of the bridging halogen. The energy of the absorption edge of the bromo-bridged sulfate PBSW is comparable to WRS4) and $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$.27)

Table 4. The Energy of the Intervalence Charge-Transfer Absorption Edges P and Bands Q at 4.2 K

Complex	$P/10^3\ cm^{-1}$	$Q/10^3\ cm^{-1}$
PBHS	8.4	15.6
PIHS	6.4	21.4
PBSW	17.7	21.1
PISW	9.5	20.9

We consider that the influence of substituting the counterion on these charge-transfer absorption edges is explained by the network of the hydrogen bonds which play a role of the bond between a platinum atom and an adjacent platinum on a chain by way of the amine (NH_2) and the counterion (Y) as shown in Fig. 5. The hydrogensulfates with the univalence counterion have more hydrogen bonds than the sulfates with the bivalence counterion, because the molar ratio of the counterions for a platinum atom in the hydrogensulfates is twice the ratio in the sulfates. Thus, the bond between a platinum atom and an adjacent platinum atom on a chain in the univalence counterion complexes is more strongly supported by the outerchain bridge of the hydrogen bond than that in the bivalence counterion complexes. The energy difference between the electronic states of Pt(II) and those of Pt(IV) in the univalence counterion complexes is smaller than that in the bivalence counterion complexes. Consequently, the energy of the absorption edge due to the charge-transfer transition from the d_{z^2} of Pt(II) to the d_{z^2} of Pt(IV) in the univalence counterion complexes is lower than that in the bivalence counterion complexes.

Furthermore, the result that the influence of the substitution of the counterion on the Pt mixed-valence state is comparable to the influence of the substitution of the bridging halogen, suggests that the formation of the WRA mixed-valence complexes can be interpreted by two contributions, as follows. (1)

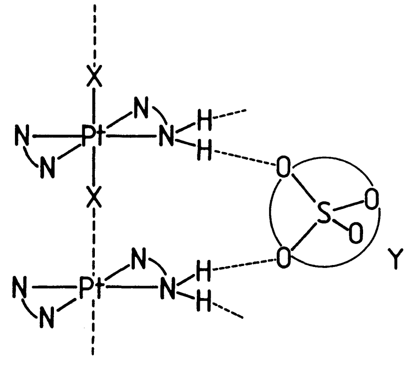

Fig. 5. The linkage between Pt(II) and Pt(IV) on a chain by hydrogen bonds through amines and counterions.

The charge-transfer interaction between the Pt(II) and Pt(IV) atoms becomes stronger in order of Cl, Br, and I which are the bridging halogen, because the energy of the intervalence charge-transfer absorption bands⁷⁾ and the energy distinction between the Pt(II) and Pt(IV) peaks in the XPS measurement⁵⁾ decrease in order of Cl, Br, and I. These results are in accordance with that the overlap integral between Pt(II) and Pt(IV) increase in the order of Cl, Br, and I. Accordingly, the ability to form the mixed-valence complexes increases in the order of Cl, Br, and I. (2) The charge-transfer interaction between the Pt(II) and Pt(IV) in the mixed-valence complexes having more counterions per a platinum atom is stronger than that in the complexes having less counterions, because the counterions link $[Pt^{IV}X_2(en)_2]^{2+}$ with $[Pt^{II}(en)_2]^{2+}$ on a chain by hydrogen bonds as shown in Fig. 5. Consequently, the charge-transfer interaction between the Pt(II) and Pt(IV) in the hydrogensulfates is stronger than that in the sulfates. In other words, the ability to form the mixed-valence complexes in the hydrogensulfates is larger than that in the sulfates.

In the energy region below the charge-transfer absorption edge P, weak absorption bands have been observed in the single crystal spectra of the sulfates PBSW and PISW for *E*//chain. This weak absorption band of PISW is noted by A in Fig. 4, and the weak absorption bands of PBSW are noted by A, B, and C in Fig. 3. The weak absorption band A of PISW, which has been recently reported partially in our previous paper,²⁸⁾ and the weak absorption bands A, B, and C of PBSW will be attributed to the transition related to some kinds of defects, namely, Pt(III), Pt(IV)Pt(II)Pt(II)Pt(IV), and Pt(II)Pt(IV)Pt(IV)Pt(II) on individual Pt chains. In the case of the hydrogensulfats PBHS and PIHS, however, these weak absorption bands could not be observed. This result can be explained by the following consideration. In the hydrogensulfates, it is difficult to produce these defects, because the hydrogen bond network strongly links $[Pt^{IV}X_2(en)_2]^{2+}$ to $[Pt^{II}(en)_2]^{2+}$ on individual chains. On the other hand, in the sulfates, the defects are easily produced, because the hydrogen bond network weakly links the Pt atoms. Investigation of the dependence of the weak absorption bands on compounds will be also necessary.

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