3906 © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***62,*** *3906—3910 (1989)* [Vol. 62, No. 12

Study of Mixed-Valence State in Halogen-Bridged Mixed-Valence Platinum(II,IV) Complexes by Temperature Dependence of Intervalence Charge-Transfer Spectra

Nobuyuki MATSUSHITA,*,† Norimichi KOJIMA, Toshiro BAN, and Ikuji TSUJIKAWA
Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606

(Received June 7, 1989)

The low-energy absorption edge due to the intervalence charge-transfer (IVCT) transition from Pt^{II} to Pt^{IV} has been investigated at 4.2 K and room temperature in single crystals of $[Pt(en)_2][PtBr_2(en)_2]Y_4$ {Y=ClO_4(PBC), HSO_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=Cl(PCSW), Br(PBSW), I(PISW)}. The IVCT absorption edges in PCSW, PBSW, and PISW shifted to the lower-energy side (i.e. red shift), while those in PBC, PBHS, and PIHS shifted to the higher-energy side (i.e. blue shift) with an increase in temperature.. We consider that the thermal effect of the valence fluctuation of the Pt mixed-valence state causes a red shift of the IVCT absorption edge and that the thermal effect of the hydrogen bond between the Pt^{II} complex ion and the Pt^{IV} complex ion causes a blue shift of the IVCT absorption edge. These two effects coexist and compete with each other in one complex. The dominant effect of the two effects determines the direction of the shift of the IVCT absorption edge, namely, the temperature dependence of the Pt mixed-valence state.

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 the viewpoints of physics and chemistry as a model of one-dimensional mixed-valence compounds. Figure 1 shows the structure of the Pt chain bridged by halogens in these Wolffram's Red Salt Analogues (WRA) mixed-valence complexes. The bridging halogen is not at the middle point between Pt^{II} and Pt^{IV}, but closer to Pt^{IV} than Pt^{II}. The electronic state of Pt is not strictly bivalent or quadrivalent, and approaches that of Pt^{III} by the medium of a charge-transfer interaction between the electronic state of Pt^{II} and that of Pt^{IV}.

The solid state properties in WRS and WRA mixed-valence complexes as a one-dimensional electron system have been investigated both experimentally and theoretically on the basis of the extended Peierls-Hubbard model.[4,5] The dependence of the solid state properties and the mixed-valence state on chemical members of the complexes has been investigated, mainly through substitution of the metal atom and the bridging halogen. Very recently, we reported the investigation on the idea that the influence of the substitution of a counter ion on the mixed-valence state can be interpreted by a hydrogen bond network from a comparison of the optical properties of the sulfate complexes and the hydrogensulfate complexes at 4.2 K.[6] On the other hand, it has been reported that the lattice constants along the Pt chain of $[Pt(NH_3)_4][PtX_2(NH_3)_4](HSO_4)_4$ (X=Cl, Br)[7,8] decrease, while those of $[Pt(NH_3)_4][PtI_2(NH_3)_4](HSO_4)_4\cdot 2H_2O$[8] and $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ (X=Cl, Br, I),[9] where en denotes ethylenediamine, increase with an increase in temperature. These results show that there are two kinds of temperature dependences regarding the Pt-Pt distance: One is that the Pt-Pt distance becomes longer with an increase in temperature; the other is that the Pt-Pt distance becomes shorter with an increase in temperature. This suggests that there are also two kinds of temperature dependences regarding the Pt mixed-valence state. We expect that the temperature dependence of the Pt mixed-valence state is dominated by the constituents of the complexes as the metal ion, the bridging halogen, the in-plane ligand amine and the counter ion. However, the temperature dependence of the mixed-valence state has not yet been investigated in detail. We have investigated the temperature dependence of the optical properties in some WRA mixed-valence complexes in order to clarify the temperature dependence of the mixed-valence state. In this paper we report on the optical properties of single crystals at 4.2 K and at room temperature in $[Pt(en)_2][PtX_2(en)_2](SO_4)_2\cdot 6H_2O$ {X=Cl(PCSW), Br(PBSW), I(PISW)}, $[Pt(en)_2][PtBr_2(en)_2]Y_4$ {Y=ClO_4(PBC), HSO_4(PBHS)}, $[Pt(en)_2][PtI_2(en)_2](HSO_4)_4\cdot 4H_2O$ (PIHS). In addition, we also report on the synthesis, structure and the mixed-valence state of a new WRA mixed-valence complex, PCSW. From these experimental results, we discuss the temperature dependence of the Pt mixed-valence state on the basis of the hydrogen bond network.

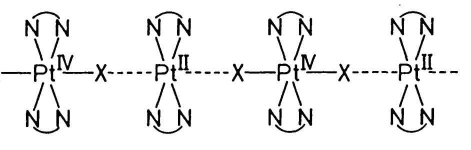

Fig. 1. The Pt chain structure of the halogen-bridged mixed-valence platinum complexes.

---

† Present address: Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153.

Experimental

Preparation. The Pt^{II}-Pt^{IV} mixed-valence complexes (PBHS, PIHS, PBSW, PISW) were prepared; these single crystals were obtained according to a previously described method.(6) The PBC was prepared by a procedure of Bekaroglu et al.(10) Single crystals of the low-temperature phase** of PBC were obtained at 13 °C by recrystallization from an aqueous solution. The above-mentioned mixed-valence complexes were identified by elemental analysis and a powder X-ray diffraction method.

$[Pt(en)_2][PtCl_2(en)_2](SO_4)_2 \cdot 6H_2O$ (PCSW): $[PtCl_2(en)_2](HSO_4)_2$ was obtained by the oxidation of $[Pt(en)_2]Cl_2$ with an aqueous hydrogen peroxide solution, and then by the addition of a small amount of hydrochloric acid and an excess of aqueous sulfuric acid to the oxidized platinum complex solution. Its Pt^{IV} complex (1.7 mmol) and $[Pt(en)_2]Cl_2$ (1.7 mmol) were dissolved in water (ca. 100mL). Yellow plate-like single crystals, which show dichroism, were obtained by a slow concentration of this colorless solution. Found: C, 9.63; H, 4.46; N, 11.31; O, 22.44; S, 6.45; Cl,7.06%. Calcd for $C_8H_{44}Cl_2N_8O_{14}Pt_2S_2$: C, 9.61; H, 4.44; N, 11.21; O, 22.41; S, 6.42; Cl, 6.89%.

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 (20 °C for PBC) on a Rigaku diffractometer using the θ-2θ scan technique and graphite-monochromated Cu $K\alpha$ radiation (λ=1.5418 Å). It was confirmed that crystals of PBC were the low-temperature phase. The crystals of PBC in the low-temperature phase were used for measurements of the absorption spectra.

The TGA of PCSW 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 and room temperature with a Jasco CT-100 spectrometer using a tungsten lamp for the light source and a Glan-Taylor 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 measured at 4.2 K was placed in a double glass Dewar's vessel and immersed in liquid helium to cool. The measurement at room temperature was carried out by irradiating the sample with monochromatic light to prevent thermo-damage of the single crystal due to white light.

Results and Discussion

PCSW. TGA shows that the content of the crystallized water (10.8%) calculated from the chemical formula of PCSW corresponds with the weight loss (10.6%, 48—121 °C) on heating. The powder X-ray diffraction pattern shows that PCSW is isomorphous to PBSW and PISW in structure. The lattice constants of PCSW (a=13.74, b=11.54, c=9.19 Å, β=101.7°) was determined by the powder X-ray diffraction pattern of PCSW with index numbers which were numbered by reference to that of PBSW and PISW. To our knowledge, it is the first example that Cl-, Br-, and I-bridged complexes are isomorphous in the WRA mixed-valence complexes whose chemical entities are the same, except for the bridging halogen. Figure 2 shows the absorption spectra of a single crystal of PCSW at 4.2 K. The absorption edge P for the light polarized parallel to the Pt chain axis ($\boldsymbol{E}/\!/$ chain) is the low-energy absorption edge due to the IVCT transition from the d_{z^2} of Pt^{II} to the d_{z^2} of Pt^{IV}. The energy of the IVCT absorption edge of PCSW (22.3×10^3 cm^{-1}) is higher than that of PBSW (17.7×10^3 cm^{-1})(6) and PISW (9.5×10^3 cm^{-1}).(6) The energies of the IVCT absorption edge in complexes comprising a bivalent counter ion are in the order I<Br<Cl, as well as those in complexes comprising a univalent counter ion. The energy of the IVCT absorption edge of PCSW is higher than that of $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (PCC) (19.1×10^3 cm^{-1})(11) as well as that of PBSW, being higher than that of PBHS (8.4×10^3 cm^{-1})(6) and PBC (7.5×10^3 cm^{-1}). In other words, the energy of the IVCT absorption edge of a complex comprising a bivalent counter ion is higher than that of the complexes comprising a univalent counter ion, also in the chloro-bridged mixed-valence complexes. As previously described in our paper,(6) complexes comprising a univalent counter ion have more hydrogen bonds which link a platinum atom with an adjacent platinum on the same chain by way of the amine and the counter ion than the complexes comprising a bivalent counter ion. This is because the molar ratio of the counter ion for a platinum atom in the former complexes is twice as large as that in the latter complexes. Thus, the bond between a platinum atom and an adjacent platinum atom on the same chain in univalent counter ion complexes is more strongly supported by the hydrogen bond network than that in

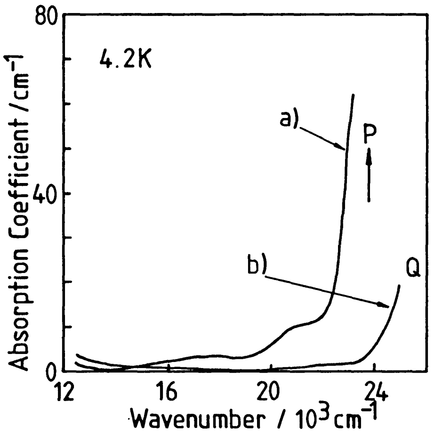

Fig. 2. Single crystal absorption spectra of $[Pt(en)_2][PtCl_2(en)_2](SO_4)_2 \cdot 6H_2O$ (PCSW) at 4.2 K. Curve a) is the spectrum for the light polarized parallel to the Pt chain axis ($\boldsymbol{E}/\!/$chain). Curve b) is the spectrum for the light polarized perpendicular to the Pt chain axis ($\boldsymbol{E}\perp$chain).

** The structure phase transition occurs in PBC at ca. 30 °C. The high-temperature phase is orthorhombic and the low-temperature phase is monoclinic.

the bivalent counter ion complexes. Therefore, the result of PCSW and PCC can also be explained by the effect of this hydrogen bond network. The peak energy of the IVCT band obtained by a Kramers-Kronig transformation of the reflection spectra of $[Pt(chxn)_2][PtCl_2(chxn)_2](ClO_4)_4$ (Pt-chxn-Cl-ClO_4) (3.2 eV), where chxn denotes 1,2-cyclohexanediamine, is much higher than that of PCC (2.72 eV),[4] and the crystal color of Pt-chxn-Cl-ClO_4 is the same yellow as that of PCSW. These results show that the mixed-valence state of PCSW is comparable to that of Pt-chxn-Cl-ClO_4. We can explain the change in the mixed-valence state with a change from en to chxn as follows. The distinction between the electronic state of Pt^{II} and that of Pt^{IV} becomes large with a decrease in the effect of the hydrogen bond network, since the C_6H_{10} ring of chxn blocks the formation of the hydrogen bonds between the $-NH_2$ of chxn and the counter ion ClO_4^-. The influence of the substitution from the univalent counter ion as ClO_4^- or HSO_4^- to the bivalent counter ion as SO_4^{2-} on the mixed-valence state is comparable to that of the substitution of the in-plane ligand amine from en to chxn. In other words, this fact is proof that the hydrogen bond between the counter ion and the amine contributes to the mixed-valence state.

Temperature Dependence of the Mixed-Valence State. Figures 3—5 show the IVCT absorption edges for the *E*//chain at 4.2 K and at room temperature in PBC, PBHS, and PIHS, respectively; Table 1 shows those energies. The energies of these IVCT absorption edges at room temperature are higher than those at 4.2 K. Namely, the IVCT absorption edges in PBC, PBHS, and PIHS shifted to the higher-energy side with an increase in temperature. This blue shift is opposite to a broadening of the spectra due to an increase in temperature. Therefore, this result shows that the energy distinction between the electronic state of the Pt^{II} and that of the Pt^{IV} in the mixed-valence state increases with an increase in temperature.

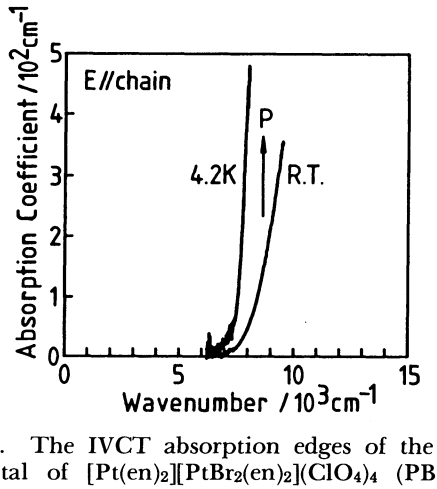

Fig. 3. The IVCT absorption edges of the single crystal of $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$ (PBC) for *E*//chain at 4.2 K and room temperature (R.T.).

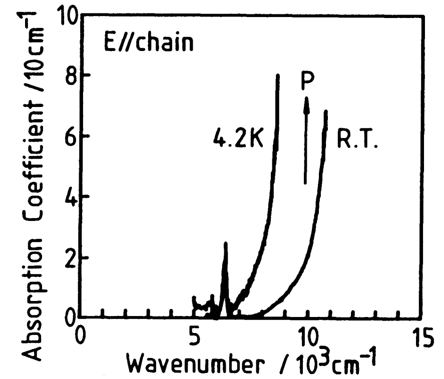

Fig. 4. The IVCT absorption edges of the single crystal of $[Pt(en)_2][PtBr_2(en)_2](HSO_4)_4$ (PBHS) for *E*//chain at 4.2 K and room temperature (R.T.).

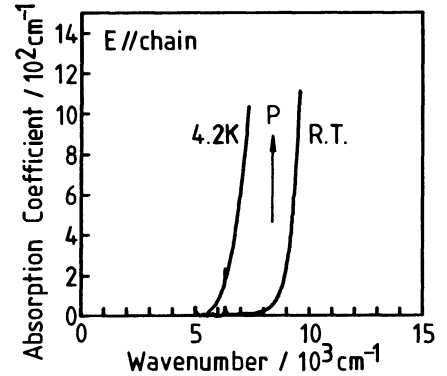

Fig. 5. The IVCT absorption edges of the single crystal of $[Pt(en)_2][PtI_2(en)_2](HSO_4)_4 \cdot 4H_2O$ (PIHS) for *E*//chain at 4.2 K and room temperature (R.T.).

Table 1. The Energy of the IVCT Absorption Edges at 4.2 K and Room Temperature

Complex	Energy/10^3 cm^{-1}	
	4.2 K	Room temp
PBC	7.5	8.3
PBHS	8.4	10.2
PIHS	6.4	9.0
PCSW	22.3	19.8
PBSW	17.7	14.8
PISW	9.5	7.3

Figures 6—8 show the IVCT absorption edges for the *E*//chain at 4.2 K and at room temperature in PCSW, PBSW, and PISW, respectively; Table 1 shows those energies. The energies of these IVCT absorption edges at room temperature are lower than those at 4.2 K. Namely, the IVCT absorption edges in PCSW, PBSW, and PISW shifted to the lower-energy side with an increase in temperature. This result shows that the energy distinction between the electronic state of the Pt^{II} and that of the Pt^{IV} in the mixed-valence state decreases with an increase in temperature, for the following reasons. The lower-energy side shift, i.e. the red shift (2000—3000 cm^{-1}), is much larger than

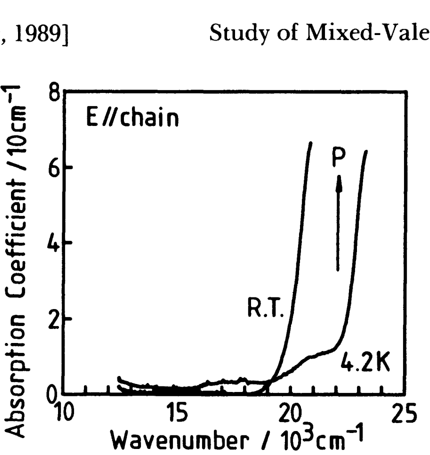

Fig. 6. The IVCT absorption edges of the single crystal of $[\mathrm{Pt(en)_2}][\mathrm{PtCl_2(en)_2}](\mathrm{SO_4})_2\cdot 6\mathrm{H_2O}$ (PCSW) for *E*//chain at 4.2 K and room temperature (R.T.).

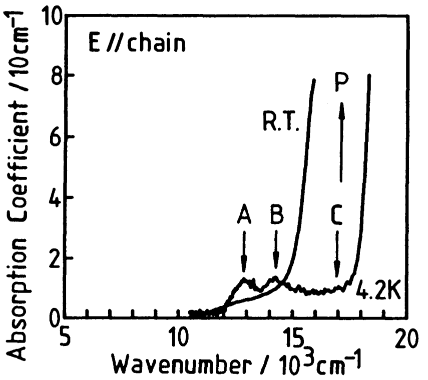

Fig. 7. The IVCT absorption edges of the single crystal of $[\mathrm{Pt(en)_2}][\mathrm{PtBr_2(en)_2}](\mathrm{SO_4})_2\cdot 6\mathrm{H_2O}$ (PBSW) for *E*//chain at 4.2 K and room temperature (R.T.).

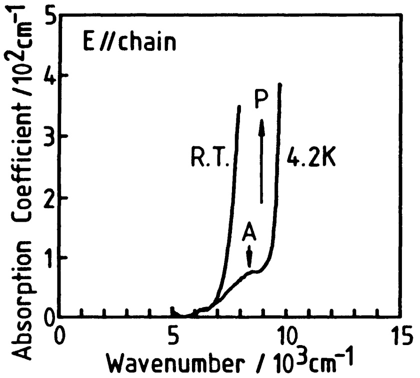

Fig. 8. The IVCT absorption edges of the single crystal of $[\mathrm{Pt(en)_2}][\mathrm{PtI_2(en)_2}](\mathrm{SO_4})_2\cdot 6\mathrm{H_2O}$ (PISW) for *E*//chain at 4.2 K and room temperature (R.T.).

the temperature broadening of the spectra. Its large red shift cannot be explained by both a broadening of the spectra and an increase in the energy distinction between the electronic state of the $\mathrm{Pt^{II}}$ and that of the $\mathrm{Pt^{IV}}$, which was mentioned above. In addition, we have found that the peak energy of the reflection spectra of PBSW at room temperature is lower than that at 77 K.[12] The result of the reflection spectra is consistent with the absorption spectral result of PBSW. Therefore, the result of the red shift of the IVCT absorption edge shows that the energy distinction between the electronic state of $\mathrm{Pt^{II}}$ and that of $\mathrm{Pt^{IV}}$ in the mixed-valence state decreases with an increase in temperature.

We found that there are two kinds in the temperature dependences of the mixed-valence state from the absorption spectra. These two dependences are consistent with the two types of temperature dependences of the mixed-valence state obtained from the structural result: that there are two kinds in the temperature dependences of the Pt-Pt distance along the Pt chain. To interpret the two types of temperature dependences of the mixed-valence state, we propose two types of thermal effects contributing to the mixed-valence state as follows.

One is an effect that the electronic state of the $\mathrm{Pt^{II}}$ and that of the $\mathrm{Pt^{IV}}$ approach each other with an increase in temperature. A positional fluctuation of the bridging halogen becomes vigorous by a thermal excitation of the $\mathrm{Pt^{IV}}$-X stretching vibration with an increase in temperature. This fluctuation induces a valence fluctuation of the Pt mixed-valence state by the medium of the electron-phonon coupling, which is one of characteristics of this WRA system. This valence fluctuation becomes vigorous with an increase in temperature, and approaches the electronic state of the $\mathrm{Pt^{II}}$ and that of the $\mathrm{Pt^{IV}}$ to that of the $\mathrm{Pt^{III}}$, respectively. Consequently, the distinction between the energy level of the d_{z^2} of $\mathrm{Pt^{II}}$ and that of $\mathrm{Pt^{IV}}$ in the mixed-valence state decreases with an increase in temperature. As a result, this change in the Pt electronic state causes a red shift of the IVCT absorption edge. Equally, the negative thermal expansion coefficient of the lattice constant along the Pt chain axis of $[\mathrm{Pt(NH_3)_4}][\mathrm{PtX_2(NH_3)_4}](\mathrm{HSO_4})_4$ (X=Cl, Br)[7,8] is theoretically interpreted as the valence fluctuation.[13]

The other is an effect that the electronic state of the $\mathrm{Pt^{II}}$ and that of the $\mathrm{Pt^{IV}}$ are more distinguishable from each other with an increase in temperature. Positional fluctuations of the hydrogen atom of the in-plane ligand amine and the oxygen atom of the counter ion become vigorous by thermal excitation with an increase in temperature. These fluctuations weaken the link by the hydrogen bond between the $\mathrm{Pt^{II}}$ complex ion and the $\mathrm{Pt^{IV}}$ complex ion. Consequently, the weak link of the hydrogen bond weakens the intervalence charge-transfer bond between the $\mathrm{Pt^{II}}$and the $\mathrm{Pt^{IV}}$. Therefore, the electronic state of the $\mathrm{Pt^{II}}$ and that of the $\mathrm{Pt^{IV}}$ at higher temperatures become more distinguishable than those at lower temperatures. As a result, this change in the Pt electronic state causes a blue shift of the IVCT absorption edge.

In a comparison between the crystal structure of $[\mathrm{Pt(NH_3)_4}][\mathrm{PtBr_2(NH_3)_4}](\mathrm{HSO_4})_4$ at 298 K and that at 134 K, the Pt-Pt distance becomes long, and the N(-H)···O distance becomes short with a decrease in temperature.[8] The change of the Pt–Pt distance is consistent with the red shift, and the change of the N(–H)···O distance is consistent with the blue shift. This result regarding the structure shows that both effects causing the red and blue shifts coexist together and compete with each other in one WRA mixed-valence complex, since changes in both the Pt–Pt distance and the N(–H)···O distance coexist. In addition, from the results concerning the IVCT absorption edge, the dominant effect of the two competing effects determines the direction of the shift of the IVCT absorption edge. In the sulfate complexes, PCSW, PBSW, and PISW, the effect of the valence fluctuation due to the thermal vibration of the bridging halogen (namely, the effect causing the red shift) dominates. In PBC, PBHS, and PIHS, the effect regarding the weakening of the hydrogen bond link due to the thermal vibration (namely, the effect causing the blue shift) dominates. Furthermore, we consider which of the thermal effects (the valence fluctuation or the hydrogen bond) dominates the temperature dependence of the mixed-valence state. This dominance can be explained from the effect of the hydrogen bond network. As mentioned above, the dependence of the energy of the IVCT absorption edges on the substitution of the counter ion and that of the in-plane ligand amine is explained from this effect of the hydrogen bond network. Relatively speaking, the perchlorate and hydrogensulfate complexes comprising the univalent counter ion belong to a system in which the effect of the hydrogen bond network is stronger, while the sulfate complexes comprising the bivalent counter ion belong to a system in which that effect is weaker. This classification is used because the composition ratio of the counter ions for a platinum atom in the former is twice as much as that in the latter.[6] First, in the former system, in which the effect of the hydrogen bond network is stronger, the temperature dependence of the mixed-valence state is dominated by the thermal effect of the hydrogen bond rather than the thermal effect of the valence fluctuation. Therefore, the energy distinction between the electronic state of $\mathrm{Pt^{II}}$ and that of $\mathrm{Pt^{IV}}$ becomes larger, namely, the IVCT absorption edge shows a blue shift with an increase in temperature. On the other hand, in the latter system, in which the effect of the hydrogen bond network is weaker, the temperature dependence of the mixed-valence state is dominated by the thermal effect of the valence fluctuation rather than the thermal effect of the hydrogen bond. Therefore, the energy distinction between the electronic state of $\mathrm{Pt^{II}}$ and that of $\mathrm{Pt^{IV}}$ becomes smaller, namely, the IVCT absorption edge shows a red shift with an increase in temperature.

In the above discussion, the mixed-valence state and its temperature dependence in the perchlorate and hydrogensulfate complexes are not only dominated by the direct contribution due to the interaction between the $\mathrm{Pt^{II}}$ and the $\mathrm{Pt^{IV}}$ through the bridging halogen, but are also dominated by the hydrogen bond between the amine and the counter ion. On the other hand, the mixed-valence state and its temperature dependence in the sulfate complexes are almost dominated by the direct contribution and are little dominated by the hydrogen bond.

To confirm the temperature dependences of the mixed-valence state by the reflection spectra, measurements of the reflection spectra in PBC, PBHS, PIHS, PCSW, and PISW are in progress. To clarify the relation between the temperature dependence of the IVCT spectra and that of the structure, studies of the temperature dependence of the crystal unit cell for PBHS, PIHS, PCSW, PBSW and PISW, and that of the IVCT absorption edges of $\mathrm{[Pt(NH_3)_4][PtX_2(NH_3)_4](HSO_4)_4}$ (X=Cl, Br) and $\mathrm{[Pt(NH_3)_4][PtI_2(NH_3)_4](HSO_4)_4\cdot 2H_2O}$ are necessary.

The authors wish to thank Dr. Koshiro Toriumi of I.M.S. and Dr. Masahiro Yamashita of Nagoya University for valuable discussions concerning the crystal structure. We are also indebted to Dr. Naohilo Watanabe of Kyoto University for his kind help and advice concerning data processing computer programs. This study was supported by a Grant-in-Aid for Scientific Research No. 63540485 from the Ministry of Education, Science and Culture.

References

1) H. J. Keller, "Extended Linear Chain Compounds," ed by J. S. Miller, Plenum, New York (1982), p. 357.

2) R. J. H. Clark, "Mixed-Valence Compounds," ed by D. B. Brown, Reidel, Dordrecht (1980), p. 271.

3) K. Nasu, M. Yamashita, T. Mitani, and S. Kurita, *Butsuri*, **41**, 317 (1986).

4) Y. Wada, T. Mitani, M. Yamashita, and T. Koda, *J. Phys. Soc. Jpn.*, **54**, 3143 (1985).

5) K. Nasu, *J. Phys. Soc. Jpn.*, **52**, 3865 (1983); **53**, 302 (1984); **53**, 427 (1984).

6) N. Matsushita, N. Kojima, T. Ban, and I. Tsujikawa, *Bull. Chem. Soc. Jpn.*, **62**, 1785 (1989).

7) M. Tanaka, I. Tsujikawa, K. Toriumi, and T. Ito, *Acta Crystallogr., Sect. B*, **38**, 2793 (1982).

8) M. Tanaka and I. Tsujikawa, *Butsuri*, **41**, 275 (1986).

9) K. Toriumi and M. Yamashita, private communication.

10) O. Bekaroglu, H. Breer, H. Endres, H. J. Keller, and H. Nam-Gung, *Inorg. Chim. Acta*, **21**, 183 (1977).

11) M. Tanaka, S. Kurita, T. Kojima, and Y. Yamada, *Chem. Phys.*, **91**, 257 (1984).

12) N. Matsushita, N. Kojima, N. Watanabe, and T. Ban, in preparation for publication.

13) T. Murao, *Phys. Rev. B*, **35**, 6051 (1987).