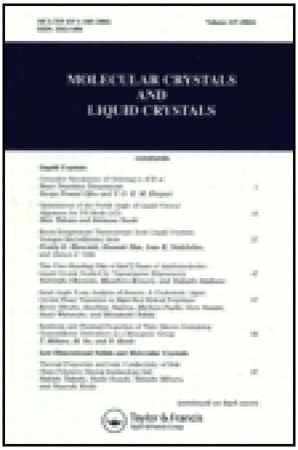

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Midgap Absorption Spectra in Various Kinds of Halogen Bridged Mixed-Valence Pt Complexes

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MIDGAP ABSORPTION SPECTRA IN VARIOUS KINDS OF HALOGEN BRIDGED MIXED-VALENCE Pt COMPLEXES

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Abstract We have investigated several kinds of midgap absorption spectra due to the mismatch of valence alternation(nonlinear excitations such as solitons and polarons) in various kinds of halogen bridged mixed-valence Pt complexes, $[Pt(en)_2][PtX_2(en)_2](SO_4)_2\cdot 6H_2O$ (X=Cl, Br and I), $[PtX_2(en)][PtX_4(en)]$ (X=Cl and Br), and $[Pt(NH_3)_4][PtCl_2(NH_3)_4](HSO_4)_4$. Also we investigated the relationship between the stability of the mismatch of valence alternation and the crystal structure.

INTRODUCTION

In recent years, one-dimensional halogen-bridged mixed-valence complexes have been investigated intensively from viewpoints of physics and chemistry as a model of one-dimensional mixed-valence system. The valence of the Pt atoms in the halogen bridged Pt chain is alternate, and this valence alternation of Pt(II) and Pt(IV) consists in two fold degeneracy system. So that various kinds of mismatch of valence alternation(nonlinear excitations such as kink-solitons and polarons) are expected in these complexes. Recently, several authors have observed the photo-induced absorption effect for several weak absorption bands(midgap bands) below the intervalence charge transfer(IVCT) band corresponding to the $Pt^{II}(5d_z2)\rightarrow Pt^{IV}(5d_z2)$ transition in this system, and have discussed the relation between the origin of the midgap bands and the mismatch of valence alternation as solitons and polarons.[1-6] However, this relation has not been elucidated perfectly. The number of the midgap bands and the decay time of the photo-induced absorption effect remarkably depend on the kind of Pt complexes. In the present paper, we report midgap absorption bands due to the mismatch of valence alternation in various kinds of mixed valence Pt complexes and discuss the relationship between the stability of the mismatch of valence alternation and the crystal

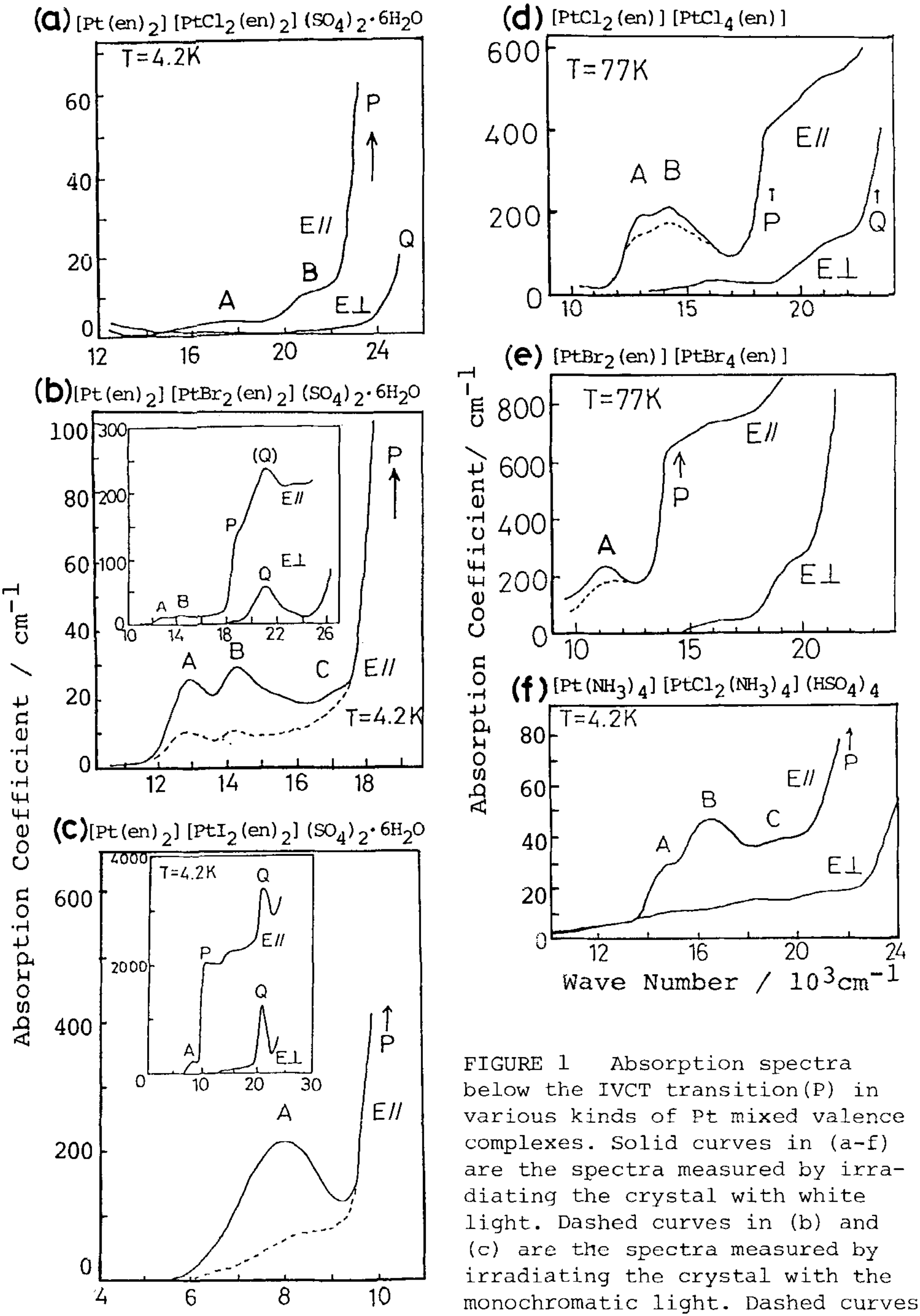

FIGURE 1 Absorption spectra below the IVCT transition(P) in various kinds of Pt mixed valence complexes. Solid curves in (a-f) are the spectra measured by irradiating the crystal with white light. Dashed curves in (b) and (c) are the spectra measured by irradiating the crystal with the monochromatic light. Dashed curves in (d) and (e) are the spectra measured by the light below the IVCT band. E// and E⊥ denote the electric vectors of the incident light parallel and perpendicular to the chain axis, respectively.

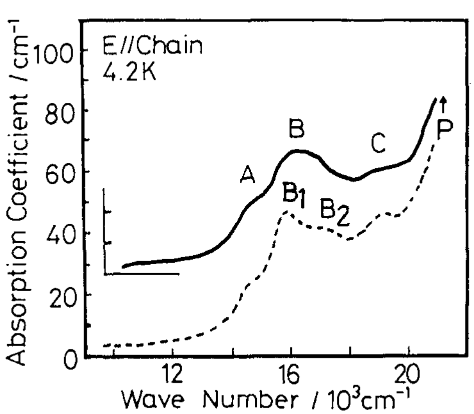

FIGURE 2 Midgap absorption spectra in $[Pt(NH_3)_4][PtCl_2(NH_3)_4](HSO_4)_4$. Solid curve is the spectra measured by irradiating the crystal with white light. Dashed curve is the spectra measured by irradiating the crystal with the monochromatic light.

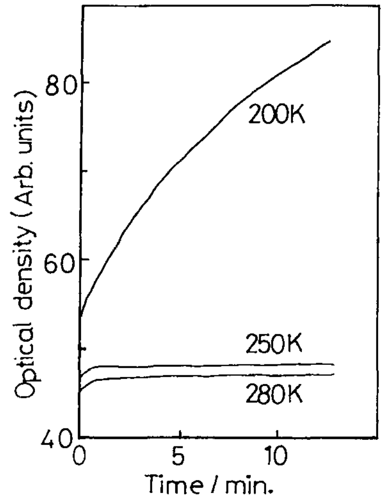

FIGURE 3 Development of the photo-induced absorption effect of the B band of $[PtCl_2(en)][PtCl_4(en)]$ at various temperatures. Time 0 denotes the point when a filter is removed to irradiate the sample with the light in the region of the IVCT band.

structure. Moreover, we discuss the migration of the mismatch of valence alternation.

RESULTS AND DISCUSSION

Figure 1 shows the IVCT bands(P and Q denote the $Pt^{II}(5d_{z}2) \rightarrow Pt^{IV}(5d_{z}2)$ and the $Pt^{II}(5d_{yz,zx}) \rightarrow Pt^{IV}(5d_{z}2)$ transitions, respectively) and midgap absorption bands(A-C) in $[Pt(en)_2][PtX_2(en)_2](SO_4)_2 \cdot 6H_2O$(X=Cl:PCSW, X=Br:PBSW, X=I:PISW), $[PtX_2(en)][PtX_4(en)]$(X=Cl:PEC, X=Br:PEB), and $[Pt(NH_3)_4][PtX_2(NH_3)_4](HSO_4)_4$(ACS). The number of the midgap bands in PCSW, PBSW, PISW, PEC, PEB, and ACS are 2, 3, 1, 2, 1, and 4, respectively. In the case of ACS, as shown in Fig. 2, it is obvious that at least four midgap absorption bands(A, B_1, B_2, C) exist below the IVCT band.

The characteristic properties of the midgap absorption bands in these complexes are summarized as follows.

(1) Midgap absorption bands of all complexes appear below the absorption edge of the IVCT band only for the light of E // chain.

(2) Midgap absorption bands in PBSW, PISW, PEC, PEB, and ACS exhibit the photo-induced absorption effect, which are shown in Figs. 1 and 2.
(3) In the case of PBSW, the intensity of the C band is much weaker than those of the A and B bands, but it is remarkably enhanced by the Au-doping. The Au^{III} doping disturbs the Pt valence state, and it probably increases the mismatch of the Pt valence alternation in the relaxation process of the charge transfer exciton.
(4) In the case of ACS, the photo-induced absorption effect of the B_2 band is significantly stronger than those of the A, B_1, and C bands.
(5) As shown in Fig. 3, the development of the photo-induced absorption effect of the midgap bands in PEC remarkably depends on temperature. PEC undergoes a structural phase transition at about 240K.[7] The crystal structures of the low and high temperature phases are monoclinic(a=5.495Å, b=13.460Å, c=9.653Å, β=93.29° at 117K) and orthorhombic(a=5.517Å, b=13.571Å, c=9.731Å at 291K), respectively.[7] In the case of the high temperature phase($T > 240K$), the absorption coefficients of the A and B bands increased when the sample was irradiated with the light in the region of the IVCT band, and became the steady state during a few minutes. On the other hand, their absorption coefficients decreased when the irradiating light was stopped, and became the steady state during several minutes. The midgap absorption bands in PBSW, PISW, and ACS also show the similar time dependence. In the case of the low temperature phase($T < 240K$), the absorption coefficients increased monotonously during several tens of minutes with irradiating the light in the region of the IVCT band, but they did not decrease when the irradiating light was stopped. From these results, it is obvious that the mismatch of valence alternation in the low temperature phase of PEC is significantly more stable than that in the high temperature phase of PEC.

The time dependence of the photo-induced absorption effect of the midgap bands in PEC resembles closely that of the midgap absorption bands(A and B) in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$(PCC).[2] The intensities of the A and B bands in PCC, which were increased by irradiating with the light in the region of the IVCT band, did not decrease at 77K, but the stable photo-induced absorption effect was not observed at room temperature.[2] PCC also undergoes a structural phase transition like PEC.[8] The crystal structure of the low temperature phase ($T < 295K$) of PCC is monoclinic($P2_1/a$), where the Pt-X-Pt chain is nonlinear(i.e. zigzag). On the other hand, the crystal structure of the high temperature phase($T > 295K$) of PCC is orthorhombic(Icma), where the Pt-X-Pt chain is linear. Therefore, the mismatch of valence alternation in the low temperature phase with zigzag Pt-X-Pt chain of PCC is significantly more stable than that in the high temperature phase with linear Pt-X-Pt chain of PCC. In connection with this, the following should be noted. Most of the mixed valence Pt complexes which have midgap absorption bands,(for example, $[Pt(en)_2][PtX_2(en)_2](SO_4)_2 \cdot 6H_2O$(X=Cl, Br, and I)[9], $[PtX_2(en)][PtX_4(en)]$(X=Cl and Br)[10], $[Pt(NH_3)_4][PtCl_2(NH_3)_4](HSO_4)_4$[11]), have zigzag Pt chains.

From above mentioned results, we arrived at the conclusion that the potential barrier of processes from the metastable states such as the mismatch of valence alternation to the ground state in the zigzag Pt-X-Pt chain is large and it is responsible for the stability of the mismatch of valence alternation.

Here, we focus the transfer mechanism of the mismatch of valence alternation. From the time dependence of the photo-induced absorption effect of midgap bands, it is obvious that the photo-induced mismatches of valence alternation in MX-chains migrate generally, and soliton pairs or polaron pairs are recombined in the ground state. We classify the transfer mechanism of the mismatches of valence alternation(S^0, S^+, S^-, P^+, and P^-) in the mixed valence MX-chain, which is shown in Fig. 4. In the case that the difference in valence is 2, such as mixed valence Pt complexes, the migrations of S^0, $S^\pm$, and $P^\pm$ are induced by two-electrons transfer. On the other hand, in the case that the difference in valence is 1, such as mixed valence Cu complexes, the migrations of $S^\pm$ and $P^\pm$ are induced by one-electron transfer. It is worth noting that the migrations of $S^\pm$ and $P^\pm$ in the case(II) resemble closely those of the domain wall soliton($\downarrow\ \uparrow\ \downarrow\ \underline{\uparrow\ \uparrow}\ \downarrow\ \uparrow$) and the magnon($\uparrow\ \downarrow\ \uparrow\ \underline{\uparrow}\ \uparrow\ \downarrow\ \uparrow$) in one-dimensional Ising-like antiferromagnets such as $CsCoCl_3$. Studies on the behavior of the nonlinear excitations in the one-dimensional mixed valence complexes where the difference in valence is one are in progress.

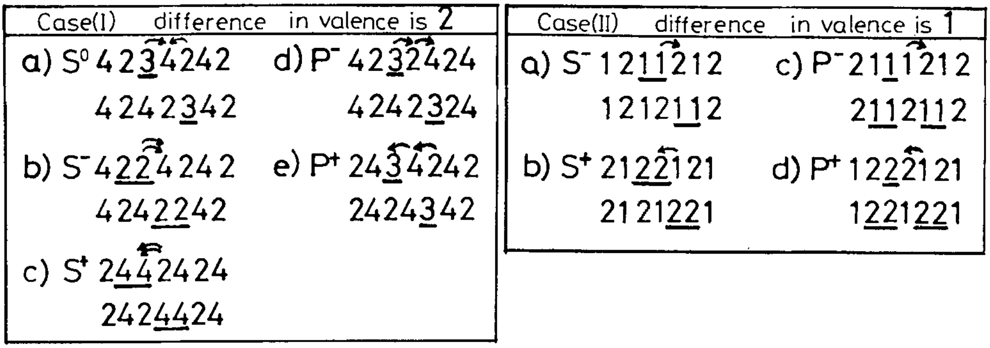

FIGURE 4 Transport mechanism of the mismatch of valence alternation in mixed valence MX-chain. Arabic numerals show the valence states in MX-chain. S^0, $S^{\pm}$ and $P^{\pm}$ denote a neutral soliton, charged solitons and polarons, respectively. ↷ shows the electron transfer.

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