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### Creations of Solitons and Polarons in MX-Chain Compounds, {[Pt(en)<sub>2</sub>][PtX<sub>2</sub>(en)<sub>2</sub>]}<sub>3</sub>(CuX<sub>4</sub>)<sub>4</sub> (X=Cl and Br)

H. Aso<sup>a</sup>, T. Manabe<sup>a</sup>, T. Kawashima<sup>b</sup>, T. Ishii<sup>a</sup>, H. Miyasaka<sup>a</sup>, H. Matasuzaka<sup>a</sup>, M. Yamashita<sup>a</sup>, Hassanuddin<sup>c</sup>, N. Kuroda<sup>c</sup> & M. Shiro<sup>d</sup>

<sup>a</sup> Graduate School of Science, Tokyo Metropolitan University and PRESTO(JST), 1-1 Minamiohsawa, Hachioji, Tokyo, 192-0397, Japan

<sup>b</sup> Graduate School of Human Informatics, Nagoya University, Nagoya, 464-8601, Japan

<sup>c</sup> Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto, 860-8555, Japan

<sup>d</sup> Rigaku, Matsubara-cho, Akishima, Tokyo, 196-8666, Japan

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## Creations of Solitons and Polarons in MX-Chain Compounds, $\{[\text{Pt}(\text{en})_2][\text{PtX}_2(\text{en})_2]\}_3(\text{CuX}_4)_4 (\text{X} = \text{Cl and Br})$

H. ASO<sup>a</sup>, T. MANABE<sup>a</sup>, T. KAWASHIMA<sup>b</sup>, T. ISHII<sup>a</sup>,  
 H. MIYASAKA<sup>a</sup>, H. MATASUZAKA<sup>a</sup>, M. YAMASHITA<sup>a</sup>,  
 HASSANUDDIN<sup>c</sup>, N. KURODA<sup>c</sup> and M. SHIRO<sup>d</sup>

<sup>a</sup>*Graduate School of Science, Tokyo Metropolitan University and  
 PRESTO(JST), 1-1 Minamiohsawa, Hachioji, Tokyo 192-0397, Japan,*

<sup>b</sup>*Graduate School of Human Informatics, Nagoya University, Nagoya,  
 464-8601, Japan,*

<sup>c</sup>*Faculty of Engineering, Kumamoto University, Kurokami,  
 Kumamoto 860-8555, Japan and*

<sup>d</sup>*Rigaku, Matsubara-cho, Akishima, Tokyo 196-8666, Japan*

The creations of solitons and polarons in the  $\{[\text{Pt}(\text{en})_2][\text{PtX}_2(\text{en})_2]\}_3(\text{CuX}_4)_4$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ ) which consist of the double linear chain structures of the main one-dimensional halogen-bridged Pt(II)-Pt(IV) mixed-valence units and one-dimensional counteranions of trigonal bipyramidal Cu(I) ions, have been investigated by the absorption spectra, photo-induced absorption spectra, and ESR spectra. The ESR signals of the Pt(III) and Cu(II) species, which were introduced during the synthetic process, are observed in these compounds. The relative intensities of d-d transitions and ESR spectra of Cu(II) species in counteranions are consistent with each other in the Cl-bridged compounds obtained by pH control. The photo-induced absorption of the Cl-bridged compound is observed in the mid-gap region, which is attributable to the soliton. The doping effect by  $\text{Br}_2$  was investigated for the Br-bridged compounds. The relative intensities of d-d transition and ESR spectra in Cu(II) increase with increasing exposure time. However, the electrical conductivities do not increase. Therefore, the induced Pt(III) species are attributable to neutral solitons.

**Key Words :** MX-chain : soliton : polaron.

## INTRODUCTION

Recently quasi-one-dimensional halogen-bridged Pt, Pd and Ni mixed-valence complexes (abbreviated as MX-chain) have been attracting much attention because they show very interesting physical properties such as intense intervalence charge transfer bands, progressive overtones of resonance Raman spectra, luminescence spectra with large Stokes-shifts, midgap absorptions attributable to solitons and polarons, and large third-order nonlinear optical properties[1, 2]. Their ground states are degenerated as observed in trans-polyacetylene. Therefore, from the theoretical viewpoints, the solitons and polarons are expected to exist in these compounds as observed in trans-polyacetylene. Kuroda *et al.* experimentally observed the solitons in  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$  for the first time[3]. Okamoto *et al.* succeeded in controlling the creation of the solitons by using the difference of dimensionalities of CDW states[4]. Among these MX-chain compounds, the compounds with the counteranions of Cu(I) ions were reported[5]. These compounds are formulated as  $\{[\text{Pt}(\text{en})_2][\text{PtX}_2(\text{en})_2]\}_3(\text{CuX}_4)_4$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ ), which consist of double linear chains of the main halogen-bridged Pt(II)-Pt(IV) units and halogen-bridged square bipyramidal Cu(I) units. However, the ESR spectra show the overlap of the Cu(II) and Pt(III) species. This result indicates that the introduction of Cu(II) species into Cu(I) species in the counteranion carried out at the same time doping into the Pt(II)-Pt(IV) linear-chain, forming the Pt(III) species. In this way, the amount of Cu(II) species in the counteranions are considered to be closely related with the amounts of the soliton or polaron in the Pt main chains. Although so far many studies on solitons and polarons in the MX-chain compounds have been carried out, the studies on doping effect are rare.

In this study, we will describe two types of doping effects on  $\{[\text{Pt}(\text{en})_2][\text{PtX}_2(\text{en})_2]\}_3(\text{CuX}_4)_4$ , that is, the pH control for  $\text{X}=\text{Cl}$  and  $\text{Br}_2$  doping for  $\text{X}=\text{Br}$ .

## EXPERIMENTAL

Starting materials  $\{[\text{Pt}(\text{en})_2][\text{PtX}_2(\text{en})_2]\}_3(\text{CuX}_4)_4$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ ) were prepared by the mixture of equimolar amounts of  $[\text{Pt}(\text{en})_2]\text{X}_2$  and  $\text{CuX}_2$  in aqueous solutions. After a week, the needles of the compounds were obtained. The pH controls were carried out for  $\text{X}=\text{Cl}$  by dropping  $\text{HCl}$  solutions into the starting mixture solutions of  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  and  $\text{CuCl}_2$ . The  $\text{Br}_2$  doping was carried out for the  $\text{Br}$ -bridged compound in the decicators.

## RESULTS AND DISCUSSION

The structure of the  $\text{Cl}$ -bridged compound is shown in Fig. 1. In the main chain, the planar  $[\text{Pt}(\text{en})_2]$  units and the octahedral  $[\text{PtX}_2(\text{en})_2]$  units are stacked alternatively, forming the linear chain structures. In the parallel with the main chain, the counteranions of  $\text{Cu}(\text{I})$  ions also form linear chain structures, where the trigonal bipyramidal  $\text{Cu}(\text{I})$  ions are bridged with halogen ions. The  $\text{Pt}(\text{II})$ - $\text{Pt}(\text{IV})$  distance along the chain is consistent with the  $\text{Cu}(\text{I})$ - $\text{Cu}(\text{I})$  distance. The  $\text{Pt}(\text{II})$ - $\text{Pt}(\text{IV})$  distance in the  $\text{Cl}$ -bridged compound (5.234 Å) is shorter than that in  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$  (5.403 Å). The  $\text{Pt}(\text{IV})$ - $\text{Cl}$  and  $\text{Pt}(\text{II})\cdots\text{Cl}$  distances in the  $\text{Cl}$ -bridged compound are 2.321 and 2.913 Å, respectively, while those in  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$  are 2.318 and 3.098 Å, respectively. Therefore, the oxidation state in the  $\text{Cl}$ -bridged compound is more approaching to the  $\text{Pt}(\text{III})$  state compared with that in  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ .

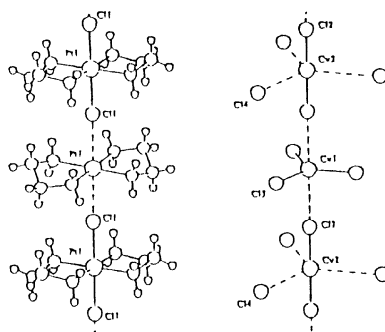


Fig. 1 Crystal structure of the Cl-bridged compound.

The ESR spectrum shows the overlaps of the Cu(II) and Pt(III) species in the Cl-bridged compound. This result indicates that the introduction of Cu(II) species into Cu(I) species in the counteranion carried out at the same time doping into the Pt(II)-Pt(IV) linear-chain, forming the Pt(III) species. Correspondingly, the d-d transition of the Cu(II) species are also observed around 1.3 eV in the absorption spectra. The pH dependence of the ESR spectra and d-d transitions was investigated by dropping HCl solutions. In Fig.2, the relative integrated intensities of the ESR spectra and d-d transitions are plotted against the amount of the drops of HCl. The induced Cu(II) species in the counterions must create the Pt(III) species in the main chains. Therefore, we can control the creation of the solitons or polarons of the Pt(III) species in the main Pt chains by controlling the pH.

The photo-induced absorption spectrum of the Cl-bridged compound was carried out at various temperatures as shown in Fig. 3. At 140K, the photo-induced absorption was observed in the midgap region (1.4 eV),

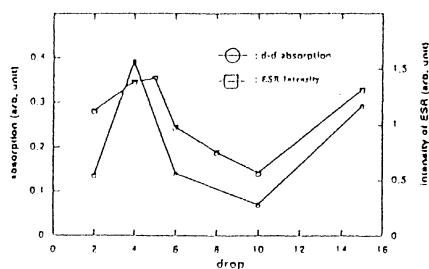


Fig.2 Relative integrated intensities of the ESR spectra and d-d transitions

which is almost at the midpoint of the intervalence charge transfer band from the Pt(II) units to the Pt(IV) units along the chain axis. Therefore, the midgap absorption is reasonably assigned to the soliton.

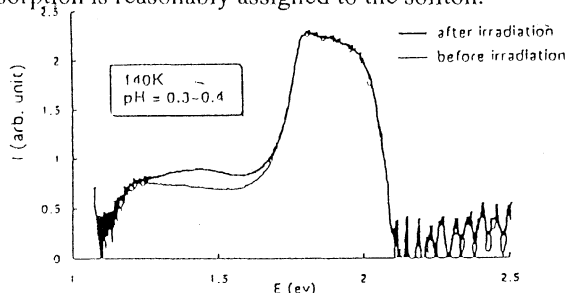


Fig. 3 Photo-induced absorption spectrum of the Cl-bridged compound.

Time dependence of doping was carried out up to 100 minutes in the decicator by vapor exposure of  $\text{Br}_2$  to the crystalline samples of the Br compound. The intensities of the absorptions around 1.5 eV increase with the increase of the exposure time. This absorption is attributable to the d-d transition of the Cu(II) species, which are created by the  $\text{Br}_2$  doping. In the ESR spectra, the signals of Cu(II) species which are observed around  $g=2$  are increasing. The integrated intensities increase with the increase of the exposure time. The relative intensities of the d-d transitions and ESR signals are shown in Fig. 4.

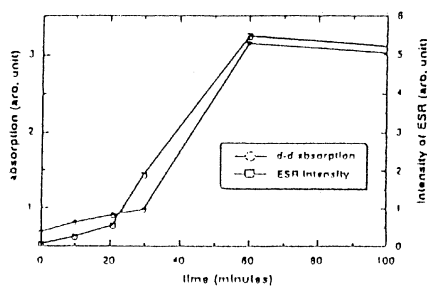


Fig. 4 Relative intensities of the d-d transitions and ESR of the Br-bridged compound.

Their behaviors are similar to each other. Accordingly the amounts of the Cu(II) species increase by Br<sub>2</sub> doping in the counteranion. As a result, the Pt(III) species may increase in the main chain. The single-crystal electrical conductivities of these doped compounds do not increase or are almost constant. Therefore, the Pt(III) species are considered as the neutral solitons.

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#### REFERENCES

1. H. Okamoto and M. Yamashita, Bull. Chem. Soc. Jpn., 71, 2023(1998)
2. H. Kishida et al., Nature, 405, 929(2000)
3. N. Kuroda et al., Phys. Rev. Lett., 58, 2212(1987)
4. H. Okamoto et al., Phys. Rev. Lett., 69, 247(1992)
5. R. J. H. Robin, et al., J. Chem. Soc., Dalton., 2498(1980)