Solitons, polarons and their dynamics in mixed-valence halogen-bridged MX-chains

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This article describes the photo-generation processes of elementary excitations such as solitons and polarons, and their dynamics in the one-dimensional (1D) halogen-bridged Pt compound [Pt(en)2Br](ClO4)2. Spin-solitons were photo-generated via relaxation processes of CT excitons and self-trapped excitons, made evident by photo-induced absorption and photo-induced electron spin resonance spectra. Polarons were not generated from CT excitons. Diffusion of spin-solitons on the 1D chain was studied quantitatively by analysing 1H NMR spin-lattice relaxation times ($T_1$).

Keywords: halogen-bridged MX-chain; soliton; exciton; photo-induced absorption spectrum; nuclear magnetic resonance

1. Introduction

One-dimensional (1D) halogen-bridged metal complexes (MX-chains) have attracted much attention from many chemists and physicists owing to the variety of their electronic states and their many attractive physical properties such as intense charge transfer bands (Tanaka et al. 1984; Wada et al. 1985), overtone progressions in the resonance Raman spectra (Clark et al. 1976; Campbell et al. 1978; Clark 1984, 1990), intense luminescence spectra with large Stokes shifts (Tanino & Kobayashi 1983), photo-generation (Okamoto et al. 1992) and long-range migration (Kimura et al. 1998) of solitons and polarons, and large third-order optical nonlinearity (Kishida et al. 2000). They also provide 1D model compounds of high $T_c$ copper oxide superconductors.

This system has been extensively studied theoretically by the extended Peierls–Hubbard model (Nasu 1983, 1984), in which the electron–phonon interaction ($S$), electron transfer ($T$) and on-site and nearest neighbour-site Coulomb repulsion energies ($U$ and $V$, respectively) compete or cooperate with each other. It has been established that the Ni compounds take the Ni$^{III}$ averaged valence or Mott–Hubbard (MH) states, due to the strong $U$, where the bridging halide ions are located at the midpoints between the neighbouring two metal ions (figure 1a). In this case, the half-filled metallic band splits into the lower- and upper-Hubbard bands composed of Ni$^{III}$d$_z^2$ orbitals with a Hubbard gap of approximately 5 eV. Therefore, all Ni compounds belong to the class III category

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of mixed-valence compounds proposed by Robin & Day (1967). On the other hand, the Pt and Pd compounds take the M_{II}–M_{IV} mixed-valence or charge density wave (CDW) states owing to the strong S, where the bridging halide ions are displaced from the midpoints between the neighbouring two metal ions. Accordingly, the half-filled metallic band splits into the occupied valence band composed of an M_{II}d_{z}^{2} band and the unoccupied conduction band composed of an M_{IV}d_{z}^{2} band with a finite Peierls gap (figure 1b). Therefore, Pt and Pd compounds belong to the Robin–Day class II category (Robin & Day 1967).

A characteristic electronic structure in mixed-valence MX-chain compounds is the doubly degenerate groundstate shown as

\[ \cdots M^{2+}X\cdots M^{4+}X\cdots M^{2+}X\cdots M^{4+}X\cdots M^{2+}X\cdots M^{4+}X\cdots M^{2+}X\cdots M^{4+}X\cdots \]

which is analogous to trans-polyacetylene. Photo- or thermal excitation of the doubly degenerate groundstate forms soliton and polaron pairs as illustrated in figure 2a–c. In the spin-soliton, domain walls form at the boundary of the degenerate two electronic states with opposite phase, i.e. -2-4-2-4- and -4-2-4-, and can migrate along the chain over long ranges by forming a ‘spin-soliton’ expressed as -2-4-3^{0}-2-4-, which includes a paramagnetic M_{III}^{3+} site. For a spin-soliton, a phase mismatch occurs at the boundary and no extra charge appears on the chain. Therefore, spin-solitons are also called neutral-solitons. When a
divalent or tetravalent site is inserted at the boundary instead, expressed as 
\[-2-4-2\] \(K\) \[-2-4-\] or \[-2-4-4\] \(C\) \[-2-4-\], charged-solitons with a positive or a negative extra charge are formed. In this case, the chain has no electron spins.

In the polaron, on the other hand, no mismatch of the phase is needed, but inserted \(M^3\) \(C\) sites have paramagnetic spins as well as extra charge, as given by 
\[-2-4-3\] \(C\) \[-4-2-\] or \[-4-2-3\] \(K\) \[-2-4-\).

The solitons and polarons migrate along the chain over long ranges, and usually vanish by a recombination process within a finite lifetime.

In this article, we focus on the generation of elementary excitons such as solitons and polarons, and their dynamics in mixed-valence MX-chain compounds.

### 2. Photo-generation and detection of solitons, polarons and excitons

Solitons, polarons and excitons can be generated by photo-irradiation (Okamoto & Yamashita 1998). Photo-generation of solitons, polarons and excitons is strongly dependent on the optical gap energies \(\Delta E\), the latter being attributable to the charge-transfer (CT) transition from \(M^{2+}\) species to \(M^{4+}\) species, forming a CT exciton. Since lattice motion is much slower than electron transfer (Frank–Condon principle), bridging halogens are located at the original position just after the photo-excitation. Therefore, this situation is schematically expressed as figure 3b. In the 1D system, since there is no energy barrier to lattice relaxation, the CT exciton immediately induces a local lattice distortion, i.e. halogen motion, and relaxes to a metastable state, which is a self-trapped exciton (STE; figure 3c). In many cases, luminescence from an STE is observed with a large Stokes shift amounting to half of \(\Delta E\). Such a large Stokes shift comes from the large lattice relaxation energy of the STE due to the halogen motion.
Spin-soliton pairs are formed during the relaxation process of STEs. The mechanism of spin-soliton formation is illustrated in figure 3c. The relaxation process A in figure 3c affords the original electronic structure (groundstate), whereas process B affords spin-soliton pairs as shown in figure 3d. This soliton pair can move on the 1D chain with finite activation energy. Polaron pairs, on the other hand, cannot be formed from STEs and are formed from electron-hole pairs with higher energy than CT excitons.

The photo-induced solitons and polarons can be detected by photo-induced absorption (PA) and photo-induced electron spin resonance (PESR) spectroscopies. In the PA spectra, solitons and polarons are detected as mid-gap absorptions. PA spectra of [Pt(en)₂Br](ClO₄)₂ (figure 4) show a triplet structure, a₁, a₂, b. The time characteristics of each band have been investigated. Band b decays in a manner different from a₁ and a₂, which show the same decay characteristics. Therefore, the optically excited states include two different types of photo-product associated with the doublet a₁ and a₂ and mid-gap structure b.

Comparing the energies of the PA bands in figure 4 with the theoretical predictions in figure 5, it is natural to assign the doublet to polarons and the b band to a spin- or charged-soliton. PESR spectra of [Pt(en)₂Br](ClO₄)₂ indicate that the b band can be assigned to a spin-soliton.

### 3. Detection of the soliton dynamics by NMR

Solitons and polarons are induced not only by light but also by chain defects. Since a spin-soliton has no extra charge, a sole soliton can be generated with no charge compensation. Therefore, a small number of spin-solitons are in the as-grown crystals.

The NMR relaxation measurement is a sensitive probe for obtaining information from a small number of paramagnetic spins, because even a trace of electron spins can make a strong relaxation mechanism owing to the large

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Figure 4. PA spectrum of [Pt(en)₂Br](ClO₄)₂ at 77 K.

Figure 5. Schematic electronic structure of the (a) spin-soliton, (b) charged-soliton and (c) polaron.
magnetic moment of electron spins (approx. 10³ times larger than nuclear spins; Ikeda 2004). The ¹H NMR spin-lattice relaxation time (T₁) measured in [Pt(en)₂Br](ClO₄)₂ showed the presence of two kinds of proton with fast and slow relaxation, and the relative magnitudes of these two kinds of ¹H magnetization show temperature-dependent behaviour, i.e. the magnetization of the fast component rapidly decreases upon heating.

The fast relaxing component did not give a single T₁ but distributed T₁ values. This component was assigned to protons located in the neighbourhood of trapped or fixed paramagnetic M₃⁺ sites and/or at chain ends. For probes far enough away from paramagnetic M₃⁺ sites, the spin-diffusion mechanism, which enables the nuclear-magnetization propagation via mutual flips of spins in neighbouring protons with no mass migration, becomes dominant over electron–phonon magnetic dipolar interactions. Protons located in this region give a constant T₁ corresponding to the observed long T₁ component. Determined T₁ values of the slow component in [Pt(en)₂Br](ClO₄)₂ are shown in figure 6. A gradual T₁ decrease upon heating from 85 to 200 K and a sharp decrease to phase transition temperature were observed.

From the temperature-dependent ¹H relaxation together with the ESR data, it has been revealed that spin concentration originating from paramagnetic Pt₃⁺ species in crystals is almost temperature independent (Kawamori et al. 1985). Therefore, the following model of the spin dynamics can be derived. Paramagnetic sites fixed in 1D chains at low temperatures begin to move apart from the trapped sites upon heating, obtaining the thermal excitation energy. This means that the number of fixed paramagnetic spins decreases, whereas the moving spin number increases with temperature, consistent with the observed results. Upon heating, the protons along the chain feel an averaged magnetic field made by rapidly diffusing electrons. From these considerations, the increase in the number of protons having the long T₁ and the gradual decrease of the T₁ value on heating could be reasonably recognized.

Figure 6. ¹H T₁ of the slowly relaxing component in [Pt(en)₂Br](ClO₄)₂ at 20.96 (plus) and 40.14 (closed circle) MHz. T_tr is the phase transition temperatures.

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The present model of the electron-spin migration can be supported by the temperature dependence studies of the ESR linewidth (Kawamori et al. 1985), which showed a gradual narrowing upon heating attributable to the motional effect.

The rapid decrease of the fast $T_1$ component above 200 K shown in figure 6 shows the effect of the phase transition $^{1}H T_1$ due to lattice motions.

For a quantitative discussion of the observed $T_1$, the dimensionality of the electron-spin motion has to be investigated in connection with the Larmor frequency dependence of $T_1$. Nuclear relaxation by rapidly diffusing electrons in low-dimensional systems has been studied theoretically (Devreux et al. 1974; Devreux 1982). It has been reported that the nuclear relaxation rate due to randomly jumping electron spins, under the condition that the diffusion rate $D^*/\gamma_e \gamma_N^2$, where $\gamma_e$ and $\gamma_N$ are electron and nuclear Larmor frequencies, respectively, is given by Hamaue et al. (1981)

$$T_1 = kT\chi_s \left[ \frac{3}{5} d^2 f(\gamma_N) + \left( a^2 + \frac{7}{5} d^2 \right) f(\gamma_e) \right],$$

where $f(\omega)$ denotes the spectrum density, and $d$, $a$ and $\chi_s$ are anisotropic and isotropic parts of the hyperfine coupling between protons and electrons, and the normalized electron susceptibility per metal site, respectively. When electrons diffuse along 1D chains, the spectral density is expressed as (Devreux 1982)

$$f_{1D}(\omega) = \frac{1}{\sqrt{2D^*/\gamma_e}} - \frac{2\gamma\lambda}{2D^*};$$

where $\lambda$ is called the delocalization length and $\nu$ is given by 0.33 when $\lambda > 5$. $D^*$ is defined using the 1D diffusion constant $D$ and the inter-site distance $b$ in the chains as $D^* = D/b$.

In the present 1D diffusion model, the coupling between proton and electron spins is assumed to be approximately dipolar, then equation (3.1) is rewritten as

$$T_1^{-1} = kT\chi_s \left[ \frac{3}{5} d^2 f_{1D}(\gamma_N) + \frac{7}{5} d^2 f_{1D}(\gamma_e) \right].$$

If one combines equations (3.2) and (3.3), the $^1H T_1$ contributed by the 1D diffusion electron spins is assumed to be

$$T_1^{-1} = kT\chi_s \frac{d^2}{5} \left[ \left( 3 + 7 \sqrt{\gamma_N^2/\gamma_e} \right) \frac{1}{\sqrt{2D^*/\gamma_N^2}} - \frac{3.3\lambda}{3D^*} \right],$$

allowing $D^*$ and $\lambda$ to be derived from experimental data. Larmor frequency dependences of $T_1$ observed for $[Pt(en)_2Br](ClO_4)_2$ (figure 7) can be well interpreted by equation (3.4), supporting the 1D diffusion of electron spins. From the slope of the plots, the diffusion rate $D^*$ can be estimated by using the dipolar coupling constant $d$ calculated from the crystal data, and $\chi_s$ can be estimated by assuming that the concentration of the diffusing electron spins is proportional to the magnetization of the slow component.

The activation energy for electron-spin diffusion in $[Pt(en)_2Br](ClO_4)_2$ was evaluated to be $17 \pm 2$ meV by assuming the Arrhenius relation for the temperature dependence of $D^*$. It is noted that this value of $E_a$ is much smaller than that (840 meV) determined from electrical conductivity data (Hamaue et al. 1981). If unpaired spins are assumed to be the charge-carrier contribution.
to the conductivity $\sigma$, the 1D conductivity $\sigma_{\text{NMR}}$ derived from NMR is expressed by $D^*$ using the Nernst–Einstein relation given by

$$\sigma_{\text{NMR}} = \frac{n e^2 b^2 D^*}{kT}.$$  \hspace{1cm} (3.5)

Here, $n$ and $e$ are the charge-carrier concentration and the electronic charge, respectively. $\sigma_{\text{NMR}} = 10^{-1}\text{ S m}^{-1}$ was obtained at 303 K by the values of determined $D^*$, reported $n$ and $b$ (Kawamori et al. 1985), giving a conductivity $10^7$ times higher than that ($10^{-9}\text{ S m}^{-1}$) reported (Hamaue et al. 1981) for $[\text{Pt(en)}_2\text{Br}](\text{ClO}_4)_2$. For this disagreement between the NMR and the electrical conductivity results, the carriers of spin and charge are considered to be different in the present system. This indicates that the diffusing spin carriers detected from $^1\text{H}$ $T_1$ can mostly be attributed to neutral solitons.

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