Unprecedented Soliton Formation Mechanism in Quasi-One-Dimensional Chloro-Bridged Pt^{II}-Pt^{IV} Mixed-Valence Compound, {[Pt(en)$_2$][PtCl$_2$(en)$_2$]}$_3$(CuCl$_4$)$_4$·12H$_2$O

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A new type of complex consisting of double liner-chain structure {[Pt(en)$_2$][PtCl$_2$(en)$_2$]}$_3$(CuCl$_4$)$_4$·12H$_2$O was synthesized. High concentration (ca. 200 times larger than the literature) of neutral soliton (Pt^{III} component) formation was found. This unprecedented soliton formation mechanism will be discussed.

Recently, quasi-one-dimensional halogen-bridged mixed-valence compounds (hereafter abbreviated as MX-chains) have been extensively investigated, since they exhibit a wide range of interesting physical properties. These include intense and dichroic intervalence charge-transfer bands, progressive resonance Raman spectra, luminescence spectra with large Stokes-shifts, midgap absorptions attributable to solitons and polarons, large third-order nonlinear optical properties, one-dimensional model compounds of high T_C copper oxide superconductors, etc.[1] Indeed, more recently a gigantic third-order nonlinear optical susceptibility has been observed in [Ni(chxn)$_2$Br]Br$_2$ ($\approx 10^{-4}$ esu).[2]

In most MX-chains of Pt and Pd, owing to the strong electron-phonon interaction, the bridging halogens are displaced from the midpoints between the neighboring two metal atoms, giving rise to CDW states, or M^{II}–M^{IV} mixed-valence states ($\cdots$M$^{II}\cdots$X–M^{IV}–X$\cdots$M$^{II}\cdots$). Accordingly, the half-filled metallic band is split into an occupied valence band and an unoccupied conduction band with a finite Peierls gap. Therefore, these compounds belong to the class II type of the Robin–Day classification for the mixed-valence complexes.[1a] The compounds are formulated as [M^{II}(AA)$_2$][M^{IV}X$_2$(AA)$_2$]Y$_4$ (M^{II}–M^{IV}=Pt^{II}–Pt^{IV}, Pd^{II}–Pd^{IV}, Ni^{II}–Pt^{IV}, Pd^{II}–Pt^{IV}, and Cu^{II}–Pt^{IV}; X=Cl, Br, I, and mixed-halides; AA = ethylenediamine (en), 1R,2R-diaminocyclohexane (chxn), etc.; Y=ClO$_4$, BF$_4$, X, etc.).[3] The ground states of the M^{II}–M^{IV} mixed-valence compounds are degenerated as observed in *trans*-polyacetylene.[4] 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 [Pt(en)$_2$][PtCl$_2$(en)$_2$](ClO$_4$)$_4$ for the first time.[1h] In the compound, the Pt^{III} sites are considered as a neutral soliton, judging from the ESR spectrum. The Pt^{III} sites are considered as domain walls in the degenerated electronic states. Among these MX-
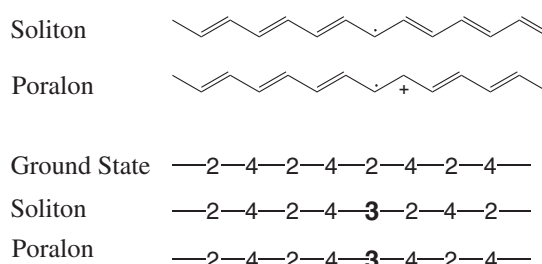
Figure 1. Schematic drawing of the electronic structure of quasi-one-dimensional chain. Arabic numerals show the positive valence numbers of platinum ions.

chain compounds, the compounds with the Cu^{I} counter anions were reported previously.[5] These compounds are dehydrated types of {[Pt(en)$_2$][PtX$_2$(en)$_2$]}$_3$(CuX$_4$)$_4$ (X=Cl and Br), which consist of double linear chains of the main halogen-bridged Pt^{II}-Pt^{IV} units and halogen-bridged quasi-trigonal-bipyramidal Cu(I) units. In these {[Pt(en)$_2$][PtX$_2$(en)$_2$]}$_3$(CuX$_4$)$_4$ (X=Cl and Br) compounds the Cu^{I} ions are considered to be changed into Cu^{II} ions, which make the Cu-Cu distance shorter and are ESR active. Therefore, we will focus on the {[Pt(en)$_2$][PtX$_2$(en)$_2$]}$_3$(CuX$_4$)$_4$ compounds. Fortunately, we have synthesized a new type of hydrated {[Pt(en)$_2$][PtCl$_2$(en)$_2$]}$_3$(CuCl$_4$)$_4$·12H$_2$O according to the similar method reported previously.[5,6] In this paper, we will describe the unprecedented soliton formation mechanism detected by ESR spectrum of this compound.

The structure of the compound is shown in Figure 2.[7] In the main Pt-Cl chain, the planar [Pt^{II}(en)$_2$] units and the octahedral [Pt^{IV}Cl$_2$(en)$_2$] units are stacked alternatively, forming the linear chain structures. The bridging Cl$^-$ ions are disordered with half occupancy. In the parallel direction with the main chain, the Cu^{I}
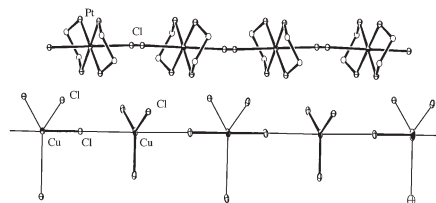
Figure 2. The structure of {[Pt(en)$_2$][PtCl$_2$(en)$_2$]}$_3$(CuCl$_4$)$_4$·12H$_2$O. Water molecules are omitted.

counter anions also form linear chain structures, where the quasi-trigonal-bipyramidal Cu(I) ions are bridged with halogen ions. The bridging Cl^- ions are located at midpoints between two Cu ions.

The Pt^{II}–Pt^{IV} distance along the chain is consistent with the Cu^I–Cu^I distance. The Pt^{II}–Pt^{IV} distance in this compound (5.234 Å) is shorter than that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (5.403 Å). The Pt^{IV}–Cl and $Pt^{II}\cdots$Cl distances in the compound are 2.321 and 2.913 Å, respectively, while those in $[Pt(en)_2]$ $[PtCl_2(en)_2](ClO_4)_4$ are 2.318 and 3.085 Å, respectively. Therefore, the displacement of the bridging Cl ion in this compound is smaller than that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$. This indicates that the oxidation state in this compound is approaching the Pt^{III} state compared with that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$.

The electrical conductive spectrum obtained by the Kramers–Kronig transformation of the single crystal reflectance spectrum along the chain axes is measured. The intervalence charge-transfer band from Pt^{II} to Pt^{IV} species of this compound is observed at 2.4 eV along the chain axes. The peak energy of this compound is lower than that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (2.7 eV).[1f] This implies that the oxidation state of this compound is approaching the Pt^{III} state compared with that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$. Such a result is consistent with that of the crystal structure. The photoinduced absorption spectrum was measured at 150 K. The single mid-gap absorption at ca. 1.3 eV is observed, which is almost at half energy of the intervalence charge-transfer band (2.4 eV).

The ESR spectrum of this compound at 20 K is shown in Figure 3. This spectrum can be simulated into the Cu^{II} and Pt^{III} species. Since the Pt^{II}, Pt^{IV} and Cu^I ions are diamagnetic and ESR silent, this result indicates that the introduction of Cu^{II} species into Cu^I species in the counteranion makes the Cu–Cu distance shorter and carries out the creation of Pt^{III} species. The Pt^{III} species in this compound are considered to be the neutral solitons judging from the analogy of ClO_4 compound.

This consideration is primarily arisen from the photoinduced absorption spectrum, which shows only a single mid-gap absorption peak. In the case of the polaron formation, it is essentially expected to show two mid-gap peaks in the absorption spectrum. In addition, the ESR spectrum of Pt^{III} species obtained from the simulation showed five lines which are attributed to the hyperfine splitting due to the ^{195}Pt nuclei ($I = 1/2$). This splitting
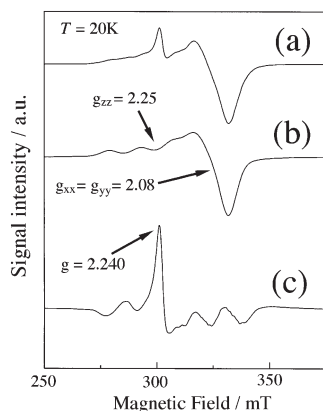
pattern is expected from the case that the unpaired electron of the Pt^{III} ion spreads into two Pt sites.[8b] Such ESR signal is consistent with that of $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$, in which the neutral solitons are stably generated.

The concentration of the Pt^{III} component in this compound (0.37%) is by ca. 200 times larger than that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (0.0015%), where the reference used is $CuSO_4\cdot5H_2O$. Such a high concentration of the Pt^{III} component (neutral soliton) in this compound is considered to be carried out by the following two reasons; 1) The oxidation state of this compound is approaching the Pt^{III} state compared with that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ as shown in the crystal structures and electronic spectra. 2) The Cu^I ion is easily converted into the Cu^{II} ion, which makes the Cu–Cu distance shorter. Such a shorter Cu–Cu distance makes the Pt oxidation states approaching the averaged states and induces the creation of Pt^{III}.

References and Notes

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6   Elemental analyses for $Pt_6Cu_4Cl_{22}C_{24}H_{120}N_{24} O_{12}$: Calcd; C, 9.17; H, 3.85; N, 10.70, found; C, 9.17; H, 3.57; N, 10.64.

7   Crystal system is hexagonal, space group $P6_3/m$ (no. 176), $a = 15.587(3)$ Å, $c = 10.463(2)$ Å, $V = 2201.3(6)$ Å^3. The final cycle of full-matrix least-squares refinement was based on 1160 observed reflections ($I > 2.00\sigma(I)$) and 83 variable parameters and converged with unweighted and weighted agreement factors of: $R = 0.038$, $R_w = 0.057$, G.O.F. = 1.09. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 200699. Copies of the data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Figure 3. (a) Experimental EPR spectrum, (b) Simulated spectrum of Cu^{2+}, (c) Reproduced spectrum of Pt^{3+}.