Mixed-Valence Compounds

DOI: 10.1002/ange.200602987

Halogen-Bridged Pt^{II}/Pt^{IV} Mixed-Valence Ladder Compounds**

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Low-dimensional electronic systems have been attracting much attention for a long time in solid-state chemistry and physics. Among them, one-dimensional (1D) electronic systems have been an attractive target because many characteristic physical properties have been observed in them, such as Mott–Hubbard, charge-density-wave (CDW), and spin-density-wave (SDW) states in organic (semi)conductors,[1,2] as well as nonlinear excitations such as solitons and polarons in π-conjugated polymers [3,4] and slow relaxation of magnetization in several Ising-type ferro- or ferrimagnetic compounds.[5–7] Two-dimensional (2D) electronic systems have also been of interest for the past several decades. Many materials with Perovskite structures have been the target of research. To date, many attractive physical properties have been reported, such as colossal magnetoresistance (CMR) in manganese oxides[8,9] and high-temperature superconductivity in copper oxides, among others.[10,11]

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[**] This work was partly supported by a Grant-in Aid for Creative Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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In ladder systems, which can be classified as the boundary region between 1D and 2D systems, on the other hand, only a few studies have been made although further interesting physical properties are expected. Our purpose in this study is to establish a synthetic strategy for ladder compounds.

Our target compounds are the halogen-bridged 1D metal compounds (MX chains). These compounds have been attractive materials because of their highly isolated 1D electronic structures, which are formed by d_{z^2} orbitals of the metal centers and p_z orbitals of the bridging halides. In these compounds, various electronic states can be realized by substituting components such as central metals (M), in-plane ligands (L), bridging halides (X), and counteranions (Y). The MX-chain compounds with a mixed-valence structure $\text{-X}\cdots\text{M}^{2+}\cdots\text{X-M}^{4+}\text{-}$ (M = Pd, Pt; X = Cl, Br, I) have been extensively studied as 1D materials with strong electron–phonon interactions (S). Their Peierls-distorted 1D compounds show unique optical and dynamical properties such as progressive overtones in resonance Raman spectra[12] and luminescence with a large Stokes shift,[13] as well as the long-range migration of spin solitons and polarons along 1D chains.[14]

If a single-chain system can be expanded to a ladder-chain system, it is expected that the system can take two valence arrangements, namely in-phase and out-of-phase types (Figure 1). Such a variety in the valence arrangements is interesting in the fields of chemistry and physics. Moreover, novel interactions are expected through connection of the 1D chains. Although more than 300 halogen-bridged MX-chain compounds have been synthesized so far, all compounds have single-chain structures. We have succeeded in synthesizing ladder-type, halogen-bridged platinum complexes for the first time in which 1D chains are connected by the 2,2′-bipyrimidine (bpym) ligand: $\{(\mu\text{-bpym})[\text{Pt}^{\text{II}}(\text{en})]_2\}\{(\mu\text{-bpym})[\text{Pt}^{\text{IV}}\text{X}_2(\text{en})]_2\}\text{X}_2(\text{ClO}_4)_6\cdot 2\,\text{H}_2\text{O}$ (X = Br (**1**), Cl (**2**); en = ethylenediamine) and $\{(\mu\text{-bpym})[\text{Pt}^{\text{II}}(\text{en})]_2\}\{(\mu\text{-bpym})[\text{Pt}^{\text{IV}}\text{X}_2(\text{en})]_2\}\text{X}_8\cdot 4\,\text{H}_2\text{O}$ (X = I (**3**), Br (**4**)). Herein, we report the syntheses, crystal structures, and optical properties of these complexes.

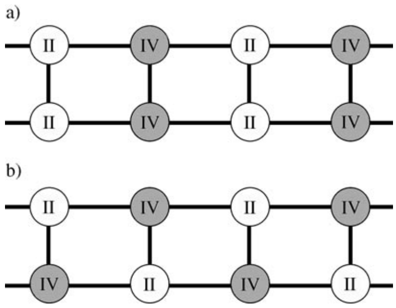

Figure 1. In-phase (a) and out-of-phase (b) valence arrangements in the mixed-valence ladder system.

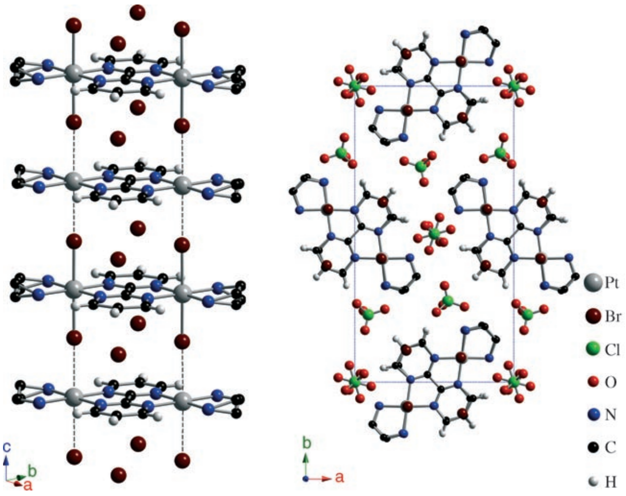

Figure 2. Perspective views of the 3D packing of **1**. H atoms of the en ligands have been omitted for clarity.

Figure 2 shows two perspective views of the crystal structure of bromide-bridged platinum compound **1**. The {Pt(en)} moiety is connected by a bpym ligand, thus forming a binuclear $\{(\mu\text{-bpym})[\text{Pt(en)}]_2\}$ unit. This unit is bridged by bromide ions to form a ladder structure. Each ladder is weakly connected through the hydrogen bond between the amino protons of the en ligands and perchlorate ions of the counteranions. The shortest Pt–Pt separations along the leg and rung directions within the ladder are 5.534 and 5.466 Å, respectively, whereas that between the ladders is 8.561 Å, thus indicating that each ladder is isolated from one other. The bridging bromide ions lie closer to the Pt^{IV} centers, thus indicating the $\text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}}$ mixed valence or CDW state of this compound. Therefore, this compound belongs to the class II compounds of the Robin–Day classification.[15] This compound has an in-phase valence arrangement as shown in Figure 1 a. Generally, in the 2D mixed-valence compounds, the out-of-phase valence arrangements are stabilized rather than the in-phase valence arrangements owing to Coulomb interactions. This trend is inconsistent with our result. In compound **1**, nonbonded bromide anions are located at the sandwich position between two bpym ligands with half occupancies. Usually, a negative charge stabilizes the high oxidation state. The bromide anions lie closer to the Pt^{IV} centers; therefore, these bromide anions can stabilize the in-phase valence arrangement.

Figure 3 shows two perspective views of the crystal structure of iodide-bridged platinum compound **3**. The fundamental intraladder structure is almost the same as that of **1**. The shortest Pt–Pt separations along the leg and rung directions within the ladder are 5.833 and 5.468 Å, respectively, whereas that between the ladders is 7.933 Å. Compared with the crystal structure of compound **1**, two significant differences are found, depending on the counteranions: 1) two water molecules are located at the sandwich position between two bpym ligands (no halide anions) and 2) the bridging halide ions are disordered. The valence arrangement of this compound has not been clarified as yet because of the disorder of the bridging halide ions. However, because nonbonded halide anions that were found in compound **1** are absent in compound **3**, this compound might have out-of-phase valence arrangement (Figure 1 b).

Figure 4 shows an X-ray oscillation photograph of **1** and **3**. In the case of compound **1**, very weak superlattice reflections

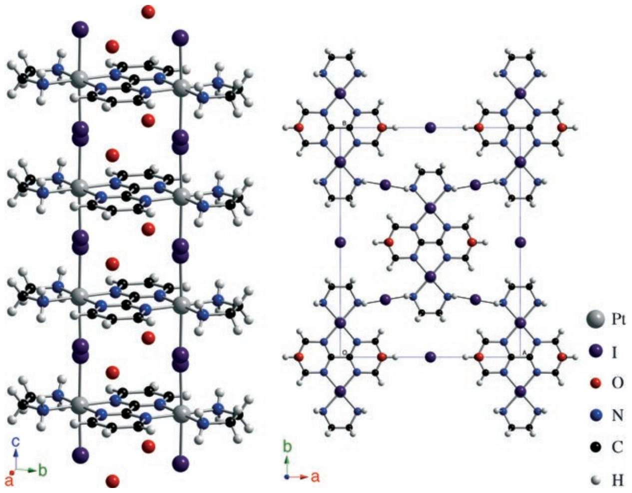

Figure 3. Perspective views of the 3D packing of **3**.

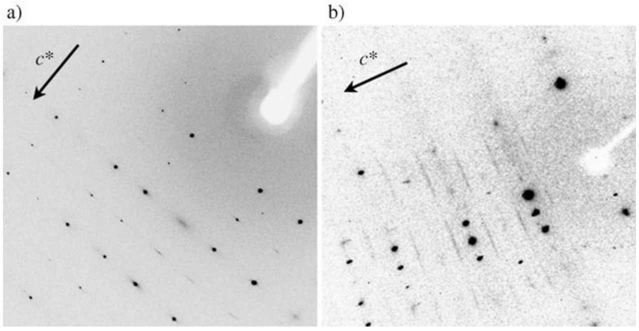

Figure 4. X-ray oscillation photograph in **1** (a) and **3** (b).

at $h,k,l+{}^1/_2$ were observed which correspond to the two-fold periodicity along the c^* direction (leg direction). The line width of these superlattice reflections is as sharp as those of the main reflections, thus indicating that this compound has a long-range ordered charge arrangement. On the other hand, in the case of compound **3**, diffuse scatterings with finite line width at $h,k,l+{}^1/_2$ were observed. This finding suggests that compound **3** has some short-range ordered charge arrangement. We have succeeded in controlling the charge arrangement of ladder compounds by variation of the counteranions.

The selected interatomic separations and the distortion parameter (d) of the described compounds, defined as $\{r(\mathrm{Pt^{II}}\cdots\mathrm{X})-r(\mathrm{Pt^{IV}}\text{-}\mathrm{X})\}/\{r(\mathrm{Pt^{II}}\cdots\mathrm{Pt^{IV}})\}$, are listed in Table 1. Here, the d parameter shows the degree of displacement of the bridging halide ions from the midpoints between the two neighboring Pt ions. In other words, this value is an index to estimate the electron–phonon interaction and the band gap. In the described ladder compounds, the d parameters are dependent on the bridging halide ions and increase in the order I, Br, Cl. This result suggests that the band gap was controlled by changing bridging halide ions.

Table 1: Comparison of the interatomic separations [Å] and the distortion parameter (d) for **1**–**4**.

Compound	$\mathrm{Pt^{II}}\cdots\mathrm{Pt^{IV}}$	$\mathrm{Pt^{II}}\cdots\mathrm{X}$	$\mathrm{Pt^{IV}}\text{–}\mathrm{X}$	d[a]
1	5.534	3.057	2.478	0.105
2	5.435	3.119	2.317	0.148
3	5.833	3.156	2.678	0.082
4	5.482	3.008	2.474	0.097

[a] Defined as $\{r(\mathrm{Pt^{II}}\cdots\mathrm{X})-r(\mathrm{Pt^{IV}}\text{–}\mathrm{X})\}/\{r(\mathrm{Pt^{II}}\cdots\mathrm{Pt^{IV}})\}$.

To acquire information about the band gap, optical conductivity spectra (Figure 5) were obtained from Kramers–Kronig transformation of the single-crystal reflectance spectra. Broad bands were observed at about 2.4, 3.7, 1.7, and 2.1 eV with shoulders (ca. 3.0 eV) in **1, 2, 3**, and **4**, respectively. By considering the trends of a series of the single-chain MX compounds,[16] these broad bands are attributable to the charge-transfer (CT) transition from $\mathrm{Pt^{II}}$ to $\mathrm{Pt^{IV}}$ species. The E_{CT} value outstandingly depends on the bridging halide ion and increases in the order I, Br, Cl. This tendency is similar to single-chain MX compounds, thus indicating that the band gap can be controlled by changing bridging halide ions. This finding is consistent with the argument of the d parameter. However, shoulders of the CT bands have not been observed in the single-chain MX chains. Although the origin of such behavior has not been clarified at the present stage, investigations on the assignment of such transitions are now in progress.

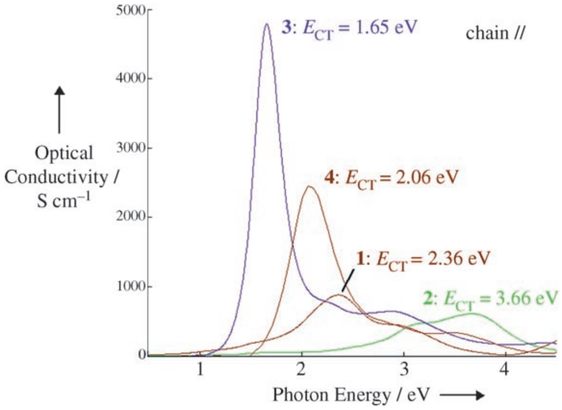

Figure 5. Optical conductivity spectra with polarization of light parallel to the chain axis compounds **1**–**4** at room temperature.

In the resonance Raman spectra (Figure 6), intense peaks attributable to the X-$\mathrm{Pt^{IV}}$-X stretching modes are observed, where the stretching modes of **1**, **2**, **3**, and **4** are at $\tilde{\nu} = 191.7$, 325.7, 124.3, and 174.4 cm^{-1}, respectively. The Raman shifts clearly depend on the bridging halide ions, which is in good agreement with the X-ray and optical conductivity results.

In summary, we have succeeded in synthesizing halogen-bridged $\mathrm{Pt^{II}}/\mathrm{Pt^{IV}}$ mixed-valence ladder compounds for the first time. In these compounds, the band gap is controlled by changing bridging halide ions. Moreover, by changing counteranions, the charge arrangements of ladder compounds can be controlled. Therefore, ladder-type MX compounds have strong advantages for studying the boundary region between 1D and 2D electronic systems. Our results will greatly contribute to the realization of attractive physical properties in the ladder system.

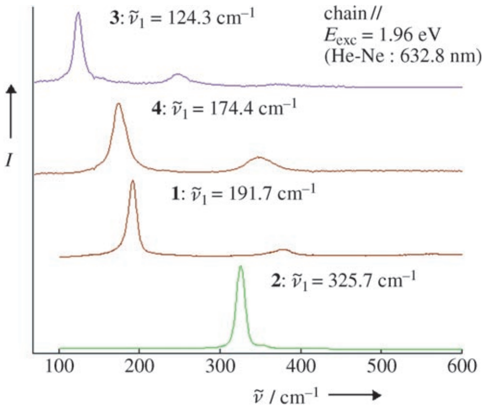

Figure 6. Polarized Raman spectra for the polarization of $z(x,x)z(x||c$ axis) at room temperature.

Experimental Section

1: $HClO_4$ (3 mL) was added to an aqueous solution (10 mL) containing $\{(\mu\text{-bpym})[Pt^{II}(en)]_2\}(NO_3)_4$ (50 mg, 0.055 mmol) and $\{(\mu\text{-bpym})[Pt^{IV}Br_2(en)]_2\}(NO_3)_4$ (67 mg, 0.054 mmol). Needle-shaped crystals were obtained after a week. Elemental analysis (%) calcd for $C_{12}H_{22}N_8Br_3Cl_3O_{12}Pt_2\cdot H_2O$: C 11.77, H 1.98, N 9.15, Br 19.57, Cl 8.69; found: C 11.77, H 2.04, N 8.94, Br 19.47, Cl 8.49.

3: I_2 vapor was allowed to slowly diffuse into a H_2O/MeOH solution containing $\{(\mu\text{-bpym})[Pt^{II}(en)]_2\}(NO_3)_4$ (50 mg, 0.055 mmol) and excess KI. Needle-shaped crystals were obtained after a week. Elemental analysis (%) calcd for $C_{12}H_{22}N_8I_6Pt_2\cdot 2H_2O$: C 9.83, H 1.79, N 7.64; found: C 9.66, H 2.14, N 7.41.

The syntheses of **2** and **4** are provided in the Supportiong Information.

X-ray crystal structure determinations were made by using a Bruker SMART 1000 (**1**, **2**) and a Rigaku Saturn CCD diffractometer (**3**, **4**) with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). Crystal data of these compounds are provided in the Supporting Information. CCDC-611172, 604141, 610578, and 610579 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: July 25, 2006

Keywords: charge transfer · coordination modes · ladder polymers · mixed-valent compounds · valence structures

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