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Tuning of Electronic Structures of Quasi-One-Dimensional Bromo-Bridged Pd^{II}–Pd^{IV} Mixed-Valence Complexes by Substituting Counter Anions

Hisamitsu Arakawa,[1] Daisuke Kawakami,[2] Shinya Takaishi,[2] Takashi Kajiwara,[2] Hitoshi Miyasaka,[1] Ken-ichi Sugiura,[1] Masahiro Yamashita,*[2] Hideo Kishida,[3] and Hiroshi Okamoto[3]

[1]Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0397

[2]Department of Chemistry, Graduate School of Science, Tohoku University & CREST(JST), Aoba-ku, Sendai 980-8578

[3]Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, 515 Kashiwanoha, Kashiwa 277-8561

Received February 15, 2006; E-mail: yamasita@agnus.chem.tohoku.ac.jp

New quasi-one-dimensional bromo-bridged Pd^{II}–Pd^{IV} mixed-valence complexes with long chain alkylsufonates $[Pd(en)_2][PdBr_2(en)](C_nH_{2n+1}SO_3)_4 \cdot 2H_2O$ (en = ethylenediamine, $n = 7$, 8, 9, and 10) were synthesized. With increasing alkyl-chain length (n) of the counter anions, the Pd^{II}···Pd^{IV} distances decreased, indicating that the oxidation states of the Pd atoms are close to the Pd^{III} state.

Quasi-one-dimensional halogen-bridged mixed-valence complexes (MX chains) have been attracting much attention because they show very interesting physical properties, such as intense and dichroic inter-valence charge-transfer bands, progression in the resonance Raman spectra, luminescence spectra with large Stokes-shifts, large third-order nonlinear optical properties, midgap absorptions attributable to solitons, polarons, etc.[1] Theoretically, these MX chains are considered to be extended Peierls–Hubbard systems, where electron-phonon interaction (S), electron transfer (T), on- and neighbor-site Coulomb repulsion energies (U and V, respectively) compete or cooperate with each other.[2]

The Pt and Pd complexes take charge density wave (CDW) or M^{II}–M^{IV} mixed-valence states due to S, where the bridging halides are displaced from the midpoints between the neighboring two metal ions (Fig. 1a). Therefore, these Pt and Pd complexes are class II type for mixed-valence compounds in the Robin and Day classification.[3] In these MX chain complexes, the CDW amplitudes can be tuned by varying metal ions, bridging halide ions, in-plane ligands, and counter anions.[4] Moreover, the dimensionalities of the CDW can be controlled by using the intra- and inter-chain hydrogen-bond networks.[5]

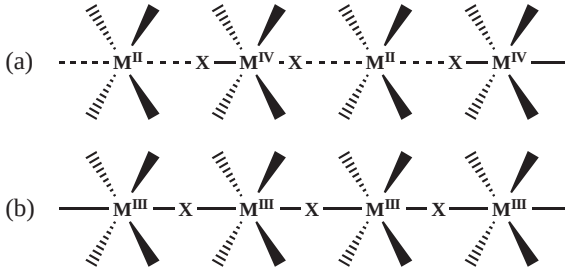

Fig. 1. Structure of M^{II}–M^{IV} mixed-valence complexes of Pt and Pd (a), and M^{III} complexes of Ni (b).

On the other hand, Ni complexes take Ni^{III} Mott–Hubbard states due to the strong U, where the bridging halides are located at the midpoints between neighboring two Ni atoms (Fig. 1b). Very strong antiferromagnetic interactions among spins located on the Ni^{III} d_{z^2} orbitals through the bridging halide ions are observed in these complexes.[6] Therefore, the Ni complexes are class III type for mixed-valence compounds in the Robin and Day classification. These complexes have also been of recent interest in applied science because a gigantic third-order nonlinear optical susceptibility ($\approx 10^{-4}$ e.s.u.) has been observed for $[Ni^{III}(chxn)_2Br]Br_2$ (chxn = 1*R*,2*R*-diaminocyclohexane).[7]

More recently, a new series of MX chains, that is, the Ni–Pd mixed-metal complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$, have been synthesized, where S on the Pd sites and U on the Ni sites compete with each other. With an increase in the Ni component, the Pd^{II}–Pd^{IV} mixed-valence state gradually changed to the Pd^{III} state due to the stronger U on the Ni site (≈ 5 eV) compared with S on the Pd site (≈ 1 eV).[8] Their local electronic structures, such as Mott–Hubbard state, CDW state, and soliton, have been directly observed by scanning tunneling microscopy (STM) for the first time.[9]

The number of Pd^{II}–Pd^{IV} mixed-valence complexes is less than that of Pt^{II}–Pt^{IV} mixed-valence complexes, because the Pd^{IV} states are less stable compared with the Pt^{IV} states. Therefore, the counter ions of Pd^{II}–Pd^{IV} complexes with ethylenediamine (en) ligand occur only with ClO_4^- and BF_4^-,[10] affording relatively weak T. In order to promote interaction between the Pd^{II} site and the Pd^{IV} site, or to generate the Pd^{III} Mott–Hubbard state, we have synthesized new Pd^{II}–Pd^{IV} mixed-valence complexes with en as an in-plane ligand by substituting the counter anions with $C_nH_{2n+1}SO_3^-$ ($n = 7$, 8, 9, and 10), which are expected to form different hydrogen-bonds between NH_2 of en and O of $C_nH_{2n+1}SO_3^-$, as well as cause fastener effects. Similar Pt^{II}–Pt^{IV} mixed-valence complexes have been studied by Matsushita and Taira.[11] However, no Pd complexes with $C_nH_{2n+1}SO_3^-$ counter anions have been reported.

Single-crystal X-ray structure determination was carried out for all complexes at 93 K. Figure 2 shows two perspective views of the $n = 7$ complex. The planar $[Pd(en)_2]$ units are

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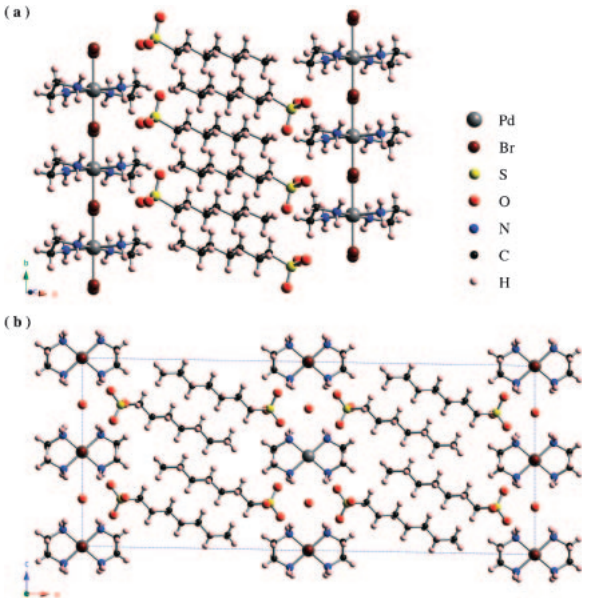

Fig. 2. Perspective views of the 3D packing of $[Pd(en)_2][PdBr_2(en)_2](C_7H_{15}SO_3)_4$.

Table 1. Comparison of the Interatomic Distances along the Chains (Å)

n	Pd^{II}–Pd^{IV}	Pd^{IV}–X	X···Pd^{II}	d[a)]
7	5.283(4)	2.498(4)	2.785(4)	0.054
8	5.3018(9)	2.499(3)	2.803(3)	0.057
9	5.274(3)	2.496(4)	2.778(4)	0.053
10	5.292(4)	2.489(4)	2.803(4)	0.059
ClO_4	5.407	2.496	2.911	0.077

a) $d = \{(X\cdots Pd^{II}) - (Pd^{IV}–X)\}/(Pd^{II}\cdots Pd^{IV})$.

bridged by Br ions, which are disordered at positions away from the midpoints between two neighboring Pd ions with half occupancies, thus forming linear chain Pd^{II}–Pd^{IV} mixed-valence structures. In order to understand the inter-chain valence arrangement, X-ray diffuse scattering was measured for these complexes. As a result, a rod-shaped diffuse scattering was observed in all complexes, indicating that these complexes are in a two-dimensional CDW state, where the CDW phase is ordered in the *bc*-plane.[5] As a comparison with the complex of ClO_4^-, the relevant bond distances are listed in Table 1. The Pd···Pd distance, Pd^{IV}–Br and Pd^{II}···Br bond lengths of the $n = 7$ complex are 5.283, 2.499, and 2.784 Å, respectively, while those in $[Pd(en)_2][PdBr_2(en)_2](ClO_4)_4$ are 5.407, 2.496, and 2.911 Å, respectively.[12] The degrees of displacements of the bridging halide ions from the midpoints between two neighboring Pd ions, defined as $\{(X\cdots Pd^{II}) - (Pd^{IV}–X)\}/(Pd^{II}\cdots Pd^{IV})$, are 0.054 for the former complex and 0.077 for the latter. Therefore, the oxidation state of the present complex is closer to Pd^{III}, namely a Robin–Day class III complex, than the complex with ClO_4^-.

Single-crystal reflectance spectra of $[Pd(en)_2][PdBr_2(en)_2](C_nH_{2n+1}SO_3)_4$ ($n = 7$, 8, 9, and 10) were measured at room temperature. Optical conductivities obtained from the Kramers–Kronig transformation are shown in Fig. 3. The $n =$ 7 complex showed an intense band at 1.03 eV. This is attributed to a charge-transfer (CT) transition from the Pd^{II} species to the Pd^{IV} species along the chain. According to theoretical studies,[13] the energy of the CT bands in mixed-valence compounds is given a $2S - U$, if T and V are neglected. The lower CT energy of the present complex than the complex of ClO_4 (1.13 eV[14]) is a consequence of a decrease in S, suggesting that the charge delocalization of this complex is larger than that of the complex of ClO_4. This is consistent with the finding that the displacement of the bridging bromide ions in the present complexes is smaller than that of the complexes of ClO_4^- as discussed above. This can be explained by the difference in the hydrogen-bond modes, i.e., HN···O···HN (via one atom) in the present complexes, while NH···O–Cl–O···HN (via three atoms) in complex of ClO_4^-.

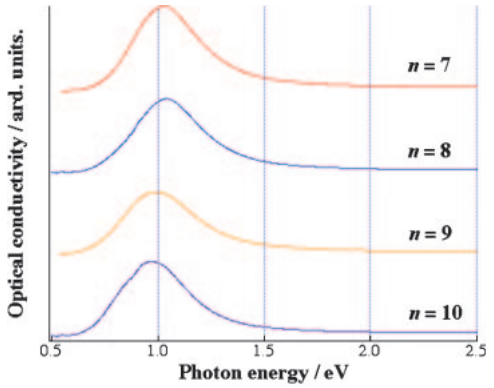

Fig. 3. Optical conductivity spectra with polarization of light parallel to the b axis in $[Pd(en)_2][PdBr_2(en)_2](C_nH_{2n+1}SO_3)_4$ ($n = 7$, 8, 9, and 10).

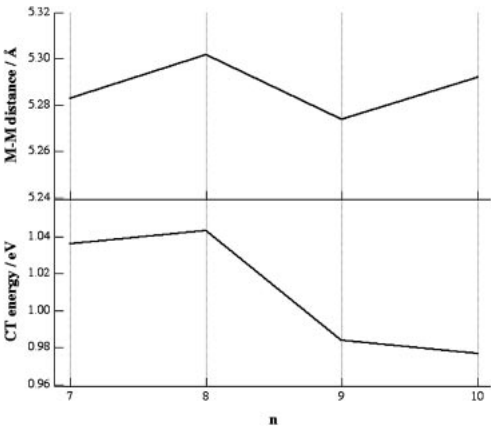

Fig. 4. The parity behavior of the M–M distance and the CT energy of $[Pd(en)_2][PdBr_2(en)_2](C_nH_{2n+1}SO_3)_4$ ($n =$ 7, 8, 9, and 10).

Moreover, the Pd···Pd distance and the CT energy decreased with increasing alkyl-chain length with parity behavior as shown in Fig. 4. The unit cell angle β also shows this parity behavior depending on the alkyl-chain length, i.e., $\beta =$ 91.033(9), 97.060(11), 93.456(7), and 99.086(9)° for $n = 7$, 8, 9, and 10, respectively. This is presumably due to the difference in the crystal packing arising from the difference in the alkyl-chain length.

In this work, the new quasi-one-dimensional bromo-bridged Pd^{II}–Pd^{IV} mixed-valence complexes with long chain alkylsulfonates counter anion were synthesized. These complexes have a different hydrogen-bond mode from that of complexes with ClO_4^-. The results of X-ray and optical conductivity measurements indicates that the oxidation states of Pd atoms approach the Pd^{III} state with increasing alkyl-chain length, which is presumably due to the fastener effects of the long alkyl-chains of the counter anions.

Experimental

Syntheses. The starting material, $[Pd(en)_2]Br_2$ was synthesized by mixing $PdBr_2$ (3 g, 11.3 mmol) and ethylenediamine (4.5 g, 74.8 mmol) in aqueous solution: 4.06 g (10.5 mmol, 93.2%). The compound $[Pd(en)_2][PdBr_2(en)](C_nH_{2n+1}SO_3)_4 \cdot 2H_2O$ ($n = 7$, 8, 9, and 10) were obtained by diffusing Br_2 gas to the 5 mL aqueous solution containing $C_nH_{2n+1}SO_3Na$ ($n = 7$, 8, 9, and 10) (300 mg, excess) and $[Pd(en)_2]Br_2$ (100 mg, 0.259 mmol).

Single crystal X-ray structure was determined using RIGAKU MSC SATURN CCD diffractometer with graphite monochromator Mo Kα ($\lambda = 0.7107$ Å). Crystal data for $[Pd(en)_2][PdBr_2(en)](C_7H_{15}SO_3)_4 \cdot 2H_2O$ at 93(2) K: $M_r = 683.03$, monoclinic, space group $C2/c$, $a = 36.48(3)$ Å, $b = 5.283(4)$ Å, $c = 15.237(11)$ Å, $\beta = 91.033(9)^\circ$, $V = 2936(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.545$ g cm^{-3}, final $R = 0.0407$, $wR = 0.0996$, GOF = 1.111 with $I > 2.00\sigma(I)$. Crystal data for $[Pd(en)_2][PdBr_2(en)](C_8H_{17}SO_3)_4 \cdot 2H_2O$ at 93(2) K: $M_r = 711.09$, monoclinic, space group $C2/c$, $a = 37.762(8)$ Å, $b = 5.3018(9)$ Å, $c = 15.290(4)$ Å, $\beta = 97.060(11)^\circ$, $V = 3037.9(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.555$ g cm^{-3}, final $R = 0.0489$, $wR = 0.1048$ GOF = 1.120 with $I > 2.00\sigma(I)$. Crystal data for $[Pd(en)_2][PdBr_2(en)](C_9H_{19}SO_3)_4 \cdot 2H_2O$ at 93(2) K: $M_r = 739.14$, monoclinic, space group $C2/c$, $a = 41.31(2)$ Å, $b = 5.274(3)$ Å, $c = 15.234(9)$ Å, $\beta = 93.456(7)^\circ$, $V = 3313(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.482$ g cm^{-3}, final $R = 0.0455$, $wR = 0.0919$, GOF = 1.143 with $I > 2.00\sigma(I)$. Crystal data for $[Pd(en)_2][PdBr_2(en)](C_{10}H_{21}SO_3)_4 \cdot 2H_2O$ at 93(2) K: $M_r = 767.19$, monoclinic, space group $C2/c$, $a = 42.75(3)$ Å, $b = 5.292(4)$ Å, $c = 15.311(11)$ Å, $\beta = 99.086(9)^\circ$, $V = 3420(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.490$ g cm^{-3}, final $R = 0.0471$, $wR = 0.0909$, GOF = 1.142 with $I > 2.00\sigma(I)$. Crystallographic dates have been deposited with Cambridge Crystallographic Date Centre: Deposition number CCDC-291564, 291565, 291566, and 291567 for compound $n = 7$, 8, 9, and 10, respectively. Copies of the date can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Date Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Polarized reflectivity spectra were obtained by using a specially designed spectrometer with a 25 cm grating monochromator and an optical microscope.

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