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Structural Study of Electronic States in Quasi-One-Dimensional Halogen-Bridged Mixed-Metal Complexes $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$

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The electronic structures of quasi-one-dimensional halogen-bridged mixed-metal compounds $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ were investigated by means of powder X-ray diffraction measurements. Unit cell lengths of all directions obeyed a linear relationship when $x < 0.9$, whereas those deviated when $x > 0.9$ especially in the case of the *b* and *c* axes. This deviation can be explained by a phase change from an M^{III} Mott−Hubbard state to an $M^{II}-M^{IV}$ charge-density-wave state because of chemical pressure caused by the substitution of Pd ions into $[Pd(chxn)_2Br]Br_2$ with smaller Ni ions.

Quasi-one-dimensional (1D) halogen-bridged nickel, palladium, and platinum compounds (MX chains) have interesting chemical and physical properties, such as an intense and dichroic charge-transfer band,[1] progressive overtones in the resonance Raman spectra,[2] midgap absorptions attributable to solitons and polarons,[3] gigantic third-order nonlinear optical susceptibility,[4] spin Peierls transition,[5] etc. These compounds are in highly isolated 1D electronic systems with −M−X−M−X− 1D linear chain structures composed of the d_{z^2} orbital of metal ions (M) and p_z orbitals of the bridging halide ions (X). These MX chains are considered to be a Peierls−Hubbard system, where the electron−phonon interaction (*S*), the transfer integral (*T*), and the on-site and nearest-neighbor Coulomb repulsion energies (*U* and *V*, respectively) strongly compete with each other.[6] All platinum and palladium compounds form $M^{II}-M^{IV}$ mixed-valence states, where the bridging halide ions are displaced from the midpoints between two neighboring metal ions ($-X\cdots M^{II}\cdots X-M^{IV}-X\cdots$) as a consequence of the large *S* value (Figure 1a).[7] These platinum and palladium compounds are Robin−Day class II mixed-valence complexes.[8] This state is noted as a charge-density-wave (CDW) state.

On the other hand, the nickel complexes form the average Ni^{III} or Mott−Hubbard (MH) states, where the bridging halide ions are located at the midpoints between the two neighboring nickel atoms, represented as $-X-Ni^{III}-X-Ni^{III}-X-$, due to a large *U* value (Figure 1b).[9] These nickel compounds are Robin−Day class III complexes.[8]

Recently, a series of single crystals of quasi-1D bromo-bridged nickel and palladium mixed-metal complexes, $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$, have been synthesized.[10] The electronic structures of these complexes have been extensively studied by means of electron spin resonance,[11] infrared,[12] optical conductivity spectroscopies,[12] X-ray diffuse scattering,[13] and scanning tunneling microscopy.[14] It has been found that the oxidation states of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ change when $x \approx 0.9$. In other words, these compounds are in

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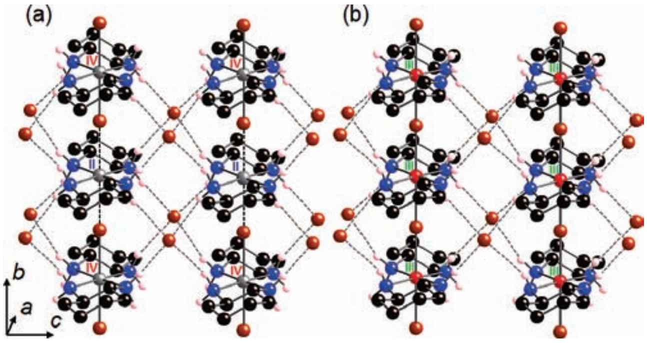

Figure 1. Crystal structures of (a) $[Pd(chxn)_2Br]Br_2$ and (b) $[Ni(chxn)_2Br]Br_2$. Dashed lines show hydrogen bonds (gray) and $Pd^{II}-Br$ interactions (black). Hydrogen atoms bonding to carbon atoms are omitted for clarity. Color code: red, Ni; gray, Pd; brown, Br; blue, N; black, C; pink, H.

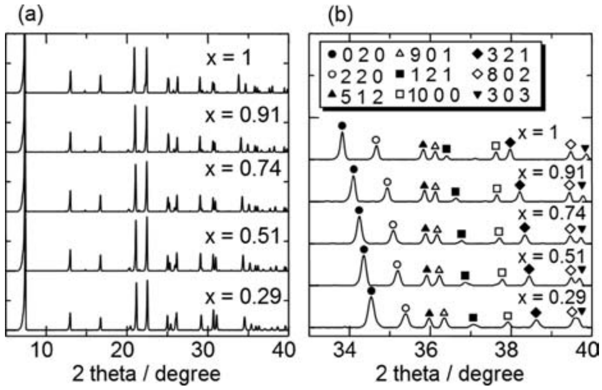

Figure 2. (a) PXRD patterns of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ with selected x values. (b) Magnification of part a in the range of $33° \leq 2\theta \leq 40°$. Inset: Miller indices of each peak.

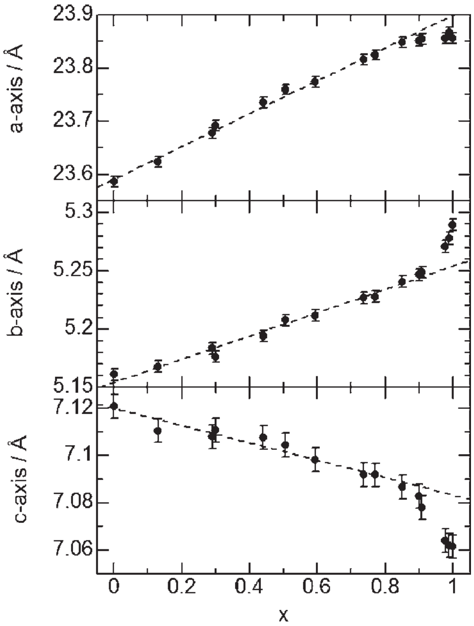

Figure 3. Change in the unit cell parameters of a series of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ in relation to x. Dashed lines indicate fitted values with a linear relationship in $x < 0.90$.

a MH state when $x < 0.9$ and in a CDW state when $x > 0.9$. However, the chemical or physical origin of this crossover has not been clarified yet. In order to clarify the origin of this crossover, we have measured powder X-ray diffraction (PXRD) patterns of a series of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ and tried to clarify the origin from a structural viewpoint.

Single crystals of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ were prepared by using a previously reported electrochemical oxidation method.[10] PXRD patterns were acquired on a Rigaku RINT powder diffractometer with graphite-monochromated Cu Kα radiation. PXRD patterns were fitted by using the LeBail method[15] incorporated in the *Rietica* software. The ratios of Ni and Pd ions were determined by using inductively coupled plasma emission measurements on a Shimadzu ICPS 7510 plasma spectrometer.

Figure 2 shows PXRD patterns of a few $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ complexes at room temperature. All of the compounds showed similar PXRD patterns, and they could be fitted with the space group of *I*222, showing that the crystal structures of each compound are isomorphous. The PXRD patterns shifted gradually with an increase in x, indicating that the unit cell parameters continuously changed and that there was no phase separation. Although a slight broadening of the peaks in nickel–palladium mixed-metal complexes compared to pure nickel or palladium complexes, which may originate from a distribution of x in the crystal, was observed, it is small enough to discuss the x dependency.

Figure 3 shows the unit cell parameters of a series of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ in relation to x. The unit cell lengths of the *a* and *b* axes increased with an increase in x, which is consistent with the finding that the valence orbitals of Pd 4d are spatially wider than those of Ni 3d. On the other hand, the length of the *c* axis decreased with an increase in x. This finding is explained as follows: Because the 1D chain runs along the *b* axis, its length should be directly influenced by the substitution. In fact, as mentioned above, the unit cell length increased in this direction with an increase in x. On the other hand, the 1D chains are connected to each other via hydrogen bonds (N–H···Br···H–N) along the *c* axis, as shown in Figure 1. Therefore, in order to maintain the hydrogen bonding, the length of the *c* axis decreased with an increase in x.

The unit cell length in each direction obeys a linear relationship when $x < 0.9$, whereas it deviates from the line when $x > 0.9$, especially in the case of the *b* and *c* axes. The x dependence of the unit cell length of the *b* axis (parallel to 1D chain) could be influenced by the electronic state of the compound. As mentioned above, $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ is in MH and CDW states below and above $x = 0.9$, respectively. Therefore, the linear relationship in the unit cell length of the *b* axis when $x < 0.9$ corresponds to twice the linear summation of the $Ni^{III}-Br$ and $Pd^{III}-Br$ bond lengths. The deviation from the line when $x > 0.9$ is probably due to an increase in the M···M distance because the complex enters a CDW state.

Recently, for the first time, we synthesized the Pd^{III} compound (MH state) $[Pd(en)_2Br](C_nY)_2 \cdot H_2O$ (C_nY = dialkylsulfosuccinate) by making use of the attractive force between the alkyl chains, which acts as a form of chemical pressure.[16] We have shown that $[Pd(en)_2Br](C_5Y)_2 \cdot H_2O$

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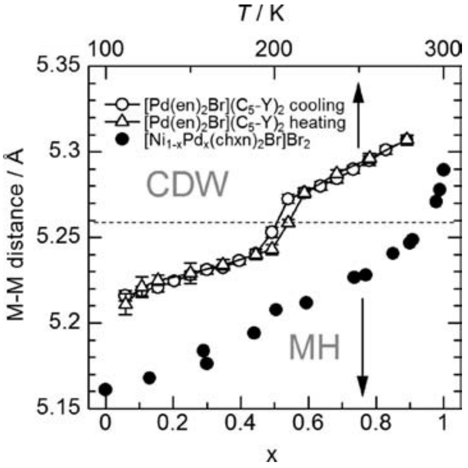

Figure 4. Temperature dependence of the Pd···Pd distance along the 1D chain in $[Pd(en)_2Br](C_5Y)_2 \cdot H_2O$ (upper scale) together with the x dependence of the M···M distance in $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ (lower scale).

undergoes a novel phase transition between the MH and CDW states at 205 K. Figure 4 shows the temperature dependence of the Pd···Pd distance in $[Pd(en)_2Br](C_5Y)_2 \cdot H_2O$ along the 1D chain (upper scale) together with the x dependence of the M···M distance in $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ (lower scale). In both systems, the electronic state changed at an M···M distance of ca. 5.26 Å. In other words, the CDW and MH states are the ground states when the Pd···Pd distance is longer and shorter than 5.26 Å, respectively. This result suggests that the Pd···Pd distance is a boundary between the CDW and MH states.

If the Pd−Br bond is ionic, the potential energy of the Br ion can be determined by using the Born−Mayer equation. In the Pd^{IV}−Br···Pd^{II} mixed-valence system, the energy of the Br ions forms a double-minimum potential, i.e., the summation of two potential curves. The two minima correspond to Pd^{IV}−Br···Pd^{II} (red curve) and Pd^{II}···Br−Pd^{IV} (blue curve), as shown in Figure 5a. When the Pd···Pd distance becomes shorter, the two minima of the Br ions approach each other and finally form a single-minimum potential at the midpoint between two neighboring Pd ions, as shown in Figure 5b. In this situation, all of the Pd ions should be equivalent, and the Pd^{III} MH state will be stabilized. In the present system, we think that the boundary distance between the double-minimum and single-minimum potentials is ca. 5.26 Å.

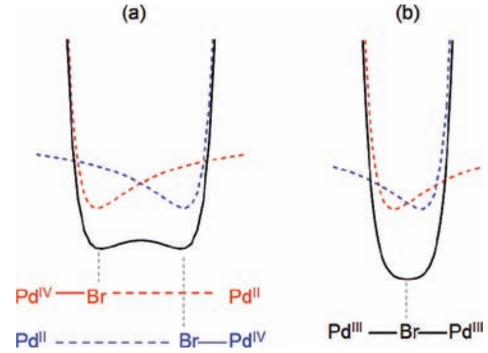

Figure 5. Potential energy curve of the bridging Br ion in the (a) CDW and (b) MH states.

Finally, we have concluded that the origin of the crossover between the MH and CDW states in $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ was due to the shortening of the Pd···Pd distance when Pd ions were substituted with smaller Ni ions. In other words, a chemical pressure effect occurred.

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Supporting Information Available: Schematic drawing of the N−H symmetrical stretching mode in $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$, (b) IR spectra in several $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$, and (c) peak energy values of the N−H symmetrical stretching mode in a series of $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ as a function of x. This material is available free of charge via the Internet at http://pubs.acs.org.