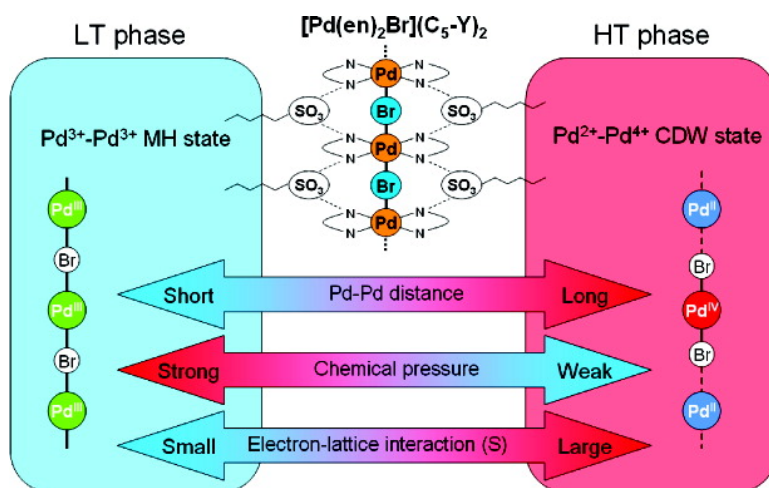


Charge-Density-Wave to Mott#Hubbard Phase Transition in Quasi-One-Dimensional Bromo-Bridged Pd Compounds

Shinya Takaishi, Mitsuhiro Takamura, Takashi Kajiwara, Hitoshi Miyasaka, Masahiro Yamashita, Muneaki Iwata, Hiroyuki Matsuzaki, Hiroshi Okamoto, Hisaaki Tanaka, Shin-ichi Kuroda, Hiroyuki Nishikawa, Hiroki Oshio, Kenichi Kato, and Masaki Takata

J. Am. Chem. Soc., **2008**, 130 (36), 12080-12084 • DOI: 10.1021/ja8032026 • Publication Date (Web): 16 August 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Charge-Density-Wave to Mott–Hubbard Phase Transition in Quasi-One-Dimensional Bromo-Bridged Pd Compounds

Shinya Takaishi,^{*,†} Mitsuhiro Takamura,[†] Takashi Kajiwara,[†] Hitoshi Miyasaka,[†] Masahiro Yamashita,^{*,†} Muneaki Iwata,[‡] Hiroyuki Matsuzaki,[‡] Hiroshi Okamoto,[‡] Hisaaki Tanaka,[§] Shin-ichi Kuroda,[§] Hiroyuki Nishikawa,^{||} Hiroki Oshio,^{||} Kenichi Kato,^{⊥,¶} and Masaki Takata^{⊥,¶}

Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aza-aoba, Aramaki, Sendai 980-8578, Japan, Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa 277-8561, Japan, Department of Applied Physics, Graduate School of Engineering, Nagoya University, Furocho, Chikusa-ku, Nagoya 464-8603, Japan, Department of Chemistry, The University of Tsukuba, 1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan, RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan, and Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198 Japan

Received April 30, 2008; E-mail: takaishi@agnus.chem.tohoku.ac.jp; yamasita@agnus.chem.tohoku.ac.jp

Abstract: A $\text{Pd}^{\text{III}}\text{—Br—Pd}^{\text{III}}$ Mott–Hubbard state was observed in a quasi-one-dimensional bromo-bridged Pd compound $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5\text{—Y})_2\cdot\text{H}_2\text{O}$ (en = ethylenediamine, $\text{C}_5\text{—Y}$ = dipentylsulfosuccinate) for the first time. The phase transition between Mott–Hubbard and charge-density-wave states occurred at 206 ± 2 K and was confirmed by using X-ray, ESR, Raman and electronic spectroscopies, electrical resistivity, and heat capacity. From X-ray powder diffraction patterns and Raman spectra of a series of Pd–Br compounds, $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n\text{—Y})_2\cdot\text{H}_2\text{O}$ ($n = 4, 5, 6, 7, 8, 9,$ and 12), chemical pressure from the alkyl chains of the counterions caused the phase transition.

Introduction

Recently, there has been much interest in one-dimensional (1D) electron systems, or quantum wires, because they have many characteristic physical properties, such as spin-density-wave (SDW) and charge-density-wave (CDW) states in organic conductors;¹ a soliton, polaron, and bipolaron in π -conjugated polymers;² slow relaxation of magnetization in several ferro- or ferrimagnetic compounds,³ etc. One-dimensional (1D) mixed-valence Wolfram's red salt analogues, that is, halogen-bridged MX chains, have been attracting much attention. Many interesting chemical and physical properties, such as an intense and

dichroic charge transfer band,⁴ overtone progressions in the resonant Raman spectra,⁵ midgap absorptions attributable to solitons and polarons,⁶ gigantic third-order nonlinear optical susceptibility,⁷ thermochromism in the organic media,⁸ and insertion of a 1D chain into artificial peptides,⁹ have been reported. These compounds form highly isolated 1D electron systems, such as —M—X—M—X— 1D linear chain structures, composed of the d_{z^2} orbitals of metal ions (M) and the p_z orbitals of bridging halide ions (X). These MX chains are thought to be Peierls–Hubbard systems, where the transfer integral (t), the on-site and nearest neighbor-site Coulomb repulsion (U and V , respectively), and the electron–lattice interaction (S) strongly compete with each other.¹⁰ Pt and Pd compounds form mixed-valence states, represented as $\text{—X}\cdots\text{M}^{\text{II}}\cdots\text{X—M}^{\text{IV}}\text{—X}\cdots$, as a consequence of a strong S value ($S > U$). These compounds are Robin–Day class II mixed-valence complexes.¹¹ Their

[†] Tohoku University.

[‡] The University of Tokyo.

[§] Nagoya University.

^{||} The University of Tsukuba.

[⊥] RIKEN Spring-8 Center.

[¶] Japan Synchrotron Radiation Research Institute.

- (1) (a) Andrieux, A.; Jerome, D.; Bechgaard, K. *J. Phys. Lett.* **1981**, *42*, 87–90. (b) Forro, L.; Bouffard, S.; Pouget, J. P. *J. Phys. Lett.* **1984**, *45*, 453–459. (c) Hasegawa, T.; Kagoshima, S.; Mochida, T.; Sugiura, S.; Iwasa, Y. *Solid State Commun.* **1997**, *103*, 489–493.
- (2) (a) Goldberg, I. B.; Crowe, H. R.; Newman, P. R.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1979**, *70*, 1132–1136. (b) Su, W. P.; Schrieffer, J. R.; Heeger, A. *J. Phys. Rev. B* **1980**, *22*, 2099–2111.
- (3) (a) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760–1763. (b) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. *J. Am. Chem. Soc.* **2002**, *124*, 12837–12844. (c) Lescouezec, R.; Vaissermann, J.; Ruiz-Perez, C.; Lloret, F.; Carrasco, R.; Julve, M.; Verdager, M.; Dromzee, Y.; Gatteschi, D.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1483–1486.

- (4) (a) Tanaka, M.; Kurita, S.; Kojima, T.; Yamada, Y. *Chem. Phys.* **1984**, *91*, 257–65. (b) Wada, Y.; Mitani, T.; Yamashita, M.; Koda, T. *J. Phys. Soc. Jpn.* **1985**, *54*, 3143–3153.

- (5) (a) Clark, R. J. H.; Franks, M. L.; Trumble, W. R. *Chem. Phys. Lett.* **1976**, *41*, 287–292. (b) Clark, R. J. H.; Kurmoo, M.; Mountney, D. N.; Toftlund, H. *J. Chem. Soc., Dalton Trans.* **1982**, 1982, 1851–1860. (c) Clark, R. J. H. *Chem. Soc. Rev.* **1990**, *19*, 107–131.

- (6) Tanino, H.; Kobayashi, K. *J. Phys. Soc. Jpn.* **1983**, *52*, 1446–1456.
- (7) (a) Iwasa, Y.; Funatsu, E.; Hasegawa, T.; Koda, T.; Yamashita, M. *Appl. Phys. Lett.* **1991**, *59*, 2219–2221. (b) Kishida, H.; Matsuzaki, H.; Okamoto, H.; Manabe, T.; Yamashita, M.; Taguchi, Y.; Tokura, Y. *Nature* **2000**, *405*, 929–932.

- (8) Kimizuka, N.; Lee, S. H.; Kunitake, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 389–391.

- (9) Tanaka, K.; Kaneko, K.; Shionoya, M. *Dalton Trans.* **2007**, 2007, 5369–5371.

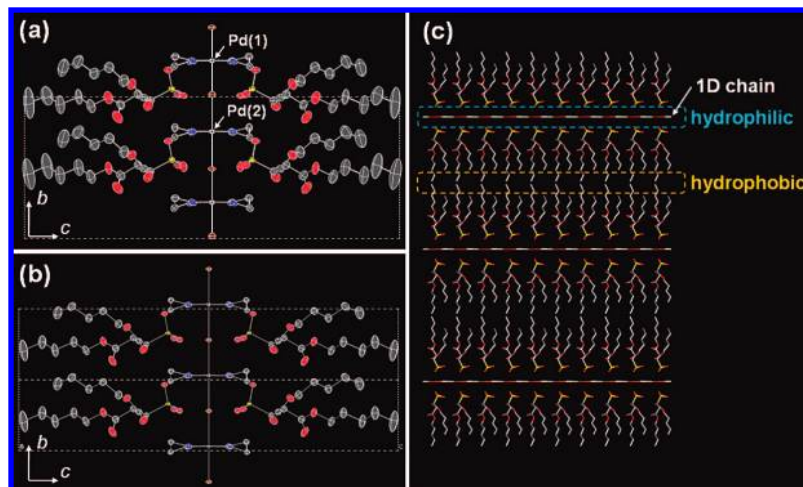


Figure 1. Crystal structure of $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$. ORTEP drawing (a) at 259 K and (b) at 162 K and of (c) crystal packing. Water molecules and hydrogen atoms are omitted for clarity. White, Pd; brown, Br; blue, N; yellow, S; red, O; gray, C.

Peierls distorted 1D structure has been noted to be in a charge-density-wave (CDW) state.

On the other hand, Ni complexes crystallize in an average-valent Mott–Hubbard (MH) state, expressed as $-\text{X}-\text{Ni}^{\text{III}}-\text{X}-\text{Ni}^{\text{III}}-\text{X}-$, due to a strong U value ($U > S$). These compounds are in a Robin–Day class III state.¹¹ Although more than 300 compounds have been synthesized since Wolfram reported the mixed-valence salt $[\text{Pt}^{\text{II}}(\text{NH}_2\text{C}_2\text{H}_5)_4][\text{Pt}^{\text{IV}}(\text{NH}_2\text{C}_2\text{H}_5)_4\text{Cl}_2]\text{Cl}_4\cdot 4\text{H}_2\text{O}$ in 1900, all of the Ni compounds and Pd and Pt compounds form MH and CDW states, respectively, without exception. If $S \approx U$, a phase transition between CDW and MH states can occur. It is difficult to control U structurally because U is usually dependent on M itself. On the other hand, S is dependent on not only M and X but also the 1D chain structure. In other words, S is reduced by shortening the M–X–M bond lengths. Therefore, chemical pressure can effectively reduce S . Herein, to the best of our knowledge, we report the first observation of a temperature induced CDW to MH phase transition under ambient pressure in a Pd compound by introducing long alkyl chains as counterions, which can cause effective chemical pressure. The mechanism for the phase transition between CDW and MH states will also be discussed.

Experimental Section

Sodium salts of the counterions $\text{NaC}_n\text{-Y}$ ($\text{C}_n\text{-Y} =$ dialkylsulfosuccinate) were prepared using a previously reported method.¹² $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n\text{-Y})_2\cdot\text{H}_2\text{O}$ ($n = 4, 5, 6, 7, 8, 9,$ and 12) was synthesized by slowly diffusing Br_2 vapor into a 1:1 $\text{H}_2\text{O}/\text{THF}$ solution of $\text{Pd}(\text{en})_2\text{Br}_2$ and $\text{NaC}_n\text{-Y}$. Single crystal structures were determined on a Bruker SMART CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). ESR spectra were measured on a Bruker EMX spectrometer equipped with a gas-flow type cryostat Oxford ESR 900. Raman spectra were measured on a Renishaw Raman spectrometer. Polarized reflectivity spectra were obtained by using a specially designed spectrometer with a 25 cm grating monochromator and an optical microscope. Current–voltage characteristics were measured using a Keithley

2611 source meter, and electrical resistivity measurements were carried out using an Agilent 34420A nanovoltmeter. X-ray powder diffraction patterns were measured on a Rigaku RINT-TTR III diffractometer for $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n\text{-Y})_2\cdot\text{H}_2\text{O}$ ($n = 4, 5, 6, 7,$ and 8) and on a Debye–Scherrer camera in the beamline 02B2¹³ combined with the synchrotron radiated X-ray source installed at SPring-8 for $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n\text{-Y})_2\cdot\text{H}_2\text{O}$ ($n = 9$ and 12). Lattice parameters were refined using the LeBail method.¹⁴

Results and Discussion

Results of X-ray crystal structure analysis for $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$ at 259 and 162 K are shown in Figure 1a and 1b, respectively. At both temperatures, the $\text{Pd}(\text{en})_2$ moieties are bridged by bromide ions, forming 1D chains. There are hydrogen bonds between two oxygen atoms of the sulfonate ion and the amino protons of the en ligand. The compound has a lamellar structure, and the counterions separate the hydrophobic and hydrophilic spaces. The 1D Pd–Br chain lies in the hydrophilic space (Figure 1c).

There was a remarkable difference in the periodicity of the crystal structures at the two temperatures. At 259 K, the lattice parameters a and b were two times longer than those at 162 K. This difference was clear in the superlattice reflections (see Supporting Information). At 259 K, the Pd(1)–Br bond lengths are 2.512 and 2.497 Å , whereas the Pd(2)–Br bond lengths are 2.783 and 2.776 Å . Because a Pd^{II}–Br distance is usually longer than a Pd^{IV}–Br distance, Pd(1) and Pd(2) were assigned to be Pd^{IV} and Pd^{II}, respectively. Therefore, this indicates that the present compound is in a 3D-ordered CDW state ($\cdots\text{Pd}^{\text{II}}\cdots\text{X}-\text{Pd}^{\text{IV}}-\text{X}\cdots\text{Pd}^{\text{II}}\cdots$) at this temperature. At 162 K, on the other hand, the 2-fold periodicity disappeared, and all of the Pd ions became equivalent. The Pd–Br bond lengths are 2.613 and 2.604 Å , which are intermediate between Pd^{II}–Br and Pd^{IV}–Br bond lengths, suggesting that this compound is in an MH state ($-\text{Pd}^{\text{III}}-\text{X}-\text{Pd}^{\text{III}}-\text{X}-\text{Pd}^{\text{III}}-$) at 162 K.

Figure 2 shows the temperature dependence of the average neighboring Pd–Pd distance along the chain. The average Pd–Pd distance in $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$ at 293 K is 5.31 Å . This distance is longer than that in $[\text{Pd}(\text{chxn})_2\text{Br}]\text{Br}_2$ (chxn

(10) (a) Nasu, K. *J. Phys. Soc. Jpn.* **1984**, *52*, 3865–3873. (b) Webber-Milbrodt, S. M.; Gammel, J. T.; Bishop, A. R., Jr. *Phys. Rev. B* **1992**, *45*, 6435–6458. (c) Iwano, K.; Nasu, K. *J. Phys. Soc. Jpn.* **1992**, *61*, 1380–1389.

(11) Robin, M. B.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247–422.

(12) Dufour, B.; Rannou, P.; Djurado, D.; Janeczka, H.; Zagorska, M.; de Geyer, A.; Travers, J. -P.; Pron, A. *Chem. Mater.* **2003**, *15*, 1587–1592.

(13) Takata, M.; Nishibori, E.; Kato, K.; Kubota, Y.; Kuroiwa, Y.; Sakata, M. *Adv. X-ray Anal.* **2002**, *45*, 377–384.

(14) Le Bail, A.; Duroy, H.; Fourquet, J. L. *Mater. Res. Bull.* **1998**, *23*, 447–452.

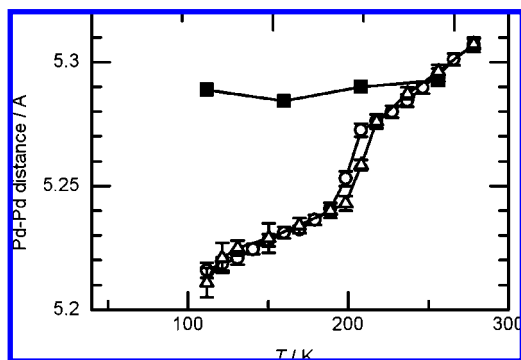


Figure 2. Temperature dependence of the average Pd–Pd distance in $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5\text{--Y})_2\cdot\text{H}_2\text{O}$ during the cooling (circle) and heating (triangle) processes together with that in $[\text{Pd}(\text{chxn})_2\text{Br}]\text{Br}_2$ (square).

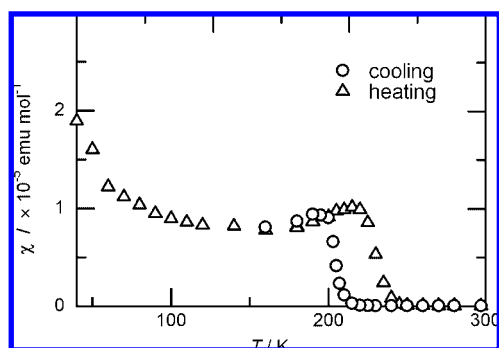


Figure 3. Temperature dependence of the spin susceptibility for $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5\text{--Y})_2\cdot\text{H}_2\text{O}$.

= 1*R*,2*R*-diaminocyclohexane), which has the shortest Pd–Pd distance thus far reported and is in a CDW state.¹⁵ Upon lowering the temperature, this distance decreased by ca. 2% and became 5.21 Å at 110 K, whereas that of $[\text{Pd}(\text{chxn})_2\text{Br}]\text{Br}_2$ showed almost no temperature dependence. Such a large temperature dependence in the present compound is thought to be due to suppression of the thermal motion of the alkyl chains. In addition, a discontinuity in the Pd–Pd distance with a small hysteresis was clearly observed at ca. 205 K. This indicates that some first-order phase transition occurs at this temperature.

In order to confirm that a phase transition occurs, electron spin resonance (ESR) spectra were acquired. Because CDW and MH states should show diamagnetic and paramagnetic (antiferromagnetic) behaviors, respectively, the two states can be determined using ESR signals. ESR spectra at various temperatures are shown in the Supporting Information. Figure 3 shows the temperature dependence of the spin susceptibility obtained by integrating the first derivative of the ESR signal twice. Around room temperature, very weak ESR signals on the order of 10^{-8} emu mol⁻¹ were observed. This result is in agreement with the structural data, which indicate that this compound is in a diamagnetic CDW state at room temperature. On the other hand, the spin susceptibility below 200 K was on the order of 10^{-5} emu mol⁻¹. This could be due to paramagnetic behavior coupled with a strong antiferromagnetic interaction, which is characteristic of compounds in an MH state.¹⁶ The Curie ($1/T$) contribution below 100 K, which is 0.14% of the spin concentration, is probably due to the existence of an odd number of Pd³⁺ ions ($S = 1/2$) in the domains or short chains. A clear discontinuity in the spin susceptibility was observed at ca. 205

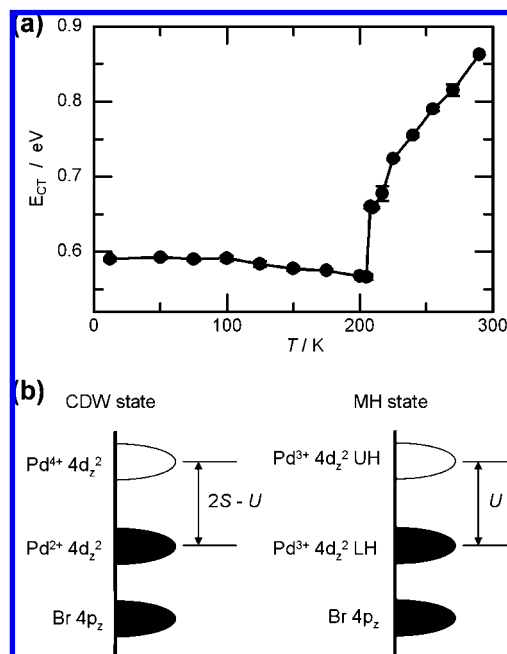


Figure 4. (a) Temperature dependence of the charge transfer energy determined from the peak in the optical conductivity spectra. (b) Proposed band structures in the CDW and MH states.

± 5 and $230 \text{ K} \pm 5 \text{ K}$ in the cooling and heating processes, respectively. We concluded that the discontinuity corresponds to a first-order phase transition between CDW and MH states.

Figure 4a shows the temperature dependence of the charge transfer (CT) energy, which was determined from the optical conductivity spectra, shown in the Supporting Information. A clear discontinuity in the electronic transition energy was observed at $206 \pm 2 \text{ K}$ as well. This temperature is similar to those observed in the crystal structure and ESR results. In the high temperature (HT) phase, the peak energy decreased from 0.86 eV (290 K) to 0.66 eV (210 K). On the other hand, the peak energy barely changed with a change in the temperature in the low temperature (LT) phase. This can be understood by considering the origin of the electronic transition. Figure 4b shows the band structures for the CDW and MH states proposed based on the Peierls–Hubbard model.¹⁰ In the CDW state, the lowest electronic transition is a CT transition from the Pd^{II} to Pd^{IV} d_z^2 band. In this case, the CT energy (E_{CT}) is $2S - U$ if V and t are ignored. In the MH state, on the other hand, the lowest electronic transition is that from a lower Hubbard band to an upper Hubbard band, of which $E_{\text{CT}} = U$. Because almost no temperature dependence was observed in the LT phase, whereas there was a large temperature dependence of the CT energy in the HT phase, S , not U , decreases as the Pd–Pd distance becomes shorter.

Figure 5 shows the temperature dependence of the Raman spectra. In the HT phase, an intense Raman peak was observed at ca. 130 cm^{-1} , which was assigned to the Br–Pd–Br symmetrical stretching mode ($\nu(\text{Br--Pd--Br})$). However, the peak disappeared in the LT phase. It is well-known that this stretching mode is allowed in the CDW state and forbidden in the MH state. This result clearly indicates that this compound undergoes a phase transition from CDW to MH states.

(15) Hazell, A. *Acta Crystallogr., Sect. C* **1991**, *47*, 962–966.

(16) Okamoto, H.; Toriumi, K.; Mitani, T.; Yamashita, M. *Phys. Rev. B* **1990**, *42*, 10381–10387.

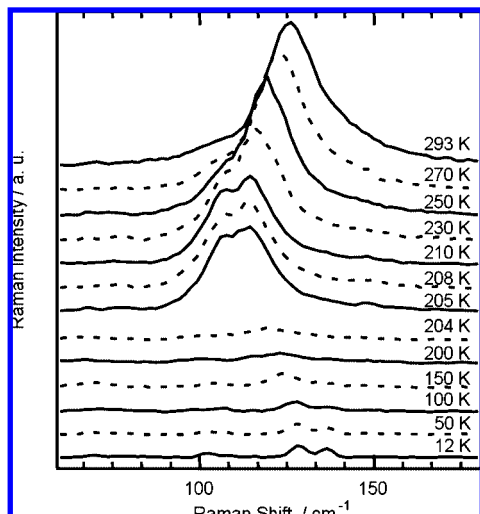


Figure 5. Temperature dependence of the Raman spectra for $[\text{Pd}(\text{en})_2\text{Br}]\cdot(\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$.

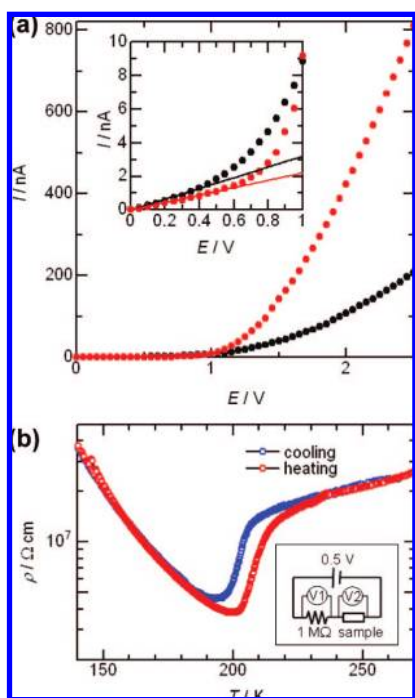


Figure 6. (a) Current (I)–voltage (E) characteristics for $[\text{Pd}(\text{en})_2\text{Br}]\cdot(\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$ at 215 K (black) and 145 K (red). Inset shows low voltage region magnified. (b) Temperature dependence of electrical resistivity for $[\text{Pd}(\text{en})_2\text{Br}]\cdot(\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$. Inset is the electrical circuit used in this measurement.

Figure 6a shows current (I)–voltage (E) characteristics for $[\text{Pd}(\text{en})_2\text{Br}]\cdot(\text{C}_5\text{-Y})_2\cdot\text{H}_2\text{O}$. In both phases, nonlinearity of the I – E characteristics was observed above ca. 0.5 V. In the CDW state, it is known that electrical conduction above a threshold voltage (E_T) is explained by the sliding of the CDWs, which carries a current with only small incremental changes in the electric field.¹⁷ On the other hand, nonlinear conduction in an MH state is not well understood; however, there may be a depinning effect of the conducting carrier due to the electron correlation. Anyway, in order to exclude such a depinning effect,

(17) McDonald, R. D.; Harrison, N.; Balicas, L.; Kim, K. H.; Singleton, J.; Chi, X. *Phys. Rev. Lett.* **2004**, *93*, 076405.

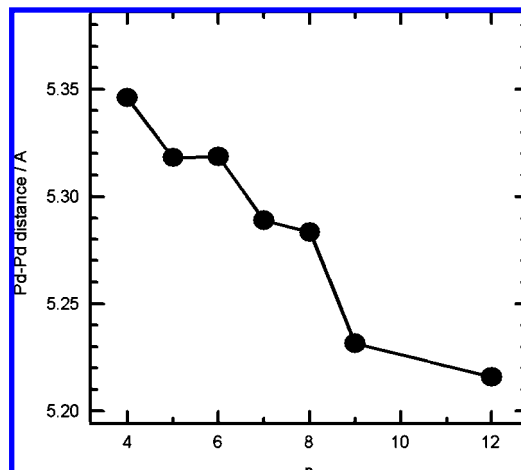


Figure 7. Nearest neighboring Pd–Pd distance as a function of the alkyl chain length.

we measured the electrical resistivity at a low voltage (0.5 V). Figure 6b shows the temperature dependence of the electrical resistivity. Below the critical temperature (T_c), the electrical conductivity increased with a decrease in the temperature. The electrical resistivity could be fitted by using an Arrhenius model ($\rho = \rho_0 \exp(E_a/2k_B T)$), and the activation energy (E_a) was determined to be 205.8 meV. This value is much smaller than the optical gap (~ 0.6 eV) probably because of an indirect band gap in this compound.

Above T_c , on the other hand, the electrical resistivity decreased with a decrease in the temperature. Such a metallic temperature dependence is not observed in CDW compounds because the CDW state, which is a consequence of the Peierls transition, has a finite band gap. This anomalous behavior is probably due to change of the activation energy (E_a) caused by change of the Pd–Pd distance.

In addition, a drastic decrease in the resistivity was observed just above T_c . This behavior is explained by a charge fluctuation due to the phase transition accompanied by CT. This behavior has also been observed in a tetrathiafulvalene (TTF)–chloranil (CA) salt, which shows a neutral (N) to ionic (I) phase transition.¹⁸

From the crystal structures, spin susceptibility, optical conductivity spectra, Raman spectra, and electrical resistivity, we concluded that a first-order phase transition between CDW and MH states occurs at $T_c = 206 \pm 2$ K. This phase transition was also confirmed using a heat capacity measurement ($\Delta H = 1.554 \pm 0.011$ kJ mol^{−1}, $\Delta S = 7.48 \pm 0.05$ J K^{−1} mol^{−1}; see Supporting Information).

In order to clarify the origin of the phase transition, we synthesized a series of Pd–Br compounds $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n\text{-Y})_2\cdot\text{H}_2\text{O}$ ($n = 4, 5, 6, 7, 8, 9,$ and 12) with different alkyl chain lengths. We determined the nearest neighboring Pd–Pd distance of these compounds from the X-ray powder diffraction (XRPD) patterns. Increasing the alkyl chain length caused the Pd–Pd distance to decrease dramatically even at room temperature, as shown in Figure 7, suggesting that the attractive force between the alkyl chains of the counterions becomes stronger with an increase in the alkyl chain length. In other words, the attractive force acting between the alkyl chains is the origin of the chemical pressure.

(18) Mitani, T.; Kaneko, Y.; Tanuma, S.; Tokura, Y.; Koda, T.; Saito, G. *Phys. Rev. B* **1987**, *35*, 427–429.

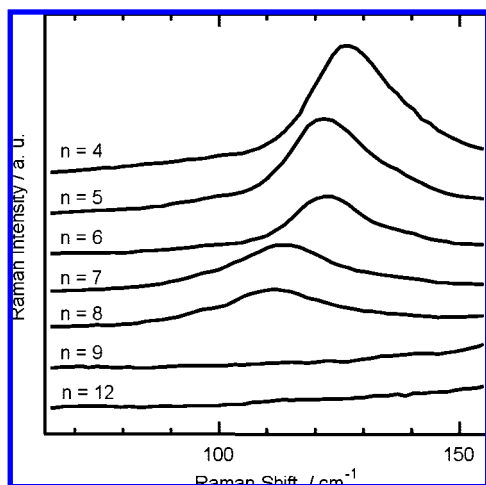


Figure 8. Raman spectra of $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n-\text{Y})_2\cdot\text{H}_2\text{O}$ ($4 \leq n \leq 12$).

Figure 8 shows Raman spectra of the series of Pd–Br compounds at room temperature. An intense Raman peak attributed to $\nu(\text{Br}-\text{Pd}-\text{Br})$ was observed for the compounds with short alkyl chains ($n \leq 8$), whereas it was not observed for the compounds with longer alkyl chains ($n \geq 9$). Therefore, the compounds with short ($n \leq 8$) and long ($n \geq 9$) alkyl chains are in CDW and MH states, respectively, at room temperature. As shown in Figure 7, the nearest Pd–Pd distances in $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_8-\text{Y})_2\cdot\text{H}_2\text{O}$ and $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_9-\text{Y})_2\cdot\text{H}_2\text{O}$ at room temperature were determined to be 5.283 and 5.232 Å, respectively. This finding is in agreement with the result of the temperature dependency studies on $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5-\text{Y})_2\cdot\text{H}_2\text{O}$ (boundary between CDW and MH phase is at a Pd–Pd distance of ca. 5.26–5.27 Å). Therefore, the Pd–Pd distance is the main factor determining the electronic state of these compounds.

We measured the temperature dependence of the Raman spectra and determined the T_c for the series of Pd–Br compounds (Raman spectra are shown in the Supporting Information). Figure 9 shows the phase diagram of these compounds. With an increase in the alkyl chain length, T_c steadily increased.

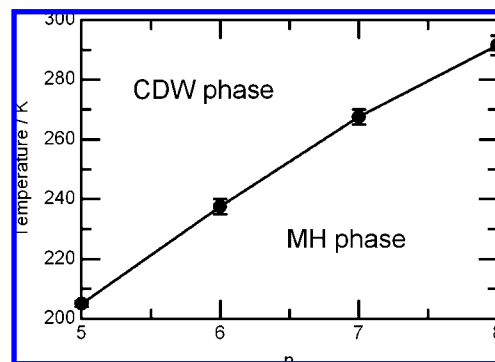


Figure 9. Phase diagram for $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n-\text{Y})_2\cdot\text{H}_2\text{O}$.

We concluded that the attractive force between the alkyl chains and the thermal motion of the alkyl chains originally compete in this system. We were able to control the electronic state of the compounds via the temperature and alkyl chain lengths.

Acknowledgment. Authors wish to acknowledge Prof. Y. Nakazawa and Dr. Y. Miyazaki at Osaka University for the heat capacity measurements and Dr. F. Iwahori at Nihon University for the X-ray measurements at low temperatures. Authors also acknowledge Prof. N. Kimizuka and Dr. K. Kuroiwa at Kyushu University for the helpful discussions about syntheses of counterions. This work was partly supported by a Grant-in Aid for Creative Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology.

Supporting Information Available: X-ray crystallographic information at 162 and 259 K in CIF format, temperature dependence of the X-ray oscillation photographs, ESR spectra, optical reflectivity and the optical conductivity spectra, and heat capacity data for $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_5-\text{Y})_2\cdot\text{H}_2\text{O}$. Temperature dependence of the Raman spectra in $[\text{Pd}(\text{en})_2\text{Br}](\text{C}_n-\text{Y})_2\cdot\text{H}_2\text{O}$ ($n = 6, 7, \text{ and } 8$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA8032026