

## Halogen-bridged Pd Chain complex with Superior Electrical Conductivity

○ Mohammad Rasel Mian<sup>1</sup>, Hiroaki Iguchi<sup>1</sup>, Shinya Takaishi<sup>1</sup>, Hiroshi Okamoto<sup>2</sup>, Hisaaki Tanaka<sup>3</sup>, Shin-ichi Kuroda<sup>3</sup>, Masahiro Yamashita<sup>1</sup>

<sup>1</sup> Department of Chemistry, Tohoku University, Japan

<sup>2</sup> Department of Advanced Materials Science, The University of Tokyo, Japan

<sup>3</sup> Department of Applied Physics, Nagoya University, Japan

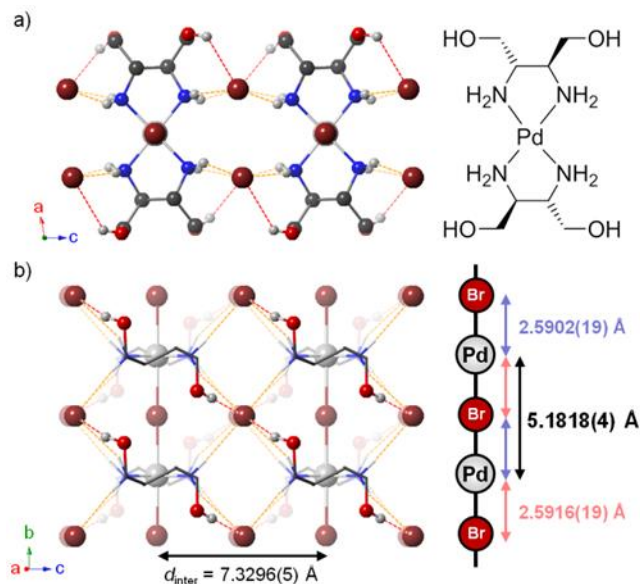
**[Abstract]** Br-bridged Pd chain complex with the Pd ion in an uncommon +3 oxidation state, [Pd(dabdOH)<sub>2</sub>Br]Br<sub>2</sub> (**1**)<sup>1</sup> and [Pd(dabdOH)<sub>2</sub>Br](SO<sub>4</sub>)<sub>2</sub>•3H<sub>2</sub>O (**1**), were prepared using a new method involving multiple hydrogen bonds. The chain complex **1** exhibited superior electrical conductivity and thermal stability. An in-plane ligand with an additional hydrogen donor group (hydroxy group), (2S,3S)-2,3-diaminobutane-1,4-diol (dabdOH), was used to create a multiple-hydrogen-bond network, which effectively shrinks the Pd–Br–Pd distance, stabilizing the Pd(III) state up to its decomposition temperature (443 K for **1** and 425 K for **2** respectively). **1** shows semi-conducting behavior with quite high electrical conductivity (3–38 S cm<sup>-1</sup> for **1** and 0.01 S cm<sup>-1</sup> for **2** at room temperature), which is 10<sup>6</sup> times larger than the previous record for analogous PdBr chains. Indeed, **1** is the most conductive MX-type chain complex reported so far.

**[Introduction]** The chemistry of Pd(III) Compounds has much attracted researchers' attention in both applied and basic sciences due to their intrinsic physical properties which depend strongly on the oxidation state of metal. For example, gigantic third-order nonlinearities<sup>2</sup> and ultrafast optical switching<sup>3</sup> has been discovered in Ni(III) chain complexes. So far, all Ni complexes are in Ni(III) averaged valence (AV) states, whereas Pd and Pt complexes are generally in M<sup>2+</sup>/M<sup>4+</sup> mixed valence (MV) state. However, Ni ions are very labile, which is very difficult to introduce into various supramolecular architectures, such as nanowire,<sup>4</sup> nanotube.<sup>5</sup> On the other hand, Pd ions are substitutionally inert, Pd-based MX chains AV states are promising for new strongly-correlated electron systems with small band gaps. Recently, we have successfully synthesized bromine-bridged Pd(III) chain complexes by using chemical pressure.<sup>6</sup> However, their low crystallinity and fragility prevents detailed study of their electronic states and to realize intrinsic unique properties. Therefore, a new synthetic strategy is necessary.

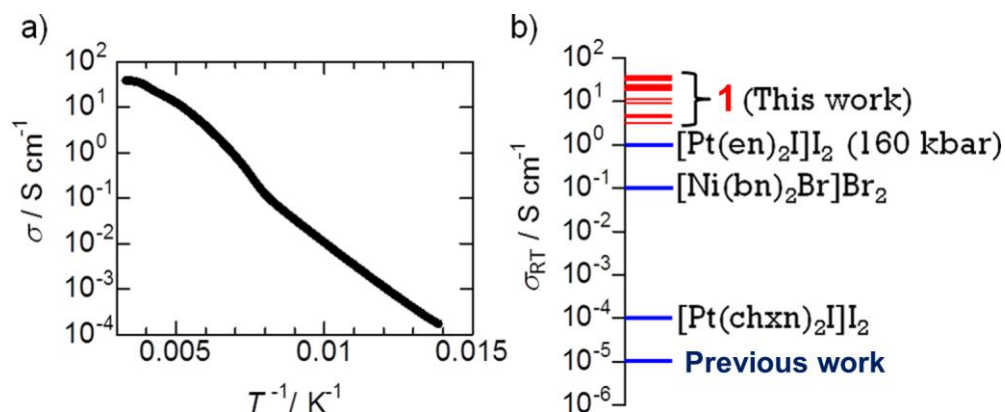
**[Methods]** The ligand (dabdOH) is synthesized from L-(+)-tartaric acid and reacts with PdBr<sub>2</sub> in water at 55 °C to give [Pd(dabdOH)<sub>2</sub>]Br<sub>2</sub>. The desired Pd(III) complex, **1**, is synthesized by slowly diffusing Br<sub>2</sub> vapor in the [Pd(dabdOH)<sub>2</sub>]Br<sub>2</sub> solution. On the other hand, Na<sub>2</sub>SO<sub>4</sub> is used in [Pd(dabdOH)<sub>2</sub>]Br<sub>2</sub> solution for the synthesis of complex **2**.

**[Results and Discussion]** The crystal structure of **1** at 93 K is shown in figure 1. The hydrogen bond between the amino groups and Br<sup>-</sup> counteranions (hereafter abbreviated as Br<sub>(Y)</sub>) supports the 1D chain structure along the *b* axis and connects neighboring chains along the *c* axis. The shortest distance between the oxygen atoms of the ligand and Br(Y), i.e., d(O⋯Br(Y)), was 3.163 Å, indicating that additional hydrogen bonds are formed. d(Pd–Br–Pd) was determined to be 5.1818(4) Å, which is the shortest d(Pd–Br–Pd) reported so far. The distances between bridging Br<sup>-</sup> and the Pd ion (d(Pd–Br)) were 2.5902(19) Å and 2.5916(19) Å. They suggest that the Pd ion is in a Pd(III) AV state because the bridging Br<sup>-</sup> is nearly equidistant from the two Pd ions. Thus, an uncommon and rare oxidation state +3 has

been isolated in **1** and **2** up to their decomposition temperature (443 K for **1** and 425 K for **2** respectively). Our method is significant for three reasons. First, shortest Pd–Br–Pd distance of all reported Pd–X chains, and thus, the Pd(III) state is stabilized up to the decomposition temperature (for example **1** and **2**). Second, the PdBr chain exhibited superior electrical conductivity ( $3\text{--}38\text{ S cm}^{-1}$  for **1** and  $0.01\text{ S cm}^{-1}$  for **2** at room temperature), making **1** (6-order higher than previous record)<sup>1</sup> comparable to the most conducting 1D coordination polymers reported to date. Third, high crystallinity and robustness are suitable for optical and physical property measurements.



**Fig. 1.** Crystal structure of **1** with (a) the chemical structure of the  $[\text{Pd}(\text{dabdOH})_2]$  unit and (b) schematic representation of the chain structure and selected distances.  $\text{NH}\cdots\text{Br}_{(\text{Y})}$  and  $\text{OH}\cdots\text{Br}_{(\text{Y})}$  hydrogen bonds are represented as orange and red dotted lines, respectively. H atoms connected to the C atoms are omitted for clarity. Light gray, Pd; brown, Br; red, O; blue, N; black, C; and gray, H.



**Fig. 2.** a) Temperature dependence of the electrical conductivity ( $\sigma$ ) of **1** along the chain axis. b)  $\sigma$  at room temperature ( $\sigma_{\text{RT}}$ ) of previous work and several similar MX chains (data taken from ref. no 1). Data for 12 crystals of **1** (red) are shown to express the reproducibility.

## [References]

- [1] M. R. Mian *et al.* *J. Am. Chem. Soc.* **139**, 6562 (2017).
- [2] Kishida *et al.* *Nature* **405**, 929 (2000).
- [3] Tao *et al.* *Adv Mater.* **19**, 2707 (2007).
- [4] D. Kawakami *et al.* *Angew. Chem. Int. Ed.* **45**, 7214 (2006).
- [5] K. Otsuba *et al.* *nature Mater.* **10**, 2915(2011).
- [6] S. Takaishi *et al.* *J. Am. Chem. Soc.* **130**, 12080 (2008).