Mixed Charge-Ordering State of MMX-Type Quasi-One-Dimensional Iodide-Bridged Platinum Complexes with Binary Countercations

Hiroaki Iguchi,[†] Shinya Takaishi,[†] Takashi Kajiwara,[†] Hitoshi Miyasaka,[†] Masahiro Yamashita,[*,†]
Hiroyuki Matsuzaki,[‡] and Hiroshi Okamoto[‡]

*Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aza-aoba, Aramaki,
Sendai 980-8578, Japan, and Department of Advanced Materials Science, Graduate School of Frontier Sciences,
The University of Tokyo and CREST (JST), Kashiwa 277-8561, Japan*

Received October 7, 2008; E-mail: yamasita@agnus.chem.tohoku.ac.jp

The electronic states of quasi-one-dimensional (Q1D) materials have played an important role in bringing about new physical properties for the materials.[1−4] In particular, many interesting physical properties[5−7] in Q1D halogen-bridged metal complexes (hereafter abbreviated as MX-chains) are due to their unique charge-ordering (CO) states.[8] The CO states of Q1D materials can be switched by external stimuli.[5,9] The multistability of the CO states originates from the competition or cooperation among several factors, such as electron−phonon interactions, electron transfer, Coulombic repulsion, etc.

Recently, Q1D halogen-bridged dinuclear metal complexes (hereafter abbreviated as MMX-chains) have been extensively studied as an extension to the MX-chain systems.[10] On the basis of theoretical calculations and experimental data, the electronic states of the MMX-chains can be classified into the following four CO states and are also known to be strongly correlated to the position of the bridging halide ion.

(a) average-valence (AV) state
$$-M^{2.5+}-M^{2.5+}-X-M^{2.5+}-M^{2.5+}-X-$$

(b) charge-density-wave (CDW) state
$$\cdots M^{2+}-M^{2+}\cdots\cdots X-M^{3+}-M^{3+}-X\cdots$$

(c) charge-polarization (CP) state
$$\cdots M^{2+}-M^{3+}-X\cdots\cdots M^{2+}-M^{3+}-X\cdots$$

(d) alternating charge-polarization (ACP) state
$$\cdots M^{2+}-M^{3+}-X-M^{3+}-M^{2+}\cdots\cdots X\cdots$$

The larger number of degrees of freedom of the electrons in the MMX-chains than those in the MX-chains cause a larger variety of CO states and smaller energy gaps among them.[11] Each CO state exhibits various physical properties. Therefore, MMX-chains have the potential to be used as multifunctional switching materials.

Since all of the MMX-chains thus far synthesized are in one of these four CO states without exception, new CO states in MMX-chains are very important not only for producing switching materials but also for bringing about new physical and chemical properties of low-dimensional materials. In this communication, we report a new CO state in MMX-chains with binary countercations, $K_2(H_3NCH_2CHMe-CH_2NH_3)[Pt_2(pop)_4I]\cdot 4H_2O$ (pop = $P_2H_2O_5{}^{2-}$) (**1**).

MMX-chains synthesized to date are categorized into two ligand systems: dithioacetate (dta), $[M_2(RCS_2)_4I]$ (M = Ni, Pt; R = alkyl chain group)[12] and diphosphite (pop), $A_4[Pt_2(pop)_4X]\cdot nH_2O$ or $A'_2[Pt_2(pop)_4X]\cdot nH_2O$ (A = alkali metal, alkyl ammonium, etc.; A' = alkyldiammonium; X = Cl, Br, and I).[13] In order to develop new CO states, we studied the pop system because its chain structure can be controlled more easily than that of the dta system by introducing various countercations. We synthesized **1** with two different kinds of countercations (binary system). It should be noted
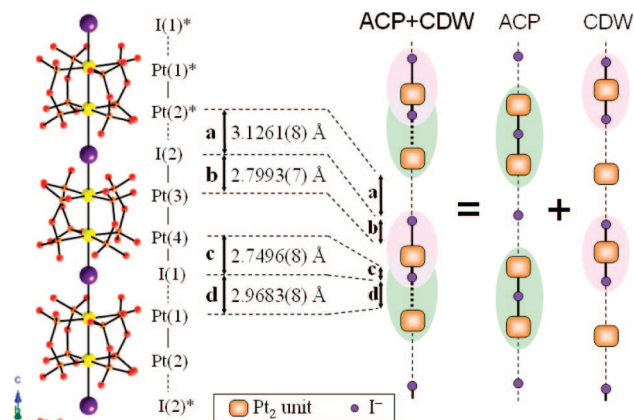

Figure 1. Crystal structure of **1** (red, O; orange, P; purple, I; yellow, Pt) and schematic chain structure in ACP+CDW (**1**), ACP and CDW states. The countercations, lattice water, and hydrogen atoms are omitted for clarity.

that all of the known MMX-chains with the pop ligand include only one type of countercation (unitary system).

The crystal structure of **1** at 100 K is shown in Figure 1. Two neighboring Pt_2 units are bridged by an I^- ion, forming a $\cdots Pt-Pt-I-Pt-Pt-I\cdots$ linear-chain structure along the c-axis. Interestingly, there are two different Pt−I−Pt distances (c + d: 5.7179(11) Å; a + b: 5.9254(11) Å), which induce a 2-fold periodicity along the chain. This structural feature is characteristic of the ACP state, which has not been observed in the pop system to the best of our knowledge. However, the displacement of the bridging I^- ions from the midpoint between neighboring Pt_2 units indicates that the CO state is not a simple ACP state. Focusing on the Pt−I bond lengths, one Pt_2 unit is coordinated by neighboring I^- ions with short Pt−I bond lengths (c: 2.7496(8) Å; b: 2.7993(7) Å), whereas the other is coordinated by I^- ions with a long Pt····I bond length (d: 2.9683(8) Å; a: 3.1261(8) Å). This structural feature is characteristic of the CDW state, except that there is only one Pt−I−Pt distance in compounds in a simple CDW state. Therefore, the CO state of **1** was concluded to be a mixture of the ACP and CDW states (ACP+CDW state), which has never been synthesized or predicted theoretically to our knowledge. Schematic representations of the structure in each CO state are shown in Figure 1. The positions of the bridging I^- ions are three-dimensionally (3D) ordered. The 2-fold periodicity along the c-axis with a 3D ordered structure in **1** was verified by the strong superlattice reflections observed in an X-ray oscillation photograph. The 3D ordered structure is very rare, and the first example has been reported only recently.[14] The mechanisms which realize the 3D ordered ACP+CDW state are uncertain. However, the polar orientation of $H_3NCH_2CHMeCH_2NH_3{}^{2+}$ ions (Figure S2, Supporting Information) may play a role in this mechanism.
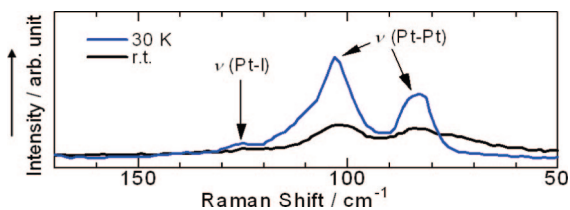
[†] Tohoku University.
[‡] The University of Tokyo.

Figure 2. Polarized Raman spectra for the polarization of $z(x,x)z$ ($x \parallel c$ axis) at 30 K and room temperature (r.t.). Two strong signals attributed to the stretching mode ν (Pt−Pt) and weak band at around 124 cm^{-1} attributed to the stretching mode ν (Pt−I) are observed.
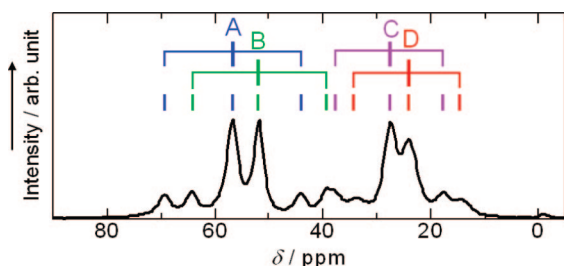

Figure 3. ^{31}P MAS NMR spectrum of **1** in the solid state. Satellite lines on the both sides of the peak are due to the coupling between ^{31}P and ^{125}Pt. Four groups of peaks (A to D) are assigned to four kinds of P atom.

Raman spectroscopy is the powerful tool for investigating the electronic states of MX-chains, MMX-chains, and other mixed valence compounds.[13b,c,15] Polarized Raman spectra of **1** at 30 K and room temperature (Figure 2) were measured to confirm the CO state in **1**. On the basis of previous reports,[16] the two strong signals at 84 and 103 cm^{-1} were assigned to be the stretching mode ν (Pt−Pt) of the Pt$_2$ unit, indicating that there are two different Pt$_2$ units. A relatively weak band was also observed at ∼124 cm^{-1}, although it was not observed at room temperature because of low resolution. This band was assigned to the Pt−I stretching mode, which is activated by the displacement of I$^-$ ions from the midpoint between the neighboring Pt$_2$ units. These findings are consistent with the crystal structure of **1** discussed above. Therefore, **1** was thought to be in an ACP+CDW state. Because the Raman peak did not shift, the ACP+CDW state is stable from room temperature to at least ∼30 K.

^{31}P MAS NMR spectroscopy was performed in order to clarify the CO state of **1**. According to previous work reported by Kimura et al.,[17] the ^{31}P chemical shift (δ) depends on the crystal field around the P atom and the paramagnetic shift, δ_P, which is larger for P atoms coordinated to Pt ions in a low oxidation state. Therefore, ^{31}P MAS NMR spectroscopy can provide information about not only the environment of the P atoms but also the charges of the Pt ions. In addition, the coupling constant (J) between ^{31}P and ^{195}Pt ($I = {}^1/_2$, natural abundance = 33.8%) also yields information about the oxidation state of the Pt ions.[18] The value of J for a four-coordinated Pt^{2+} complex is larger than that of the six-coordinated Pt^{3+} complex. Figure 3 shows a ^{31}P MAS NMR spectrum of **1** at room temperature. Four intense peaks were observed and attributed to four inequivalent P atoms (A−D), which is consistent with the crystal structure. The other small peaks were assigned to be satellites due to the coupling between ^{31}P and ^{195}Pt. Chemical shifts (δ) and coupling constants (J) for K$_4$[Pt$_2$(pop)$_4$]·2H$_2$O, K$_4$[Pt$_2$(pop)$_4$I$_2$], and **1** are listed in Table 1. K$_4$[Pt$_2$(pop)$_4$]·2H$_2$O and K$_4$[Pt$_2$(pop)$_4$I$_2$] were regarded as Pt^{2+} and Pt^{3+} complexes, respectively. According to the δ and J values,

Table 1. ^{31}P Chemical Shifts (δ) and Coupling Constants (J) of Pt^{2+}, Pt^{3+} Complexes and Compound **1**

	δ/ppm		J (Pt−P)/kHz	
K$_4$[Pt$_2$(pop)$_4$]·2H$_2$O^a	65 ± 2.0		3.4 ± 0.1	
K$_4$[Pt$_2$(pop)$_4$I$_2$]^b		22.01		2.20
compound **1**^{c}	51.83 (B)	24.11 (D)	3.05 (B)	2.34 (D)
	56.85 (A)	27.52 (C)	3.05 (A)	2.45 (C)

^{a} See ref 17. ^{b} See Figure S3, Supporting Information. ^{c} A to D present each P atom in Figure 3.

which are related to the charges of the Pt ions as mentioned above, the oxidation state of the Pt ion coordinated by P atoms A and B is lower than that of the Pt ion coordinated by P atoms C and D. The differences in the δ and J values of **1** and K$_4$[Pt$_2$(pop)$_4$]·2H$_2$O or K$_4$[Pt$_2$(pop)$_4$I$_2$] indicate that **1** is a Robin−Day class II mixed-valence compound.[8a] The slight difference between the δ values (3−5 ppm) of the P atoms is due to the difference between the charges of Pt ions and the differences in the crystal fields around the P atoms. Therefore, the ^{31}P MAS NMR spectrum supports the presence of a new ACP+CDW CO state.

Further measurements to estimate the accurate charges of each Pt atom are now in progress.

Supporting Information Available: Additional experimental details and X-ray crystallographic information of compound **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ferraris, J. P.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948–949. (b) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578–580.
(2) Sauteret, C.; Hermann, J.-P.; Frey, R.; Pradère, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R. *Phys. Rev. Lett.* **1976**, *36*, 956–959.
(3) Haldane, F. D. M. *Phys. Rev. Lett.* **1983**, *50*, 1153–1156.
(4) Miller, J. S. *Extended Linear Chain Compounds*; Plenum Press: New York, 1982; Vol. 1−3.
(5) Iwai, S.; Okamoto, H. *J. Phys. Soc. Jpn.* **2006**, *75*, 011007.
(6) Kishida, H.; Matsuzaki, H.; Okamoto, H.; Manabe, T.; Yamashita, M.; Taguchi, Y.; Tokura, Y. *Nature* **2000**, *405*, 929–932.
(7) Okamoto, H.; Yamashita, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2023–2039.
(8) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *9*, 247–422. (b) Day, P. In *Low-Dimensional Cooperative Phenomena*; Keller, H. J., Ed.; Plenum Press: New York, 1974; pp 191−214.
(9) Brossard, L.; Ribault, M.; Valade, L.; Cassoux, P. *Phys. Rev. B* **1990**, *42*, 3935–3943.
(10) Yamashita, M.; Takaishi, S.; Kobayashi, A.; Kitagawa, H.; Matsuzaki, H.; Okamoto, H. *Coord. Chem. Rev.* **2006**, *250*, 2335–2346.
(11) Kuwabara, M.; Yonemitsu, K. *J. Mater. Chem.* **2001**, *11*, 2163–2175.
(12) (a) Bellitto, C.; Flamini, A.; Gastaldi, L.; Scaramuzza, L. *Inorg. Chem.* **1983**, *22*, 444–449. (b) Kitagawa, H.; Onodera, N.; Sonoyama, T.; Yamamoto, M.; Fukawa, T.; Mitani, T.; Seto, M.; Maeda, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10068–10080.
(13) (a) Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604–4607. (b) Kurmoo, M.; Clark, R. J. H. *Inorg. Chem.* **1985**, *24*, 4420–4425. (c) Clark, R. J. H.; Kurmoo, M.; Dawes, H. M.; Hursthouse, M. B. *Inorg. Chem.* **1986**, *25*, 409–412.
(14) Matsunaga, S.; Takizawa, K.; Kawakami, D.; Iguchi, H.; Takaishi, S.; Kajiwara, T.; Miyasaka, H.; Yamashita, M.; Matsuzaki, H.; Okamoto, H. *Eur. J. Inorg. Chem.* **2008**, 3269–3273.
(15) (a) Clark, R. J. H. *Chem. Soc. Rev.* **1984**, *13*, 219–244. (b) Clark, R. J. H. *Chem. Soc. Rev.* **1990**, *19*, 107–131.
(16) Matsuzaki, H.; Matsuoka, T.; Kishida, H.; Takizawa, K.; Miyasaka, H.; Sugiura, K.-i.; Yamashita, M.; Okamoto, H. *Phys. Rev. Lett.* **2003**, *90*, 046401.
(17) Kimura, N.; Ohki, H.; Ikeda, R.; Yamashita, M. *Chem. Phys. Lett.* **1994**, *220*, 40–45.
(18) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1980**, 145–147.

JA807901P