

Charge Fluctuation in MMX Chain Compounds, $A_4[Pt_2(pop)_4I] \cdot nH_2O$

M. Yamashita,^{*,†} S. Miya,[†] T. Kawashima,[†] T. Manabe,[†]
T. Sonoyama,[‡] H. Kitagawa,[‡] T. Mitani,[‡] H. Okamoto,[§] and
R. Ikeda^{||}

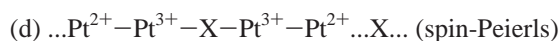
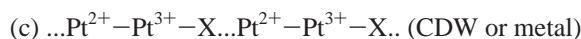
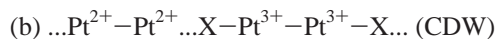
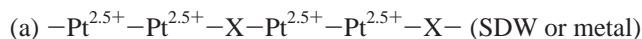
Graduate School of Human Informatics and PRESTO(JST)
Nagoya University
Chikusa-ku Nagoya 464-8601, Japan
Japan Advanced Institute of Science and Technology
Ishikawa 923-1292, Japan
Department of Applied Physics, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
Department of Chemistry, University of Tsukuba
Tsukuba 305-8571, Japan

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Recently quasi-one-dimensional halogen-bridged mixed-valence compounds (MX chains) have been attracting much attention because they show very interesting physical properties such as intense and dichroic intervalence charge-transfer bands, progressive resonance Raman spectra, luminescence spectra with large Stokes-shifts, large third-order nonlinear optical properties, midgap absorptions attributable to solitons and polarons, one-dimensional model compounds of high T_c copperoxide superconductors etc.¹ Theoretically these MX chains are considered as Peierls–Hubbard systems, where the electron–phonon interaction (S), the electron transfer (T), the intra- and intersites Coulomb repulsion energies (U and V, respectively) compete or cooperate with each other.² The Pt and Pd compounds have charge density wave states (CDW) due to the strong electron–phonon interaction, where the bridging halogens are distorted from the midpoints between the neighboring two metal ions. In these compounds, the CDW strengths are tuned by substituting the metal ions, bridging halogens, in-plane ligands, and counteranions. Moreover, the dimensionalities of the CDW can be controlled by using the intra- and interchain hydrogen-bond networks. On the other hand, the Ni compounds have spin density wave states (SDW) due to the strong electron–correlation, where the bridging halogens are located at the midpoints between neighboring two Ni atoms.³ The very strong antiferromagnetic interactions among the spin located on the $Ni^{3+}d_x^2$ orbitals through the bridging halogen ions are observed in these compounds.

As a development of the MX chains, the MMX chains which have binuclear metal units in quasi-one-dimensional structures were reported.⁴ There are four possibilities of the oxidation states depending on the positions of the bridging halogens. In these

compounds, the phase transitions or charge fluctuations among these oxidation states are expected due to the smaller gaps.⁵



So far, two types of MMX chains have been reported, that is, $[M_2(dta)_4I]$ ($M = Pt$ and Ni ; $dta = CH_3CS_2^-$) and $A_4[Pt_2(pop)_4X] \cdot nH_2O$ ($A = K$ and NH_4 ; $X = Cl$, Br , I ; $pop = P_2O_5H_2^{2-}$; $n = 0, 2$, and 3). In the $A_4[Pt_2(pop)_4X] \cdot nH_2O$, the Cl - and Br -bridged complexes have been extensively investigated by X-ray single crystal structure determinations, resonance Raman spectra, optical spectra, solid-state ^{31}P NMR, etc., and are found to have structures (b). On the other hand, the I -bridged compounds have not been investigated as much because their single crystals could not be obtained. The electron–phonon interaction in I -bridged complexes are expected to be weaker, compared with those in the Cl - and Br -bridged compounds. Therefore, the I -bridged compounds are more delocalized, and then it may enable them to take various oxidation states or phase transitions. In this paper, we will report the Raman spectra and X-ray photoelectron spectroscopy of $A_4[Pt_2(pop)_4I] \cdot nH_2O$ ($A = Li, NH_4$, and Cs ; $n = 0, 2$ and 3).

The starting compounds, $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2(pop)_4I_2]$ were synthesized according to the literatures.^{4a,6} $A_4[Pt_2(pop)_4I] \cdot nH_2O$ ($A = Li, n = 3$; $A = NH_4, n = 2$; $A = Cs, n = 0$) were synthesized by adding the excess amounts of ANO_3 into the aqueous solutions of the equimolar amounts of $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2(pop)_4I_2]$. Recrystallizations were carried out from the aqueous solutions by adding ANO_3 . The numbers of the water molecules were determined by TGA-50 (Shimadzu Science Co.). Elemental analyses of Li^+ , K^+ , and Cs^+ were performed by ICP method. Elemental analyses of N and H were also performed by the usual method in the Institute for Molecular Science. Raman spectra were measured with Ar^+ excitation using a JASCO NR-1800 laser Raman spectrometer. The measurements of the XP spectra were performed using an ESCALAB MKII (VG Scientific Co.) photoelectron spectrometer with $Mg K\alpha$ ($h\nu = 1253.6$ eV) as an exciting light source.

Raman spectra of these compounds were measured at various temperatures. Their spectra are shown in Figure 1 and 2, respectively. The Li compound shows the singlet signal around 90 cm^{-1} . On the other hand, the Cs compounds show the doublet signals around 100 cm^{-1} , although their intensities are different from each other. The Raman spectra of the NH_4 compounds depend on the temperature as shown in Figure 2, that is, the singlet signal at room temperature and the doublet signal at low temperature. Their transition is repeatedly observed. From these results, the Li compound has a structure (a) $-Pt^{2.5+}-Pt^{2.5+}-I-Pt^{2.5+}-Pt^{2.5+}-I-$, and the Cs compound has a structure (b) $\dots Pt^{2+}-Pt^{2+} \dots I-Pt^{3+}-Pt^{3+}-I \dots$. The NH_4 compound has a struc-

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[†] Nagoya University.

[‡] Japan Advanced Institute of Science and Technology.

[§] The University of Tokyo.

^{||} University of Tsukuba.

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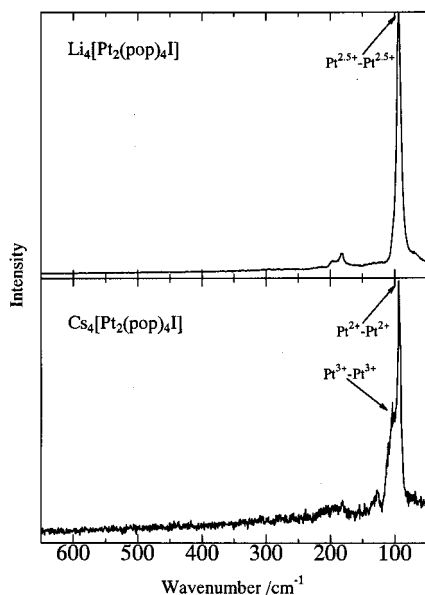


Figure 1. Raman spectra of $A = \text{Li}$ and Cs in $A_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot n\text{H}_2\text{O}$.

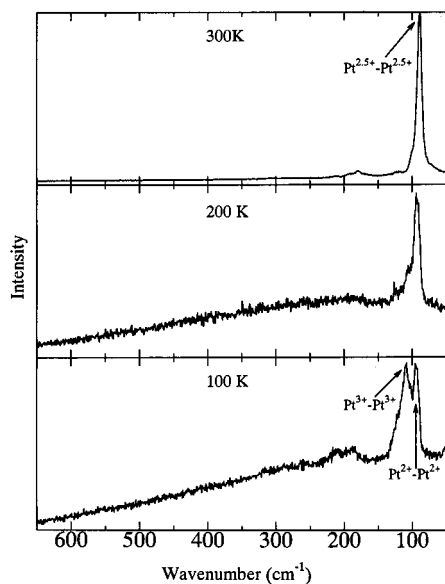


Figure 2. Temperature dependence of Raman spectra of $(\text{NH}_4)_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot 2\text{H}_2\text{O}$.

ture (a) $-\text{Pt}^{2.5+}-\text{Pt}^{2.5+}-\text{I}-\text{Pt}^{2.5+}-\text{Pt}^{2.5+}-\text{I}-$ at room temperature and a structure (b) $\dots\text{Pt}^{2+}-\text{Pt}^{2+}\dots\text{I}-\text{Pt}^{3+}-\text{Pt}^{3+}-\text{I}\dots$ at low temperature. That is, the charge fluctuation between (a) and (b) occurred in the NH_4 compound (Figure 2).

To directly investigate their oxidation states, the XP spectra were measured for $A = \text{Li}$ and Cs at 77 K, and for NH_4 at room temperature and 77 K (Figures 3 and 4). The XP spectrum of $A = \text{Li}$ is composed of $4f_{7/2}$ and $4f_{5/2}$ of $\text{Pt}^{2.5+}$, while the XP spectrum of $A = \text{Cs}$ is broad then could be resolved into four components, that is, $4f_{7/2}$ and $4f_{5/2}$ of Pt^{2+} and Pt^{3+} . The XP spectra of NH_4 composed of $4f_{7/2}$ and $4f_{5/2}$ of $\text{Pt}^{2.5+}$ at room temperature, and could be resolved into $4f_{7/2}$ and $4f_{5/2}$ of Pt^{2+} and Pt^{3+} at 77 K. Their binding energies are listed in Table 1. Their values are reasonably corresponding to their oxidation states. These results are consistent with those of Raman spectra.

The Li compound has a structure (a) and the Cs compound has a structure (b). The NH_4 compound shows the charge fluctuation between (a) and (b). Therefore, such interesting phenomena may depend on the ionic radius of Li , NH_4 , and Cs or the numbers of the water molecules. More detail investigations are now in progress.

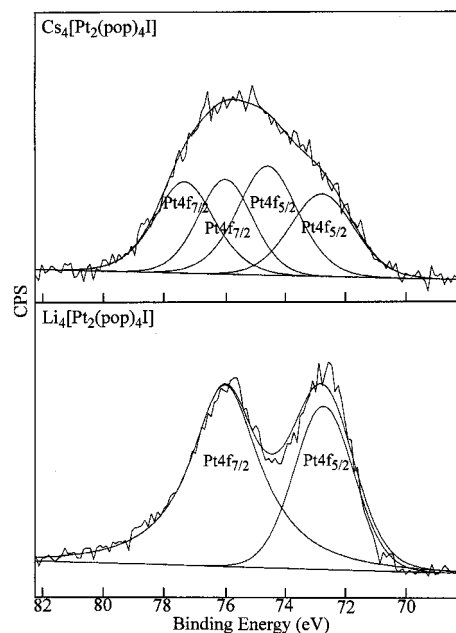


Figure 3. XP spectra of Pt atoms of $A = \text{Li}$ and Cs in $A_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot n\text{H}_2\text{O}$.

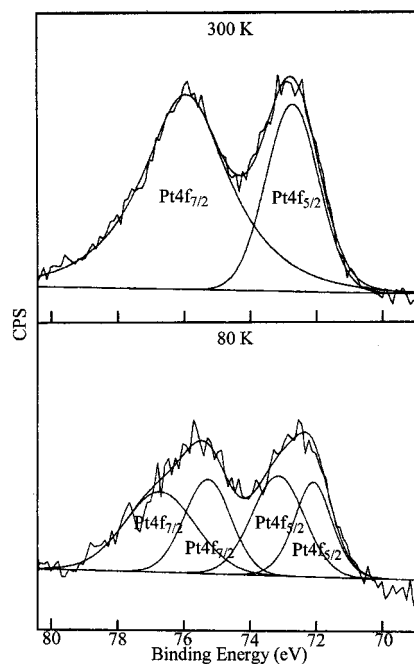


Figure 4. XP spectra of Pt atoms of $(\text{NH}_4)_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot 2\text{H}_2\text{O}$ at room temperature (top) and 77 K (bottom).

Table 1. Binding Energies of Pt Atoms in $R_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot n\text{H}_2\text{O}$ (eV)

	Pt^{2+}		$\text{Pt}^{2.5+}$		Pt^{3+}	
	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$
$\text{Li}_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot 3\text{H}_2\text{O}$			72.70	75.95		
$(\text{NH}_4)_4[\text{Pt}_2(\text{pop})_4\text{I}] \cdot 2\text{H}_2\text{O}$						
rt			72.73	75.96		
77 K	72.17	75.40			73.22	76.82
$\text{Cs}_4[\text{Pt}_2(\text{pop})_4\text{I}]$	72.26	75.33			73.48	76.70

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