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Introduction

The electronic states in the one-dimensional (1D) electron system play a key role in bringing about a variety of attractive physical properties such as high conductivity,^{1,2} large optical nonlinearity,^{3,4} Luttinger liquid behavior,⁵ ultra-fast optical responses,⁶ *etc.* Quasi-1D halogen-bridged metal complexes, which also show attractive physical properties originating from the 1D electron system,^{4,6–8} have a robust chain structure derived from the coordination bonds between the metal ions (M) and the bridging halide ions (X). Some of them show the reversible adsorption and desorption of molecules with reten-

Predominance of covalency in water-vaporresponsive MMX-type chain complexes revealed by ¹²⁹I Mössbauer spectroscopy†

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¹²⁹I Mössbauer spectroscopy was applied to water-vapor-responsive MMX-type quasi-one-dimensional iodide-bridged Pt complexes (MMX chains) in order to investigate their electronic state quantitatively. Two sets of octuplets observed in K₂(H₃NC₃H₆NH₃)[Pt₂(pop)₄]·4H₂O (**2·4H₂O**) and one octuplet observed in K₂(*cis*-H₃NCH₂CH=CHCH₂NH₃)[Pt₂(pop)₄]·4H₂O (**1·4H₂O**) and dehydrated complexes (**1** and **2**) indicate a unique alternating charge-polarization + charge-density-wave (ACP + CDW) electronic state and a charge-density-wave (CDW) electronic state, respectively. These spectra correspond to their crystal structure and the change of electronic states upon dehydration. Since these complexes consist of an alternating array of positively charged and negatively charged layers, the charge on the iodide ion (ρ_{1S}) was discussed on the basis of the isomer shift (IS). The ρ_{1S} of the water-vapor-responsive MMX chains was mainly –0.13 to –0.21, which are the smallest of all MMX chains reported so far. Hence, it indicates that the negative charge on the iodide ion is strongly donated to the Pt ion in these complexes. This covalent interaction predominates in the ACP + CDW state as well as in the CDW state. Therefore, the ACP + CDW state is in fact the CDW state with the ACP-type lattice distortion. Because the ρ_{1S} became smaller with the decreasing Pt–I–Pt distance, it can be concluded that the covalent interaction plays an important role in determining the electronic states of the MMX chains with pop (= P₂H₂O₅²⁻) ligands.

tion of crystallinity^{9–11} and with the change of the electronic states,¹¹ indicating that they are promising multifunctional vapor-induced switching materials.

Quasi-1D halogen-bridged metal complexes consisting of paddle-wheel-type dinuclear complexes, the so-called MMX chains, have higher degrees of freedom of the electrons than those consisting of mononuclear complexes (MX chains), inducing a larger variety of electronic states in MMX chains. On the basis of theoretical calculations¹² and experimental data, the electronic states of the MMX chains have been classified into the following four states:

(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+} $\cdots X$ \cdots



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[†]Electronic supplementary information (ESI) available: Analysis of ¹²⁹I Mössbauer spectra and other detailed discussions including Fig. S1. See DOI: 10.1039/c4dt00627e

These electronic states are strongly correlated with the position of the bridging halide ion, which is at the midpoint between two metal ions in the AV state and is close to the higher-oxidized metal ion in other states. Strictly, formal oxidation numbers, 3+ and 2+, should be represented as $(3 - \delta)$ + and $(2 + \delta)$ +, respectively. The AV state is a Robin–Day class III system, whereas the other three are class II systems.¹³

MMX chains synthesized to date are classified into two categories on the basis of their ligands. A high conductivity,¹⁴ metal-insulator transition,¹⁴ and the formation of nanowires on a substrate¹⁵ have been reported in a dithioacetate (dta) system, $[M_2(RCS_2)_4I]$ (M = Ni, and Pt; R = alkyl chain group). However, the adjustable components are limited to the metal ions (Ni and Pt) and the alkyl chain groups in the dta system. On the other hand, in a diphosphite (pop) system, $Y_4[Pt_2(pop)_4X] \cdot nH_2O$ and $Y'_2[Pt_2(pop)_4X] \cdot nH_2O$ (Y = alkali metal, alkyl ammonium, etc.; $Y' = alkyldiammonium; X = Cl^{-}$, Br⁻, and I⁻; pop = $P_2H_2O_5^{2-}$),^{11,16} the negatively charged chains require countercations, of which there are a huge number of possible candidates. Furthermore, removing lattice water molecules can change the electronic states of the MMX chains.¹¹ Therefore, the pop system is a more promising target to realize the new electronic states and to study the change of electronic states upon chemical external stimuli such as adsorption-desorption of molecules.

Recently, we rationally designed more robust MMX chains with binary countercations, $A_2B[Pt_2(pop)_4I]\cdot nH_2O(A^+ = K^+ and Rb^+; B^{2+} = aliphatic diammonium ion; <math>n = 2$ and 4),¹⁷ which show reversible dehydration/rehydration when B^{2+} is $H_3NCH_2CHXCH_2NH_3^{2+}$ (X = H, Me, Cl) or *cis/trans*- $H_3NCH_2CH=CHCH_2NH_3^{2+}$.^{17b,c} Although the electronic state of $K_2(cis-H_3NCH_2CH=CHCH_2NH_3)[Pt_2(pop)_4I]\cdot 4H_2O(1\cdot 4H_2O)$ is the typical CDW state,^{17c} $K_2(H_3NC_3H_6NH_3)[Pt_2(pop)_4I]\cdot 4H_2O$ (2·4H₂O) forms a new ACP + CDW electronic state (…Pt^{(2+a)+}-Pt^{(2+b)+}…I-Pt^{(3-c)+}-Pt^{(3-d)+}-I…; 0 < a, b, c, d < 0.5; a, c < b, d).^{17b} Dehydration of 2·4H₂O changes the structure as shown in Fig. 1 and also changes the electronic state from the ACP + CDW state to the narrow-gapped CDW state,^{17b} which contains thermally activated Pt³⁺ spins as mobile solitons.¹⁸



5.6305(8) Å

5.9786(9) A

Estimating the charge on the metal or halide ion in MMX chains is quite important to understand the electronic states. ¹²⁹I Mössbauer spectroscopy is a powerful tool for determining the charge on the iodide ion quantitatively. So far, $[Pt_2(MeCS_2)_4I]$ and $[Pt_2(EtCS_2)_4I]$ forming the ACP state, $(H_3NC_6H_{12}NH_3)_2[Pt_2(pop)_4I]$ forming the CDW state, $(Et_2NH_2)_4[Pt_2(pop)_4I]$ forming the CDW state, $(Et_2NH_2)_4[Pt_2(pop)_4I]$ forming the CP state, and their precursor $Pt(III)_2$ complexes have been studied by ¹²⁹I Mössbauer spectroscopy. ^{14d,19} Herein, we study the characteristics of the new ACP + CDW state in **2·4H_2O** and its change upon dehydration by comparing the similar complex, **1·4H_2O**, and other MMX chains in the pop system. In addition, we discuss the origin of the charge variation in the pop system.

Experimental section

Materials

All of the commercially available chemicals were of reagent grade and used as received. The starting $Pt(II)_2$ complex, $K_4[Pt_2(pop)_4]\cdot 2H_2O$, was synthesized from K_2PtCl_4 and H_3PO_3 following the reported procedures.²⁰

Synthesis of ¹²⁹I-enriched MMX chains

The starting $Pt(III)_2$ complex, ¹²⁹I-enriched $K_4[Pt_2(pop)_4I_2]$, was synthesized at Kyoto University Reactor (KUR) using 5 mL of Na¹²⁹I aqueous solution containing 36 mg (0.28 mmol) of ¹²⁹I with 105 mg (0.74 mmol) of Na₂SO₃ and 5 mg (0.17 mmol) of formaldehyde. The impurities were removed and ¹²⁹I-enriched $K_4[Pt_2(pop)_4I_2]$ was synthesized by the following chemical reactions. The reaction temperature was roughly controlled using a hotplate.

Reaction I

$$2Na^{129}I + xNa_2SO_3 + yHCHO + xCa(NO_3)_2$$

$$\rightarrow 2Na^{129}I + xCaSO_3 + 2xNaNO_3 + vHCHO$$

Reaction II

$$2Na^{129}I + 2xNaNO_3 + yHCHO + Pb(NO_3)_2$$

$$\rightarrow Pb^{129}I_2 + (2x+2)NaNO_3 + yHCHO$$

Reaction III

$$Pb^{129}I_2 + K_2CO_3 \rightarrow 2K^{129}I + PbCO_3 \downarrow$$

Reaction IV

12.8445(12) A

2.8445(12) A

12.8445(12) A

1 2.8445(12) Å

¢

Pt Pt

þ

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$$K^{129}I + {}^{127}I_2 \to K^{129}I^{127}I_2$$

Reaction V

$$\begin{split} \mathrm{K}^{129}\mathrm{I}^{127}\mathrm{I}_2 + \mathrm{K}_4[\mathrm{Pt}_2(\mathrm{pop})_4] \cdot 2\mathrm{H}_2\mathrm{O} &\rightarrow \mathrm{K}_4[\mathrm{Pt}_2(\mathrm{pop})_4\mathrm{I}_2] \downarrow \\ &+ \mathrm{KI} + 2\mathrm{H}_2\mathrm{O} \end{split}$$

Reactions I–V. A Heated aqueous solution (5 mL) containing Na¹²⁹I (0.28 mmol) was added to 0.17 mL of 2.53 M Ca(NO₃)₂ aqueous solution (102 mg, 0.43 mmol), followed by filtration of the resulting white powder. The filtrate was heated at 30-40 °C overnight to slowly concentrate the solution by half.

2.990(3) A

2.641(3) Å

2.828(6) Å

3.151(6) Å

Pt

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After being cooled to room temperature, the colorless crystals (CaSO₃) were separated by decantation, and then the solution was added to 0.11 mL of 1.25 M Pb(NO₃)₂ aqueous solution (46 mg, 0.14 mmol). The resulting yellow powder $(Pb^{129}I_2)$ was filtered and washed three times with methanol. Pb¹²⁹I₂ was again dissolved in hot water (20 mL) and was added to 0.145 mL of 1.25 M K₂CO₃ aqueous solution (25 mg, 0.18 mmol) to form a white suspension. After the centrifugation and the filtration, the clear solution was heated at 60-70 °C to reduce the volume to about 5 mL, cooled to room temperature, and ¹²⁷I₂ (85.3 mg, 0.336 mmol) was added. To the resulting homogeneous solution, $K_4[Pt_2(pop)_4] \cdot 2H_2O$ (391 mg, 0.338 mmol) was added and heated at 30-40 °C for 2 h, followed by addition of methanol (approx. 50 mL) to precipitate ¹²⁹I-enriched $K_4[Pt_2(pop)_4I_2]$. The brown solid was washed with methanol and dried by heating (331 mg, 0.24 mmol, 85%).

¹²⁹I-enriched $K_2(cis-H_3NCH_2CH=CHCH_2NH_3)[Pt_2(pop)_4I]$ -4H₂O (1·4H₂O). The synthesis of 1·4H₂O was carried out by following the reported procedure for the non-enriched complex.^{17c} 21.5 mL of the Pt₂ complexes in water (containing 165 mg (0.14 mmol) of $K_4[Pt_2(pop)_4]\cdot 2H_2O$ and 168 mg (0.12 mmol) of $K_4[Pt_2(pop)_4I_2]$) and 21 mL of the aqueous salt solution (containing 42 mg (0.20 mmol) of *cis*-H₃NCH₂CH=CHCH₂NH₃(NO₃)₂ and 808 mg (8.00 mmol) of KNO₃) were mixed and allowed to stand for 2 days. 1·4H₂O was obtained as glossy brown cubic crystals (217 mg, 68%).

¹²⁹I-enriched K₂(H₃NC₃H₆NH₃)[Pt₂(pop)₄I]·4H₂O (2·4H₂O). The synthesis of 2·4H₂O was carried out by following the reported procedure for the non-enriched complex.^{17b} 10.8 mL of the Pt₂ complexes in water (containing 81 mg (0.070 mmol) of K₄[Pt₂(pop)₄]·2H₂O and 80 mg (0.058 mmol) of K₄[Pt₂(pop)₄I₂]), 0.72 mL of 250 mM H₃NC₃H₆NH₃SO₄ aqueous solution (31 mg, 0.18 mmol), and 4.00 mL of 900 mM KNO₃ aqueous solution (364 mg, 3.6 mmol) were mixed and allowed to stand for 2 days. 2·4H₂O was obtained as glossy brown cubic crystals (144 mg, 85%).

Dehydration method

For dehydration, $1.4H_2O$ was heated at 75 °C under vacuum $(8 \times 10^{-2} \text{ Pa})$ for 17 h, and $2.4H_2O$ was heated at 70 °C under vacuum $(8 \times 10^{-2} \text{ Pa})$ for 19 h. This condition is stronger than the previous one, which can complete dehydration.^{17*b*,*c*} Each dehydrated sample 1 and 2 was put into the plastic bag and sealed with a sealer in order to avoid exposure to air. The sealing was carried out in a glove bag filled with dry nitrogen gas.

¹²⁹I Mössbauer spectroscopy

The 27.7 keV γ -ray generated from ¹²⁹Te was used for obtaining the ¹²⁹I Mössbauer spectrum. In this study, a ¹²⁹Te source was obtained by neutron irradiation of enriched ⁶⁶Zn¹²⁸Te in the nuclear reaction ¹²⁸Te $(n,\gamma)^{129}$ Te at KUR. Since the half-life of ¹²⁹Te is 69.6 minutes, the measurement of ¹²⁹I Mössbauer spectra (typically continued for four hours) was accumulated four to six times with the repeatedly irradiated ¹²⁹Te source in order to obtain distinct spectra using a constant-acceleration spectrometer with a NaI(Tl) scintillation counter. The source and the absorber were cooled with a home-made closed-cycle refrigerator system using helium gas as the working medium.

Analysis of ¹²⁹I Mössbauer spectra

The spectra were analyzed by the least-squares fitting with Lorentzian lines using the MossWinn software.²¹ The detailed explanation of ¹²⁹I Mössbauer spectra is given in some references.^{19,22} In Mössbauer spectroscopy, the energy of the γ -ray is controlled by changing the relative velocity of the source. The difference between the nuclear transition energy of the source and that of the absorber is called the isomer shift (IS) and is customarily denoted by the relative velocity to the ZnTe source. The quadrupole coupling constant (QCC), which is a direct measure of the electric field gradient (EFG) at the iodine nucleus, is the other important parameter available from the Mössbauer spectra. The charge on the ¹²⁹I can be calculated from IS ($\rho_{\rm IS}$) or QCC ($\rho_{\rm QCC}$) as described in the ESI.[†]

Results and discussion

¹²⁹I Mössbauer spectra of 1·4H₂O, 2·4H₂O and their dehydrated states

¹²⁹I Mössbauer spectra of $1.4H_2O$ and 1 at 14 K are shown in Fig. 2. The best fit for each spectrum was obtained with one octuplet. Therefore, there is only one chemically independent iodide site in both $1.4H_2O$ and 1, consistent with their CDW electronic state. As shown in Table 1, the Mössbauer parameters of $1.4H_2O$ and 1 were nearly identical, indicating that the electronic state was not changed by the dehydration. The ¹²⁹I Mössbauer spectra of $2.4H_2O$ and 2 at 14 K are shown in Fig. 3. Apparently, the spectrum of $2.4H_2O$ consists of two sets of octuplets while that of 2 consists of one octuplet. These spectra correspond to the crystal structure.^{17b} Since $2.4H_2O$ is in the ACP + CDW state, two chemically independent iodide ions exist due to the ACP-like distortion. This distortion dis-



Fig. 2 ^{129}I Mössbauer spectra of $1{\cdot}4H_2O$ and 1 measured at 14 K. The solid lines were fitted with the data.

Table 1	Mössbauer para	meters and Pt-I-P	t distance (d(Pt-I-	–Pt)) for MMX	chains and their	precursors
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	Electronic state	T/\mathbf{K}	$IS^a/mm s^{-1}$	QCC ^b /MHz	$\rho_{\rm IS}{}^c$	$\rho_{\rm QCC}{}^d$	Ref.	d(Pt–I–Pt)/ Å
pop system								
1.4H ₂ O	CDW	14	0.751(15)	-1506(45)	-0.14(2)	-0.34(2)	This work	$5.7623(18)^{e}$
1	CDW	14	0.759(15)	-1512(45)	-0.13(2)	-0.34(2)	This work	5.679 ^f
$2 \cdot 4H_2O \cdot I_a$	ACP + CDW	14	0.639(13)	-1625(49)	-0.21(2)	-0.29(2)	This work	$5.6305(8)^{g}$
$2 \cdot 4H_2 O \cdot I_b$			0.359(7)	-1327(40)	-0.40(2)	-0.42(2)		5.9786(9) ^g
2	CDW	14	0.757(15)	-1471(44)	-0.14(2)	-0.36(2)	This work	$5.689(2)^{g}$
(H ₃ NC ₆ H ₁₂ NH ₃) ₂ [Pt ₂ (pop) ₄ I]	CDW	15	0.47(8)	-1680(50)	-0.33(5)	-0.27(2)	19 <i>b</i>	5.916^{h}
$(Et_2NH_2)_4[Pt_2(pop)_4I]$	CP	15	0.31(7)	-1567(47)	-0.43(4)	-0.32(2)	19 <i>b</i>	6.665^{i}
$K_4[Pt_2(pop)_4I_2]$	Discrete	16	0.15(7)	-1530(46)	-0.54(4)	-0.33(2)	19 <i>b</i>	
dta system								
[Pt ₂ (MeCS ₂) ₄ I]-I ₂	ACP	16	0.28(8)	-1180(36)	-0.45	-0.49	14d, 19a	$5.914(2)^{j}$
$[Pt_2(MeCS_2)_4I]$ -Ib			0.56(8)	-1380(40)	-0.27	-0.40	,	$5.914(2)^{j}$
Pt ₂ (EtCS ₂) ₄ I]-I _a	ACP	11	0.35(8)	-1213(36)	-0.41(5)	-0.47(2)	19 <i>b</i>	$5.860(2)^{k}$
Pt ₂ (EtCS ₂) ₄ I-I _b			0.50(8)	-1432(43)	-0.31(5)	-0.38(2)		$5.917(2)^{k}$
$[Pt_2(MeCS_2)_4I_2]$	Discrete	16	0.17(7)	-1172(35)	-0.53(4)	-0.49(2)	19 <i>b</i>	
$[Pt_2(EtCS_2)_4I_2]$	Discrete	16	0.22(7)	-1177(35)	-0.49(4)	-0.49(2)	19 <i>b</i>	

^{*a*} Referenced to ZnTe. ^{*b*} Converted to QCC value of ¹²⁷I. ^{*c*} Calculated from eqn (2) in the ESI. ^{*d*} Calculated from eqn (4) in the ESI. ^{*e*} At 100 K, see ref. 17*c*. ^{*f*} Estimated from the lattice constant obtained from the powder X-ray diffraction pattern (lattice constant along the chain axis of 1 is 0.01 Å shorter than that of 2). ^{*g*} At 100 K, see ref. 17*b*. ^{*h*} At room temperature, see ref. 23. ^{*i*} At 93 K, see ref. 23. ^{*j*} Calculated from the lattice constant along the chain axis and Pt–Pt distance at 91 K, see ref. 24. ^{*k*} At 48 K, see ref. 14*f*.



Fig. 3 129 I Mössbauer spectra of 2·4H₂O and 2 measured at 14 K. The red and blue solid lines indicate the I_a and I_b components, respectively. The black solid lines were fitted with the data.

appears by the dehydration; therefore, the change of the ^{129}I Mössbauer spectra from $2{\cdot}4H_2O$ to 2 supports the change of the electronic state from the ACP + CDW state to the CDW state.

Reliability of $\rho_{\rm QCC}$ in 1·4H₂O, 2·4H₂O and their dehydrated states

It has been reported that the arrangement of cations and anions around the iodide ions occasionally affects the QCC value and induces inaccurate ρ_{QCC} .^{19b} In **1·4H₂O**, **1**, **2·4H₂O** and **2**, the ρ_{QCC} is significantly larger than the ρ_{IS} as shown in Table **1**. This difference is attributable to the characteristic molecular packing in these complexes. The three-dimensional hydrogen-bond and coordination-bond networks in present complexes constrain each [Pt₂(pop)₄] unit to arrange in the same *ab* plane, named "synchronized" packing^{17c} (*e.g.* the structure of $1.4H_2O$ is shown in Fig. 4). Therefore, an iodide ion, two K⁺ ions and four H₂O molecules (if hydrated) per formula are located in the same layer, which has a positive charge in average. On the other hand, the other layer consisting of a $[Pt_2(pop)_4]^{3-}$ unit and an aliphatic diammonium ion per formula has a negative charge in average. In other words, the iodide ions and the Pt ions are in the positively charged and negatively charged layer, respectively (Fig. 4). Although the Pt ions along the *c* axis (chain axis) mainly contribute to the EFG at the iodine nucleus, the arrangement of the charged layers should decrease the EFG, resulting in a smaller QCC



Fig. 4 Schematic representation of the charged layer in $1.4H_2O$. H_2O molecules and hydrogen atoms are omitted for clarity. Iodide ions, K⁺ ions and *cis*- H_3NCH_2CH =CHCH₂NH₃²⁺ ions are disordered. Pt yellow, I purple, K brown, P orange, O red, N blue, C black.

and a larger $\rho_{\rm QCC}$ observed in the present complexes. Consequently, it can be concluded that the $\rho_{\rm QCC}$ is not appropriate to discuss the quantitative value of the iodine charge in the pop system. This high susceptibility of QCC to the surrounding charges is also supported by the relationship between QCC and IS as discussed in the ESI† and Fig. S1 therein. Therefore we focus on the $\rho_{\rm IS}$ from now on.

Iodine charge of 1.4H2O, 2.4H2O and their dehydrated states

As shown in Table 1, the $\rho_{\rm IS}$ values of 1, 1-4H₂O, and 2 are -0.13(2), -0.14(2), and -0.14(2), respectively, which are the smallest of all MMX chains. So far, the smallest values of $\rho_{\rm IS}$ are -0.27 for $[{\rm Pt}_2({\rm MeCS}_2)_4{\rm I}]$ in the dta system^{14d,19a} and -0.33(5) for $({\rm H}_3{\rm NC}_6{\rm H}_{12}{\rm NH}_3)_2[{\rm Pt}_2({\rm pop})_4{\rm I}]$ in the pop system.^{19b} Accordingly, the negative charge on the iodide ion is strongly donated to the Pt ion in the case of $1\cdot4{\rm H}_2{\rm O}$, 1 and 2. This result corresponds to the previous report that the covalent interaction is more dominant in the CDW state compared with the Coulomb interaction.^{19b}

The two chemically independent iodide ions in 2·4H₂O are denoted by Ia and Ib. The Ia is located between higher oxidized Pt ions with shorter Pt–I–Pt distance (*d*(Pt–I–Pt)), and the I_b is located between lower oxidized Pt ions with longer d(Pt-I-Pt). The smaller $\rho_{\rm IS}$ of -0.21(2) can be assigned as the value derived from the I_a in $2 \cdot 4H_2O$, because the environment around the iodide ion in 2 (e.g. $\rho_{IS} = -0.14(2)$, d(Pt-I-Pt) =5.689(2) Å) is close to that around I_a in 2·4H₂O (e.g. $d(Pt-I_a-Pt) =$ 5.6305(8) Å) rather than that around I_b in 2·4H₂O (e.g. d(Pt-I_b-Pt) = 5.9786(9) Å). Thus, the ρ_{IS} of I_b in 2.4H₂O is -0.40(2). This assignment is in contrast to the previous results that I_a is more negative than I_b , observed in $[Pt_2(MeCS_2)_4I]^{14d,19a}$ and [Pt₂(EtCS₂)₄I],^{19b} which forms the ACP state. In the pointcharge model, the short d(Pt-I-Pt) destabilizes the $5d_{z2}$ orbitals of Pt ions and stabilizes the $5p_z$ orbital of iodide ions. Therefore, the more negative iodide ions and more positive Pt ions are preferred in shorter d(Pt-I-Pt) if the Coulomb interaction is dominant. On the other hand, the overlap integral between these orbitals should be larger and the charge donation from the iodide ion to Pt ions is enhanced in shorter d(Pt-I-Pt) if the covalent interaction is dominant. Since I_a is more positive than Ib in 2.4H2O, it can be concluded that the covalent interaction predominates in the ACP + CDW state as well as the CDW state,^{19b} whereas the Coulomb interaction predominates in the ACP state. This is also supported by the reported optical conductivity spectra, which reveal that the electronic structure in the ACP + CDW state is similar to that in the CDW state.^{17c} Consequently, the ACP + CDW state can be regarded as the CDW state with the ACP-type lattice distortion.

The origin of the opposite result is probably the quite short d(Pt-I-Pt) in 2·4H₂O. The $d(\text{Pt-I}_{a}-\text{Pt})$ in 2·4H₂O (5.6305(8) Å) is 0.23 Å shorter than that in $[\text{Pt}_2(\text{EtCS}_2)_4\text{I}]$ (5.860(2) Å).^{19b} In addition, the shortest Pt-I distance (d(Pt-I)) in 2·4H₂O (2.641(3) Å; Fig. 1) is 0.29 Å shorter than that in $[\text{Pt}_2(\text{EtCS}_2)_4\text{I}]$ (2.93 Å). Consequently, short d(Pt-I-Pt) and d(Pt-I) enhance the overlap between the orbitals and charge donation from

iodide ions to Pt ions. The short d(Pt-I-Pt) in MMX chains with binary countercations originates from the coordination bonds between K⁺ and oxygen atoms of pop ligands.^{17c} The calculated small ρ_{IS} values in the present complexes are valid even under the predominance of the covalent interaction as described in the ESI.[†]

Dependence of the iodine charge on the Pt-I-Pt distance

As discussed above, smaller ρ_{IS} values observed in **1·4H**₂**O**, **2·4H**₂**O** and their dehydrated states indicate that the covalent interaction is stronger in MMX chains with binary countercations. It is more clearly expressed by the relationship between ρ_{IS} and d(Pt-I-Pt) as shown in Fig. 5. Kobayashi *et al.* reported that the ρ_{IS} of the discrete Pt(III)₂ complex in the pop system, K₄[Pt₂(pop)₄I₂], is -0.54(4).^{19b} This negative charge is donated to the other Pt ion at the opposite side when the iodide ion bridges two [Pt₂(pop)₄] units in the 1D chain. Therefore, the decrease of the d(Pt-I-Pt) increases the charge donation from iodide ions to Pt ions, resulting in smaller ρ_{IS} . The strength of the covalent interaction determines the electronic states of the MMX chains in the pop system.

On the other hand, the difference in $\rho_{\rm IS}$ between I_a and I_b is relatively large in the dta system, though the difference in d(Pt-I-Pt) is very small or smaller than the resolution limit of the single crystal X-ray structural analysis. Thus, there is no relationship between $\rho_{\rm IS}$ and d(Pt-I-Pt) in the dta system, which is consistent with the previous report that the Coulomb interaction is more dominant in the ACP state in the dta system.^{19b} This difference between the pop and the dta system is probably related to the charge of each ligand and the presence or absence of countercations. Since the monovalent anionic ligand (RCS₂⁻) and the neutral 1D chain in the dta system produce a 1D electron system without perturbation, various electronic states are observed in the same compound in the dta system (*e.g.* the AV state above 300 K, the CP state from 300 K to 80 K, and the ACP state below 80 K for



Fig. 5 Relationship between d(Pt-I-Pt) and ρ_{15} of MMX chains in the pop system shown in Table 1. Dashed line indicates the ρ_{15} of $Pt(III)_2$ complex, K₄[Pt₂(pop)₄I₂], ($\rho_{15} = -0.54(4)$).^{19b} It can be regarded as the extreme value of ρ_{15} in MMX chains ($d(Pt-I-Pt) = \infty$).

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 $[Pt_2(MeCS_2)_4I]^{14d}$). This multistability is intrinsic to the 1D electron system. In contrast, the anionic 1D chain in the pop system requires countercations, which induce the short d(Pt-I-Pt) and strong covalent interaction and thus suppress the appearance of the ACP state in $1.4H_2O$, $2.4H_2O$ and dehydrated complexes. Furthermore, divalent anionic ligands (pop^{2-}) and countercations can be regarded as the periodic potentials, which interfere with the Coulomb interaction between Pt ions and iodide ions and thus bring about the dominance of the covalent interaction. Therefore, it can be concluded that the covalent interaction plays a crucial role in the dta system.

Conclusions

The electronic states of water-vapor-responsive MMX chains in the pop system, $K_2(cis-H_3NCH_2CH=CHCH_2NH_3^{2+})$ [Pt₂(pop)₄I]· $4H_2O$ (1·4H₂O), $K_2(H_3NC_3H_6NH_3)[Pt_2(pop)_4I]\cdot 4H_2O$ (2·4H₂O) and their dehydrated complexes 1 and 2, were studied by ¹²⁹I Mössbauer spectroscopy. In the case of 1.4H₂O, 1 and 2, one octuplet was observed in the 129I Mössbauer spectra, consistent with the CDW electronic state. On the other hand, the spectrum of 2.4H2O consists of two sets of octuplets, corresponding to the ACP + CDW electronic state. These charges on the iodide ions (ρ_{IS}) are calculated from the isomer shift (IS) but not from the quadrupole coupling constant (QCC), which was affected by the arrangement of cations and anions. The electronic states with the exact charge of iodide ions and the formal charge of Pt ions can be represented as follows: $\cdots [Pt^{2^{+}}-Pt^{2^{+}}]\cdots I^{0.14-}-[Pt^{3^{+}}-Pt^{3^{+}}]-I^{0.14-}\cdots \text{ for the CDW state in } 2, \text{ and } \cdots [Pt^{(2+a)_{+}}-Pt^{(2+b)_{+}}]\cdots I_{a}^{0.21-}-[Pt^{(3-c)_{+}}-Pt^{(3-d)_{+}}]-I_{b}^{0.40-}\cdots$ for the ACP + CDW state in $2 \cdot 4H_2O$. Consequently, we successfully confirmed the change of the electronic state from the ACP + CDW state to the CDW state upon dehydration by ¹²⁹I Mössbauer spectroscopy. The ρ_{IS} values of 1·4H₂O, 1 and 2 (-0.13 to -0.14) are the smallest of all MMX chains reported so far. Accordingly, the negative charge on the iodide ion is strongly donated to the Pt ion in these complexes. In 2.4H2O, more positive I_a bridges higher oxidized Pt ions with shorter Pt-I-Pt distance (d(Pt-I-Pt)) and more negative Ib bridges lower oxidized Pt ions with longer d(Pt-I-Pt). This result is in contrast to the assignment in the case of the MMX chains in the dta system forming the ACP state, indicating that the covalent interaction predominates in the ACP + CDW state as well as in the CDW state.^{19b} Combined with the optical conductivity spectra of 2·4H₂O, it can be concluded that the ACP + CDW state is regarded as the CDW state with the ACP-type lattice distortion. In the pop system, the $\rho_{\rm IS}$ became smaller as d(Pt-I-Pt) decreased, and thus as the charge donation from iodide ions to Pt ions increased. In addition, pop²⁻ and countercations can interfere with the Coulomb interaction between Pt ions and iodide ions. Therefore, the covalent interaction plays a crucial role in determining the electronic states of the MMX chains in the pop system.

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