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Three-Dimensionally Ordered CDW State in Quasi-One-Dimensional Iodo-Bridged Dinuclear Platinum Mixed-Valence Compounds, $A_4[Pt_2I(pop)_4]\cdot nH_2O$ (A = Aromatic Ammonium Cations)

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Linear-chain iodo-bridged dinuclear Pt mixed-valence compounds with aromatic ammonium countercations, $A_4[Pt_2I(pop)_4]\cdot nH_2O$ [pop = $P_2O_5H_2^{2-}$, A = benzyl ammonium (n = 2; **1**), anilinium (n = 2; **2**), and p-methoxy anilinium (n = 2; **3**)], that have three-dimensionally ordered structures were synthesized. In the case of **1**–**3** the aromatic ammonium countercations were located between neighboring Pt chains and stacked in 1D columns. π–π Interactions between the phenyl rings and hydrogen bonds between the $–NH_3^+$ moieties and the oxygen atoms of the pop ligand link the Pt chains together, thus giving rise to a three-dimensionally ordered CDW state. This is the first observation of this phenomenon in compounds of this type.

Introduction

Recently, quasi-one-dimensional halogen-bridged mixed-valence compounds (MX chains) have been the subject of much attention because they have interesting properties, such as intense and dichroic intervalence charge-transfer bands, progressive overtones in resonance Raman spectra, large third-order nonlinear optical properties, and midgap absorptions attributable to solitons and polarons. They also have large Stokes shifts in their luminescence spectra, and they can act as one-dimensional model compounds of high T_c copper oxide superconductors, etc.[1] Theoretically, MX chains may be thought of as Peierls–Hubbard systems, in which electron-phonon interactions (S), electron transfers (T), and intra- and intersite Coulomb repulsion energies (U and V, respectively) compete or cooperate with each other.[2] Pt and Pd compounds adopt a charge density wave (CDW) or M^{II}–M^{IV} mixed-valence states from the electron–phonon interactions (S). Therefore, these complexes are Robin–Day Type II mixed-valence compounds.[3] In contrast, Ni complexes adopt Ni^{III} Mott–Hubbard states because of strong electron correlations (U) and are therefore classified as Robin–Day Type III complexes. In a recent study a very large third-order nonlinear optical susceptibility (ca. 10^{-4} e.s.u.) has been reported for $[Ni^{III}(chxn)_2Br]Br_2$ (chxn = 1R,2R-diaminocyclohexane).[4]

As an extension of MX chain systems, quasi-one-dimensional halogen-bridged dinuclear Pt complexes (MMX chains) have been reported.[5,6] Theoretically, the mixed-valence states of MMX chain systems may be classified into the following four groups, which strongly depend on the positions of the bridging halogen ions:

(a) $–Pt^{2.5+}–Pt^{2.5+}–X–Pt^{2.5+}–Pt^{2.5+}–X–$

[average-valence (AV) state]

(b) $\cdots Pt^{2+}–Pt^{2+}\cdots X–Pt^{3+}–Pt^{3+}–X\cdots$

[charge-density-wave (CDW) state]

(c) $\cdots Pt^{2+}–Pt^{3+}–X\cdots Pt^{2+}–Pt^{3+}–X\cdots$

[charge-polarization (CP) state]

(d) $\cdots Pt^{2+}–Pt^{3+}–X–Pt^{3+}–Pt^{2+}\cdots X\cdots$

[alternating charge-polarization (ACP) state]

So far, two types of MMX chains have been reported: a dta-system[5] and a pop-system.[6] In the former, the Pt–Pt dimer units are coordinated by four dithioacetate (dta) derivatives forming lantern structures, and these units are bridged by iodide ions to form neutral linear chains. The latter compounds have the chemical formulae $A_4[Pt_2(pop)_4X]\cdot nH_2O$ or $A'_2[Pt_2(pop)_4X]\cdot nH_2O$ (pop = $P_2H_2O_5^{2-}$; A = K, Na, Li, Cs, Rb, alkyl ammonium, etc.; A′ = alkyldiammonium; X = Cl, Br, and I). We have synthesized more

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than 50 compounds by substituting the cations and bridging halogens. Since there are significant interactions between the p_z orbitals of the bridging iodide ions and the d_{z^2} orbitals of the platinum ions in the I-bridged compounds, various oxidation states are stable. The oxidation states of iodo-bridged MMX compounds with pop ligands depend on the Pt–I–Pt distances; that is, the compounds with the shortest, intermediate, and longest Pt–I–Pt distances are in AV, CDW, and CP states, respectively. CP state compounds, in particular, have the potential to exhibit ferroelectric and second-order optical nonlinear effects but these effects have not yet been observed, and they adopt only one-dimensional ordering because of their weak interchain interactions. We have recently reported pressure and photo-induced phase changes between the CP and CDW states in $\{(C_2H_5)_2NH_2\}_4[Pt_2I(pop)_4]\cdot 4H_2O$.[7] We have also reported vapochromic behavior in $\{NH_3(CH_2)_nNH_3\}_2[Pt_2I(pop)_4]\cdot 4H_2O$, which was accompanied by a phase change between the CP and CDW state with an increase or decrease in the temperature.[8] If a three-dimensionally ordered CP state can be constructed it may be possible to develop multi-switching devices, which convert between the CP state (ferroelectric, second-order optical nonlinear effect, paramagnetic) and the CDW state (non-dielectric, third-order optical nonlinear effect, diamagnetic) depending on pressure and photo and/or temperature-induced effects. In order to construct a three-dimensionally ordered charge state it is necessary to control the interchain interactions. Thus, we used aromatic ammonium cations in order to create π–π interactions and hydrogen bonds.

In this paper, we report on the first examples of three-dimensionally ordered CDW states in quasi-one-dimensional halogen-bridged dinuclear Pt mixed-valence compounds with aromatic ammonium countercations, $A_4[Pt_2I(pop)_4]\cdot nH_2O$ [A = benzyl ammonium ($n = 2$; **1**), anilinium ($n = 2$; **2**) and *p*-methoxyanilinium ($n = 2$; **3**)]. For comparison, we also report on a *p*-carboxyanilinium compound ($n = 6$; **4**), which does not have a three-dimensionally ordered CDW state.

Results and Discussion

Crystallographic Details

A perspective view of the crystal structure of **1** at 200 K is shown in Figure 1. Two Pt atoms are linked by four pop ligands to form a dinuclear $Pt_2(pop)_4$ unit. The two neighboring $Pt_2(pop)_4$ units are bridged by an I ion, and the chain structure is constructed along a diagonal line of the unit cell. Two types of $Pt_2(pop)_4$ units alternate in this chain structure: one dimer contains Pt^{2+} ions and the other contains Pt^{3+} ions with axial positions coordinated by I ions ($[Pt_2I_2(pop)_4]$). The selected interatomic distances of compounds **1**–**4** and the precursor compounds are listed in Table 1. The intradimer Pt–Pt distances of the $[Pt^{2+}{}_2(pop)_4]$ unit and the $[Pt^{3+}{}_2I_2(pop)_4]$ unit in structure **1** are 2.9121 Å and 2.7606 Å, respectively. These distances are consistent with the intradimer Pt–Pt distance reported for the precursors $K_4[Pt^{2+}{}_2(pop)_4]\cdot 2H_2O$ (2.925 Å)[6a] and $K_4[Pt^{3+}{}_2I_2(pop)_4]$ (2.754 Å)[9] and suggest that compound **1** is in a CDW state, i.e. $\cdots Pt^{2+}–Pt^{2+}\cdots I–Pt^{3+}–Pt^{3+}–I\cdots$. In all previously reported pop compounds the bridging iodide ions have been disordered, with half occupancies at the displaced positions from the midpoints between neighboring Pt dimer units. However, the bridging iodide of **1** was not disordered. This indicates that the charge structure of **1** is a three-dimensionally ordered CDW state. The benzyl ammonium countercations are located between the neighboring Pt chains and stacked in a 1D-column structure. A slipped-parallel type π–π interaction was observed between the phenyl rings of the benzylammonium countercations (nearest C···C distance: ca. 3.4 Å). The $–NH_3^+$ moieties of the benzyl ammonium cations form hydrogen bonds with the oxygen atoms of the pop ligand connecting the Pt chain. The π–π interactions and hydrogen bonds seem to cause the three-dimensional ordering.

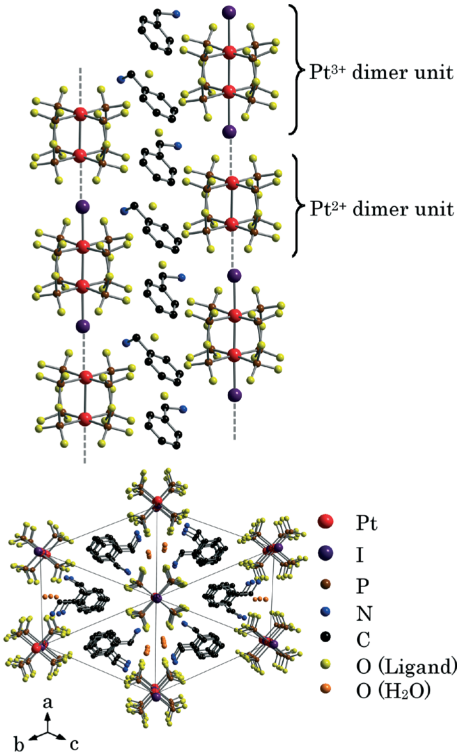

Figure 1. Perspective views of the 3D packing of **1**. H atoms have been omitted for clarity.

Table 1. Comparison of interatomic distances [Å] and lowest energy CT bands E_1 [eV].

	$Pt^{II}–Pt^{II}$	$Pt^{III}–Pt^{III}$	Pt–I–Pt	E_1
1	2.9121(4)	2.7606(4)	6.287	1.644
2	2.9277(5)	2.7729(5)	6.144	–[a]
3	2.9219(3)	2.7768(3)	5.968	–[a]
4	2.877		6.116	1.486
$K_4[Pt^{2+}{}_2(pop)_4]\cdot 2H_2O$[b]	2.925	–	–	–
$K_4[Pt^{3+}{}_2I_2(pop)_4]$[c]	–	2.754	–	–

[a] Spectra of compounds **2** and **3** could not be measured due to their efflorescence. [b] Ref.[6a] [c] Ref.[9]

In the case of **2** and **3**, the bridging iodide ion was also not disordered and two types of $Pt_2(pop)_4$ units alternate in the chain structure. The intradimer Pt–Pt distances of the $[Pt^{2+}{}_2(pop)_4]$ and $[Pt^{3+}{}_2I_2(pop)_4]$ units are consistent with those of the precursors. Therefore, **2** and **3** are in a CDW state with three-dimensional ordering. π–π Interactions and hydrogen bonds similar to those of **1** were also found, resulting in the formation of similar three-dimensionally ordered CDW states.

On the other hand, in compound **4**, two neighboring $[Pt_2(pop)_4]$ units were bridged by I ions, thus forming a Pt–Pt–I linear chain along the *b* axis (Figure 2). The bridging I ions of compound **4** were disordered, with half occupancies at positions displaced from the midpoints between the neighboring dinuclear Pt units. The disordered bridging I ion indicates that the charge ordering is not three-dimensional but one-dimensional. Because the *p*-ammonium benzoic acid countercation forms a dimer structure with hydrogen bonding between neighboring carboxyl groups, π–π interactions cannot exist between the phenyl rings. Therefore, the charge ordering of compound **4** is not three-dimensional.

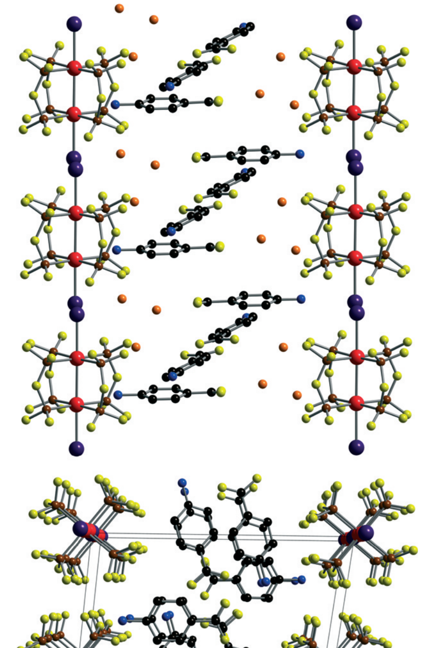

Figure 2. Perspective views of the 3D packing of **4**. H atoms have been omitted for clarity.

Compound **4** is in either a CDW or CP state, because the bridging I ions are disordered and the intradimer Pt–Pt distance is 2.877 Å, which is intermediate between those of $K_4[Pt^{2+}{}_2(pop)_4]\cdot 2H_2O$ (2.925 Å) and $K_4[Pt^{3+}{}_2I_2(pop)_4]$ (2.754 Å). However, because the charge ordering state of compound **4** is not three-dimensional, it is difficult to determine whether **4** is in a CDW or CP state by using X-ray structural analysis. The electronic structure of the iodo-bridged pop systems can be estimated from interdimer Pt–Pt separation of the Pt–I–Pt moiety.[7] In the case of compound **4**, however, the Pt–I–Pt distance is 6.116 Å, and this distance is on the boundary between a CDW and CP state (ca. 6.1 Å). Therefore, the electronic structure of compound **4** cannot be determined from the Pt–I–Pt distance.

Single-Crystal Reflectance Spectroscopy

Single-crystal reflectance spectra of compounds **1** and **4** were measured at room temperature, and optical conductivities obtained by using the Kramers–Kronig transformation are shown in Figure 3. The spectra of these compounds have similar shapes. A large peak is observed around 1.5 eV (E_1), and weak peaks are observed around 2–4 eV (E_2, E_3, and E_4). Similar to the previously reported iodo-bridged pop compounds, the optical gap energies E_2–E_4 were not dependent on the countercations and interdimer Pt–I–Pt distances.[7] Therefore, E_2, E_3, and E_4 were assigned to be intradimer transitions. In relation to $K_4[Pt^{3+}{}_2I_2(pop)_4]$, E_2, E_3, and E_4 were assigned to be intradimer transitions from bridging I ions to neighboring Pt^{III} ions, from bridging I ions to the other Pt^{III} ions, and from Pt^{III} to Pt^{III} ions, respectively.[10,11] In contrast, as observed in a previous report,[7] the optical gap energy E_1 was observed only with the 1D-chain structure and varied over the range 0.5–2.5 eV depending on the countercations and interdimer Pt–I–Pt distance. Therefore, E_1 was assigned as an interdimer transition from Pt^{II} to Pt^{III} ions. This assignment is also supported by a previously reported theoretical study.[11]

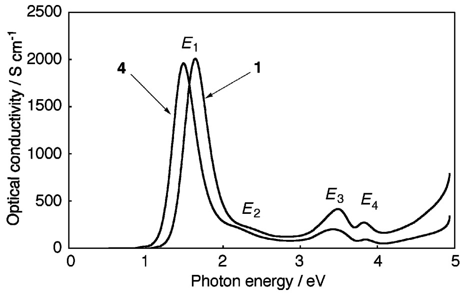

Figure 3. Optical conductivity spectra of compounds **1** and **4** at room temperature.

Matsuzaki et al. have reported the syntheses of the iodo-bridged pop compounds with various alkali metals (Na, Rb, and Cs) and alkylammonium countercations [NH_4, $C_nH_{2n+1}NH_3$, $(C_nH_{2n+1})_2NH_2$, and $NH_3(C_nH_{2n})NH_3$], and have demonstrated that the substitution of these countercations dramatically affects the charge-ordering states depending upon the interdimer Pt–I–Pt distance.[7] In the phase diagram that they have reported there is a boundary between the CDW and CP states at ca. 6.1 Å, and the charge-ordering state changes from a CDW to a CP state with an increase in the interdimer Pt–I–Pt distance. The relevant interdimer Pt–I–Pt distances of compounds **1**–**4** are listed in Table 1. From an X-ray structure analysis it can be seen that compounds **1**–**3** are in a CDW state. Based on the phase diagram, compound **3** is in a CDW state, whereas

Table 2. Crystal data and refinement parameters for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{28}H_{52}IN_4O_{22}P_8Pt_2$	$C_{24}H_{44}IN_4O_{22}P_8Pt_2$	$C_{28}H_{52}IN_4O_{26}P_8Pt_2$	$C_{28}H_{48}IN_4O_{32}P_8Pt_2$
M_r [g mol^{-1}]	1561.58	1505.47	1625.58	1717.54
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.3016(12)	10.6996(12)	10.5656(11)	8.949(8)
b [Å]	14.7049(16)	13.8966(15)	15.4293(16)	8.991(9)
c [Å]	15.2580(17)	16.4147(18)	16.3601(17)	17.12(2)
α [°]	112.643(2)	87.505(2)	78.379(2)	89.90(4)
β [°]	93.498(2)	80.080(2)	78.582(2)	83.71(4)
γ [°]	98.735(3)	67.508(2)	75.291(2)	71.14(2)
V [Å^3]	2293.2(4)	2220.6(4)	2496.2(4)	1294.6(2)
Z	2	2	2	2
D_{cal} [g cm^3]	2.256	2.252	2.163	2.110
T [K]	200(2)	200(2)	200(2)	173.1
$R_1[I > 2\sigma(I)]$[a]	0.0327	0.0427	0.0298	0.0595
$wR_2[I > 2\sigma(I)]$[b]	0.0587	0.0888	0.0546	0.1470
GOFs	0.815	0.839	0.893	1.381

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

compounds **1** and **2** are in a CP state. Thus, because of the interchain interactions three-dimensionally ordered pop compounds with aromatic ammonium countercations have a different phase diagram from those of pop compounds with alkali metals and alkylammoniums that are not three-dimensionally ordered.

Conclusions

We synthesized iodo-bridged dinuclear Pt compounds with a three-dimensionally ordered CDW state by using countercations that can form hydrogen bonds with the pop ligands as well as π–π interactions with the phenyl rings of aromatic ammonium countercations. Three-dimensionally ordered pop compounds have a different phase diagram from those of pop compounds that are not three-dimensionally ordered because of the interchain interactions. We are currently trying to prepare compounds with three-dimensionally ordered CP states, which should show very interesting physical properties such as ferroelectric and second-order nonlinear optical effects.

Experimental Section

General Procedures and Materials: All chemicals and solvents used in these syntheses were reagent grade. The starting compounds $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2I_2(pop)_4]$ were synthesized as described in the literature.[6,12] Single crystals of $A_4[Pt_2I(pop)_4]\cdot nH_2O$ [A = benzylammonium (n = 2; **1**), anilinium (n = 2; **2**), and p-methoxyanilinium (n = 2; **3**), p-carboxyanilinium (n = 6; **4**)] were obtained by diffusion of an aqueous solution of ANO_3 into an aqueous solution of equimolar amounts of $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2I_2(pop)_4]$ over a few days. An elemental analysis was carried out at the Elemental Analytical Center of Tokyo Metropolitan University. $C_{28}H_{52}IN_4O_{22}P_8Pt_2$ (**1**, 1561.61): calcd. C 21.54, H 3.36, N 3.59; found C 21.45, H 3.23, N 3.59. $C_{24}H_{44}IN_4O_{22}P_8Pt_2$ (**2**, 1505.50): calcd. C 19.15, H 2.95, N 3.72; found C 19.06, H 3.00, N 3.73. $C_{28}H_{48}IN_4O_{32}P_8Pt_2$ (**4**, 1717.57): calcd. C 19.18, H 2.99, N 3.20; found C 19.49, H 2.97, N 3.16. An elemental analysis could not be carried out for compound **3** because it decomposed.

Crystallographic Data Collection: For compounds **1**–**3**, X-ray data were collected with a Bruker SMART1000 diffractometer at 200 K. For compound **4**, an X-ray data collection was carried out with a Rigaku AFC7R diffractometer at 173 K. The structures were solved by using direct methods and refined by using least-squares on F^2 with the SHELX-97 program.[13] Crystal data are summarized in Table 2.

CCDC-668561 (for **1**), -668562 (for **2**), -668563 (for **3**), -668564 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical Measurements: In ordert to measure the polarized reflectance spectra the light from a halogen–tungsten incandescent lamp was focused with a concave mirror onto the entrance slit of a 25-cm grating monochromator (JASCO CD 25). Monochromatic light from the exit slit was passed through a polarizer and focused on a specific surface of a single-crystal sample by using an optical microscope. The reflected light from the sample was focused using a concave mirror on the detector (a PdS cell or a photomultiplier tube). Optical conductivity spectra were obtained by using the Kramers–Kronig transformation on the polarized reflectance spectra.

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