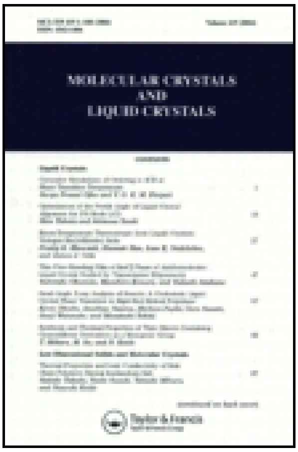

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Crystal and Electronic Structures of Quasi-One-Dimensional Halogen-Bridged Binuclear Platinum Complexes, $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (n=2-6)

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Crystal and Electronic Structures of Quasi-One-Dimensional Halogen-Bridged Binuclear Platinum Complexes, $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (n = 2-6)

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The crystal structures of $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (pop=$O(PO_2H)_2^{2-}$, n=2-6) have been determined. Judging from the results of the X-ray structural analyses and Raman spectra, 1–D electronic structures of these compounds are consider to be ...Pt^{2+}–Pt^{3+}–X ...Pt^{2+}–Pt^{3+}–X... charge–polarized states.

Keywords: MMX-chain compounds; halogen-bridged mixed-valence complexes

INTRODUCTION

Recently quasi-one-dimensional halogen-bridged -M-X-M-X- (M=Ni, Pd, Pt) compounds (MX-chain compounds) have been attracting much attention [1]. As an extension of the MX chain compounds, the MMX chain compounds which have binuclear units in quasi-one-dimensional structures were reported [2-7]. There are four possibilities of the charge modulation depending on the deviation of the bridging halogen ions from the midpoints between two adjacent binuclear units.

(a)-X-$Pt^{2.5+}$-$Pt^{2.5+}$-X-$Pt^{2.5+}$-$Pt^{2.5+}$-X- (Mott-Hubbard state).
(b)– X...Pt^{2+}-Pt^{2+}....X – Pt^{3+}-Pt^{3+} – X .... (CDW state)
(c)-X....Pt^{2+}-Pt^{3+}-X....Pt^{2+}-Pt^{3+}-X.... (charge polarized state)
(d)....X....Pt^{2+}-Pt^{3+}-X-Pt^{3+}-Pt^{2+}....X....(spin-Peierls state)

In these compounds, the phase transition and/or charge fluctuations among these oxidation states are expected due to the smaller band gaps [8, 9]. So the structure and physical properties of the MMX chain compounds, $A_4[Pt_2(pop)_4X]{\bullet}nH_2O$ (A=Li, Na, K, Rb, Cs, NH_4; X=Cl, Br, I; pop=$O(PO_2H)_2^{2-}$), have been investigated. But the I-bridged MMX chain compounds have not been investigated so much, because less quality of their single crystal could not be suitable for X-ray structural analysis. The electron-phonon interaction in the case of I-bridged complexes are expected to be weaker in comparison with those in the Cl^- and Br^- bridged compounds. Therefore, these electronic structures are expected to be more delocalized, and there are the possibility of taking the additional oxidation states or phase transitions. In this paper we report the synthesis and the electronic structures of new quasi-one-dimensional halogen-bridged binuclear mixed-valence compounds, $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (n=2 -6).

EXPERIMENTAL

The starting compounds, $K_4[Pt_2^{II}(pop)_4]$ and $K_4[Pt_2^{III}(pop)_4I_2]$ were synthesized according to the literatures [2, 8-11]. $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ were synthesized by adding the excess amounts of $(C_nH_{2n+1})_2NH{\bullet}HNO_3$ into the aqueous solutions of the equimolar amounts of $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2(pop)_4I_2]$.

Recrystallization were carried out from the aqueous solution. Crystal structures were determined by single crystal X-ray diffraction method (Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo-Kα radiation). Raman spectra were measured with Ar^+ excitation using a JASCO NR-1800 laser Raman Spectrometer.

RESULTS AND DISCUSSIONS

Crystal Structure : The perspective drawings of the chain structure of $\{(C_3H_7)_2NH_2\}_4[Pt_2(pop)_4I]$ with atomic numbering systems are presented in Fig. 1. Crystallographic data are summarized in Table1. Two Pt atoms are bridged by four pyrophosphato ligands (pop^{2-}) to form a binuclear $Pt_2(pop)_4$ unit. The Pt_2 units are also bridged by iodine ion to construct a linear-chain structure. The linear chains of n=2 and 5 (C2 and C5) compounds are not straight and a little bit bent to form a

Table1 Crystallographic Data

	n=2 (C2)	n=3 (C3)	n=4 (C4)	n=5 (C5)	n=6 (C6)
Formula	C16H56IN4P8Pt2	C24H72IN4P8Pt2	C32H88IN4P8Pt2	C40H104IN4P8Pt2	C48H120IN4P8Pt2
Formula weight	1389.51	1501.72	1613.94	1726.135	1838.35
Crystal system	monoclinic	tetragonal	tetragonal	triclinic	monoclinic
Space group	C2/m	P4nc	P4212	P-1	C2/c
a (Å)	17.709(1)	16.521(1)	16.8625(3)	12.521(3)	37.687(5)
b (Å)	14.954(1)	16.521(1)	16.8625(3)	15.969(4)	9.098(2)
c (Å)	9.8345(7)	9.1014(6)	8.7734(2)	8.993(1)	23.459(3)
α (Å)	90	90	90	104.61(1)	90
β (Å)	121.952(4)	90	90	180.645(5)	111.491
γ (Å)	90	90	90	71.072(6)	90
V ($Å^3$)	2209.9(3)	2484.1(3)	2494.66(8)	1589.2	7484(2)
Z	2	2	2	1	4
Dx(g/cm^{-3})	2.088	2.008	2.148	1.803	1.631
Temperature(°C)	23	23	-160	-120	-120
Crystal Dimensions (mm)	0.20×0.10×0.10	0.50×0.20×0.10	0.30×0.10×0.10	0.20×0.15×0.10	0.30×0.10×0.10
R1[a]	0.039	0.035	0.040	0.058	0.044
Rw[b]	0.102	0.088	0.137	0.156	0.096
GOF	1.40	1.18	1.36	2.31	1.09
Reflections measured	9986	8320	23212	10560	30205
Independent reflections	2083	787	1685	5011	3002

[a] $R1 = \Sigma ||Fo|-|Fc|| / \Sigma |Fo|$, [b] $Rw = [\Sigma \omega (Fo^2-Fc^2)^2 / \Sigma \omega (Fo^2)^2]^{1/2}$

Table2 Selected bond distances (Å)and angles(°).

	n=2	n=3	n=4	n=5	n=6
Pt-Pt	2.8586(6)	2.850(1)	2.8469(8)	2.8485(8)	2.863(2)
Pt-I	2.718(1)	2.733(5)	2.739(3)	2.745(1)	2.746(6)
Pt-I		2.773(7)	2.745(3)		2.748(6)
ΔI	1.575(3)	0.746(4)	0.442(5)	0.668(2)	0.742(5)
Pt-I-I	167.2(2)	180.00	180.00	168.3(4)	180.00

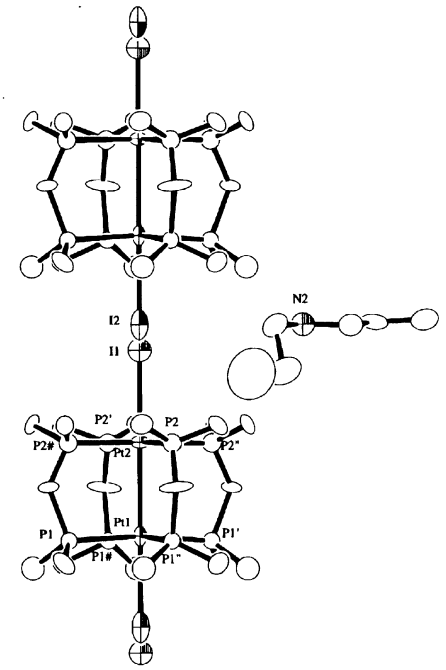

Figure 1. An ORTEP drawing of $\{(C_3H_7)_2NH_2\}_4[Pt_2(pop)_4I]$ with atom numbering scheme.

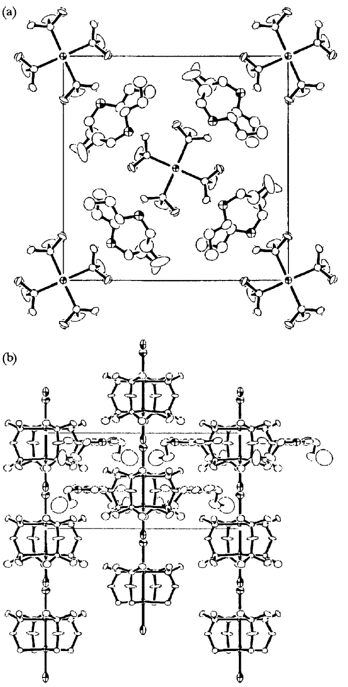

Figure 2. A stereoscopic view of $\{(C_3H_7)_2NH_2\}_4[Pt_2(pop)_4I]$ from (a) c-axis, (b) a-axis.

zigzag structures, in contrast to the straight chains in the n=3, 4 and 6 (C3, C4 and C6) compounds. As has been observed previously for the Br^- and Cl^- bridged compounds, the bridging I ion are disordered over two sites with an occupancy factor of 0.5. The positional disorder of the halogen atoms separates into the short Pt-X and long Pt...X distances which can be attributed to the Pt^{III}-X and Pt^{II}...X distances, respectively. The observed chain structures can be interpreted by the following two structural models, that is, all of which require positional disorder among the chains (b) and (c) states. The Pt-Pt distance of Pt_2 units are observed to be 2.847Å - 2.863Å, which are the intermediate values among those of the corresponding Pt^{II}-Pt^{II} (2.925Å) and Pt^{III}-Pt^{III} (2.754Å) complexes of discrete structures.

Raman Spectra :

Raman spectroscopy has been used widely to study the vibrational and structural properties of MX-chain and MMX-chain compounds. In the case of (c) state, where the Pt-Pt distances of the Pt_2 units are uniform, the Pt-Pt stretching mode ,$\nu(Pt^{II}-Pt^{III})$, should be a singlet. In addition, since the iodine ion were located in a little deviated position from the midpoint between the Pt_2 units, ν(Pt-I) would be a Raman-active. In the case of (b) state, since the Pt-Pt distances are different from each other, ν(Pt-Pt) mode is expected to be a doublet and the ν(Pt-I) mode would be allowed.

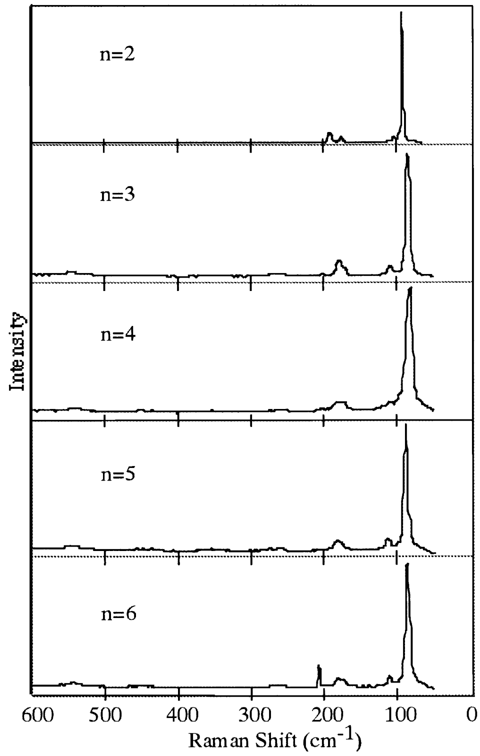

Figure 3. Raman spectra of $\{(C_nH_{2n+1})_2NH_2\}[Pt_2(pop)_4I]$

The results of the Raman spectra of these compounds are shown Fig. 3. This phenomena can be observed at 116cm^{-1}, suggesting that $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ compounds have the oxidation state of (c) -$X...Pt^{2+}-Pt^{3+}-X...Pt^{2+}-Pt^{3+}-X....$. This is in good agreement with the results of the X-ray structural analysis.

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