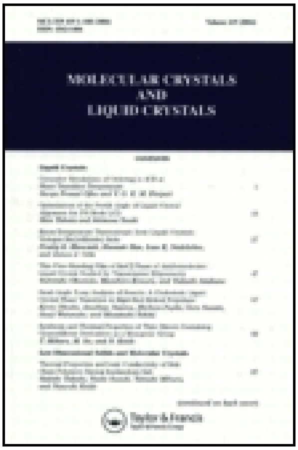

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Charge Fluctuation in Quasi-One-Dimensional Halogen-Bridged Platinum Binuclear Mixed-Valence Compounds, $A_4[Pt_2(pop)_4I]\cdot nH_2O$

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To cite this article: Takuya Kawashima, Shuji Miya, Toshio Manabe, Masahiro Yamashita, Kouichi Takizawa, Tomohiko Ishii, Hiroyuki Matsuzaka, Takuya Sonoyama, Hirosi Kitagawa, Tadaoki Mitani, Hiroyuki Matsuzaki, Hideo Kishida, Hiroshi Okamoto & Ryuichi Ikeda (2000): Charge Fluctuation in Quasi-One-Dimensional Halogen-Bridged Platinum Binuclear Mixed-Valence Compounds, $A_4[Pt_2(pop)_4I]\cdot nH_2O$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 145-150

To link to this article: http://dx.doi.org/10.1080/10587250008038258

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 145-150
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Charge Fluctuation in Quasi-One-Dimensional Halogen-Bridged Platinum Binuclear Mixed-Valence Compounds, $A_4[Pt_2(pop)_4I]\cdot nH_2O$

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New quasi-one-dimensional halogen-bridged platinum binuclear mixed-valence compounds, $A_4[Pt_2(pop)_4I]\cdot nH_2O$ (A= alkaline metal and NH_4, and; n=0, 2 and 4) have been synthesized. The Li, Na and K compounds take structures $-Pt^{2.5+}-Pt^{2.5+}-X-Pt^{2.5+}-Pt^{2.5+}-X-$ (a). On the other hand, the Cs and Rb compounds take structures $\ldots Pt^{2+}-Pt^{2+}\ldots X-Pt^{3+}-Pt^{3+}-X\ldots$ (b). Interestingly, the NH_4 compound takes a phase transition between (a) and (b) around 200K.

Keywords: phase transitions; mixed-valence complexes

INTRODUCTION

Quasi-one-dimensional halogen-bridged Pt, Pd and Ni complexes (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 Tc copperoxide superconductors, etc [1-3]. As a development of the MX chains, the MMX chains which have binuclear metal units in quasi-one-dimensional structures were reported [4-11]. 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 [12,13].

(a)-$Pt^{2.5+}$-$Pt^{2.5+}$-X-$Pt^{2.5+}$-$Pt^{2.5+}$-X- (SDW or metal)
(b)...Pt^{2+}-Pt^{2+}...X-Pt^{3+}-Pt^{3+}-X... (CDW)
(c)...Pt^{2+}-Pt^{3+}-X...Pt^{2+}-Pt^{3+}-X.. (SDW or metal)
(d)...Pt^{2+}-Pt^{3+}-X-Pt^{3+}-Pt^{2+}...X... (Spin-Peierls)

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 and 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 so 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. We will report new quasi-one-dimensional halogen-bridged binuclear mixed-valence compounds, $A_4[Pt_2(pop)_4I]\cdot nH_2O$ (A= alkaline metal and NH_4 ; n=0, 2 and 4).

EXPERIMENTAL

The starting compounds, $K_4[Pt_2(pop)_4]$ and $K_4[Pt_2(pop)_4I_2]$ were synthesized according to the literatures [4,14-17]. $A_4[Pt_2(pop)_4I]\cdot nH_2O$ (A=Li, n=4; A=Na, K, Rb and 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 $K_4[Pt_2(pop)_4I_2]$ [18]. Recrystallization 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.). Crystal structures of $Li_4[Pt_2(pop)_4I]\cdot 4H_2O$ was determined by the single crystal X-ray diffraction method (Rigaku

AFC7R diffractometer with graphite monochromated Mg-Kα radiation). The complexes is crystallized in tetragonal, space group P4, Z=1: a=9.523(2),c=8.797(3)Å, V=797.8(4)Å^3. Raman spectra were measured with Ar$^+$ excitation using a JASCO NR-1800 laser Raman spectrometer. The measurements of the XP spectra were performed using ESCALAB MKII (VG Scientific Co.) photoelectrometer with Mg-Kα (hv=1253.6 eV) as an exciting light source.

RESULTS AND DISCUSSIONS

The perspective drawing of the chain structures of $Li_4[Pt_2(pop)_4I]\cdot 4H_2O$ is presented in Figure.1. Relevant interatomic distances and angles are listed in Table I. The structure consists of a linear chain with a –Pt-Pt-I-Pt-Pt-I repeating unit along the c axis. Two Pt atoms are bridged by four pyrophosphato ligands ($P_2O_5H_2^{2-}$=pop) to form a binuclear $Pt_2(pop)_4$ unit. The bridging I ions are located on the midpoint between the two $Pt_2(pop)_4$ unit. This result means that all Pt atoms are equivalent or +2.5.

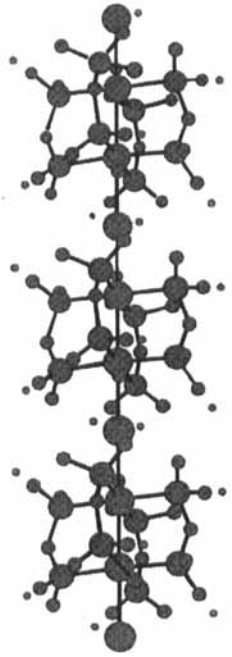

FIGURE 1. Structure of $Li_4[Pt_2(pop)_4I]\cdot 4H_2O$

TABLE 1. Selected Bond distances (Å) and angles(°)

atom-atom	distance
Pt(1)-Pt(1)	2.859(6)
Pt(1)-I(1)	2.969(3)
Pt(1)-P(1)	2.33(4)
Pt(1)-P(2)	2.35(3)
P(1)-O(11)	1.53(5)
P(1)-O(14)	1.73(4)
P(1)-O(15)	1.36(9)
P(2)-O(2)	1.60(4)
P(2)-O(3)	1.54(9)
P(2)-O(14)	1.44(5)

atom-atom-atom	angle
Pt(1)-Pt(1)-I(1)	180.0
Pt(1)-Pt(1)-P(1)	90.3(6)
Pt(1)-Pt(1)-P(2)	92.5(10)
I(1)-Pt(1)-P(1)	89.7(6)
I(1)-Pt(1)-P(2)	87.5(10)
P(1)-Pt(1)-P(1)	179(1)
P(1)-Pt(1)-P(2)	89(1)
P(1)-Pt(1)-P(2)	90(1)
P(2)-Pt(1)-P(2)	175(1)
Pt(1)-P(1)-O(11)	118(2)
O(11)-P(1)-O(14)	99(3)
O(14)-P(1)-O(15)	120(3)
O(2)-P(2)-O(3)	104(3)
P(1)-O(14)-P(2)	138(3)
Li(3)-Li(3)-Li(3)	88.9(7)

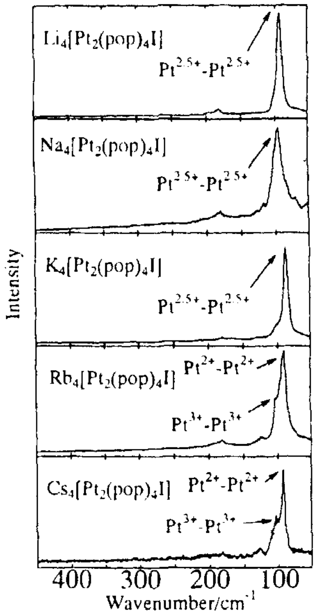

FIGURE 2.
Raman spectra of $A_4[Pt_2(pop)_4I]\ nH_2O$

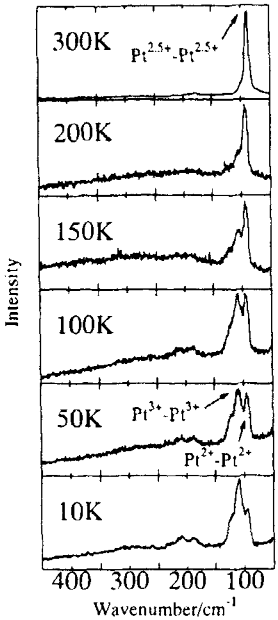

FIGURE 3. Temperature dependence
Raman spectra of $(NH_4)_4[Pt_2(pop)_4I]\ 2H_2O$

Raman spectra of these compounds were measured at various temperatures. Their spectra were shown in Figure.2 and 3, respectively. The compounds with Li, Na and K show the singlet signal around 90 cm^{-1}. Therefore, they are reasonably attributable to the ν($Pt^{2.5+}$-$Pt^{2.5+}$). On the other hand, the compounds with Rb and Cs show the doublet signals around 100 cm^{-1}. Therefore, the lower and higher signals are attributable to the ν(Pt^{2+}-Pt^{2+}) and ν(Pt^{3+}-Pt^{3+}). The Raman spectra of the NH_4 compound depend on the temperature as shown in Figure. 3, that is, the singlet signal at room temperature and the doublet signal at low temperature. The transition is repeatedly observed. Form these results, the compounds with Li, Na and K have structures (a) -$Pt^{2.5+}$-$Pt^{2.5+}$-I-$Pt^{2.5+}$-$Pt^{2.5+}$-I-, and the compounds with Rb and Cs have structures (b)...Pt^{2+}-Pt^{2+}...I-Pt^{3+}-Pt^{3+}-I... The NH_4 compound has a structure (a)-$Pt^{2.5+}$-$Pt^{2.5+}$-I-$Pt^{2.5+}$-$Pt^{2.5+}$-I- at room temperature and a structure (b)...Pt^{2+}-Pt^{2+}...I-Pt^{3+}-Pt^{3+}-I..at low temperature. That is, the charge fluctuation between (a) and (b) is occurred in the NH_4 compound.

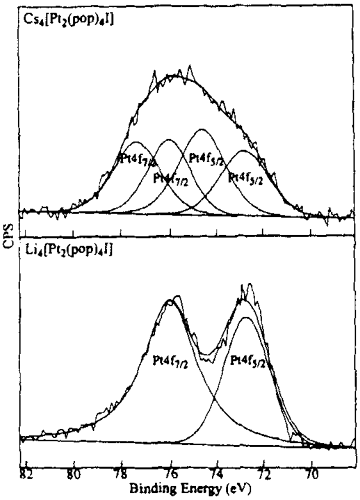

FIGURE 4. XP spectra of Pt Atoms of A=Li and Cs in $A_4[Pt_2(pop)_4I]\cdot nH_2O$

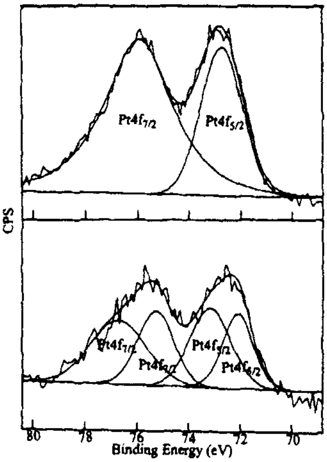

FIGURE 5. XP spectra of Pt Atoms of $(NH_4)_4[Pt_2(pop)_4I]\cdot 2H_2O$ at room temperature (top) and 77K (bottom)

TABLE 2. Binding Energies of Pt Atoms in $A_4[Pt_2(pop)_4I]\cdot nH_2O$

	Pt^{2+}		$Pt^{2.5+}$		Pt^{3+}	
	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$
$Li_4[Pt_2(pop)_4I]\cdot 4H_2O$			72.70	75.95		
$Na_4[Pt_2(pop)_4I]\cdot 2H_2O$			72.86	75.81		
$K_4[Pt_2(pop)_4I]\cdot 2H_2O$			72.91	76.12		
$(NH_4)_4[Pt_2(pop)_4I]\cdot 2H_2O$ (rt)			72.73	75.96		
$(NH_4)_4[Pt_2(pop)_4I]\cdot 2H_2O$ (77K)	72.17	75.40			73.32	76.82
$Rb_4[Pt_2(pop)_4I]\cdot 2H_2O$	72.26	75.33			73.48	76.70
$Cs_4[Pt_2(pop)_4I]$	72.78	75.95			74.56	77.22

In order to directly investigate their oxidation states, the XP spectra were measured for A=Li, Na, K, Rb and Cs at 77K, and for NH_4 at room temperature and 77K. The XP spectra of A=Li, Na and K compose of $4f_{7/2}$ and $4f_{5/2}$ of $Pt^{2.5+}$, while the XP spectra of A=Rb and Cs are 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 $4f_{7/5}$ and $4f_{5/2}$ of $Pt^{2.5+}$ at room temperature, and could be resolved into $4f_{7/2}$ and $4f_{5/2}$ of Pt^{2+} and Pt^{3+} at 77K. Their binding energies are listed in Table III. Their values are reasonably corresponding to their oxidation states. These results are consistent with those of Raman spectra.

The compounds with Li, Na and K have structures (a) and the compounds with Rb and Cs have structures (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, Na, K, Pb, Cs and NH_4 or the numbers of the water molecules. More recently we have obtained the compounds with different water molecules. Therefore, the number of water molecules is very important in this system.

Acknowledgments

This was partly supported by Grant-in-Aid for Scientific Research on Priority Areas ("Metal-assembled Complexes") from Ministry of Education, Science, Sports and Culture, Japan.

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