

ESR Observations of Dehydration-Induced Electronic Phase Changes in Iodo-Bridged Diplatinum Complexes

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Quasi-one-dimensional (Q1D) halogen(*X*)-bridged binuclear metal(*M*)-complexes, so called *MMX*-chains have been attracting much interest because of their wide variety of valence ordering state, such as averaged valence (AV) state [$-\text{Pt}^{2.5+}-\text{Pt}^{2.5+}-$], charge polarization (CP) state [$-\text{Pt}^{2+}-\text{Pt}^{3+}-$], charge-density-wave (CDW) states [$-\text{Pt}^{2+}-\text{Pt}^{2+}-\text{Pt}^{3+}-\text{Pt}^{3+}-$] and alternate charge polarization (ACP) state [$-\text{Pt}^{2+}-\text{Pt}^{3+}-\text{Pt}^{3+}-\text{Pt}^{2+}-$], due to the direct *M-M* bonding in 1D chain. The former two states are paramagnetic states with the unpaired electron residing on the Pt^{3+} ions ($S=1/2$), whereas latter states are nonmagnetic with the lattice dimerizations. In the complexes with (pop)-ligands (pop= $\text{P}_2\text{H}_2\text{O}_5^{2-}$), the electronic state is controlled by the counteraction or crystalline water, forming AV, CDW, and CP states as the distance of the metal dimer, $d_{\text{Pt-I-Pt}}$, increases [1].

In this study, we apply the ESR technique, which has been a powerful tool in determining the valence states of the Pt ions in *MMX*-chain complexes [2], to a newly synthesized complex $\text{K}_2(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Pt}_2(\text{pop})_4\text{I}]\cdot 4\text{H}_2\text{O}$ (**1**) which includes two kinds of counteractions. This complex shows ACP-like structural characteristics in the X-ray analyses, which have never been observed in the (pop)-ligand systems. Moreover, dehydration of this complex induces a remarkable and reversible change of the electronic state into a possible CDW state, whereas a small amount of paramagnetic contribution has been detected by the ^{31}P NMR spectra. Fig. 1 shows the spin susceptibility of complex (**1**) before and after dehydration, caused by evacuating the sample tube, shown by open and solid circles, respectively. The dashed curves show the fittings by the Curie law. Inset shows the change of the ESR signal by dehydration. In the dehydrated complex, we observe a remarkable enhancement of the spin susceptibility from the Curie law for high temperatures caused by the activation of Pt^{3+} spins, showing a good agreement with the NMR results. This implies the crossover of the electronic state into a possible AV state for high temperatures, considering the short $d_{\text{Pt-I-Pt}}$ in the dehydrated complex.

[1] H. Matsuzaki *et al.*, Phys. Rev. Lett. 90, (2003) 046401.

[2] H. Tanaka *et al.*, Phys. Rev. B 73, (2006) 245102; Phys. Rev. B 78, (2008) 033104.

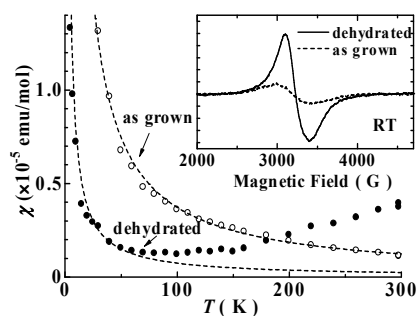


Fig. 1. Temperature dependences of spin susceptibility before and after dehydration. Inset shows the ESR signals at RT.