A platinum-dimer based metal–organic framework having a pre-installed cationic guest for proton conduction

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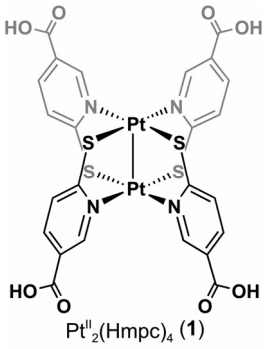
Solid-state proton conductors have been of particular interest of researchers because of its potential use for fuel cells. Among them, metal–organic frameworks (MOFs), which have networked structure made from metal ions and organic ligands have provided diverse research platform for proton conduction in recent years. In this work, we have newly synthesized a novel MOF based on the divalent platinum dimer complex with free carboxyl group, $Pt^{II}_2(Hmpc)_4$ (**1**; H_2mpc = 6-mercaptopyridine-3-carboxylic acid).



$Pt^{II}_2(Hmpc)_4$ (**1**)

Title MOF (**2**) was synthesized according to following reaction:

1 + Cl_2 + $CoCl_2 \cdot 6H_2O$ →$[Pt^{III}_2(mpc)_4Cl_2Co^{III}(DMA)(HDMA)\cdot solvent]_n$ (**2**)

Figure 1 shows the X-ray crystal structure of **2** at 100 K. **2** crystallizes in monoclinic space group $P2_1/n$ (a = 17.822(2), b = 9.0411(8), c = 30.291(3) Å, β = 106.966(1)°, V = 4668.4(8) Å^3). In this framework, Co(III) ions are coordinated with three fourth of the carboxyl groups of the platinum dimer unit to form the 2D-layer structure. In addition, a dimethylammonium cation (HDMA) is trapped as a guest inside the pore through hydrogen bonding network with free carboxyl group of the ligand. Alternate current impedance measurement revealed a high proton conduction of 10^{-3} Scm^{-1}. Details are presented.

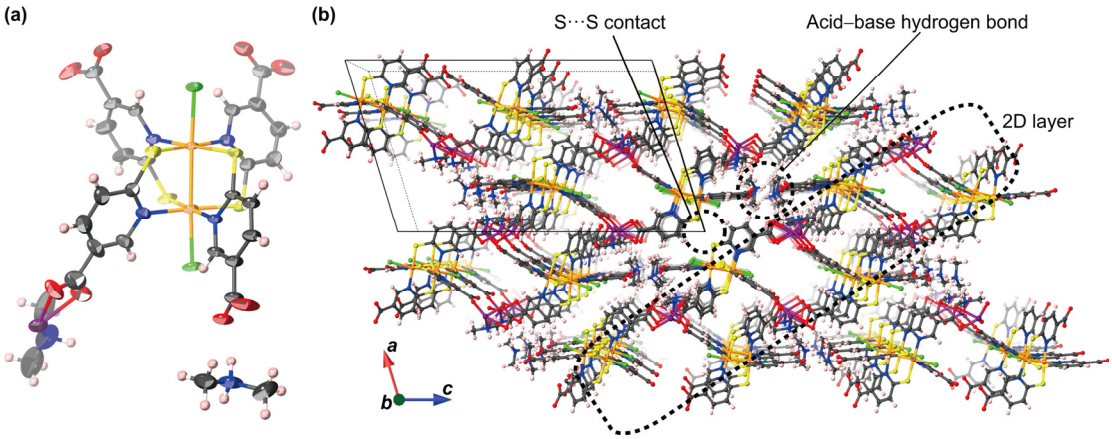


Figure 1. Crystal structure of **2** at 100 K. (a) Asymmetric unit of **2**. (b) 3D packing structure along the *b*-axis. Platinum, chlorine, carbon, nitrogen, oxygen, and hydrogen atoms are shown in orange, green, grey, blue, red and pink, respectively.

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