Electronic Supplementary Information for

Three Dimensional Porous Hofmann Clathrate $[M^{II}Pt^{II}(CN)_4]_\infty$ (M = Co, Ni)
Synthesized by Using Postsynthetic Reductive Elimination

Takuro Okamora, a Bin Wu, a,b Hiroaki Iguchi, a Brian K. Breedlove, a Masahiro Yamashita, a,b,d Wataru Kosaka, c Hitoshi Miyasaka, c Shinya Takaishi, *, a

aDepartment of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aza-aoba, Aramaki, Sendai 980-8578, Japan
bAdvanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan
cInstitute for Materials Research, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan
dSchool of Materials Science and Engineering, Nankai University, Tianjin 300350, China.

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I. Materials.

K$_2$PtCl$_4$ was obtained by Mitsuwa Chemicals Co., Ltd, and used as received. KCN, AgNO$_3$, Co(NO$_3$)$_2$·6H$_2$O, NiBr·3H$_2$O, and Br$_2$ were obtained by Wako Pure Chemical Industries, Ltd, and used as received.

II. Characterization and Instrumental Procedures

Single-crystal X-ray diffraction collected on Bruker APEX-II diffractometer with an APEX II CCD detector and JAPAN thermal Engineering Co., Ltd Cryo system DX-CS190LD. N$_2$ isotherm at 77 K was performed using microtrac Bell sorp Max. Thermogravimetric analysis was performed using Shimadzu DTG-60H under a N$_2$ gas flow (50 ml/min) or aerobic condition with a sweep rate of 1 K/min unless otherwise noted. Powder X-ray diffraction (PXRD) of 1, 1', 2, and 2' were measured in air (0–2θ scan) using Bruker PHASER diffractometer with Cu Kα radiation source. PXRD of 1' and 2' were measured in dry N$_2$ atmosphere (transmission geometry with a sealed capillary) using Rigaku RINT2000 diffractometer. Magnetic susceptibilities were measured using Quantum Design MPMS-5 SQUID magnetometer under 1000 Oe DC field. UV-Vis-NIR spectra were measured using Shimadzu UV-3100PC spectrometer with an integrating sphere unit. Diffuse reflectance spectra were transformed to absorbance spectra using Kubelka-Munk function. FT-IR spectra were measured using Jasco FT-IR 4200 spectrometer with ATR unit. ICP-OES measurements were performed in Shimadzu ICPE-9000 installed at the research and analytical center for giant molecules in Tohoku university. Emissions at 228.616(1), 231.604(1) and 214.423(1) nm are used for Co, Ni and Pt elements, respectively.

III. Syntheses

Synthesis of 1
To 5 ml of aqueous solution of K$_2$PtCl$_4$ 415 mg (1.00 mmol) was added KCN 260 mg (4.00 mmol) and stirred until the solution became colorless. AgNO$_3$ 679 mg (4.00 mmol) was added and stirred ca. 24 h under dark. The precipitate (AgCl) was filtered off by celite filtration. Approximately 250 mg (~1.5 eq) of Br$_2$ was added and stirred for 30 min, and then heated to 50 °C for another 30 min to remove excess of Br$_2$ in the solution. After cooling, to the solution was added 5 ml of 0.2 M aqueous solution of Co(NO$_3$)$_2$·6H$_2$O and stand overnight. Obtained orange color crystals of [Co(H$_2$O)$_2$Pt(CN)$_4$Br$_2$]$_{\infty}$ 10/3(H$_2$O) (1) were collected by filtration. (Yield 507 mg, 0.83 mmol, 83 %)

Synthesis of 2
To 5 ml of aqueous solution of K₂PtCl₄ 415 mg (1.00 mmol) was added KCN 260 mg (4.00 mmol) and stirred until the solution became colorless. AgNO₃ 679 mg (4.00 mmol) was added and stirred ca. 24 h under dark. The precipitate (AgCl) was filtered off by celite filtration. Approximately 250 mg (~1.5 eq) of Br₂ was added and stirred for 30 min, and then heated to 50 °C for another 30 min to remove excess of Br₂ in the solution. After cooling, to the solution was added 5 ml of 0.2 M aqueous solution of NiBr₂·3H₂O and stand overnight. Obtained yellow color crystals of [Ni(H₂O)₂Pt(CN)₄Br₂]ₓ · 8/3(H₂O) (2) were collected by filtration. (Yield 534 mg, 0.89 mmol, 89%)
Fig. S1 Experimental PXRD patterns of Hofmann clathrate synthesized by mixing 0.2 M aquesous K$_2$Pt(CN)$_4$ and 0.2 M Co(NO$_3$)$_2$ (a) or NiBr$_2$ (b), respectively. The PXRD patterns was well indexed by assuming the following parameters, Tetragonal, $a = 7.41$ Å, $c = 7.99$ Å for (a) and Tetragonal, $a = 7.33$ Å, $c = 8.00$ Å for (b), by using DASH software containing in the CSD software package. Fig. 1(c) shows the PXRD pattern simulated from the crystal structure shown in the inset of Fig. 1(c). Color code; White: Pt, Gray: C, Blue: N, Green, Ni. Red: O.
Table S1 Crystallographic data of 1 (rt and 70 °C) and 2 (rt)

<table>
<thead>
<tr>
<th></th>
<th>1 (rt)</th>
<th>1 (70 °C)</th>
<th>2 (rt)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>C₄Br₂Co₁N₄O₅Pt₃</td>
<td>C₁₂Br₆Co₁₂N₁₂O₁₄Pt₃</td>
<td>C₁₂Br₆N₁₂N₁₂O₁₄Pt₃</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>603.17</td>
<td>1777.67</td>
<td>1176.95</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Trigonal</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>R-3m</td>
<td>Pm-3m</td>
<td>Pm-3m</td>
</tr>
<tr>
<td><strong>Crystal size (mm³)</strong></td>
<td>0.20×0.20×0.20</td>
<td>0.20×0.20×0.20</td>
<td>0.20×0.20×0.20</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>14.997(3)</td>
<td>10.4037(8)</td>
<td>10.338(9)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>17.444(3)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>3397.6(17)</td>
<td>1126.1(3)</td>
<td>1105(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>9</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
<td>293(2)</td>
<td>343(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td><strong>μ (mm⁻¹)</strong></td>
<td>15.652</td>
<td>15.741</td>
<td>16.197</td>
</tr>
<tr>
<td><strong>ρcalcd</strong></td>
<td>2.607</td>
<td>2.612</td>
<td>2.695</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>2379</td>
<td>793</td>
<td>804</td>
</tr>
<tr>
<td><strong>GOF on F²</strong></td>
<td>1.170</td>
<td>1.140</td>
<td>1.115</td>
</tr>
<tr>
<td><strong>R₁, wR₂ [I &gt; 2σ]</strong></td>
<td>0.0376, 0.0818</td>
<td>0.0199, 0.0530</td>
<td>0.0292, 0.0646</td>
</tr>
<tr>
<td><strong>R₁, wR₂ [all data]</strong></td>
<td>0.0395, 0.0824</td>
<td>0.0209, 0.0537</td>
<td>0.0347, 0.0662</td>
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<tr>
<td><strong>Reflns. measured</strong></td>
<td>1389</td>
<td>340</td>
<td>326</td>
</tr>
<tr>
<td><strong>CCDC No.</strong></td>
<td>1503125</td>
<td>1503126</td>
<td>1503124</td>
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Table S2 Experimental and calculated data of elemental analyses

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Br</th>
<th>Co</th>
<th>Ni</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>found for 1</strong></td>
<td>8.007</td>
<td>1.757</td>
<td>9.135</td>
<td>25.84</td>
<td>9.47</td>
<td>-</td>
<td>31.67</td>
</tr>
<tr>
<td>calcd. for C_4H_{10.67}Br_2Co_1N_4O_5.33Pt_1</td>
<td>7.83</td>
<td>1.75</td>
<td>9.13</td>
<td>26.03</td>
<td>9.60</td>
<td>-</td>
<td>31.77</td>
</tr>
<tr>
<td><strong>found for 1''</strong></td>
<td>9.786</td>
<td>3.251</td>
<td>11.075</td>
<td>0.74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calcd. for C_4H_{16}Co_1N_4O_5Pt_1</td>
<td>9.57</td>
<td>3.21</td>
<td>11.16</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>found for 2</strong></td>
<td>7.983</td>
<td>1.916</td>
<td>8.964</td>
<td>25.49</td>
<td>-</td>
<td>9.43</td>
<td>32.29</td>
</tr>
<tr>
<td>calcd. for C_4H_{9.33}Br_2Ni_1N_4O_4.67Pt_1</td>
<td>7.98</td>
<td>1.56</td>
<td>9.31</td>
<td>26.56</td>
<td>-</td>
<td>9.75</td>
<td>32.42</td>
</tr>
<tr>
<td><strong>found for 2''</strong></td>
<td>10.142</td>
<td>2.642</td>
<td>11.278</td>
<td>0.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calcd. for C_4H_{14}Co_1N_4O_5Pt_1</td>
<td>9.93</td>
<td>2.92</td>
<td>11.58</td>
<td>0.00</td>
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</table>
Fig. S2 Calculated void space of 1 (upper) and 1' (lower) with a probe radius of 1.4 Å (left), 1.65 Å (middle), and 1.82 Å (right), respectively.
Fig. S3 Magnetic susceptibility of 1, 1', 1", 2, 2' and 2" under 1000 Oe.
Discussion about the magnetic susceptibility

The magnetic susceptibilities of \( 2, 2', \) and \( 2'' \) were fitted by \( S = 1 \) van Vleck’s equation as follows,

\[
\chi_{iso} = \frac{2Ng^2\mu_B^2}{3kT} \left[ \frac{2kT \exp(-D/kT)}{D} - \frac{2kT \exp(-D/kT)}{1 + 2\exp(-D/kT)} \right]
\]

where \( N, \mu_B \) and \( k \) represent Avogadro constant, Bohr magneton and Boltzmann constant, respectively. The best fit parameters are \( g = 2.18 \) and \( D = +13.1 \) K for \( 2 \) (red curve), \( g = 1.99 \) and \( D = +34.2 \) K for \( 2' \) (green curve), and \( g = 2.16 \) and \( D = +15.0 \) K for \( 2'' \) (blue curve). For \( 1, 1', \) and \( 1'' \), no modeling was conducted due to overparametrization. The magnetic susceptibility of \( 1 \) and \( 1'' \) (\( 2 \) and \( 2'' \)) are mostly identical, suggesting that Co (Ni) ion is in the same coordination geometry. On the other hand, the susceptibility of \( 1' \) and \( 2' \) is different from those of \( 1 \) and \( 2 \), respectiliby, indicating that the local coordination environment chaged by the removal of the axial water molecules.
Fig. S4 FT-IR spectra of 1, 1', 1'', 2, 2', and 2''.
Fig S5 Calculated IR spectra of (a) $[\text{Pt(CN)}_4\text{Br}_2]^{2-}$ and (b) $[\text{Pt(CN)}_4\text{Br}_2]^{2-}$. For the DFT calculation, structural optimization was performed before frequency calculation with LANL2DZ basis set. The peaks 2165.09 and 2115.42 cm$^{-1}$ are assigned to CN stretching mode.
Fig. S6 TG/DTA of 1 and 2 up to 600°C (5°C/min) under aerobic condition. The exothermic weight loss at around 400 °C and 500 °C in 1 and 2, respectively, corresponds to the thermal decomposition. The final product was a mixture of Pt and Co₃O₄ in the case of 1 and NiO in the case of 2, confirmed by using powder X-ray diffraction (PXRD) patterns of the decomposed compounds (Fig. S7).
Fig. S7 PXRD patterns of 1 and 2 after heating up to 600°C in air together with simulated patterns of Pt, Co$_3$O$_4$ and NiO for comparison.
Fig. S8 UV-vis-NIR spectra of 1, 1', 1", 2, 2' and 2" together with those of aqueous solution of K$_2$Pt(CN)$_4$Br$_2$ and K$_2$Pt(CN)$_4$. 

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\frac{\text{Absorbance (Kubelka-Munk function)}}{\text{a.u.}}}{\frac{\text{Wavelength / nm}}{}}
**Discussion about UV-vis-NIR spectra**

Comparing the spectra of 1, 1', 1'', 2, 2', and 2'' as well as those of aqueous K$_2$Pt(CN)$_4$ and K$_2$Pt(CN)$_4$Br$_2$, the intense peaks at the UV ($\lambda < 400$nm) region can be attributable to Pt species because the spectrum shape depends on the oxidation state of Pt center and independent of M' (M' = Co or Ni). Thus, we have normalize the absorbance of the compounds by using peak heights of them in UV region. On the other hand, the peaks in the vis-NIR region (400nm < $\lambda$ < 1500 nm) can be assigned to d-d transition of M' ions because no prominent peak was observed in the aqueous solution of K$_2$Pt(CN)$_4$ and K$_2$Pt(CN)$_4$Br$_2$. 1 and 1'' (or 2 and 2'') showed quite similar spectra at vis-NIR region, reflecting the similar coordination environment of M' ions between them. The spectra of 1' and 2' is similar with those of 1'' and 2'' in the UV region, respectively, whereas quite different in the vis-NIR region, which can be explained by the difference in the local coordination environment of M' ions. The larger absorbance in 1' than 1 or 1'' should be due to the relaxation of Laporte rule in the tetrahedral geometry.
Fig. S9 Simulated and experimental PXRD patterns of 1 and 2 at room temperature.
Fig. S10. Time evolution of the weight loss in 1 at 100°C under N₂ atmosphere.
**Discussion about the local coordination environment of anhydrous 1' and 2'**

Here we discuss the local coordination environment of 1' (M' = Co) and 2' (M' = Ni). For 2', PXRD pattern did not change except for the peak intensity by removing axial water molecules, indicating that the MOF skeleton does not change. Thus, we can simply conclude that Ni ion in 2' have a square planer geometry. This is also supported by the finding that the yellow color of 2' is typical in the square planer Ni^{2+} complexes.

On the other hand, consideration of the local environment of 1' is not straightforward because of significant change in the PXRD pattern as well as lost of long range lattice ordering by removing axial water molecules. However, FT-IR spectrum of 1' showed a clear single peak at 2186 cm\(^{-1}\) (Fig. S4), suggesting that 1' has a uniform local structure. In addition, UV-vis spectrum showed much larger absorbance was observed. This suggests that relaxation of Laporte's selection rule, which usually occurs by d-p hybridization in the tetrahedral geometry. Especially, the peak at 585 nm with a shoulder peak at 540 nm (right fig.) is quite similar with the UV-vis spectrum of Co[Au(CN)\(_2\)]\(_2\) with a tetrahedral coordination geometry (590 nm, 550 nm(sh)).\(^\text{S2}\) Thus, we estimated that Co ion is in tetrahedral coordination geometry. Transformation from square planer to tetrahedral geometry in the framework should accompanied by the Co-N bond cleavage and reformation, causing poor crystallinity of 1'.
Reference
