

Systematic Structural Control of Multichromic Platinum(II)-Diimine Complexes Ranging from Ionic Solid to Coordination Polymer

Atsushi Kobayashi,* Hirofumi Hara, Tsubasa Yonemura, Ho-Chol Chang and Masako Kato*

Division of Chemistry, Faculty of Science, Hokkaido University, North-10 West-8, Kita-ku, Sapporo
060-0810, Japan

Supporting Information

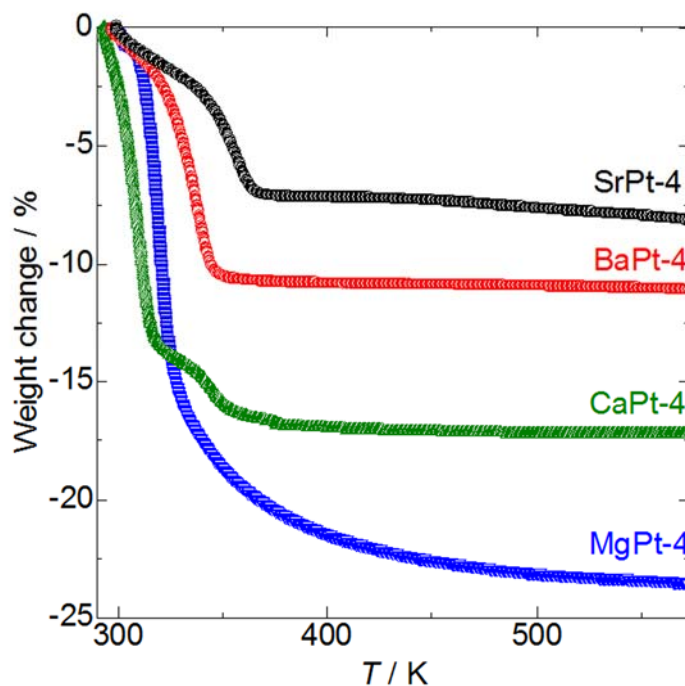


Figure S1. TG curves of **MgPt-4·9H₂O**, **CaPt-4·6H₂O**, **SrPt-4·3H₂O** and **BaPt-4·5H₂O**. (1 K/min heating, Ar flow rate: 300 ml/min)

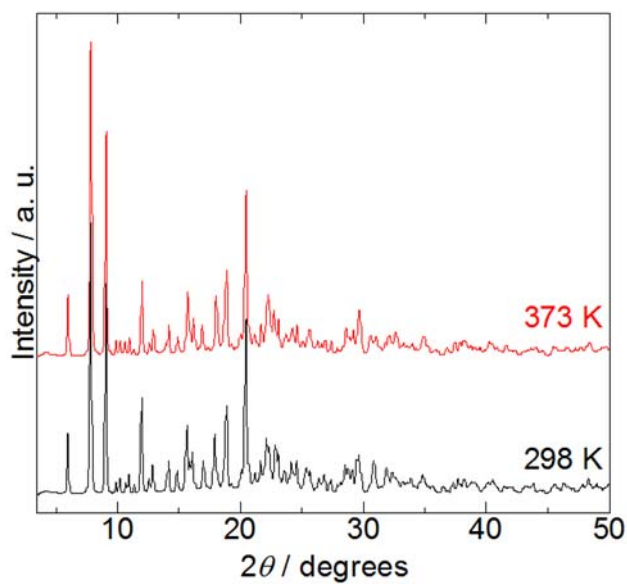


Figure S2. PXRD patterns of **BaPt-4.5H₂O** at 298 (black) and 373 K (red). $\lambda = 1.200(1)$ Å.

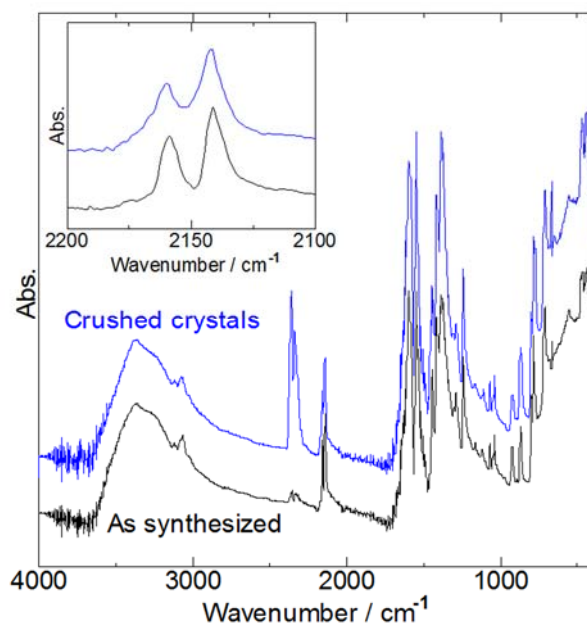


Figure S3. IR spectra of as synthesized **CaPt-4.6H₂O** (black) and the crushed crystals (blue). Inset shows the expansion of the $\nu(\text{C}\equiv\text{N})$ vibration band region around 2150 cm⁻¹.

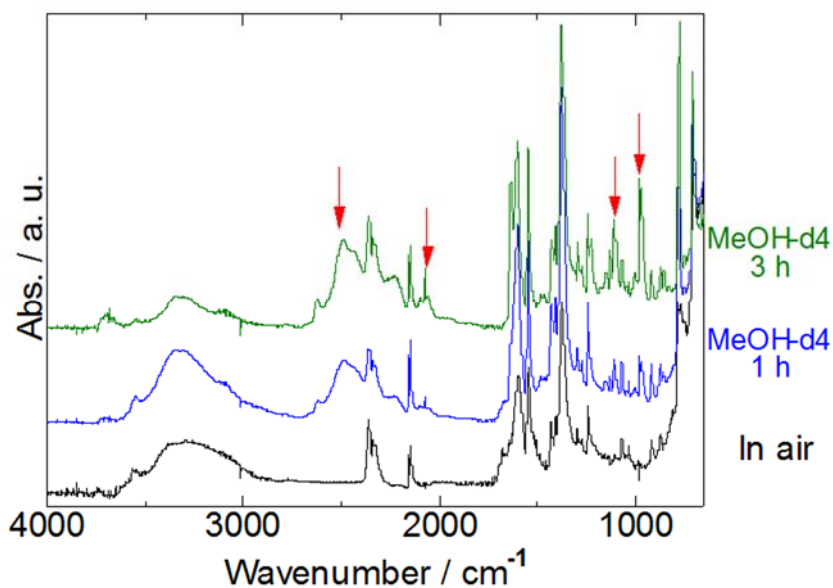


Figure S4. IR spectral change of as-synthesized **MgPt-4.9H₂O** (black) under exposure to methanol-d₄ vapour at room temperature. Red arrows indicate the band assigned to the adsorbed methanol-d₄.

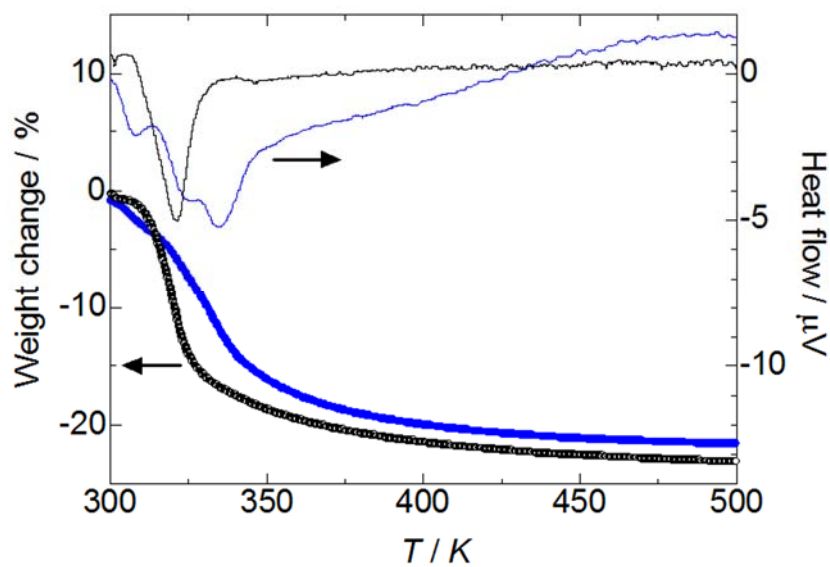


Figure S5. TG-DTA analyses of **MgPt-4.9H₂O** (black) before and (blue) after exposing it to MeOH vapour at room temperature for 1 day.

Table S1. Selected bond lengths of the metalloligand [Pt(CN)₂(4,4'-dcbpy)]²⁻.

| | Na₂Pt-4· 5H₂O^a | MgPt-4· 9H₂O | CaPt-4· 6H₂O | SrPt-4· 3H₂O | BaPt-4· 5H₂O |
|-----------------------|--|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Pt1-N1 | 2.047(4) | 2.043(6) | 2.042(4) | 2.011(12) | 2.053(6) |
| Pt1-N2 | 2.047(4) | 2.058(9) | 2.050(4) | 2.042(15) | 2.034(5) |
| Pt1-C13 | 1.944(5) | 1.960(11) | 1.946(5) | 1.97(2) | 1.944(7) |
| Pt1-C14 | 1.955(4) | 1.961(8) | 1.948(5) | 1.966(16) | 1.953(8) |
| M-O1 (carboxylate) | - | 2.084(7) | 2.355(3) 2.618(3) | 2.555(12) 2.765(11) | 2.748(5) 2.873(5) |
| M-O2 (carboxylate) | - | - | 2.489(4) | 2.615(11) 2.707(11) | 2.743(5) 2.876(5) |
| M-O3 (carboxylate) | - | - | 2.537(3) | 2.734(12) | 2.906(5) |
| M-O4 (carboxylate) | 2.344(4) | - | 2.505(3) | 2.652(14) | 2.813(5) |
| M-O5 (water) | 2.396(3) 2.392(4) | 2.057(7) | 2.387(3) | 2.615(14) | 2.780(5) |
| M-O6 (water) | 2.551(5) 2.370(4) | 2.089(8) | 2.417(3) | 2.632(14) | 2.819(5) |
| M-O7 (water) | 2.404(4) | 2.074(9) | 2.409(4) | - | - |
| M-O8 (water) | 2.435(3) 2.394(4) | 2.075(8) | - | - | - |
| M-O9 (water) | 2.419(3) 2.492(4) | 2.076(11) | - | - | - |
| M-N3(cyano) | 2.553(4) | - | - | - | - |
| M-N4(cyano) | 2.618(4) | - | - | 2.675(14) | 2.918(6) |
| N1-C1 | 1.348(6) | 1.336(15) | 1.338(7) | 1.41(2) | 1.341(9) |
| N1-C5 | 1.377(6) | 1.368(13) | 1.350(6) | 1.37(2) | 1.349(9) |
| N2-C6 | 1.363(6) | 1.351(10) | 1.365(6) | 1.37(2) | 1.381(10) |
| N2-C10 | 1.357(6) | 1.344(14) | 1.335(7) | 1.33(2) | 1.331(9) |
| N3-C13 | 1.146(7) | 1.124(16) | 1.141(6) | 1.11(2) | 1.150(10) |
| N4-C14 | 1.151(6) | 1.137(12) | 1.140(7) | 1.14(2) | 1.147(11) |
| O1-C11 | 1.246(6) | 1.262(11) | 1.243(6) | 1.21(2) | 1.258(9) |

| | | | | | |
|--------|----------|-----------|----------|-----------|-----------|
| O2-C11 | 1.272(6) | 1.243(12) | 1.263(6) | 1.224(19) | 1.262(9) |
| O3-C12 | 1.255(5) | 1.241(10) | 1.251(6) | 1.23(2) | 1.256(10) |
| O4-C12 | 1.241(5) | 1.308(13) | 1.253(6) | 1.25(2) | 1.258(10) |
| C1-C2 | 1.378(7) | 1.371(12) | 1.367(8) | 1.38(2) | 1.372(11) |
| C2-C3 | 1.390(6) | 1.389(15) | 1.389(7) | 1.39(2) | 1.391(10) |
| C3-C4 | 1.390(6) | 1.391(15) | 1.410(7) | 1.36(2) | 1.403(10) |
| C3-C11 | 1.508(7) | 1.525(11) | 1.499(7) | 1.55(2) | 1.489(11) |
| C4-C5 | 1.370(7) | 1.380(11) | 1.380(7) | 1.41(2) | 1.388(11) |
| C5-C6 | 1.478(6) | 1.475(15) | 1.477(7) | 1.42(2) | 1.478(10) |
| C6-C7 | 1.398(6) | 1.404(15) | 1.376(6) | 1.38(2) | 1.389(10) |
| C7-C8 | 1.375(6) | 1.388(15) | 1.382(7) | 1.39(2) | 1.391(10) |
| C8-C9 | 1.385(6) | 1.384(12) | 1.385(7) | 1.37(2) | 1.386(11) |
| C8-C12 | 1.536(6) | 1.508(17) | 1.526(7) | 1.57(2) | 1.516(11) |
| C9-C10 | 1.384(6) | 1.385(17) | 1.363(7) | 1.37(2) | 1.378(10) |

^a Ref. 1

Elemental analyses of as synthesized and crushed MgPt-4·9H₂O

Calcd. for [Mg(H₂O)₅][Pt(CN)₂(4,4'-dcbpy)]·4H₂O : C 24.88, H 3.58, N 8.29.

Found for as synthesized crystals : C 24.41, H 3.39, N 8.35.

Found for the crushed sample: C 24.43, H 3.22, N 8.32.

Elemental analysis of the sample obtained from exposure MgPt-4·9H₂O to MeOH vapour

Calcd. for {Mg[Pt(CN)₂(4,4'-dcbpy)]·6H₂O·MeOH} : C 27.56, H 3.39, N 8.57.

Found : C 27.31, H 2.99, N 8.39.

Reference

1) A. Kobayashi, T. Yonemura, M. Kato, *Eur. J. Inorg. Chem.* 2010, 2465-2470.