

Supporting Information

Methylated Molybdoplatinate — Its Unexpected Ability to Absorb Methanol

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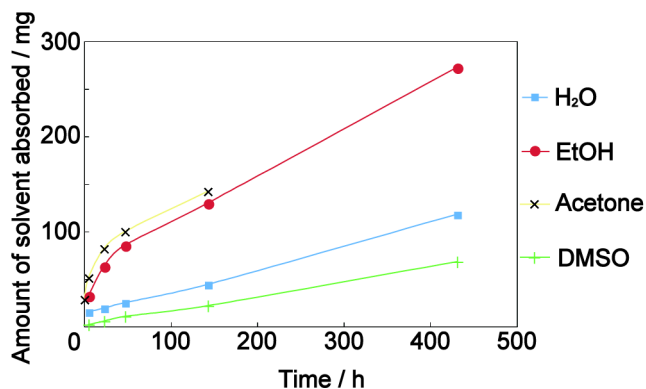


Figure S1. Absorption of different polar solvents by 100 mg of **2**.

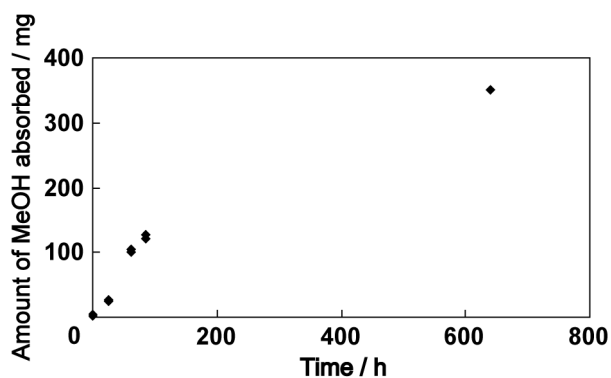


Figure S2. Absorption of MeOH by 100 mg of TBA₄**1**·6MeOH.

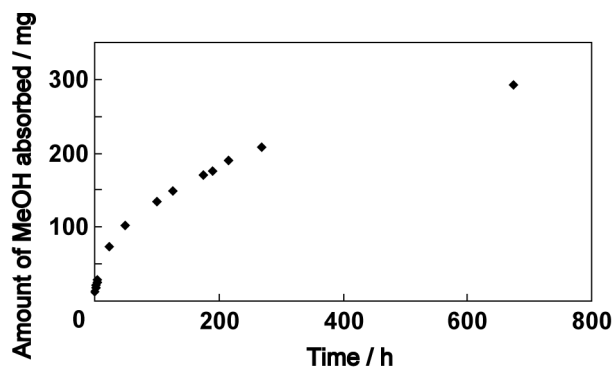


Figure S3. Absorption of MeOH by 100 mg of TBA₇**3**·8H₂O.

Description of the disorder observed in the crystal of $\text{TBA}_4\mathbf{1} \cdot 6\text{MeOH}$

An asymmetric unit contains two tetrabutylammonium (TAB) cations with their central nitrogen atoms labeled as N1 and N2. One of the four terminal methyl groups of the TBA cation centered by N2 is disordered over two sites (labeled as C32A and C32B). Their site occupancies are 0.620(13) and 0.380(13), respectively. There are three independent methanol molecules of crystallization in an asymmetric unit. They are labeled as C33 and O13, C34 and O14, and C35 and O15. The methanol molecules labeled as C35 and O15 is disordered over two sites. The major part consist of C35A and O15A with the site occupancies of 0.812(6) and the minor part consist of C35B and O15B with the site occupancies of 0.188(6).

Description of the disorder observed in the crystal of $\text{TBA}_7\mathbf{3} \cdot 8\text{H}_2\text{O}$

An asymmetric unit contains eight independent tetrabutylammonium (TBA) cations with their central nitrogen atoms labeled as N1-N8. TBA cations centered by N1-N6 are well apart from the crystallographic symmetry elements and thus show site occupancies of 1.0. Only two terminal methyl groups are disordered over respective two sites, C48 of TBA centered by N3 and C96 of TBA centered by N6. They are labeled as C48A, C48B, C96A and C96B and show occupancies of 0.653(18), 0.347(18), 0.63(3) and 0.37(3), respectively. On the other hand, TBA cations centered by N7 and N8 are located very close to inversion centers [at (0, 0, 1/2) and (1/2, 1/2, 0), respectively] and thus show site occupancies of 0.5. Therefore, total number of TBA cations in an asymmetric unit is $6+0.5 \times 2=7$.

Electron density around the inversion center at (0, 0, 1/2) show three independent and thus total of six branches with the shape similar to a double dagger. It was successfully interpreted as two TBA cations that are slightly displaced to each other and partially overlapping. They are related by the inversion center at (0, 0, 1/2). The point of intersection of the one of the horizontal lines and the vertical line of double dagger was interpreted as the nitrogen atom of this TBA and

labeled as N7. The horizontal lines passing through N7 were interpreted as two butyl groups, namely C97-C98-C99-C100 and C101-C102-C103-C104. For these 8 atoms (C97-C104), the site occupancies were fixed to 0.5 and the fractional coordinates were freely refined. The vertical line going up was assigned as a butyl group and labeled as C105-C106-C107-C108. The vertical line going down was assigned as the last butyl group and labeled as C109-C110-C111-C112. C109, C110, C111 and C112 are related to N7, C105, C106 and C107 by the inversion center at (0, 0, 1/2). For these 8 atoms (N7, C105-C107 and C109-C112), the site occupancies were fixed to 0.5 and the fractional coordinates were constrained to follow the center of symmetry. Since there is no atom at the position related to C108 by the inversion center at (0, 0, 1/2), the fractional coordinate of C108 was freely refined. Its occupancy was fixed to 0.5. In CIF, `_atom_site_disorder_group` for these atoms are set to -1 (negative value for this entry means that the symmetry operation does not apply to the relevant disorder group). The drawing of the molecule together with its symmetry related component is shown in Figure S4.

Electron density around the inversion center at (1/2, 1/2, 0) has a triply fused hexagonal motifs at its center. It was also successfully interpreted as two TBA cations that are located close to and are related by the inversion center. In CIF, `_atom_site_disorder_group` for these atoms are set to -2. The drawing of the molecule together with its symmetry equivalent one is shown in Figure S5.

Water molecules in this crystal are also disordered. A group of 4 water molecules out of 8 water molecules in the asymmetric unit are located close to the polyoxometalate centered by Pt02. Among them, OW1, OW2 and OW4 are well separated from other components and were successfully refined with their site occupancy of 1.0. OW3A and OW3B are close to each other and their site occupancies were refined with the constraint that the sum of them is fixed to 1.0. Their site occupancies are 0.503(18) and 0.497(18). In CIF, `_atom_site_disorder_group` for these atoms are set to 7 and 8.

The remaining 4 water molecules are located close to the polyoxometalate centered by Pt01.

Among them, OW5 is well separated from other components and was successfully refined with their site occupancy of 1.0. The remaining water molecules are disordered over two sites, which are grouped into two sets, first comprising of OW6A, OW7A and OW8A and the second comprising of OW6B, OW7B and OW8B. Although interatomic distances are 1.975 Å for OW6A-OW6B, 1.729 Å for OW7A-OW7B, 2.524 Å for OW8A-OW8B, 2.120 Å for OW6A-OW7B and 2.194 Å for OW7A-OW6B, there are no contacts shorter than 2.8 Å within each disorder group after this disorder assignment. The site occupancies are 0.555(11) and 0.445(11) and _atom_site_disorder_group are set to 9 and 10 for the atoms labeled with A and B, respectively.

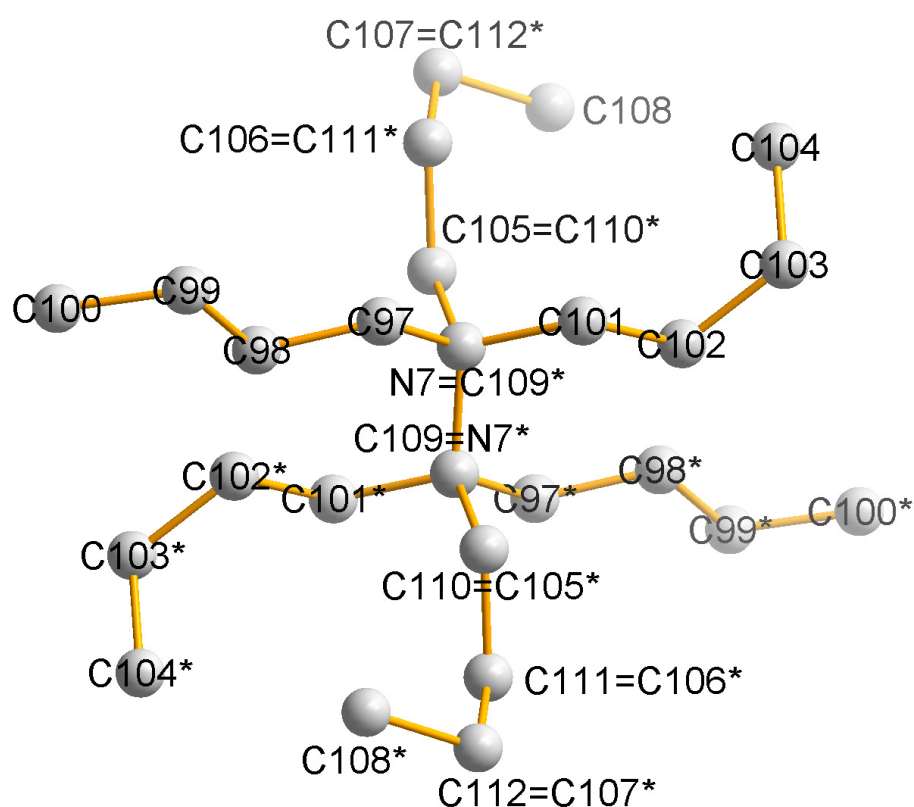


Figure S4. Drawing of the tetrabutylammonium cation centered by N8 and its symmetry equivalent molecule. Atoms labeled with # are related to those labeled without # by the inversion center. Contacts within 2.0 Å between the molecules are shown in broken lines.

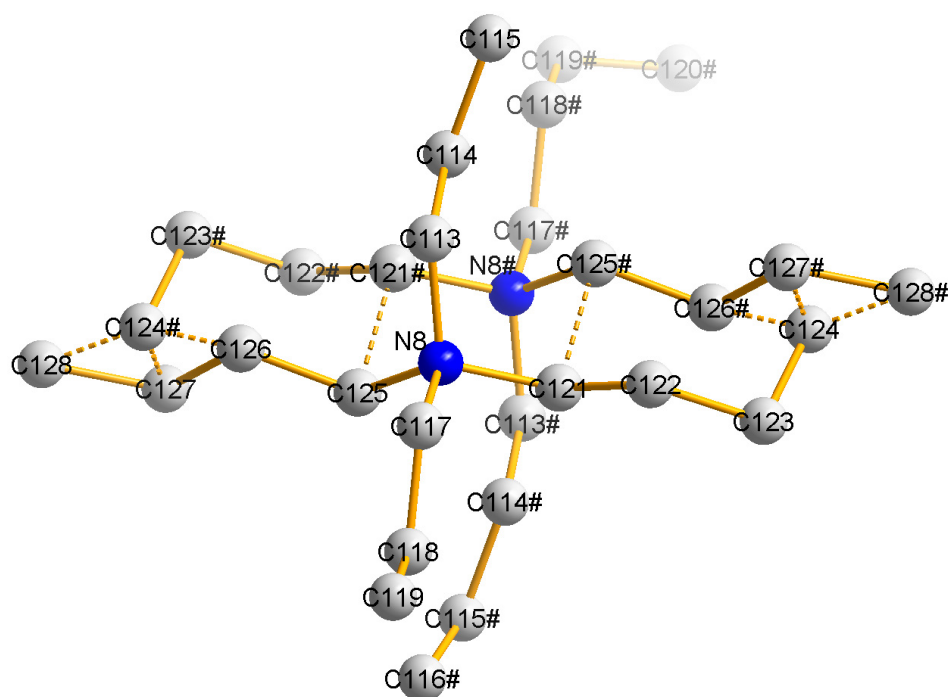


Figure S5. Drawing of the tetrabutylammonium cation centered by N8 and its symmetry equivalent molecule. Atoms labeled with # are related to those labeled without # by the inversion center. Contacts within 2.0 Å between the molecules are shown in broken lines.