

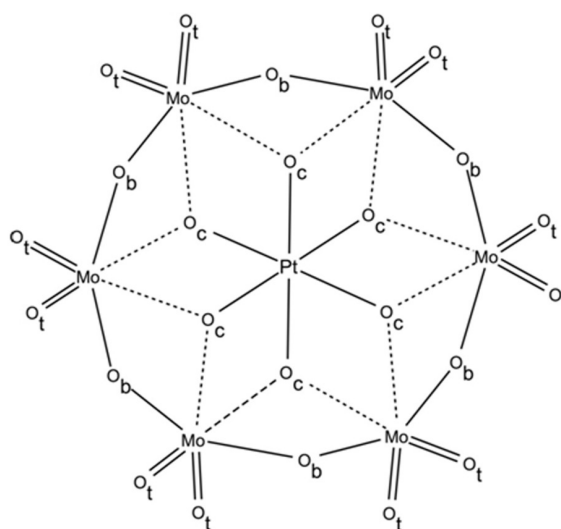
# Studies of Robust, Hydrogen-Bonded Polyanion Aggregates

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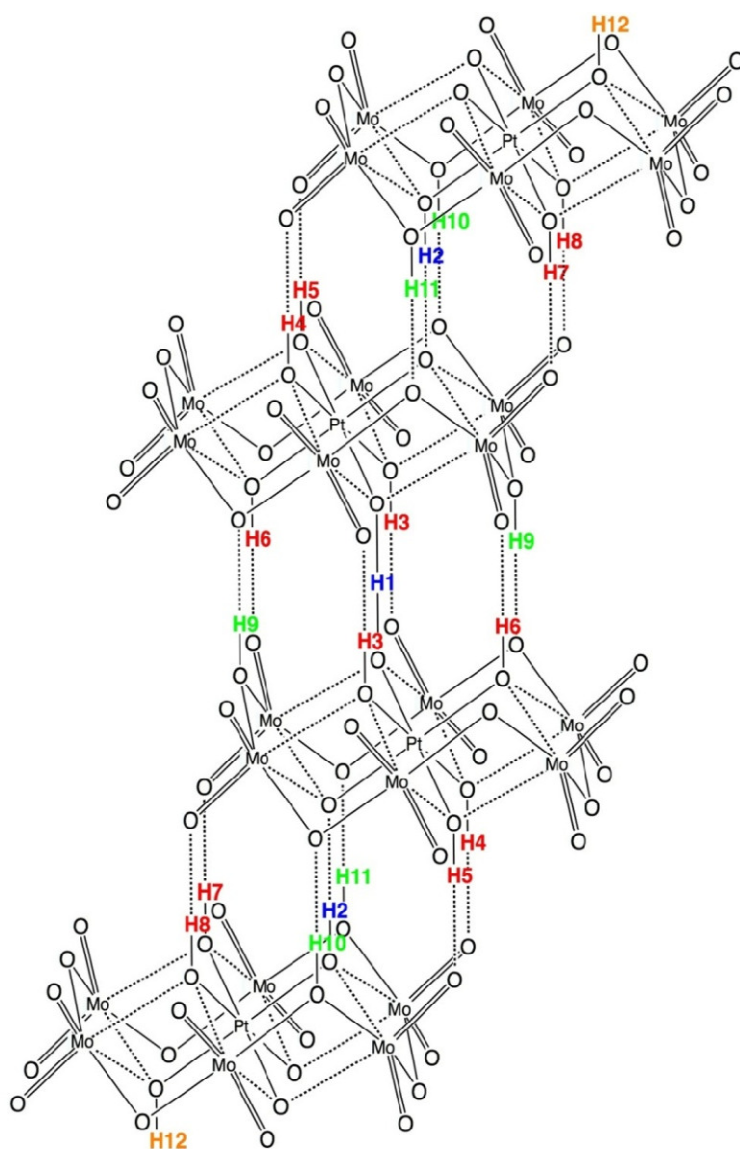
The lability and/or instability of hydrogen-bonded inorganic aggregates studied to date have in general<sup>1</sup> precluded structural characterization in solution except at extremely low temperature<sup>2</sup>. In contrast, the solution chemistry of stable synthetic and natural organic hydrogen-bonded aggregates such as supramolecular polymers<sup>3</sup> and G-quadruplexes<sup>4</sup> is well understood. The present work focuses on three remarkably stable hydrogen-bonded inorganic aggregates based on protonated  $[\text{PtMo}_6\text{O}_{24}]^{8-}$  polyanion units (see Figure 1).



**Figure 1:** The  $[\text{PtMo}_6\text{O}_{24}]^{8-}$  anion.

The tetrameric platinomolybdate  $[(\text{PtMo}_6\text{O}_{24})_4\text{H}_{21}(\text{H}_5\text{O}_2)_2][(\text{n-C}_4\text{H}_9)_4\text{N}]_9$ ,  $[\text{H}_2\text{TET}]\text{TBA}_9$ , was prepared from the reaction of  $\text{K}_2\text{Pt}(\text{OH})_6$  with  $\text{K}_2\text{MoO}_4$  and acidification of the reaction solution followed by precipitation with tetra-*n*-butylammonium bromide. A single-crystal X-ray diffraction study<sup>5</sup> showed that each pair of nearest-neighbor protonated  $[\text{PtMo}_6\text{O}_{24}]^{8-}$  units was linked by seven hydrogen bonds (Figure 2), including four  $\text{O}_c\text{H}\cdots\text{O}_t$  hydrogen bonds, whose hydrogen atoms are colored red in Figure 2; one  $\text{O}_c\text{H}\cdots\text{O}_c$  bond, whose hydrogen atom is colored blue in Figure 2; and two  $\text{O}_b\text{H}\cdots\text{O}_b$  bonds, whose hydrogen atoms are colored green in Figure 2, where oxygen atoms are labeled as in Figure 1. The  $^{195}\text{Pt}$  NMR spectrum of the  $[\text{H}_2\text{TET}]\text{TBA}_9$  in 1:4 (v/v)  $\text{CD}_3\text{CN}/\text{CDCl}_3$  showed two resonances of equal intensity, consistent with the retention of the tetrameric structure in solution. The  $^1\text{H}$  NMR spectrum of  $[\text{H}_2\text{TET}]\text{TBA}_9$  at room temperature displayed eight narrow resonances, two broad resonances, and a broad “water resonance”. A variable temperature  $^1\text{H}$  NMR experiment showed that the two broad resonances and the water resonance narrowed with decreasing temperature, suggesting rapid chemical exchange among the protons responsible for these resonances. The sharp resonances were assigned to H1-H8 in Figure 2, while the broad resonances were assigned to two of the three H9-H11 protons, where the third proton was presumably exchange-broadened

beyond recognition or dissociated. A 2D EXSY experiment allowed for a more detailed assignment of the H1-H8 protons.



**Figure 2:** The  $[(\text{PtMo}_6\text{O}_{24})_4\text{H}_{23}]^{9-}$  anion ( $\text{H}_2\text{TET}$ ).

Cooperative hydrogen-bonding effects likely play a role in stabilizing the  $\text{H}_2\text{TET}$  anion. Analysis of the X-ray crystallographic data revealed the potential for cooperative and anticooperative hydrogen-bonding effects similar to those observed in polypeptides<sup>6</sup>. Four types of quasiplanar hydrogen-bonded molybdenum-oxygen chains, analogous to peptide chains, are observed. If cooperative hydrogen bonding effects are key determinants of proton chemical shifts in  $\text{H}_2\text{TET}$  as they are in hydrogen-bonded peptide chains<sup>7</sup>, all eight sharp resonances in the  $^1\text{H}$  NMR spectrum can be assigned among the H1-H8 protons. A “proton exclusion” effect was observed where in no case both the  $\text{O}_b$  atom and  $\text{O}_c$  atom bridging the same pair of molybdenum atoms are protonated. Invocation of proton exclusion restricts the potential for tautomerism in the anion, and excludes all of the potential constitutional isomers except for the observed configuration.

Reaction of  $[\text{H}_2\text{TET}]\text{TBA}_9$  with a large excess of triethylamine led to the formation of the analytically pure platinumomolybdate  $[(\text{PtMo}_6\text{O}_{24})_3\text{H}_{15}][(\text{n-C}_4\text{H}_9)_4\text{N}]_6[(\text{C}_2\text{H}_5)_3\text{NH}]_3$ , ( $\text{H}_2\text{TRI TBA}_6\text{TEAH}_3$ ). Crystallization of this material from acetonitrile/toluene gave a solvated salt of the  $[(\text{PtMo}_6\text{O}_{24})_3\text{H}_{16}]^{8-}$  ( $\text{H}_2\text{TRI}$ ) anion, while crystallization from acetonitrile/diethyl ether gave a salt of the  $[(\text{PtMo}_6\text{O}_{24})_3\text{H}_{14}]^{10-}$  ( $\text{TRI}$ ) anion. The protonated  $[\text{PtMo}_6\text{O}_{24}]^{8-}$  units of the trimeric anions were linked through the same seven hydrogen bond motif observed in the tetramer. The transformation of the tetramer to the trimer was monitored by  $^1\text{H}$  and  $^{195}\text{Pt}$  NMR titrations of  $\text{H}_2\text{TET}$  with triethylamine in hydrated 1:4 (v/v)  $\text{CD}_3\text{CN}/\text{CDCl}_3$  solution, demonstrating that  $\text{H}_2\text{TET}$  first dissociates to  $\text{TET}$  in solution, converts to  $\text{H}_2\text{TRI}$  with the addition of

triethylamine, and then converts to **HTRI** with the addition of further triethylamine. Proton NMR spectra of **H<sub>2</sub>TRI/HTRI** mixtures showed five sharp peaks, indicating that the trimers adopt the same structural configurations observed in **H<sub>2</sub>TET**. The <sup>1</sup>H NMR resonances were assigned with the aid of a 2D EXSY experiment. Addition of water to a solution containing **H<sub>2</sub>TET** and five equivalents of water gave the <sup>1</sup>H NMR spectrum expected for a hydrogen-bonded platinomolybdate dimer of the type previously observed by Saski and Lee in the solid state.<sup>8</sup> Cooperative hydrogen bonding effects similar to those observed in the tetramer were also observed in the trimer, and correlations between chemical shifts of protons occupying the same position in similar hydrogen-bonded molybdenum-oxygen chains in the tetramer and trimer were observed and rationalized.

## References

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