Pd₄L₈ interlocked cage with halogen ions bound in its cavities

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Pd₄L₈ interlocked cages, where two Pd₂L₄ cages are quadruply interlocked, are stabilized by three anions trapped in between Pd(II) ions.¹ It was found that the $[Pd_21_4]^{4+}$ cage originally reported by Hooley and his coworkers² was converted into a $(Cl^-)_3 \subset [Pd_41_8]^{8+}$ interlocked cage with three Cl⁻ ions as template anions. F⁻ can also play as a template to form a $(F^-)_3 \subset [Pd_41_8]^{8+}$ interlocked cage, whereas Br⁻ did not produce the interlocked cage at all. Interestingly, the *J*-coupling between F⁻ and pyridyl hydrogen atoms was observed in both ¹H and ¹⁹F NMR spectra of the $(F^-)_3 \subset [Pd_41_8]^{8+}$ interlocked cage. The F⁻ is equally coupled with neighboring eight pyridyl hydrogen atoms. The observation of this type *J*-coupling of CH…F⁻ hydrogen bonds $(^{h1}J_{HF})$ at room temperature is rare. This

observation indicates that the $(X^{-})_{3} \subset [Pd_{4}1_{8}]^{8+}$ interlocked cage is stabilized not only by the electrostatic interaction between X⁻ and Pd²⁺ but also by relatively $CH \cdots X^{-}$ strong hydrogen bonds. It was also found that Cl⁻ ions trapped in the $(Cl^{-})_{3} \subset [Pd_{4}\mathbf{1}_{8}]^{8+}$ interlocked cage can be replaced with F⁻ ion(s) in a stepwise manner to form $(Cl^{-}\cdot F^{-}\cdot Cl^{-}) \subset [Pd_4\mathbf{1}_8]^{8+}$ and $(\mathbf{F}^{-}\cdot\mathbf{C}\mathbf{l}^{-}\cdot\mathbf{F}^{-})\subset [\mathbf{P}\mathbf{d}_{4}\mathbf{1}_{8}]^{8+}$

interlocked cages, respectively. The arrangement of F^- and Cl^- in the interlocked cages was unambiguously determined by the observation of the ${}^{h1}J_{HF}$ coupling around the trapped F^- ion(s) in their ¹H NMR spectra.



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