

Coordinative Equilibrium at Open Metal Sites in a Paddlewheel Metal-Organic Framework

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Coordination bondings have been extensively studied in contemporary chemistry since their nature has broadly been employed in academia and industry. Most studies of coordination bondings have been achieved only with strongly coordinating metal complexes because of their ubiquity in nature. By contrast, weak coordination bonding has been considered a polar interaction only, while studies for differing weak chemical bonds and polar interactions are challenging. Meanwhile, metal-organic frameworks (MOFs) are a structurally well-defined crystalline subset of porous materials comprising metal ions and multitopic organic linkers. Among them, paddlewheel-type MOFs with open metal sites (OMSs) such as HKUST-1 can be an excellent platform to observe the weak coordination bonding because the nanopores in the HKUST-1 can spatially confine a molecule such as a trichloromethane (TCM) that has lone-paired electrons on its neutral chlorine atom. Although the TCM has been considered as a non-Lewis-base molecule based on its chemical inertness, we postulated that the spatial confinement of TCM could enhance the probability of possible coordination of its lone-paired electrons at the metal center. In this poster, we present the existence of weak coordination bonding, demonstrating a “coordination equilibrium” that arises between the TCM and strong Lewis-base molecules such as H_2O , MeOH , EtOH , DMF , and PhOH . The coordination equilibrium was demonstrated by using an in situ ^1H nuclear magnetic resonance analysis. Further, Raman results that support the possible weak coordination bonding of TCM are provided.