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In Situ X-ray Absorption Spectroscopy Studies of Kinetic Interaction between Platinum(II) Ions and UiO-66 Series Metal–Organic Frameworks

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ABSTRACT: The interaction of guest Pt(II) ions with UiO-66–X (X = NH2, H, NO2, OMe, F) series metal–organic frameworks (MOFs) in aqueous solution was investigated using in situ X-ray absorption spectroscopy. All of these MOFs were found to be able to coordinate with Pt(II) ions. The Pt(II) ions in UiO-66–X MOFs generally coordinate with 1.6–2.4 Cl and 1.4–2.4 N or O atoms. We also studied the time evolution of the coordination structure and found that Pt(II) maintained a coordination number of 4 throughout the whole process. Furthermore, the kinetic parameters of the interaction of Pt(II) ions with UiO-66–X series MOFs (X = NH2, H, NO2, OMe, F) were determined by combinational linear fitting of extended X-ray absorption fine structure (EXAFS) spectra of the samples. The Pt(II) adsorption rate constants were found to be 0.063 h−1 for UiO-66–NH2 and 0.011–0.017 h−1 for other UiO-66–X (X = H, NO2, OMe, F) MOFs, which means that Pt(II) adsorption in UiO-66–NH2 is 4–6 times faster than that in other UiO-66 series MOFs. FTIR studies suggested that the carboxyl groups could be the major host ligands binding with Pt(II) ions in UiO-66 series MOFs, except for UiO-66–NH2, in which amino groups coordinate with Pt(II) ions.

INTRODUCTION

Metal–organic frameworks (MOFs) are interesting coordination polymers due to their potential applications as permanently porous host materials for guest ions, molecules, and gases. Postsynthetic modifications can be used to change the structure and composition of the organic linker and therefore change the pore volume, surface area, and chemical properties of the MOF.1,2 These changes, along with the addition of guest metal ions to the MOF, can be used to solve application-specific problems, such as hydrogen gas storage,3–5 catalysis,6–9 chemical adsorption and separation,10–12 sensing of organic molecules, gases, and ions,13,14 as well as drug delivery.15 The loading of guest metal ions into MOFs is mostly carried out in the solution phase with a conventional wet-chemistry strategy.16–18 Functional groups on MOF linkers, such as –NH2, –SH,11 and –COOH,20 are generally considered as the key factors for efficient encapsulation of metal ions.

The coordination of metal ions with common organic ligands, dendrimers, and polymers has been extensively studied.21–23 For example, Crooks and co-workers studied the binding of PtCl52− anions with hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers with UV–vis spectroscopy. From their study, the formation of PtCl5(H2O)4+n−2 (n ≤ 3) is the key step that leads to the coordination of Pt(II) with the amino group in the PAMAM dendrimer.24 Considering the importance and broad applications of MOFs as host materials for guest metal ions, no detailed studies have been carried out on the coordination mechanism of metal ions within MOFs, particularly the coordination kinetics.

We chose the UiO-66 MOF, which consists of Zr6O4(OH)4 (H2O)4 clusters and 1,4-benzenedicarboxylate (BDC) linkers, as the host material in our studies because UiO-66 has superior thermal and chemical stability.25 It has been reported that UiO-66 could maintain its crystalline structure up to 540 °C and tolerate most common neutral solvents. A series of isoreticular UiO-66 MOFs could be synthesized by using functionalized BDC linkers with various functional groups, such as –NH2, –NO2, –F, and –OMe. Functionalized BDC linkers can be introduced into the MOF either before the synthesis or via postsynthetic modifications of UiO-66 MOFs.26 In our previous study, we found that Pt(II) ions could be efficiently adsorbed inside of the cages of UiO-66–NH2 via a conventional wetness impregnation approach in aqueous solution.16 Potassium tetrachloroplatinate (K2PtCl4) was found to be a good metal precursor, and the amino group in the MOF (UiO-66–NH2) was essential for the efficient loading of Pt(II) into the MOF. We also found that both the functional groups and MOF’s porous structure are important in controlling the coordination structure of metal ions.27 The loaded Pt(II) ions were further reduced to metallic Pt nanoclusters that had the...
same size as the octahedral cages of UiO-66–NH$_2$ (1.2 nm) and were uniformly dispersed throughout the MOF. These Pt nanoclusters, confined within UiO-66–NH$_2$ showed superior chemoselectivity in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol than Pt nanoclusters supported on other materials.\(^1\) This study on the binding process of Pt(II) ions with MOFs and its kinetics would shed light on the loading mechanism and preparation condition of these hybridized materials. A deep understanding of the metal loading mechanism in MOFs would help the design and synthesis of other functionalized MOF materials involving guest metal ions for their various applications.

UV−vis spectroscopy is a traditional technique to study the interaction of metal ions and ligands. Unfortunately, it is not practical to adopt UV−vis spectroscopy to study MOFs in the solution phase due to the strong light scattering by large MOF particles (typically several hundred nanometers). X-ray absorption spectroscopy (XAS), another sophisticated in situ technique that is suitable for exploring the local coordination environment of metal ions, was therefore employed to study this system. Herein, we present the results of the coordination structure of Pt(II) ions adsorbed within isoreticular UiO-66−X MOFs (X = NH$_2$, NO$_2$, F, OMe). UiO-66−X MOFs were synthesized by substituting the H$_2$BDC linker with other functionalized linkers. Briefly, ZrCl$_4$ (0.40 g, 1.71 mmol, Acros Organics) was dissolved in 100 mL of DMF at room temperature by sonication. For UiO-66−NH$_2$, 2-aminoterephthalic acid (0.31 g, 1.71 mmol, Acros Organics) was dissolved in the ZrCl$_4$ solution. For UiO-66−NO$_2$, 2-nitroterephthalic acid (0.36 g, 1.71 mmol) was dissolved in the ZrCl$_4$ solution. For UiO-66−F, 2-fluoroterephthalic acid (0.32 g, 1.71 mmol, Alfa Aesar) was dissolved in the Zr solution. For UiO-66−OMe, 2-methoxyterephthalic acid (0.34 g, 1.71 mmol) was dissolved in the ZrCl$_4$ solution. A small amount of water (0.13 mL, 6.84 mmol) was added to the solution, which is essential to get the well-ordered material. The Teflon cup was transferred to a preheated oven at 120 °C. After 24 h, the Teflon cup was removed from the oven and cooled to room temperature. The precipitate was isolated and purified using the same procedure as that described for the synthesis of UiO-66.

**Experimental Section**

**Synthesis of UiO-66.** UiO-66 was synthesized and purified by a similar procedure as that reported.\(^2\) All syntheses were performed in 480 mL Teflon PFA wide mouth jars. The following is a detailed synthesis procedure for UiO-66: Zirconium(IV) chloride (ZrCl$_4$ 0.40 g, 1.71 mmol, Acros Organics) was dissolved in 100 mL of N,N'-dimethylformamide (DMF) at room temperature by sonication. 1,4-Benzendicarboxylic acid (H$_2$BDC 0.28 g, 1.71 mmol, Sigma-Aldrich) was added to the clear solution in an equimolar ratio with regard to ZrCl$_4$. A small amount of water (0.13 mL, 6.84 mmol) was added to the solution, which is essential to get the well-ordered material.\(^2\) The tightly capped jars were placed in a preheated oven at 120 °C for 24 h under static conditions. After 24 h, the solutions were cooled to room temperature, and the precipitates were isolated by centrifugation. The solids were washed with 40 mL of DMF three times, followed by washing with 40 mL of methanol three times. During each wash, the MOF suspension was kept at room temperature for 12 h to allow solvent exchange before being centrifuged. The solvent was decanted, and the MOF powder was dried at 150 °C under vacuum.

**Synthesis of 2-Fluoroterephthalic Acid.**\(^2\) Dimethyl-2-fluoroterephthalate (0.5 g, 2.36 mmol, Matrix Scientific) was dissolved in 20 mL of aqueous sodium hydroxide (NaOH, 1.0 M) at 353 K for 30 min with continuous stirring. After 30 min, the clear solution was cooled down to room temperature. Concentrated hydrochloric acid (HCl, assay 37%) was added dropwise to the solution while stirring until the pH reached 1. The resultant white precipitate was recovered by vacuum filtration and washed with copious amounts of water to remove the excess acid. The white powder was vacuum-dried overnight at room temperature.

**Synthesis of 2-Methoxyterephthalic Acid.**\(^2\) 2,5-Dimethylanisole (0.60 g, 4.40 mmol) and potassium permanganate (KMnO$_4$, 3.47 g, 22.0 mmol) were dissolved in 20 mL of H$_2$O. The solution was refluxed for 5 h. After cooling down to room temperature, the suspension was separated by vacuum filtration. Concentrated HCl (assay 37%) was added dropwise to the filtrate until the pH reached 1. The resultant white precipitate was recovered by vacuum filtration and washed with copious amounts of water to remove the excess acid. The white powder was vacuum-dried overnight at room temperature.

**Synthesis of Functionalized UiO-66–X (X = NH$_2$, NO$_2$, F, OMe).** UiO-66–X MOFs were synthesized by substituting the H$_2$BDC linker with other functionalized linkers. Briefly, ZrCl$_4$ (0.40 g, 1.71 mmol, Acros Organics) was dissolved in 100 mL of DMF at room temperature by sonication. For UiO-66–NH$_2$, 2-aminoterephthalic acid (0.31 g, 1.71 mmol, Acros Organics) was dissolved in the ZrCl$_4$ solution. For UiO-66–NO$_2$, 2-nitroterephthalic acid (0.36 g, 1.71 mmol) was dissolved in the ZrCl$_4$ solution. For UiO-66–F, 2-fluoroterephthalic acid (0.32 g, 1.71 mmol, Alfa Aesar) was dissolved in the Zr solution. For UiO-66–OMe, 2-methoxyterephthalic acid (0.34 g, 1.71 mmol) was dissolved in the ZrCl$_4$ solution. A small amount of water (0.13 mL, 6.84 mmol) was added to the solution, which is essential to get the well-ordered material. The Teflon cup was transferred to a preheated oven at 120 °C. After 24 h, the Teflon cup was removed from the oven and cooled to room temperature. The precipitate was isolated and purified using the same procedure as that described for the synthesis of UiO-66.

**In Situ XAS Studies.** In situ X-ray absorption spectra were measured at beamlines 10-ID-B and 9-BM-B at the Advanced Photon Source at Argonne National Laboratory. The data were collected in transmission mode at the Pt L$_3$-edge (11.564 keV). During in situ measurements, a home-built XAS liquid cell equipped with Kapton windows was employed. The liquid cell was constructed to enable efficient magnetic stirring with a micro stir bar (3 mm × 3 mm) at the bottom. The thickness of the liquid sample was set to 5 mm. Under the conditions in current experiments, the total absorption length was measured to be ~2−2.5, with an edge jump of ~0.05−0.10.

Before the XAS experiment, each one of these UiO-66–X series MOFs (20.0 mg) was dispersed uniformly in deionized water (0.3 mL) using sonication for 30 min. The suspension solution was transferred into the XAS liquid cell with a syringe. An appropriate amount of K$_2$PtCl$_4$ (2.13 mg) was dissolved in deionized water (0.10 mL) to make a fresh solution. The K$_2$PtCl$_4$ solution was also injected into the MOF suspension solution using a syringe. The cell was immediately sealed with a septum and placed at the prealigned position in the X-ray beam path. Magnetic stirring and X-ray measurements were started immediately. The interval between the mixing process and XAS measurements was typically ~5 min. Each scan for in situ XAS measurements takes 4 min.

In situ XAS spectra were collected continuously for the first hour for each sample after injecting the K$_2$PtCl$_4$ solution and then were remeasured at 2, 4, 8, 12, 16, 20, 24, 28, 32, 36 h. During each measurement, a bulk Pt foil reference was placed between the transmission and reference ion chambers to allow simultaneous energy calibration for each XAS scan. Multiple scans (2−4) were merged into one data set for XAS analysis if they were collected continuously.

XAS spectra of the reference samples were collected in transmission mode using finely ground powders dispersed on Kapton tape. The solid powder samples after kinetic studies were separated from solution and dried at room temperature. These powder samples were measured in a transmission mode after being pressed into a hollow stainless steel cylinder. The
sample thickness was adjusted to get a total absorption length below 2.5.

For XAS analysis, the software at the beamline was used to perform deadtime correction and energy calibration. The Athena program, which is an interface to IFEFFIT and FEFFIT, was used for glitch removal, energy alignment, pre-edge subtraction, postedge normalization, and conversion to $k$-space.\textsuperscript{30,31} All X-ray absorption near-edge structure (XANES) spectra were calibrated by setting the Pt $L_1$-edge energy to 11564.0 eV in the reference channel (Pt foil). Extended X-ray absorption fine structure (EXAFS) data were fitted in $R$-space using the theoretical models constructed from FEFF 6.\textsuperscript{32–34} $K_2PtCl_4$ and $Pt(NH_2CH_2CH_2NH_2)Cl_2$ powders were used as the experimental standards to determine amplitude reduction factors ($S_0^2$) of Pt–Cl and Pt–N, which are 0.84 and 0.89, respectively. Because oxygen is adjacent to nitrogen in the periodical table, nitrogen is a good approximation of oxygen. Thus, we adopted the same amplitude reduction factor of Pt–N (0.89) for the Pt–O path during EXAFS fitting. The energy shifts ($\Delta E$) and Debye–Waller factor ($\sigma^2$) of the two paths of Pt–Cl and Pt–N/O were set to be the same value, respectively, to minimize the uncertainty of fitting parameters. In most cases, we did not observe significant changes in the total coordination number of the two paths, irrespective of whether it was constrained to a fixed value of 4 or not, which agrees with the typical square-planar coordination structure of Pt(II) complexes.

For combinational linear fitting of EXAFS, we considered the EXAFS equation\textsuperscript{35}\textsuperscript{35}

$$\chi(k) = \sum_i N_i S^2_i F_i(k) e^{-2k\sigma^2_i} e^{-2R_i/\lambda(k)} \sin[2kR_i + \delta_i(k)]$$

(1)

where $N_i$ is the number of atoms in the coordination shell $i$ and $\sigma^2_i$ is the mean-square variation of distances (also called the Debye–Waller factor) about the average $R_i$ to atoms in the $i$th shell. The above parameters can be determined during EXAFS fitting. The amplitude reduction factor ($S_0^2$) is determined with experimental standards as mentioned above, while other parameters such as the effective scattering amplitude ($F_i(k)$), effective scattering phase shift ($\delta_i(k)$), and mean-free path ($\lambda(k)$) are calculated with FEFF.

The above equation can be easily rewritten as follows

$$\chi(k) = c_1 \sum_i N_i S^2_i F_i(k)e^{-2k\sigma^2_i} e^{-2R_i/\lambda(k)} \sin[2kR_i + \delta_i(k)] + c_2 \sum_j N_j S^2_j F_j(k)e^{-2k\sigma^2_j} e^{-2R_j/\lambda(k)} \sin[2kR_j + \delta_j(k)]$$

(2)

where $i$ and $j$ represent the $i$th and $j$th shell of two different components in the sample, respectively. $c_1$ and $c_2$ represent the relative concentration of the two different components in the sample, respectively, and they have the restriction

$$c_1 + c_2 = 1$$

(3)

After mixing $K_2PtCl_4$ with the MOF, we assumed that Pt(II) exists in two formats, as free $K_2PtCl_4$ and coordinated in the MOF. Therefore, the relative concentration of free $K_2PtCl_4$ ($c_1$) and Pt(II) ions adsorbed in the MOF ($c_2$) could be derived by combinational linear fitting of EXAFS of the mixture solution using EXAFS of free $K_2PtCl_4$ and separated MOFs containing Pt(II) ions as the standard spectra. During combinational linear fitting of EXAFS, all of the data were derived under the following conditions: $k = 3.5–10$, $r = 1.0–2.5$, $k$-weight = 3. The fitting procedure was carried out in $k$-space using the imaginary portion of the EXAFS function in the Athena program.

**Other Characterizations.** Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed using an Agilent Cary 670 FTIR equipped with a linearized MCT detector, a Harrick diffuse reflectance accessory, and a Praying Mantis high-temperature reaction chamber. An appropriate amount of MOF sample was diluted with KBr powder (10 or 5 wt % MOF). After being ground into a fine powder, the diluted sample was packed in the sample cup, followed by a degassing process at 150 °C using a high-vacuum diffusion pump at 2 × 10$^{-4}$ Torr for 1 h. After cooling down to room temperature, the spectra were recorded at 1 cm$^{-1}$ resolution within 4000–700 cm$^{-1}$. Kubelka–Munk correction was applied to generate the spectra for quantitative analysis. The loadings of platinum in MOFs were determined using an inductively coupled plasma mass spectrometer (ICP-MS, X Series II, Thermo Scientific).

**RESULTS AND DISCUSSION**

**Coordination Structure of $K_2PtCl_4$ with UiO-66 Series MOFs.** The normalized XANES of $K_2PtCl_4$ in UiO-66–$NH_2$
aqueous solution measured at extended reaction time is shown in Figure 1a. More XANES spectra at various reaction times are also shown in Figure S1 (Supporting Information). The absorption edge energy was found to shift gradually from 11564.1 to 11564.3 eV after 36 h, along with the white line of XANES varying from 11566.3 to 11567.0 eV. Compared with standard samples (K\textsubscript{2}PtCl\textsubscript{4}, Pt(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})Cl\textsubscript{2}, Pt-(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2}; see Figure S3 (Supporting Information)), the absorption edge energy changes suggest the coordination of the amine group with Pt(II) ions during loading. It is notable that at least one isosbestic point (11574 eV) was observed, suggesting that two dominant coordination structures of Pt(II) ions coexist in the solution, K\textsubscript{2}PtCl\textsubscript{4} and Pt(II)-adsorbed in UiO-66−NH\textsubscript{2}. The subtle changes in XANES indicate no dramatic variation on the local coordination environment of Pt(II) ions, that is, the typical planar structure of the Pt(II) complex could be maintained in MOF cages.

The coordination number, bond length, and adjacent element type around Pt(II) could be derived by fitting EXAFS spectra. As shown in the EXAFS of Pt(II) ions in the presence of UiO-66−NH\textsubscript{2} (Figure 2), the intensity of the first coordination shell (Pt−Cl/N/O) decreased significantly, accompanied by peak position shifts to lower bond lengths during the whole loading process, indicating ligand exchange from Cl to N or O atoms.

The EXAFS fitting results are summarized in Figure 3 and Table 1. After mixing K\textsubscript{2}PtCl\textsubscript{4} and UiO-66−NH\textsubscript{2} in water, the coordination number of Pt−Cl decreased rapidly at the beginning and then reached a plateau of ~2.0 after 10 h. On the contrary, the coordination number of N or O atoms increased to ~1−2 at the initial stage and then was maintained at ~2.0 after 10 h. The total coordination number of Pt−Cl and Pt−N/O was found to be constant (~4) during the whole loading process, indicating that the typical square-planar structure of Pt(II) complex was maintained in MOF cages, which is consistent with XANES results discussed above.

The coordination of Pt(II) ions with UiO-66 series MOFs containing other functional groups (−H, −F, −NO\textsubscript{2}, and −OMe) was also observed, as shown by the EXAFS spectra in Figure 4. By measuring XAS of separated MOF samples containing Pt(II) ions after in situ XAS studies, the intensity of the first coordination shell was found to be generally low for all Pt(II)-adsorbed MOF samples with various functional groups (−NH\textsubscript{2}, −H, −F, −NO\textsubscript{2}, −OMe), indicating the coordination of lighter atoms (compared with Cl) with Pt(II). In addition, XANES of Pt(II) ions adsorbed in UiO-66−NH\textsubscript{2} is almost identical to that of the Pt(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})Cl\textsubscript{2} standard sample (Figure 5), suggesting that Pt(II) ions maintained the square-planar coordination structure in MOF cages. For other UiO-66 series MOFs, the intensity of the primary peak of XANES increased, and the white line position shifted to higher energy, compared with the Pt(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})Cl\textsubscript{2} standard sample, indicating the coordination of Pt(II) with more electronegative atoms (i.e., O). Furthermore, the time evolution of EXAFS results of UiO-66−X samples (X = H, F, NO\textsubscript{2}, OMe) in K\textsubscript{2}PtCl\textsubscript{4} solution shows a similar trend, as shown in Figures S4−S11 (Supporting Information). That is, the intensity of the first coordination shell decreases, and the peak position shifts to lower bond length at extended reaction time (Figures S4−S7, Supporting Information), indicating the coordination of Pt(II) ions with oxygen-containing ligands. On the basis of the EXAFS fitting of Pt−Cl and Pt−O paths, the coordination numbers of Pt−Cl decreased from 4 to ~2.5 after 36 h, while that of the Pt−O path increased from 0 to ~1.5 in these UiO-66−X (X = H, F, NO\textsubscript{2}, OMe) MOFs (Figures S8−S11, Supporting Information). The similar kinetic evolution of the Pt(II) adsorption process in these MOFs suggests that similar coordination structures were formed.

The EXAFS fitting results of separated UiO-66 series samples containing Pt(II) ions are listed in Table 1. The coordination numbers of Pt−Cl were found to be 1.6−2.4. The coordination shell of Pt−N/O has a coordination number varying in the range of 1.4−2.4. Furthermore, the similar coordination number of 2 for all Pt(II)-adsorbed MOF samples could result from the geometric restriction of the MOF structure. On the basis of DFT calculations, it is unlikely that three −NH\textsubscript{2} groups coordinate with Pt(II) ions in UiO-66−NH\textsubscript{2}. In all of the fitting results, the bond length of Pt−Cl was generally kept at 2.22−2.27 Å, with the Pt−N/O bond length maintained at ~2.0 after 10 h. The total coordination number of Pt−Cl and Pt−N/O was found to be constant (~4) during the whole loading process, indicating that the typical square-planar structure of Pt(II) complex was maintained in MOF cages, which is consistent with XANES results discussed above.

The coordination of Pt(II) ions with UiO-66 series MOFs containing other functional groups (−H, −F, −NO\textsubscript{2}, and −OMe) was also observed, as shown by the EXAFS spectra in Figure 4. By measuring XAS of separated MOF samples containing Pt(II) ions after in situ XAS studies, the intensity of the first coordination shell was found to be generally low for all Pt(II)-adsorbed MOF samples with various functional groups (−NH\textsubscript{2}, −H, −F, −NO\textsubscript{2}, −OMe), indicating the coordination of lighter atoms (compared with Cl) with Pt(II). In addition, XANES of Pt(II) ions adsorbed in UiO-66−NH\textsubscript{2} is almost identical to that of the Pt(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})Cl\textsubscript{2} standard sample (Figure 5), suggesting that Pt(II) ions maintained the square-planar coordination structure in MOF cages. For other UiO-66 series MOFs, the intensity of the primary peak of XANES increased, and the white line position shifted to higher energy, compared with the Pt(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})Cl\textsubscript{2} standard sample, indicating the coordination of Pt(II) with more electronegative atoms (i.e., O). Furthermore, the time evolution of EXAFS results of UiO-66−X samples (X = H, F, NO\textsubscript{2}, OMe) in K\textsubscript{2}PtCl\textsubscript{4} solution shows a similar trend, as shown in Figures S4−S11 (Supporting Information). That is, the intensity of the first coordination shell decreases, and the peak position shifts to lower bond length at extended reaction time (Figures S4−S7, Supporting Information), indicating the coordination of Pt(II) ions with oxygen-containing ligands. On the basis of the EXAFS fitting of Pt−Cl and Pt−O paths, the coordination numbers of Pt−Cl decreased from 4 to ~2.5 after 36 h, while that of the Pt−O path increased from 0 to ~1.5 in these UiO-66−X (X = H, F, NO\textsubscript{2}, OMe) MOFs (Figures S8−S11, Supporting Information). The similar kinetic evolution of the Pt(II) adsorption process in these MOFs suggests that similar coordination structures were formed.

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between 1.95 and 2.00 Å. These bond length values agree with typical parameters of Pt(II) complexes in the literature.36,37

Kinetics of Pt(II) Ion Coordination with UiO-66 Series MOFs. It is difficult to determine the individual concentration of $\text{K}_2\text{PtCl}_4$ and Pt(II) ions adsorbed in MOFs during the loading process by combinational linear fitting of XANES due to the subtle changes in XANES (selected spectra in Figure 1a and b and full spectra in Figures S1 and S2, Supporting Information). However, the differences in their EXAFS spectra are obvious (Figure 2), probably because of the exchange of ligands around Pt(II) with different coordination bond distances. Therefore, it is possible to obtain the relative molar ratio of the two major coordination structures of Pt(II) ions with combinational linear fitting of the EXAFS with freshly made $\text{K}_2\text{PtCl}_4$ and Pt(II) adsorbed in MOFs. Here, we assume that Pt(II) exists in two formats, as free $\text{K}_2\text{PtCl}_4$ and coordinated in the MOF. At the initial state of the loading process, we assume that there is no $\text{K}_2\text{PtCl}_4$−MOF interaction. We used the EXAFS spectrum acquired from freshly prepared $\text{K}_2\text{PtCl}_4$ solution as the standard spectrum for the initial state. After mixing $\text{K}_2\text{PtCl}_4$ with MOF for 36 h, we separated the MOF containing Pt(II) from the solution and measured its EXAFS spectrum, which was used as the standard spectrum for the final state. After mixing $\text{K}_2\text{PtCl}_4$ with the MOF, there was a net transfer of Pt(II) ions from $\text{K}_2\text{PtCl}_4$ into MOF along with changes in the coordination environment of Pt(II). For EXAFS spectra acquired at different time intervals during the Pt(II) adsorption process, we could estimate the amount of Pt(II) in $\text{K}_2\text{PtCl}_4$ and in the MOF by combinational linear fitting of these EXAFS spectra with the standard ones acquired from freshly made $\text{K}_2\text{PtCl}_4$ (initial state) and Pt(II) ions adsorbed in MOFs (final state).

The time evolutions of the concentrations of $\text{K}_2\text{PtCl}_4$ and Pt(II) adsorbed in the UiO-66−$\text{NH}_2$ MOF in aqueous solution are shown in Figure 6a. The data could be fitted with a first-order linear equation (Figure 6b).

Consider the coordination of $\text{K}_2\text{PtCl}_4$ with the UiO-66−$\text{NH}_2$ MOF as follows

![Figure 4. Comparison of Fourier-transformed Pt $L_3$-edge EXAFS of separated UiO-66 series MOFs containing Pt(II) ions with various functional groups after 36 h; $k = 3.5$−$10.0$ and k-weight = 3.](image)

![Figure 5. Comparison of Pt $L_3$-edge XANES of separated UiO-66 series MOFs containing Pt(II) ions with various functional groups after 36 h, and standard samples; $k = 3.5$−$10.0$ and k-weight = 3.](image)

# Table 1. EXAFS Fitting Results of Separated UiO-66 Series MOFs Containing Pt(II) Ions after In Situ XAS Studies.4

<table>
<thead>
<tr>
<th>sample</th>
<th>bond length (Å)</th>
<th>coordination number</th>
<th>bond length (Å)</th>
<th>coordination number</th>
<th>DW factor ($10^{-4}$ Å$^2$)</th>
<th>energy shift (eV)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(II), UiO-66</td>
<td>2.26(2)</td>
<td>1.97(3)</td>
<td>1.6(2)</td>
<td>2.4(2)</td>
<td>14 (9)</td>
<td>5.8 (25)</td>
<td>0.011</td>
</tr>
<tr>
<td>Pt(II), UiO-66−$\text{NH}_2$</td>
<td>2.27(2)</td>
<td>2.00(3)</td>
<td>2.0(4)</td>
<td>2.0(4)</td>
<td>25 (15)</td>
<td>5.6 (24)</td>
<td>0.014</td>
</tr>
<tr>
<td>Pt(II), UiO-66−$\text{OMe}$</td>
<td>2.22(3)</td>
<td>1.95(2)</td>
<td>2.4(8)</td>
<td>1.4(7)</td>
<td>46 (22)</td>
<td>1.7 (27)</td>
<td>0.019</td>
</tr>
<tr>
<td>Pt(II), UiO-66−$\text{NO}_2$</td>
<td>2.26(2)</td>
<td>1.94(3)</td>
<td>2.1(3)</td>
<td>1.9(4)</td>
<td>26c</td>
<td>3.2 (32)</td>
<td>0.032</td>
</tr>
<tr>
<td>Pt(II), UiO-66−F</td>
<td>2.26(2)</td>
<td>1.98(2)</td>
<td>1.6(4)</td>
<td>2.4(4)</td>
<td>33 (27)</td>
<td>5.6 (24)</td>
<td>0.016</td>
</tr>
</tbody>
</table>

4The number in bracket indicates the deviation of the last digit of the fitting results. bDebye–Waller (DW) factor. The same values of the parameters for Pt−Cl and Pt−N/O shells were used in the fitting. cThe parameter was fixed in the fitting.

![Figure 6. (a) Kinetic evolution of $\text{K}_2\text{PtCl}_4$ and Pt(II) ions adsorbed in UiO-66−$\text{NH}_2$ in aqueous solution and (b) linear fitting of the $\text{K}_2\text{PtCl}_4$ concentration with an extended reaction time.](image)
The rate constants (\(k\)) for the adsorption of K\(_2\)PtCl\(_4\) at a reaction time \(t\) are found to be 0.013 ± 0.004 h\(^{-1}\). The initial concentration of K\(_2\)PtCl\(_4\) (13 mM) is close to the initial concentration of K\(_2\)PtCl\(_4\). From the linear fitting, we obtained the rate constant for the adsorption of K\(_2\)PtCl\(_4\) in UiO-66 (Figures 6 and 7), where \(a\) is the rate constant, \([A]\) represents the concentration of K\(_2\)PtCl\(_4\), and \([A]_0\) represents the initial concentration of K\(_2\)PtCl\(_4\) (13 mM). The half-life is in the range of 41–63 h for all the MOFs except for UiO-66–NH\(_2\) (11 h). Among all UiO-66–X MOFs (X = NH\(_2\), H, NO\(_2\), OMe, F), UiO-66–NH\(_2\) has the highest reaction rate during the coordination with K\(_2\)PtCl\(_4\), while UiO-66–F has the lowest.

The half-life was calculated to be 53 h.

In the case of UiO-66, the reaction rate is only ~20% of that of UiO-66–NH\(_2\). We also calculated from eq 5 using the above kinetic results that ~39% of the total Pt was adsorbed in UiO-66 after mixing K\(_2\)PtCl\(_4\) and the MOF for 36 h (defined as the loading efficiency). However, ICP-MS analysis only gave 29% Pt loading efficiency (Table 3). The washing process during separation of the MOF could be responsible for the divergence between ICP-MS and in situ XAS results because a portion of Pt(II) ions adsorbed in the MOF could be removed while washing with water.

**Table 3. ICP-MS Results of Pt Loading in Separated UiO-66 Series MOFs after In Situ XAS Studies**

<table>
<thead>
<tr>
<th>sample</th>
<th>Pt loading amount (wt %)</th>
<th>Pt loading efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(II), UiO-66</td>
<td>1.43</td>
<td>29</td>
</tr>
<tr>
<td>Pt(II), UiO-66–NH(_2)</td>
<td>4.72</td>
<td>94</td>
</tr>
<tr>
<td>Pt(II), UiO-66–OMe</td>
<td>1.07</td>
<td>21</td>
</tr>
<tr>
<td>Pt(II), UiO-66–NO(_2)</td>
<td>0.87</td>
<td>17</td>
</tr>
<tr>
<td>Pt(II), UiO-66–F</td>
<td>0.78</td>
<td>16</td>
</tr>
</tbody>
</table>

*Loading efficiency is defined as the actual Pt loading amount divided by the theoretical Pt loading amount. We used 5 wt% Pt theoretical loading amount in all samples.*

**Figure 7.** (a) Kinetic evolution of K\(_2\)PtCl\(_4\) and Pt(II) ions adsorbed in UiO-66 in aqueous solution and (b) linear fitting of the K\(_2\)PtCl\(_4\) concentration with an extended reaction time.

\[
K_2PtCl_4 + nZrO(CO)_2C_8H_5NH_2 = K_{2-n}PtCl_4-n(ZrO(CO)_2C_6H_5NH_2) + nKCl
\]

where \(n\) is between 0 and 2. Because the concentration of the amino group in UiO-66–NH\(_2\) is 180 mM, which is 13 times higher than that of K\(_2\)PtCl\(_4\) (13 mM), we assume that the concentration of available amino groups remained constant during the whole kinetic study. Combined with the linear fitting curve shown in Figure 6, the coordination of Pt(II) ions with the UiO-66–NH\(_2\) MOF can be considered as a quasi-first-order reaction.

For a first-order reaction, we have

\[
\ln[A] = -at + \ln[A]_0
\]

where \(a\) is the rate constant, \([A]\) represents the concentration of K\(_2\)PtCl\(_4\) at a reaction time \(t\), and \([A]_0\) represents the initial concentration of K\(_2\)PtCl\(_4\). From the linear fitting in Figure 6b, we obtained the rate constant for the adsorption of K\(_2\)PtCl\(_4\) in UiO-66–NH\(_2\) MOF (\(a = 0.063 ± 0.004\ h^{-1}\)).

The rate constants (\(a\)) of UiO-66 series MOFs are very close to each other (0.011–0.013 h\(^{-1}\)). The half-life is in the range of 41–63 h for all the MOFs except for UiO-66–N\(_2\) (11 h). Among all UiO-66–X MOFs (X = NH\(_2\), H, NO\(_2\), OMe, F), UiO-66–NH\(_2\) has the highest reaction rate during the coordination with K\(_2\)PtCl\(_4\), while UiO-66–F has the lowest.

**Table 2. Kinetic Results of K\(_2\)PtCl\(_4\) Coordination with UiO-66 Series MOFs Obtained from In Situ XAS Studies**

<table>
<thead>
<tr>
<th>sample</th>
<th>(a) (h(^{-1}))</th>
<th>([A]_0) (mM)</th>
<th>(t_{1/2}) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(II), UiO-66</td>
<td>0.013 ± 0.002</td>
<td>11.3 ± 0.4</td>
<td>53</td>
</tr>
<tr>
<td>Pt(II), UiO-66–NH(_2)</td>
<td>0.063 ± 0.004</td>
<td>10.0 ± 0.7</td>
<td>11</td>
</tr>
<tr>
<td>Pt(II), UiO-66–OMe</td>
<td>0.017 ± 0.002</td>
<td>12.5 ± 0.4</td>
<td>41</td>
</tr>
<tr>
<td>Pt(II), UiO-66–NO(_2)</td>
<td>0.017 ± 0.002</td>
<td>12.0 ± 0.4</td>
<td>41</td>
</tr>
<tr>
<td>Pt(II), UiO-66–F</td>
<td>0.011 ± 0.002</td>
<td>12.2 ± 0.4</td>
<td>63</td>
</tr>
</tbody>
</table>

In the case of UiO-66, the reaction rate is only ~20% of that of UiO-66–NH\(_2\). We also calculated from eq 5 using the above kinetic results that ~39% of the total Pt was adsorbed in UiO-66 after mixing K\(_2\)PtCl\(_4\) and the MOF for 36 h (defined as the loading efficiency). However, ICP-MS analysis only gave 29% Pt loading efficiency (Table 3). The washing process during the coordination environment after Pt(II) ions are adsorbed in all UiO-66 series MOFs studied in this work.

On the basis of dynamic nuclear polarization enhanced solid-state \(^{15}\)N NMR spectroscopy, XAS, and DFT calculations, we have confirmed that one Pt(II) ion coordinates with two neighboring –NH\(_2\) groups in UiO-66–NH\(_2\) and two chloride groups in the square-planar coordination structure in the UiO-66 series MOFs.
octahedral cages of UiO-66–NH$_2$.$^{27}$ However, for other UiO-66 series MOFs without an amino group, other functional groups must coordinate with Pt(II). We think that hydroxyl groups from zirconium oxide clusters and/or carboxyl groups from BDC linkers could coordinate with Pt(II) ions.

To investigate the interaction of Pt(II) ions with hydroxyl or carboxyl functional groups of UiO-66 series MOFs, we carried out DRIFTS experiments. As shown in Figures S12–S16 (Supporting Information), all spectra were scaled based on the C=C ring vibration peak at $\sim$1390 cm$^{-1}$. $^{39}$ except for UiO-66–OMe MOF, in which the carboxyl group peak at 1563 cm$^{-1}$ was used due to the very weak peak from benzene ring vibration. In the case of UiO-66, it can be observed that the asymmetric stretching vibration (O=C=O) of carboxyl groups at 1580–1600 cm$^{-1}$ was dramatically suppressed after loading K$_2$PtCl$_4$ (Figure S12, Supporting Information), suggesting the coordination of carboxyl groups with Pt(II) ions. For UiO-66–NH$_2$, significant changes were seen from the amino group (Figure S13, Supporting Information). After loading K$_2$PtCl$_4$, symmetric and asymmetric stretching vibrations of the amino group (H–N–H) red shifted from 3393 and 3500 cm$^{-1}$ to 3381 and 3490 cm$^{-1}$, respectively, indicating the coordination of Pt(II) ions with the NH$_2$ group. In addition, the intensity of the C–N stretching vibration peak at 1257 cm$^{-1}$ decreased after binding to Pt(II). In comparison, no obvious changes were found in the carboxyl group peaks, although the intensity of the hydroxyl group vibration decreased after loading Pt(II) ions. These results indicate that the major coordination site in UiO-66–NH$_2$ could be the amino group. In UiO-66–F and UiO-66–NO$_2$, the intensity of carboxyl group peaks decreased slightly (Figures S14 and S15, Supporting Information), while in UiO-66–OMe, these peaks shifted to a lower wavenumber (Figure S16, Supporting Information). However, we did not observe significant shifts in the stretching vibration signal of hydroxyl groups at $\sim$3670 cm$^{-1}$. In fact, in some MOFs, such as UiO-66–OMe, this signal could not be detected both before and after loading Pt(II) ions, implying that the hydroxyl group is not the key factor for binding Pt.

In all, these FTIR results suggest that carboxyl groups at the defect sites of UiO-66 MOFs could be the major coordination sites for Pt(II) ions in all UiO-66 series MOFs studied in this work, except for UiO-66–NH$_2$ in which the amino group could be the main host ligand. The defect sites could come from dangling carboxyl groups either on the surface or in the bulk of the MOFs.

![Figure 8](http://pubs.acs.org.)

**CONCLUSIONS**

Using XAS, we found that all of the UiO-66 series MOFs included in this work were able to coordinate with K$_2$PtCl$_4$ in aqueous solution, which could be the key for the loading of metal precursors into the cages of these MOFs. The four-coordinate square-planar structure of Pt(II) was maintained in UiO-66 series MOFs. The numbers of Cl and N/O atoms coordinated with Pt(II) were found to be 1.6–2.4 and 1.4–2.4, respectively. The MOF’s crystalline structure could be responsible for this result due to the geometric restriction that it provides.

The time evolutions of the concentration of K$_2$PtCl$_4$ and Pt(II) adsorbed in UiO-66–NH$_2$ and other UiO-66 MOFs were studied with the combinational linear fitting of EXAFS. The coordination reaction of K$_2$PtCl$_4$ with UiO-66 series MOFs was found to be first order with respect to the concentration of K$_2$PtCl$_4$. The rate constant was determined to be 0.011–0.017 h$^{-1}$ for UiO-66 series MOFs except for UiO-66–NH$_2$, which has the highest rate constant of 0.063 h$^{-1}$. The half-life was calculated to be 41–63 h for UiO-66 series MOFs except for UiO-66–NH$_2$ which is 11 h.

DRIFTS studies showed that carboxyl group vibrations were generally suppressed after loading Pt(II) ions, suggesting that the carboxyl group could be the possible host ligand coordinated to Pt(II) ions in UiO-66–X MOFs (X = H, F, NO$_2$, OMe). UiO-66–NH$_2$ is an exception, in which the amino group is the major coordination site for binding Pt(II) ions. This different coordination mechanism could explain the faster coordination kinetics of Pt(II) with UiO-66–NH$_2$ than that with other UiO-66 MOFs.

**ASSOCIATED CONTENT**

* Supporting Information

XANES and EXAFS of Pt(II) ions in the presence of UiO-66 series MOFs; EXAFS fitting results at extended reaction time; DRIFT spectra of MOF samples before and after loading Pt(II) ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
MOFs, metal–organic frameworks; FTIR, Fourier transform infrared; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; ICP-MS, inductively coupled plasma mass spectroscopy; UV–vis, ultraviolet–visible spectroscopy; XAS, X-ray absorption spectroscopy; XANES, X-ray absorption near-edge structure; EXAFS, extended X-ray absorption fine structure; DFT, density functional theory; DMF, N,N′-dimethylformamide; PAMAM, poly(amido amine)

REFERENCES