Probing the Structure of Planar Molecular Cobalt Hydroxide Cations in Water by EXAFS Spectroscopy

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Molecular cobalt-oxide materials gain increasing interest as catalysts for artificial photosynthesis since Nocera group revealed the cobalt-phosphate oxygen-evolution catalyst [1] comprises domains of planar cobalt-oxide clusters which are modelled with, on the basis of EXAFS analysis, a discrete heptanuclear $\{Co_7\}$-O/OH cluster [2].

We herein demonstrate planar water-soluble cobalt hydroxide clusters can be synthesized by the reaction of Co(II) cations with *fac*-$\{Co(tacn)\}^{3+}$ cation complex (tacn = 1,4,7-triazacyclononane) in aqueous alkaline solution. As shown in Fig. 1, the role of *fac*-$\{Co(tacn)\}^{3+}$ is to cap the peripheral sites of a labile molecular $\{Co\}_x$ hydroxo cluster so that its bulky tacn ligand terminates further hydrolysis-condensation reactions and hence prevents precipitation of the bulk cobalt hydroxide [3]. Moreover, the metal–hydroxo frameworks are strengthened by multiple intramolecular hydrogen bonds. By using this strategy, we successfully obtained two cobalt hydroxide cluster cations $\mathbf{Co^{III}_2Co^{II}_2}^{4+}$ and $\mathbf{Co^{III}_6Co^{II}_7}^{8+}$ which are composed of a $\{Co_2\}$ or a $\{Co_7\}$ cobalt(II) hydroxo core surrounded by outer shell of inert *fac*-$\{Co(tacn)\}^{3+}$ units, and all cobalt centers are coplanar (Fig. 1). These cations readily dissolve in water, and we show here that their solid-state structures are preserved in solution, as verified by solution-state EXAFS analysis.

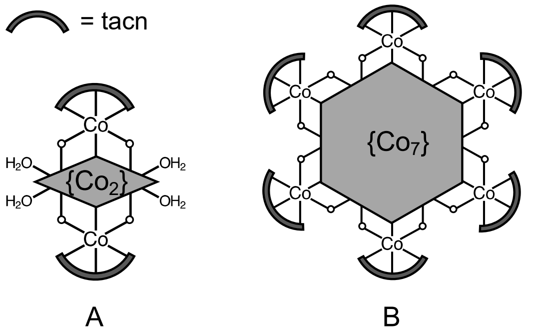

Fig. 1. Diagrams showing solid-state structures of $\mathbf{Co^{III}_2Co^{II}_2}^{4+}$ (A) and $\mathbf{Co^{III}_6Co^{II}_7}^{8+}$ (B) cations.

EXAFS Co K-edge data for $\mathbf{Co^{III}_2Co^{II}_2}^{4+}$ and $\mathbf{Co^{III}_6Co^{II}_7}^{8+}$ in water were collected by using Ritsumeikan synchrotron radiation BL-3, and the Fourier-transformed spectra are given in Fig. 2. The spectra show both first and second shell attributed to Co–O or Co–N primary sphere coordination bonds and Co···Co interactions in the secondary coordination sphere, respectively. To determine Co···Co distances in solution-state, we performed FEFF-fitting to the experimental spectra by simulating theoretical spectra based on single-crystal X-ray crystallographic parameters. The fitting gave an average Co···Co distance of 3.05 Å for $\mathbf{Co^{III}_2Co^{II}_2}^{4+}$ and 3.07 Å for $\mathbf{Co^{III}_6Co^{II}_7}^{8+}$; these distances are close to those of obtained from X-ray crystallography: 3.08 and 3.03 Å, respectively. EXAFS analyses therefore evidence that the cobalt–hydroxo frameworks dissolve intact in aqueous solution.

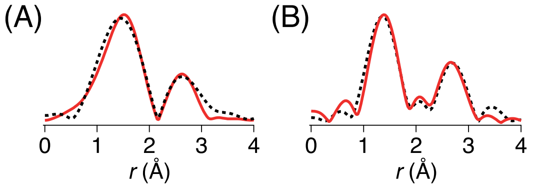

Fig. 2. Fourier-transformed EXAFS spectra of $\mathbf{Co^{III}_2Co^{II}_2}^{4+}$ (A) and $\mathbf{Co^{III}_6Co^{II}_7}^{8+}$ (B) in water. Black dashed and red solid traces are experimental and simulated spectra, respectively.

In summary, we have synthesized two cobalt hydroxide clusters whose structures are related to the molecular domains of cobalt-phosphate water-oxidation catalyst. EXAFS spectra of these clusters in water exhibit distinct secondary Co···Co coordination shell and hence verify the integrity of the hydroxo frameworks upon dissolution. This work proves *fac*-$\{Co(tacn)\}^{3+}$ cation complex is a remarkable capping group for labile metal–hydroxo clusters because not only it assembles the clusters but also it ensures cluster stability in aqueous solution so that it is possible to study structure-function relationship of metal-oxides in solution.

References

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(3) Sugiarto, T. Tagami, K. Kawamoto, and Y. Hayashi, *Dalton Trans.*, **2018**, *47*, 9657.