

遷移金属 2 価イオンの水酸化物形成過程における中間化学種の安定化と構造解明

EXAFS study on stability of planar cobalt(II) and nickel(II) hydroxo clusters in water

スギアルト, 林 宜仁

Sugiarto and Yoshihito Hayashi

金沢大学理工研究域物質化学系

Department of Chemistry, Graduate School of Natural Science and Technology, Kanazawa University,
Kakuma, Kanazawa 920-1192, Japan

e-mail: hayashi@se.kanazawa-u.ac.jp

水溶液中でのニッケルおよびコバルト二価イオンの 2 量体から平面型水酸化物クラスターへの成長を Co および Ni 吸収端を用いた EXAFS 測定により観測した。

We synthesized a group of planar cobalt hydroxide or nickel hydroxide cation clusters Co_2M_2 and Co_6M_7 ($\text{M} = \text{Co}^{2+}$ or Ni^{2+}). Their stability in water is confirmed by EXAFS spectroscopy.

Keywords: EXAFS, cobalt hydroxide, nickel hydroxide, aqueous chemistry

Background and research objectives

Molecular cobalt-oxide and nickel-oxide clusters have attracted attention since Nocera group discovered that cobalt-phosphate [1] and nickel-borate [2] oxygen-evolution catalysts are in fact composed of domains of cobalt or nickel oxo/hydroxo in molecular dimensions [3, 4]. Their group further proposed, on the basis of EXAFS analysis, a planar heptanuclear cobalt-oxo/hydroxo cluster to model the surfaces of cobalt-phosphate catalysts [4].

The research aim is to synthesize a planar molecular cobalt(II) or a nickel(II) hydroxo cluster which dissolves intact in water thus its solution properties can be investigated at a molecular level. To isolate those labile hydroxo clusters from aqueous solution, we use a cation complex $\text{fac}\{-\text{Co}(\text{tacn})\}^{3+}$ ($\text{tacn} = 1,4,7\text{-triazacyclononane}$) as a protecting group [5, 6] to terminate a peripheral site on a metal hydroxo species from a hydrolysis-condensation reaction of cobalt(II) or nickel(II) cations so that the precipitation of the bulk metal hydroxides in alkaline condition is prevented. As a result, we obtained a new family of planar molecular cobalt or nickel hydroxide cations Co_2M_2 and Co_6M_7 ($\text{M} = \text{Co}^{\text{II}}$ or Ni^{II}). Herein, we report an EXAFS study of Co_2M_2 and Co_6M_7 in water as well as in solid states.

Experiment

Co_2M_2 and Co_6M_7 were synthesized by the reaction of $\text{fac}\{-\text{Co}(\text{tacn})(\text{OH}_2)_3\}^{3+}$ with cobalt(II) or nickel(II) cations in water pH 6 and 12, respectively. Solid-state (BN pellets) and solution-state (in water) EXAFS spectra of the clusters were collected in Ritsumeikan University SR center BL-3. For each sample, a minimum three sets of data were collected and were merged and processed by using Athena program. The experimental spectra were analyzed by running FEFF program in Artemis.

Results and discussion

Clusters Co_2M_2 or Co_6M_7 ($\text{M} = \text{Co}^{\text{II}}$ or Ni^{II}) comprise a $\{\text{M}^{\text{II}}_2\}$ - or a $\{\text{M}^{\text{II}}_7\}$ -hydroxo core which is capped by two or six $\text{fac}\{-\text{Co}(\text{tacn})\}^{3+}$ units, as illustrated in Fig. 1.

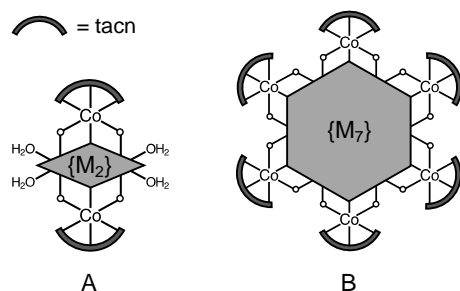


Fig. 1. Schematic representations of (A) Co_2M_2 and (B) Co_6M_7 .

Fig. 2 shows solid- and solution-state EXAFS r -space spectra of Co_2M_2 and Co_6M_7 (Co K-edge spectra for Co_2Co_2 and Co_6Co_7 and Ni K-edge for Co_2Ni_2 and Co_6Ni_7). In general, the spectra display two shells corresponding to the primary and secondary coordination spheres of the absorber metals. Because the second shell peaks are observed clearly, it assures the structure frameworks of the metal(II)–hydroxo core are maintained upon dissolution in water. We tried to extract $\text{M}\cdots\text{M}$ distances from the experimental spectra by fitting with FEFF program, and we found that the metal–metal distances are close to those of observed in the data from single-crystal structures. For example, the average $\text{Co}\cdots\text{Co}$ distance in Co_6Co_7 in the crystal structure is 3.03 Å and solution-state EXAFS gives a value of 3.07 Å. Also, the $\text{Ni}\cdots\text{Ni}$ distance in Co_6Ni_7 found by crystallography and solution-state EXAFS is 3.06 and 3.03 Å, respectively. This indicates the heptanuclear metal(II)–hydroxo core dissolves intact in water.

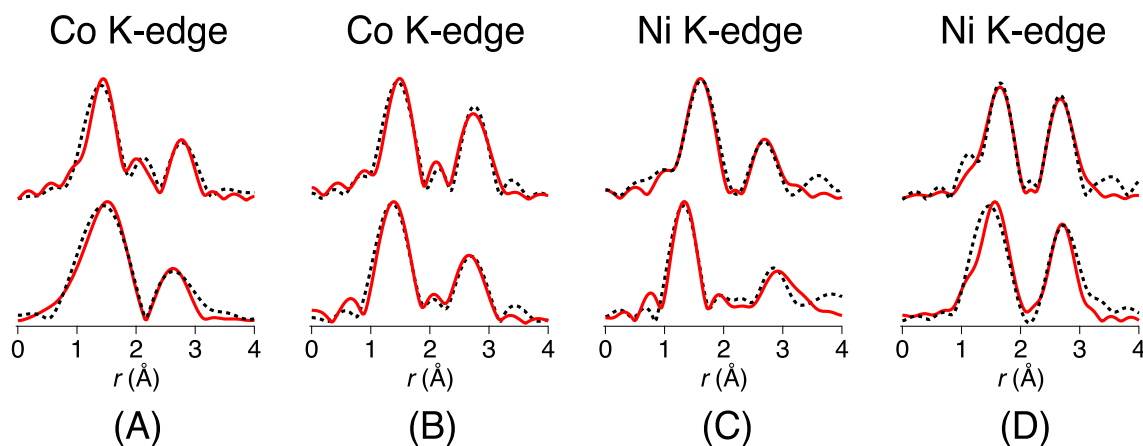


Fig. 2. Solid-state (top traces) and solution-state (bottom traces) r -space EXAFS spectra of (A) Co_2Co_2 , (B) Co_6Co_7 , (C) Co_2Ni_2 , and (D) Co_6Ni_7 . Black dashed and red solid traces are experimental and simulated spectra, respectively.

In summary, the solution state EXAFS data shows a good agreement with the solid state data which uses an authentic sample structurally certified by single-crystal X-ray analysis, and the distance parameters derived from EXAFS were matched well with crystallographic data. The distinct observation of the second coordination sphere peaks of $\text{M}\cdots\text{M}$ interactions ensures the retention of each cluster framework when it dissolves in water. These EXAFS observations are convincing evidence to support our idea that the interactions of planar metal(II)–hydroxo clusters can be trapped by using $\text{fac-}\{\text{Co}(\text{tacn})\}^{3+}$ as the protecting group, and these molecular metal hydroxides are stable in water.

References

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