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COMMUNICATION

Efficient Removal of Perchlorate Ion from Water by Water-insoluble M_2L_4 Type CompoundMasaru Mochizuki,^a Tatsunari Inoue,^a Katsunori Yamanishi,^b Shiori Koike,^a Mitsuru Kondo,^{*,a,c} Liang Zhang,^d and Hiromi Aoki^d

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Reaction of $CuSO_4 \cdot 5H_2O$ with 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (*m*-bbitrb) provides a new positively charged M_2L_4 type molecule, $[SO_4 \subset Cu_2(m\text{-bbitrb})_4]SO_4$. This compound includes SO_4^{2-} inside and outside the cationic cage. Despite this compound being insoluble in water, it shows high efficient perchlorate removal activity from water by the exchange with SO_4^{2-} outside the cage.

Materials which show anion-exchange property have attracted intense attentions as useful methods for removal of toxic anions from water. One of the recent tough targets of the anions that should be removed from water is perchlorate ion (ClO_4^-). The anion interferes with the thyroid's uptake of iodide ion, which is an essential component of growth hormones produced in the thyroid gland. Therefore, ingestion of excess ClO_4^- would seriously affect the growth of newborns and children.¹ In 2005, the U.S. Environmental Protection Agency (EPA) announced that the acceptable exposure level of this anion was 24.5 ppb in drinking water.² However, reduction of the concentration of the anion to the low concentration level in a short period is difficult because of its high solubility.³

Numerous coordination compounds with M_2L_4 cationic cages have been reported to date.⁴ Their cages include various guest molecules such as anions,⁵⁻⁷ neutral molecules,⁸ and metal complexes.⁹ Among them, the self-assembled M_2L_4 cages which are constructed by metal ions and bis(imidazole)- or bis(benzimidazole)-type neutral ligands have attracted attention as molecular capsules for anions.^{6,7} Many of them have been isolated with hydrophobic anions such as ClO_4^- , BF_4^- , and $CF_3SO_3^-$ within the cationic cages. This is because the hydrophobic anions assist the self-assembled construction of the M_2L_4 frameworks.^{6,7,10} In contrast, M_2L_4 -type molecular capsules including sulfate ion, which is a harmless anion, were not known for the series of coordination compounds constructed by bis(imidazole)- or bis(benzimidazole)-type ligands.

We have recently shown that ClO_4^- in aqueous solutions can be removed by encapsulating it in a water-insoluble M_2L_4 molecular capsule.¹¹ This method, however, could not remove ClO_4^- from water to below 1 ppm concentration level. On continuing works, we have succeeded in isolation of a new water-insoluble M_2L_4 type compound that includes SO_4^{2-} inside and outside the cage. This compound removed ClO_4^- from water efficiently. Here, we report the synthesis, structure, and the high

perchlorate removal activities from water of the compound.

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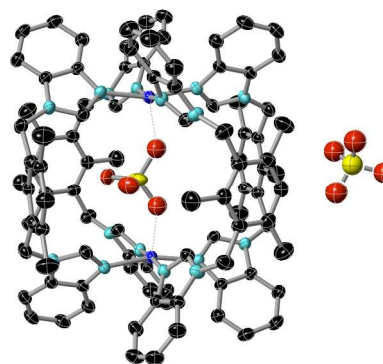


Figure 1. Molecular structure of $1-SO_4$. Disorders of SO_4^{2-} inside the cage, and hydrogen atoms are omitted for clarity. Color code: blue, copper; red, oxygen; yellow, sulfur; sky-blue, nitrogen; black, carbon.

Compound $1-SO_4$ was obtained as blue microcrystals by evaporation of an EtOH/ H_2O mixed solution of $CuSO_4 \cdot 5H_2O$ and *m*-bbitrb on heating. Single crystals for X-ray diffraction analysis were grown by slow evaporation of an EtOH/ H_2O solution of the product in a test tube for a few months. Figure 1 shows the M_2L_4 type capsule structure of $1-SO_4$ bearing SO_4^{2-} inside and outside the cage. The SO_4^{2-} inside the cage associates with the two Cu^{2+} with Cu—O distances of 2.143 (8) Å. These distances are shorter than the Cu—O distance (2.388 (4) Å) between ClO_4^- and Cu^{2+} in $[ClO_4 \subset Cu_2(m\text{-bbitrb})_4](ClO_4)_2](ClO_4)$ (**2**) that was reported by Su and co-workers.⁶ The coordination of SO_4^{2-} pulls the Cu^{2+} toward the center of the capsule. The Cu^{2+} of $1-SO_4$ is withdrawn about 0.202 (2) Å to the center of the capsule from the N_4 plane that is defined by four nitrogen atoms at the coordination condition, while Cu^{2+} of **2** remains in the N_4 plane. As a result the Cu...Cu distance of the M_2L_4 cage of $1-SO_4$ (about 6.6 Å) is shorter than that of **2** (7.36 Å). This is the first M_2L_4 -type molecule capturing divalent anions in M_2L_4 cationic cages constructed by bis(imidazole)- or bis(benzimidazole)-type ligands.

It was found that $1-SO_4$ has high activity for removal of ClO_4^- ion from water despite the compound being insoluble in water. Figure 2a shows changes the concentrations of anions in the

aqueous solution as a function of time after addition of 0.20 g (0.10 mmol) of **1-SO₄** to an aqueous solution (100 mL) containing NaF, NaCl, NaBr, NaNO₃, NaClO₄, and Na₂SO₄ at the same concentration (1.0 mM). The change in the concentration of each anion was monitored using ion chromatography. As shown in the chart, 1.0 mM ClO₄⁻ was reduced to about 0.070 mM at 5 min, and then 0.013 mM within 30 min. Other anions, NO₃⁻ and Br⁻, were also reduced from 1.0 mM to about 0.55 mM and 0.80 mM, respectively, at 30 min. Concentrations of Cl⁻ and F⁻ were not changed essentially. The concentration of SO₄²⁻ was increased from 1.0 mM to 1.73 mM at 30 min. This increase corresponds to the decreases of concentrations of other anions, indicating that SO₄²⁻ of **1-SO₄**, which is insoluble in water, was exchanged with the anions during the reaction.

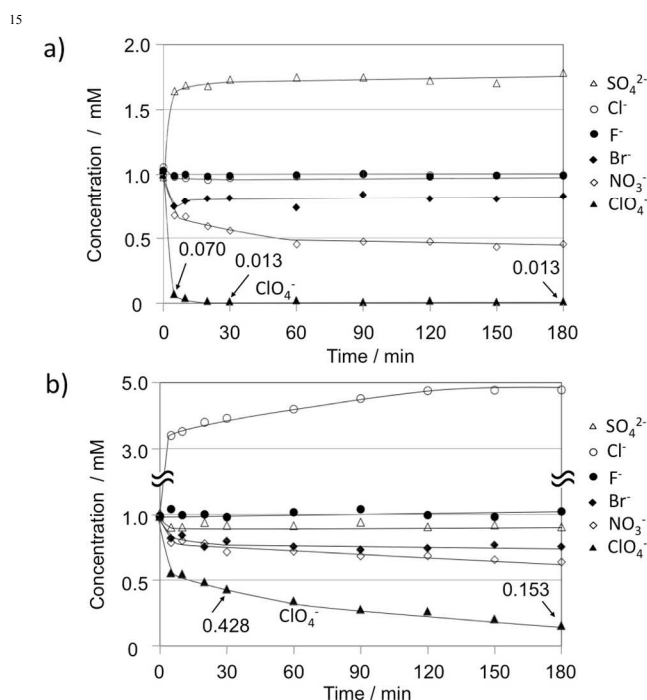


Figure 2. Changes of concentration of anions in an aqueous solution (100 mL), containing NaF, NaCl, NaBr, NaNO₃, NaClO₄, and Na₂SO₄ (all 0.1 mmol) after addition of **1-SO₄** (0.20 g, 0.1 mmol) (a) and anion-exchange resin PuroLite A530E (0.20 g) (b).

To estimate the ClO₄⁻ removal ability of **1-SO₄**, a similar experiment was carried out for comparison using an anion-exchange resin (PuroLite A530E),¹² which has been widely used for ClO₄⁻ removal.¹³ This study showed that 1.0 mM ClO₄⁻ was reduced to about 0.42 mM at 30 min and 0.15 mM at 180 min (Figure 2b). Three other anions, NO₃⁻, Br⁻, and SO₄²⁻, were reduced from 1.0 mM to 0.71 mM, 0.79 mM, and 0.91 mM, respectively, at 30 min. The concentration of Cl⁻, which is originally included in the resin, increased corresponding to the decreases of concentrations of other anions. This result shows that **1-SO₄** efficiently removes ClO₄⁻ from water. This ability could arise from the hydrophobic space created among the [SO₄ ⊂ Cu₂(*m*-bbitr_b)₄]²⁺ units, which encapsulates the hydrophobic anion ClO₄⁻ in preference to SO₄²⁻. This study showed that **1-SO₄** can remove ClO₄⁻ effectively from aqueous solutions even in the presence of other anions.

To study the anion exchange reaction shown by Figure 2a, structure of the reaction product was determined by single crystal X-ray analysis technique at 173 K (Figure 3) and elemental analysis (Supporting Information). Immersion of **1-SO₄** in an aqueous solution that contained excess NaClO₄ for a few days provided a blue powder. The solution remained colorless throughout the reaction. After careful washing of the reaction product with water, the obtained product was recrystallized from MeCN. The single-crystal X-ray diffraction study confirmed that the product was [SO₄ ⊂ Cu₂(*m*-bbitr_b)₄](ClO₄)₂·4MeCN (**1-ClO₄**). The overall structure is shown in Figure 3. Molecular structure of the cationic unit of **1-ClO₄** is essentially same to that of **1-SO₄**. This result clearly demonstrates that only SO₄²⁻ outside the cage was exchanged with ClO₄⁻ by the anion-exchange reactions. Compound **1-ClO₄** was also insoluble in water, meaning that ClO₄⁻ was separated from the aqueous solution by treatment with **1-SO₄**.

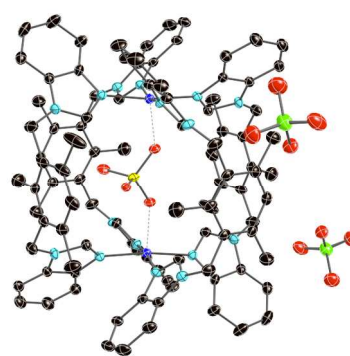


Figure 3. Molecular structure of **1-ClO₄**. Disorders of SO₄²⁻ inside the cage, ClO₄⁻ outside the cage, and hydrogen atoms are omitted for clarity. Color code: blue, copper; red, oxygen; yellow, sulfur; sky-blue, nitrogen; black, carbon; green, chlorine.

Although the solution in Figure 2a remained colorless throughout the experiment, the concentration of Cu²⁺ dissolved in the solution was determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES). This measurement detected only 0.13 mg L⁻¹ of Cu²⁺ in the aqueous solutions after the ClO₄⁻ removal experiment. This value is lower than the concentration in drinking water mandated by the World Health Organization (2 mg L⁻¹).¹⁴ These results show that **1-SO₄** has high potential as a material for removal of ClO₄⁻ from water for many purposes.

Since the ClO₄⁻ removal speed by **1-SO₄** was very fast, we have attempted to prepare a **1-SO₄**-fixed filter. The filter was made from a commercially available syringe filter (ϕ 40 mm, 0.2 μm pores). The fixation of **1-SO₄** on the membrane was achieved by filtration of a powder sample of **1-SO₄** suspended in water using the syringe filter. After the aqueous solution of NaClO₄ (ca. 1,000 ppb for ClO₄⁻) was passed through the filter under hand-pressure, it was found that the concentration of ClO₄⁻ was reduced to ca. 12 ppb for ClO₄⁻. The ion chromatography charts are shown in Figure 4. This result means that the **1-SO₄** is useful for convenient removal of ClO₄⁻ from water in a short time period.

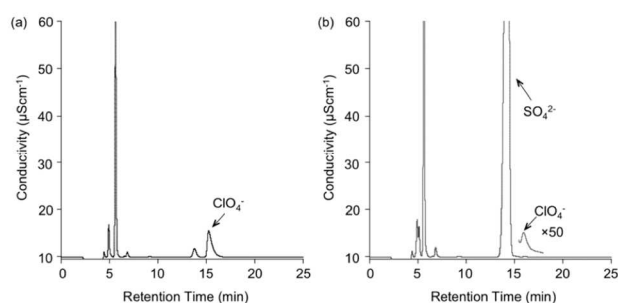


Figure 4. Ion chromatograph charts of the aqueous solution of NaClO_4 (ca. 1000 ppb) (6.0 mL) before (a) and after (b) passing through the syringe filter fixed with **1-SO₄**.

Although removal of ClO_4^- by anion-exchange resins is currently a promising method, the resins are generally difficult to regenerate for reuse.¹⁵ We confirmed that **1-SO₄** is conveniently regenerated for reuse after the ClO_4^- removal experiments. As summarized in the Supporting Information (p. S18), analytically pure *m*-bbitr_b was recovered by a general procedure from the reaction products obtained after ClO_4^- removal experiments in about 53% yield. The ligand could be used for re-preparation of **1-SO₄**.

In conclusion, we have prepared a new water-insoluble M_2L_4 type compound that includes SO_4^{2-} inside and outside the cage. The compound removed ClO_4^- from water by exchange with SO_4^{2-} outside the cage of the compound. The activity was useful for reduction of ClO_4^- in water to lower concentration level. The removal reactions were not interfered by other general anions. The compound was conveniently regenerated by general chemical procedure from the obtained product after the ClO_4^- removal experiments. While many anion-exchange resins have been developed, utilizations of positively charged nano-scale molecules as anion-exchange materials were not explored well. This work reveals that coordination compounds have high potentials as new anion-exchange materials.

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Notes and references

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† Electronic supplementary information (ESI) available: Materials and methods, crystallographic data, XRD charts, UV-vis. reflectance spectra, IR spectra. 854022 (1-SO₄), CCDC 854021 (1-ClO₄). For ESI and crystallographic data in CIF or other electronic format see DOI: xx.xxxx/xxxxxxxxxxx.

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Graphical Abstract

High efficient perchlorate removal from water by water-insoluble M_2L_4 type molecule is described.

Removal of Perchlorate Ion from Water in the Short Period

