Removal of Perchlorate Anion from an Aqueous Solution by Encapsulation in an Anion-templated Self-assembled Molecular Capsule

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A new M_2L_4-type molecular capsule was prepared and characterized. It is shown that the anion-templated self-assembled construction is useful for selective removal of perchlorate anion from aqueous solution.

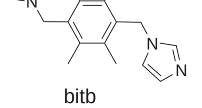
Perchlorate anion is one of the most difficult anions to be separated from an aqueous solution.[1] Even $KClO_4$, which shows one of the lowest solubilities among perchlorate salts, dissolves 15 g of the salt in 1 L of water. Actually, there are no metal ions that effectively precipitate perchlorate anion from water. That is why the creation of cationic hosts that can precipitate the perchlorate anion from aqueous solution are unique subjects in host–guest chemistry.

Positively charged cages made up of metal–organic frameworks recognize the target anions by the sizes and shapes of the anions, coordination at the metal sites, and hydrogen bonds with the cage frameworks.[2] Water molecules, however, significantly inhibit the chemical interactions by competitive coordination to the metal sites and hydrogen-bonding sites.[3] That is why the selective encapsulation of the target anions within cages has not been established in aqueous solution.

M_2L_4-type cationic molecular capsules were synthesized from bis(benzoimidazole)-type ligands.[4] Although various anions and water molecules have been successfully encapsulated within the cationic cages, selective encapsulation of target guests has not been developed.

Recently, we selected 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bitb; Scheme 1) for the preparation of a new self-assembled metal complex, and have successfully isolated a new M_2L_4-type metal complex $[ClO_4 \subset Cu_2(bitb)_4(ClO_4)_2]ClO_4$ (**1**) by treatment of bitb with $Cu(ClO_4)_2 \cdot 6H_2O$. As a unique new finding for this self-assembled system, dependency of the capsule structure formation on the perchlorate anion concentration was observed. This paper describes the characterization of the molecular capsule and successful utilization of the anion-templated self-assembled process to remove perchlorate anion from an aqueous solution.

The bitb was prepared from a reaction of dibromodurene and imidazole according to the literature method.[5] The treatment of $Cu(ClO_4)_2 \cdot 6H_2O$ (37.1 mg, 0.1 mmol) with two equiv of bitb (58.9 mg, 0.2 mmol) in MeCN/H_2O (1:1) media (40 mL) yielded complex **1** as deep purple crystalline material in about 72% yield (Elemental analysis (%) Calcd for $C_{72}H_{88}Cl_4Cu_2N_{16}O_{16}$: C, 50.80; H, 5.21; N, 13.16. Found: C, 50.68; H, 4.74; N, 13.10). The single-crystal X-ray analysis demonstrated the capsule structure of complex **1**.[6]



bitb

Scheme 1. Structure of bitb.

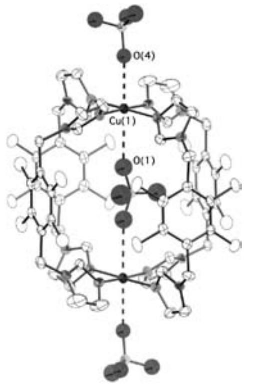


Figure 1. Capsule structure of complex **1**. A crystallographic inversion center is located in the center of the capsule framework. The perchlorate anion in the cage is disordered over two positions, one of which is shown. Hydrogen atoms and a metal-free perchlorate anion are omitted for clarity.

As shown in Figure 1, one of the perchlorate anions per formula unit is encapsulated in the cage, which has a size of about $6.5 \times 6.5 \times 5.0$ Å^3. This anion is located around an inversion center and therefore treated as being disordered. The perchlorate anion weakly associates with the two Cu^{II} sites [Cu(1)···O(1) = 2.87(1) Å]. The other two perchlorate anions outside weakly associate with each Cu^{II} site [Cu(1)···O(4) = 2.642(8) Å]. The remaining perchlorate anion is located among the capsule molecules without significant interactions to the molecular capsule.

To understand if the capsule structure is retained in solution, we measured the ESI mass spectrum of an MeCN solution of complex **1**. The spectrum observed shows two peaks, which are ascribed to $[ClO_4 \subset Cu_2(bitb)_4]^{3+}$ and $[ClO_4 \subset Cu_2(bitb)_4(ClO_4)]^{2+}$ (Supporting Information).[7] This result clearly demonstrates that the cage structure is retained in solution.

To study the selective encapsulation of perchlorate anion by the cationic cage of complex **1**, we have monitored the change in the absorption spectrum upon addition of $NaClO_4$(aq) to a mixture of $CuSO_4 \cdot 5H_2O$ and 2 equiv of bitb. As shown in Figure 2, the absorption band with a maximum at 610 nm gradually shifts to shorter wavelength. When 0.5 equiv of $NaClO_4$(aq) was added

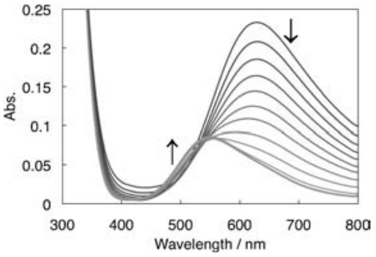


Figure 2. Absorption change when 20 µL of $NaClO_4$(aq) ($10\,mmol\,L^{-1}$) was added stepwisely to a mixed MeCN/H_2O (1:1) solution (1.6 mL) of $CuSO_4{\cdot}5H_2O$ ($2.5\,mmol\,L^{-1}$) and bitb ($5.0\,mmol\,L^{-1}$).

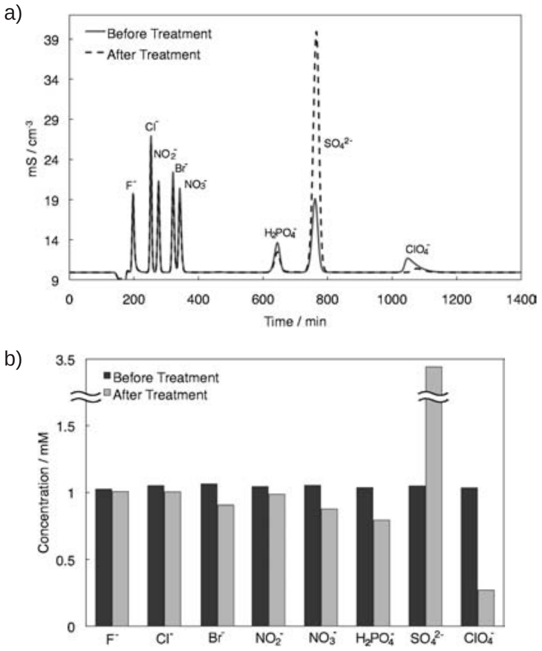


Figure 3. Ion chromatogram before and after the addition of $CuSO_4{\cdot}5H_2O$ and bitb to the aqueous solution of various salts (a). Summary of the changes in concentration of each anion (b). Increase of concentration of $SO_4{}^{2-}$ corresponds to the added $CuSO_4{\cdot}5H_2O$.

to 1 equiv of $CuSO_4{\cdot}5H_2O$, the shift was essentially stopped. The resulting absorption spectrum is consistent with that of complex **1** (Supporting Information).[7] This means that the $[ClO_4 \subset Cu_2(bitb)_4]^{3+}$ capsule is formed by self-assembly even in the presence of $SO_4{}^{2-}$ in an aqueous solution.

Moreover, we have successfully isolated complex **1** by evaporation of a MeCN/H_2O mixed solution of $NaClO_4$, $CuSO_4{\cdot}5H_2O$, and bitb.[8] Obviously, the perchlorate anion plays an important role in the formation of the cationic cage of complex **1**.

This finding prompted us to remove perchlorate anion from aqueous solution by encapsulation in the self-assembled cage. We have succeeded in the separation of perchlorate anion in 80% yield from an aqueous solution of $NaClO_4$ by addition of 2 equiv of $CuSO_4{\cdot}5H_2O$ and 4 equiv of bitb within 1 h. Moreover, we have shown that there is preferential removal of the perchlorate anion. Figure 3a shows the change in the ion chromatogram before and after the addition of $CuSO_4{\cdot}5H_2O$ (63 mg, 0.25 mmol) and bitb (148 mg, 0.5 mmol) to an aqueous solution (100 mL), containing eight kinds of salts (NaF, NaCl, NaBr, $NaNO_2$, $NaNO_3$, $NaH_2PO_4{\cdot}2H_2O$, Na_2SO_4, and $NaClO_4$) all at the same concentration ($1\,mmol\,L^{-1}$). The solution was stood for 2 h without stirring. During the experiment, a white powder of bitb changed to a pale purple powder because of conversion to complex **1**. The changes in the concentrations of these anions in the supernatant were monitored by ion chromatography. The results are summarized in Figure 3, showing the preferential removal of perchlorate anion among the various anions in the solution.

To the best of our knowledge, this is the first example of anion receptors that remove perchlorate anion from an aqueous solution. Further studies of the self-assembled molecular capsule system are in progress.

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References and Notes

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6 This complex crystallizes as **1**·4MeCN. Crystallographic data for the complex: $C_{80}H_{100}C_{14}Cu_2N_{20}O_{16}$, $M_r = 1866.70$, monoclinic, space group $C2/c$ (No. 15), $a = 25.805(4)$, $b = 13.152(2)$, $c = 29.799(5)$ Å, $\beta = 117.737(5)^\circ$, $V = 8951(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.385\,g\,cm^{-3}$, $\mu(Mo\,K\alpha) = 0.706\,mm^{-1}$, $T = 293$ K, $\lambda = 0.7107$ Å, ω scan. Of a total of 32288 reflections collected, 8328 were independent ($R_{int} = 0.042$). The structure was solved by direct methods and refined by full-matrix least squares on F. Final $R1$ $[I > 2\sigma(I)] = 0.0984$ and $wR2 = 0.1578$ (all data); GOF = 1.498. CCDC 715771.

7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

8 Identification was carried out by determination of cell parameter; $a = 25.86(5)$, $b = 13.16(3)$, $c = 29.00(6)$ Å, $\beta = 114.49(1)^\circ$, $V = 8981(33)$ Å^3.

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