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Preferential Removal of Perchlorate ion from Water by Self-assembled Construction of Cationic 3D Coordination Frameworks with Methylene Units

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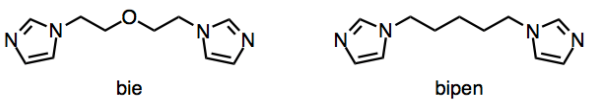
Four new Co(II)-coordination polymers have been prepared from treatments of a Co^{II} source with 2,2′-bis(1*H*-imidazolyl-1-yl)ether (bie) or 1,5-bis(1*H*-imidazol-1-yl)pentane (bipen), which are bis-imidazole-type ligands with hydrophobic polymethylene units. Structural characterizations have shown that their compounds create hydrophobic cavities for anions in their cationic 3D coordination frameworks. The self-assembled construction of the frameworks in aqueous solutions containing various inorganic anions trapped perchlorate ion selectively in the cavities. Because the product is insoluble in water, perchlorate ion was selectively removed from the aqueous solutions.

Removal of perchlorate ion (ClO_4^-) from aqueous solutions is quite difficult because of the ion's high solubility in water[1,2] This anion is also highly soluble in organic solvents due to the hydrophobic property.[3-5] Because this anion is harmful for newborns and children,[6,7] the development of ClO_4^- removal methods from aqueous solutions is an important goal. We have succeeded in preferential removal of ClO_4^- from aqueous solutions by selective trapping in a water-insoluble coordination cage.[8] Treatment of an aqueous solution containing ClO_4^- and other inorganic anions with Cu^{II} ion and the hydrophobic bis-imidazole-type ligand, L, removes ClO_4^- from the solutions by formation of a water-insoluble Cu_2L_4-type molecular capsule that traps ClO_4^- within it. We have also shown that ClO_4^- is trapped preferentially in the space between cationic molecular capsules with bis-benzimidazole-type ligands.[9] These studies indicate that the hydrophobic space created in the cationic coordination frameworks is useful for trapping ClO_4^-.



Scheme 1. Bie and bipen structures.

The self-assembled formation of water-insoluble cationic coordination frameworks bearing hydrophobic spaces in aqueous solutions would be useful for preferential removals of ClO_4^- from aqueous solutions by selectively trapping the anion in the cavities. Because coordination polymers are generally insoluble in water, formations of coordination polymers bearing cationic hydrophobic cavities in aqueous solutions could be useful for removal of ClO_4^- from aqueous solutions. In this work, we have selected two bis-imidazole-type ligands with hydrophobic chain units, bie and bipen, to construct water-insoluble coordination polymers bearing hydrophobic cavities for ClO_4^-. The ligand structures are illustrated in Scheme 1.

Numerous coordination polymers have been synthesized by using rigid bridging ligands such as pyrazine, 4,4′-bipyridine, and terephthalate to create porous materials with stable channels.[10-16] These compounds, which are called metal-organic-frameworks when they have porous frameworks, have shown various zeolite-like functions such as heterogeneous catalysis, gas adsorption, molecular separation, and anion exchanges. On the other hand, syntheses and characterizations of coordination polymers constructed by bridging ligands bearing polymethylene units are still rare[17-22] because their fragile networks have been considered to be difficult to create functional frameworks. This paper describes the syntheses and crystal structures of four new Co(II)-coordination polymers with bie and bipen, and the ClO_4^- removal functions from the aqueous media by self-assembled formations of the coordination polymers.

The ligands, bie[17] and bipen,[18] were prepared according to the methods in the literature. Compounds $[Co(bie)_3](ClO_4)_2$ (**1**) and $[Co(bipen)_3](ClO_4)_2$ (**3**) were obtained as single crystals by diffusion of a MeOH solution of the bridging ligand into an aqueous solution of $Co(ClO_4)_2{\cdot}6H_2O$. Compounds $[Co(bie)_3](NO_3)_2$ (**2**) and $[Co(bipen)_3](NO_3)_2$ (**4**) were obtained as single crystals by diffusion treatments of the ligand with $Co(NO_3)_2{\cdot}6H_2O$ in MeOH or acetone solution. The synthetic procedures are summarized in the Supporting Information (SI). Single-crystal X-ray diffraction studies have shown that **1**–**3**, which crystallized in the centric space group trigonal $R\bar{3}$(h), are crystallographically isostructural.[23] Although **4** has remarkably longer *c* axis compared to other thee compounds, the network motif is essentially same to **1**–**3**. Therefore, only the crystal structure of **1** is described in detail in this manuscript.

Figure 1a shows a crystallographic independent unit of **1**, which consists of a Co^{II} ion, parts of bie and a ClO_4^- ion. The Co^{II} center is based on the octahedron with six imidazole nitrogen atoms of bie (Co(1)—N(1) = 2.1703(19) Å) (Figure 1b). As shown in Figure 1a, the bie ligand was remarkably disordered in **1**; O(1), C(4), and C(5) were solved at 50% occupation. Part of the coordination framework is shown in Figure 2a to show the disorder of the bie. This figure shows bie with blue and red methylene units. It is easily understandable that the disorder around the six Co^{II} ions is either a set of the Co-bie-Co with blue methylene units or with red methylene units. Figure 2b shows the overall structure of **1** after rationally omitting the disorders of the bie.

The framework is constructed of three kinds of Co-bie chains, which run along the ($a - b - c$), ($a + b - c$), and ($2a + b + c$) vectors. As shown in this figure, channel-like cavities are created among the bie frameworks along the *a* and *b* axes. The cavities are filled with ClO_4^-. The channel window (2.9 Å × 1.0 Å) is not large enough for the release and reinclusion of anions.

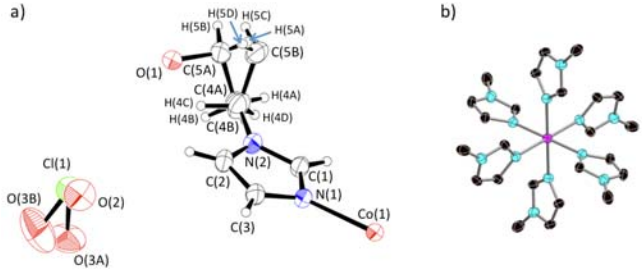


Figure 1. The crystallographically independent unit of **1** (a). Thermal ellipsoids of the coordination environment of **1** at 30% probabilities (b). Hydrogen atoms are omitted for clarity in (b).

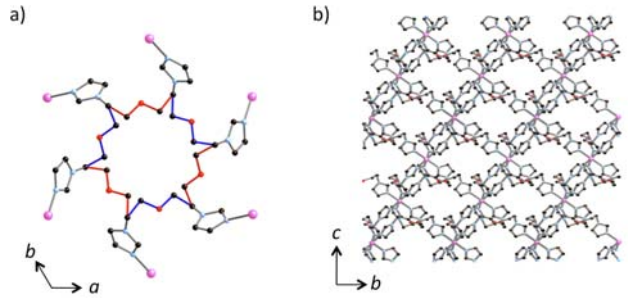


Figure 2. Aspects of connections between the Co^{II} ions by disordered bie ligands of **1** (a). Each blue and red methylene units reveal a set of the disordered bie ligand. The 3D framework as viewed along the *a* axis (b). Perchlorate ions and hydrogen atoms are omitted for clarity. Color code: pink, cobalt; red, oxygen; sky-blue, nitrogen; black, carbon.

Single crystal X-ray analyses of **1**–**3** were carried out at room temperature, while the measurement of **4** was carried out at 173K because this crystal lost the crystallinity under air at room temperature. In contrast to **1**–**3**, **4** included three co-crystallized water molecules per a Co^{II} ion. Although **4** has a similar 3D network motif to **1**–**3**, the framework broadens remarkably along the *c* axis, creating the larger channel-like cavities with the channel window of 4.9 Å × 2.1 Å. The cavities are filled with NO_3^- ions and water molecules.

Crystal structure characterizations of **1**–**4** have shown that the counteranions are located in the hydrophobic cavities in the 3D frameworks of their compounds. These results prompted us to study the removal of ClO_4^- from aqueous solutions by constructing the Co-bie and Co-bipen coordination polymers.

Changes in concentrations of ClO_4^- over time were monitored by ion chromatography for aqueous solutions (50.0 mL) of $Co(ClO_4)_2{\cdot}6H_2O$ (115 mg, 0.25 mmol) after mixing with bie (154 mg, 0.75 mmol) or bipen (153 mg, 0.75 mmol). With the Co-bie system, 10 mM of ClO_4^- (0.50 mmol in the solution) was reduced to 1.8 mM in 10 min. and 1.4 mM in 180 min. (Figure S5 in the SI). Although similar treatment was carried out for $Co(NO_3)_2{\cdot}6H_2O$ with bie in an aqueous solution, the nitrate concentration was not reduced much (Figure S9 in the SI), meaning that formation of **2** would not proceed well in aqueous media.

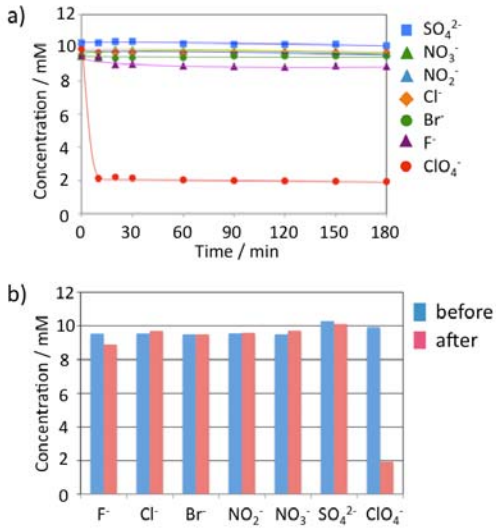


Figure 3. Changes of concentrations of anions in an aqueous solution (50 mL), containing NaF, NaBr, $NaClO_4$, $NaNO_2$, Na_2SO_4 (all 0.5 mmol) and $CoCl_2{\bullet}6H_2O$ (59.5 mg, 0.25 mmol), after mixing with bie (154 mg, 0.75 mmol) (a). Summary of the changes in concentration of each anion (b).

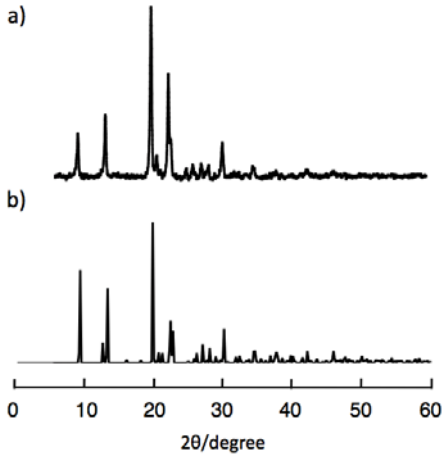


Figure 4. XRPD (Cu K□) pattern of a solid sample obtained by the anion removal experiment (a) with the simulated XRPD pattern for **1** (b).

We studied the selectivity to anions removed from water by the formation of the Co-bie coordination polymer. Figure 3a shows the changes in concentration of anions as functions over time in an aqueous solution (50.0 mL) that contained 5.00 mM of Co^{II} ion and 10 mM each of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, and ClO_4^-, after mixing with bie (154 mg, 0.75 mmol) at room temperature. The concentration of ClO_4^- was reduced from 10 mM to 2.1 mM in 10 min. and 1.9 mM in 180 min. The changes of concentrations of anions are summarized in Figure 3b. Concentrations of other anions were not much reduced. The pink solid obtained after the treatment was confirmed to be **1** by measurements of X-ray powder diffraction (XRPD) pattern (Figure 4). These results indicate

that formation of **1** proceeds even in aqueous solutions, and reduced the concentrations of ClO_4^- in the aqueous solutions selectively. To the best of our knowledge, this is the first example that shows ClO_4^- was removed from aqueous solutions by using self-assembled constructions of coordination polymers.

With the Co-bipen system, reduction in concentration of ClO_4^- (10 mM; 0.50 mmol in 50.0 mL) was not effective compared to the Co-bie system. The concentration was only reduced to 8.8 mM in 30 min. and 3.4 mM in 180 min by treatment with Co(II) ion (0.25 mmol) and bipen (0.75 mmol). (Figure S7 in the SI). Although the removal efficiency was lower than that of the Co-bie system, treatment by bipen also removed ClO_4^- from aqueous solution selectively (Figure S8 in the SI). The XRPD measurement of the pink solid obtained after the treatment indicated the formations of unidentified products in addition to **3** (Figure S9 in the SI). This result shows that formation of **3** did not proceed well compared to the Co-bie system in the aqueous solution.

Although formation of **3** is useful for removal of ClO_4^- from aqueous solutions in the short period, it was difficult to reduce the concentration of the anion to below 0.10 mM because **3** is slightly soluble in the aqueous solution.[24] For example, when an aqueous solution (50 mL) containing $NaClO_4$ (0.50 mmol) was treated with excess Co(II) ion (2.5 mmol) and bie (7.5 mmol), concentration of ClO_4^- in the solution was 0.18 mM at 10min. and 0.13 mM at 180 min. after mixing (Figure S6 in the SI).

Because the Co-bie frameworks showed higher affinities to ClO_4^- than with other inorganic anions, we examined whether NO_3^- in **2** was exchanged with ClO_4^- to yield **1** in aqueous solutions. A solid sample of **2** (40.1 mg, 0.05 mmol) was immersed in aqueous solutions (100 mL), and changes in the concentrations of anions in the solutions were monitored by ion chromatography. After 3 h, concentrations of ClO_4^- were essentially not decreased (Figure S10 in the SI). This result means that the channel windows of Co-bie/bipen frameworks are too small to allow anion exchange reactions. Thus, the anions are securely trapped in the cationic 3D frameworks.

In summary, we have synthesized and structurally characterized four new Co(II)-coordination polymers with bie and bipen ligands. They have 3D coordination frameworks with hydrophobic cavities for anions. The self-assembled formations in the aqueous solutions removed ClO_4^- from aqueous solutions by trapping the anion in the hydrophobic space in the Co-bie and Co-bipen frameworks. For the two systems, the Co-bie system showed higher ClO_4^- removal activities.

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23 Data collections were carried out on a Rigaku VariMax Saturn (Mo $K\alpha$ radiation, 1.2 kW rotating anode). Crystal data for **1**: $C_{30}H_{42}Cl_2CoN_{12}O_{11}$ (Mw = 876.57), trigonal, $R\bar{3}$(h) (No. 148), $a = b$ = 13.7773 (5) Å, c = 18.2177 (11) Å, V = 2994.7 (3) Å^3, Z = 3, ρ(calcd) = 1.458 gcm^{-3}, μ(Mo Kα) = 0.634 mm^{-1}, λ = 0.71075 Å, ω scan, T = 298 K, reflections collected/unique reflections/parameters refined: 15273/1493/117, R_{int} = 0.0349, final R_1 = 0.0482 ($I > 2\sigma(I)$), wR_2 = 0.1215 (all data), GOF = 1.071. CCDC 1053738. Crystal data for **2**: $C_{30}H_{42}CoN_{14}O_9$ (Mw = 801.68), trigonal, $R\bar{3}$(h) (No. 148), $a = b$ = 13.8038(4) Å, c = 16.8272 (9) Å, V = 2776.8 (4) Å^3, Z = 3, ρ(calcd) = 1.438 gcm^{-3}, μ(Mo Kα) = 0.535 mm^{-1}, λ = 0.71075 Å, ω scan, T = 298 K, reflections collected/unique reflections/parameters refined: 14851/1396/123, R_{int} = 0.0354, final R_1 = 0.0354 ($I > 2\sigma(I)$), wR_2 = 0.079 (all data), GOF = 1.151. CCDC 1053739. Crystal data for **3**: $C_{33}H_{48}Cl_2CoN_{12}O_8$ (Mw = 870.66), trigonal, $R\bar{3}$(h) (No. 148), $a = b$ = 13.7655 (7) Å, c = 18.2214 (11) Å, V = 2990.2 (3) Å^3, Z = 3, ρ(calcd) = 1.450 gcm^{-3}, μ(Mo Kα) = 0.629 mm^{-1}, λ = 0.71075 Å, ω scan, T = 298 K, reflections collected/unique reflections/parameters refined: 15831/1518/117, R_{int} = 0.0299, final R_1 = 0.0600 ($I > 2\sigma(I)$), wR_2 = 0.1544 (all data), GOF = 1.045. CCDC 1053740. Crystal data for **4**: $C_{33}H_{54}CoN_{14}O_9$ (Mw = 849.81), trigonal, $R\bar{3}$(h) (No. 148), $a = b$ = 13.1007 (12) Å, c = 25.985 (5) Å, V = 3862.3 (9) Å^3, Z = 3, ρ(calcd) = 1.096 gcm^{-3}, μ(Mo Kα) = 0.388 mm^{-1}, λ = 0.71075 Å, ω scan, T = 173 K, reflections collected/unique reflections/parameters refined: 20208/1946/130, R_{int} = 0.0357, final R_1 = 0.0822 ($I > 2\sigma(I)$), wR_2 = 0.2433 (all data), GOF = 1.59. CCDC 1053741.

24 When **3** (0.15 mmol) was added in an aqueous solution (30 mL), about 0.2 mM of ClO_4^- was detected (Figure S11 in SI). That observation indicates that about 0.003 mmol of **3** could be dissolved in 30 mL of water.