Preferential Removal of Perchlorate Ion from Water Using Self-assembled Constructions of Cationic 3D Coordination Frameworks with Methylene Units

Murakami Aya, Yamanishi Katsunori, Sone Eriko, Kondo Mitsuru

Chemistry Letters

Volume 44

Number 7

Page range 1007-1009

Year 2015-05-13

Copyright (C) 2015 The Chemical Society of Japan. All Rights Reserved.

URL http://hdl.handle.net/10297/9010
doi: 10.1246/cl.150316

<table>
<thead>
<tr>
<th>著者</th>
<th>Murakami Aya, Yamanishi Katsunori, Sone Eriko, Kondo Mitsuru</th>
</tr>
</thead>
<tbody>
<tr>
<td>版面</td>
<td>1007-1009</td>
</tr>
<tr>
<td>出版</td>
<td>Chemistry Letters</td>
</tr>
<tr>
<td>権利</td>
<td>Copyright (C) 2015 The Chemical Society of Japan. All Rights Reserved.</td>
</tr>
</tbody>
</table>

doi: 10.1246/cl.150316
Four new Co(II)-coordination polymers have been prepared from treatments of a Co<sup>II</sup> source with 2,2'<sup>-</sup>bis(1H-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.

**Scheme 1.** Bie and bipen structures.

The self-assembled formation of water-insoluble cationic coordination frameworks bearing hydrophobic cavities in aqueous solutions would be useful for preferential removals of ClO<sub>4</sub><sup>-</sup> 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<sub>4</sub><sup>-</sup> 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<sub>4</sub><sup>-</sup>. The ligand structures are illustrated in Scheme 1.
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 along the bie frameworks along the \(a\) and \(b\) axes. The cavities are filled with ClO\(_4^–\). The channel window (2.9 Å \(\times\) 1.0 Å) is not large enough for the release and reincclusion 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).

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\(^{III}\) 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 \(\times\) 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 mL) of Co(ClO\(_4^–\))\(_2\)·6H\(_2\)O (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\(_3^–\))·6H\(_2\)O 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 2.** Aspects of connections between the Co\(^{III}\) 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.

**Figure 3.** Changes of concentrations of anions in an aqueous solution (50 mL), containing NaF, NaBr, NaClO\(_4^–\), NaNO\(_2^–\), Na\(_2\)SO\(_4^–\), NaNO\(_3^–\), NaClO\(_4^–\), NaClO\(_4^–\), NaNO\(_2^–\) (all 0.5 mmol) and CoCl\(_2\)·6H\(_2\)O (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\(_\alpha\) ) 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\(^{III}\) 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. 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 10 min. 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 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.

References and Notes

4. Agency for Toxic Substances and Disease Registry, Toxicological Profile for Perchlorates, Chapter 4, Chemical and physical information; Department of Health and Human Services: Atlanta, GA; http://www.atsdr.cdc.gov/toxprofiles/tp162-c5.pdf.