Selective incarceration and extraction of oxoanion contaminants from aqueous media by self-assembled nanojars

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Introduction
Selective binding and extraction of anions by artificial receptors is one of the most far-reaching areas of supramolecular chemistry, with implications in chemical, biological and environmental sciences. The extraction of kosmotropic anions from aqueous media is challenging, due to their large hydration energies (affinity for water). We have recently shown that a class of toroidal copper(II)-hydroxide/pyrazolate complexes (nanojars), with the formula \([\text{Cu}_n\text{OH}(\text{pz})]_m\), \(n = 27–36\), totally incarcerate kosmotropic anions with an unprecedented strength. Lined by H-bond donors on the inside and hydrophobic on the outside, these \(\sim 2 \text{ nm}\) sized assemblies selectively extract kosmotropic anions from mixtures with chaotropic anions (low hydration energies). Up to twelve hydrogen bonds from the neutral host assembly wrap around and sequester anions from aqueous solutions, similarly to their analogs in living organisms, such as the sulfate- and phosphate-binding proteins. Tetrabutylammonium “lids” seal the nanojars and render the encapsulated anion completely buried and inaccessible, so that, for example, sulfate is not precipitated out as BaSO\(_4\) by Ba\(^{2+}\) ions.

Mechanism of formation (by ESI-MS)

KOSMOTROPIC anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>The HOFMEISTER series</th>
<th>CHAOTROPIC anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{PO}_4^{3–})</td>
<td>(\text{CO}_3^{2–})</td>
<td>(\text{CO}_3^{2–})</td>
</tr>
<tr>
<td>(\text{SO}_4^{2–})</td>
<td>(\text{Cl}^{–})</td>
<td>(\text{Br}^{–})</td>
</tr>
<tr>
<td>(\text{NO}_3^{–})</td>
<td>(\text{SCN}^{–})</td>
<td>(\text{I}^{–})</td>
</tr>
<tr>
<td>(\text{ClO}_4^{–})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(-2773\) \(-1315\) \(-1090\) \(-347\) \(-321\) \(-306\) \(-280\) \(-275\) \(-214\)

- LARGE hydration energies - difficult to extract from \(\text{H}_2\text{O}\)
- SMALL hydration energies - easy to extract from \(\text{H}_2\text{O}\)

Mass spectrometric studies

Summary
Effect of peripheral pyrazole ligand substitution on nanojar structure and stability
Homoeptropic nanojars can be obtained with pyrazoles shown in green; those in orange can only form heteroeptropic nanojars, and the ones in red do not form nanojars under similar conditions. Substitution of the 4-position does not effect nanojar formation; straight chains in the 3-position are also tolerated, and favor the \(\text{Cu}_{27}\) nanojar; two bulky substituents in the 3,5-positions prevent nanojar formation. Substituents with donor ability are not tolerated at any position of the pyrazole ligand.

Three- or four-ring (from six to fourteen-membered) assemblies, comprised of two smaller outer rings and one or two larger inner rings, have been observed in solution and/or in the solid state. The absence of the 11-membered ring could be explained by considering its size too large for a smaller inner ring, and too small for a larger inner ring.

Acknowledgments
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