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Polyoxometalates

Inorganic Cryptand: Size-Selective Strong Metallic Cation Encapsulation by a Disilicoicosatungstate (Si_2W_{20}) Polyoxometalate**

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A large number of macrocyclic organic compounds that are capable of binding metallic cations are found in natural systems and can be artificially synthesized. Selective recognition has been applied to diverse processes, such as sensors, artificial enzymes, and antibiotics.[1] Although encapsulation behavior depends on the sizes of the metallic cations and macrocyclic cavities, and other factors, such as solvents,[2] precise size-selective encapsulation is difficult because of the conformational flexibility of the organic ligands.

Polyoxometalates (POMs) are robust, discrete, and structurally well-defined oxide clusters that are mainly composed of high-valent transition metals (such as W^{VI}, Mo^{VI}, V^{V}).[3] One of the key characteristics of POMs is a strong affinity for metallic cations. Certain POMs can selectively trap divalent cations, such as Ca^{2+}, in the presence of monovalent cations, such as Na^+.[4] These water-soluble anions can be potentially useful for applications, such as detergents, that involve cation binding and exchange. Some kinds of POMs capture metallic cations in their cavities upon formation[5] or by substitution.[6] For example, Na^+ is captured in the center of the Preyssler-type POM $[Na\subset P_5W_{30}O_{110}]^{14-}$ and can be substituted by the cations with almost the same size under hydrothermal conditions.[6] Furthermore, there are few examples of the encapsulation of metallic cations by the guest-free form of POMs: tungstoarsenates of $[MAs^{III}{}_4W_{40}O_{140}]^{(28-n)-}$ (M^{n+} = Na^+, K^+, Ba^{2+}) encapsulate NH_4^+, Ag^+, and Co^{2+},[7] and a supramolecular POM based on $[AsW_9O_{33}]^{9-}$ and $[Mo_3S_4]^{4+}$ selectively encapsulates Cu^+ and Ag^+.[8] There is also a fourth class of the cation-trapping POMs in which the cations can either be trapped in a cluster cavity with closed or open pores, and an equilibrium is observed in the case of open pores.[9]

Recently, we have synthesized a dimeric γ-Keggin POM, $[H_n(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{(8-n)-}$ (H_n-**1**; $n = 1$, 2), by the dehydrative condensation of the silicodecatungstate $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$.[10] As POM **1** has a rigid cavity between two $[\gamma\text{-}SiW_{10}O_{32}]^0$ cluster units, size-selective metallic cation encapsulation is expected. Herein, we report size-selective, strong, metallic cation encapsulation by **1**.

The fully deprotonated form of **1**, $[(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{8-}$, was prepared by the reaction of the tetra-*n*-butylammonium (TBA) salt of H_1-**1** with the proton scavenger 2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (BEMP), which features extremely strong basicity, low nucleophilicity, and solubility in organic solvents.[11] The ^{29}Si NMR spectrum of the fully deprotonated form of **1** in acetonitrile showed a signal at $\delta = -85.8$ ppm (Supporting Information, Figure S1a), and the ^{183}W NMR spectrum showed three signals at $\delta = -133.8$, -134.7, and -200.0 ppm, with an integrated intensity ratio of 2:1:2 (Supporting Information, Figure S2). The NMR spectroscopic data are in accord with D_{2h} symmetry.

When one equivalent of $Pb(OTf)_2$ was added to an acetonitrile solution of **1**, one new ^{29}Si NMR signal appeared at $\delta = -79.9$ ppm (Figure 1a) and three broad ^{183}W NMR signals appeared at $\delta = -91.9$, -123.2, and -146.2 ppm with the integrated intensity ratio of 1:2:2 (Figure 1b).[12] The ^{207}Pb NMR spectrum has one sharp signal at $\delta = -2755$ ppm (Figure 1c); the broad signal of the parent $Pb(OTf)_2$ ($\delta = -3407$ ppm in MeCN; Supporting Information, Figure S3) was not observed. The cold-spray ionization mass spectrum of Pb-**1** (CSI-MS, positive mode) has three intense signals at $m/z = 3484.12$, 4564.83, and 6725.38, with isotopic distributions that agree with the formulations $[TBA_8\{Pb(SiW_{10}O_{32})_2(\mu\text{-}O)_4\}]^{2+}$, $[TBA_{15}\{Pb(SiW_{10}O_{32})_2(\mu\text{-}O)_4\}_2]^{3+}$, and $[TBA_7\{Pb(SiW_{10}O_{32})_2(\mu\text{-}O)_4\}]^+$, respectively (Supporting Information, Figure S4). These NMR and CSI-MS data show the formation of a single species, and that the parent structure of **1** is maintained upon complexation with Pb^{2+}.

Yellow single crystals of Pb-**1** suitable for X-ray crystallography were successfully obtained from acetonitrile solution of **1** with one equivalent of $Pb(OTf)_2$ by vapor diffusion of methanol (Figure 2). The dimeric γ-Keggin structure of **1** is maintained after encapsulation of Pb^{2+}. One Pb^{2+} ion is located inside the cluster framework of **1**; the position deviates from the center of **1**, and the Pb^{2+} ion is positioned at one of two disordered sites. The results of the elemental analysis and mass spectrometry support the composition of Pb-**1** as being $[Pb\subset(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{6-}$. The encapsulated Pb^{2+} ion is coordinated to ten oxygen atoms: Two oxygen atoms at the conjunction of two γ-Keggin structures ($Pb{-}O_{conj}$ 2.60 Å), four oxygen atoms on the Si-O-W bridging position

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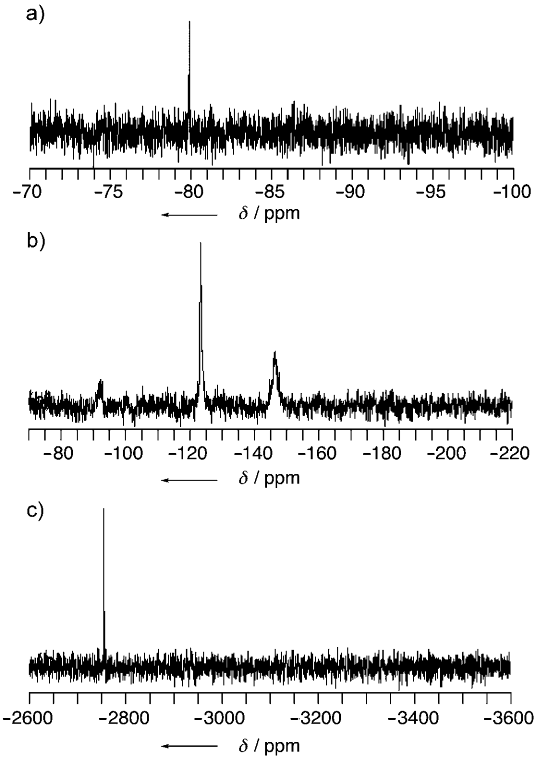


Figure 1. a) ^{29}Si, b) ^{183}W, and c) ^{207}Pb NMR spectra of **1** with one equivalent of $Pb(OTf)_2$.

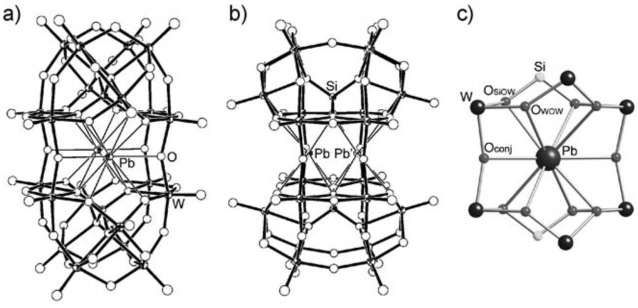


Figure 2. Molecular structure of Pb-**1**. a, b) Two mutually orthogonal views; c) A ball-and-stick representation of the coordination sphere of Pb^{2+}.

($Pb{-}O_{SiOW}$ 2.67–2.87 Å), and four oxygen atoms on the corner-shared W-O-W bridging position ($Pb{-}O_{WOW}$ 2.83–2.90 Å). The coordination environment of Pb^{2+} is similar to those of organic cryptands.[13] It was confirmed that the dissolution of Pb-**1** in acetonitrile gave almost the same ^{29}Si and ^{207}Pb NMR spectra as those shown in Figure 1 a and c, respectively.

The observed metal cation encapsulation of **1** is also supported by the results with the DFT calculation. The HOMO of **1** showed that the orbitals on the oxygen atoms surrounding the cavity were directed to the center of **1** (Supporting Information, Figure S5). This is probably the reason why **1** can encapsulate metal cations in the cavity.

Next, encapsulation of other dicationic metallic ions was examined. Dicyclohexano[18]crown-6 (DCH-18C6) complexes were used as metal cation sources owing to the insolubility of metal salts in acetonitrile. When one equivalent of $[Sr(DCH\text{-}18C6)]^{2+}$ was added, one new ^{29}Si NMR signal appeared at $\delta = -79.6$ ppm (Supporting Information, Figure S1 c), in the same manner as that of $Pb(OTf)_2$. The molecular structure of Sr-**1** was essentially identical with that of Pb-**1**; one metallic cation was located inside the cavity of **1** and the position was deviated from the center of the cavity (Supporting Information, Figure S6). In contrast, no new ^{29}Si NMR signals appeared when one equivalent of Ba^{2+} was added (Supporting Information, Figure S1 d). The compound Ba•H_3O-**1** was successfully synthesized by the reaction of **1** with $Ba(NO_3)_2$. The X-ray crystallographic data showed that larger Ba^{2+} was not encapsulated, but coordinated to the outer W=O moieties (Figure 3 a). The ^{29}Si NMR and X-ray crystallographic data indicate that **1** could encapsulate Sr^{2+} (ionic radius, 1.40 Å) as well as Pb^{2+} (1.43 Å), but larger Ba^{2+} (1.56 Å) could not be encapsulated in the cavity. The size-selective encapsulation ability was also observed for monocationic metallic ions. The patterns of ^{29}Si NMR signals of a 1:1 mixture of **1** and $[M(DCH\text{-}18C6)]^{+}$[14] showed that the larger Cs^{+} ion (1.88 Å) was not encapsulated, but Na^{+} (1.32 Å), Ag^{+} (1.42 Å), K^{+} (1.65 Å), and Rb^{+} (1.75 Å) were (Supporting Information, Figure S1 e–i).[17,19] The molecular structure of $[Ag\subset(SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{7-}$ (Ag-**1**) could be confirmed by X-ray crystallography (Figure 3 b).[20]

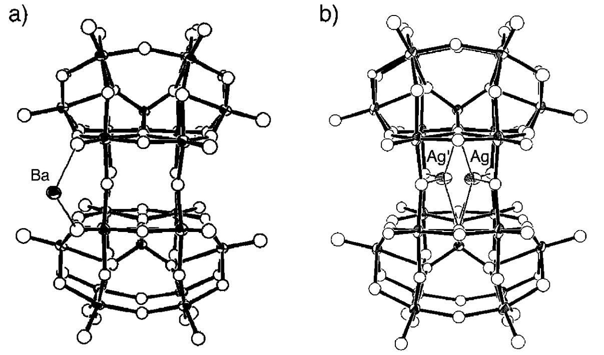
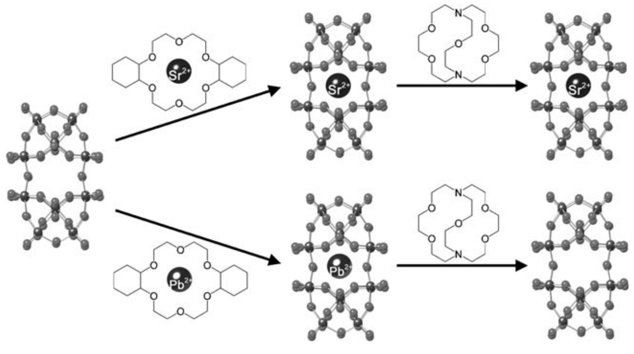


Figure 3. Molecular structures of a) Ba-**1** and b) Ag-**1**. The silver atom in Ag-**1** is crystallographically disordered over two positions, Ag and Ag′.

The metal-cation-encapsulating ability of **1** was compared with DCH-18C6 and 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-[8.8.5]tricosane ([2.2.1]cryptand) (Scheme 1). When one equivalent of $[Pb(DCH\text{-}18C6)](NO_3)_2$ was added to the MeCN solution of **1**, the ^{29}Si NMR signal appeared at $\delta = -79.9$ ppm, with disappearance of the corresponding signal of guest-free **1** (Supporting Information, Figure S7), and a ^{207}Pb NMR signal of Pb-**1** appeared at $\delta = -2755$ ppm, with disappearance of the signal at $\delta = -3350$ ppm for $[Pb(DCH\text{-}18C6)](NO_3)_2$ (Supporting Information, Figure S8). These NMR data show that **1** can encapsulate Pb^{2+} more strongly than DCH-18C6. In the same way as that of Pb^{2+}, a new



Scheme 1. Transfer of Pb^{2+} and Sr^{2+} ions from dicyclohexano[18]crown-6 to **1**, and the reaction of the resulting Pb-**1** and Sr-**1** complexes with [2.2.1]cryptand.

^{29}Si NMR signal appeared at $\delta = -79.6$ ppm with disappearance of the signal of guest-free **1** upon the addition of one equivalent of $[Sr(DCH\text{-}18C6)](NO_3)_2$ to the solution of **1**, which also indicates stronger encapsulation of Sr^{2+} by **1** than DCH-18C6. Furthermore, the affinity of **1** to Sr^{2+} was much stronger than that of organic [2.2.1]cryptand. The ^{29}Si NMR spectrum of Sr-**1** was unchanged by the addition of [2.2.1]cryptand to the solution of Sr-**1**, even after 72 h at 333 K (Supporting Information, Figure S9).[21] To our knowledge, **1** is the first inorganic cryptand that encapsulates metal cations more strongly than organic cryptands. In contrast, reaction of Pb-**1** with [2.2.1]cryptand resulted in the regeneration of guest-free **1** without decomposition of the POM framework (Supporting Information, Figure S10).[23]

In conclusion, the cage-like disilicoicosatungstate **1** encapsulates smaller dicationic Pb^{2+} and Sr^{2+} ions and monocationic Ag^+, Na^+, K^+, and Rb^+ ions. POM **1** is a stronger inorganic Sr^{2+}-capturing agent than organic cryptands; larger Ba^{2+} and Cs^+ ions are not included.

Experimental Section

Details of the experimental procedures, including crystallographic studies, are given in Supporting Information. CCDC 728161 (Pb-**1**), 728162 (Sr-**1**), 728163 (TEA_7·[Ag-**1**]·2 MeCN), and 728160 (TBA_5·[Ba·H_3O-**1**]·3 H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] When one equivalent of Ag^+ was added, the signal was split into a doublet by coupling between ^{29}Si and Ag ($J = 1.3$ Hz). A similar Si–Ag coupling has been reported[15] because silver is composed of two stable isotopes with $I = 1/2$: ^{107}Ag (natural abundance: 51.82 %) and ^{109}Ag (48.18 %).[16] On the other hand, when one equivalent of Pb^{2+}, Ca^{2+}, Sr^{2+}, Na^+, K^+, or Rb^+ was added, the signal splitting was not observed, probably because of the low natural abundance of the NMR active nucleus (^{207}Pb: $I = 1/2$, 22.1 %) or high relaxation rate of quadrupolar nuclei (^{43}Ca: $I = 7/2$, ^{87}Sr: $I = 9/2$, ^{23}Na: $I = 3/2$, ^{39}K: $I = 3/2$, ^{85}Rb: $I = 5/2$).

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[17] The larger Cs^+ ion could not be encapsulated into **1**, but Na^+ and K^+ could, although the stability constant of $[Cs(DCH\text{-}18C6)]^+$ (Log $K = 4.26$) is smaller than those of $[Na(DCH\text{-}18C6)]^+$ (5.20)

and $[K(DCH\text{-}18C6)]^+$ (5.63) in MeCN.[18] This shows the size-selective encapsulation of monocationic metallic cations from DCH-18C6 to the cavity of **1**.

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[19] La-**1** was successfully synthesized in the same way as that of Ba•H_3O-**1**. La^{3+} (1.30 Å) was not encapsulated, and coordinated to outer W=O groups. Therefore, the encapsulation of metallic cations for **1** depends not only on size, but also on charge. This effect is probably because the stronger electrostatic interaction of **1** with multivalent cations leads to the stabilization even by the outer W=O groups.

[20] The Ag^+ ion encapsulated in Ag-**1** was located closely to the center of the cavity and had a larger temperature factor than those of the Pb^{2+} and Sr^{2+} ions in Pb-**1** and Sr-**1**. The DFT calculation showed that an Ag atom at the center of the cavity was the most stable in $[Ag\subset(SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{7-}$ (Supporting Information, Figure S11), whereas the position of the Ag^+ ion in Ag-**1** could not be strictly determined by the X-ray analysis.

[21] Although the ligand exchange rate of Sr^{2+} is quite high,[22] the NMR spectrum of the solution of Sr-**1** was not significantly changed after one equivalent of [2.2.1]cryptand was added at 333 K and the solution was kept for 10 days. This fact suggests that Sr-**1** is thermodynamically stable even in the presence of [2.2.1]cryptand. Although the metal cation transfer reaction from $[Sr([2.2.1])]^{2+}$ to **1** was also attempted by the addition of one equivalent of $[Sr([2.2.1])](NO_3)_2$ to **1**, a precipitate of the $[Sr([2.2.1])]^{2+}$ salt of **1** was instantly formed, and the formation of Sr-**1** could not be confirmed.

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[23] Upon addition of one equivalent of [2.2.1]cryptand to the acetonitrile solution of Pb-**1**, one sharp ^{29}Si NMR signal appeared at $\delta = -85.8$ ppm with disappearance of the signal of Pb-**1** at $\delta = -79.6$ ppm, thus indicating the regeneration of **1**.