to Ni brought about by cation binding.

The loss of d–d absorption was used to determine an apparent association constant in acetone for Na^+ of $K_a(Na^+) = 1400\ M^{-1}$ by fitting to eq 1 (Figure 2),[13] where ϵ_A is $A_{obs}/[\mathbf{1}]$, ϵ_F is the

$$[Na^+]/(\epsilon_A - \epsilon_F) = [Na^+]/(\epsilon_B - \epsilon_F) + 1/K_a(\epsilon_B - \epsilon_F) \quad (1)$$

extinction coefficient for the free complex, and ϵ_B is the extinction coefficient for the complex in the presence of excess Na^+. The binding constants are based on the **1** monomer, in order to compare them directly with those determined by Gokel et al.[4] The value of $K_a(Na^+)$ is in acceptable agreement with that determined by Gokel et al. by the ion-selective electrode method.[14] Our method of determining binding constants is advantageous relative to ion-selective electrode methods in that a standard such as 18-crown-6 is not required for accurate determination. Furthermore, eq 1 is frequently used for determining the binding constants for small-molecule substrates with macromolecules,[13] thus extending the analogy of the Ni system to actual biological self-assembly. The fact that we have observed an apparent binding constant for $NaClO_4$ that is similar to that observed by Gokel for Na(picrate) provides strong evidence that the complexes are ionophores in their own right and do not require picrate anion for cation binding.

It has been noted previously that the cation selectivity for **1** is much greater than that for simple podands.[3] The binding constant for Na^+ determined here also parallels this finding,[15] being much greater than that for hexaglyme ($K_a(Na^+) = 36\ M^{-1}$).[16] In fact, while the binding constant for **1** is much less than that for 18-crown-6 ($K_a(Na^+) = 23\,000\ M^{-1}$),[17] it is identical to that for 15-crown-5[18] and significantly larger than that for 12-crown-4 ($K_a(Na^+) = 57\ M^{-1}$).[19] The apparent binding constant was determined for Li^+ to be $K_a(Li^+) = 2100\ M^{-1}$. It has been pointed out that **2** and other cation-binding complexes containing positive charges exhibit the selectivity $Li^+ > Na^+ > K^+$,[4] which is consistent with our results.

The implications of these findings are significant not only in understanding the self-assembly process but also in the design of ionophore systems that have high cation affinities in their own right. In the self-assembly process, it is clear that the presence of the substrate (i.e. Na^+) affects the conformation of the binding site (i.e. the nuclearity of the Ni complex). It is now clear that the presence of the alkali-metal salt alone is sufficient to induce the formation of the dinuclear, cation-bound complex. We have also shown that the association constants are similar for ClO_4^- and picrate salts, demonstrating that picrate anion is not required for efficient binding. Furthermore, the fact that the binding affinity is significantly greater than simple podands suggests that the dimerization process is playing a key role in regulating cation association. These findings indicate that synthesis of new Ni(II) ionophores will lead both to a more detailed understanding of the self-assembly process and to complexing agents with novel properties.

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Additions and Corrections

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P. A. Eldredge, K. S. Bose, D. E. Barber, R. F. Bryan, E. Sinn, A. Rheingold, and B. A. Averill*: Synthesis and Structures of the $[MoFe_6S_6(CO)_{16}]^{2-}$, $[MoFe_4S_3(CO)_{13}(PEt_3)]^{2-}$, and $[Mo_2Fe_2S_2(CO)_{12}]^{2-}$ Ions: High-Nuclearity Mo–Fe–S Clusters as Potential Precursors to Models for the FeMo-Cofactor of Nitrogenase.

Pages 2365–2375. In this paper the space group of crystals of the bis(tetraphenylarsonium) salt of cluster III, $[Mo_2Fe_2S_2(CO)_{12}]^{2-}$, is reported incorrectly as $P2_1/m$ (No. 11) rather than $P2_1/n$ (No. 14, alternate setting)—the space group actually found and used in the course of the X-ray analysis. In Figure 5, illustrating the structure of that cluster, the bond lengths Mo–C(4) and Fe–C(4) are inadvertently interchanged.—B. A. Averill