list of selected bond distances and angles is given in Table III. The molecular structure has an imposed C_2 symmetry. Cobalt is bonded to the four nitrogens in a square-planar geometry, the metal being only 0.063 (1) Å out of the N_4 plane. The six-membered chelate rings, which each have a boat conformation, tilt alternatively up and down giving rise to a double saddle-shaped conformation of the tetraanion. The pyrrole planes form dihedral angles of 34.0 (1) and 31.7 (1)° with the N_4 coordination plane. The dihedral angle between adjacent pyrroles is 123.3 (1)°, while those between the two pairs of opposite pyrroles are 112.1 (1) and 116.6 (1)°. The axial coordination sites around the metal are filled by the *meso*-methylene groups (Figure 2b). The two pairs of carbon atoms C11, C11′ and C17, C17′ cap the CoN_4 plane on both sides, their C···C separation ranging from 4.073 (4) Å for C17···C17′ to 4.707 (5) Å for C11···C11′. Four hydrogens, one from each of the aforementioned carbons, provide a flattened tetrahedral cage around the cobalt, and the Co···H distances are rather short [Co···H(112) = 2.69 Å, Co···H(172) = 2.79 Å]. The *meso*-alkyls of the porphyrinogen are forced by the conformation of the macrocycle to be in close proximity to the metal. This has been observed in the iron(III) and the oxomolybdenum(V) complexes.[2,3] The C–H bonds are able to protect and maintain unsaturated metal centers, in the meantime providing information on the C–H···metal interaction for a variety of metals and oxidation states. Such an interaction should be considered a preliminary stage in any aliphatic intramolecular C–H bond activation.[12]

There is a significant difference in the distances of the three similar Li–C bonds (Li–C1, Li–C2, Li–C3) and Li–C4 and Li–N1 (Table III), implying an η^3-bonding mode for the lithium cation to the pyrrolyl anion. The pyrrolyl anion can display thus either the σ- or π-bonding mode, depending on the electronic needs of the cation. This can occur with the central metal atom, as was found in the zirconium(IV) derivative,[3] or with cations binding at the periphery of the macrocycle, as was found in the structures of complexes **3**–**5**. We should emphasize the potential ability of the periphery of our macrocycle–metal complexes to bind metals. The structures of the zirconium(IV) complex[3] together with those of **3**–**5** show the electronic flexibility of the macrocyclic tetraanion **4**. With regard to this, in the syntheses of complexes **3**–**5** (reaction 2) the use of an excess of metal halide should be avoided, since complexes **3**–**5** react with metal halides.[13] These factors may lead us to the use of **2** for the construction of polymetallic systems. In addition, complexes **3**–**5** exemplify a bifunctional nature containing both an electron-rich transition metal and a Lewis acid in their structure. Their use for producing a significant polarization in small molecular substrates is very well-known.

Acknowledgment. We thank the U.S. Navy (Grant No. N00014-89-J-1810) and the Fonds National Suisse de la Recherche Scientifique (Grant. No 20-28470-90) for financial support. The Royal Society is also acknowledged for a European Science Fellowship to J.J.

Registry No. **2**, 139376-54-8; **3**, 139376-49-1; **4**, 139376-51-5; **5**, 139376-53-7.

Supplementary Material Available: For complex **4**, complete listings of crystallographic data, fractional atomic coordinates for hydrogen atoms, anisotropic thermal parameters, bond distances and angles, and equations of least-squares planes (5 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

---

(11) The Cu and Fe derivatives are isostructural with that of Co. The unit cell parameters are as follows: $C_{52}H_{80}CuLi_2N_4O_4$, M_r = 902.7, monoclinic, space group *C2/c*, a = 20.808 (2) Å, b = 10.946 (1) Å, c = 22.811 (2) Å, β = 104.57 (2)°, U = 5028.5 (9) Å^3, Z = 4, D_c = 1.192/g cm^{-3}; $C_{52}H_{80}FeLi_2N_4O_4$, M_r = 895.0, monoclinic, space group *C2/c*, a = 20.749 (2) Å, b = 10.930 (1) Å, c = 22.797 (2) Å, β = 104.69 (2)°, U = 5001.1 (9) Å^3, Z = 4, D_c = 1.189 g cm^{-3}.

(12) Hill, C. L. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989; p 243.

(13) Jacoby, D.; Floriani, C. Unpublished results.

Contribution from the Department of Chemistry,
North Carolina State University,
Raleigh, North Carolina 27695-8204,
and Department of Chemistry, Yale University,
New Haven, Connecticut 06511-8118

Binding of Alkali-Metal Cations by Self-Assembling Ionophore Complexes of Nickel(II)

Mark Wehr Jones,[†] Nishi Gupta,[†] Alanna Schepartz,[‡] and H. Holden Thorp*,[†]

Received October 31, 1991

The assembly of enzyme complexes to form binding sites not present in the separated subunits is an important mechanism of molecular recognition in biological systems.[1,2] Recently, a family of Ni(II) complexes has been reported that allows the self-assembly process to be modeled using small molecules.[3,4] In complexes such as **1** (Chart I), two Schiff base ligands (L = *N*-methyl-3-(2-ethoxymethoxy)salicylaldimine) containing flexible polyether chains are organized around a Ni^{2+} template to create an alkali-metal cation binding site. The complex transports picrate salts of alkali-metal cations from aqueous solution into chloroform.[3] It was shown that the complexes transport alkali-metal cations when 2 equiv of the ligand is mixed with 1 equiv of Ni^{2+}, demonstrating the self-assembly of the binding site in situ.

In a report by Gokel et al.,[4] it was shown that a related complex, **2**, is monomeric and square planar at low concentrations in chloroform solution but is octahedral in 1:1 $CHCl_3/CH_3OH$, presumably with two axial CH_3OH ligands. The binding of sodium picrate by **2** leads to a novel complex with the formula $L'_4Ni_2(H_2O)(Na(picrate))_2$ (L′ = *N*-methyl-3-methoxysalicylaldimine), which has been characterized by X-ray crystallography. Since studies thus far were performed either in methanol or by extraction from aqueous solution, it remains unclear whether a coordinating solvent is required to create the binding site or whether the presence of the alkali-metal cation alone can induce the association of the Ni complexes. Furthermore, the results of Gokel suggest that picrate anion is required for cation binding, suggesting that without a hydrophobic coordinating anion addition of the polyether chains to the complex is not sufficient for cation binding.[4] We report here three important features of complex **1**: (1) in acetone solution, the complex remains monomeric and square planar until *only* the dry alkali-metal salt is added; (2) cation binding occurs in the absence of picrate anion; (3) the binding constants for alkali-metal cations can be determined accurately in the absence of a standard using methods usually applied to biological self-assembly.

Experimental Section

Complex **1** was prepared as previously described.[3] $NaClO_4$ was recrystallized from ethanol and dried in a vacuum oven. Cyclic voltammetry was performed in acetonitrile with either 0.1 M tetrabutylammonium hexafluorophosphate or 0.1 M sodium hexafluorophosphate. Experiments were performed using a ferrocene standard in a drybox with a Pt button working electrode, Pt wire counter electrode, and a Ag wire pseudoreference electrode. Instrumental conditions were as previously described.[5a] Vapor pressure osmometry was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. A solution of 0.1 M $NaClO_4$ in acetone was used. This solution was initially calibrated using azobenzene, which gave an accurate molecular weight. Solution magnetic moments were determined in acetone-d_6 solution by the Evans method.[5b] UV–vis spectra were acquired in acetone solution using an HP8452 diode-array spectrophotometer.

Results and Discussion

The optical spectrum of **1** in acetone exhibits a d–d band at 615 nm (ϵ = 107 M^{-1} cm^{-1}) and an intense charge-transfer band at 416 nm (Figure 1). These solutions give diamagnetic proton NMR spectra, which can be readily assigned. These properties

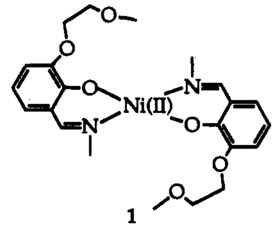
---

[†] North Carolina State University.

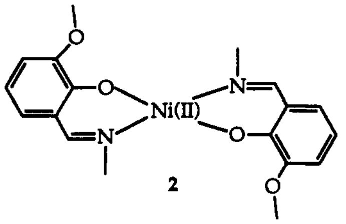
[‡] Yale University.

0020-1669/92/1331-1308$03.00/0

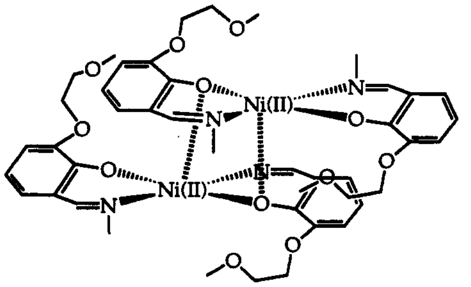
Chart I



1



2



3

Table I. Properties of Complex 1 with and without Na^+

complex	magn moment, μ_B	$E_{p,ox}$, V vs SSCE	$E_{p,red}$, V	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
1	diamagnetic	0.96	−1.59	614 (107), 416 (5700)
1 + $NaClO_4$	2.8	1.03	−1.75	366 (9100)[a]

[a] Extinction coefficient based on the monomer of 1.

are identical to those of the analogous complex without the polyether chains,[6] which is known to be square planar with a *trans*-N_2O_2 configuration, as shown in 1.[7-9] In addition, it has been shown[4] that 2 is monomeric in $CHCl_3$ solution with optical properties essentially identical to those for 1 shown in Figure 1. Complex 1 can be electrochemically oxidized and reduced, but cyclic voltammograms are irreversible in both cases, giving E_p values as shown in Table I.

Addition of an excess of $NaClO_4$ to an acetone solution of 1 leads to a substantial loss of the visible absorption and a blue shift of the charge-transfer band to 366 nm, which also increases substantially in intensity (Figure 1). These solutions exhibit paramagnetically shifted proton NMR spectra, and the Evans method gives a solution magnetic moment of 2.8 μ_B, based on the L_2Ni monomer.

On the basis of the past work of Holm[10-12] and the studies of Gokel on 2,[4] the complex with bound Na^+ appears to contain octahedral Ni^{2+} and to be dinuclear. Thus, the presence of Na^+ induces a transition in the ionophore complex, suggesting that the binding affinity is large enough to force the metal center out of its lowest energy, mononuclear conformation. The complex is harder to both oxidize and reduce in the presence of Na^+ (Table I). Vapor-pressure osmometry studies performed in 0.1 M $NaClO_4$ acetone solution give a molecular weight of 990, consistent with a L_4Ni_2 unit. This is the first conclusive evidence that the complex with bound Na^+ is dinuclear *in solution* in a solvent in which the complex is monomeric and square-planar in the absence of the alkali-metal cation. Thus, addition of dry $NaClO_4$ to an acetone solution of 1 causes a shift from a mononuclear, square-planar complex to a dinuclear complex with bound Na^+. Importantly, binding of the alkali-metal cation is not contingent upon the presence of picrate anion or a coordinating solvent. The precise solution structure of the dinuclear, Na^+-bound species remains unclear; however, Holm has shown that the complexes can associate into dinuclear structures (3).[10-12] The structure of our dinuclear species may be based on 3, with an additional ligand

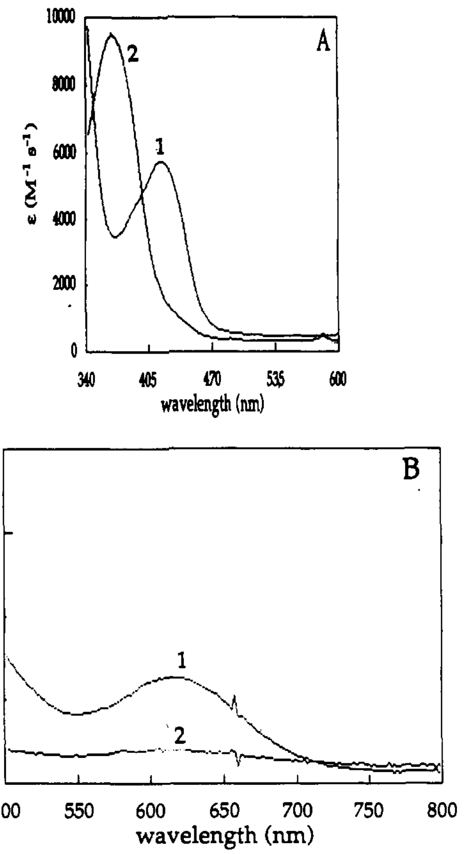


Figure 1. (A) UV–vis spectra of 1 (0.2 mM) in acetone solution (1) without and (2) with 0.1 M $NaClO_4$. (B) Optical spectra of 1 (1.0 mM) (1) without and (2) with 0.1 M $NaClO_4$.

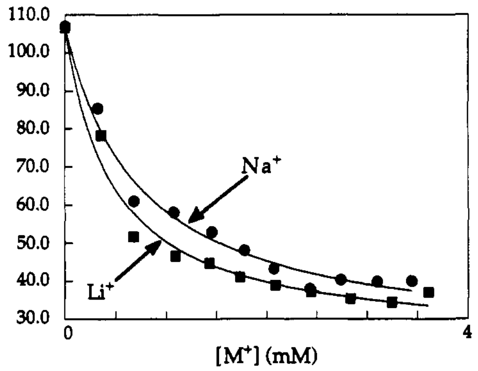


Figure 2. Plots of ϵ(614 nm) for 1 (1.0 mM) in acetone as a function of added alkali-metal cation. The solid lines were obtained from linear least-squares fits to eq 1.

---

(1) Huang, C. Y.; Rhee, S. G.; Chock, P. B. *Annu. Rev. Biochem.* **1982**, *51*, 935. Laue, F. T.-K.; Fersht, A. R. *Nature* **1987**, *326*, 811.
(2) Evans, P. R.; Hudson, P. J. *Nature* **1979**, *279*, 500.
(3) Schepartz, A.; McDevitt, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 5976.
(4) Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 7434.
(5) (a) Grover, N.; Thorp, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 7030. (b) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(6) Sacconi, L.; Paoletti, P.; Del Res, G. *J. Am. Chem. Soc.* **1957**, *79*, 4062.
(7) Simonsen, S. H.; Pfluger, C. E. *Acta Crystallogr.* **1957**, *10*, 536.
(8) Fox, M. R.; Ligafelter, E. C. *Acta Crystallogr.* **1967**, *22*, 943.
(9) Frasson, E.; Panattoni, C.; Sacconi, L. *J. Phys. Chem.* **1959**, *63*, 1908.
(10) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.
(11) Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 4683.
(12) Holm, R. H.; Swaminathan, K. *Inorg. Chem.* **1962**, *1*, 599.

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.

Acknowledgment. We are grateful to D. Powers and W. A. Kalsbeck for experimental assistance. H.H.T. thanks the National Science Foundation for a Presidential Young Investigator Award, the David and Lucile Packard Foundation for a Fellowship, the Camille and Henry Dreyfus Foundation for a New Faculty Award, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. A.S. also thanks the NSF for a Presidential Young Investigator Award and the David and Lucile Packard Foundation for a Fellowship.

---

(13) Wolfe, A.; Shimer, G. H.; Meehan, T. *Biochemistry* **1987**, *26*, 6392.
(14) Arnold, K. A.; Gokel, G. W. *J. Org. Chem.* **1986**, *51*, 5015.
(15) Inoue, Y.; Liu, Y.; Hakushi, T. In *Cation Binding by Macrocycles*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker, Inc.: New York, 1990; p 1.
(16) Buschmann, H.-J. *Z. Phys. Chem.* (*Munich*) **1984**, *139*, 113.
(17) Haymore, B. L.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *Inorg. Chem.* **1982**, *21*, 1598.
(18) Michaux, G.; Reisse, J. *J. Am. Chem. Soc.* **1982**, *104*, 6895.
(19) Buschmann, H.-J. *J. Solution Chem.* **1987**, *16*, 181.

Additions and Corrections

1991, Volume 30

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