for oxygen transfer from dioxygen ylides such as water oxide[7a,b] and carbonyl oxide, but that QCISD(T) calculations are essential for reliable energetics with the highly strained dioxirane. The barrier heights show a remarkable sensitivity to the level of theory, with deviations up to 20 kcal/mol. Although the less stable carbonyl oxide form exhibits the greater reactivity as one might anticipate, the intrinsic gas-phase reactivity of these two isomeric oxygen donors is opposite to that observed in solution.[4a] Since oxygen donation from dioxirane exhibits the higher barrier despite its weaker O–O bond and inherent ring strain, we must look elsewhere for the origin of the difference in reactivity. In addition to steric interactions, solvent effects must play a major role. It has been noted that the presence of water increases the rate of epoxidation of alkenes with dimethyldioxirane[4b] while an increase in solvent polarity has the opposite effect.[1a]

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Registry No. 1, 157-26-6; **2**, 56077-92-0; ethylene, 74-85-1.

Synthesis and Structure of the Chloride and Nitrate Inclusion Complexes of [16-Pyrimidinium crown-4]$^{4+}$

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Anion coordination chemistry has received attention because of its chemical and biological significance.[1,2] Recently it was reported that reflux of a mixture of thiamin iodide and mercuric iodide in acetone produced a cyclic polypyrimidinium cation[3] (see Scheme I). This communication reports the synthesis of another cyclic polymer, [16-pyrimidinium crown-4]$^{4+}$, and the structure of its chloride and nitrate inclusion complexes.

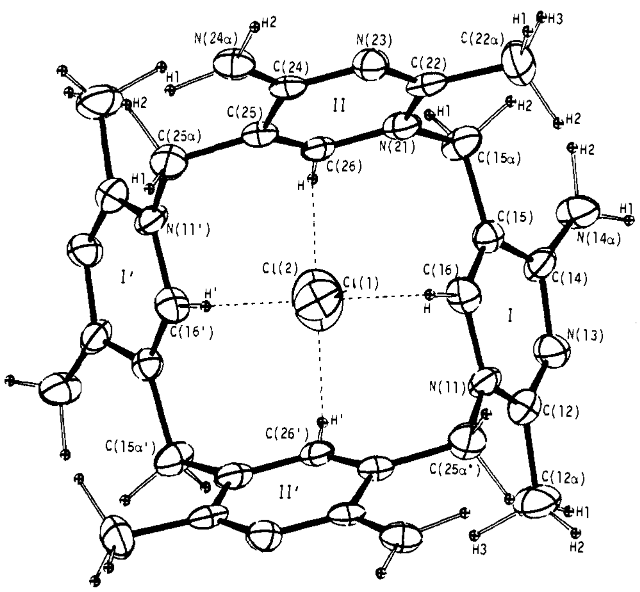


Figure 1. A top view down to 2-fold axis of [16-pyrimidinium crown-4]$^{4+}$. The crystallographic 2-fold axis passes through Cl(1) and Cl(2).

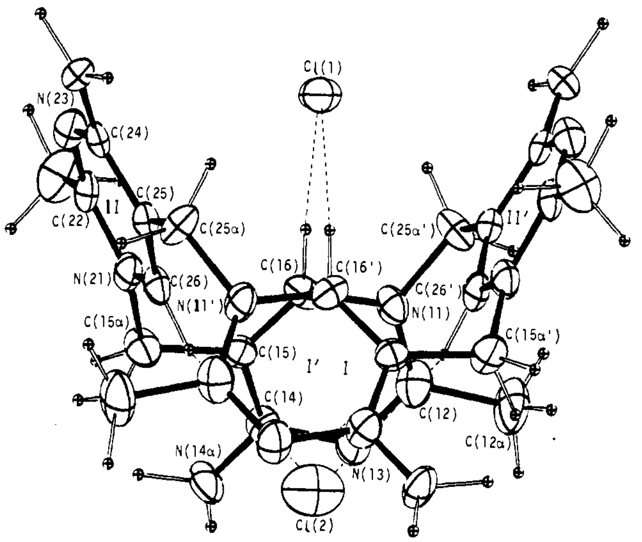
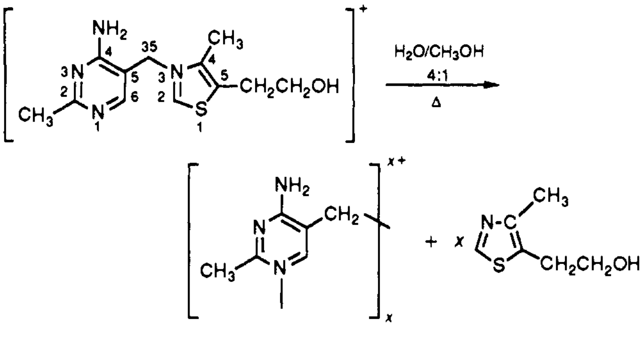


Figure 2. A side view of the [16-pyrimidinium crown-4]$^{4+}$ cation showing its interaction with Cl(1) and Cl(2).

Scheme I



Reflux of a mixture of thiamin chloride hydrochloride and $Ni(OAc)_2 \cdot 4H_2O$ (2:1 molar ratio) in methanol afforded the chloride salt of [16-pyrimidinium crown-4]$^{4+}$,[4] which also was isolated from an aqueous solution of thiamin chloride hydrochloride and $Zn(OAc)_2$. The nitrate salt was prepared as tiny, needle-like crystals by heating thiamin nitrate at 65 °C for 30 min in a 15–50% water–methanol medium.[5,6]

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[1] Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112 and references therein.

[2] (a) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547–1550. (b) Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 1550–1553. (c) Buhner, M.; Geuder, W.; Gries, W.-K.; Hung, S.; Koch, M.; Poll, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1553–1556.

[3] Cramer, R. E.; Carrie, M. J. *J. Inorg. Chem.* **1990**, *29*, 3902–3904.

[4] Cramer, R. E.; Kim, K. E.; Evangelista, R. S.; Kuwabara, E. S. *Abstracts of Papers*, 188th National Meeting of the American Chemical Society, Philadelphia, PA; American Chemical Society: Washington, DC, 1984; INOR 254.

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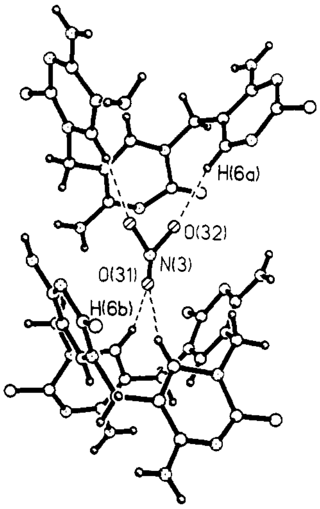

Figure 3. A side view of a nitrate ion interacting with two [16-pyrimidinium crown-4]$^{4+}$ cations. In this view, the front pyrimidinium ring of the top tetramer has been delected so that the nitrate ion can be seen.

The [16-pyrimidinium crown-4]$^{4+}$ cation (Figure 1) is cyclic wherein four 2,4,5-trisubstituted pyrimidine units are joined by methylene bridges linking the C(5) of one pyrimidine to N(1) of the next. Quaternization of the endocyclic N(1) atoms results in an overall 4+ charge for the tetramer. Bond distances and bond angles within each pyrimidinium unit are in agreement with those observed for protonated thiamin.[7] Alternating pyrimidiniums are related by a crystallographic 2-fold axis perpendicular to the mean plane of the macrocycle. Opposing pairs of hydrogen atoms, bound to the C(6) atoms (all of which are nearly coplanar), define the size of the cavity, which is no larger than 1.3 Å in diameter, too small to accommodate any anion.

The macrocycle adopts a boat conformation (Figures 2 and 3), with chloride or nitrate ions held in a pincher-like grip by opposing pyrimidinium rings. In the chloride salt the two nonequivalent chloride anions interact with the tetramer through four C(6)–H···Cl^- hydrogen bonds and through four pyrimidinium ring···Cl^- electrostatic contacts: C(16)···Cl(1) = 3.695 (8) Å, C(26)···Cl(2) = 3.787 (8) Å, H(C16)···Cl(1) = 2.65 Å, and H(C26)···Cl(2) = 2.77 Å; perpendicular distances from the Cl ion to the pyrimidine ring = 3.297 (5) Å for Cl(1)···pyrimidine ring II and 3.438 (5) Å for Cl(2)···pyrimidine ring I. The dihedral angles between the pyrimidinium rings are 73.5°, 81.5°, 120.2°, and 128.4° for planes I and II (I/II; Figure 2), I/II′, I/I′, and II/II′, respectively. The exposed side of Cl(1) is hydrogen-bonded to two water molecules and two NH_2 groups of neighboring tetramers, while Cl(2) is hydrogen-bonded to four waters. A solvated chloride anion Cl(3) and the other two water molecules act as hydrogen-bonding spacers between neighboring tetramers.

The nitrate structure is similar, with a nitrate ion wedged between opposite pyrimidinium rings, with the N(3) and O(31) atoms located on the 2-fold axis. This guest nitrate ion interacts with two tetramers, one above and one below. The closest contact between guest and host occurs between the central oxygen atom, O(31), and both of the C(6) protons of the "lower" rings: O(31)–C(6) 3.3 Å, O(31)–H(16) 2.5 Å, O(31)–H(6)–C(6) angle = 142°. The O(32) lateral oxygens form electrostatic contacts of 3.4 Å with the exocyclic N(41′). The same nitrate acts as a guest of the "upper" tetramer with a closest contact O(32)–C(6) 3.2 Å, O(32)–H(6) 2.3 Å, O(32)–H(6)–C(6) angle = 164°. The dihedral angle between the two pyrimidinium planes of the upper tetramer, which enclose the O(32) oxygens, is 129°, while the corresponding angle in the lower tetramer, which encloses O(31), is 125°. The dihedral angles between adjacent pyrimidinium rings are 74° and 97°. Of the three remaining nitrate ions per tetramer, the N(1) nitrate is located in a general position accounting for two nitrates, while the other, N(2), is found on a 2-fold axis and is disordered.

Cyclic pyrimidinium oligomers could serve as polycationic receptors for anions[8] and provide a multitude of novel structures with properties of wide significance. While we do not yet understand the parameters that govern the formation of the two products we have isolated from the oligomerization of thiamin, namely, [24-pyrimidinium crown-6]$^{6+}$ and [16-pyrimidinium crown-4]$^{4+}$, studies of the capability of these cyclized polymers to capture other biologically important polyatomic anions such as HPO_4^{2-} or HCO_3^-, in addition to monoatomic halide anions like F^-, Br^-, or I^-, are under way.

Registry No. Thiamine chloride hydrochloride, 67-03-8; [16-pyridinium crown-4]$^{4+}$ chloride salt, 135108-17-7; thiamine nitrate, 532-43-4; [16-pyridinium crown-4]$^{4+}$ nitrate salt, 135108-19-9.

Supplementary Material Available: Expermental details of the structure determination, listings of crystal data and summary of data collection, for [16-pyrimidinium crown-4]Cl_4·5.5H_2O and [16-pyrimidinium crown-4]$(NO_3)_4$, atomic parameters and anisotropic thermal parameters for [16-pyrimidinium crown-4]Cl_4·5.5H_2O, and bond lengths and angles and hydrogen bonds and other short contacts, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic displacement coefficients, H atom coordinates and isotropic parameters, and a figure depicting the crystal packing for [16-pyrimidinium crown-4]$(NO_3)_4$ (12 pages); listing of observed and calculated structure factor amplitudes for [16-pyrimidinium crown-4]Cl_4·5.5H_2O and [16-pyrimidinium crown-4]$(NO_3)_4$ (24 pages). Ordering information is given on any current masthead page.

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(5) For [16-pyrimidinium crown-4]$(NO_3)_4$: Anal. Calcd for $C_{24}N_{16}H_{32}O_{12}$: C. 39.13: N. 30.42: H, 4.38. Found: C. 39.18: N. 30.24: H. 4.39. For [16-pyrimidinium crown-4]Cl_4·5.5H_2O: Anal. Calcd for $C_{24}H_{43}Cl_4O_{4.5}N_{12}$: C. 39.52: H. 5.94: N. 23.04. Found: C. 39.83: H. 5.87: N. 23.11.

(6) For [16-pyrimidinium crown-4]$(NO_3)_4$: ^1H NMR (300 MHz. DMSO) δ 9.76. 1 H NH_2. 9.00 1 H NH_2. 7.21 1 H C(6)-H. 5.08 2 H C(35)H_2. 2.62 3 H (C21)H_3. all singlets: ^{13}C NMR (D_2O) δ 165 C(2). 163 C(4). 143 C(6). 116 C(5). 52 C(35). 22 C(21): FAB MS calcd for cation 488. obsd 485 (loss of $3H^+$): UV λ_{max} = 257 nm. log ϵ = 4.63.

(7) Cramer. R. E.: Maynard. R. B.: Ibers. J. A. *J. Am. Chem. Soc.* **1981**. *103*. 76-81.

(8) Indeed. the cyclic pyrimidinium hexamer[3] incorporates a HgI_4^{2-} anion.

γ-Cyclodextrin Template Method for Controlling Stereochemistry of Bimolecular Interactions and Reactions

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γ-Cyclodextrin, which is a cyclic compound composed of eight D-glucose residues joined by α-1,4-linkages, can include two molecular species in its large cavity.[1] Because of this unique property, γ-cyclodextrin can be used as a molecular flask or vessel, in which interactions and reactions between two guest molecules are facilitated.[1-3] Since guest species in γ-cyclodextrin are still

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(1) For references on 1:2 host–guest complexation of γ-cyclodextrin, see: (a) Ueno, A.; Moriwaki. F.; Osa. T.; Hamada, F.; Murai. K. *Tetrahedron* **1987**. *43*. 1571. (b) Ueno. A.; Moriwaki. F.; Osa. T.; Hamada, F.; Murai, K. *J. Am. Chem. Soc.* **1988**. *110*. 4323.

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