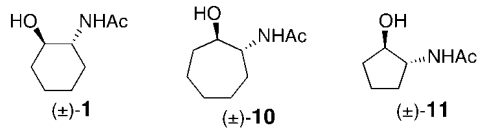
Table 2. Selectivities for various substrates in kinetic resolutions with peptide catalysts.[a]



Entry	Catalyst	Racemic substrate	Conversion	$k(R,R)/k(S,S)$
1	**3**	**1**	50%	51
2	**3**	**10**	45%	15
3	**3**	**11**	49%	27
4	**12**	**1**	53%	50
5	**12**	**10**	47%	31
6	**12**	**11**	53%	26

[a] The reactions were conducted with 1–2 mol% catalyst (5.9 mM in substrate, toluene solvent) at 25 °C. Conversions and enantioselectivities were measured by chiral GLC (Chiraldex GTA).

Once again, we found that these observations are mirrored with other substrates in this class (Table 2). Whereas catalyst **3** affords a $k_{rel} = 27$ for five-membered ring **11**, isostere **12** affords a nearly identical k_{rel} of 26 (Table 2, entries 3 and 6). For seven-membered ring **10**, catalyst **3** affords $k_{rel} = 15$; isostere **12** is actually more selective for this substrate, affording $k_{rel} = 31$ (Table 2, entries 2 and 5). These results underscore both the functional similarity of octapeptide **3** and isostere **12**, and the greater complexity in analyzing the octapeptide system. If there is a unique contact between the amides of substrates such as **1** and peptide **3**, it appears not to be at the D-Pro-Gly linkage.

In summary, we report an approach to probing the mechanisms by which peptide-based enantioselective catalysts function. Relying on conformational analogies between such catalysts and their derived alkene isosteres, we have uncovered a specific, kinetically significant amide in a tetrapeptide system. Applying the same approach to a highly selective octapeptide system, we have excluded the central amide of a β-hairpin as the kinetically significant binding site. Additional studies along these lines should provide further mechanistic insight into the inner workings of peptide-based catalysts and, potentially, their more complex enzymatic counterparts.

Received: March 21, 2001 [Z16818]

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Ion-Pair Recognition by Nucleoside Self-Assembly: Guanosine Hexadecamers Bind Cations and Anions**

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Ion-pair recognition calls for receptors with separate cation and anion binding sites. Ditopic hosts typically have these discrete binding sites built into their covalent frameworks.[1, 2] A more efficient approach might be to use noncovalent interactions to build the ion-pair receptor from multiple components.[3] Below, we describe a prime example of how

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[**] This research is sponsored by the Separations and Analysis program of the U.S. Department of Energy. J.D. thanks the Dreyfus Foundation for a Teacher-Scholar Award. We thank LaTarsha Riddick for help with experiments.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

self-assembly provides a supramolecular complex with Lewis basic and Lewis acidic sites for the simultaneous binding of cations and anions. Hydrogen-bonding, ion-dipole, and base-stacking interactions provide a tubular complex with a cation-loaded interior. Meanwhile, an array of hydrogen-bond donors on the receptor's surface enables anion coordination. The ligands, cations, and anions all cooperate to control assembly of a 22-component complex.

The G-quartet is a macrocycle formed by hydrogen-bonded guanosine units (Scheme 1).[4, 5] Alkali metal cations template G-quartet formation from guanosine nucleotides in water,[6] and these cation-filled G-quartets stack to give octamers, dodecamers, hexadecamers, and higher aggregates.[7, 8] Gottarelli's group and our group have shown that lipophilic nucleosides also self-associate in nonpolar solvents.[9–11] While G-quartet formation is undoubtedly cation-dependent, Gottarelli and co-workers made the striking discovery that lipophilic guanosine analogues could coextract chiral anions from water into organic solvents with enantioselectivity.[12] This result implies that G-quartet aggregates (G-quadruplexes) might be able to recognize ion pairs in solution. In this paper, we use X-ray crystallography and NMR spectroscopy to obtain a clearer picture of how the nucleosides, cations, and anions are organized in a lipophilic G-quadruplex.[13] While the structure and dynamics of this model system are interesting, our main point is that self-assembly can provide selective ion-pair receptors.

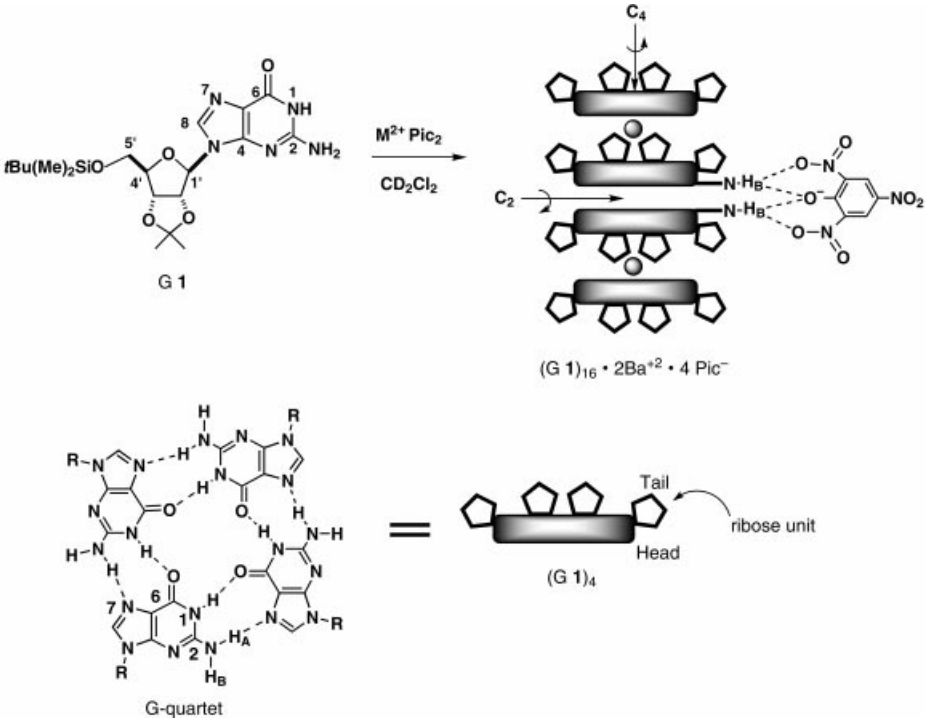
We previously determined that the K^+, Pb^{2+}, and Ba^{2+} G-quadruplexes formed from G**1** and metal picrate salts are D_4-symmetric hexadecamers in the solid state.[11b, 9d,e] As illustrated for Ba^{2+} in Scheme 1, the Pb^{2+} and Ba^{2+} G-quadruplexes consist of two C_4-symmetric $(G\mathbf{1})_8 \cdot M^{2+}$ octamers. The G-quartets within each octamer are stacked head-to-tail,[14] with a 30° rotation between layers. The divalent cations, each interacting with eight nucleosides, are well separated from their picrate counterions (> 8.5 Å). These anions are not, however, uninvolved spectators. In the solid-state, the four picrate groups join the $G_8 \cdot M^{2+}$ octamers together by hydrogen bonding with the NH_B amino protons that project from the two "inner" G-quartets (bonding of one picrate anion is shown in Scheme 1). Overall, 16 nucleosides, 2 cations, and 4 anions form a complex that has dimensions of $25 \times 25 \times 30$ Å and a molecular weight greater than 7600 Da.

This study's major goal was to determine whether the lipophilic G-quadruplex maintains its coordination to the picrate anions in solution. Does this complex exist as a picrate-bound hexadecamer, $(G\mathbf{1})_{16} \cdot 2M^{2+} \cdot 4Pic^-$, in solution, or does it dissociate to give $(G\mathbf{1})_8 \cdot M^{2+} \cdot 2Pic^-$ octamers? It is a challenge to distinguish an octamer $(G\mathbf{1})_8 \cdot M^{2+}$ from a hexadecamer $(G\mathbf{1})_{16} \cdot 2M^{2+}$ by NMR spectroscopy. Both species have the same G**1** to picrate anion ratio, making determination of stoichiometry ambiguous. Also, the ^1H NMR spectra for a C_4-symmetric $(G\mathbf{1})_8 \cdot M^{2+}$ octamer and a D_4-symmetric $(G\mathbf{1})_{16} \cdot 2M^{2+}$ hexadecamer would be indistinguishable based on symmetry considerations.

Below, we demonstrate that the picrate-bound G-quadruplex is a hexadecamer in CD_2Cl_2 solution. Strong evidence for this structure comes from NMR cross-over experiments wherein G**1** and a 1:1 mixture of Sr^{2+} and Ba^{2+} picrate salts give a 1:1:2 statistical combination of three complexes: $(G\mathbf{1})_{16} \cdot 2Ba^{2+} \cdot 4Pic^-$, $(G\mathbf{1})_{16} \cdot 2Sr^{2+} \cdot 4Pic^-$, and the "mixed" hexadecamer $(G\mathbf{1})_8 \cdot Ba^{2+} \cdot (G\mathbf{1})_8 \cdot Sr^{2+} \cdot 4Pic^-$. Other NMR spectroscopy and circular dichroism (CD) data indicate that the picrate anions bind to the G-quadruplex in solution.

Before carrying out solution experiments, we first determined that the solid-state structure of $(G\mathbf{1})_{16} \cdot 2Sr^{2+} \cdot 4Pic^-$ is isomorphous with its Ba^{2+} analogue (see the Supporting Information).[15] The octacoordinate Sr^{2+} cations are located between G-quartet layers, and two $(G\mathbf{1})_8 \cdot Sr^{2+}$ octamers stack head-to-head to give the D_4-symmetric hexadecamer, $(G\mathbf{1})_{16} \cdot 2Sr^{2+} \cdot 4Pic^-$. The four picrate anions are hydrogen bonded to the exocyclic amines of the two "inner" G_4-quartets (in the same way as illustrated for Ba^{2+} in Scheme 1).

The picrate anions that clamp together the two "inner" G-quartets in the hexadecamer's crystal structure also associate with the G-quadruplex in solution. The CD spectrum obtained after dissolving $(G\mathbf{1})_{16} \cdot 2Ba^{2+} \cdot 4Pic^-$ in CD_2Cl_2 has a prominent Cotton band at 380 nm which corresponds to the absorbance signal of the picrate anion (Figure 1 A). This induced CD band indicates that the achiral picrate anions remain stereoselectively bound to the chiral G-quadruplex in CD_2Cl_2.[12, 16]



Scheme 1. A lipophilic G-quadruplex that binds ion pairs. Pic = picrate, R = 5′-silyl-2′,3′-isopropylidene-D-ribose.

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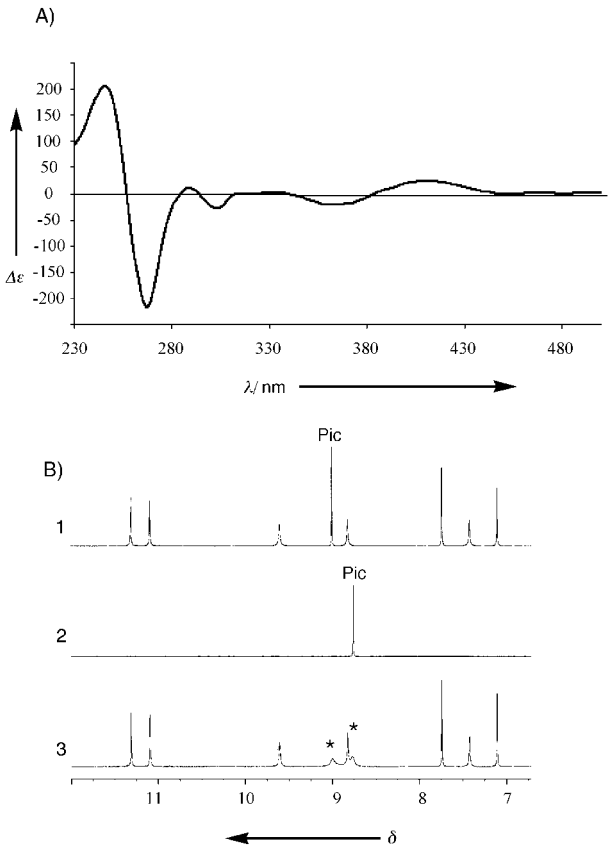

Figure 1. A) Circular dichroism spectra for $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$ (5.0×10^{-3} mM) in CH_2Cl_2 at 25 °C. The band at 256 nm corresponds to the G**1** chromophore while the induced band near 380 nm corresponds to the picrate anion. B) A region of the ^{1}H NMR spectra in CD_2Cl_2 at 25 °C and with a complex concentration of 0.6 mM for: 1) $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$, 2) [2.2.2]-cryptand$\cdot Ba^{2+}\cdot 2Pic^{-}$, and 3) a 1:1 mixture of $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$ and [2.2.2]-cryptand$\cdot Ba^{2+}\cdot 2Pic^{-}$. The asterisks identify the NMR signals which correspond to the two slowly exchanging picrate anions.

More evidence for G-quadruplex–picrate interactions in solution was obtained from ^{1}H NMR experiments. A mixture of the Ba^{2+} picrate G-quadruplex complex and [2.2.2]-cryptand/$BaPic_2$ in CD_2Cl_2 showed separate NMR signals for the picrate protons (Figure 1B). Since [2.2.2]-cryptand sequesters Ba^{2+},[17] the picrate anion should only be loosely coordinated, if at all, to the cryptate. The two different picrate proton NMR signals, marked with asterisks in spectrum 3 (Figure 1B), indicate that anion exchange between the Ba^{2+} G-quadruplex and the Ba^{2+} cryptate is slow on the chemical shift timescale, with millisecond lifetimes for the bound anion. The slow NMR exchange and the induced CD band confirm that the picrate anions remain intimately associated with the G-quadruplex in CD_2Cl_2 solution.[18]

The ^{1}H NMR data in Figure 2 show that the lipophilic G-quadruplexes are hexadecamers in solution. A water solution containing a 1:1 ratio of Ba^{2+} and Sr^{2+} picrates was stirred with a CD_2Cl_2 solution of G**1** (9.6 mM) for 24 hours. Lipophilic G**1** extracted picrate salts into CD_2Cl_2 to give a 1:1:2 ratio of three species: $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$, $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}$, and a new complex with four sets of ^{1}H NMR spectroscopic signals. A D_4-symmetric hexadecamer, such as $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$ or $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}$, has only two sets of NMR signals, one set for the two degenerate "inner" G_4-quartets and one set for the degenerate "outer" G_4-quartets. A lower-symmetry hexadecamer, such as $(G\mathbf{1})_8\cdot Ba^{2+}\cdot(G\mathbf{1})_8\cdot Sr^{2+}\cdot 4Pic^{-}$, should have four sets of NMR signals for its nonequivalent G-quartets. After the salt extraction (Figure 2C), signals are present for "inner" and "outer" H8 protons of $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$ and $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}$. Importantly, signals of the appropriate intensity for two new "inner" and two new "outer" H8 protons are also present. These four new signals must arise from the mixed hexadecamer, $(G\mathbf{1})_8\cdot Ba^{2+}\cdot(G\mathbf{1})_8\cdot Sr^{2+}\cdot 4Pic^{-}$. Two of the new H8 proton signals belong to the Ba^{2+}-bound G-quartets, while the other new H8 proton resonances are due to the G-quartets that sandwich Sr^{2+}. Scheme 2 illustrates this process. This experiment, done under thermodynamic conditions,[19] indicates that these complexes are hexadecamers in CD_2Cl_2. If the aggregates were $G_8\cdot M^{2+}$ octamers, we would not observe diagnostic NMR spectroscopic signals for a mixed complex upon extraction of Ba^{2+} and Sr^{2+} picrates.

A different cross-over experiment in CD_2Cl_2 highlights the impressive kinetic stability of these guanosine hexadecamers. Crystalline $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}$ and $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$ were combined to give a 1:1 mixture of the G-quadruplexes (0.6 mM) in CD_2Cl_2. An NMR spectroscopy stack plot shows slow formation ($t_{1/2}=42$ h) of the mixed hexadecamer $(G\mathbf{1})_8\cdot Ba^{2+}\cdot(G\mathbf{1})_8\cdot Sr^{2+}\cdot 4Pic^{-}$ (Figure 3). Again, a 1:1:2 statistical ratio of the three complexes was obtained at equilibrium.

While there are many possible mechanisms for ligand and cation exchange between $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$ and $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}$, the slow equilibration illustrated in Figure 3 implies that the four picrate anions hold the G-quadruplex together tightly in solution. If bridging interactions between bound anions and the "inner" G-quartets are significant in

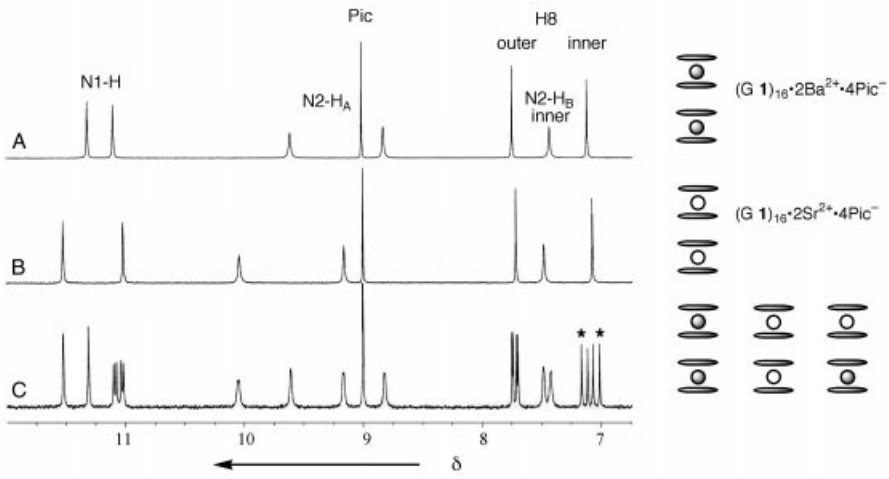

Figure 2. The "H8 region" of the ^{1}H NMR spectra: A) $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^{-}$, B) $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}$, C) after stirring a CD_2Cl_2 solution of G**1** with an aqueous solution of a 1:1 mixture of Ba^{2+} and Sr^{2+} picrates for 24 h. Spectra were recorded for samples (0.6 mM) in CD_2Cl_2 at 25 °C. The "inner" H8 proton resonances for the mixed hexadecamer $(G\mathbf{1})_8\cdot Ba^{2+}\cdot(G\mathbf{1})_8\cdot Sr^{2+}\cdot 4Pic^{-}$ are identified by asterisks.

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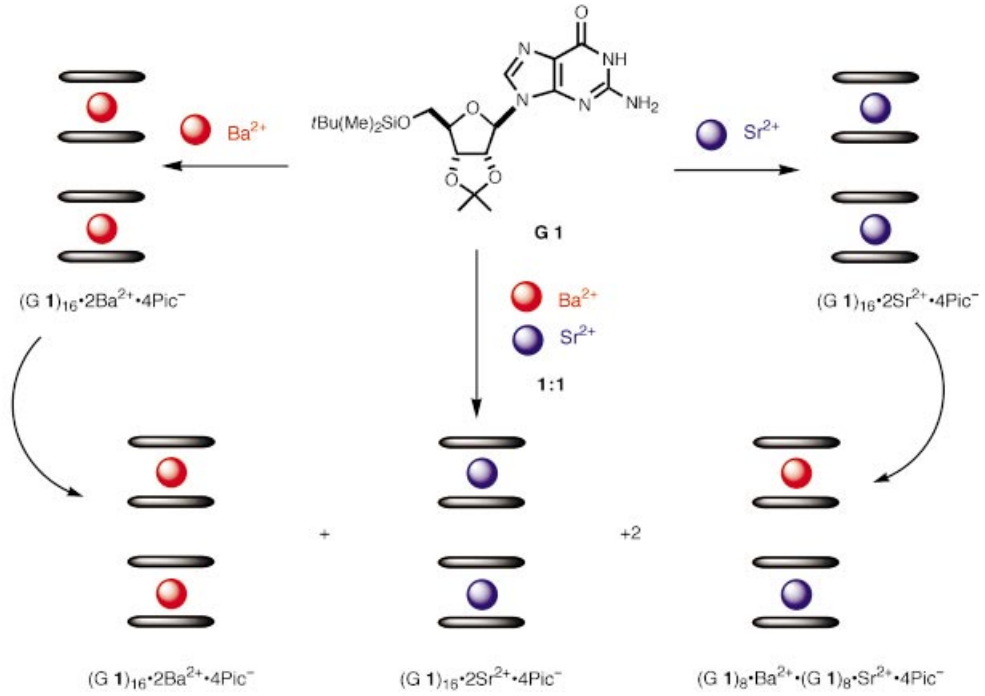

Scheme 2. Self-assembly of G**1** with Ba^{2+} and Sr^{2+} picrates gives a statistical mixture of hexadecameric G-quadruplexes.

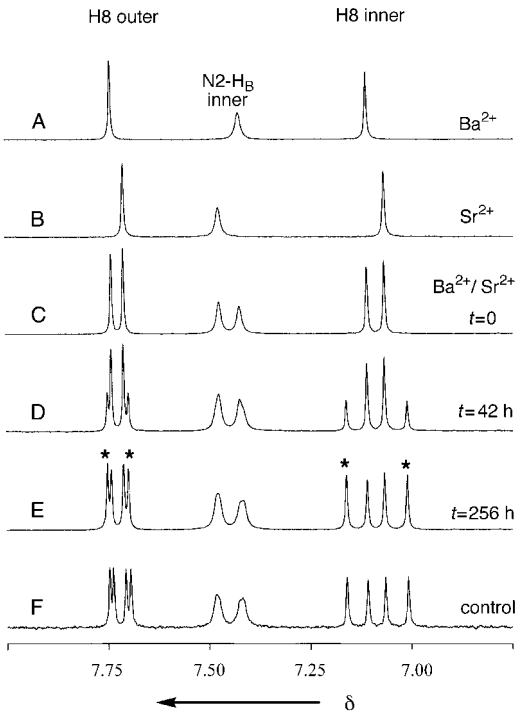

Figure 3. The "H8 region" of the ^{1}H NMR spectra for: A) $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^-$, B) $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^-$, C) a 1:1 mixture of $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^-$ and $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^-$ immediately after mixing, D) 42 h after mixing, E) 6 days after mixing, F) after stirring a CD_2Cl_2 solution of G**1** with an aqueous solution of a 1:1 mixture of Ba^{2+} and Sr^{2+} picrates for 24 h. Spectra were recorded for samples (0.6 mM) in CD_2Cl_2 at 25 °C. The H8 proton resonances for the mixed hexadecamer $(G\mathbf{1})_8\cdot Ba^{2+}\cdot(G\mathbf{1})_8\cdot Sr^{2+}\cdot 4Pic^-$ are identified by asterisks.

solution, then the anion's identity should modulate the hexadecamer's kinetic stability. Any change in the kinetic stability of the G-quadruplex due to the identity of the bound anion should be reflected in an altered formation rate for the mixed hexadecamer. Using thiocyanate, an anion that should not bridge $(G\mathbf{1})_8\cdot M^{2+}$ octamers as effectively as the picrate anion, we found that the anion can significantly affect the hexadecamer's kinetic stability. Thus, 1:1 mixtures of crystalline $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4(SCN^-)$ and $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4(SCN^-)$ also equilibrated to a statistical 1:1:2 ratio of complexes, but with a half-life of only $t_{1/2}=0.5$ h at room temperature in CD_2Cl_2. This equilibration rate for the thiocyanate complexes was approximately two orders of magnitude faster than that for the picrate complexes, $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^-$ and $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic$. This result is consistent with the G-quadruplex having a stronger affinity for the picrate anion, as compared to the thiocyanate. Finally, the lipophilic G-quadruplex appears to be cooperative in its ion-pair binding. Extraction of a water solution containing 100 equivalents of KSCN and 1 equivalent of $Ba(Pic)_2$ with a CD_2Cl_2 solution of G**1** (10 mM) showed that only $(G\mathbf{1})_{16}\cdot 2Ba^{2+}\cdot 4Pic^-$ was formed in the organic phase. This self-assembled ion-pair receptor prefers to bind the divalent Ba^{2+} over the monovalent K^+ and the picrate anion over the thiocyanate.

While G-quartets are well-known cation receptors, our most significant finding in this paper is that the anion can also help control G-quadruplex structure and stability in solution. The lipophilic G**1** and divalent picrate salts form a guanosine hexadecamer in both the crystalline state and in CD_2Cl_2 solution. Self-assembly of monomeric ligands to give ditopic receptors with discrete cation and anion binding sites promises to be a fundamentally powerful approach for selective ion-pair recognition.

Received: March 26, 2001 [Z16845]

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[15] Crystal data for $(G\mathbf{1})_{16}\cdot 2Sr^{2+}\cdot 4Pic^{-}\cdot (H_2O)_{23.25}\cdot (CH_3CN)_{3.5}$: $C_{335}H_{561}Sr_2N_{95.5}O_{131.25}Si_{16}$; $M_r = 8651.47$, crystal dimensions $0.636\times 0.455\times 0.127$ mm^3, tetragonal, space group $I4$, $a = 30.5043$, $b = 30.5043$, $c = 25.802(3)$ Å, $V = 24{,}009(3)$ Å^3, $Z = 2$, $D_x = 1.197$ mg m^{-3}, $\mu Mo_{K\alpha} = 0.347$ mm^{-1}. Data were collected on a Bruker SMART 1000 CCD diffractometer at 193(2) K. Structure determination was done by direct methods using the program XS.[20] Refinement, using the XL program,[21] was done to convergence on F^2 with $R(F) = 11.12\,\%$ and $wR(F^2) = 23.43\,\%$ for all 15685 independent reflections [$R(F) = 8.84\,\%$, $wR(F^2) = 22.09\,\%$ for those 12150 data with $F_o > 4\sigma(F_o)$]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160231. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Nickel(II) Phosphate VSB-5: A Magnetic Nanoporous Hydrogenation Catalyst with 24-Ring Tunnels**

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Aluminosilicate zeolites and related nanoporous materials are used widely in the domains of separation, ion-exchange, and shape-selective catalysis.[1–3] The majority of catalytic processes that use zeolites involve acid-catalyzed reactions, for example hydrocarbon isomerization, cracking, alkylation, and dehydration,[1, 3] though recently there has been a surge in interest in partial oxidation reactions based upon titanosilicate materials and transition metal substituted aluminophosphates.[4] It would be of great interest to create nanoporous materials that catalyze other types of reactions, such as shape-selective hydrogenations, but it has not so far proved possible to achieve this in a zeolite catalyst without introduction of extra-framework Ni and noble metal clusters. The underlying challenge here is to design a nanoporous system based on, say, nickel, that is both functional and thermally stable with respect to chemical or structural degradation.[5, 6] We recently showed that the open-framework nickel(II) phosphate, VSB-1 (Versailles – Santa Barbara-1), is sufficiently stable to be rendered nanoporous and exhibits typical zeolitic properties.[7] Furthermore, this large-pore material has interesting catalytic properties suitable for reactions that require only weak acidity.[8] Herein, we describe a second nanoporous nickel phosphate, VSB-5, which exhibits redox properties that

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[**] A.K.C. thanks the Fondation de l'Ecole Normale Supérieure and the Région de l'Ile de France for a Chaire Internationale de Recherche, Blaise Pascal. We also thank the CNRS for financial support and for providing a Poste Rouge for Q.G. and a PICS to the two groups for cooperation. The authors are indebted to D. S. Kim for his support with pore size analysis. We thank the Korean Ministry of Science and Technology (Key Research Program, KK-0005-F0) for supporting this work, and the Korea Science and Engineering Foundation (KOSEF) Fellowship for J.S.C. is gratefully acknowledged. J.S.C. was partially supported by the U.S. Department of Energy under grant DE-FG03-96ER14672. P.M.F. was supported by the National Science Foundation under the MRSEC Program (NSF-DMR-96-32716).