Based on paired experiments in benzene (200, 220 °C) and *p*-dioxane (182, 196 °C), the apparent activation enthalpy for formation of CO hydrogenation products is 40.7 ± 6% kcal/mol. This result is compatible with a strongly endothermic rate-determining (rd) step (eq 2) in which hydrogen atom transfer to CO yields formyl and cobalt tetracarbonyl radical pairs in a manner entirely analogous to the proposed[1] arene hydrogenation mechanism. Where this mechanism applies, triple-bond hydrogenation need not make use of cluster catalysts; prior hydrogen atom transfer is sufficiently bond weakening to cause the moiety to be susceptible to further reduction. Furthermore, if the H atom transfer mechanism is valid other complexes, capable of reversible hydrogen activation by reaction analogous to eq 4 and possessing metal–hydrogen bonds not too much stronger than that in $HCo(CO)_4$ (58 kcal/mol),[16a] should also be capable of CO hydrogenation. This prediction was successfully tested with the system $Mn_2(CO)_{10}$–$HMn(CO)_5$ in *p*-dioxane. The total manganese content was 0.2 or 0.6 M, the temperature was 240 °C, and the partial pressures of CO and H_2 were 102 and 204 atm, respectively. These conditions were chosen on the basis of the successful use of $HMn(CO)_5$ for arene hydrogenation[7a] by the H atom transfer–radical pair mechanism,[7b] an estimate for $D(HMn(CO)_5)$ of 64 ± 1 kcal/mol, the greater stability of $HMn(CO)_5$ than of $HCo(CO)_4$ toward loss of CO,[19c] and the less favorable equilibrium constant for the analogue of eq 4. Pseudo-first-order rate constants for the formation of methanol and total product were found to be 1.3×10^{-5} s^{-1} and $1.4_6 \times 10^{-5}$ s^{-1}, respectively, and proportionality between hydrogenation rate and concentration of $HMn(CO)_5$[17] was observed.

$$HCo(CO)_4 + CO \xrightarrow{rd} H\dot{C}O + \cdot Co(CO)_4$$

$$\Delta H^\circ(2) = 40.0 \pm 1.7 \text{ kcal/mol}^{16} \quad (2)$$

$$H\dot{C}O + HCo(CO)_4 \xrightarrow{fast} \text{products} \quad (3)$$

$$2Co(CO)_4 \xrightarrow{fast} Co_2(CO)_8 \overset{+H_2}{\rightleftharpoons} 2HCo(CO)_4 \quad (4)$$

Further mechanistic speculations[18] based on the available data would not be warranted. Efforts to ascertain the probable reaction pathway(s) via variations of temperature, pressure, solvent, catalyst concentration, and by appropriate labeling studies are underway.

The homogeneous, catalytic formation of methanol from synthesis gas by mononuclear catalysts which is now reported was unexpected because it had been so long overlooked in the very extensive review literature[19] of such systems. The further observation that the same catalyst system simultaneously converts methanol to higher alcohols, probably via the "homologation" reaction of alcohols,[20] opens the way to a detailed study of the long-sought homogeneous analogues of both the Fischer–Tropsch and methanol synthesis catalysts.

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Alkali Metal Ion Specificity in the Solution Ordering of a Nucleotide, 5′-Guanosine Monophosphate

Sir:

The 5′-guanosine monophosphate dianion (5′-GMP) was recently reported to form a regular ordered structure in aqueous solution that is slow to exchange on the ^{1}H NMR time scale.[1] The most informative evidence for structure formation was provided by the presence of four nonequivalent H(8) resonances in the limiting spectrum of the disodium salt in D_2O solution near 0 °C. The large chemical shift range for the H(8) protons (1.3 ppm) and the appearance of nonequivalent amino proton lines indicated that both base stacking and hydrogen bonding are important in the self-structuring processes. Based on these observations and consideration of infrared frequency shifts in the carbonyl stretching region, it was concluded that structure formation arises from limited stacking of planar tetramer units (I) formed by hydrogen bonding between positions N(1) and N(2) as donors and O(6) and N(7) as acceptors.[2]

The slow chemical exchange of self-assembled 5′-GMP is

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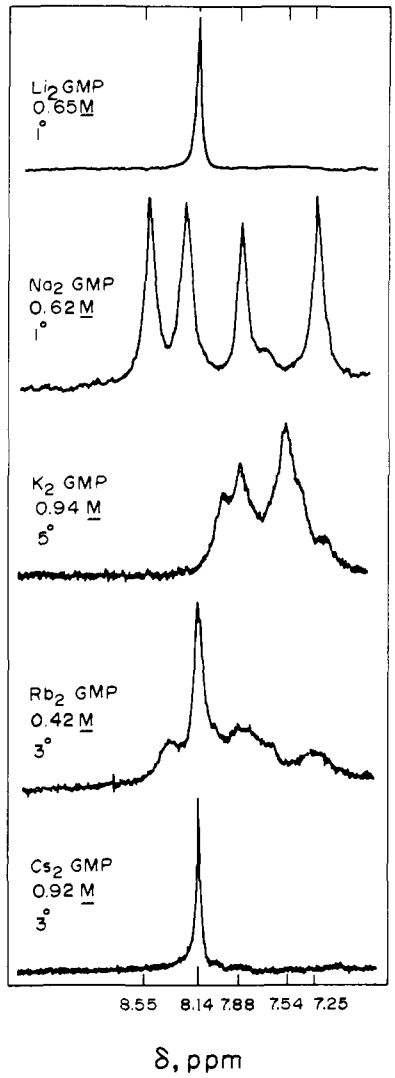
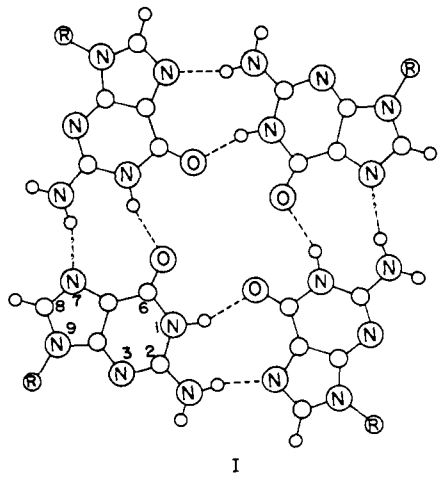


Figure 1. Limiting H(8) resonance lines (220 MHz) of the alkali metal salts of 5′-guanosine monophosphate dianion in D_2O solution. The concentrations employed approach the saturation limits, except for Na_2(5′-GMP) which is soluble to ~1.0 M. Nonequivalent environments are also observed for certain ribose protons of the Na^+, K^+, and Rb^+ salts, but the resolution is much poorer than that shown for the H(8) lines.



I

unusual insofar as all other mononucleotides or nucleosides associated via base-stacking or hydrogen-bonding interactions, including mixed systems with Watson–Crick complementarity, undergo rapid chemical exchange and give time-averaged NMR spectra in aqueous solution.[6-11] The relatively high activation energy for site exchange ($\Delta G^{\ddagger}_{25°} > 15$ kcal/mol)[1]

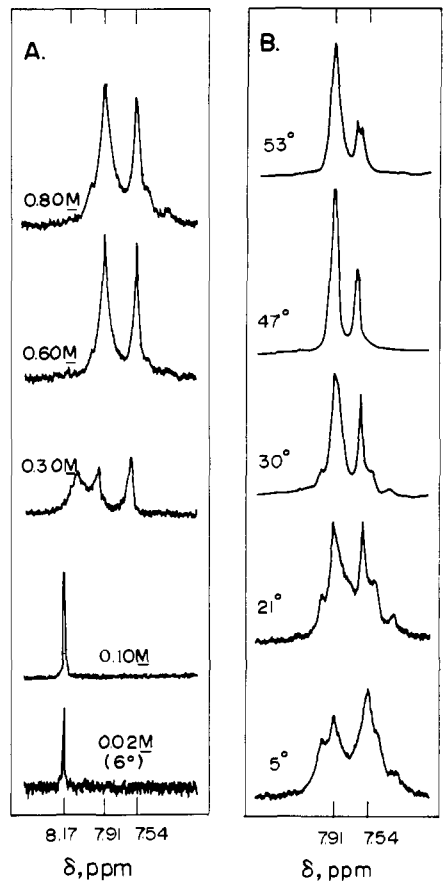


Figure 2. (A) Concentration dependence of the H(8) resonances of self-assembled K_2(5′-GMP) in D_2O solution at 20 ± 1°. (B) Temperature dependence of the H(8) lines of 0.94 M K_2(5′-GMP) in D_2O. The chemical shift values of lines in the limiting spectrum at 5° are at 8.01, 7.91, 7.54, 7.44, and 7.23 ppm relative to internal TSP. A sixth line may be present as a high-field shoulder on the 7.91-ppm resonance.

prompted us to investigate the possibility of selective complexation of the alkali metal counterion by the self-structure nucleotide. The results indicate that the self-assembly phenomenon depends dramatically on the nature of the alkali metal ion. We believe this to be the first demonstration of the ability of alkali metal ions to direct structure formation of a nucleotide through a size-selective coordination mechanism.

Figure 1 shows the limiting H(8) resonance lines of the alkali metal salts of 5′-GMP[12] in concentrated D_2O solutions near the freezing point of the solvent. It is immediately clear that, in addition to Na^+, both K^+ and Rb^+ form slowly exchanging ordered structures with multiple H(8) environments, whereas Li^+ and Cs^+ provide little or no evidence for structure formation.

In dilute solution (~0.02 M) all of the salts exhibit a single sharp H(8) line near 8.17 ppm characteristic of unassociated 5′-GMP. As the concentrations of the Li^+ and Cs^+ salts approach their saturation limits, the line shifts slightly to higher field and broadens ($\Delta\nu_{1/2} \simeq 8$ Hz), perhaps owing to some association via base stacking of monomeric units. The limiting low-temperature spectrum of Cs_2(5′-GMP) appears to give weak higher field H(8) lines which may be due to some regular structure formation, but their intensity is <5% of the total H(8) intensity.

In marked contrast to Li^+ and Cs^+, the Na^+, K^+, and Rb^+ salts each show a great degree of self-ordering. The second highest field H(8) line of Na_2(5′-GMP) has been previously shown[1] to increase in intensity at the expense of the remaining three lines as the extent of association is decreased with increasing temperature or decreasing concentration. The three

self-structure lines could be explained in terms of a head to tail stacking of three tetramer units (i.e., a dodecamer) or, alternatively, by head to tail and head to head stacking of two tetramer units.

The limiting spectrum of K_2(5′-GMP) is different from that of self-assembled Na_2(5′GMP). Based on the concentration and temperature dependence of the K_2(5′-GMP) self-structure lines (cf. Figure 2A and 2B), there appear to be at least three different structures present in solution. The higher temperatures at which ordered structures persist in the K^+ complex than in the Na^+ complex show the former to be more stable than the latter.

A third unique H(8) spectrum is provided by Rb_2(5′-GMP). The limiting spectrum of this self-assembled salt shows at least three broad self-structure lines near 8.30, 7.74, and 7.21 ppm and a sharper line near 8.08 ppm due to unstructured nucleotide. Based on the relative intensities of the self-structure lines, it is likely that more than one structure exists for self-assembled Rb_2(5′-GMP).

Although the H(8) NMR spectra are unique for each of the three structured salts, it is probable, based on IR data, that they all incorporate a hydrogen-bonding scheme analogous to that proposed for self-assembled Na_2(5′-GMP). The vibrational frequencies of the structured Na^+ salt in the C=O, C=C, and C=N stretching region occur at 1672, 1593, 1585, 1570, and 1538 cm^{-1}. A similar spectrum is observed for the self-structured K^+ and Rb^+ salts. The unassembled salts, including those of the nonstructuring Li^+ and Cs^+ ions[13] under conditions where the H(8) NMR line is slightly broadened, exhibit a distinctly different spectrum with three bands near 1665, 1580, and 1568 cm^{-1}.[14]

The binding constants for complexation of alkali metal ions by phosphate groups in polyphosphates,[15] adenine nucleotides,[16,17] and DNA[18] are known to decrease slightly with increasing metal ion radius. In contrast to this electrostatically determined order, the qualitative stability order for self-assembled 5′-GMP salts is $K^+ > Na^+$, $Rb^+ \gg Li^+$, Cs^+. Though such a stability ranking has not been observed previously in a nucleotide or polynucleotide system, similar rankings have often been observed for complexes of alkali metal ions with macrocyclic antibiotics, oligopeptides, or synthetic cyclic ethers, for example.[19] In these complexes, the specificity of binding depends upon the ability of the cyclic organic molecule to provide a cavity of appropriate size containing residues capable of complexing the metal ion. Too large an ion is excluded sterically and too small an ion is unable to bridge the distance between potential ligand residues in the cavity.

We propose that the presence of analogous binding cavities in ordered 5′-GMP is responsible for the observed ion specificity of structure formation in the following way. The center of the planar tetramer (1) is ~2.2 to 2.3 Å from the center of the carbonyl oxygens, a value very close to O–Na ligand distances observed, e.g., in the Na^+ complex of an analogue of antamanide (average distance from Na^+ to carbonyl oxygen 2.30 Å).[20] The Na^+ could easily fit in the center of the square formed by the four carbonyl oxygens without inhibiting stacking of two tetramer units (a fifth coordination to solvent above the plane of the tetramer is also possible, as in the pentacoordination observed in the antaminide analogue).[20] Li^+, with Li–O ligand distance of ~2.0–2.1 Å may be too small to bridge the necessary distance and so fail to form a complex. K^+, on the other hand, with a K–O ligand distance of 2.6–2.9 Å[19] is too large to fit in the plane. The same liganding carbonyl groups can be used, however, to form a cavity between two planar tetramers. If the interplanar spacing is 3.4 Å, the K–O distance would be 2.8 Å, and the coordination number would be eight, as observed in a number of K^+ complexes. We note that this structure would be capable of linear extension of the stack, while retaining the same coordination number and geometry. Rb^+ is similar in size to K^+ and should be capable of forming similar complexes with GMP, coordinatively intercalated between planar tetramers. Cs^+, however, is significantly larger than K^+ and cannot be sandwiched between the rings at a distance that would still permit GG stacking interactions.[22] We suggest that cavity complexation as described contributes stability to the complex, and that it is a necessary condition for self-structure formation by neutral GMP.[23]

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