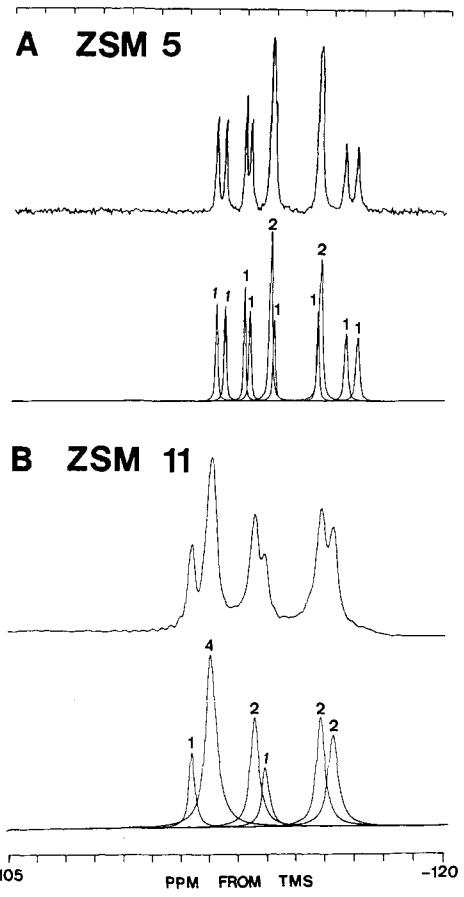

Figure 2. (A) Observed (79.5 MHz, 3914 scans, 7-s delay, and 0-Hz line broadening) and calculated ^{29}Si MAS NMR spectra of zeolite ZSM-5 at 393 K; (B) Observed (79.5 MHz, 3500 scans, 7-s delay and 0-Hz line broadening) and calculated ^{29}Si MAS NMR spectra of zeolite ZSM-11 at 373 K. The numbers in the theoretical spectra reflect the relative peak intensities.

The nature of these high-temperature phases is somewhat ambiguous at the present time. The NMR spectra may reflect a change to genuine (static) structures of different and higher symmetries. This could occur if the Si–O bond lengths were too short to exactly accommodate the lattice structure, resulting in strain and subsequent distortion from the ideal symmetry which is removed at elevated temperatures by lattice expansion. However, the spectra are also compatible with dynamic structures whose (average) structures are of higher symmetry. Thus, by their sensitivity to those cases where mobility induces apparent phase changes with the *number* of lines reflecting an associated change in the symmetry, the spectra may be reflecting more mobile lattices for zeolites in general than hitherto anticipated. The case of ZSM-39 is important in this regard as it is very dense (and hence relatively rigid) structure.

We are further investigating these systems to resolve this point, complementing the NMR data with synchrotron-based X-ray investigations at both ambient and elevated temperatures[8] which will provide greatly improved diffraction structures although it is recognized that the lattice changes detected by the NMR data may be too small to be resolved, even using synchrotron radiation. The NMR data can also be augmented by measurement of the spectra and also relaxation times of the ^{27}Al and most importantly the ^{17}O nuclei in the lattice, as their relaxation mechanisms will be via quadrupolar interactions and should directly reflect any lattice motions.

Acknowledgment. We acknowledge the financial assistance of the Natural Sciences and Engineering Research Council (Canada) in the form of an Operating Grant (CAF).

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Flavocyclodextrin as a Promising Flavoprotein Model. Efficient Electron Transfer Catalysis by Flavocyclodextrin

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Flavoproteins play key roles in electron transport,[1] respiration, photosynthesis, bioluminescence, and other oxidation–reduction systems,[2] catalyzing the electron transfer[3] from NADH (or NADPH) to the flavin and further to the electron acceptor. The function of flavoproteins may be "reconstructed" artificially by providing an appropriate self-organizing system for flavin and dihydronicotinamide to associate reversibly.

There are only two unnatural "artificial flavoprotein families" known, flavopapains[4] and flavoporphyrins,[5,6] but the latter has small association constants with the nicotinamideimidazole. Cyclodextrins (CD) are well known to associate with guests strongly and rapidly.[7] These characteristics should make it possible to prepare an artificial flavoenzyme if flavin is implanted in CD.

We wish to report the synthesis of flavo-α-cyclodextrin, **1**,[8] and its very efficient electron transport.

Compound **1** was prepared from 6-tosyl-α-cyclodextrin and 8α-bromoriboflavin according to Scheme I. Separation and purification of **1** was performed by silica gel thick-layer chromatography and Sephadex G-10 column chromatography. The structure determination was based on the following spectra and analysis [UV–vis 270 (2.5×10^4), 350 (7.3×10^3), 450 nm (1.0×10^4), IR 3380, 2940, 1708, 1585, 1548, 1155, 1080 cm^{-1}; FAB-MS 1363 $(M + H)^+$; ^1H NMR δ from Me_4Si 2.58, 2.85, 3.21, 3.5–4.0, 4.07–4.10, 4.48, 5.06, 8.01, 8.07 ppm; ^{13}C NMR δ from Me_4Si 18.16, 33.79, 35.57, 47.40, 60.01, 63.29, 68.74, 71.57–73.68, 82.12, 85.13, 101.98, 117.88, 131.78, 132.12, 134.50, 135.41, 137.41, 145.20, 150.96, 155.42, 159.80 ppm. Elemental anal. Calcd for $C_{53}H_{78}N_4O_{35}S \cdot H_2O$: C, 46.09; H, 5.84; N, 4.06. Found: C, 45.81; H, 5.67; N, 4.57.] The ^{13}C and ^1H NMR spectra showed the ordinary absorptions ascribed to 8α-S-Me riboflavin and C_6SH-α-cyclodextrin (shifted less than 1.0 ppm for ^{13}C and 0.2 ppm for ^1H) except for the following shifted absorptions: ^{13}C; Fl 8α, at 33.79; C_6 A-ring at 35.57; C_4 A-ring at 85.13. All of the observed ^1H absorption intensity ratios indicate an exactly 1:1 combination of both moieties.

The electron-transfer activities of **1** for *N*-alkyldihydronicotinamides (RNAH, **2a–c**) were studied in water, pH 7.4 at

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Scheme I

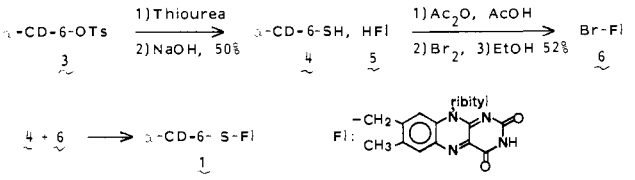

Table I. Association Constants and Rate Constants for the Reduction of Natural and Artificial Flavoenzyme

flavin	reductant	K_a (M^{-1})	k_2 (s^{-1})	$k_2 \cdot K_a$ (M^{-1} s^{-1})
NADH FMN oxidoreductase[a]	NADH	21000	15.5	326000
8α-S-flavopapain (7)[b]	benzyl-NAH	10300	0.0054	56
8α-S-flavoCD (1)[c]	*n*-hexyl-NAH	2500	0.5	1200
	isopropyl-NAH	260	0.36	94
	benzyl-NAH	1050	0.06	63

[a] 23 °C, pH 7.0, ref 9b. [b] 25 °C, pH 7.5. [c] 25 °C, pH 7.4. Rate constant for 8α-S-substituted riboflavin obtained (ca. 50 M^{-1} s^{-1}) by the Hammett extrapolation from substituted Fl's.

25 °C. The reaction was nearly quantitative as determined by electronic spectroscopy when an excess (at least 10-fold) of RNAH was used. The rates of the electron transfer from RNAH to the flavin moiety of the flavo-CD (eq 1) were measured by following

$$\mathbf{1} + \mathrm{RNAH} \overset{K_a}{\rightleftharpoons} \mathbf{1}\cdot\mathrm{RNAH} \xrightarrow[H^+]{k_2} \mathrm{RNA}^+ + \mathbf{1}\cdot\mathrm{H}_2 \qquad (1)$$

the characteristic absorption of the flavin at 450 nm by using a stopped-flow apparatus. As shown in Table I, flavo-CD **1** has reasonably large association constants of 1050, 260, and 2500 M^{-1} for benzyl-, isopropyl-, and *n*-hexyl-NAH, respectively, although smaller than 8α-S-flavopapain.[4a] The natural NADH·FMN oxidoreductase[9a] has an even larger association constant (ca. eightfold greater) for NADH which has much more extensive recognition site than RNAH. It is noteworthy that simple CD cavity confers almost the same degree of recognition as the natural enzyme.

The most interesting feature of compound **1** is the large rate constant for the electron transfer (Table I). Although the natural NADH dependent flavoprotein exhibits a 30-fold larger rate constant than **1**, the "structurally related flavopapain" **7**[4a] has a much smaller (by a factor of 90) rate constant than **1**. This suggests that the spacial arrangement of the flavin moiety relative to the bound dihydronicotinamide is much better in **1** than the flavopapain, since the latter probably has an Fl-NAH edge–edge distance of 4–14 Å, depending on the flavin internal rotation based on the X-ray crystallographic analysis of unmodified papain.[9b]

The overall efficiencies of dihydroflavin production for **1** (eq 1), expressed by $k_2 \cdot K_a$, are 63, 94, and 1200 M^{-1} with benzyl-, isopropyl-, and *n*-hexyl-NAH, respectively, larger than 56 for 8α-S-flavopapain[4a] with benzyl-NAH but smaller than 1.64×10^6 for the sterically less hindered and more electron deficient flavopapain with *n*-hexyl -NAH.[10]

Furthermore, according to our preliminary experiments, **1** exhibited efficient catalytic activities for the electron transfer from RNAH to metalloporphyrins, which are important steps in respiration and the reduction of cytochrome P-450. A typical example is the electron transfer from *n*-hexyl-NAH to TPPS·Mn^{III} catalyzed by **1** with the observed catalytic constant of 200 M^{-1} s^{-1} at 25 °C in pH 7.4 aqueous solution. The catalytic efficiency of **1** was 5.5-fold higher than FMN (see Table II). According to our preliminary experiments, artificial Fl-CD can be a good model of Fl-protein (e.g., P-450 reductase).

Table II. Rates of Flavin-Catalyzed Reduction of Mn^{III}·Porphyrin

Mn^{III} porphyrin[a]	flavin[a]	k_2[b] (M^{-1} s^{-1}) MeNAH	k_2[b] (M^{-1} s^{-1}) *n*-hexyl-NAH
MnTPPS		0.2	0.2
MnTPPS	FMN	36	31
MnTPPS	**1**	22	200
cytochrome *c*	**7**	56 (benzyl-NAH)[c]	

[a] 8×10^{-6} M. [b] $v = k[\mathrm{Mn^{III}TPPS}][\mathrm{RNAH}]$, H_2O, 25 °C, pH 7.4. [c] Reference 4 and 10.

The present observations of excellent RNAH binding and efficient electron transfer may give a promise for versatile application of flavocyclodextrin to a variety of biomimetic chemistries.

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Bifunctional Activation of Ketone with Rhodium(III) Porphyrin. Efficient Cooperation of Metal and Intramolecular Base

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The enolization of carbonyl compounds is an essential process in many organic and biological reactions. The generation of enolates as reactive intermediates in organic synthesis usually requires strongly basic conditions.[1-3] On the other hand, the enolization catalyzed by metalloenzymes such as aldolases involves an efficient cooperation of metal ion (as a Lewis acid) and a basic amino acid residue (as a Brønsted base) under neutral conditions.[4] Such a concerted acid–base cooperation, although not readily accessible by using synthetic systems,[5] is significant for the development of catalytic organic reactions under mild conditions. Now, we wish to report here that simple ketones such as acetone undergo novel bifunctional activation (enolization) with Rh(III) porphyrins having suitably located intramolecular bases.

Chlororhodium(III) complexes of *trans*- and *cis*-5,15-bis(2-hydroxy-1-naphthyl)octaethylporphyrin (**1a**-*trans* and **1a**-*cis*)[6]

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