quenching by ET from An to the photoexcited (b^-)Re^{II} center is endothermic for b = tmb, dmb, bpy, and 4-dab and thermoneutral or only weakly exothermic for b = 5-dab, deb, and bpz.[22] Third, nanosecond flash photolysis (ns-FP) provides unequivocal evidence for rapid formation of $^3An^*$ following excitation at wavelengths where light is absorbed almost exclusively (>90%) by the (b)-$Re(CO)_3$ chromophore. Excitation of each (b)ReAn complex (320 nm, 10 ns fwhm, 6 mJ/pulse) produces a strongly absorbing transient with a spectrum (λ_{max} = 425 nm, $\lambda_{shoulder}$ = 405 nm, ΔOD_{max} = 0.8) that is identical to the spectrum of $^3An^*$.[23] No other transients were observed within the time resolution of the ns-FP apparatus, indicating that $^3An^*$ is formed with $k_{EnT} \geq 10^8$ s^{-1}.

Rates for MLCT quenching (k_q) in the (b)ReAn complexes in 2-methyltetrahydrofuran solution were calculated by using the expression $k_q = (1/\tau_{(b)ReAn}) - (1/\tau_{(b)ReB})$, where τ values are MLCT emission lifetimes of corresponding (b)ReAn and (b)ReB complexes. Figure 1 shows a plot of log k_q vs ΔE_{EnT}; *note that k_q clearly increases as ΔE_{EnT} becomes less exothermic.*

In the limit of weak interchromophore electronic coupling, the rate for exchange E_nT from a donor to an acceptor is given by the following expression:[2,4,15,16]

$$k_{EnT} = \frac{2H_{DA}^2}{h}\left(\frac{\pi^3}{\lambda_s k_B T}\right)^{1/2} \exp\{-(S^D + S^A)\}\sum_{i=1}\sum_{j=1}\frac{(S^D)^{w_i}}{w_i!}\frac{(S^A)^{v_j}}{v_j!} \times \exp\left\{\frac{-(\Delta E_{EnT} + \lambda_s + w_i\hbar\omega_D + v_j\hbar\omega_A)^2}{4\lambda_s k_B T}\right\} \quad (2)$$

In eq 2, H_{DA} is the exchange coupling matrix element,[19] S^D (S^A) and $\hbar\omega_D$ ($\hbar\omega_A$) are, respectively, the unitless displacement and frequency of the dominant high-frequency mode which is displaced during E_nT in the donor (acceptor), λ_s is the sum of outer-sphere and low-frequency inner-sphere reorganization energies for de-excitation of the donor and excitation of the acceptor, the sums are taken over ground-state vibrational levels of the donor (w_i) and excited-state vibrational levels of the acceptor (v_j), and the other parameters have their usual meanings. This type of expression has been used extensively to model rate–driving force correlations for highly exothermic ET and nonradiative excited-state decay.[1-7,9,11-13]

Equation 2 was used to fit the MLCT quenching rate data for the (b)ReAn complexes; the solid line in Figure 1 was calculated by using the following parameters: $S^D = 1.0$, $S^A = 0.9$, $\hbar\omega_D = \hbar\omega_A = 1300$ cm^{-1}, $\lambda_s = 0.15$ eV, $H_{DA} = 2.2$ cm^{-1}. Several key features emerge from this fit of the experimental data. First, although the line simply represents a six-parameter fit of the rates, the values of each parameter are reasonable given the structure of the two chromophores and the nonpolar solvent.[24] Second, it is clear that the calculated line reproduces k_q well for b = tmb, dmb, bpy, and 4-dab; however, k_q is larger than predicted for b = 5-dab, deb, and bpz. As noted above, ΔG for ET from An to the photoexcited Re center is thermoneutral or slightly exothermic for the latter complexes.[22] We believe that the larger than expected k_q values for b = 5-dab, deb, and bpz arise because, in these complexes, ET is competitive with E_nT, and the k_q values represent a sum of the rates for the two processes. The relative quantum yield for $^3An^*$ formation (Φ_T^{rel}),[25] which was determined for each (d)ReAn complex, provides evidence that a process competes with E_nT in some members of the series. For b = tmb, dmb, and bpy, Φ_T^{rel} is nearly constant ($\Phi_T^{rel} \approx 1.0$, 0.9, and 1.0, respectively); however, it decreases along the series b = 4-dab, 5-dab, deb, and bpz ($\Phi_T^{rel} \approx 0.8$, 0.7, 0.5, and 0.6, respectively). This result strongly implies that $k_q \approx k_{EnT}$ for b = tmb, dmb, and bpy, but $k_q > k_{EnT}$ for the other complexes. The Φ_T^{rel} data also suggest that the divergence between k_q and k_{EnT} is most significant for the latter two complexes, which is qualitatively consistent with the comparison between theory and experiment in Figure 1.

Finally, the results presented herein imply that the total reorganization energy for E_nT is markedly less than has been observed for ET in related complexes.[9,11] Because of this difference, the optimal rate for E_nT occurs at considerably lower exothermicity than the optimal rate for ET.

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Supplementary Material Available: Synthetic details and ^1H NMR data for all compounds (3 pages). Ordering information is given on any current masthead page.

(22) ΔG values for excited-state ET (ΔG_{ET}) were estimated from $\Delta G_{ET} = E_p(An/An^+) - E_{1/2}(b/b^-) - E_{MLCT}$, where $E_p(An/An^+)$ and $E_{1/2}(b/b^-)$ are, respectively, peak and half-wave potentials for oxidation of An and reduction of b in the (b)ReAn complexes in CH_3CN, and E_{MLCT} was determined as described in ref 6. The estimated ΔG_{ET} values are as follows (eV): +0.19 (tmb), +0.13 (dmb), +0.07 (bpy), +0.02 (4-dab), 0.0 (5-dab), −0.12 (deb), −0.08 (bpz).

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NMR Assignment of Leucocin A, a Bacteriocin from *Leuconostoc gelidum*, Supported by a Stable Isotope Labeling Technique for Peptides and Proteins

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Bacteriocins are peptides or proteins produced by bacteria that display antimicrobial activity against closely related species of microorganisms.[1] Their potential as nontoxic food preservation agents, especially for dairy products and meat, has stimulated interest in the production of bacteriocins by lactic acid bacteria.[2] However, with the exception of nisin A, which is well-characterized[3] and approved for commercial use in over 45 countries,[4] only a few bacteriocins have been purified to homogeneity and had their primary sequence fully elucidated.[5] This lack of in-

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Figure 1. Primary sequence of leucocin A with one disulfide bridge between cysteines 9 and 14 not shown. The solid bars represent identified short-range NOEs: NH^{i}–NH^{i+1} (d_{NN}), $C_{\alpha}H^{i}$–NH^{i+1} ($d_{\alpha N}$), and CH^{i}(other)–NH^{i+1} ($d_{other\text{-}N}$) observed in DMSO with 0.25% CF_3COOH (TFA) at 303 K (A) and 90% water with 10% DMSO and 0.2% TFA at 283 K (B).

formation about their chemical structures and modes of action has retarded their commercial development. Recently, we isolated the bacteriocin, leucocin A, produced by *Leuconostoc gelidum* UAL-187,[6] and determined its sequence of 37 amino acids (Figure 1) by a combination of chemical, spectral, and genetic methods.[7] We now describe the ^{13}C labeling of leucocin through use of a widely applicable stable isotope labeling technique for peptides and proteins and assign its complete ^{1}H and ^{13}C NMR spectra.

Development of multidimensional NMR techniques allows efficient analysis of peptide and protein structures in solution.[8,9] Although the problems of spectral overlap in 2D ^{1}H frequency space with increasing size of the biomolecules can often be overcome by new multidimensional NMR techniques assisted by multiple ^{15}N and ^{13}C labeling,[9] the isotope-bearing proteins can be difficult and expensive to obtain. This is due both to the cost of multiply labeled amino acid precursors and [U-^{13}C]glucose used in fermentative production of proteins as well as to the failure of many biological systems to grow or produce desired metabolites on simple defined media. Our approach to overcoming these obstacles involves preparation of a complex labeled medium by cultivation of cyanobacteria (e.g., *Anabaena* sp.) on inexpensive sodium [^{13}C]bicarbonate as the sole carbon source.[10] Following this strategy, continuous addition of sodium [^{13}C]bicarbonate (30% isotopic purity) to three fermentations of *Anabaena* sp. (9 L each) over 7–10 days under a controlled nitrogen atmosphere yields a labeled cell mass (24 g) that can be hydrolyzed by pepsin and chymopapain to provide a uniformly labeled mixture of amino acids and peptides (17 g).[11] Although conventional acid hydrolysis of algal protein destroys many sensitive constituents and gives an amino acid mixture that frequently fails to support growth of microorganisms without extensive supplementation, the enzymatically formed peptone is an excellent nutrient medium for various bacteria (including *Escherichia coli*). Its use in a 1.7-L cultivation of *Leuconostoc gelidum* UAL-187 yielded 1.7 mg of [U-^{13}C]leucocin A.[12]

Since leucocin A aggregates in pure water, the NMR studies were performed in DMSO-d_6 (0.2% trifluoroacetic acid (TFA)) and in 90% water/10% DMSO (0.2% TFA, unlabeled sample only). Sequential assignments were achieved by ^{1}H spin system identification in 2D double-quantum-filtered (DQF) COSY[13] and 2D TOCSY[14] spectra which were linked with distance information taken from 2D NOESY[15] data, as first proposed by Wüthrich.[8a] Bleaching effects due to solvent suppression were clarified by recording spectra at different temperatures.[16] The high number of glycine residues and the unusual amino acid sequence, Asn-Gly-Gly-Asn-Gly (residues 31–35), cause extensive resonance overlap, especially in DMSO. To overcome these difficulties, information on interresidue NH–NH, $C_{\alpha}H$–NH, and $C_{\beta}H$–NH 2D NOE connectivities from NOESY spectra was also transferred back to the 2D TOCSY and DQF-COSY spectra to extend assignments in regions of overlap. This approach elucidated the complete ^{1}H NMR assignment of all 37 individual amino acids (Figure 1) in both solvents (supplementary material).

Assignments of resonances of carbons adjacent to protons were available via inverse 2D ^{13}C–^{1}H heteronuclear multiple quantum coherence (HMQC)[17] experiments measured in DMSO-d_6 (supplementary material). The [U-^{13}C]leucocin A from the *Anabaena*-derived peptone offers a considerable advantage in such measurements. For example, a 1 mM sample of the labeled leucocin gave excellent spectra in about 6.5 h using 32 scans per increment, whereas a much more concentrated solution (4 mM) of the corresponding unlabeled material produced a comparable signal to noise ratio in 52 h employing 256 scans per increment. All of the carbons could be identified in these spectra with the exception of the C_{α} atoms of both cysteines and the C_{β} resonance of threonine, which were not observable even with variation of acquisition parameters. Since the *Anabaena* cells can also be easily labeled with ^{15}N by the addition of sodium [^{15}N]nitrate,[9a] the corresponding peptone is readily available[18] for generation of isotopically substituted peptides or proteins for 3D NMR experiments. Differences in the chemical shift data of leucocin A and those determined for amino acids in random coil peptides[19] suggest a rigid conformation for residues near the disulfide bridge. Detailed studies on the three-dimensional solution structure of leucocin A and other bacteriocins are in progress.

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(12) A previously developed purification technique[7] for leucocin A was modified to a three-step procedure involving adsorption on Amberlite XAD-2 polystyrene resin, gel filtration on Sephadex LH-60, and reverse-phase HPLC. An unlabeled sample of leucocin A (8 mg) was prepared using unlabeled media described previously[7] and the new isolation protocol.
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Supplementary Material Available: Experimental procedures for production of ^{13}C-labeled peptone, fermentation and isolation of leucocin A, and acquisition of NMR data, as well as tables of ^{1}H and ^{13}C NMR assignments (11 pages). Ordering information is given on any current masthead page.

Intermolecular versus Intramolecular Hydrogen-Bonding Competition in the Complexation of Cyclitols by a Twisted Polyaza Cleft

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The complexation of monomers of biomacromolecules via hydrogen bonding and π-stacking is receiving increased attention.[1] Foremost are synthetic receptors for nucleotide bases.[2] In contrast, only a small number of hosts for monosaccharides have been developed,[3] even though practical applications for carbohydrate hosts are possible.[4] The parallel alignment or divergence of hydrogen bond donors and acceptors within nucleotide bases does not allow substantial intramolecular hydrogen bonding. Conversely, we find that the ability to form intramolecular hydrogen bonds within carbohydrate analogues (cyclitols) dominates the selectivity and strength of binding to polyaza cleft **1**.

Key steps in the synthetic pathway to **1**[5] (Scheme I) are as follows: (a) formylation of the aldol product[6] **3** with *N*,*N*-dimethylformamide dimethyl acetal,[7] (b) protection of ethyl 3,3-diaminopropenoate[8] with 3,4-dimethoxybenzyl (**4**), (c) enamine formation from **5** using trimethylsilylpyrrolidine,[9] (d) vacuum flash pyrolysis addition of ethyl glyoxylate[10] to **6**, and (e) after central pyridine formation,[11] deprotection of the amines with CF_3CO_2H.[12]

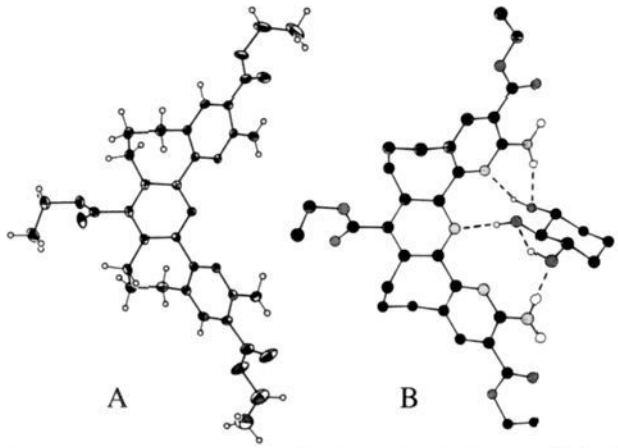


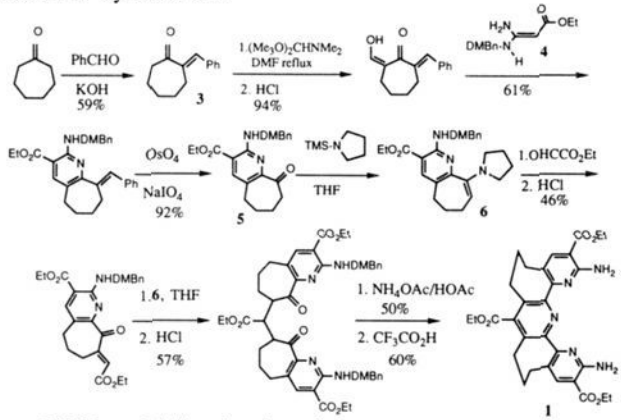
Figure 1. (A) Crystal structure of **1**. (B) Molecular dynamics derived structure for the complexation of 1,3/2-cyclohexanetriol by **1**.

Table I. Binding Constants (M^{-1})[a]

	host	
guest	**1**	**2**
cis 1,2-diol	12[a]	--
trans 1,2-diol	18[a]	2[c]
1,3/2-triol	110[b]	35[b]
1,2/3-triol	47[b]	12[a]
1,2,3-triol	39[b]	14[a]

[a] Error estimated from the percent saturation achieved is (a) 15%, (b) 10%, and (c) 100%.

Scheme I. Synthesis of **1**[a]



[a] DMBn = 3,4-dimethoxybenzyl.

Host **1** is twisted in the solid state[13] with a dihedral angle between the peripheral pyridines of 79.8° (Figure 1A). This twist opens up the cavity and allows the complexation of nonplanar substrates such as cyclitols. Figure 1B displays the dominant

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