control of *relative* stereochemistry are rare.[16]

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Supplementary Material Available: Experimental data for **5**, **10**, **11**, **12**, **17**, **18**, **20**, *d,l*-methynolide, and *d,l*-10-*epi*-methynolide (4 pages). Ordering information can be found on any current masthead page.

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Helical Ferric Ion Binders

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Ditopic metal ion binders[1,2] are of interest for the study of cooperative and allosteric effects that are crucial in enzyme regulation and related processes.[3,4] It occurred to us that triple-stranded helices could be promising structures for such studies as they may accommodate binding cavities of varying proximity in their inner space, are extendable, and may exhibit chiral recognition.[5] However, in order to generate helical conformations in tripodlike molecules, random coiling of the chains has to be avoided, possibly by noncovalent interstrand linkages.[6] In this communication we describe the first triple-stranded helices that incorporate two metal ions and are stabilized by interstrand hydrogen bonds (H bonds). These H bonds may be modulated to generate diastereomeric helices of either right- or left-handedness. The molecules are assembled from tris(2-aminoethyl)amine as an anchor, extended by L-leucine, and elongated by an alternating sequence of hydroxamate and amide groups as ligands and H bonding units, respectively. When loaded with Fe^{3+} ions, the presence of chiral amino acids and hydroxamate chromophores as probes allows the determination of the absolute configuration around each metal ion and thereby the helicity of the overall structure.

The syntheses of the monotopic binder **3** and of the ditopic binders **5** and **7** were achieved by Scheme I outlined below.[7] First, the conformation and ion-binding properties of the monotopic binder **3** were examined. The IR of **3a** shows bonded NH centered around 3310 cm^{-1} (1.8 mM, CDCl$_3$), and its NMR spectrum reveals nonequivalence of the diastereotopic $\mathrm{NCH_2C}H_2\mathrm{NH}$ protons in CDCl$_3$ ($\Delta\delta = 0.53$ ppm) and to a smaller extent in CD$_3$OD ($\Delta\delta = 0.17$ ppm). The single stranded n-PrNHCOCH(i-Bu)NHCOCH$_2$CH$_2$N(OBz)COC$_6$H$_4$OCH$_3$ shows free NH absorptions at 3430 cm^{-1} in the IR and minor nonequivalence of its diastereotopic protons in CDCl$_3$ ($\Delta\delta < 0.05$ ppm) that collapsed in CD$_3$OD. This establishes restricted conformational freedom in **3a** caused by interchain H bonds.[8] The IR of the Fe^{3+} complex, **3b-Fe**,[9] shows similarly bonded NH (3285 cm^{-1} in 4 mM CDCl$_3$),

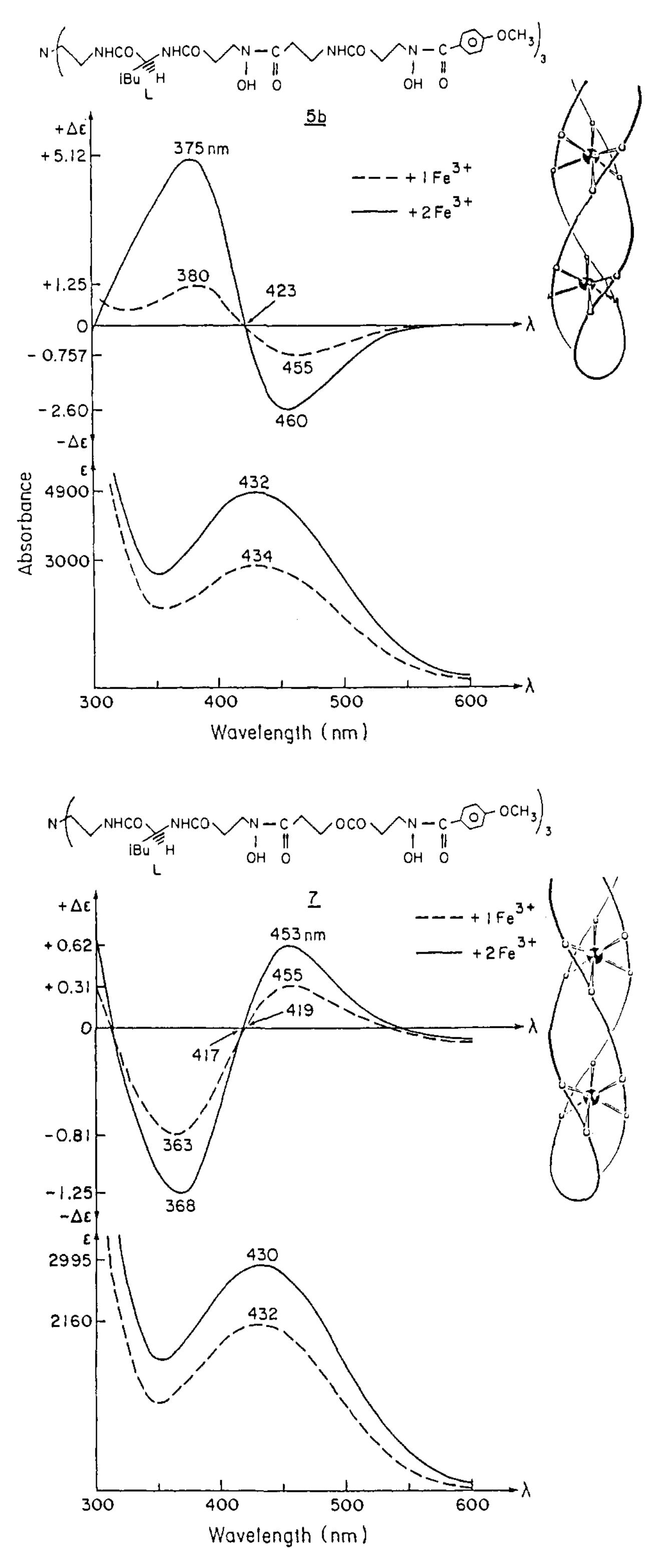

Figure 1. CD and UV spectra of **5b-Fe** (0.16 mM), **5b-2Fe** (0.16 mM), **7-Fe** (0.15 mM), and **7-2Fe** (0.15 mM) in CDCl$_3$.

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(7) The linear carboxylates **2**, **4**, and **3** were prepared by a series of condensation reactions involving 2-(hydroxylamino)propionic acid, 2-aminopropionic acid, and 4-methoxybenzoic acid. The detailed reaction procedures will be given in a full account of this work.

(8) The reliability of spectrometric IR/NMR analyses in identifying such interchain H bonds has recently bee described (ref 6).

(9) All spectroscopic data for the Fe^{3+} complexes in CDCl$_3$ were obtained with isolated, TLC purified complexes.

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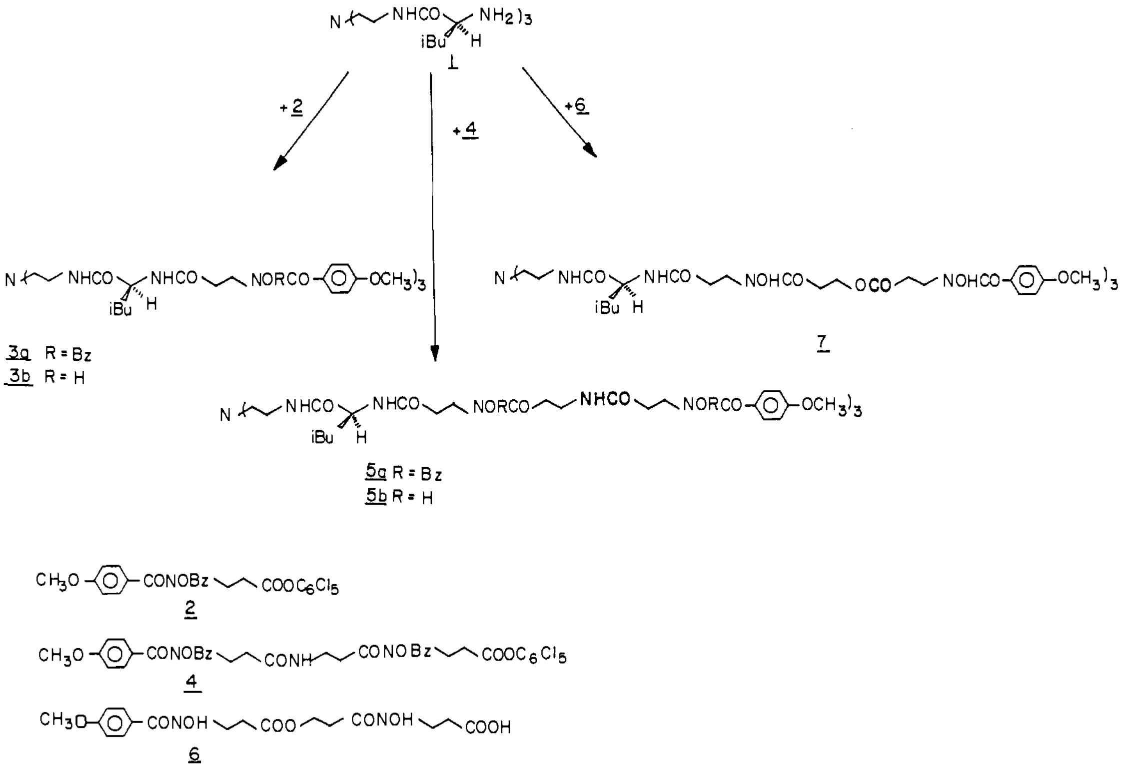
Scheme I



and its CD (0.29 mM in $CDCl_3$) reveals Cotton effects at 450 nm ($\Delta\epsilon$ = +2.4) and at 345 nm ($\Delta\epsilon$ = −3.64). This indicates predominance of the Λ-cis configuration[10] which is stabilized by H bonds.

Extension of **3** with a second set of alternating amide and hydroxamate groups yielded **5a** which also has interchain H bonds according to its IR (NH absorptions around 3300 cm^{-1}, 1.6 mM $CDCl_3$) and NMR spectra ($\Delta\delta$ = 0.39 ppm in $CDCl_3$ and $\Delta\delta$ = 0.15 ppm in CD_3OD for the diastereotopic NCH_2CH_2 protons). The absolute signs of the Cotton effects of the diferric complex **5b-2Fe** are identical with those of the monoferric complex **5b-Fe** but almost fourfold in intensity (Figure 1). This establishes identical configuration around each guest ion, Δ-cis according to the aboslute signs, and ultimately implies the presence of a right-handed helical structure. The configurations of the Fe^{3+} complexes of **5b** are thus opposite to those of the Fe^{3+} complex of **3b**. Molecular models of **5b-2Fe** point toward H bonds between the peripheral amide–NH of one strand and the central amide–CO of the adjacent strand that inverts the directionality of the remaining H bonds and thereby the preferred handedness of the Fe^{3+} complexes. The bonded NH frequencies of the isolated **5b-Fe** (3285 cm^{-1} in 1.2 mM $CDCl_3$) and **5b-2Fe** (3310 cm^{-1} in 1.2 mM $CDCl_3$) and their diminished Cotton effects in protic MeOH ($\Delta\epsilon$ = +0.60 at 374 nm for **5b-Fe**, and $\Delta\epsilon$ = −0.60 at 470 nm and $\Delta\epsilon$ = +1.90 at 390 nm for **5b-2Fe**) relative to aprotic $CDCl_3$ (Figure 1) strongly support this possibility.

In order to obtain further evidence for the role of the peripheral H bonds ditopic binder **7**, where the peripheral amides had been replaced by ester groups, was synthesized and examined. Binder **7** has its remaining amides H bonded in $CDCl_3$, as shown by its low NH frequencies (around 3275 cm^{-1} in 5 mM $CDCl_3$) and its NMR pattern. The signs of the Cotton effects of the diferric complex **7-2Fe** are identical with those of the monoferric complex **7-Fe** but twice in intensity (Figure 1). This demonstrates identical configuration for both complexes, Λ-cis according to the absolute signs, and the formation of a left-handed helix. The complexes of ester **7** thus adopt a configuration opposite to those of amide **5b** but identical with that of the monotopic binder 3b, indicating restoration of the original H bond pattern in **3**.

The generation of diastereomeric helical metal complexes of either right- or left-handedness by using the very same amino acid as a chiral constituent demonstrates the governing role of H bonds in shaping these arrangements. To which extent the nature of these H bonds may modulate the height of the pitch and thereby the proximity of the metal ions is under current investigation, as is the expansion of these systems to generate artificial ion channels.

Acknowledgment. We thank Prof. S. Lifson for fruitful discussions, R. Lazar for her devoted technical assistance, and the Minerva Foundation for support of this project.

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Electrochemical Formation of an Organic Thin Film by Disruption of Micelles

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The preparation of organic thin films has attracted considerable interest in recent years in view of their potential applications to microelectronics, optics, etc.[1] Various methods for preparing organic thin films have been presented.[2-4]

Recently, we demonstrated that a micelle formed by surfactants having a ferrocenyl moiety can be broken up into monomers when the surfactants are oxidized chemically or electrochemically and that a solubilizate is released from the micelles as the micelles

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