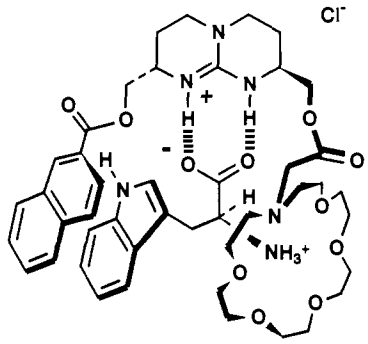

**Figure 1.** Proposed structure for a 1:1 complex between (*S,S*)-**1** and L-tryptophan.

chloride (1.7 equiv, DMF, $Et_3N$) afforded the monosubstituted naphthoyl ester **3**[10] in 50% yield. Reaction of **3** with bromoacetic acid (1,3-dicyclohexylcarbodiimide, $CH_2Cl_2$) gave **4** (82%), which upon reaction with monoazacrown ether **5**[11] ($CH_2Cl_2$, reflux, 4 days) afforded **1** in 87% yield.[12]

Despite its ionic structure, receptor **1** is scarcely soluble in water, but almost freely soluble in common organic solvents. The affinity of **1** toward amino acids was therefore determined by liquid–liquid single-extraction experiments, in which 0.5 mL of an aqueous solution of L-Trp, L-Phe, or L-Val (0.2 M) was extracted into 2 mL of a $CH_2Cl_2$ solution of **1** ($5.5 \times 10^{-3}$ M). The extraction efficiencies (i.e., fraction of receptor molecules occupied by substrate) in the organic phase, determined by NMR integration, were ca. 40% for L-Trp and L-Phe, but L-Val, without any aromatic side chain, was not detected.[13] A competition experiment with a mixture of all three amino acids (0.2 M each) resulted in 100:97:6 Phe/Trp/Val ratios.[14] The results of the extraction of a 2-mL aqueous solution of a more complex mixture of 13 amino acids ($4.9 \times 10^{-2}$ M each) by a 3-mL $CH_2Cl_2$ solution of receptor **1** ($9.7 \times 10^{-3}$ M) are shown in Table I.[15] In this case, selectivity for phenylalanine was enhanced, and some lipophilic substrates, like leucine, were also extracted to a significant extent.

Chiral recognition was confirmed by the observation (NMR) that the corresponding D-enantiomers were not extracted. Reciprocally, use of (*R,R*)-**1** allowed the extraction of D-Phe or D-Trp, but not of the L-enantiomers. A more precise account of the selectivity was achieved by HPLC analysis of diastereomeric dipeptides prepared from extracts of racemic samples of Phe or Trp and a suitable optically pure L-Leu derivative.[16] The amount of D-isomer in the extracts was lower than 0.5% for D-Trp (determined as L-Leu-D-Trp) and 2% or less for D-Phe (as L-Leu-D-Phe). This high degree of chiral recognition can be explained by the three simultaneous[2c] noncovalent interactions of the substrate with the flexible and foldable receptor. $^1$H-NMR data (upfield shifts for the naphthoyl protons) support the binding model illustrated in Figure 1 for a 1:1 complex of (*S,S*)-**1** with L-Trp. No similar model can be assembled (CPK) for the D-enantiomer.[17]

Full NMR studies of the complexes, and development of related amino acid receptors with enhanced side-chain recognition features, are currently underway.

**Supplementary Material Available:** NMR data for new compounds and details for the amino acid analyses (3 pages). Ordering information is given on any current masthead page.

(17) With the data available, the more hindered 2:1 complexes could not be ruled out, however.

## Structural and Spectroscopic Characterization of Chiral Ferric Tris-Catecholamides: Unraveling the Design of Enterobactin

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Enterobactin, a siderophore of *Escherichia coli*, is remarkable not only in forming the most stable known complex of iron[1] but also in preferentially forming a specific tris-chelate isomer with labile metal ions.[2] Efficient iron accumulation, including recognition at the cell receptor,[3] depends on these features. Furthermore, the Δ conformation assigned to [Fe(enterobactin)]$^{3-}$ ($\mathbf{Ent}_{Fe}$)[4] is unusual among siderophores.[5,6] The source of stereospecific chelation has been ascribed to nonbonded interactions rather than steric strain within the chiral backbone.[7] Similar interactions between peripheral appendages in tris-bidentate metal chelates have been identified as important energetic contributors to the diastereomeric distributions[8,9] and the thermodynamic stability[10] of kinetically labile metal complexes. The role of these weakly polar interactions,[11] especially between aromatic groups packed in a herringbone fashion, has only recently been appreciated in stabilizing protein structures and metal complexes.[12] Moreover, ligands incorporating aromatic rings which stereospecifically ligate labile metals have potential application in asymmetric induction in organic transformations.[13] A group of ferric and gallium complexes have been synthesized and structurally characterized that provide insights into enterobactin's

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(12) All new compounds were characterized by a full complement of high-resolution spectra.
(13) No Phe and Trp extraction was observed when the dinaphthoyl guanidinium derivative was employed as receptor.
(14) For the analysis of amino acid mixtures the organic layer was washed twice with water and the aqueous solution evaporated. The resulting amino acid extract was dissolved in 1 mL of buffer (Beckman Na-S) and determined in a Beckman 6300 analyzer (ion-exchange column, postcolumn ninhydrin reaction).
(15) For the 13-amino acid mixture, a 50-μL aliquot was first injected to determine residues present at low concentrations. The sample was next diluted 1:10 for more accurate analysis of residues at higher concentration (Leu, Phe, Trp).
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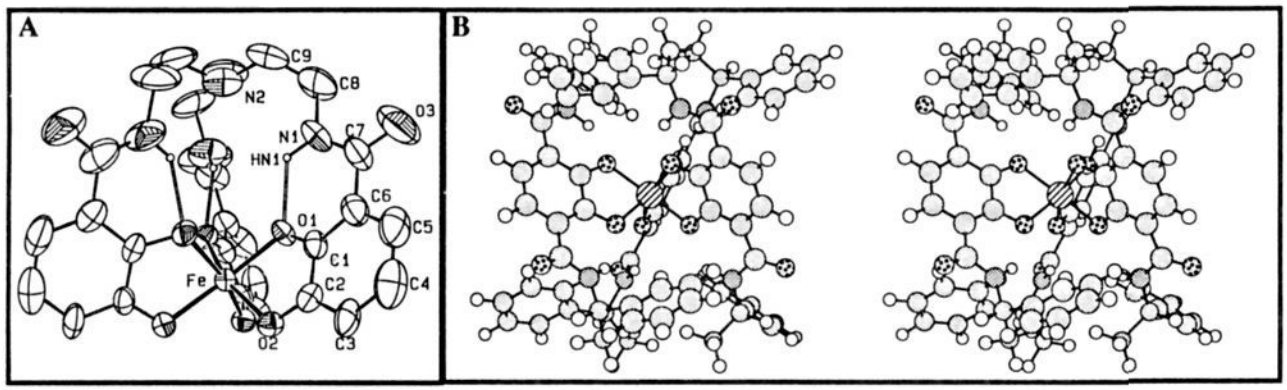
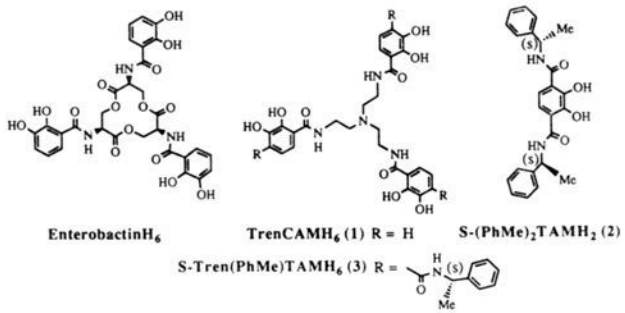



**Figure 1.** (A) Structure of the complete anion of $\mathbf{1}_{Fe}$. Selected structural parameters (Å, deg): Fe–O1, 1.990 (6); Fe–O2, 2.028 (7); O1–Fe–O2, 79.5 (3); HN1–O1, 1.951. Twist angle 37.4, Δ chirality. (B) Stereoview of the complete anion of $\mathbf{2}_{Fe}$. Selected structural parameters (Å, deg): Fe–O1, 2.020 (5); Fe–O2, 1.999 (6); O1–Fe–O2, 79.8 (2); HN1–O1, 1.797; HN2–O2, 1.853. Twist angle 41.5, Λ chirality.

**Scheme I**




stereospecificity and metal coordination geometry and allow a definitive assignment of the stereochemistry in $\mathbf{Ent}_{Fe}$.

The ligands TrenCAMH$_6$ (**1**)[14] and (*S*)-(PhMe)$_2$TAMH$_2$ (**2**) are shown in Scheme I.[15] Crystal structures of [Fe(TrenCAM)]$^{3-}$ ($\mathbf{1}_{Fe}$) and [Fe((*S*)-(PhMe)$_2$TAM)$_3$]$^{3-}$ ($\mathbf{2}_{Fe}$) (parts A and B, respectively, of Figure 1) display the desired tris-chelated coordination. The dearth of precise structural data of ferric exocyclic catecholate complexes is striking in light of their physiological importance: $\mathbf{1}_{Fe}$ is the first structurally characterized ferric complex with a ligand topology similar to that of enterobactin.[16] Both compounds crystallize in acentric, cubic space groups with crystallographically imposed 3-fold symmetry of the anions.[17] In the structure solution of $\mathbf{2}_{Fe}$, the chirality of the methine carbon (*S*) allows unambiguous assignment of the Λ configuration at the metal, while in the structure solution of $\mathbf{1}_{Fe}$, refinements of both crystal enantiomers support the Δ form.[18] Except for the slightly smaller twist angles of 41.5° ($\mathbf{2}_{Fe}$) and 37.4° ($\mathbf{1}_{Fe}$), these coordination geometries are consistent with known ferric catecholate structures.[19] The lesser twist of $\mathbf{1}_{Fe}$, as well as other metrical parameters,[20] suggest that the tren cap is restrictive to tris-catecholamide coordination. This could account in part for the $10^6$ difference (ca. 8 kcal/mol) in stability as compared to $\mathbf{Ent}_{Fe}$.[21] Both structures show inward positioning of the amide protons, which interact strongly with the *o*-hydroxy oxygens,[22] a positioning highly conserved in all metal complexes of this ligand class.[16,21]

The lability of d$^5$ ferric complexes in aqueous environments normally precludes optical resolution.[23] Attempts to resolve $\mathbf{1}_{Fe}$ in solution have been unsuccessful. Ligand chirality, however, can induce a preference between the Δ and Λ diastereomers as found for $\mathbf{Ent}_{Fe}$. The CD activity in the LMCT absorption (~540 nm) of both $\mathbf{2}_{Fe}$ and $\mathbf{3}_{Fe}$ (**3** has half of the chiral appendages of **2**, arranged in an all-cis fashion; see Scheme I) indicates that a chiral preference is retained in solution, with that of $\mathbf{2}_{Fe}$ nearly equivalent to that of $\mathbf{Ent}_{Fe}$ and more than twice that of $\mathbf{3}_{Fe}$.[24] Comparison of the CD spectrum of $\mathbf{2}_{Fe}$ in solution and in the solid state[25] with the CD spectrum of $\mathbf{Ent}_{Fe}$, in addition to the crystal structure of $\mathbf{2}_{Fe}$, allows definitive assignment of the Δ isomer for $\mathbf{Ent}_{Fe}$. Quantification of the Λ:Δ ratios of $\mathbf{2}_{Fe}$ and $\mathbf{3}_{Fe}$ is, however, not reliable with CD spectroscopy.[26] The gallium complexes [Ga((*S*)-(PhMe)$_2$TAM)$_3$]$^{3-}$ ($\mathbf{2}_{Ga}$) and [Ga((*S*)-Tren(PhMe)-TAM)]$^{3-}$ ($\mathbf{3}_{Ga}$) have therefore been synthesized to determine the ratio by $^1$H NMR.[27,28] In aqueous solution, $\mathbf{2}_{Ga}$ exists as a *single* isomer, as is found for $\mathbf{Ent}_{Ga}$;[29] the Λ:Δ ratio of $\mathbf{3}_{Ga}$ is found to be 85:15. These ratios correspond to a stabilization of the Λ isomer of $\mathbf{2}_{Ga}$ of more than twice that of $\mathbf{3}_{Ga}$ (2.8 kcal/mol vs 1.0 kcal/mol; 300 K), a result consistent with the CD data of $\mathbf{2}_{Fe}$ and $\mathbf{3}_{Fe}$. This nonlinear increase in stereoselective stabilization from $\mathbf{3}_{Fe}$ to $\mathbf{2}_{Fe}$ is indicative of cooperativity between the top and lower chiral appendages in $\mathbf{2}_{Fe}$. The isomeric preference and cooperativity of these metal complexes can be rationalized through the interactions present in the solid-state structure of $\mathbf{2}_{Fe}$ and easily visualized in Figure 1B. The preferred trans configuration of an amide proton to a methine proton in conjunction with the amide hydrogen bonding promotes the interactions among adjacent chiral groups by directing them inward. Favorable aryl/aryl and methyl/aryl interactions result upon stereospecific chelation; these are reduced

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(19) The twist angle is defined by the $O_1$–M–$O_2$ angle of a single catecholate ligand projected onto the plane perpendicular to the idealized 3-fold axis.

(20) Most notable is the abnormal positioning of the amide hydrogen bond.

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(24) CD data, λ (nm), Δε ($M^{-1}$ $cm^{-1}$) ($H_2O$, pH > 8.0): $\mathbf{Ent}_{Fe}$, 530, −4.0; $\mathbf{2}_{Fe}$, 541, +3.8; $\mathbf{3}_{Fe}$, 536, +1.5.

(25) As a KBr pellet of pulverized X-ray quality crystals; λ = 541 nm, CD sign is positive (Δε not determined).

(26) Small variations in the LMCT bands among the complexes can cause variations in the Δε values and hence significant changes in the estimate of the minor isomer when the ratio is far from unity, since this is a difference measurement.

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upon isomerization. Moreover, the cooperativity operative in $\mathbf{2}_{Fe}$ results from the chiral interactions of one trigonal face predisposing the other toward assembling in an analogous fashion, thus enhancing the same metal chirality.

These results show that the amide proton is an important feature in the stability of metal complexes of enterobactin. The solid- and solution-state CD spectra of $\mathbf{2}_{Fe}$ in combination with the crystal structure of $\mathbf{2}_{Fe}$ confirm the $\Delta$ chirality for $\mathbf{Ent}_{Fe}$. Most importantly, we have shown that, in an aqueous environment, complexes of labile metals of defined stereospecificity can be synthesized using simple bidentate ligands, relying solely on weakly polar interactions. Interactions peripheral to the immediate metal coordination environment measurably impact the selectivity and stability of metal complexes, suggesting new avenues in the design of stereospecific metal chelators.

**Acknowledgment**. This research was supported by National Institutes of Health Grant AI 11744. T.D.P.S. thanks the NSF for a postdoctoral fellowship (1988-1990, CHE-8809111).

**Supplementary Material Available:** Synthetic details and tables of atomic coordinates and thermal parameters for $[Fe(S\text{-}(PhMe)_2TAM)_3](Me_4N)_3$ and $[Fe(TrenCAM)]K_3$ (5 pages). Ordering information is given on any current masthead page.

## A New Class of Organized Self-Assembled Monolayers: Alkane Thiols on GaAs (100)

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Self-assembled monolayers (SAMs) have been of intense interest in the past few years, but actual examples of highly organized films[2] are limited almost exclusively to those formed on oxide and coinage metal substrates, as shown by the major systems of alkylsiloxanes on natively oxidized $SiO_2$,[3] *n*-alkanoic acids on natively oxidized Al[4] and Ag,[5] dialkyl disulfides,[6] dialkyl sulfides,[7] and alkanethiols on Au,[8] and alkanethiols on natively oxidized Ag.[9] Since a key potential application of SAMs is in chemically

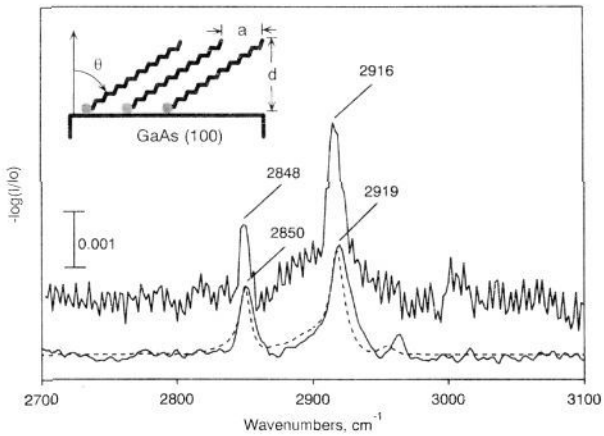


**Figure 1.** Infrared spectra of the C-H stretching modes for a self-assembled monolayer of ODT formed on both sides of a GaAs wafer with a (100) surface orientation. The lower plot is a transmission spectrum (solid line) and a simulation (dashed line) for an average single-chain structure with a chain tilt of 57° and a twist of 45°. The upper plot is the reflection spectrum taken at a 55° angle of incidence with a p-polarized beam. The intensity scales are in absorbance units for transmitted and reflected power, respectively, ratioed against a film-free sample. The inset at the upper left shows a schematic representation of a self-assembled monolayer of ODT on GaAs (100). The thickness ($d$), chain spacing ($a$), and chain tilt angle ($\theta$) dimensions are shown. The balls at the surface represent sulfur.

specific electrochemical and electronic devices, as demonstrated by the intense interest in applying the thiol/Au system to modified electrodes and sensors,[8a,b,10] it is notable that no examples of organized SAMs *bonded directly* to a bare semiconductor substrate surface have been reported. We now report the discovery of a new class of organized monolayers derived from the self-assembly of alkanethiols directly onto the bare GaAs (100) surface. That viable S/GaAs chemistry might exist to allow self-assembly has been indicated by current studies which show that room temperature coverage of GaAs by deposits of inorganic sulfide salts,[11] $P_2S_5$,[12] and simple organothiol compounds (six carbons or less)[13] exerts significant effects on electron-hole pair recombination velocities. We have produced SAMs from alkanethiols, $X(CH_2)_nSH$ for $X = CH_3$ with $n = 11$-$21$ and $X = CO_2H$ and $CO_2CH_3$ with $n = 15$. The bulk of our characterization has been on octadecanethiol (ODT, $X = CH_3$, and $n = 17$), and for brevity we focus on these results which show that the monolayer consists of a stable, highly organized assembly of tilted, conformationally ordered alkyl chains, chemically bonded directly to the bare GaAs surface.

Semiinsulating (dopant density $10^{15}$ cm$^{-3}$) *n*-type GaAs single crystals of (100) orientation and polished on two sides (Macom Co., Boston, MA) were washed with pure ethanol and exposed to UV light and ozone to remove trace organics.[14] The native

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