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Synthesis, Characterization, and Photobehavior of Δ- and Λ-*fac*-Tris((*S*)-tryptophanato)chromium(III)

Noel A. P. Kane-Maguire,* T. W. Hanks,* Dennis G. Jurs, Ronald M. Tollison, Ann L. Heatherington, Laurel M. Ritzenthaler, Luanne M. McNulty, and Hugh M. Wilson

Department of Chemistry, Furman University, Greenville, South Carolina 29613

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The complexes Δ-*fac*-Cr(*S*-trp)$_3$ and Λ-*fac*-Cr(*S*-trp)$_3$ (where *S*-trp is the unsymmetric bidentate ligand (*S*)-tryptophanato) have been prepared by heating [Cr(en)$_3$]Cl$_3$ with excess *S*-trpH in water or dimethyl sulfoxide (DMSO) solution. The two diastereoisomeric species are separated by extracting the initial solid product with acetone, in which only Δ-*fac*-Cr(*S*-trp)$_3$ is soluble. Geometric isomer identifications are made from an analysis of uv−visible spectral data and indicate isolation of just the *facial* isomer. Optical isomer assignments are based on circular dichroism (CD) measurements. Photochemical studies in DMSO solution reveal that on ligand-field (d−d) excitation at 488 nm the Δ-*fac*-Cr(*S*-trp)$_3$ isomer is essentially photoinert, while the Λ-*fac*-Cr(*S*-trp)$_3$ isomer undergoes complete conversion to Δ-*fac*-Cr(*S*-trp)$_3$ with a quantum yield of 0.03. Complete photoinversion demonstrates a key stereochemical role for the asymmetric C of (*S*)-tryptophan. The observation of the same inversion process thermally (at elevated temperatures) indicates that the Δ-*fac*-Cr(*S*-trp)$_3$ diastereoisomer has a considerably higher stability than that of the Λ species. This conclusion is in accord with molecular mechanics calculations, which estimate the Δ diastereoisomer to be more stable by 7 kcal mol^{-1}. The observation of optical inversion without *fac* → *mer* geometric isomerism is suggestive of a Bailar trigonal twist mechanism and may constitute the first example of a photoinduced Bailar twist. Using X-ray crystallographic data available for the glycine analog, a normalized chelate bite value of 1.31 is estimated for the *fac*-Cr(*S*-trp)$_3$ system. Consistent with our experimental data, recent theoretical studies by Rodger and Johnson conclude that a Bailar twist will be energetically preferred over a Ray and Dutt twist for bite values less than 1.4.

Introduction

The pathways of intramolecular rearrangements remain an elusive problem in mechanistic inorganic chemistry.[1−12] Experimental distinctions between various twist and one-bond rupture mechanisms might in principle be obtained by employing tris-chelate complexes of the type M(A−B)$_3$, which contain three unsymmetrical bidentate ligands, A−B. Such species can exist as *meridional* and *facial* geometric isomers, as well as exhibiting optical isomerism. Studies of thermal and photochemical intramolecular processes involving unsymmetrical β-diketone and tropolone complexes have been especially popular, and in several cases experimental evidence argues for a twist pathway.[3,4,6−8]

The application of **tris(α-amino acidate (AA)) complexes** in such mechanistic studies (where the ligand is an unsymmetric N−O type bidentate) is presently restricted to one early report by Denning and Piper[2] on Co(III) complexes with (*S*)-proline and (*S*)-leucine. For several known Co(III) and Rh(III) systems,[13] the facial and meridional isomers have distinguishable uv−visible spectra—an attractive feature lacking in the tris(β-diketone) species. Similar differences are anticipated for analogous Cr(III) complexes. However, to date relatively few tris(α-amino acidate) Cr(III) systems have been fully characterized,[14−16] and to our knowledge no photochemical investigations have been reported. We have therefore initiated a program directed at examining the thermal and photochemical behavior of such Cr(III) systems. In this report we describe the synthesis, characterization, and photobehavior of the two diastereoisomeric species Δ-*fac*-Cr(*S*-trp)$_3$ and Λ-*fac*-Cr(*S*-trp)$_3$ (where *S*-trp is (*S*)-tryptophanato).

Experimental Section

Instrumentation. Electronic absorption spectra were recorded on a HP8452A diode array spectrophotometer. Optical rotation data were obtained using a Perkin-Elmer MC 241 polarimeter, while a JASCO 710 spectropolarimeter was employed for circular dichroism (CD) measurements. An argon ion laser (Spectra-Physics Stabilite 2016) and a Rayonet RPR-100 photochemical reactor were employed for 488- and 350-nm irradiations, respectively. Conductance measurements were determined using a Markson Electromark analyzer (Model 4403).

Materials. The free ligand (*S*)-tryptophan was used as obtained from Fisher Scientific. The complex [Cr(en)$_3$]Cl$_3$·3H$_2$O was prepared by the method of Gillard and Mitchell,[17] except that dimethylformamide rather than methanol was employed as solvent. All elemental analyses (C, H, N) were performed by Midwest Microlab.

Synthesis of *fac*-Tris(*S*)-tryptophanato)chromium(III). Method 1 (Water Solvent). A 0.6 g (1.9 × 10^{-3} mol) sample of [Cr(en)$_3$]-

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$Cl_3 \cdot 3H_2O$ was added with stirring to a hot suspension of 2.0 g (9.6×10^{-3} mol) of (*S*)-tryptophan in 30 mL of water. After several minutes of stirring at 80–90 °C, precipitation of red-violet *fac*-Cr(*S*-trp)$_3$ began. After heating was continued for 25 min, the reaction mixture was filtered hot to remove solid product, which was then washed with 200 mL of hot water (to remove some contamination with free tryptophan) and sucked dry. A separation of the *fac*-Cr(*S*-trp)$_3$ product into its Λ and Δ stereoisomers was effected by stirring the material with 50 mL of acetone and filtering. The acetone-insoluble fraction, (+)$_{546}$-*fac*-Cr(*S*-trp)$_3$ (Λ-isomer—see later), was washed with a further 25 mL of acetone and sucked dry (0.60 g, 48%). Anal. Calcd for Cr-$(C_{11}H_{11}N_2O_2)_3 \cdot 2H_2O$: C, 56.80; H, 5.35; N, 12.04. Found: C, 56.66; H, 5.10; N, 11.82. The acetone-soluble fraction, (−)$_{546}$-*fac*-Cr(*S*-trp)$_3$ (the Δ isomer), was precipitated from the deep red 50-mL acetone extract by adding 400 mL of ether and then suction-filtered (0.20 g, 16%). Anal. Calcd for $Cr(C_{11}H_{11}N_2O_2)_3 \cdot 2H_2O$: C, 56.80; H, 5.35; N, 12.04. Found: C, 56.50; H, 5.08; N, 11.89.

Method 2 (Dimethyl Sulfoxide Solvent). When the reaction is carried out under identical conditions except for the replacement of H_2O by DMSO, the reaction product remains in solution. Subsequent addition of excess water (200–400 mL) results in the isolation of solid *fac*-Cr(*S*-trp)$_3$, almost exclusively as the (−)$_{546}$ isomer, Δ-*fac*-Cr(*S*-trp)$_3$.

Quantum Yield Calculations. The quantum yield for photoinversion of Λ-(+)$_{546}$-*fac*-Cr(*S*-trp)$_3$ to Δ-(−)$_{546}$-*fac*-Cr(*S*-trp)$_3$ in dimethyl sulfoxide (DMSO) solution was determined as follows. Absorbance-matched solutions ($A_{488} = 1.10$, 5-cm cell) of (−)$_D$-$Cr(en)_3^{3+}$ and Λ-(+)$_{546}$-*fac*-Cr(*S*-trp)$_3$ were irradiated at 488 nm for 11 min (complex concentrations of 5.50×10^{-3} and 2.32×10^{-3} M, respectively). The observed percent reaction for these two solutions was determined from the optical rotation changes at 336 nm. Using a value of 0.44 for the quantum yield for the loss of optical activity of (−)$_D$-$Cr(en)_3^{3+}$,[18] the quantum yield for Λ-*fac*-Cr(*S*-trp)$_3$ photoinversion could then be calculated.

Theoretical Calculations. Molecular mechanics calculations on Λ-(+)$_{546}$-*fac*-Cr(*S*-trp)$_3$ and Δ-(−)$_{546}$-*fac*-Cr(*S*-trp)$_3$ were carried out on an Apple Macintosh Ci equipped with a Tektronix Corp. CAChe modeling engine. Standard Allinger MM2/MMP2 parameters[19] were used where available. These were augmented by algorithms within the CAChe molecular mechanics package which estimate force field parameters not treated by Allinger.[20] Ligands were arranged about the chromium in an octahedral geometry with initial Cr–N and Cr–O bond lengths taken from the X-ray crystal coordinates for *fac*-tris(glycinato)-chromium(III).[14] An initial optimization of the structure was performed using the conjugate gradient method; no symmetry constraints were placed on the structure.

The only freely rotating portions of the molecule are the carbon–carbon bonds of the tryptophan methylene linkage. To search for the global minimum, a crude potential energy surface was generated by driving the six dihedral angles (in 15° increments) involved in the three linkages and calculating the energy, without geometry optimization, at each point. Starting from the lowest energy conformer, the dihedral angles were sequentially driven (in 15° increments) with full geometry optimization using the conjugate gradient method at each step. The lowest energy conformation at each dihedral was held constant while the subsequent dihedrals were driven. The four lowest energy structures from this procedure were then minimized using the block-diagonal Newton–Ralphson technique, and the lowest energy structure obtained was used for comparison to the other isomers.

Results and Discussion

Synthesis. The synthetic procedure involved heating an aqueous or DMSO solution of $Cr(en)_3^{3+}$ with excess (*S*)-tryptophan. Subsequent extraction with acetone separated the product into acetone-soluble and -insoluble fractions (a similar separation is achieved with ethanol). Microanalyses and conductance measurements in DMSO are consistent with the isolation of isomers of Cr(*S*-trp)$_3$.

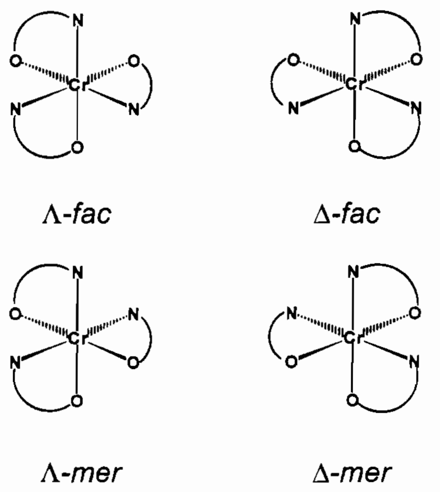
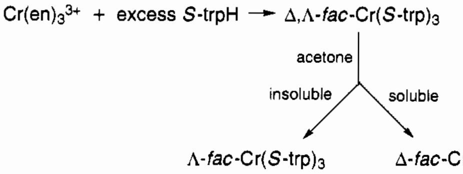
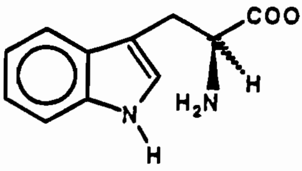


Figure 1. The four isomers of Cr(AA)$_3$ systems.



The asymmetric center in (*S*)-tryptophan accounts for the unusual ease of separation of these stereoisomers, since Λ- and Δ-*fac*-Cr(*S*-trp)$_3$ are diastereoisomers rather than enantiomers. Both isomers are soluble in aprotic solvents, and our solution studies have been carried out primarily in DMSO. The isomeric assignments above are based on UV–visible and CD studies described below.

Isomeric Assignments. The neutrality of the Cr(*S*-trp)$_3$ products is consistent with (*S*)-tryptophan binding as a bidentate ligand in the deprotonated form:



Unsymmetric metal binding occurs via the lone pairs on the amine N and the carboxylic O, and as a result two geometric isomers (*facial* and *meridional*) are possible for the tris-bidentate Cr(*S*-trp)$_3$ species. In addition, each of these can exist in two optical forms—namely the Δ and Λ absolute configurations (see Figure 1). Geometric isomer identifications have been made from an analysis of UV–visible spectral data, while optical isomer (absolute configuration) assignments have been based on CD studies.

Analogous Cr(III) and Co(III) complexes often have similar UV–visible absorption spectra associated with their **ligand-field (d–d) transitions.** For many Co(AA)$_3$ complexes all possible isomers have been isolated and spectrally characterized.[13] For the *facial* and *meridional* isomers their two d–d absorption bands have reverse intensities, and the longer wavelength absorption is broader in the *meridional* case. From the sole X-ray crystallographic study on a Cr(AA)$_3$ system,[14]

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Table 1. Absorption and CD Data for Cr(*S*-trp)$_3$ in DMSO

	λ, nm (ϵ)	
	abs	CD
Λ-*fac*	518 (143); 392 (111)	570 (−0.64); 504 (+2.35); 391 (−0.93)
Δ-*fac*	515 (90); 387 (81)	492 (−1.30); 386 (+0.11)

Cr(gly)$_3$ was found to be the *facial* isomer, and its UV−visible spectrum matches closely that for *fac*-Co(gly)$_3$. Absorption maxima and associated molar absorptivities in DMSO for the two diastereomeric Cr(*S*-trp)$_3$ species isolated in the present study are collated in Table 1 (see supplementary material for original spectra). In both cases, the longer wavelength UV−visible absorption band is more intense than that at shorter wavelength, in agreement with a *facial* geometric isomer assignment. Oki[16] and Yoshimura and co-workers[15] have also reported the isolation of only the *facial* isomer for several related Cr(AA)$_3$ systems.

From a polarimetric study on the Cr(*S*-trp)$_3$ products, the acetone-soluble and -insoluble isomers are levo- and dextrorotatory at 578 nm, i.e. (−)$_{578}$-***fac*-Cr(*S*-trp)$_3$** and (+)$_{578}$-***fac*-Cr(*S*-trp)$_3$,** with specific rotations of −300 and +80°, respectively. The CD spectra for these two products in DMSO are shown in Figure 2 (see also Table 1). As expected, the two CD spectra exhibit a nearly mirror-image relationship with respect to each other. The acetone-soluble and -insoluble isomers are assigned the Δ and Λ absolute configurations, respectively, by the close correspondence of their CD spectra with that reported for Δ- and Λ-*fac*-Cr(*S*-ala)$_3$[15] (where *S*-ala is (*S*)-alaninato).

Photochemical Studies. Our studies on Cr(*S*-trp)$_3$ in DMSO solution indicate that, on d−d excitation (488 nm, Ar ion laser), the Δ-*fac*-Cr(*S*-trp)$_3$ isomer is essentially photoinert, while the Λ-*fac*-Cr(*S*-trp)$_3$ isomer undergoes photoconversion to Δ-*fac*-Cr(*S*-trp)$_3$ with a quantum yield of 0.03. We find no evidence for photosubstitution of coordinated tryptophan. Our evidence for $\Lambda \rightarrow \Delta$ photoinversion is based on CD (Figure 3) and UV−vis (supplementary material) spectral changes on 488-nm irradiation of Λ-*fac*-Cr(*S*-trp)$_3$. Three isosbestic points are observed in successive absorption spectra during the photolysis of Λ-*fac*-Cr(*S*-trp)$_3$. The wavelengths involved (370, 438, and 463 nm) are in excellent agreement with those of the intersection points of the overlaid spectra of Δ-*fac*-Cr(*S*-trp)$_3$ and Λ-*fac*-Cr(*S*-trp)$_3$. Such data provide compelling evidence for $\Lambda \rightarrow \Delta$ photoinversion about the Cr(III) center being the sole photoreaction. Further support is provided by the presence of two clean isodichroic points in the CD spectral data for Λ-*fac*-Cr(*S*-trp)$_3$ photolysis (Figure 3). On extended photolysis, the resulting CD spectrum matches within experimental error that observed for Δ-*fac*-Cr(*S*-trp)$_3$, which indicates that inversion is complete.

There are two main conclusions drawn from this photochemical study:

1. Complete inversion about Cr(III) demonstrates a key stereochemical role for the asymmetric C of (*S*)-tryptophan. The absence of any detectable Λ-*fac*-Cr(*S*-trp)$_3$ on photoinitiated equilibration does not automatically require that the Δ-*fac*-Cr(*S*-trp)$_3$ diastereoisomer is more stable. There are ample precedents of photoisomerizations resulting in the preferential formation of the less stable isomer.[21] However, in the present system, complete Λ-*fac*-Cr(*S*-trp)$_3$ to Δ-*fac*-Cr(*S*-trp)$_3$ inversion is also observed thermally at elevated temperatures (for example, $t_{1/2}$ for inversion in DMSO solution is 160 min at 80 °C).[22] Furthermore, a more stable Δ-*fac*-Cr(*S*-trp)$_3$ isomer is in accord with molecular mechanics calculations (vide infra).[23]

2. Optical inversion without *fac* → *mer* geometric isomerism is suggestive of a trigonal twist mechanism about the true C_3 axis (Bailar twist). All other twist processes (such as the Ray and Dutt rhombic twist about a pseudo-C_3 axis) and one-ended bond rupture mechanisms either yield inversion and geometric isomerism or yield geometric isomerism in the absence of inversion. Diagrammatic representations of the trigonal and rhombic twists are shown in Figures 4 and 5, respectively.

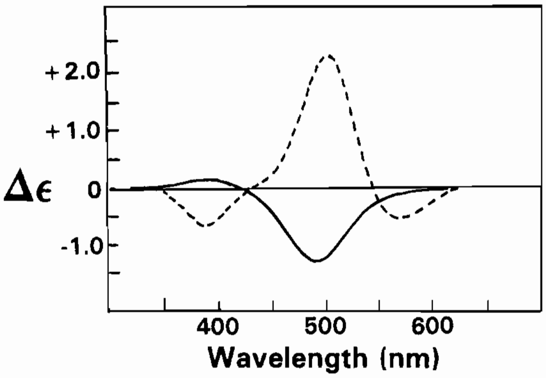

Figure 2. Circular dichroism spectra in DMSO solution of the acetone-soluble Δ-*fac*-Cr(*S*-trp)$_3$ isomer (—) and acetone-insoluble Λ-*fac*-Cr(*S*-trp)$_3$ isomer (- - -).

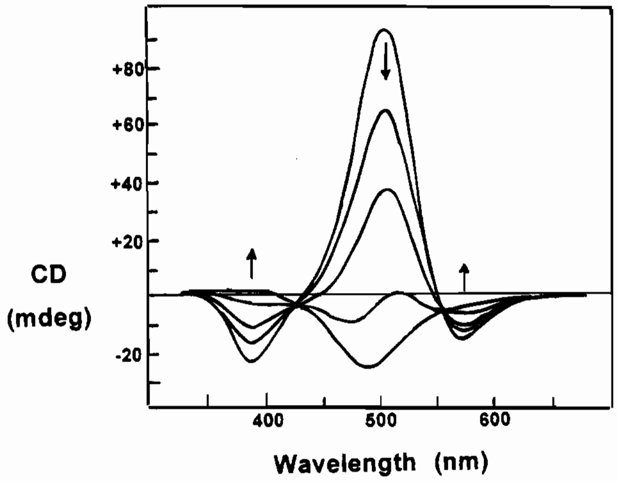

Figure 3. Circular dichroism spectral changes for a 1.0 × 10^{-3} M solution of Λ-*fac*-Cr(*S*-trp)$_3$ in DMSO (1 cm cell) upon 488-nm photolysis for 0, 4, 9, 19, and 29 min.

Our observations on Λ-*fac*-Cr(*S*-trp)$_3$ inversion may constitute the first example of a photoinduced Bailar twist. It has been suggested previously on theoretical grounds that the $^4T_{2g}$ excited state of tris-chelate Cr(III) complexes may facilitate intramolecular twist processes.[26] Our present findings are also of interest in the light of recent theoretical studies by Rodger and Johnson[12] on the relative likelihood of Bailar versus Ray and Dutt twists for tris-chelate systems. They suggest that the critical determining factor is the size of the normalized bite, *b*,

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(21) We thank a reviewer for constructive comments on this point.

(22) Heatherington, A. L.; Ritzenthaler, L. M.; Kane-Maguire, N. A. P. Unpublished results. Thermal inversion is a minor factor at the temperature of the photochemical study (22 °C), for which a thermal half-life of 60 h is estimated.

(23) Partial photoinversions have previously been reported by Vagg and Williams for a series of Ru(II) complexes of the general form [Ru(diimine)$_2$(AA)]$^{n+}$ (where diimine is 1,10-phenanthroline or 2,2′-bipyridine and AA is a bidentate α-amino acidate anion).[24,25] For the case where AA is (*S*)-tryptophanato and the diimine is phenanthroline, the photoequilibrated system contained the Δ and Λ isomers in a 4:1 ratio.

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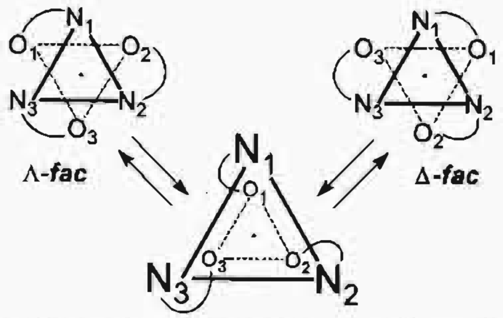

Figure 4. Bailar trigonal twist for Cr(AA)$_3$ systems, showing movement about the real C_3 axis.

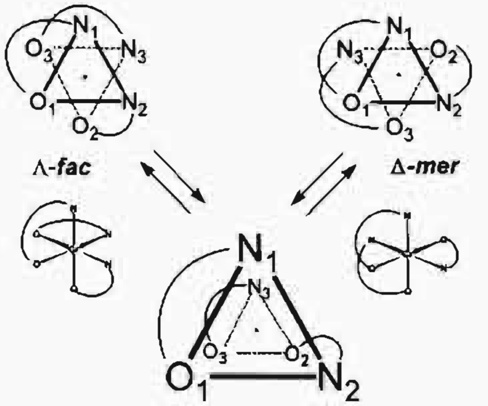

Figure 5. Ray and Dutt rhombic twist for Cr(AA)$_3$ systems, showing movement about one of the pseudo-C_3 axes.

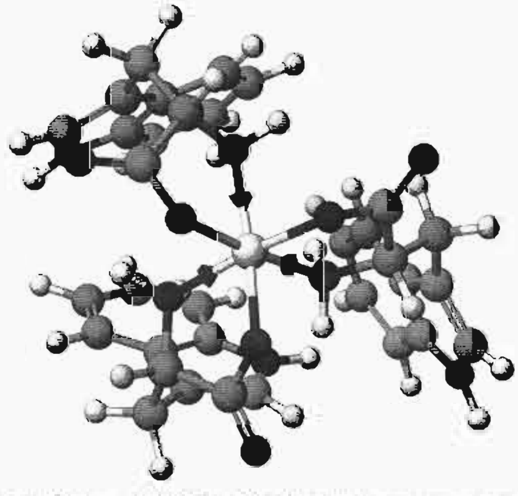

Figure 6. Energy-minimized Δ-*fac*-Cr(*S*-trp)$_3$ structure derived from molecular mechanics calculations.

for the system (where the bite is defined as the distance between the donor atoms of the chelate ring divided by the metal−donor atom distance). They conclude that a Bailar twist will be energetically preferred if the bite value is less than 1.4. Although we do not have direct information on the size of *b* for the *fac*-Cr(*S*-trp)$_3$ species, we expect the value to be very similar to that for *fac*-Cr(gly)$_3$. Using X-ray crystallographic data available for the glycine case, we estimate a *b* value of 1.31 for our *fac*-Cr(*S*-trp)$_3$ system—a number within the range favoring a Bailar twist mechanism.

Theoretical Calculations. Support for the structural assignments made by the spectroscopic methods were obtained from molecular mechanics calculations carried out on the Δ-*fac*-Cr-(*S*-trp)$_3$ and Λ-*fac*-Cr(*S*-trp)$_3$ isomers.[27] The final minimum energy structures for the two diastereomers are shown in Figures 6 and 7. The calculated heats of formation were −15.2 and −8.2 kcal mol^{-1} for the Δ and Λ isomers, respectively. *The Δ isomer is calculated to be more stable than the Λ by approximately 7 kcal mol^{-1}.* This result is in accord with our observation of complete conversion to the Δ-*fac*-Cr(*S*-trp)$_3$ isomer upon thermal or photoassisted equilibration. It is of interest that the synthesis of Cr(*S*-trp)$_3$ when carried out in aqueous solution yields primarily the less stable Λ-*fac*-Cr(*S*-trp)$_3$ isomer. In contrast, preparations carried out in DMSO solution (in which both isomers are soluble), yield almost exclusively the more stable Δ-*fac*-Cr(*S*-trp)$_3$ isomer. These observations suggest that either the reaction in water is kinetically rather than thermodynamically controlled or the Λ product is considerably less soluble in aqueous solution.

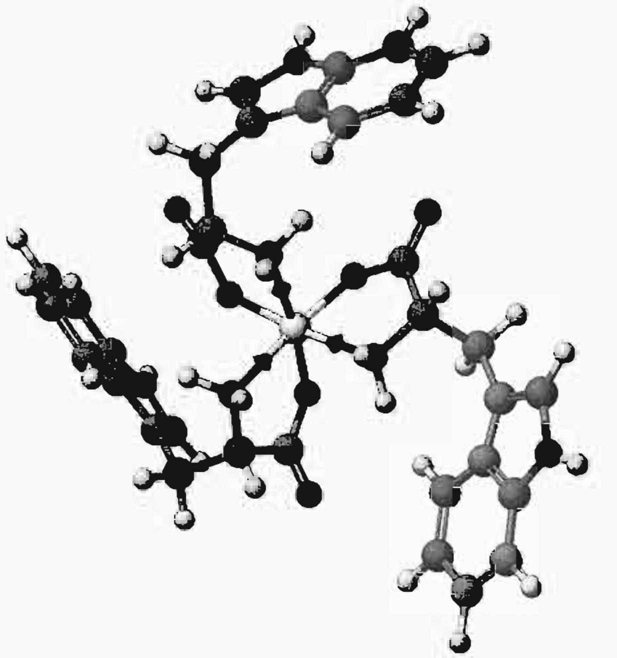

Figure 7. Energy minimized Λ-*fac*-Cr(*S*-trp)$_3$ structure derived from molecular mechanics calculations.

In the final minimized Δ and Λ structures, the bond lengths and geometries about the chromium did not vary significantly from each other or from those reported for *fac*-Cr(gly)$_3$. The calculated energy differences, therefore, arise primarily from the different orientations of the indole rings about the metal chelate (see Figures 6 and 7). The Δ isomer appears to be more congested than the Λ, but the van der Waals term for the Λ isomer is only slightly lower in energy than that for the Δ. In fact, there is little difference in the bond stretch, bond and dihedral angles, or torsion terms. It is only the electrostatic and hydrogen bond terms which differ significantly.

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Supplementary Material Available: Figure S1, displaying the uv−visible absorption spectra in DMSO of Λ-*fac*-Cr(*S*-trp)$_3$ and Δ-*fac*-Cr-(*S*-trp)$_3$, and Figure S2, exhibiting the absorption spectral changes upon 488-nm photolysis in DMSO (2 pages). Ordering information is given on any current masthead page.

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