Coordination Chemistry of Microbial Iron Transport. 42. Structural and Spectroscopic Characterization of Diastereomeric Cr(III) and Co(III) Complexes of Desferriferrithiocin[1]

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Abstract: Desferriferrithiocin, $DFFTH_2$ (**1**), is a novel siderophore produced by *Streptomyces antibioticus* and acts as a mediator for iron uptake in this organism. It contains neither catecholate nor hydroxamate functional groups and is tridentate, via a central nitrogen, a phenolate oxygen, and a carboxylate oxygen. It is known to form 2 to 1 complexes with ferric ion. There are potentially several geometric isomers for the ML_2 complex. In order to prepare kinetically stable complexes of this chiral ligand, Fe^{3+} has been replaced by Cr^{3+} and Co^{3+}. There are two diastereomeric Co^{3+} complexes that form from $Na_3[Co(CO_3)_3]$ and $DFFTH_2$ in aqueous solution. These have been separated by chromatographic (HPLC) techniques and characterized by electrophoresis, FAB mass spectra, NMR spectra, and VIS/UV and CD spectra. Reaction of the siderophore ligand with $CrCl_3\cdot 3THF$ in dry acetone in the presence of excess triethylamine gives a mixture of two diastereomeric chromium complexes, $[Et_3NH][Cr(DFFT)_2]$, in 70% yield. These diastereomers have been separated by HPLC and characterized by microanalysis, FAB mass spectroscopy, VIS/UV and CD spectroscopy, and single-crystal X-ray diffraction. The structure analyses have established that the complexes are meridional isomers that differ in their chirality at the metal center. The first isomer, **A** (produced in relative abundance of 62.5%), is a greenish-brown solid whose color in solution varies greatly with the solvent. According to the IUPAC convention, this isomer has a Λ (or **A**) absolute configuration. When isolated from acetonitrile/water solutions as the tetramethylammonium salt of **A**, the compound $[(CH_3)_4N][Cr(DFFT)_2]\cdot 0.5H_2O$ (**2**) crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 10.592 Å, b = 18.702 (7) Å, c = 27.407 (5) Å, V = 5429 (4) Å^3, and Z = 8; the two metal complexes in the asymmetric unit are essentially identical. The absolute configuration of the ligand is confirmed to be *S*. The second isomer, with a Δ (or **C**) absolute configuration (isolated in relative abundance of 37.5%), crystallizes from methanol/2-propanol as the potassium salt $K[Cr(DFFT)_2]\cdot 2C_3H_8O$ (**3**). Crystals of this salt conform to space group $P2_1$ with a = 9.643 (2) Å, b = 13.913 (3) Å, c = 12.350 (4) Å, β = 112.14 (2)°, V = 1536.6 (13) Å^3, and Z = 2. The structure of **2** was determined from 12422 unique data (h, $k \pm l$) measured at −105 °C. Refinement of 694 variables against 10587 observed data gave R = 3.7%, R_w = 4.8, and GOF = 1.97. The structure of **3** was determined from 3655 unique data ($\pm h,k \pm l$) measured at −105 °C. Refinement of 378 variables against 2126 observed data gave R = 3.2%, R_w = 3.4%, and GOF = 1.08. Although isomers **A** and **C** have metal coordination geometries that are essentially mirror images, the chirality of the ligand makes these diastereomers rather than enantiomers. The solid-state structures of these isomers are discussed in relation to their CD spectra, which are novel in being essentially the same for the low-energy T_{2g} manifold while mirror image for the T_{1g} manifold. [The same spectral features are apparent for the Co^{3+} complexes.] The CD spectra are qualitatively explained on the basis of these electronic transitions for an octahedral complex; the two isomers both have a distorted octahedral geometry that is approximately D_{2d} in symmetry. The further perturbation of this ligand field involves an S_4 symmetry distortion which affects T_1 and T_2 symmetries differently and can be used as a simple rationale for the unusual relationship of the spectra.

The solubilization and mediation of iron uptake by aerobic microbes occurs via the production of low molecular weight ligands that have very high affinities for ferric ion.[2-4] We have been concerned with the characterization of the coordination chemistry of these compounds (the siderophores) and the mechanisms by which they deliver iron to the microbial cell. It has been shown that the microbial transport process generally involves a recognition of the geometry and chirality at the metal center of the siderophore complex. Most of the more than 100 naturally occurring siderophores are hexadentate in order to completely encapsulate a six-coordinate ferric ion; typically these ligands incorporate three bidentate ligand groups that form complexes with approximate trigonal symmetry. We report here a new kind of chirality at the metal center of a siderophore complex and describe how this leads to a novel relationship between the circular dichroism spectra of the pairs of cobalt(III) and chromium(III) diastereomeric metal complexes.

Iron uptake and inhibition studies with a number of siderophores, semisynthetic siderophores, and synthetic siderophore analogues have demonstrated remarkable stereospecificity and enantioselectivity of the microbial receptors.[2,3] One well-studied example is the siderophore enterobactin, a tricatecholate ligand produced by *E. coli* and other enteric bacteria. The absolute configuration of the metal complex of enterobactin was established for the chromic complex by comparing the CD spectrum with resolved tris(catecholato)chromate(III) and trihydroxamate siderophore complexes such as chromic (desferriferrichrome).[5] The metal complex of enterobactin has trigonal symmetry, and these studies established that the absolute configuration at the metal center is Δ.[6] The formation of only one chirality at the metal center is imposed by the optical activity of the enterobactin ligand, which is formed from naturally occurring *l*-serine. When the synthetic mirror image enterobactin was made it did not deliver iron to the cell,[7] presumably because the resultant Λ absolute configuration at the metal center was not recognized by the enterobactin receptor of *E. coli*. In order to probe the role of the metal center chirality, kinetically inert complexes have been formed by replacing ferric ion with chromic ion; these were shown to be useful probes of siderophore mediated iron uptake.[8,9] Recently,

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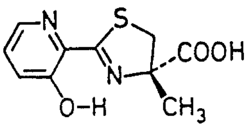
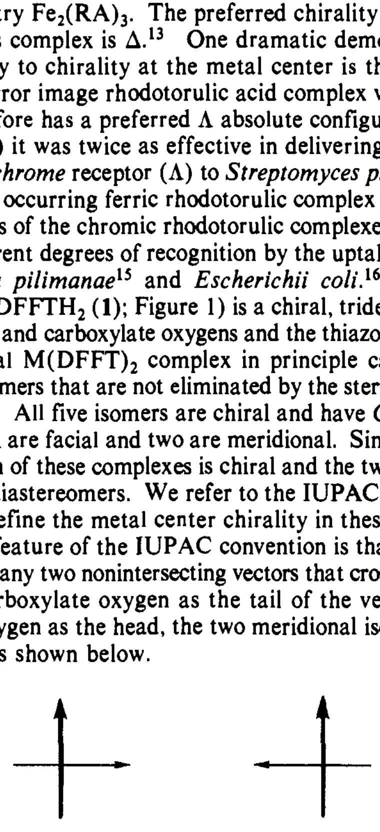


Figure 1. (*S*)-Desferriferrithiocin (metal-free ferrithiocin).

kinetically inert complexes of enterobactin and synthetic analogues have been used to further probe this stereospecificity.[10] This work has established the role of the metal center in the receptor recognition of the ferric enterobactin complex.

A similar metal center recognition has been found in hydroxamate siderophore mediation of iron uptake. The trihydroxamate ferrichrome, unlike enterobactin, preferentially forms a Λ metal center.[11] The synthetic mirror image of this siderophore (a Δ metal center) was also found not to be an effective iron transport agent.[12] Another hydroxamate ligand, rhodotorulic acid, contains only two hydroxamate groups and forms an iron complex with a stoichiometry $Fe_2(RA)_3$. The preferred chirality of the metal center in this complex is Δ.[13] One dramatic demonstration of the sensitivity to chirality at the metal center is that when the synthetic mirror image rhodotorulic acid complex was prepared (which therefore has a preferred Λ absolute configuration at the metal center) it was twice as effective in delivering iron via the cellular *ferrichrome* receptor (Λ) to *Streptomyces pilosus* as was the naturally occurring ferric rhodotorulic complex (Δ).[14] Similarly, isomers of the chromic rhodotorulic complexes were found to have different degrees of recognition by the uptake systems of *Rhodotorula pilimanae*[15] and *Escherichii coli*.[16] Desferriferrithiocin ($DFFTH_2$ (**1**); Figure 1) is a chiral, tridentate ligand, via phenolate and carboxylate oxygens and the thiazoline nitrogen. Its octahedral $M(DFFT)_2$ complex in principle can form five geometric isomers that are not eliminated by the steric constraints of the ligand. All five isomers are chiral and have C_2 symmetry; three of them are facial and two are meridional. Since the ligand is chiral, each of these complexes is chiral and the two meridional isomers are diastereomers. We refer to the IUPAC convention[17] in order to define the metal center chirality in these complexes. The central feature of the IUPAC convention is that chirality is generated by any two nonintersecting vectors that cross each other. With the carboxylate oxygen as the tail of the vector and the phenolate oxygen as the head, the two meridional isomers can be diagramed as shown below.



In this diagram the bold-faced arrow is intended to be above the plane of the lighter arrow. Shown below each is the absolute configuration that is thus defined. Since, however, these vector pairs are not formed by two simple skew chelate rings, the earlier IUPAC proposal does not strictly apply. A more general definition of C (clockwise) or A (anticlockwise) has been put forward.[18] This designation for these complexes is also shown and it will be used throughout this paper to designate the diastereomeric isomers of both the Co and Cr complexes.

Desferriferrithiocin is a chiral siderophore that was first isolated in 1980 from *Streptomyces antibioticus*.[19] Like two other recently identified siderophores, anguibactin[20] and pyochelin,[21,22] $DFFTH_2$ contains a thiazoline ring. The chirality of carbon(IV) of the thiazoline ring in desferriferrithiocin has an *S* absolute configuration, opposite that of *l*-cysteine. A preliminary report on the stability of the iron complex has appeared,[23] and a 1:1 five-coordinate copper complex has recently been reported.[24] However, nothing of relevance to the coordination properties of this compound in octahedral complexes has been known. We report here the preparation and characterization of several kinetically inert complexes of this ligand, the separation of two pairs of the cobaltic and chromic isomers, their structural and physical characterization, and correlation of the structures with their circular dichroism spectra.

Experimental Section

General. Acetone was dried over 4 Å molecular sieves and distilled prior to use. Reactive metal reagents $CrCl_3\cdot 3THF$ and $Na_3[Co(CO_3)_3]\cdot 3H_2O$ were prepared according to the literature procedures.[25,26] Triethylamine was distilled from sodium. Desferriferrithiocin (**1**) was a gift from Ciba Geigy. Unless otherwise specified, other starting materials were commercial analyzed reagents. Elemental analyses were performed by the Microanalytical Laboratory, University of California, Berkeley. Proton NMR spectra were recorded on a custom-built 200-MHz FT instrument. Vis/UV and CD spectra were recorded with use of 1 cm path length cells on Hewlett-Packard HP8450A and Jasco J500-C spectrometers, respectively. Mass spectra were recorded in the UCB Mass Spectrometer Facility. Spectra were obtained on a Vacuum Generators Analytical FAB mass spectrometer, Model ZAB2-EQ, with a cesium ion gun.

$[Co(DFFT)_2]^-$ Syntheses. Preparation of $Na[Co(DFFT)_2]$. A solution of desferriferrithiocin ($DFFTH_2$) (477 mg, 2.00 mmol) in 20 mL of water was added to 360 mg (0.99 mmol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$. The reaction mixture was stirred 48 h at room temperature in the dark and then filtered through a fine glass frit. The reddish-brown filtrate was cautiously neutralized with ca. 3 mL of 0.4 M HCl added in portions to give a solution of pH 6.8. Following lyophilization, 614 mg of crude product was obtained. Paper electrophoresis (0.05 M HEPES buffer, pH 8.0, constant current 40 mA) of the crude product showed three spots, all negative ions. The fastest moving spot (yellow-green) is a minor unidentified impurity (probably an oxidation product of the ligand). The middle spot (light orange) is assigned as a cobaltous complex, based on its R_f (twice as fast as the Co(III) complex) and on the portion NMR spectrum of this fraction, which showed paramagnetically broadened lines. The slowest moving spot (dark brown) is the expected cobaltic complex: it has the same R_f as the Cr(III) complex, and the proton NMR spectrum of this extracted spot shows no paramagnetic broadening. Furthermore, the NMR spectra (discussed later) confirm the presence of two distinct isomers of the complex.

Further purification and isomer separation of the cobalt(III) isomers was achieved by HPLC with a Hamilton PRP-1 semipreparative column (10 × 250 mm) and an ion-pairing solvent system (0.01 M NH_4OAc, pH 8.86 for both solvent A (H_2O) and solvent B (MeOH)). The crude mixture of isomers (20 mg/200 μL of solvent A) was injected on to the PRP column and eluted at a flow rate of 5 mL/min with the following gradient: 10–20% B (2%/min); 20–30% B (1%/min); 30–45% B (1.5%/min); and 45–55% B (1%/min).

Two peaks eluting before 3.3 min were discarded, and the two isomers C and A eluted at 20.7 and 24.4 min, respectively. The solutions of pure isomers were evaporated to dryness, applied to an AG50W-X4 ion ex-

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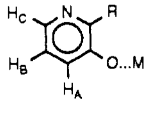
Table I. ^{1}H NMR Spectra of Desferriferrithiocin ($DFFTH_2$) and the Isomeric Na[Co$(DFFT)_2$] Complexes[a]

		free $DFFTH_2$ ligand	Na[Co$(DFFT)_2$] isomer A	Na[Co$(DFFT)_2$] isomer C
CH_3		1.67 ppm (s, 3 H)	1.88 (s)	1.91 (s)
CH_2		3.38 ppm (d, 1 H) (^2J = 11.6 Hz) 3.80 ppm (d, 1 H)	3.89 (d) (^2J = 11.2 Hz) 4.44 (d)	3.77 (d) (^2J = 11.3 Hz) 4.19 (d)
	**A**	7.43 ppm (m, 2 H)	6.88 (dd) J_{AB} = 8.7 Hz	7.45 (dd) J_{AB} = 8.7 Hz
	B		7.06 (dd) J_{AC} = 1.2 Hz	7.32 (dd) J_{AC} = 1.2 Hz
	C	8.04 ppm (dd, 1 H) J_{AC} = 1.9 Hz, J_{BC} = 3.9 Hz	7.91 (dd) J_{BC} = 4.3 Hz	8.00 (dd) J_{BC} = 4.2 Hz

[a] Proton NMR spectra were performed in D_2O at 200 MHz with trimethylsilylpropionate-d_4 (TSP) as a reference.

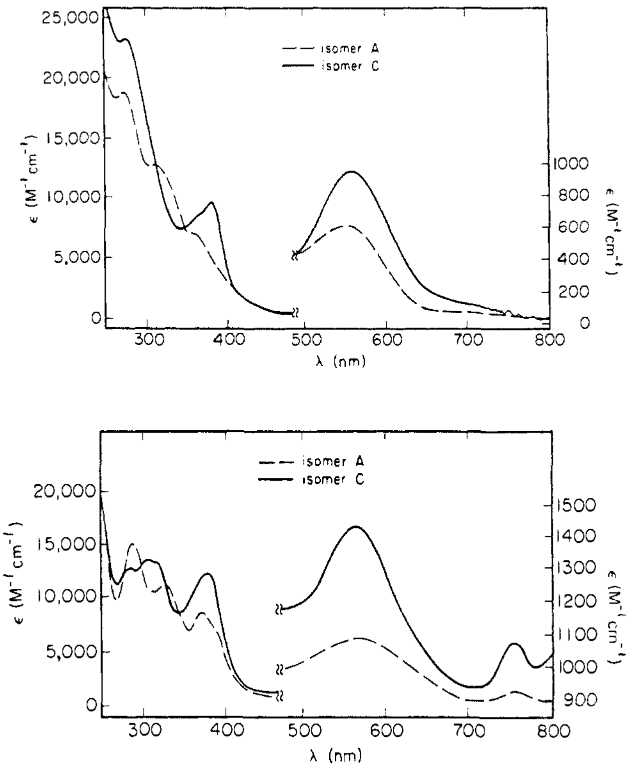


Figure 2. Vis/UV spectra of the A and C isomers of [M$(DFFT)_2$]$^-$ complexes (M = Co, Cr) in methanol: (upper panel) cobaltic complexes; (lower panel) chromic complexes.

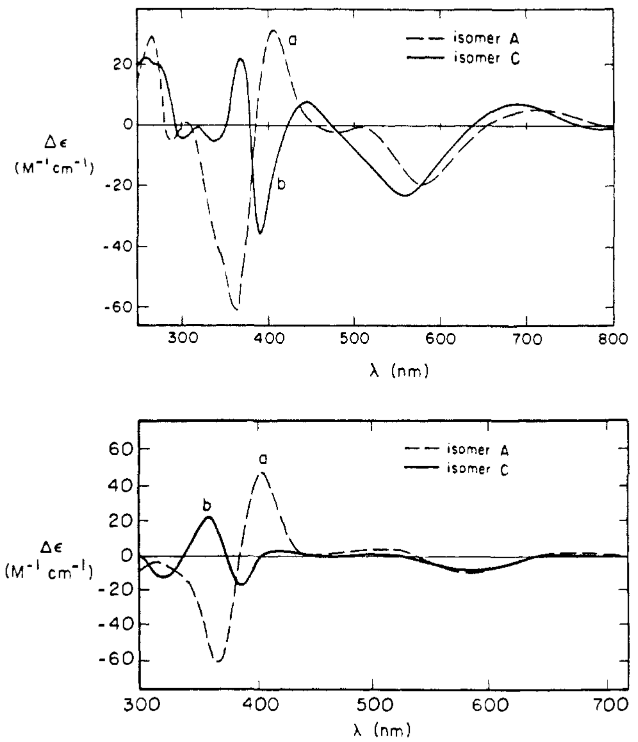


Figure 3. Circular dichroism spectra of the A and C isomers of [M$(DFFT)_2$]$^-$ complexes (M = Co, Cr) in methanol: (upper panel) cobaltic complexes; (lower panel) chromic complexes; (a) Na^+ salt of isomer A from compound **2**; (b) Na^+ salt of isomer C from compound **3**.

change column (Na^+ form, 100–200 mesh, 7 × 240 mm), and eluted with water. The solutions were then lyophilized to give the sodium salts. These samples were characterized by proton NMR, FAB mass spectra, and VIS/UV and CD spectroscopic characterization. NMR spectra are recorded in Table I.

[Cr$(DFFT)_2$]$^-$ Syntheses. Preparation of [Et_3NH][Cr$(DFFT)_2$]. Desferriferrithiocin (0.200 g, 0.84 mmol) was dissolved in acetone (125 mL) under argon. $CrCl_3 \cdot 3THF$ (0.160 g, 0.43 mmol) and triethylamine (0.25 g, 2.5 mmol) were added and the resulting greenish-brown solution was refluxed for 1.5 h and subsequently stirred at room temperature for 24 h. The light green precipitate was removed by filtration and the resulting dark brown filtrate was evaporated to dryness. The residue was dissolved in methanol and applied to a Sephadex LH-20 column (2.7 × 30 cm) and eluted with methanol. Evaporation of the methanol followed by vacuum drying gave [Et_3NH][Cr$(DFFT)_2$] in 70% yield (0.188 g, 0.3 mM) as a mixture of isomers. Calcd. (Found) for $C_{26}H_{32}N_5O_6S_2Cr$: C, 49.83 (49.60); H, 5.15 (5.48); N, 11.17 (10.98); S, 10.23 (9.88); Cr, 8.29 (7.34). Negative ion FABMS: *m/e* (ref abundance) 524 (100%).

Preparation of [Na][Cr$(DFFT)_2$]. Clean separation of the [Cr$(DFFT)_2$]$^-$ isomers was achieved by HPLC with use of a Hamilton PRP1 semipreparative column (10 × 250 mm), a flow rate of 5 mL/min, and an ion pairing solvent system 0.01 M NH_4OAc, pH 8.86 for A(H_2O) and B(MeOH). An isomeric mixture of [Et_3NH][Cr$(DFFT)_2$] (170 mg) was dissolved in 8.5 mL of solvent A; 500 μL of this solution was injected onto the column. The isomers were eluted with use of a gradient of 10–40% B (15%/min) and then 40–100% B (6%/min). Isomer A eluted at 16.3 min and isomer C at 18.6 min. The procedure was repeated until the entire sample was separated. The solvent was stripped from the solutions of the separated isomers and the resulting solids were applied to a cation exchange column (AG50W-X8, Na^+ form, 4 × 32 cm), eluted with H_2O, and evaporated to dryness. Final purification was achieved by chromatography on Sephadex LH-20 (solvent methanol). The yield is 100 mg of Na[isomer A] (62.5%) and 60 mg of Na[isomer C] (37.5%). Negative ion FABMS: *m/e* (rel abundance), assigned as isomer A, 524 (100%), [Cr$(DFFT)_2$]$^{1-}$; isomer C, 524 (100%), [Cr$(DFFT)_2$]$^-$.

Preparation of K^+ Salts. Approximately 10 mg of Na[isomer A] was applied to cation exchange column (AG50W-X8, K^+ form, 2.5 × 10 cm) and eluted with water. The purple fraction was roto-evaporated to dryness. The same procedure was repeated for 10 mg of Na[isomer C]. Solid K[isomer A] forms dark green thin plates. Solid K[isomer C] was obtained as a purple powder.

Preparation of [$(CH_3)_4N$]$^+$ Salts. Approximately 10 mg of Na[isomer A] and Na[isomer C] were applied to a cation exchange column (AG50W-X8 [$(CH_3)_4N$]$^+$ form, 10 × 40 mm) and eluted with water. After removal of the solvent, brownish-green solids of [$(CH_3)_4N$] and [isomer A] and [$(CH_3)_4N$] [isomer C] were obtained.

Spectroscopic Measurements. Solutions of the cobalt complexes were prepared by dissolving the pure samples (from HPLC) in methanol. About 2.7 mg of each isomer was diluted in methanol to 50 mL. After spectroscopic analyses, these solutions were analyzed for cobalt by atomic absorption; isomer A was determined to be 51.6 × 10^{-6} M and isomer C 74.7 × 10^{-6} M in cobalt. The extinction coefficients for the spectra

Table II. VIS/UV and CD Spectral Characteristics of $M(DFFT)_2^-$ Complexes (M = Co, Cr; Both A and C Isomers in Methanol Solutions)

visible				CD			
isomer A		isomer C		isomer A		isomer C	
λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	$\Delta\epsilon$, M^{-1} cm^{-1}	λ_{max}, nm	$\Delta\epsilon$, M^{-1} cm^{-1}
273	18780	276	23250	266	+31.7	259	24.3
						274	21.9
311	12770	365	8490	287	−6.8	300	−4.9
						336	−5.7
356	7000	380	9570	362[b]	−64.9	368	+23.9
550	597	560	945	405	+33.2	390	−38.5
				476	−2.6	445	+8.3
				578	−21.4	559	−25.2
				714	+5.9	692	+7.1
289	15165	284	13158			320	−11.9
		303	13932	366	−64.5	360	+15.7
326	11776	315	13692	402	+48.5	384	−16.0
369	9586	378	12621	515	+3.5	415	+3.1
574	1073	574	1454	580	−9.7	580	−7.7
				670	+3.5	670	+2.0

[a] Concentrations Na[isomer A] = 51.6×10^{-6} M, Na[isomer C] = 74.7×10^{-6} M. [b] There is a shoulder at 342 ($\Delta\epsilon \approx -42.3$). [c] Concentrations Na[isomer A] = 43.7×10^{-6} M, Na[isomer C] = 34.26×10^{-6} M, 1 cm path length.

are based on these concentrations. Absorption maxima for the shoulders were determined with use of derivative ($\delta A/\delta\lambda$) spectra. Solutions of the chromium complexes were prepared: 0.748 mg of Na[isomer A] and 0.527 mg of Na[isomer C] were each dissolved in 25 mL of MeOH. The concentrations of the solutions were measured by atomic absorption: Na[isomer A] 43.7×10^{-6} M, Na[isomer A] 34.23×10^{-6} M.

Solution spectra were obtained in methanol rather than water in order to lessen the probability of isomerization. Vis/UV spectra appear in Figure 2 and CD spectra in Figure 3. Data for all spectra are given in Table II.

Crystallization and X-ray Data Collection. $[(CH_3)_4N][Cr(DFFT)_2]\cdot 0.5H_2O$ (**2**, [isomer A]) crystallized from CH_3CN/H_2O (5:1, v:v) as thin greenish-brown plates. A suitable specimen with the dimensions 0.41 × 0.31 × 0.08 mm was mounted in a thin-walled glass capillary. The symmetry of the crystal lattice (orthorhombic) and preliminary cell constants were obtaned by a series of precession photographs. The crystal was then transferred onto an automatic Enraf-Nonius CAD-4 diffractometer for data collection. Final cell parameters were obtained by least-squares refinement of the angular settings of 24 reflections in the 2θ range $25.6° \leq 2\theta \leq 26.7°$.[27]

Applying θ–2θ scan techniques and Mo Kα radiation, all intensity data ($0 \leq h \leq 13$, $0 \leq k \leq 24$, $-35 \leq l \leq 35$) were collected at −105 °C in the range $3° \leq 2\theta \leq 55°$. A variable scan width of $(0.66 + 0.35 \tan\theta)°$ and a maximal scan time of 45 s were employed. The intensities of three standard reflections [(−1,5,16), (4,9,−4), (5,0,−12)] were remeasured after each 200 intensity measurements. A new orientation matrix was calculated from an array of 24 reflections, if any of the orientation standards was offset from its predicted position by more than 0.1°. Azimuthal scans were recorded at the end of the data collection for five reflections near $\chi = 90°$ in 10° increments of rotation of the crystal about the diffraction vector.

Crystals of $K[Cr(DFFT)_2]\cdot 2C_3H_8O$ (**3**, [isomer C]) formed from a concentrated methanol/2-propanol (1:20, v:v) solution at 4 °C as bright red parallelepipeds. A crystal of dimension 0.32 × 0.15 × 0.11 mm was prepared as for the data collection of **2**. Precession photographs yielded the symmetry of the crystal lattice (monoclinic) and preliminary cell constants. Final cell parameters were obtained as for **2** in the 2θ range $19.6° \leq 2\theta \leq 26.6°$.

Data collection proceeded as for **2** with a maximum scan time of 45 s, a variable scan width of $(0.65 + 0.35 \tan\theta)°$ and three intensity and orientation standards [(3,−3,−6], (−3,−5,5), (2,4,−6)] being monitored throughout the data collection. All data ($-12 \leq h \leq 12$, $0 \leq k \leq 18$, $-16 \leq l \leq 16$) were collected at −105 °C in the 2θ range $3° \leq 2\theta \leq 55°$. Azimuthal scans were recorded for two reflections at the end of the data collection.

Table III. Summary of Crystal Data for Compounds **2** and **3**

	$[(CH_3)_4N][Cr(DFFT)_2]\cdot 0.5H_2O$ (**2**, [isomer A])	$K[Cr(DFFT)_2]\cdot 2C_3H_8O$ (**3**, [isomer C])
compd	$[(CH_3)_4N][Cr(DFFT)_2]\cdot 0.5H_2O$	$K[Cr(DFFT)_2]\cdot 2C_3H_8O$
formula	$C_{24}H_{29}CrN_5O_{6.5}S_2$	$C_{26}H_{32}CrKN_4O_8S_2$
fw	607.7	683.8
Z	8	2
asymmetric unit	two ion pairs and one H_2O	one ion pair and two 2-propanol
space group	$P2_12_12_1$	$P2_1$
a, Å	10.592 (2)	9.643 (2)
b, Å	18.702 (7)	13.913 (3)
c, Å	27.407 (5)	12.350 (4)
β, deg		112.14 (2)
V, Å^3	5429 (4)	1536.6 (13)
d_0, g/cm^3	1.46	1.47
d_c, g/cm^3	1.49	1.48
μ, cm^{-1}	6.06	6.80

Structure Solution and Refinement for 2. The raw data (13 778 intensities) for **2** were converted into structure factor amplitudes (and their esd's) by correcting for scan speed, background, and Lorentz and polarization effects.[28,29] An inspection of the list of intensity standards revealed that no decay correction was necessary (maximum loss of intensity was 1.9% over the 184.5-h X-ray exposure time). The azimuthal scan data showed a variation of ±6.1% for the average curve. An empirical absorption correction[28] was applied (maximum and minimum correction factors 1.000 and 0.939, respectively). Systematically absent data and all redundant data ($h0l$, $l < 0$; $0kl$, $l < 0$) were rejected, leaving 12 422 unique data $h,k,\pm l$.

The structure was solved by direct methods[28,30] and refined with standard least-squares and Fourier techniques. The asymmetric unit contains two ion pairs of $[(CH_3)_4N][Cr(DFFT)_2]$ and one water molecule. All non-hydrogen atoms were refined with anisotropic thermal parameters. Although a difference Fourier map revealed the positions of almost all hydrogen atoms, they were placed at calculated[31] positions with isotropic temperature factors 1.3 times the B_{eq} of the parent atom. The hydrogen atoms at the water molecule (O7) could not be found and were not included in the structure model.

Refinement of the crystal enantiomer in which the ligand absolute configuration is S gave $R = 0.040$ ($R_w = 0.054$) versus $R = 0.046$ ($R_w = 0.060$) for refinement of the mirror image enantiomer. This provides an unequivocal assignment of the ligand and metal center chiralities.

Rejection of nine strong overlapping reflections in the final cycles of refinement gave agreement factors $R = 0.037$, $R_w = 0.048$, and GOF = 1.969 for 10 587 data with $I \geq 3\sigma(I)$ and 694 variables. A difference Fourier map calculated from the final structure factors had a maximum and minimum of 0.69 and −0.56 e$^-$/Å^3, respectively.

Structure Solution and Refinement for 3. The 7304 raw data were converted into structure factor amplitudes with no decay correction (maximum change in intensity was 0.1% over the 98.1 h of X-ray exposure time). The azimuthal scan data showed a variation of ±7.5%. An empirical absorption correction was applied (maximum and minimum correction factors 1.000 and 0.923, respectively). Systematically absent data (for $P2_1$) were removed from the data set and redundant data were averaged $R_{av} = 0.029$, based on F_o), leaving 3655 unique data.

The structure was solved by heavy-atom methods. The asymmetric unit contains one ion pair $K[Cr(DFFT)_2]$ and two 2-propanol molecules coordinated to the K^+ cation. Although a difference Fourier map calculated after anisotropic refinement of all non-hydrogen atoms revealed the positional parameters of all hydrogen atoms (except for the two iPrOH protons), these were added at calculated positions[31] as in **2** (except for the two iPrOH protons, which were not added to the structure model).

Refinement of both crystal enantiomers again confirmed the absolute configuration of the chiral carbon atoms in the ligand as S. The final residuals are as follows: $R = 0.032$, $R_w = 0.034$, and GOF = 1.079 for 2126 data with $I \geq 3\sigma(I)$ and 378 variables. The strongest peaks in a final difference Fourier map were 0.317 and −0.232 e$^-$/Å^3, respectively.

Some important crystal data for **2** and **3** are presented in Table III. The two independent molecules (both A configuration) in the asymmetric unit of **2** are labeled a and b. Selected bond distances and angles for **2**

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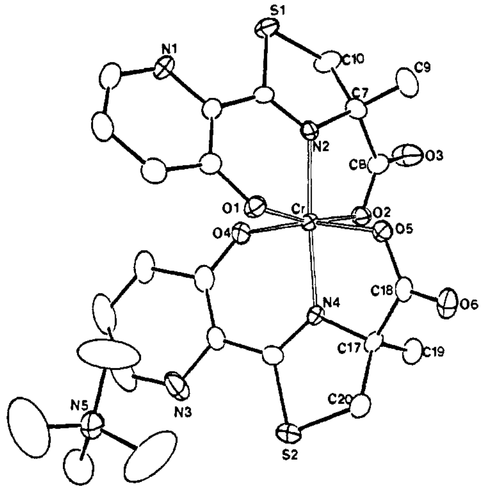

Figure 4. An ORTEP diagram of one of the two cation pairs in the asymmetric unit of **2** (molecule a). Hydrogen atoms are omitted for clarity.

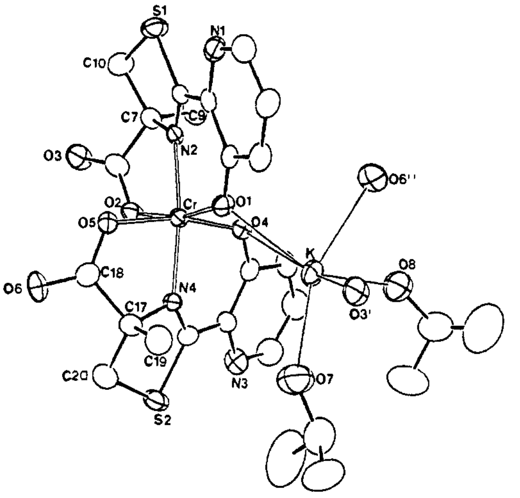

Figure 5. An ORTEP diagram of the ion pair in **3**. Primed atoms represent transformed coordinates [symmetry code: (') $(1 - x, y, z)$; ('') $(1 - x, y - {}^1/_2, 1 - z)$].

and **3** are summarized in Table IV. One of the two identical ion pairs in the asymmetric unit of **2** (molecule a) is shown in Figure 4. Figure 5 shows an ion pair of **3** and the two 2-propanol molecules. The coordination environment around Cr for **2** (molecule a) and **3** is compared in Figure 6.

Additional figures and tables pertinent to the crystal structures of **2** and **3** can be found in the supplementary material.[32]

Results and Discussion

Synthesis, Separation, and Characterization of the Cobaltic Isomers. DFFTH$_2$ (**1**) reacts with Na$_3$((Co(CO$_3$)$_3$)·3H$_2$O in water at room temperature to give a mixture of two meridional isomers of Na(Co(DFFT)$_2$). Paper electrophoresis indicated the presence of some cobaltous impurity in the final mixture. The kinetically inert d^6 isomers are separable by HPLC. Isomer A is reddish-brown in methanol and water solutions, while isomer C is purple. No isomerization was observed in methanol solutions after a month at room temperature. Results of FAB negative ion mass spectra of the cobalt complexes were essentially the same when either nitrobenzyl alcohol or thioglycerol/glycerol matrices are used. Results for the latter will be reported. For the molecular formula $C_{20}H_{16}N_4O_6S_2CoNa$ (the neutral sodium salt) of isomers a and b, the average mass is 554.415. The most abundant isotopic species is 553.9. The strongest peak in the mass spectrum was at 554. This is assigned as the deprotonated cobalt*ous* complex, and the relative intensity of the peaks found clustered at this point correspond to the computed isotope distribution for the formula given. The cobalt(III) complex is apparently reduced in the course of ionization in the mass spectrometer, a relatively common event in cases where the metal may readily be reduced by one electron. Other major peaks seen in the fragmentation pattern were 259 (NaDFFTH$^-$) and 193 (DFFTH$^-$–CO$_2$). Proton NMR spectra of the diamagnetic cobaltic complexes in D$_2$O established the absence of cobaltous species (no paramagnetic broadening) and isomeric purity of the two cobalt(III) complexes. Figure 7 displays the aromatic region of the spectra of both isomers, compared to that of DFFTH$_2$ alone. The chemical shifts of the aromatic protons are significantly different for both isomers, so that impurities of a few percent would have been readily discernible. On the basis of comparison with tabulated results,[33] peak assignments and coupling constants are given in Table I. Unlike the chemical shifts, coupling constants are nearly identical between both isomers.

Table IV. Selected Bond Distances (Å) and Angles (deg) for **2** and **3**[a]

	2		
	molecule a	molecule b	**3**
	Distance		
Cr–O1	1.950 (2)	1.959 (2)	1.947 (4)
Cr–O2	1.989 (2)	2.013 (2)	1.992 (4)
Cr–O4	1.948 (2)	1.955 (2)	1.944 (4)
Cr–O5	1.992 (2)	1.993 (2)	2.008 (5)
Cr–N2	1.989 (2)	1.979 (2)	1.989 (4)
Cr–N4	1.984 (2)	1.986 (2)	1.990 (5)
	Angle		
O1–Cr–O2	166.52 (6)	166.52 (7)	168.34 (15)
O1–Cr–O4	87.88 (7)	88.16 (7)	91.0 (2)
O1–Cr–O5	90.70 (7)	90.95 (6)	91.7 (2)
O1–Cr–N2	86.86 (7)	87.66 (7)	87.8 (2)
O1–Cr–N4	98.00 (7)	94.95 (7)	98.3 (2)
O2–Cr–O4	93.35 (7)	92.06 (7)	93.0 (2)
O2–Cr–O5	90.97 (7)	91.79 (7)	86.8 (2)
O2–Cr–N2	79.68 (7)	78.90 (7)	80.8 (2)
O2–Cr–N4	95.46 (7)	98.52 (7)	92.8 (2)
O4–Cr–O5	167.24 (6)	167.07 (7)	167.5 (2)
O4–Cr–N2	92.76 (7)	95.02 (7)	97.7 (2)
O4–Cr–N4	87.91 (7)	87.51 (7)	87.7 (2)
O5–Cr–N2	99.82 (7)	97.83 (7)	94.6 (2)
O5–Cr–N4	79.73 (7)	79.72 (7)	79.9 (2)
N2–Cr–N4	175.12 (8)	176.43 (8)	171.9 (2)

[a] The numbering scheme is identical for the anions of **2** (molecules a and b) and **3**.

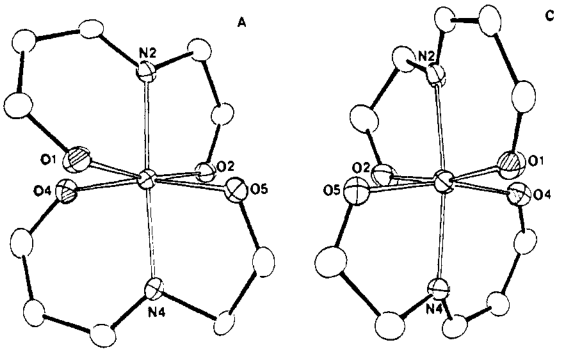

Figure 6. The coordination environment around Cr (A versus C, respectively) for **2** and **3** showing the mirror relationship between the coordination geometries. The phenolate oxygen atoms are cross-hatched to distinguish them from the carboxylate oxygen atoms.

Synthesis, Separation, and Characterization of the Chromic Isomers. DFFTH$_2$ (**1**) reacts with CrCl$_3$·3THF in the presence of an excess of triethylamine in dry acetone to yield an isomeric mixture of [Et$_3$NH][Cr(DFFT)$_2$]. The kinetically inert diastereomeric d^3 chromium(III) [(DFFT)$_2$]$^-$ isomers are separable by

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(32) See the statement regarding supplementary material in the last paragraph of this manuscript.

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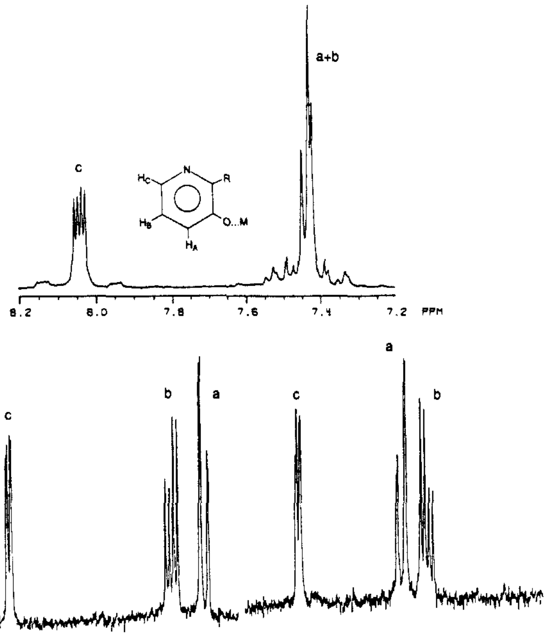


Figure 7. Aromatic region of the 200-MHz proton NMR spectra of the ligand (top) and both isomers of the Na[Co(DFFT)$_2$] (bottom), showing the assignments of the abc proton system (inset).

HPLC. Isomerization was not observed as long as the temperature of solutions of the isomers was not raised over 40 °C. The initially obtained isomer mixture contained only two isomers, which were isolated as the sodium salts Na[isomer A] (63%, a greenish-brown solid) and Na[isomer C] (a purple solid). The physical properties of the two compounds are quite different. For a given cation M$^+$, M[isomer A] is typically much more soluble than M[isomer C] in organic solvents. For example, K[isomer A] is soluble in MeOH, EtOH, 2-propanol, diglyme, and acetonitrile, while K[isomer C] is only soluble in MeOH. The color of K[isomer A] varies with solvent polarity. A diglyme solution is yellow, while an aqueous solution is purple. The isomers have been characterized by elemental analysis, negative ion FAB mass spectroscopy, and single-crystal X-ray diffraction.

Crystallographic Characterization. Isomer A was crystallized as the tetramethylammonium salt, **2** (Figure 4), and isomer C as the potassium salt (Figure 5). The [Cr(DFFT)$_2$]$^-$ anions in **2** and **3** are both meridional isomers. The absolute configuration of the chiral carbon atom of the ligand is *S* for all ligands in **2** and **3**. However, the chirality at the metal center is Λ or A for **2** and Δ or C[17,18] for **3** (Figure 6). Thus, the anions of **2** and **3** are diastereomers with identical absolute configuration of the chiral carbon atoms of the ligands and enantiomeric metal coordination geometry.

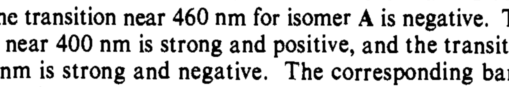
In both structures two desferriferrithiocin ligands coordinate to the metal center via one phenolate oxygen of the hydroxypyridine, one oxygen of the carboxylate group, and the nitrogen atom of the thiazoline ring. This creates a distorted octahedral meridional coordination environment for the chromium ion. Distances and angles in the anions of **2** and **3** are almost identical. The Cr–O(hydroxypyridine) distances fall in the range 1.941 (4) Å to 1.959 (2) Å (average 1.950 (6) Å) and the Cr–O(carboxylate) distance lies between 1.989 (2) and 2.013 (2) Å (average 1.998 (10) Å). The difference between the two types of Cr–O distance is consistent with the greater ligand field strength, and hence stronger Cr–O bond, for phenolate as a ligand compared to carboxylate.

The Cr–N distances fall in the range 1.979 (2) to 1.995 (4) Å (average 1.987 (5) Å). While a 1:1 five-coordinate copper complex of desferriferrithiocin recently has been reported and structurally characterized,[24] compounds **2** and **3** are the first metal complexes of the desferriferrithiocin ligand analogous to the octahedral ferric complex to be characterized by X-ray diffraction. It may be instructive to compare the bond lengths in **2** and **3** to M–O distances in metal complexes of natural and synthetic siderophore ligands to obtain an estimate of the relative stability of the chromic desferriferrithiocin complexes. Various ferric complexes of naturally occurring hydroxamates have been structurally characterized[11,34,36] and chromic complexes of synthetic hydroxamates are also known.[37] If one corrects for the larger (0.03 Å) effective ionic radius of high-spin Fe(III) compared to Cr(III),[38] it can be seen that the average Cr–O(hydroxypyridine) distance in **2** and **3** compares well with the M–O(*N*-hydroxyl oxygen) distances in ferric and chromic hydroxamate complexes, while the average Cr–O(carboxylate) distance in **2** and **3** is equal within 3 esd's to the M–O(carbonyl oxygen) distance in the hydroxamate complexes.

Interpretation of the CD Spectra. Both the cobaltic and chromic complexes show similar VIS/UV spectra (Table II and Figures 2 and 3). The series of bands in the ultraviolet are presumably ligand-to-metal charge-transfer bands. The broad absorption band in the visible region corresponds to the low-energy T manifold for an octahedral complex. The higher energy manifold in the VIS/UV spectra is obscured by the charge-transfer bands but can be inferred from the CD spectra. The ground state and spin-allowed excited states for an octahedral low-spin d^6 complex are $^1A_{1g}$, $^1T_{1g}$, and $^1T_{2g}$ (in order of increasing energy). The corresponding term symbols for chromic complexes are $^4A_{2g}$, $^4T_{2g}$, and $^4T_{1g}$. For both the cobaltic and chromic complexes, therefore, there are two spin-allowed d–d transitions of symmetry T_{1g} (low energy) and T_{2g} (high energy). Although there are some small differences in features, the cobaltic and chromic complexes are similar enough so that the following analysis of the cobaltic complex is intended also to apply to the chromic complexes.

The most striking feature of the circular dichroism spectra is that the A and C isomers show two bands in portions of their spectra due to the T_{1g} manifold that are essentially the same. The bands near 700 nm are positive and the more intense bands near 570 nm are negative. In contrast, the higher energy T_{2g} manifold shows three bands that are *antimeric* between the A and C complexes! The transition near 460 nm for isomer A is negative. The transition near 400 nm is strong and positive, and the transition near 360 nm is strong and negative. The corresponding bands seen in the C isomer follow this pattern, but with opposite signs. Finally, at still higher energy the bands are again of the same sign. The latter transitions are assigned to charge-transfer transitions, as previously noted.

The following is offered as a simple rationalization of what is clearly a rather complicated spectroscopic problem. We will use a descending symmetry approach starting with O_h symmetry and begin by noting that the meridional isomers of these bis(N,O$_2$) complexes have approximately D_{2d} symmetry if the geometry is idealized and the carboxylate and phenolate ligands are viewed as equivalent. Shown below is a sketch viewed down the nitrogen axis (one of the 4-fold axes of the parent octahedron) for this D_{2d} symmetry complex, which is not optically active (solid lines are above, dashed lines below). When a distinction is made between the two oxygen atoms (carboxylate and phenolate) the metal center becomes chiral, generating the C and A isomers. These now have



O′ = phenolate oxygen; O = carboxylate oxygen

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only C_2 symmetry, with the S_4 symmetry operation factored out of the parent D_{2d} structure. In the O_h group, the characters for the S_4 operation of the O_h representations are +1 for T_{1g} and −1 for T_{2g}. A perturbation of the symmetry from O_h by removal of the S_4 operation therefore predicts that the low energy manifold transition should generate CD transitions with the same signs for both the **A** and **C** isomers, while the high energy manifold should generate transitions of opposite sign. This is consistent with the observed spectra.

Conclusion

Diastereomeric (**A** and **C**) chromic complexes of the chiral ligand (*S*)-desferriferrithiocin have been synthesized, separated, and fully characterized. Previous studies have shown that for chiral ligands such as enterobactin or ferrichrome the synthesis of the enantiomeric ligand causes the preferred metal ion chirality also to be enantiomeric. For instance, microbial discrimination between natural Δ-ferric enterobactin and the synthetic Λ-ferric enantioenterobactin really involves a response to two changes of chirality: the ligand structure and metal ion coordination geometry. In principle the response to these two changes cannot be separated. The cobaltic and chromic complexes are pairs of two diastereomeric isomers **A** and **C** in which the ligand chirality remains unchanged. With these complexes the effect of only the metal ion coordination chirality for siderophore-related iron transport can be probed.

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Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond distances and angles, and root-mean-square amplitudes of thermal vibration, and two fully labeled plots of **2** and **3** (21 pages); listing of calculated and observed structure factor amplitudes for **2** and **3** (95 pages). Ordering information is given on any current masthead page.

Main-Group–Organotransition-Metal Chemistry: The Cyclopentadienylchromium Polyiodides Including $[(C_5Me_5)_2Cr_2I_3^+]_2[I_{16}^{2-}]$

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Contribution from the School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. *Received June 1, 1989*

Abstract: The reaction of $[Cp^*Cr(CO)_2]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and I_2 affords a compound of the empirical formula Cp^*CrI_3 (**2**). Single-crystal X-ray diffraction shows **2** to be a polymer, $\{[Cp^*CrI(\mu\text{-}I)]_2\cdot[Cp^*Cr(I_3)(\mu\text{-}I)]_2\}_n$ [monoclinic $P2_1/c$; a = 15.658 (2), b = 8.504 (1), c = 23.242 (4) Å; β = 102.48 (1)°; V = 3021.7 (9) Å^3; Z = 2; ρ_{calc} = 2.497 g cm^{-3}; 3014 observed reflections $I > 2.58\sigma(I)$; R = 0.039, R_w = 0.041]. ^{1}H NMR studies show that in chlorinated solvents **2** dissociates into $[Cp^*CrI(\mu\text{-}I)]_2$ (**1**), the latter of which can be prepared by reduction of **2** with Zn/Hg. Treatment of **2** with high concentrations of I_2 (I/Cr of >6) gives $Cp^*CrI_{5.5}$ (**3**), which is formulated as $[Cp^*_2Cr_2(\mu\text{-}I)_3]_2[I_{16}]$ [monoclinic, $P2_1/c$; a = 14.744 (2), b = 22.864 (4), c = 23.267 (5) Å; β = 93.77 (2)°; V = 7827 (4) Å^3, Z = 4; ρ_{calc} = 3.005 g cm^{-3}; 6153 observed reflections $I > 2.58\sigma(I)$; R = 0.054, R_w = 0.063]. The cation exhibits a short Cr–Cr distance of 3.00 (1) Å indicative of Cr(III)–Cr(III) bonding. This cation is imbedded within a three-dimensional polyiodide lattice based upon I_{16}^{2-} subunits. The I_{16}^{2-} cluster is comprised of an I_2-linked pair of roughly planar $(I_2)_3I^-$ subunits.

It is well-known that very few inorganic transition-metal compounds can be dissolved intact in noncoordinating solvents. The solution chemistry of inorganic fragments can, however, be studied by using solubilizing organic coligands. The cyclopentadienyl (Cp = C_5H_5) ligands are particularly ideal in this regard since most Cp complexes are soluble in nonpolar solvents and the Cp–M bond is very robust. The solubility characteristics, as well as the redox properties, can be further modified through the use of alkyl substituents on the Cp ligand.

In exploring the chemistry of such organic-solubilized inorganic fragments, we and others have focused on compounds of the type $[CpME_n]_m$ where E is a main-group atom such as sulfur,[1] oxygen,[2] or phosphorus.[3] This class of CpM–main-group compounds is quite extensive for the chlorides and bromides,[4] but the iodides have received little attention. Iodine and iodides exhibit extensive Lewis acid–base chemistry, and with the large van der Waals radius for iodide (2.15 Å),[5] organometallic iodides might be expected to adopt extended interactions in the solid state. Indeed, "Cp^*IrI_3" ($Cp^* = C_5Me_5$) is a one-dimensional polymer comprised of $[Cp^*Ir(\mu\text{-}I)I]_2$ subunits linked by I_2 molecules that interact with terminal iodo ligands.[6] Likewise, $Pt(I_2)I[C_6H_3(CH_2NMe_2)_2]$ contains an infinite chain of molecules with $I_2\cdots I^-$ ($\mu\text{-}I_3^-$) linkages.[7]

The present study of cyclopentadienylchromium iodides grew out our search for organometallic electron *acceptors*.[8] We had

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