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Coordination Chemistry of Microbial Iron Transport Compounds. 14. Isolation and Structural Characterization of *trans*-Tris(benzohydroxamato)chromium(III)-2-(2-Propanol)[1]

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The isolation of crystalline solids of the cis and trans isomers of tris(benzohydroxamato)chromium(III), $Cr(benz)_3$, is reported. The structure of the bis(isopropyl alcohol) adduct of the trans isomer has been determined by three-dimensional single-crystal X-ray diffraction using automated counter methods. The spectroscopic assignment of geometric configuration is confirmed. The trans complex is a trigonally distorted octahedron. The twist angle (the projection of the top trigonal face onto the bottom) is 47.4 (1)° for $Cr(benz)_3$ compared with 35.7 (3)° for the analogous ferric complex; these are 60 and 0° for octahedral and trigonal-prismatic structures, respectively. The Cr–O bond lengths average 1.960 (4) and 1.984 (5) Å for the *N*-hydroxyl and carbonyl oxygens, while the corresponding distances in the ferric complex are 1.98 (1) and 2.06 (2) Å. The more nearly octahedral geometry of the chromic complex is ascribed to ligand field stabilization. The O–Cr–O and O–Fe–O chelate angles average 81.0 (2) and 78.7 (5)°, respectively. The trans chromic complex is presumably a model structure for the trans chromic complex of rhodotorulic acid. Green crystals of *trans*-$Cr(benz)_3{\cdot}2(CH_3)_2CH(OH)$ conform to space group $P\bar{1}$ with $a = 10.792$ (2) Å, $b = 11.242$ (2) Å, $c = 14.148$ (6) Å, $\alpha = 77.71$ (2)°, $\beta = 66.16$ (2)°, $\gamma = 71.85$ (1)°, $V = 1484$ (3) Å^3, $Z = 2$, $\rho_{calcd} = 1.299$ g cm^{-3}, and $\rho_{obsd} = 1.298$ g cm^{-3}. The structure was solved by direct phasing methods followed by full-matrix least-squares and Fourier techniques. In the final refinement with all nonhydrogen atoms given anisotropic thermal parameters, the 3206 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 5.0\%$ and $R_w = 6.9\%$.

Introduction

The siderophores are low molecular weight compounds which are manufactured by microbes in order to facilitate the uptake of ferric iron.[3,4] Replacing the ferric ion (a high-spin d^5 system) by the chromic ion (d^3) produces inert complexes which may be used as powerful biological probes in studying the iron transport mechanism in living microbes. Furthermore, the absorption and circular dichroism spectra of these complexes can be used to determine both their geometries and absolute configurations.[5-7]

Tris(benzohydroxamato)chromium(III) was originally prepared as a simple model for chromium complexes of the trihydroxamate siderophores.[5] Unlike tris(benzohydroxamato)iron(III), which crystallizes in the cis geometry, the chromic complex was found to exist in two geometrical isomers in solution. These isomers have been separated by chromatographic techniques and characterized in solution as cis and trans. The geometries of these isomers were assigned on the basis of their chromatographic and spectroscopic properties, where the trans geometry was assigned to the less polar isomer with the greater R_f value.[6] We have now isolated the two geometric isomers of tris(benzohydroxamato)chromium(III) in pure solid forms. The trans isomer was recrystallized from a 2-propanol/heptane mixture, and its X-ray structural determination confirms the original assignment of its geometry.

High-spin ferric ion and chromic ion are within 0.03 Å in ionic radius.[8] The geometries of the chromic complexes are of interest both to characterize the coordination sites of the siderophore complexes and to determine the fundamentals of the coordination chemistry of the hydroxamate transition-metal complexes, including the degree to which chromic complexes mimic the naturally occurring ferric siderophores. We have recently reported the characterization of the complexes formed by rhodotorulic acid, a dihydroxamate siderophore.[9,10] One of the chromic complexes has been assigned a Δ-trans geometry on the basis of its spectroscopic properties in comparison to those of model complexes, including that described in this paper.

We report here the isolation of the geometric isomers of tris(benzohydroxamato)chromium(III) and the single-crystal structural analysis of the complex *trans*-tris(benzohydroxamato)chromium(III)-2-(2-propanol).

Experimental Section

Materials. Analytical grade solvents were used throughout the preparations. The tetrahydrofuran adduct of chromic chloride $CrCl_3{\cdot}3THF$ was prepared by literature methods[11] and protected from moisture. Sodium benzohydroxamate was prepared from hydroxylamine and ethyl benzoate in the presence of excess sodium methoxide.

Microanalyses. Microanalyses were performed by the microanalytical laboratory of the Department of Chemistry, University of California, Berkeley.

Physical Measurements. Visible absorption spectra were measured with a Cary Model 118 UV-vis spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer in KBr pellets or as Nujol mulls between KBr disks.

Isomer Separations. The cis and trans geometric isomers of tris(benzohydroxamato)chromium(III) were originally separated in solution on silica gel using a chloroform/methanol solution, in which both isomers isomerize within a few hours.[5] The two isomers were separated during this work by extracting the cis isomer into chloroform, leaving the chloroform-insoluble trans isomer behind.

The tetrahydrofuran adduct of $CrCl_3$, 11.2 g (30 mmol), and sodium benzohydroxamate, 14.2 g (90 mmol), were heated under reflux in acetone solution (500 mL) in the dark for 4 h. The volume of the solution was reduced to about 100 mL, and chloroform (1 L) was added. The mixture was then transferred to a separatory funnel and extracted with 1 L of water. The trans isomer, which is insoluble in chloroform, precipitated and was removed by filtration, washed with water, and dried in vacuo over P_2O_5. The chloroform layer, containing the chloroform-soluble cis isomer, was further extracted with water and dried over anhydrous Na_2SO_4. The volume of the solvent was reduced to 20 mL, and the cis isomer was precipitated by the addition of petroleum ether.

The cis isomer is quite stable toward isomerization in chloroform, some other halocarbons, and dry ketones and very unstable in alcohols, while the trans isomer is stable in alcohols. Both isomers are unstable toward isomerization in a chloroform/methanol mixture. The cis isomer can be quantitatively converted to trans by eluting a chloroform solution of the cis isomer through a silica gel column, allowing the solvent to evaporate completely, and then washing the column with methanol.

The trans isomer was recrystallized from a 2-propanol/heptane mixture as the disolvated species, mp 210 °C dec. Anal. Calcd for $Cr(C_7H_6NO_2)_3{\cdot}2C_3H_8O$: C, 55.01; H, 5.94; N, 7.17. Found: C, 55.35; H, 5.90; N, 7.19. Absorption spectrum (methanol solution) [λ_{max}, nm (ϵ)]: 602 (83.9), 400 (112).

The cis isomer decomposes slowly above 240 °C. Absorption spectrum (chloroform solution) [λ_{max}, nm (ϵ)]: 588 (82.1), 418 (127).

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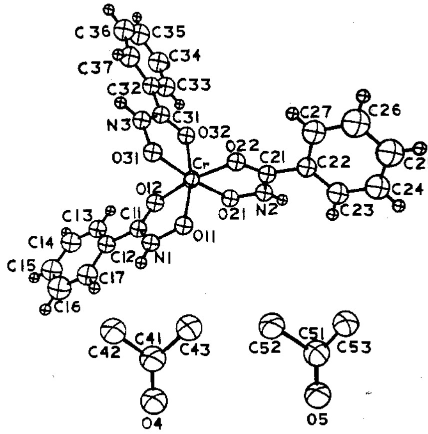

Figure 1. An ORTEP drawing of *trans*-Cr(benz)$_3$ looking down the molecular pseudo-threefold axis, with the numbering scheme of the atoms including the 2-propanol molecules, whose orientations in the figure are unrelated to the chromium complex.

Both the unsolvated *cis*- and *trans*-Cr(benz)$_3$ complexes show similar infrared spectra throughout the 4000–400-cm^{-1} region, with no difference from that reported previously for the mixture of both isomers. The Fe(benz)$_3$ complex, which crystallizes in the cis geometry, also has a similar infrared spectrum from 4000 to 600 cm^{-1}, with a shift in band positions in the 600–400-cm^{-1} region. This difference is attributed to the difference in twist angles between the Cr and Fe complexes, described later.

Unit Cell and Diffraction Data

Preliminary cell dimensions were obtained by the program SEARCH[12] to obtain the positions of 25 reflections. Crystal data, obtained by a least-squares fit to the setting angles of these 25 accurately centered reflections, are given in Table I.

Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer controlled by a PDP-8/E computer, using monochromatic Mo Kα radiation. The intensities of all unique reflections ($+h$, $\pm k$, $\pm l$) with $3° < 2\theta < 50°$ were measured using the θ–2θ scan technique. The θ scan angle was calculated as $(0.60 + 0.35 \tan \theta)°$, and an aperture with a height of 4 mm and a variable width [width (mm) = $2.50 + 0.50 \tan \theta$] was located 173 mm from the crystal. For each reflection the scan angle was extended 25% on either side to estimate the background count. The scan time was variable, with a maximum of 80 s. The intensity of a standard reflection, monitored every 5400 s of X-ray exposure, showed no significant fluctuations. Three orientation standard reflections were monitored after every 50 reflections, and a new orientation matrix was calculated if the setting angles had changed by more than 0.1° in any axis. An attenuator decreasing the intensity of the diffracted beam by a factor of 18.17 was inserted into the beam when the prescan indicated an intensity too high for accurate counting ($I > 50\,000$ counts/s).

The 3453 data were reduced to F^2 and $\sigma(F^2)$ as previously described,[12,13] with modifications to account for the variable scan speed. The parameter p, introduced to prevent overweighting of the strong reflections,[14] was set at 0.04. Lorentz and polarization corrections were made, but neither decomposition nor absorption corrections were considered necessary (μ = 4.15 cm^{-1}). The crystal density was determined by flotation in CCl$_4$/cyclohexane to be 1.298 (5) g cm^{-3}; that calculated for 2 formula units/cell was 1.299 g cm^{-3}.

Table I. Summary of Crystal Data for $Cr(benz)_3\cdot 2(CH_3)_2CH(OH)$

mol formula	$Cr(C_6H_5\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{|}{N}}H)_3\cdot 2(CH_3)_2CH(OH)$
mol wt	460.39
space group	$P\bar{1}$
a^a	10.792 (2) Å
b^a	11.242 (2) Å
c^a	14.146 (6) Å
α^a	77.71 (2)°
β^a	66.16 (2)°
γ^a	71.85 (1)°
cell vol	1484 (3) Å^3
formula units/cell, Z	2
calcd density	1.299 g cm^{-3}
obsd density	1.298 g cm^{-3}
cryst dimensions	0.58 × 0.57 × 0.21 mm
abs coeff, μ	4.15 cm^{-1}

[a] Ambient temperature of 23 °C. Mo Kα_1 radiation, λ 0.709 26 Å.

Solution and Refinement of the Structure

Solution of the phase problem was accomplished by use of the MULTAN[12] program series, using the 300 highest E values. From the E map with the highest figure of merit, the positions of the chromium atom and all but a few of the benzohydroxamate atoms were located. The remainder of the structure was determined and refined using standard difference Fourier and least-squares techniques. Full-matrix least-squares refinements were carried out using the 3206 reflections with $F_o^2 > 3\sigma(F_o^2)$.[15–18] The phenyl hydrogen atoms were inserted in calculated positions such that the C–H bond bisected the C–C–C angle of the ring, the C–H bond was 0.95 Å, and the isotropic temperature factor was 8.0 Å^2. Correction for the methyl hydrogen atoms of the 2-propanol molecules assuming freely rotating groups was carried out using the program ROTOR.[12] Hydrogen atoms on the nitrogens were located in a difference Fourier map and included as fixed atoms with an isotropic temperature factor of 8.0 Å^2.

Final refinement using anisotropic temperature factors for all nonhydrogen atoms led to convergence with R = 5.0%, R_w = 6.8%, and the error in an observation of unit weight of 2.4.[12]

The largest peaks in the final difference Fourier map (0.47 and 0.43 e Å^{-3}) are close to the 2-propanol carbons (1.28 and 1.45 Å) and seem the result of a slight disorder of the solvent molecules. Table II gives the positional and thermal parameters of the nonhydrogen atoms, and Table III gives the positional parameters calculated for the hydrogen atoms.

Description of the Structure

A perspective view of the structure with the numbering scheme used is shown in Figure 1, and a stereoview is given in Figure 2. Each molecule contains three five-membered chelate rings composed of the chromium atom and a hydroxamate group. The rings are arranged in the trans geometry with the chromium atom coordinated in an octahedral array to six oxygen atoms. The chromium(III) complex is neutral, and a difference Fourier map late in the refinement clearly showed the hydrogens located on the nitrogens of the hydroxamate groups. Bond lengths and angles are given in

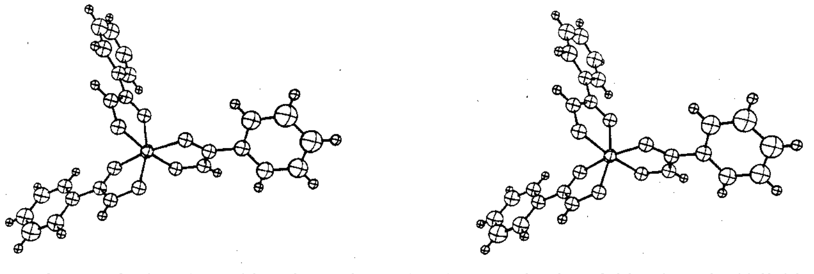

Figure 2. A stereoscopic view of *trans*-Cr(benz)$_3$ looking down the molecular pseudo-threefold axis. The individual atoms are drawn at 30% probability contours of the thermal motion.

Table II. Positional and Thermal Parameters ($\times 10^4$) for the Nonhydrogen Atoms in $Cr(benz)_3$

atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.44993 (6)	0.83970 (5)	0.87317 (5)	113.5 (8)	71.3 (6)	58.7 (5)	−21.6 (5)	−37.2 (5)	−5.9 (4)
O_{11}	0.4940 (2)	0.8333 (2)	0.9960 (2)	115 (3)	81 (3)	63 (2)	−9 (2)	−41 (2)	−11 (2)
O_{12}	0.2663 (3)	0.9352 (2)	0.9620 (2)	114 (3)	99 (3)	69 (2)	−18 (2)	−44 (2)	−19 (2)
O_{21}	0.3938 (3)	0.6817 (2)	0.9115 (2)	115 (3)	80 (3)	69 (2)	−25 (2)	−21 (2)	−10 (2)
O_{22}	0.6342 (3)	0.7247 (2)	0.8025 (2)	121 (3)	70 (3)	64 (2)	−24 (2)	−28 (2)	−5 (2)
O_{31}	0.5176 (3)	0.9929 (2)	0.8167 (2)	138 (4)	78 (3)	71 (2)	−30 (3)	−58 (2)	0 (2)
O_{32}	0.3901 (3)	0.8898 (2)	0.7516 (2)	138 (4)	80 (3)	63 (2)	−34 (2)	−46 (2)	−2 (2)
O_4	0.4291 (3)	0.3604 (2)	0.8767 (2)	123 (4)	102 (3)	94 (2)	−27 (3)	−46 (2)	0 (2)
O_5	0.4277 (4)	0.7303 (4)	0.3185 (3)	289 (7)	164 (5)	121 (3)	−134 (5)	−5 (4)	−25 (3)
N_1	0.3866 (3)	0.9175 (3)	1.0612 (2)	111 (4)	78 (3)	59 (2)	−22 (3)	−35 (2)	−7 (2)
N_2	0.5087 (3)	0.5844 (3)	0.8740 (2)	125 (4)	71 (3)	67 (2)	−25 (3)	−26 (3)	−10 (2)
N_3	0.4738 (3)	1.0540 (3)	0.7371 (2)	132 (4)	81 (3)	60 (2)	−26 (3)	−42 (3)	−3 (2)
C_{11}	0.2733 (4)	0.9663 (3)	1.0410 (3)	102 (5)	76 (4)	63 (3)	−27 (3)	−32 (3)	−3 (2)
C_{12}	0.1534 (4)	1.0570 (4)	1.1078 (3)	100 (5)	94 (4)	74 (3)	−32 (3)	−29 (3)	−15 (3)
C_{13}	0.0363 (4)	1.1075 (4)	1.0803 (4)	117 (5)	114 (5)	96 (4)	−21 (4)	−42 (4)	−26 (3)
C_{14}	−0.0774 (4)	1.1927 (5)	1.1401 (4)	106 (6)	142 (6)	132 (5)	−15 (5)	−46 (4)	−31 (4)
C_{15}	−0.0750 (5)	1.2268 (5)	1.2266 (4)	118 (6)	172 (7)	118 (5)	−15 (5)	−16 (4)	−59 (5)
C_{16}	0.0401 (5)	1.1784 (6)	1.2533 (4)	152 (7)	230 (8)	104 (4)	−22 (6)	−30 (5)	−82 (5)
C_{17}	0.1539 (4)	1.0933 (5)	1.1946 (4)	109 (5)	188 (7)	90 (4)	−11 (5)	−32 (4)	−53 (4)
C_{21}	0.6293 (4)	0.6101 (3)	0.8198 (3)	121 (5)	77 (4)	52 (3)	−25 (3)	−28 (3)	−5 (2)
C_{22}	0.7577 (4)	0.5069 (3)	0.7834 (3)	131 (5)	79 (4)	68 (3)	−26 (4)	−29 (3)	−9 (3)
C_{23}	0.7713 (5)	0.3887 (4)	0.8376 (4)	142 (6)	88 (4)	92 (4)	−19 (4)	−32 (4)	−3 (3)
C_{24}	0.8937 (6)	0.2961 (4)	0.8027 (5)	175 (8)	90 (5)	138 (5)	−9 (5)	−48 (5)	8 (4)
C_{25}	1.0019 (5)	0.3201 (5)	0.7148 (5)	143 (7)	114 (6)	163 (6)	7 (5)	−20 (5)	−28 (5)
C_{26}	0.9886 (4)	0.4359 (5)	0.6609 (5)	148 (7)	146 (7)	133 (5)	−13 (5)	7 (5)	−12 (5)
C_{27}	0.8688 (5)	0.5297 (4)	0.6950 (4)	141 (6)	107 (5)	108 (4)	−22 (4)	−6 (4)	−1 (4)
C_{31}	0.4092 (4)	0.9966 (3)	0.7064 (3)	104 (5)	83 (4)	56 (3)	−9 (3)	−29 (3)	−15 (3)
C_{32}	0.3566 (4)	1.0571 (4)	0.6216 (3)	127 (5)	83 (4)	56 (3)	−5 (4)	−31 (3)	−11 (3)
C_{33}	0.2638 (5)	1.0098 (4)	0.6074 (4)	211 (8)	118 (5)	98 (4)	−32 (5)	−92 (5)	0 (3)
C_{34}	0.2162 (6)	1.0593 (5)	0.5270 (5)	248 (10)	157 (7)	131 (5)	−36 (6)	−127 (6)	−8 (5)
C_{35}	0.2634 (7)	1.1538 (5)	0.4592 (4)	259 (10)	146 (7)	89 (4)	5 (7)	−96 (6)	−10 (4)
C_{36}	0.3526 (6)	1.2044 (5)	0.4724 (4)	226 (9)	127 (6)	75 (4)	−12 (6)	−57 (5)	8 (3)
C_{37}	0.3998 (5)	1.1581 (4)	0.5541 (3)	167 (6)	120 (5)	72 (3)	−28 (5)	−41 (4)	−5 (3)
C_{41}	0.2842 (7)	0.3722 (8)	0.8982 (5)	192 (10)	390 (14)	102 (5)	−29 (9)	−85 (6)	−39 (7)
C_{42}	0.1973 (7)	0.4091 (8)	0.9989 (6)	168 (9)	376 (14)	134 (7)	−31 (9)	−64 (6)	−19 (8)
C_{43}	0.2424 (10)	0.397 (2)	0.829 (1)	196 (14)	1830 (80)	343 (17)	190 (30)	−120 (13)	−620 (30)
C_{51}	0.3115 (9)	0.6851 (9)	0.3805 (6)	331 (15)	216 (11)	146 (7)	−123 (11)	13 (8)	−27 (7)
C_{52}	0.356 (2)	0.578 (2)	0.435 (1)	830 (50)	660 (40)	420 (30)	−500 (40)	−180 (30)	310 (30)
C_{53}	0.211 (2)	0.770 (2)	0.436 (2)	560 (40)	740 (40)	550 (30)	−390 (30)	220 (30)	−460 (30)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Positional Parameters for the Fixed Hydrogen Atoms[a]

atom	x	y	z
H_{13}	0.034	1.082	1.020
H_{14}	−0.157	1.227	1.122
H_{15}	−0.157	1.286	1.267
H_{16}	0.039	1.201	1.316
H_{17}	0.232	1.056	1.215
H_{23}	0.694	0.370	0.898
H_{24}	0.898	0.212	0.841
H_{25}	1.091	0.250	0.694
H_{26}	1.062	0.450	0.593
H_{27}	0.860	0.615	0.656
H_{33}	0.235	0.937	0.652
H_{34}	0.143	1.031	0.521
H_{35}	0.239	1.185	0.400
H_{36}	0.382	1.276	0.423
H_{37}	0.465	1.192	0.563
H_{41}	0.279	0.442	0.897
$H(N_1)$	0.407	0.933	1.113
$H(N_2)$	0.479	0.505	0.888
$H(N_3)$	0.500	1.136	0.699

[a] The subscript of each hydrogen atom is the same as that of the carbon atom to which it is attached. $B_{iso} = 8.0$ Å^2.

Tables IV and V, respectively. Figure 3, a stereoview of four unit cells looking down the molecular pseudo-threefold axis, shows the approximate hexagonal close packing of the molecules. Hydrogen bonding involving the 2-propanol molecules occurs between O_4 and O_{11}, O_5 and N_3, O_4 and O_5, and O_4 and N_2 with intermolecular distances of 2.662 (4), 2.783 (5), 2.796 (5) and 2.891 (4) Å, respectively.

Table IV. Bond Distances (Å) for $Cr(benz)_3$

$Cr-O_{11}$	1.960 (2)	N_1-C_{11}	1.294 (4)
$Cr-O_{21}$	1.952 (2)	N_2-C_{21}	1.303 (5)
$Cr-O_{31}$	1.966 (2)	N_3-C_{31}	1.318 (5)
mean[a]	1.960 (4)	mean	1.305 (7)
$Cr-O_{12}$	1.974 (3)	$C_{11}-C_{12}$	1.486 (5)
$Cr-O_{22}$	1.991 (2)	$C_{21}-C_{22}$	1.485 (5)
$Cr-O_{32}$	1.988 (2)	$C_{31}-C_{32}$	1.478 (5)
mean	1.984 (5)	mean	1.483 (2)
$O_{11}-N_1$	1.384 (4)	mean phenyl C–C	1.373 (3)
$O_{21}-N_2$	1.374 (4)		
$O_{31}-N_3$	1.364 (4)	$C_{41}-C_{42}$	1.418 (9)
mean	1.374 (6)	$C_{41}-C_{43}$	1.181 (14)
$O_{12}-C_{11}$	1.276 (4)	$C_{41}-O_4$	1.435 (7)
$O_{22}-C_{21}$	1.273 (4)	$C_{51}-C_{52}$	1.352 (16)
$O_{32}-C_{31}$	1.271 (4)	$C_{51}-C_{53}$	1.295 (15)
mean	1.273 (2)	$C_{51}-O_5$	1.385 (8)

[a] The standard deviation of the mean is given by $\sigma^2(\bar{x}) = \Sigma(x_i - \bar{x})^2/[n(n-1)]$.

Discussion

Tris(benzohydroxamato)chromium(III), $Cr(benz)_3$, is the first chromic complex of a hydroxamic acid derivative whose structure has been determined by X-ray diffraction. The structures of the cis isomer of $Fe(benz)_3$,[19] (ethylenediamine)zinc(II) benzohydroxamate,[20] and various Sn(IV) complexes of hydroxamic acid derivatives[21-25] have been reported. The uncomplexed acid appears in the structure of acetohydroxamic acid monohydrate[26] and is present as free benzohydroxamic acid in the zinc complex just mentioned.[20]

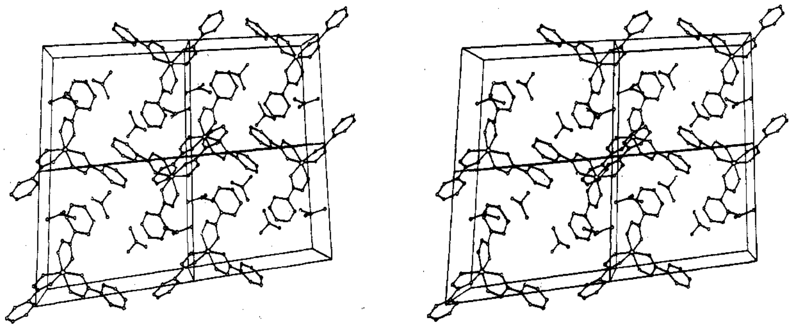

Figure 3. A stereoscopic packing diagram of *trans*-Cr(benz)$_3$ showing four unit cells down the molecular pseudo-threefold axis. The individual atoms are drawn at 30% probability contours of the thermal motion.

Table V. Bond Angles (deg) for Cr(benz)$_3$

O_{11}–Cr–O_{12}	81.1 (1)	O_{12}–C_{11}–N_1	118.6 (3)
O_{21}–Cr–O_{22}	81.1 (1)	O_{22}–C_{21}–N_2	118.2 (3)
O_{31}–Cr–O_{32}	80.7 (1)	O_{32}–C_{31}–N_3	119.5 (3)
O_{11}–Cr–O_{32}	166.4 (1)	O_{12}–C_{11}–C_{12}	120.2 (3)
O_{12}–Cr–O_{22}	171.3 (1)	N_1–C_{11}–C_{12}	121.2 (3)
O_{21}–Cr–O_{31}	172.8 (1)	O_{22}–C_{21}–C_{22}	121.5 (3)
O_{11}–Cr–O_{21}	96.8 (1)	N_2–C_{21}–C_{22}	120.2 (3)
O_{11}–Cr–O_{22}	92.8 (1)	O_{32}–C_{31}–C_{32}	120.2 (3)
O_{11}–Cr–O_{31}	88.8 (1)	N_3–C_{31}–C_{32}	120.3 (3)
O_{12}–Cr–O_{21}	93.4 (1)	C_{11}–C_{12}–C_{13}	118.0 (4)
O_{12}–Cr–O_{31}	91.9 (1)	C_{11}–C_{12}–C_{17}	123.0 (4)
O_{12}–Cr–O_{32}	90.5 (1)	C_{21}–C_{22}–C_{23}	121.7 (4)
O_{21}–Cr–O_{32}	94.3 (1)	C_{21}–C_{22}–C_{27}	119.7 (4)
O_{22}–Cr–O_{31}	94.2 (1)	C_{31}–C_{32}–C_{33}	118.7 (4)
O_{22}–Cr–O_{32}	96.6 (1)	C_{31}–C_{32}–C_{37}	122.9 (4)
Cr–O_{11}–N_1	108.2 (2)	mean phenyl C–C–C	120.0 (2)
Cr–O_{21}–N_2	109.6 (2)		
Cr–O_{31}–N_3	110.3 (2)	C_{24}–C_{41}–C_{43}	121.8 (8)
Cr–O_{12}–C_{11}	111.7 (2)	C_{42}–C_{41}–O_4	112.1 (6)
Cr–O_{22}–C_{21}	112.4 (2)	C_{43}–C_{41}–O_4	119.8 (9)
Cr–O_{32}–C_{31}	111.9 (2)	C_{52}–C_{51}–C_{53}	115.3 (14)
O_{11}–N_1–C_{11}	118.1 (3)	C_{52}–C_{51}–O_5	107.4 (10)
O_{21}–N_2–C_{21}	118.5 (3)	C_{53}–C_{51}–O_5	112.0 (9)
O_{31}–N_3–C_{31}	116.8 (3)		

While the ferric hydroxamates, both Fe(benz)$_3$[19] and the siderophores,[27–30] crystallize as the cis isomers, the isomer of Cr(benz)$_3$ used in this study occurs in the previously unobserved trans geometry.

The average metal–(*N*-hydroxyl oxygen) distance for Cr(benz)$_3$ is 1.960 (4) Å while the average metal–(carbonyl oxygen) distance is 1.984 (5) Å. These distances are 1.98 (1) and 2.06 (1) Å for Fe(benz)$_3$, 1.98 (2) and 2.04 (2) Å for ferrichrome A,[27] and 1.95 (2) and 2.01 (2) Å for ferrioxamine E.[28] The longer M–O distances in the ferric complexes are consistent with the slightly larger ionic radius of Fe(III),[8] while the difference between the two types of M–O bond lengths (averages of 1.97 (1) and 2.04 (1) Å) shows that a greater portion of charge resides on the *N*-hydroxyl oxygen atoms than on the carbonyl oxygen atoms. The magnitude of the difference between the two types of bond lengths is considerably larger in the ferric than in the chromic complexes and can be attributed to a crystal-field effect in which a pure octahedral symmetry is more favorable for the chromic complex. To analyze this effect it is of interest to further compare the coordination geometries of Fe(benz)$_3$ and Cr(benz)$_3$.

By looking down the threefold axis in Fe(benz)$_3$ and the pseudo-threefold axis in Cr(benz)$_3$ the coordination octahedra can be visualized as two trigonal faces connected by two kinds of edges (Figure 4). The shortest O–O distances occur between oxygens of the same hydroxamate group, the longest occur between oxygens of different hydroxamates, and intermediate distances occur in the edges of the trigonal faces.

Two theoretical models have been presented for the detailed analysis of tris-chelate geometries.[31,32] The ligand bite (the ratio of the ring O–O distances to the M–O distance) and the twist angle are useful in describing the variations from octahedral to trigonal-prismatic geometry. These structural parameters are compared in Table VI. An empirical relation between the ligand bite, *b*, and the twist angle has been presented: twist angle = $(-73.9 + 94.10b)°$.[33] Although hydroxamate complexes were not used in obtaining this equation, the observed and calculated twist angles for Cr(benz)$_3$ are in good agreement (47.4, 48.2°). On the other hand, the values for Fe(benz)$_3$ are in poor agreement (35.7, 43.9°). This large discrepancy is partially due to the 4° angle between the trigonal faces. This angle is very near 0° in Cr(benz)$_3$, as it is in most six-coordinate structures.[34]

The larger size of the ferric ion is expected to increase the distortions of the metal–hydroxamate ring, forcing the twist angle to decrease. However, as in a similar study of chromic and ferric catecholate structures,[33] the difference in M–O bond length is not large enough to account for the 12° difference in twist angle, which must be attributed to a difference in electronic configuration. A theoretical study of the difference in crystal field stabilization energy (ΔCFSE) between trig-

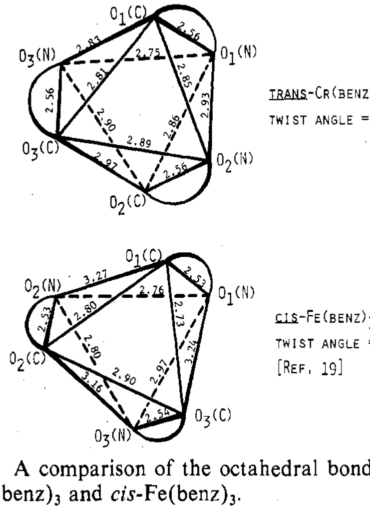

Figure 4. A comparison of the octahedral bonding geometries of *trans*-Cr(benz)$_3$ and *cis*-Fe(benz)$_3$.

Table VI. Comparison of Structural Parameters for *trans*-Cr(benz)$_3$ and *cis*-Fe(benz)$_3$

parameter	Cr(benz)$_3$	Fe(benz)$_3$[a]
mean M–OC dist, Å[b]	1.984 (5)	2.06 (2)
mean M–ON dist, Å	1.960 (4)	1.98 (1)
mean O–O ring dist, Å	2.561 (2)	2.530 (4)
mean ring O–M–O angle, deg	81.0 (2)	78.8 (5)
ligand bite[c]	1.30	1.25
trigonal twist angle, deg[c]	47.4 (1)	35.7 (3)
calcd twist angle, deg[d]	48.2	43.9

[a] Reference 19. [b] The standard deviations in the means are computed from the variance, $\sigma^2(\bar{x}) = \Sigma(x - \bar{x})^2/[n(n-1)]$. [c] Ratio of O–O distance to M–O distance; see ref 34. [d] From the linear correlation given in the text; see ref 33.

Table VII. Least-Squares Planes through the Hydroxamate Chelate Rings[a]

plane	atoms in plane	*A*	*B*	*C*	*D*
1	$O_{11}, N_1, C_{11}, O_{12}$	4.616	8.993	−3.984	5.806
2	$O_{21}, N_2, C_{21}, O_{22}$	5.955	1.759	13.871	16.185
3	$O_{31}, N_3, C_{31}, O_{32}$	5.947	−3.565	−5.976	−5.342

Δ(1), Å		Δ(2), Å		Δ(3), Å	
O_{11}	−0.0005	O_{21}	0.0017	O_{31}	0.0007
N_1	0.0016	N_2	−0.0051	N_3	−0.0018
C_{11}	−0.0024	C_{21}	0.0069	C_{31}	0.0024
O_{12}	0.0008	O_{22}	−0.0020	O_{32}	−0.0007
Cr	0.343	Cr	0.083	Cr	−0.193
C_{12}	−0.006	C_{22}	0.085	C_{32}	−0.020
$H(N_1)$	0.025	$H(N_2)$	−0.122	$H(N_3)$	0.083

[a] The planes are expressed in the form $Ax + By + Cz + D$, in which x, y, and z are fractional coordinates and D is the distance from the plane to the origin in Å.

onal-prismatic and octahedral geometries has been presented.[34] The value of ΔCFSE for conversion of the ferric complex geometry to that of the chromic complex is estimated from the twist angles to be $0.8Dq$. By following the reasoning used in the catecholate study,[33] a bending force constant may be obtained for this twist. The value found, 0.3 mdyn $Å^{-1}$, is of the same order of magnitude as angle bending force constants determined by IR spectroscopy.[35] The conclusion is the same as that of the catecholate study: The calculated change in CFSE is sufficiently large to account for the differences in twist angles between the chromic and the ferric complexes.

The hydroxamate rings are planar as shown by the least-squares planes given in Table VII. The rather large out-of-plane distance of the chromium atom from one of the planes (0.34 Å) stands out but is similar to what has been observed in the Sn(IV) complex,[23] where metal-to-plane distances of 0.82 and 0.63 Å were reported.

In summary, the trans isomer of tris(benzohydroxamato)chromium(III) conforms to a trigonally distorted octahedral structure. While the chromium–(*N*-hydroxyl oxygen) bond lengths are shorter by 0.02 Å than the chromium–(carbonyl oxygen) bond lengths, this difference is 0.08 Å in the ferric complexes. The trigonal twist angle of the chromic complex [47.4 (1)°] compared to the ferric complex [35.7 (3)°] also is a measure of the relative distortion from octahedral geometry. Both parameters show that the chromic complex is more nearly octahedral, a phenomenon ascribed to ligand field stabilization. These geometries are presumed to correspond to those for the coordination sites in the corresponding siderophore complexes such as the Δ-trans chromic complex of rhodotorulic acid.[9,10]

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Supplementary Material Available: Structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 13: J. V. McArdle, S. R. Sofen, S. R. Cooper, and K. N. Raymond, *Inorg. Chem.*, **17**, 3075 (1978).

(2) U.S.A.I.D. Fellow.

(3) K. N. Raymond, *Adv. Chem. Ser.*, **No. 162**, 33–54 (1977).

(4) J. B. Neilands, Ed., "Microbial Iron Metabolism", Academic Press, New York, 1974.

(5) J. Leong and K. N. Raymond, *J. Am. Chem. Soc.*, **96**, 1757 (1974).

(6) S. Isied, G. Kuo, and K. N. Raymond, *J. Am. Chem. Soc.*, **98**, 1763 (1976).

(7) K. Abu-Dari and K. N. Raymond, *Inorg. Chem.*, **16**, 807 (1977).

(8) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

(9) C. J. Carrano and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 501 (1978).

(10) C. J. Carrano and K. N. Raymond, *J. Am. Chem. Soc.*, **100**, 5371 (1978).

(11) J. P. Collman and E. T. Kittleman, *Inorg. Synth.*, **8**, 149 (1966).

(12) The Enraf-Nonius Fortran system operates the CAD-4 diffractometer. In addition to locally written programs for the CDC 7600, the following programs or modifications were used: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; ORFFE, a function and error program by Busing and Levy; ORTEP 2, by Johnson; ROTOR, a program to handle freely rotating groups; MULTAN, a program series for direct-methods phase determination by Germain, Main, and Woolfson.

(13) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

(14) E. C. Baker, L. D. Brown, and K. N. Raymond, *Inorg. Chem.*, **14**, 1376 (1975).

(15) Definitions of the indicators are $R = \sum|F_o - F_c|/\sum|F_o|$ and $R_w = [\sum w(F_o - F_c)^2/\sum w|F_o|^2]^{1/2}$; the error in an observation of unit weight is $[\sum w(F_o - F_c)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v the number of variables.

(16) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(17) R. F. Stewart, E. T. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(18) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(19) V. H. J. Lindner and S. Gottlicher, *Acta Crystallogr., Sect. B*, **25**, 832 (1969).

(20) S. Gottlicher and P. Ochensreiter, *Chem. Ber.*, **107**, 391 (1974).

(21) P. G. Harrison and T. J. King, *J. Chem. Soc., Dalton Trans.*, 2298 (1974).

(22) T. J. King and P. G. Harrison, *J. Chem. Soc., Chem. Commun.*, 815 (1972).

(23) P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 1414 (1976).

(24) P. G. Harrison, T. J. King, and R. C. Phillips, *J. Chem. Soc., Dalton Trans.*, 2317 (1975).

(25) P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 826 (1975).

(26) B. H. Bracher and W. H. Small, *Acta Crystallogr., Sect. B*, **26**, 1705 (1970).

(27) A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Am. Chem. Soc.*, **88**, 1810 (1966).

(28) D. van der Helm and M. Poling, *J. Am. Chem. Soc.*, **98**, 82 (1976).

(29) E. Hough and D. Rogers, *Biochem. Biophys. Res. Commun.*, **57**, 73 (1974).

(30) R. Norrestam, B. Stensland, and C.-I. Branden, *J. Mol. Biol.*, **99**, 501 (1975).

(31) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).

(32) A. Avdeef and J. P. Fackler, Jr., *Inorg. Chem.*, **14**, 2002 (1975).

(33) K. N. Raymond, S. S. Isied, L. D. Brown, F. R. Fronczek, and J. H. Nibert, *J. Am. Chem. Soc.*, **98**, 1767 (1976).

(34) R. A. D. Wentworth, *Coord. Chem. Rev.*, **9**, 171 (1972–3).

(35) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds", Wiley, New York, 1968.