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Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Coordination Chemistry of Microbial Iron Transport Compounds. 25. Proton-Dependent Cobalt(III) Spin States. Structure of the Sodium Salt of *trans*-Tris(benzohydroximato)cobaltate(III)[1]

KAMAL ABU-DARI, SUSAN J. BARCLAY, PAUL E. RILEY, and KENNETH N. RAYMOND*

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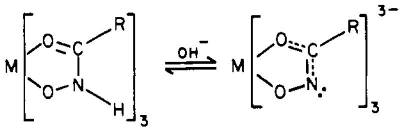
Complexes of cobalt(III) with hydroxamic acids [RC(O)N(OH)R′] are described. Coordination occurs through the two oxygen atoms after the loss of the NOH proton. For tris(hydroxamate) complexes with R′ = alkyl the complexes are low spin; when R′ = H or when R contains an electron-withdrawing group, the complexes are paramagnetic. However, the tris(hydroximato)cobaltate(III) trianion complexes, which result from further deprotonation of the hydroxamate complexes when R′ = H, are low spin. Thus there is a reversible, proton-dependent transition between low- and high-spin states in the hydrox*i*mate and hydrox*a*mate complexes. An unusual feature of the Co(III) complexes is that, while the low-spin hydrox*i*mato $[CoL_3]^{3-}$ complex is thermally stable, the high-spin hydrox*a*mato $[Co(HL)_3]^0$ complex ultimately undergoes an internal redox reaction resulting in oxidation of the ligand by the metal ion. The structure of the (nitrogen deprotonated) trans isomer of tris(benzohydroximato)cobaltate(III), as the salt $Na_3[Co(C_7H_5NO_2)_3]\cdot 8H_2O\cdot C_2H_5OH$, has been determined by single-crystal X-ray diffraction techniques with data obtained by counter methods. The material crystallizes as dark green prisms in the monoclinic space group $P2_1/n$ with a = 10.360 (1) Å, b = 11.118 (2) Å, c = 28.403 (5) Å, β = 93.64 (1)° and is isostructural with the previously reported Cr(III) complex. The Co(III) complex possesses a trans geometry in which the O_C and O_N atoms of one chelate ring are trans to an O_C and an O_N atom of one of the other two chelate rings. The coordination geometry about Co(III) approximates that of a trigonally distorted octahedron. As in the structure of the Cr(III) complex, the lengthening of the C–O bonds and the shortening of the C–N bonds indicate that much of the negative charge on the deprotonated nitrogen atoms is delocalized over the N—C═O portions of the ligands. The calculated (1.47) and measured (1.44 g cm^{-3}) densities are consistent with four formula units of the salt per unit cell. Full-matrix least-squares refinement of the structure with use of the 3906 reflections with $F_o^2 > 3\sigma(F_o^2)$ have converged with R and R_w indices of 0.035 and 0.048, respectively.

Introduction

The siderophores are low molecular weight compounds that are manufactured by microbes to facilitate the uptake of Fe(III).[2] The most common functional groups of the siderophores are the catecholate and hydroxamate moieties—which act as strong bidentate chelating agents. Somewhat recently, we expanded our study of the coordination chemistries of the catecholate and hydrox*a*mate groups to that of the hydrox*i*mate group, which may be derived from the tris(hydroxamate) complex in the presence of strong base.



This work was initiated with the preparation and structural characterization of the cis and trans isomers of the Cr(III) complexes of benzohydroximate ([benz-H]$^{2-}$).[2] The Cr(III) ion was chosen because it forms well-characterized cis and trans complexes with deferriferrioxamine B,[3] rhodotorulic acid,[4] and simple hydroxamate[5] ligands. In contrast, only the cis isomers of siderophore complexes with Fe(III) have been characterized. We now report the synthesis and crystal structure of the *trans*-$[Co(benz\text{-}H)_3]^{3-}$ complex, in which the metal ion is essentially the same size as the octahedrally coordinated Fe(III) ion.[6] An unusual, and we believe unprecedented, feature of the Co(III) complexes is that a low-spin to high-spin conversion takes place upon protonation of the hydrox*i*mato complex to form the neutral hydrox*a*mato complex.

Experimental Section

Materials. Analytical grade solvents and reagents were used as supplied, without additional purification. Sodium benzohydroxamate was prepared as previously reported.[7] Sodium *p*-nitrobenzohydroxamate and sebacodihydroxamic acid were prepared by the same method using ethyl *p*-nitrobenzoate and methyl sebacate, respectively. The L-tyrosinehydroxamic acid was obtained by the method of Bade.[8]

Microanalysis. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley.

Physical Measurements. Visible absorption spectra were measured with a Cary Model 118 UV-visible spectrophotometer. Circular dichroism spectra were measured by using a Jasco-J20 automatic recording spectropolarimeter. Low-temperature magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating-sample magnetometer used with a homogeneous magnetic field produced by a Varian Associates 12-in. electromagnet capable of a maximum field strength of 12.5 kG. A liquid-helium Dewar produced sample temperatures in the range 3.8–80 K, which were measured by a calibrated GaAs diode approximately 1 cm above the sample (~60 mg) in a sample holder machined from a Kel-F rod. The magnetometer was calibrated with $HgCo(NCS)_4$,[9] and the resulting susceptibilities were corrected for underlying diamagnetism.[10] Room-temperature magnetic susceptibility measurements were obtained by using the Gouy technique, and solution measurements were obtained by the NMR method.[11] Electrochemical measurements were performed by using the three-electrode configuration with hanging mercury drop working electrode, platinum wire auxiliary, and saturated calomel reference electrode. Triangular waves were generated by the Princeton Applied

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(1) Previous paper in the series: Wong, G. B.; Kappel, M. J.; Raymond, K. N.; Matzanke, B.; Winkelmann, G. *J. Am. Chem. Soc.* **1983**, *105*, 810.

(2) Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1980**, *19*, 2034 and references therein.

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(4) Carrano, C. J.; Raymond, K. N. *J. Chem. Soc., Chem. Commun.* **1978**, 501. Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5371.

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

(6) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(7) Abu-Dari, K.; Ekstrand, J. D.; Freyberg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 108.

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(9) St. Räde, H. *J. Phys. Chem.* **1973**, *77*, 424.

(10) Mabbs, F. E.; Machin, D. J. "Magnetism and Transition Metal Complexes"; Chapman and Hall: London, 1973.

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Research (PAR) 175 programmer in conjunction with the PAR L73 potentiostat. The scan rate was 100 mV/s. All potentials are reported vs. SCE and are uncorrected for liquid-junction potentials. The solvent used was acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Potentiometric titrations were carried out by using standardized HNO_3 as titrant at 10 °C and 0.1 M ionic strength (KNO_3) in aqueous solution. The pH measurements were made by using a Brinkmann Instruments Model pH-102 digital meter equipped with a glass calomel combination electrode (Sigma).

Syntheses. Tris(benzohydroxamato)cobalt(III). A degassed aqueous solution of sodium cobaltinitrite (6.05 g, 15 mmol) was added quickly to a degassed aqueous solution of sodium benzohydroxamate (7.16 g, 45 mmol). The temperatures of both solutions had previously been adjusted to 22 to 25 °C. The mixture was stirred for about 2 min, and the green precipitate was removed by filtration, washed with small portions of water and Et_2O, and dried in vacuo over P_2O_5. The dried material was stored at −5 °C. The yield is variable, 50–70%. The compound undergoes a sudden, internal oxidation–reduction reaction when heated to about 90 °C, with a resultant sharp change in color from green to pink; it decomposes slowly at room temperature to the pink [Co(II)] material. The IR spectrum of the green Co(III) complex is similar to those of tris(benzohydroxamato)iron(III) and -chromium(III) complexes.

Anal. Calcd for $Co(C_7H_6NO_2)_3 \cdot 1.5H_2O$: C, 51.02; H, 4.28; N, 8.50; Co, 11.92. Found: C, 51.23; H, 3.97; N, 8.50; Co, 11.9.

Cobalt(III) hydroxamato complexes with *p*-nitrobenzohydroxamic acid, *N*-methylbenzohydroxamic acid, L-tyrosinehydroxamic acid, sebacodihydroxamic acid, and deferriferrichrome A have been prepared by similar methods, and the appropriate hydroxamic acid.

Tris(L-tyrosinehydroxamato)cobalt(III). Degassed aqueous solutions of sodium cobaltinitrite (5 mmol) and L-tyrosinehydroxamic acid hydrochloride (15 mmol) were combined. The resultant brown solution was filtered and neutralized with sodium hydroxide solution. The brown precipitate was removed by filtration, washed with small portions of water, and dried over P_2O_5.

Sodium Tris(benzohydroximato)cobaltate(III). Tris(benzohydroxamato)cobalt(III) hydrate, $Co(C_7H_6NO_2)_3 \cdot 1.5H_2$ (4.94 g, 10.0 mmol), was dissolved in degassed aqueous sodium hydroxide solution (60 mL, 2.5 M). The resultant solution was filtered, and the volume was reduced under vacuum. The resultant green precipitate was filtered, washed with a small amount of cold water, and dried in vacuo over P_2O_5.

Anal. Calcd for $Na_3Co(C_7H_5NO_2)_3 \cdot 5H_2O$: C, 40.46; H, 4.04; N, 6.74; Co, 9.45. Found: C, 40.4; H, 3.6; N, 6.4; Co, 9.6.

Other cobalt(III) hydroximate complexes have been obtained similarly. A preparation of the benzohydroximato complex that gave diffraction-quality crystals and that is shown to be exclusively the trans isomer is the following.

Sodium *trans*-[Tris(benzohydroximato)cobaltate(III)]. The parent complex, $Co(C_7H_6NO_2)_3 \cdot 1.5H_2O$ (4.94 g, 10.0 mmol), was dissolved in a degassed aqueous solution of sodium hydroxide (60 mL, 2.5 M). The solution was filtered and concentrated under reduced pressure until it became turbid. It was then heated to ~80 °C, diluted with ethanol (20 mL), and set aside to crystallize. After 2 weeks, dark green prisms of the title compound were obtained after slow evaporation of this solution.

Anal. Calcd for $Na_3[Co(C_7H_5NO_2)_3] \cdot 8H_2O \cdot C_2H_5OH$: C, 38.17; H, 5.11; N, 5.80; Na, 9.53. Found: C, 38.25; H, 4.89; N, 5.82; Na 9.84. The density, 1.44 g cm^{-3}, was determined by flotation in CCl_4/ethanol solutions.

Barium Bis(benzohydroximato)(benzohydroxamato)cobaltate(III). Methanolic solutions of sodium hydroxide (20 mmol) and tris(benzohydroxamato)cobalt(III) (freshly prepared, 4.94 g, 10 mmol) were combined. The resultant green solution was filtered and treated with an aqueous solution of barium chloride (40 mmol). The precipitate was filtered, washed with water, and dried in vacuo over P_2O_5. The complex is diamagnetic.

Anal. Calcd for $BaCo(C_7H_5NO_2)_2(C_7H_6NO_2) \cdot 4H_2O$: C, 37.38; H, 3.58; N, 6.22; Ba, 20.35. Found: C, 36.18; H, 3.09; N, 5.74; Ba, 23.4; Na, 0.0.

The compound is probably contaminated with $Ba_3[Co(C_7H_5NO_2)_3]_2 \cdot 4H_2O$. Anal. Calcd: C, 35.71; H, 2.71; N, 5.95; Ba, 29.16.

Resolution of Λ-Sodium Tris(benzohydroximato)cobaltate(III). To a stirred solution of sodium tris(benzohydroximato)cobaltate(III), 8.62 g (1 mmol) in absolute ethanol, added dropwise to an aqueous solution of Λ-$Co(en)_3I_3 \cdot H_2O$, 0.32 g (0.5 mmol). The mixture was stirred for 5 min and the precipitate removed by filtration. The filtrate was treated again with 0.25 mmol of $Co(en)_3I_3$ and the precipitate again removed. The filtrate containing the remaining resolved hydroximate complex was diluted with water and frozen at liquid-nitrogen temperature until the CD spectrum was recorded. The predominant geometry of the complex in solution is (from comparison with the crystalline material) presumably trans, although no direct measurement was made of the *geometric* isomeric purity in solution.

Table I. Crystallographic Summary

a, Å	10.360 (1)	mol formula of salt	$C_{21}H_{15}N_3O_6CoNa_3$
b, Å	11.118 (2)	fw of salt	533.27
c, Å	28.430 (5)	*Z*	4
β, deg	93.64 (1)	cryst syst	monoclinic
V, Å^3	3268 (2)	systematic reflcn absences	$0k0$, $k = 2n + 1$ $h0l$, $h + l = 2n + 1$
2*θ* range for cell constants, deg	20.0–37.7	space group[b]	$P2_1/n$
d_{measd},[a] g cm^{-3}	1.44	*F*(000), electrons	1504
d_{calcd}, g cm^{-3}	1.47		
check reflcns	no significant decay during 115 h of exposure		
2*θ* range for data collection, deg	3.0–50.0		
total reflcns measd	5405		
data cryst dimens, mm	0.20 × 0.30 × 0.30		
data cryst faces	$(110), (\bar{1}\bar{1}0), (1\bar{1}0), (\bar{1}10), (001), (00\bar{1})$		
abs coeff, *μ*(Mo K*α*),[c] cm^{-1}	6.28		

[a] Flotation in a mixture of CCl_4 and C_2H_5OH. [b] An alternative setting of space group $P2_1/c$, with equivalent positions $\pm(x, y, z)$, $\pm(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$. [c] Examination of five reflections with $\chi \simeq 90°$ at regular intervals ($\Delta 2\theta = 5$–$8°$) throughout the limits of data collection showed an average variation in normalized transmission factors of 0.96–1.00; hence, correction for absorption was not applied to the intensity data.

X-ray Crystallography. A well-formed crystal was wedged into a thin-walled capillary and examined by precession photography. These photographs established that the compound is isostructural with the previously reported trans Cr(III) complex, $Na_3[Cr(benz\text{-}H)_3] \cdot 8H_2O \cdot C_2H_5OH$,[2] in space group $P2_1/n$. Hence description of the structure and its analysis will be kept to a minimum. Preliminary study of intense, low-angle reflections from this crystal with an Enraf-Nonius CAD 4 automated diffractometer indicated that the crystal had good mosaic character; the peak widths at half peak height, as determined by *ω* scans with a receiving aperature of 1 mm, were ~0.33°. Intensity and unit cell data were gathered in accordance with previously delineated procedures.[12] Crystal data and those variables of data collection relevant to this study are presented in Table I. The measured intensities were reduced and assigned standard deviations with $p = 0.02$.[12] Since this structure is isostructural with that of the trans Cr(III) salt, least-squares refinement was initiated with the fractional coordinates determined for the trans Cr(III) species by using only reflections with $F_o^2 > 3\sigma(F_o^2)$.[13] Full-matrix least-squares refinement with use of neutral atom scattering factors,[12] in which non-hydrogen atoms were treated anisotropically, converged with $R = 0.035$, $R_w = 0.048$, and an error in an observation of unit weight of 1.90 for 3906 observations and 406 variables.[13] Hydrogen atoms of the $[benz\text{-}H]^{2-}$ ligands were fixed at idealized positions,[14] while those of the ethanol and water molecules were maintained at positions estimated from a difference electron density map.[15] The largest peaks on a final difference Fourier map were ~0.25 e Å^{-3} and were close to the positions of the carbon atoms of C_2H_5OH. Examination of

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(12) Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

(13) The computer program package used in this study is cited in ref 12. The function minimized in refinment was $\sum w(|F_o| - |F_c|)^2$. The details of the weighting scheme and the definitions of the error indices are also presented in ref 12.

(14) The C–H bonds were constrained to 0.95 Å in accordance with a previous report: Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(15) The positions of the methyl hydrogen atoms of the ethanol molecule were ill-defined and hence excluded from refinement. All hydrogen atoms were assigned isotropic thermal parameters of 5.0 Å^2.

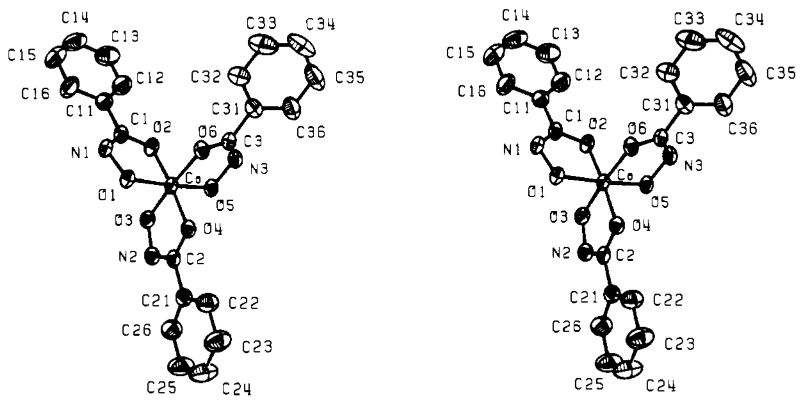

Figure 1. Stereoscopic view of the [Co(benz-H)$_3$]$^{3-}$ ion, illustrating the atom-numbering scheme used herein. Atoms are shown as ellipsoids of 50% probability; hydrogen atoms have been omitted for clarity.

Table VI. Selected Interatomic Distances (Å) and Angles (deg)[a]

Co-O(1)	1.905 (1)	O(6)-C(3)	1.314 (3)
Co-O(2)	1.884 (2)	N(1)-C(1)	1.300 (3)
Co-O(3)	1.866 (2)	N(2)-C(2)	1.285 (3)
Co-O(4)	1.914 (2)	N(3)-C(3)	1.295 (3)
Co-O(5)	1.879 (1)	C(1)-C(11)	1.478 (3)
Co-O(6)	1.925 (2)	C(2)-C(21)	1.488 (3)
O(1)-N(1)	1.416 (2)	C(3)-C(31)	1.484 (3)
O(2)-C(1)	1.315 (3)	mean phenyl C-C[b]	1.379 (3)
O(3)-N(2)	1.409 (3)	O(1)···O(2)	2.557 (2)
O(4)-C(2)	1.319 (3)	O(3)···O(4)	2.539 (2)
O(5)-N(3)	1.413 (3)	O(5)···O(6)	2.557 (2)

O(1)-Co-O(2)	84.85 (7)	O(5)-N(3)-C(3)	111.9 (2)
O(3)-Co-O(4)	84.39 (7)	N(3)-C(3)-O(6)	123.5 (2)
O(5)-Co-O(6)	84.45 (7)	C(3)-O(6)-Co	107.0 (1)
Co-O(1)-N(1)	110.4 (1)	N(1)-C(1)-C(11)	119.6 (2)
O(1)-N(1)-C(1)	112.1 (1)	O(2)-C(1)-C(11)	117.4 (2)
N(1)-C(1)-O(2)	123.0 (2)	N(2)-C(2)-C(21)	118.8 (2)
C(1)-O(2)-Co	109.6 (1)	O(4)-C(2)-C(21)	118.6 (2)
Co-O(3)-N(2)	111.8 (1)	N(3)-C(3)-C(31)	118.6 (2)
O(3)-N(2)-C(2)	112.4 (2)	O(6)-C(3)-C(31)	117.9 (2)
N(2)-C(2)-O(4)	122.6 (2)	obsd trigonal twist angle (ϕ)[c]	54.7 (8)
C(2)-O(4)-Co	108.8 (1)		
Co-O(5)-N(3)	110.3 (1)	calcd trigonal twist angle[d]	52.7

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. [b] The mean distance is obtained from $\bar{l} = \Sigma_i l_i/n$, and its variance from $\sigma^2(\bar{l}) = \Sigma_i(l_i - \bar{l})^2/[n(n-1)]$. [c] The trigonal twist angle is obtained by averaging the three torsion angles defined by the centroids CEN(1) and CEN(2) of the faces "normal" to the molecular pseudo-C_3 axis and the pairs of oxygen atoms composing each chelate ring, e.g., O(1)/CEN(1)/CEN(2)/O(2). [d] The average of three values given by the expression $\phi = -73.9 + 94.10b$, where b is the ratio of O···O distance within a chelate ring to the metal-O bond length.[18]

$|F_o|$ vs. $|F_c|$ at the end of refinement showed no trends as a function of $|F_o|$, $(\sin\theta)/\lambda$, or Miller index.

Tables of positional parameters of the non-hydrogen atoms with esd's as derived from the least-squares inverse matrix (Table II), anisotropic thermal parameters (Table III), hydrogen atom parameters (Table IV), and observed and calculated structure factor amplitudes (Table V) are available as supplementary material.[16]

Discussion

Figure 1 is a stereoscopic view of the [Co(benz-H)$_3$]$^{3-}$ complex and illustrates the atom numbering scheme used here and in the report of the structure of [Cr(benz-H)$_3$]$^{3-}$.[17] Bond lengths and bond angles are summarized in Table VI. The crystal structure consists of [Co(benz-H)$_3$]$^{3-}$ ions, Na$^+$ ions, and water and ethanol molecules, all of which are linked together by an elaborate network of hydrogen bonds. This is discussed in greater detail for the isostructural Cr(III) salt.[2]

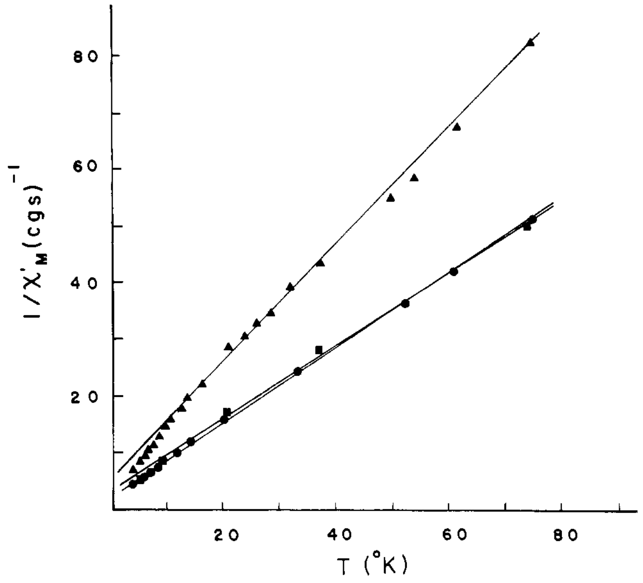

Figure 2. Inverse molar susceptibility (corrected for diamagnetic contributions) ($1/\chi_m'$) vs. temperature (K). The correlation coefficients are 0.999 for the high- ($T > 12$) and low- ($T < 12$ K) temperature data of tris(benzohydroxamato)cobalt(III) (▲), 0.999 for tris(*p*-nitrobenzohydroxamato)cobalt(III) (●), and 0.998 for tris(sebacodihydroxamato)dicobalt(III) (■).

The Co(III) complex possesses a trans geometry in which the O$_C$ and O$_N$ atoms of chelate ring 1 are trans to the O$_C$ and O$_N$ atoms of chelate rings 2 and 3, respectively (see Figure 1), and the coordination polyhedron about Co(III) approximates that of a trigonally distorted octahedron. As in the structure of *trans*-[Cr(benz-H)$_3$]$^{3-}$, the hydroximate ligands (exclusive of the phenyl rings) are planar, with the Co(III) ion lying 0.08, 0.04, and 0.37 Å from the mean planes of rings 1, 2, and 3, respectively. The mean Co-O$_N$ bond [1.883 (11) Å] appears shorter than the mean Co-O$_C$ bond [1.908 (12) Å] by essentially the same amount as observed in the structure of *trans*-[Cr(benz-H)$_3$]$^{3-}$.

Magnetic Measurements. The magnetic properties of the benzohydroxamate, *p*-nitrobenzohydroxamate, and sebacodihydroxamate [(HN(OH)C(O)(CH$_2$)$_4$)$_2$] complexes of Co(III) are shown in Figure 2 as plots of the inverse molar susceptibilities ($1/\chi_M'$, where χ' is corrected for diamagnetic contributions) vs. temperature. The three compounds display Curie-Weiss behavior [$\chi_M = C/(T - \Theta)$], with Weiss constants

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(16) Tables II, III, IV, and V are available as supplementary material; see the paragraph at the end of the paper.

(17) Although the atoms of the *trans*-[Co(benz-H)$_3$]$^{3-}$ and *trans*-[Cr(benz-H)$_3$]$^{3-}$ structures are named identically, some of the carbon atoms of the Cr(III) complex were mislabeled; the conversion is as follows for the numbering in Figure 1 (followed by the numbering in the Cr structure): 22 (26), 23 (25), 25 (23), 26 (22), 32 (36), 33 (35), 35 (33), and 36 (32).

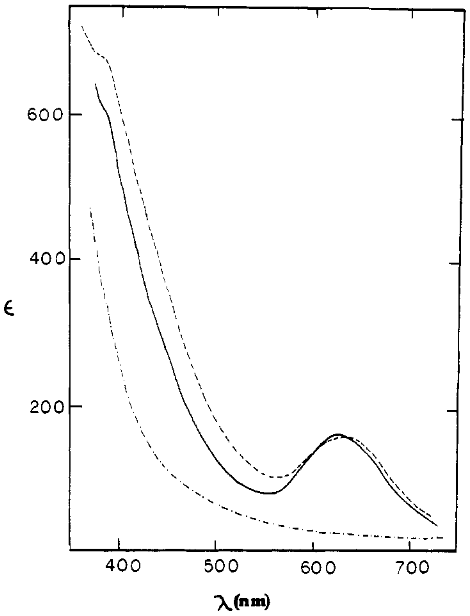

Figure 3. Visible absorption spectra of tris(benzohydroxamato)cobalt(III) (·····) in $CHCl_3$, tris(*N*-methylbenzohydroxamato)cobalt(III) (—) in $CHCl_3$, and trisodium tris(benzohydroximato)cobaltate(III) (- - -) in water.

(Θ) of −6.4, −3.6, and −5.6 K, respectively. In the range 4–12 K, the benzohydroxamato complex exhibits linear behavior, which differs from that observed above 12 K. The Weiss constant observed below 12 K is −1.9 K. The calculated magnetic moment for this complex in the range 12–80 K is 2.86 μ_B, which is lower than the room-temperature value of 4.10 μ_B. The magnetic moments for the *p*-nitrobenzohydroxamato and sebacodihydroxamato complexes are 3.52 and 3.56 μ_B, respectively. The tris(hydroximato)cobaltate(III) complexes $[CoL_3]^{3-}$ as well as bis(hydroximato)mono(hydroxamato)cobaltate(III) complexes $[CoL_2HL]^{2-}$ are diamagnetic. However the tris(*p*-nitrobenzohydroximato)cobaltate(III) trianion is *diamagnetic* in the solid state (as the sodium salt) but *paramagnetic* in aqueous solution, with a magnetic moment of 2.75 μ_B at room temperature. These results indicate that the crossover from low- to high-spin Co(III) occurs upon either the *second* or *third* protonation of the tris(hydroximato)cobaltate(III) complexes. As noted earlier, the cobalt(III) complexes with *N*-alkylhydroxamic acids are also diamagnetic at room temperature.

It is clear that cobalt(III) complexes with N-unsubstituted hydroxamic acids are not low spin and exhibit magnetic moment values that are intermediate between high and low spin. Increasing the ligand field strength by deprotonation of these hydroxamato complexes or by substitution of alkyl groups for the amino hydrogen atoms results in diamagnetic complexes that are close to the crossover between high- and low-spin states. We ascribe the paramagnetism of the *p*-nitrobenzohydroximato complex in solution to the electron-withdrawing effect of the nitro group; since the solid salt is low spin, apparently the internal pressure of the crystal in this case is sufficient to induce spin pairing.

Spectra. The visible absorption spectra of tris(benzohydroxamato)cobalt(III), tris(*N*-methylbenzohydroxamato)cobalt(III), and tris(benzohydroximato)cobaltate(III) are shown in Figure 3. The spectrum of the tris(benzohydroxamato)cobalt(III), as well as those of other high-spin cobalt(III) complexes with N-unsubstituted hydroxamic acids, shows no absorption maxima and absorbs weakly in the 900–500-nm region. This is in contrast to the spectra of the low-spin hydroximato and N-substituted hydroxamato complexes, which show an absorption maximum at ~600 nm (assigned to the transition $^1A_{1g} \rightarrow {}^1T_{1g}$) and a shoulder at ~400–450 nm ($^1A_{1g} \rightarrow {}^1T_{2g}$). Both tris(*p*-nitrobenzohydroxamato)cobalt(III) and tris(*p*-nitrobenzohydroximato)cobaltate(III) (which are paramagnetic in solution) show absorption spectra similar to those of N-unsubstituted hydroxamic acid complexes. The absorption and CD spectra of Λ-tris(benzohydroximato)cobaltate(III) are shown in Figure 4; these spectra are similar to those of Λ-*cis*-tris(hydroxamato)chromium(III) complexes. Furthermore, the CD spectrum of cobaltic deferriferrichrome A is similar to those of Λ-tris(benzohydroximato)cobaltate(III) and chromic deferri-

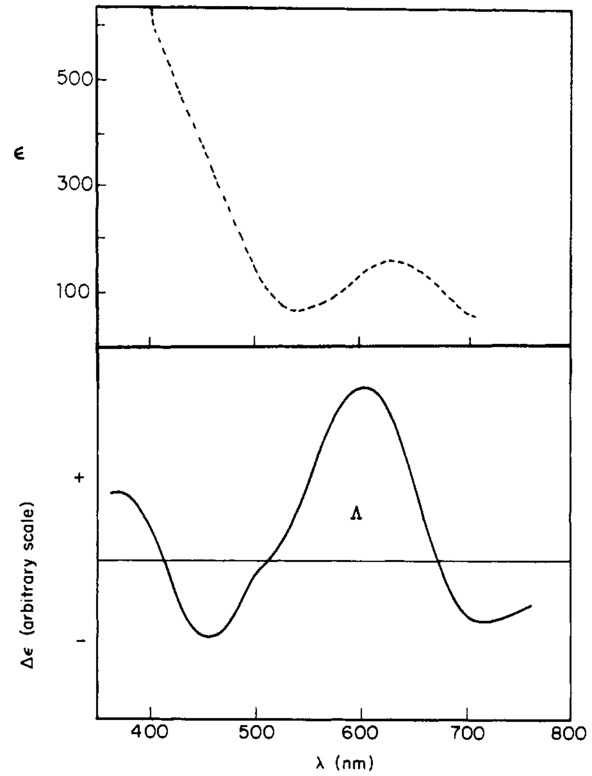

Figure 4. Visible absorption (- - -) and circular dichroism spectra (—) of trisodium tris(benzohydroximato)cobaltate(III) in water. While Δε for a pure isomer is not determined precisely, it is presumably close to the value found for the tyrosine complex (Figure 5).

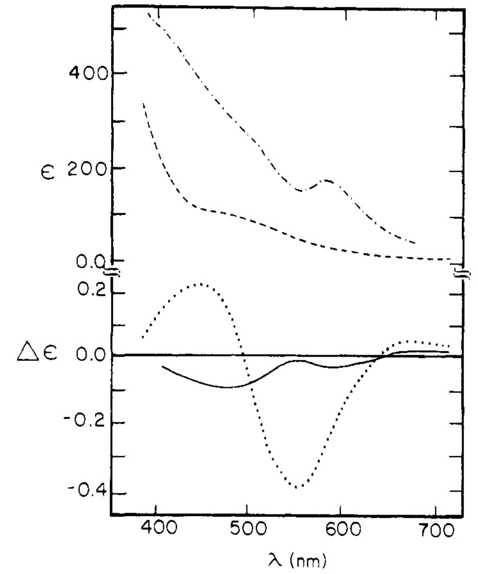

Figure 5. Visible absorption (- - -) and circular dichroism spectra (—) of tris(tyrosinehydroxamato)cobalt(III) in methanol and visible absorption (·····) and circular dichroism spectra (···) of trisodium tris(tyrosinehydroximato)cobaltate(III) in water.

ferrichrome A; these and other spectral correlations confirm that the ferric, chromic, and cobaltic complexes of deferriferrichrome A are isostructural.[19]

The absorption and CD spectra of tris(tyrosinehydroxamato)cobalt(III) and tris(tyrosinehydroximato)cobaltate(III) are shown in Figure 5. The hydroxamato complex, which apparently exists in one optical form due to the optical activity of the ligand, has an absorption spectrum similar to those of other N-unsubstituted hydroxamato complexes of cobalt(III), with no absorption maxima in the 900–500-nm region. The compound shows very weak CD activity, which is very different from that of low-spin Co(III) complexes. Upon deprotonation of tris(tyrosinehydroxamato)cobalt(III), the color changes from light brown to green (as is the case with other hydroxamato complexes), and a new CD spectrum develops (Figure 5) which is characteristic of a low-spin octahedral Co(III) complex with Δ configuration.

Potentiometric Titration. Estimates of the proton dissociation constants for the tris(benzohydroxamato)cobalt(III) complex were obtained via potentiometric titrations in aqueous solution. Due to the extreme basicity of the complex, an excess of base was added prior to titration. The titration curve shows a break at 5.5 equiv of H^+ per cobalt(III). At the end of the titration, at pH 3, the solution is clear with a white precipitate [presumably benzoic acid resulting from oxidation of the ligand by high-spin Co(III)]. Proton disssociation constants defined by

$$[Co(benz\text{-}H)_{3-n}(benz)_n]^{n-3} \overset{K_{a_n}}{\rightleftharpoons} H^+ + [Co(benz\text{-}H)_{4-n}(benz)_{n-1}]^{n-4}$$

for $n = 2–3$ were determined from the titration data in the pH range 11.5–8.5 by using the $\bar{n}$ method.[20] It was assumed that the cobalt ion remains in the +3 oxidation state during this portion of the titration and that all of the ligand is bound as the Co(III) complex. The $\bar{n}$ plot gives $pK_{a_2} \sim 11$ and $pK_{a_3} \sim 9$. The tris(benzohydroximato)cobaltate(III) anion is extremely basic, and pK_{a_1} could not be determined in aqueous solution ($K_{a_1} < 10^{-12}$).

Electrochemistry. The cyclic voltammogram (CV) of sodium tris(*p*-nitrobenzohydroximato)cobaltate(III) (which is paramagnetic in solution) displays a single, quasi-reversible, one-electron wave with a peak separation of 110 mV and a formal potential $E_f = -1.23$ V vs. SCE. The tris(benzohydroxamato)cobalt(III) complex shows similar behavior, with greater peak separation; no such behavior was observed for the low-spin tris(benzohydroximato)cobaltate(III) (as expected for all low-spin d^6 systems, since the resulting low-spin d^7 complex would be very unstable).

Summary

In conclusion, tris(hydroxamato)cobalt(III) and tris(hydroximato)cobaltate(III) complexes have been isolated and characterized. In all cases, cobalt(III) complexes with N-unsubstituted hydroxamic acids, as well as tris(*p*-nitrobenzohydroximato)cobaltate(III), are paramagnetic, with magnetic moments of about 2.7–3.6 μ_B. These values are intermediate between high-spin and low-spin d^6 complexes; they never reach the spin-only value of 4.9 μ_B expected for four unpaired electrons. The paramagnetism of these complexes is accompanied by other physical properties that are quite different from those of the diamagnetic complexes. As in other complexes of high-spin Co(III) [e.g., $Co(OH_2)_6^{3+}$ or CoF_6^{3-}], the central metal ion is a powerful oxidant and shows a reactivity very different from that of the low-spin form. The deprotonation of the neutral, paramagnetic N(proton) hydroxamate complex anions appears to be the first example of a proton-dependent spin-state change for cobalt(III) complexes.

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Registry No. $Co(HL)_3$ (HL = benzohydroxamato), 86785-19-5; $Co(HL)_3$ (HL = *p*-nitrobenzohydroxamato), 86785-20-8; $Co(HL)_3$ (HL = *N*-methylbenzohydroxamato), 86785-21-9; $Co(HL)_3$ (HL = L-tyrosinehydroxamato), 86785-22-0; $Co(HL)_3$ (HL = sebacodihydroxamato), 86785-23-1; $Na_3[Co(benz\text{-}H)_3]$, 86785-24-2; *trans*-$Na_3[Co(benz\text{-}H)_3]\cdot 8H_2O\cdot C_2H_5OH$, 86833-37-6; Λ-*trans*-$Na_3[Co(benz\text{-}H)_3]$, 86833-38-7; $Ba[CoL_2HL]$ (L = benzohydroximato), 86785-25-3; $Na_3[CoL_3]$ (L = L-tyrosinehydroximato), 86785-26-4; $Na_3[CoL_3]$ (L = *p*-nitrobenzohydroximato), 86785-27-5; Λ-$Co(en)_3I_3$, 19456-53-2; sodium cobaltinitrite, 13600-98-1.

Supplementary Material Available: Listings of fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes (Tables II–V) (26 pages). Ordering information is given on any current masthead page.

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