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Coordination Isomers of Biological Iron-Transport Compounds. 7. Preparation and Resolution of Tris(thiobenzohydroxamato)chromium(III), -cobalt(III), and (High-Spin) -iron(III) Complexes[1]

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Among the chelating functional groups found in the microbial iron-transport agents called siderophores are hydroxamate, catecholate, and thiohydroxamate. The preparation and properties of several complexes of the anion or dianion of thiobenzohydroxamic acid, PhC(=S)N(OH)H, are described. The neutral complexes tris(thiobenzohydroxamato)-chromium(III), -cobalt(III), and -iron(III) have been prepared and, after their dissolution in strong base, the salts $K_3[M(PhC(S)=N(C):)_3]$ (M = Cr, Co, Fe) were isolated. Precipitation of the anions with Λ- or Δ-tris(ethylenediamine)cobalt(III) affords resolution of the anions with the precipitated anion having an absolute configuration opposite that of the cation. Neutralization of the precipitated salt with acid and extraction with chloroform give solutions of the resolved, neutral tris(thiobenzohydroxamate) complexes—*even in the case of the high-spin ferric complex*. The half-life for racemization in chloroform at room temperature is greater than 50 h for Cr(III) and Co(III) and greater than 10 h for the Fe(III) complex. Of the two possible geometric isomers only the cis (with C_3 point symmetry) is observed for each metal. The Cr(III) and Co(III) complexes give VIS–UV absorption spectra which show the two expected d–d transitions for d^3 and low-spin d^6 octahedral complexes superimposed on a very broad charge-transfer band. The absorption maxima (ε) are 640 (230) and 480 (270) nm for Cr(III) and 635 (350) and 430 (900) nm for Co(III). The bands found in the CD spectra for the Λ isomers (Δε) are at 680 (–0.43), 600 (0.52), 490 (–0.21), 460 (–0.14), and 425 (3.1) nm for Cr(III) and 680 (–2.30), 530 (0.96), 485 (–0.54), and 375 (10.1) nm for Co(III). For both Cr and Co the lowest wavelength CD band apparently is due to charge transfer rather than the d–d manifold. Maxima are also seen in the Fe(III) VIS–UV spectrum (which appear to be charge transfer transitions) at (ε) 580 (2.4×10^3) and 490 (2.74×10^3) nm. The CD spectrum for the Λ isomer has bands at (Δε) 570 (–2.13), 490 (0.89), and 430 (–1.36) nm.

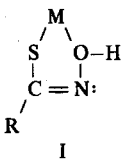
Introduction

The siderophores[2] are low molecular weight compounds which are manufactured by microbes to facilitate uptake of ferric ion. The insolubility of ferric hydroxide at physiological pH and the essential nature of iron for microbial growth apparently engendered the production of a wide range of powerful sequestering agents for ferric ion—the siderophores. The general properties of these agents[3-9] and the role of iron in microbial physiology[10] have been the subjects of recent reviews. Previous papers in this series have dealt with the coordination properties of the hydroxamate- and catecholate-containing siderophores. Two important classes of the hydroxamate type are the ferrichromes[11,12] and the ferrioxamines[13] which (except those containing substituent ionic groups) form neutral complexes using three bidentate hydroxamate monoanions. An example of the catecholate type of siderophore is enterobactin, a cyclic triester of 2,3-dihydroxy-*N*-benzoyl-*l*-serine, which forms an anionic ferric complex.[1,14]

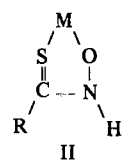
The highly specific nature of the cellular transport of at least some of the siderophores has led us to consider the possible role played by coordination isomers of these complexes. Hydroxamate and catecholate ferric complexes have been reported to be kinetically labile in aqueous solution—a property predicted by the absence of crystal field stabilization in high-spin d^5 metal ions. In contrast, the corresponding chromic complexes, though structurally the same, are kinetically inert. These kinetically inert siderophore complexes can be used as powerful chemical probes in elucidating the mechanisms of iron transport into living cells. Thus coordination isomers for model hydroxamates,[15] desferriferrichromes,[11] and ferrioxamines[13] have been isolated and characterized. The specific complex characterized as Λ-cis chromic desferriferrichrome was found to be taken up into the cells of the smut fungus *Ustilago sphaerogena* as rapidly as the native ferric complex,[12] while other types of transport behavior have been found with kinetically inert siderophore complexes in strains of the bacteria *Salmonella typhimurium* and *Escherichia coli*.[16]

A potentially new type of chelate moiety belonging to the siderophore class of compounds came with the discovery that cupric and ferric complexes of *N*-methylthioformohydroxamic acid can be isolated from culture broths of *Pseudomonas fluorescens* grown on *n*-paraffin or sucrose as the only source of carbon.[17,18] These *thio*hydroxamate compounds were found to have antibiotic activity,[17-22] a property that is shared with several hydroxamic acids.[23-25] The general chemistry of the thiohydroxamic acids forms a part of classic organic chemistry. These compounds are prepared by a variety of methods, which were reviewed recently.[26] Simple thiohydroxamic acids have pK_a's from 4.2 to 5.6,[27] compared to pK_a's of the order of 9 for the corresponding hydroxamic acids.[28] Thus the thiohydroxamic acids form metal complexes at lower pH values than corresponding hydroxamic acids. Both thiohydroxamic acids (RC(=S)N(OH)H) and *O*-methylthiohydroxamic acids ($RC(=S)N(OCH_3)H$) have like pK_a values; thus, the acidity of their compounds was proposed to be determined by the proton on nitrogen.[30] However, the *N*-alkylhydroxamic acids (RC(=O)N(OH)R′) have substantially the same acidity as the hydroxamic acids (RC(=O)N(OH)H) as well as the *O*-alkylhydroxamic acids (RC(=O)N(OR′)H).[31-34,27] This shows that the acidities of the nitrogen and oxygen functional groups in these compounds are nearly identical.

Though complexes of thioformohydroxamic acids were reported as early as 1911,[35] it was not until 1956 that metal complexes of thiobenzohydroxamic acid (PhC(=S)N(OH)H) were prepared and characterized.[36] Thiohydroxamic acids form coordinate bonds to metals via their sulfur and hydroxyl oxygen atoms. Two structures, I and II, have been suggested



I



II

for the mode of bonding. Nagata and Misukami suggested structure I[37] while Jensen et al. suggested structure II.[38] Others accepted structure I without further discussion,[19,20,39] although, as noted above, the unchanged acidity of the *N*-alkylthiohydroxamic acids makes structure I very unlikely.

X-ray data for the cis and trans isomers of bis(thioacetohydroxamato)nickel(II) established that both C–S and C–N bonds have partial double-bond character,[40-43] but the proton positions were not determined.

Both thiohydroxamic acids and hydroxamic acids form stable colored complexes with Fe(III) (and other transition metal ions) which have been used as reagents for the gravimetric and spectrophotometric determination of the metals.[44-51] The iron complexes have been established as containing high-spin Fe(III).[37,39]

We began this investigation of thiohydroxamate complexes with the assumption that the metal tris(thiohydroxamate) geometrical isomers would be more stable than the corresponding hydroxamate complexes and would allow correlation of the former's structural properties with those of the hydroxamate siderophores. This correlation, the mode of bonding of the thiohydroxamate ligand, and the preparation and resolution of several tris(thiobenzohydroxamate) complexes are the subjects of this paper. We report here the preparation of the neutral complexes $M(PhC(=O)N(O)H)_3$ (M = Cr, Fe, Co) and the corresponding potassium salts of the trinegative anions $[M(PhC(O)=N(O))_3]^{3-}$. The single geometric isomer found (cis with C_3 point symmetry) for both the anionic and neutral complexes has been resolved. To our knowledge this is the first resolution of a thiohydroxamate complex and the first reported isolation of a dianion thiohydroxamate salt. The $[M(PhC(S)=N(O):)_3]^{3-}$ complexes (M = Cr, Co) are so remarkably inert that protonation of the optically active trianion in aqueous solution gives retention of optical activity in the neutral $M(PhC(=S)N(O)H)_3$ complex. Thus the neutral complexes can be resolved by first resolving the trianion complexes in strongly basic solution, using standard precipitation procedures with optically active cations, followed by acidification and solvent extraction. To our great surprise this technique *even results in the resolution of the high-spin d^5 ferric complex.*

Experimental Section

Materials. Analytical grade solvents were used throughout the preparations. Sodium cobaltinitrite (Matheson Coleman and Bell), reagent grade, was used without further purification. The tetrahydrofuran adduct of chromic chloride, $CrCl_3 \cdot 3THF$, was prepared by literature methods and protected from moisture.[52] Sodium thiobenzohydroxamate[53] and tris(thiobenzohydroxamate)iron(III)[29] were prepared via literature procedures. The complexes Λ- and Δ-tris(ethylenediamine)cobalt(III) iodide were prepared using literature procedures.[54]

Chromatography. Kieselgel D-O silica gel was used for thin-layer chromatography on glass-coated plates, and silica gel powder 60-200 mesh (Baker) was used for column chromatography. The solvent system was 7.5:1 $CHCl_3$–methanol for both TLC and column chromatography. Spots were stained with iodine vapor.

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

Physical Measurements. Visible–UV absorption spectra of the racemic and resolved ferric, chromic, and cobaltic tris(thiobenzohydroxamate) complexes were measured in degassed chloroform, acetone, or methanol, while the spectra of the potassium salts were measured in 0.1 M degassed aqueous potassium hydroxide solutions. Visible–UV spectra were measured with a Cary Model 14 VIS–UV spectrophotometer. Circular dichroism spectra were measured using a Jasco J-20 automatic recording spectropolarimeter using chloroform solutions. Solutions of the resolved complexes were frozen immediately after resolution. The CD spectra were then completely recorded within 0.5 h after thawing. Under these conditions no significant racemization occurred during the acquisition of the CD spectrum. Infrared spectra were recorded by a Perkin-Elmer 337 spectrophotometer in KBr disks or chloroform solutions.

Approximate rates of racemization were obtained by monitoring the decrease with time of the CD bands at λ 630 nm for the cobaltic complex, 570 nm for the ferric complex, and 600 nm for the chromic complex. In each case both the Λ and the Δ enantiomers (10^{-3}–10^{-4} M concentrations) were examined.

The Preparations. All of the preparations were carried out using degassed solvents in an atmosphere of oxygen-free argon in glass Schlenk apparatus.

Tris(thiobenzohydroxamato)chromium(III). The tetrahydrofuran adduct of $CrCl_3$, 1.12 g (3 mmol), was added to a degassed solution of sodium thiobenzohydroxamate 1.75 g (10 mmol) in acetone (150 mL), the mixture was degassed again and then refluxed for 3 h. The volume of the solution was reduced to 10 mL under reduced pressure after which water (150 mL) was added with stirring. The resultant green precipitate was filtered, washed with water, and dried in vacuo over P_2O_5; yield >98%. Further purified sample was obtained by the recrystallization of the crude product from diethyl ketone–hexane mixture [mp 153 °C (uncor)]. The preparation can be carried out in methanolic solution as well. IR, cm^{-1} (relative intensities) [$CHCl_3$ solution or KBr disks]: 3150 (m), 3050 (w), 3000 (w), 2930 (w), 1550 (m), 1490 (w), 1450 (w), 1400 (m), 1255 (vs), 1190 (w), 1113 (s), 1094 (s), 1070 (s), 1000 (m), 955 (s), 933 (m), 922 (m), 917 (w), 760 (s), 715 (s), 690 (vs), 665 (s), 618 (m), 590 (w), 450 (m, b). Anal. Calcd for $Cr(C_7H_6NOS)_3 \cdot H_2O$: C, 47.90; H, 3.83; N, 7.98. Found: C, 47.98; H, 3.80; N, 7.68.

An alternative method is that reported by Cambi et al.[32] for the preparation of tris(*p*-methoxythiobenzohydroxamato)Cr(III). Although we obtained the same compound after purification, the yield was poor and the crude product was highly contaminated with insoluble chromic–hydroxo compounds.

Tris(thiobenzohydroxamato)iron(III). This complex was obtained in two forms. The green form of the complex was prepared as follows. To a solution of sodium thiobenzohydroxamate (1.575 g, 9 mmol) in acetone (150 mL) was added slowly, with stirring, $Fe(NO_3)_3 \cdot 9H_2O$ (1.212 g, 3 mmol). After 30 min the solution was filtered to remove precipitated $NaNO_3$ and evaporated to dryness under reduced pressure. The residue was redissolved in acetone, the solution was filtered, and again the solvent was evaporated to dryness. The residue was dried in vacuo over P_2O_5; yield >95%. The IR spectrum is identical with that of the chromic complex. Anal. Calcd for $Fe(C_7H_6NOS)_3 \cdot H_2O$: C, 47.56; H, 3.77; N, 7.93. Found: C, 47.83; H, 3.63; N, 8.16.

The violet form of the complex was prepared by literature procedures[29,39] and recrystallized from ethanol or ethyl methyl ketone–hexane mixture; yield >95%. Anal. Calcd for $Fe(C_7H_6NOS)_3 \cdot H_2O$: C, 47.56; H, 3.77; N, 7.93. Found: C, 47.67; H, 3.47; N, 7.83.

Tris(thiobenzohydroxamato)cobalt(III). Sodium cobaltinitrite, 1.21 g (3 mmol), was added to a degassed solution of sodium thiobenzohydroxamate, 1.75 g (10 mmol), in acetone (150 mL). The mixture was degassed again and then refluxed for 3 h. The volume was reduced to 10 mL under reduced pressure and 150 mL of degassed water was added; the green precipitate was filtered, washed with water, and dried in vacuo over P_2O_5; yield variable, 60–80%.

The compound was recrystallized from diethyl ketone–hexane mixture, mp 153 °C (uncor). The IR spectrum was identical with those of the ferric and chromic complexes. Anal. Calcd for $Co(C_7H_6NOS)_3 \cdot H_2O$: C, 47.28; H, 3.48; N, 7.87. Found: C, 47.55; H, 3.63; N, 7.81.

The Complexes $K_3[M(PhC(S)=N(O):)_3] \cdot H_2O$ (M = Cr, Co). The tris(thiobenzohydroxamato)metal complex (3 mmol) was dissolved in degassed aqueous potassium hydroxide solution (100 mL, 0.3 M). The solution was extracted with ether, the green aqueous layer was filtered, and water was evaporated at reduced pressure until the appearance of the first turbidity. The solution was then heated to the boiling point and left overnight for crystallization. Anal. Calcd for $K_3Cr(C_7H_5NOS)_3 \cdot 3.5H_2O$: C, 36.72; H, 3.23; N, 6.12; S, 14.00; K, 17.08; Cr, 7.57. Found: C, 36.72; H, 3.39; N, 6.12; S, 13.86; K, 18.5; Cr, 7.23. Calcd for $K_3Co(C_7H_5NOS)_3 \cdot 5H_2O$: C, 35.04; H, 3.50; N, 5.84. Found: C, 34.4; H, 3.6; N, 5.8. (These compounds are extremely hygroscopic and the number of H_2O molecules is that which best fits the analyses.)

Resolution of Λ-Tris(thiobenzohydroxamato)metal Complexes. For this purpose the potassium salts were used directly or prepared in situ from the metal tris-chelated complexes. To a stirred 0.1 M KOH aqueous solution containing 0.5 mmol of $K_3[M(PhC(S)=N(O))_3]$ complex at 0.5 °C was added dropwise a solution of 0.128 g (0.2 mmol) of Δ-$[Co(en)_3]I_3H_2O$ in 10 mL of H_2O. The mixture was stirred for 5 min, and the precipitate was filtered, washed thoroughly with water, and transferred while wet to a separatory funnel containing 50 mL

Table I. R_{st} Values, Band Maxima, and Extinction Coefficients for the Visible-UV and Circular Dichroism Spectra of the Tris(thiobenzohydroxamate) Complexes of Co(III), Cr(III), and Fe(III)

Compd	R_{st}[a]	Abs max, nm (ϵ[b])	CD bands, nm ($\Delta\epsilon$[b])	
			Δ	Λ
$Cr(PhC(=S)N(O)H)_3$	0.92	640 (230)	690 (+0.44)	680 (−0.43)
			600 (−0.54)	600 (+0.52)
		480 (270)	495 (+0.20)	490 (−0.21)
			460 (+0.10)	460 (−0.14)
			424 (−3.2)	425 (+3.1)
$Co(PhC(=S)N(O)H)_3$	0.82	635 (350)	680 (+2.28)	680 (−2.30)
			530 (−0.98)	530 (+0.96)
		430 sh (900)	480 (+0.57)	485 (−0.54)
			370 (−10.5)	375 (+10.1)
$Fe(PhC(=S)N(O)H)_3$	0.87	580 (2.41 × 10^3)	575 (+2.10)	570 (−2.3)
		490 (2.74 × 10^3)	490 (−0.89)	490 (+0.89)
			430 (+1.90)	430 (−1.36)
$K_3[Cr(PhC(S)=NO)_3]\cdot xH_2O$		640 (151)		
		470 (126)		
$K_3[Co(PhC(S)=NO)_3]\cdot xH_2O$		630 (540)		
		440 (1538)		

[a] R_{st} = (distance of the complex from the starting point)/(distance of the thiobenzohydroxamic acid from the starting point). [b] Units are L mol^{-1} cm^{-1}.

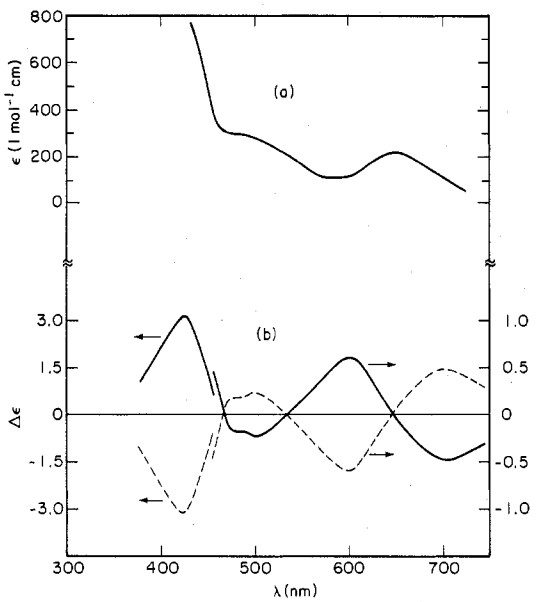


Figure 1. (a) Visible absorption spectrum of tris(thiobenzohydroxamato)chromium(III) in $CHCl_3$. (b) Circular dichroism spectra of the Δ (- - -) and Λ (—) forms of tris(thiobenzohydroxamato)chromium(III) in $CHCl_3$.

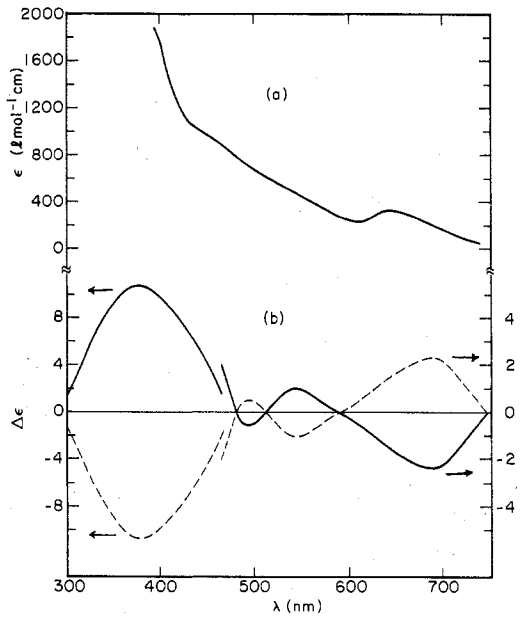


Figure 2. (a) Visible absorption spectrum of tris(thiobenzohydroxamato)cobalt(III) in $CHCl_3$. (b) Circular dichroism spectra of the Δ (- - -) and Λ (—) forms of tris(thiobenzohydroxamato)cobalt(III) in $CHCl_3$.

of water. To this was added 6 mL of 0.1 M (0.6 mmol) HCl followed by extraction with chloroform (20 mL). The chloroform was evaporated at reduced pressure to 5 mL, hexane (30 mL) was added, and the precipitate was filtered, washed with hexane, and dried in vacuo.

The Δ enantiomers were resolved similarly using Λ-$[Co(en)_3]I_3H_2O$.

Results and Discussion

Preparation and Resolution. The tris(thiobenzohydroxamate) complexes of cobalt(III), chromium(III), and iron(III), as well as their potassium salts, have been prepared and resolved into their optical isomers. This is the first time that thiohydroxamate complexes have been resolved. More remarkable, even the optical isomers of the high-spin ferric complex have been isolated and are found to be stable in chloroform solution for several hours. To our knowledge, this is the first time such a complex of ferric ion has been resolved. The spectra are shown in Figures 1–3. Although two forms (violet and green) of the neutral ferric complex were isolated, only the green form was obtained from the resolution process and so only its spectra are reported. These and other properties of the compounds are summarized in Table I. All attempts to prepare and separate the geometrical isomers of the cobalt(III) and chromium(III) compounds ended with the isolation of one single geometrical isomer which we characterize as cis. It is well-known that equilibrium isomer ratios can be affected by the solvent system used in the preparation[55] and can even result in the isolation of different single isomers as the main product in certain conditions.[56,57] However, when the chromium(III) and cobalt(III) complexes were prepared from different solvents at different temperatures, all of the isolated products were found to be the same, as shown by their chromatographic (TLC and column) behavior, their infrared spectra in both solution ($CHCl_3$) and solid (Nujol and KBr disks) states, and their absorption spectra. The latter properties and the inertness of these species also establish that the ferric complex exists as the same isomer. Attempts at fractional crystallization, which effected the partial separation of geometrical isomers of tris(thiobenzohydroxamato)chromium(III)

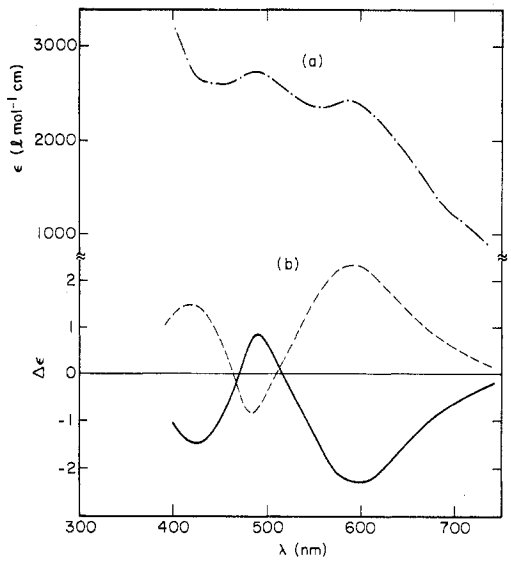


Figure 3. (a) Visible absorption spectrum of tris(thiobenzohydroxamato)iron(III). (b) Circular dichroism spectra of the Δ (- - -) and Λ (—) forms of tris(thiobenzohydroxamato)iron(III).

chelates,[58] and repeated extractions, which were used to separate the geometrical isomers of tris(acetoacetanilidato)chromium(III) chelates,[59] always gave the cis isomer. Moreover, the recrystallized tris(thiobenzohydroxamate) chelates of iron(III), chromium(III), and cobalt(III), as well as their mixed samples, melt sharply at almost the same temperature.

The possibilities that these complexes are labile and that only one geometrical isomer crystallizes preferentially were ruled out by the resolution of these chelates. The optical isomers of the chromium and cobalt chelates have a half-life for rearrangement which is greater than 50 h in chloroform solutions at room temperature. The half-life of the Fe(III) complex is greater than 10 h. These are even more stable at −60 °C, where thin-layer chromatography showed only one spot for each compound. The resolved compounds exhibit chromatographic properties which are identical with those of their racemic mixtures, which reinforces the existence of only one geometrical isomer for each.[57] The existence of only one geometrical isomer has been reported for the tris(cysteinato)cobalt(III),[60,61] potassium tris[L-cysteinesulfinato(20)-*S*,*N*]cobaltate(III),[61] and bis[bis(2-aminoethyl)sulfide]cobalt(III) bromide complexes.[57]

The chromic and cobaltic chelates are air sensitive in their solutions; therefore, all of the preparations were carried out using degassed solvents in an atmosphere of oxygen-free argon in glass Schlenk apparatus. The solutions of these complexes change their colors when exposed to air; the maxima of the low-energy transitions in the visible spectra shift at lower energy and increase in intensity. Thus even the oxygenated compounds retain their optical activity.

Metal complexes of thiohydroxamic acids dissolve in excess alkali due to the acidity of the N–H protons.[36] This behavior was reported for cobalt(III),[36] copper(II), and nickel[38] chelates, although the resulting salts previously have not been isolated and characterized. The potassium salts were obtained by reacting the tris chelates with excess potassium hydroxide solution. The compounds in the solid state are hygroscopic and air sensitive and can be converted back to the original neutral chelates by controlled neutralization with dilute acids. This behavior was used for their resolution. The neutral tris chelates also dissolve in potassium carbonate solution. The spectra of these solutions are different from those of the tripotassium salts, and no solid materials were isolated.

The infrared spectra of the potassium salts are very different from those of the neutral chelates except for those bands attributed to the phenyl rings. The strong absorption bands at 1260, 1100, and 955 cm^{-1} in the infrared spectra of the tris chelates disappear or shift positions in the potassium salts. These bands are attributed to the thioamide group (–C(=S)NH–).[30,38,62] The band at 955 cm^{-1} which disappears in the spectra of the potassium salts is attributed mainly to N–H deformation.[30,38] This was considered as evidence for the structural changes accompanying the change of the –C(=S)N(O)H group to –C(S)=N(O):.[38] The exact nature of the bonding in these complexes will be better understood after an x-ray structure analysis is completed.[63]

Spectra. The tris(thiobenzohydroxamato)chromium(III) chelate, as well as its potassium salt and the potassium salt of the cobalt(III) chelate, exhibits two absorption maxima in their visible spectra. The high-energy absorption of the cobalt(III) chelate is unresolved and appears as a shoulder due to the presence of the very strong absorption at 260 nm. These spectra are similar to those of other d^3 and spin-paired d^6 systems in octahedral ligand fields and may be assigned as $^4A_2 \rightarrow {}^4T_2$ (low energy) and $^4A_2 \rightarrow {}^4T_1$ for Cr(III) d^3 systems, and as $^1A_1 \rightarrow {}^1T_1$ (low energy) and $^1A_1 \rightarrow {}^1T_2$ for spin-paired d^6 systems, Co(III). Both geometrical isomers of related [M(A–B)$_3$] complexes (where A–B represents a bidentate ligand with two different donor atoms) have similar spectra.[64–70] The ferric chelate shows two absorption maxima at 580 and 590 nm.[27] These are assigned as charge-transfer bands, since for a high-spin d^5 system there are no spin-allowed d–d electronic transitions. In addition, the spectra of all three metal chelates have very strong absorptions at 250–260 nm. This absorption, which is also found in the ligand spectrum, is found at higher frequency in the spectra of the potassium salts of the metal chelates. It is probably an $n \rightarrow \pi^*$ transition within the ligand.

Tris metal chelates, with two different donor atoms in the chelate ring, can exist in two geometrical isomers which we have previously designated as the cis and the trans forms, both of which can exist with Λ or Δ configurations about the metal.[13,15] Each of the two d–d transitions ($A \rightarrow T_1$ and $A \rightarrow T_2$) in complexes with octahedral symmetry is expected to split into three CD bands in the spectra of the trans isomer (C_1 symmetry) and into two in the spectra of the cis isomer (C_3 symmetry). Such splitting was reported for some cobalt(III)–amino acid complexes,[63,67,70–74] although fewer bands were found in the spectra of other complexes.[71]

Two CD bands, with opposite signs, are found in the CD spectra of chromium(III) and cobalt(III) tris(thiobenzohydroxamate) complexes in the low-energy absorption region. This is interpreted as implying that these geometrical isomers are the cis isomers, which is consistent with a preliminary structure analysis.[63] Two CD bands are found in the spectrum of the cobalt(III) complex in the high-energy absorption region, while the spectrum of the chromium chelate has an additional shoulder in that region. Three CD bands were found in this region in the spectra of cis isomers of some amino acid metal chelates[67,68] and in the spectrum of (−)$[Co(ox)_3]^{3-}$ (D_3 symmetry).[75]

In the spectra of the cis isomers with C_3 symmetry the transitions $^1A \rightarrow {}^1E$ (spin-paired d^6) and $^4A \rightarrow {}^4E$ (d^3 system) should have positive chiral signs for the Λ configuration and negative signs for the Δ configurations. The transition $^1A \rightarrow {}^1A$ (spin-paired d^6) and $^4A \rightarrow {}^4A$ (d^3) should have the opposite signs to the above transitions.[71] A main difficulty arises in deciding which of the two bands from the low-energy T manifold is the E band. The order of energies of E and A levels varies from one complex to another. Although it is generally accepted that the energy order is A > E for five-membered rings formed by diamine and amino acid complexes,[63,67,70,76,79,80]

the opposite order was found for several other complexes,[66,80-83] including the chromium tris(hydroxamate) and -(catecholate) complexes.[11,13-15]

In general, the spectra and structures of the tris(thiobenzohydroxamate) complexes are similar to those of the corresponding hydroxamate complexes. Thus the energy order E > A is also expected for the tris(thiobenzohydroxamate) complexes of cobalt(III) and chromium(III). We thus assign absolute configurations to the anions which are opposite those of the $[Co(en)_3]^{3+}$ ions used to precipitate them.

The configurations of the ferric complex enantiomers are assigned as the same as those of the corresponding chromium(III) and cobalt(III) complexes precipitated with Λ- or Δ-$[Co(en)_3]^{3+}$. The CD bands at 570–575 and 490 nm appear to correspond to the absorptions at 580 and 490 nm in the visible spectrum; the CD band at 430 nm shows no such correspondence.

Due to the air sensitivity of the tris(thiobenzohydroxamato)cobalt(III) and -chromium(III) chelates, major changes were observed in the CD spectra when the solutions of the chelates were exposed to air—especially those in the low-energy region which shift to higher frequency and increase in intensity. The properties of these oxygenated species are under investigation.

In summary, neutral thiohydroxamate complexes of cobalt(III), chromium(III), and iron(III) can be resolved by first resolving the trinegative anions as salts of Λ- or Δ-$[Co(en)_3]^{3+}$. The neutral species are generated, with retention of optical activity, upon neutralization with acid and extraction into chloroform. It is very surprising that the high-spin ferric complex in chloroform solution has a half-life for racemization which is not more than an order of magnitude times faster than the corresponding cobalt(III) or chromium(III) complexes. The VIS–UV and CD spectra of the chromium(III) and cobalt(III) complexes, while very different in detail, can be related to those of hydroxamate, catecholate, and related ligand complexes. For both the Cr and Co complexes the large, low-energy CD band near 680 nm is negative for the Λ isomer.

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Registry No. $Cr(PhC(=S)N(O)H)_3$, 61477-67-6; $Co(PhC(=S)N(O)H)_3$, 61520-84-1; $Fe(PhC(=S)N(O)H)_3$, 61520-85-2; $K_3[Cr(PhC(S)=NO)_3]$, 61483-90-7; $K_3[Co(PhC(S)=NO)_3]$, 61483-91-8; Δ-$Cr(PhC(=S)N(O)H)_3$, 61520-86-3; Λ-$Cr(PhC(=S)N(O)H)_3$, 61520-87-4; Δ-$Co(PhC(=S)N(O)H)_3$, 61520-88-5; Λ-$Co(PhC(=S)N(O)H)_3$, 61520-89-6; Δ-$Fe(PhC(=S)N(O)H)_3$, 61520-90-9; Λ-$Fe(PhC(=S)N(O)H)_3$, 61521-24-2.

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Ligand Oxidation in Iron Diimine Complexes. 3. Electrochemical Oxidation of Tris(glyoxal bis(methylimine))iron(II)

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The electrochemical oxidation of tris(glyoxal bis(methylimine))iron(II), $Fe(GMI)_3^{2+}$, has been investigated using cyclic voltammetry and rotating-disk studies in 0.5 M H_2SO_4. The main reaction product is an iron(III) complex in which one of the GMI ligands is oxidized to $H_3CN{=}C(OH)CH{=}NCH_3$, thus consuming $3F$/mol of $Fe(GMI)_3^{2+}$. A reaction mechanism consisting of electrochemical oxidation of the Fe(II) to an Fe(III) complex followed by a rate-determining first-order chemical reaction is proposed. In this chemical reaction, the Fe(III) complex is intramolecularly reduced to the Fe(II) state, with concomitant oxidation of the ligand; the radical–ligand complex is then further electrochemically oxidized very rapidly. This proposed ECE mechanism is compatible with the experimental results. The rate for the intramolecular reduction of the ferric complex is 22 ± 2 s^{-1}. This value is applied to estimate a second-order rate constant of 10^9–10^{10} M^{-1} s^{-1} for the chemical oxidation of $Fe(GMI)_3^{2+}$ in this acid concentration.

Introduction

In the first two papers of this series,[2,3] it has been shown that the chemical oxidation of the low-spin iron(II) complex of the diimine ligand glyoxal bis(methylimine) ($H_3CN{=}C{-}HCH{=}NCH_3$), $Fe(GMI)_3^{2+}$, by Ce(IV) proceeds via $Fe(GMI)_3^{3+}$. This ferric complex undergoes an intramolecular one-electron transfer followed by the oxidation of this product by another $Fe(GMI)_3^{3+}$, yielding two new ligand-oxidized complexes and regenerating $Fe(GMI)_3^{2+}$. The rate of this disproportionation reaction depends very strngly on the acid concentration.[3] Spectrophotometric and potentiodynamic studies at 25 °C yielded for the disproportionation reaction the following second-order rate constants: $(2.2 \pm 0.2) \times 10^3$ and $(0.7 \pm 0.1) \times 10^3$ M^{-1} s^{-1} in 4.0 and 5.0 M H_2SO_4, respectively. Using these techniques, it was not possible to obtain rate constants for H_2SO_4 concentrations lower than 4.0 M. In 0.5 M H_2SO_4 the reaction is faster than the upper limit of detection of stopped-flow techniques.[3] In 11 M H_2SO_4,[4] a one-electron reversible oxidation of $Fe(GMI)_3^{2+}$ was observed.

The electrochemical oxidation of $Fe(GMI)_3^{2+}$ at low acid concentration (0.5 M H_2SO_4) has now been studied by means of cyclic voltammetric and rotating-disk techniques and by coulometric oxidation. The coupling of these techniques enables us to propose a mechanism for the electrochemical oxidation of $Fe(GMI)_3^{2+}$, to determine the rate constant for the intramolecular reduction of the ferric complex, and also to estimate the rate constant for the chemical oxidation at low acid concentration.

Experimental Section

The chemicals used in this study are described in part 1.[2]

A Princeton Applied Research Corp. (PARC) Model 170 electrochemistry system coupled to a 564 Tektronix storage oscilloscope was used throughout the present work. Rotating-disk measurements employed the ASR2 analytical rotator from Pine Instruments Co.; the available rotation speed was 50–10 000 rpm. Coulometric experiments were performed with the PARC Model 173 potentiostat/galvanostat with a Model 176 digital coulometer.

The electrochemical cells were glass cylinders (75-mm i.d. × 75-mm height), closed with a tightly fitting Teflon cover which held the three electrodes and the gas inlet and outlet tubes. The working electrodes were glassy carbon disks (G.C. 30 rod 3-mm diameter from Tokai Electrode Manufacturing Co., Ltd., or from Pine Instruments, diameter 7 mm); a platinum wire and a saturated calomel electrode served as the auxiliary and reference electrodes.

A coulometric cell was made of a glassy carbon crucible (50-mm i.d. × 50-mm height) closed with a tightly fitting Teflon cover which held the reference and auxiliary electrodes and the inlet–outlet tubes. The solution was magnetically stirred so that the total electrolysis was achieved in less than 1 h.

Oxygen was removed by bubbling N_2 through the solution for 30 min prior to the electrochemical measurements.

Visible absorption spectra were obtained with a Cary 17 spectrophotometer.

Results and Discussion

Typical cyclic voltammograms of $Fe(GMI)_3^{2+}$ in 0.5 M H_2SO_4, for several scan rates, are shown in Figure 1. At slower scan rates, e.g. 0.5 V s^{-1} (Figure 1a), the first anodic sweep shows only one anodic current peak at 1.15 V vs. SCE. On the cathodic sweep, the corresponding cathodic peak was not observed but a new cathodic peak at 0.6 V vs. SCE was found. On the second cycle, the corresponding anodic current peak of the more easily oxidizable couple was seen, and a significant decrease of the anodic current peak for the starting material was observed. As the scan rate was increased (Figure 1b–d) it was possible to detect the cathodic current peak corresponding to the reduction of $Fe(GMI)_3^{3+}$—i.e., the reduction of the product formed at 1.15 V vs. SCE.

Figure 2 shows the ratio of the anodic peak current (i_{pa}) to the square root of scan rate ($\nu^{1/2}$) plotted as a function of $\nu^{1/2}$. The ratio $i_{pa}/\nu^{1/2}$ is independent of $\nu^{1/2}$ for a diffusion-controlled process. Figure 2 shows that, for scan rates higher than 50 V s^{-1}, this behavior is achieved. At scan rates less than this, a chemical reaction generating another electroactive couple ($E_{1/2}$ = 0.65 V vs. SCE) takes place.

Since no *IR* correction was applied to these measurements, the anodic to cathodic peak potential separation increased with scan rate and was larger than 59 mV, the value to be expected for a one-electron reversible process.[5] However, since the anodic to cathodic peak current ratio approached unity at 100 V s^{-1} and the anodic peak potential from 5 to 50 V s^{-1} was constant within the experimental error, 1.15 ± 0.01 V vs. SCE, it is likely that the electrochemical oxidation of $Fe(GMI)_3^{2+}$ to $Fe(GMI)_3^{3+}$ is a reversible, diffusion-controlled process.

Using the plateau region of Figure 2, it is possible to calculate a diffusion coefficient for $Fe(GMI)_3^{2+}$ of (8.0 ± 0.8)