KF solutions containing 2×10^{-3} M KI (Figure 1). The frequency of the Raman line argues against its assignment to I_3^- (115 cm^{-1})[8] or PtI_4^{2-} (126 cm^{-1}).[9] There are no reports in the literature of Raman spectra of PtI_2 and PtI_4, and it was not possible to obtain spectra of these compounds under conditions similar to those existing in the electrochemical experiments. Also, the ultraviolet-visible absorption spectrum of the solution after standing at +500 mV indicated that I_3^- ions were present. The disappearance of the 174 cm^{-1} band at $E \geq 700$ mV is assumed to result from the absorption of incident and scattered light by the I_3^- solution species. The observations above tend to rule out the possibility of platinum corrosion of the type previously identified electrochemically in related systems by Argue and Banewicz.[10] The assignment of the line to adsorbed I_2 is supported not only by the line position (see above) but also by the limiting adsorption data taken from the isotherms of Johnson.[5] These data favor adsorbed I_2 rather than I_3^-. In other experiments, the failure to detect adsorbed Br_2 in experiments with 0.1 M KF, 2×10^{-3} M KBr solutions is consistent with the tendency[5] of Br^- to be oxidized to BrO^- rather than Br_2.

Turning to the molecular vibrational frequency (174 cm^{-1}) which has been assigned to adsorbed iodine: the displacement of the frequency from its gas phase value (213 cm^{-1}) to that of the crystal (180 cm^{-1}) has been attributed by Anderson and Sun[11] to the influence of intermolecular forces in the crystal. The comparable but slightly larger decrease observed in the present study for adsorbed iodine suggests that both iodine-iodine and platinum surface-iodine interactions are important. In contrast to the observations for I_2 in the crystal phase,[11] the stretching fundamental for adsorbed I_2 does not appear to be split by intermolecular coupling. The breadth of the 174-cm^{-1} band in the present study may reflect a range of intermolecular interactions present in the adsorbed phase. The displacement of the I_2 fundamental is unlikely by itself to be diagnostic of sideways or end-on coordination with the surface. Both configurations would be expected to lead to a reduction in the force constant and therefore in the fundamental frequency. However, the stereochemistry[12] of numerous 1:1 donor-acceptor complexes suggests that end-on coordination would be favored.

We conclude with a comment regarding the sensitivity of Raman spectroscopy in experiments of the type reported here. The technique, while relatively insensitive, is feasible if sophisticated technique is combined with careful electrode preparation. The sensitivity of the method is far greater for systems which exhibit resonance enhancement. However, such enhancement is restricted to molecules which specifically absorb the source radiation, and hence a distorted picture of relative populations of species may result. Resonance enhancement did not appear to be a significant factor in the present study as the intensity of the 174-cm^{-1} band was not very sensitive to a change in exciting radiation from 514 to 488 nm. Also the first overtone of the 174-cm^{-1} band was not detectable. Further, the overtone peak of crystalline I_2 has been reported as very weak in intensity.

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Coordination Isomers of Biological Iron Transport Compounds. 8.[1] The Resolution of Tris(hydroxamato) and Tris(thiohydroxamato) Complexes of High-Spin Iron(III)

Sir:

Tris metal chelates in which two different donor atoms in the chelate ring coordinate to the metal ion can exist in two geometrical isomers. We previously have designated these as the cis and trans forms—both of which can exist as either Δ or Λ optical isomers.[2] These are diagramed in Figure 1 for the cis geometrical isomers. The x-ray structure analysis of tris(benzohydroxamato)iron(III), $Fe(PhC({=}O)N({-}O)H)_3$, found a preferred cis geometry for this complex.[3] This geometry also has been found in the potassium salt of tris(thiobenzohydroxamato)chromium(III) $Cr(PhC({=}S)N({-}O)H)_3$,[4] and the isostructural ferric complex.[5] The ferric ions in both the hydroxamate and thiohydroxamate complexes are high spin with magnetic moments of 5.4–5.8. μ_B.[6-8] Thus there is no ligand field stabilization energy for these d^5 metal complexes, which have been considered to be kinetically labile.[9] Both the hydroxamate and thiohydroxamate functional groups are found in a series of compounds, called the siderophores, which are manufactured by microbes as iron transport agents.[1,10] Earlier we resolved tris(hydroxamato)chromium(III)[10] and tris(thiohydroxamato)chromium(III) and -cobalt(III).[5] *To our surprise we find the corresponding ferric complexes are resolvable by the same procedure and are very stable.* To our knowledge this is the first report of the resolution of a high-spin ferric complex which is stable in solution under ambient conditions.

The tris(thiobenzohydroxamato)iron(III) was prepared from sodium thiobenzohydroxamate and ferric nitrate in acetone, methanol, or buffered aqueous solutions. In all cases a dark green product was obtained. However, a dark violet compound was obtained from the aqueous solution of sodium thiobenzohydroxamate and ferric nitrate as described earlier.[8,11] The green and the violet products have comparable analytical data: Anal. Calcd for $Fe(PhC({=}S)N({-}O)H_3 \cdot H_2O$: C, 47.6; H, 3.8; N, 7.9. Found, green form: C, 47.8; H, 3.6; N, 8.2. Found, violet form: C, 47.7; H, 3.5; N, 7.8.

They also have similar IR spectra in the region 400–1200 cm^{-1}, and room temperature magnetic susceptibilities (Gouy technique, $\mu = 5.4\text{–}5.8\ \mu_B$) and EPR spectra characteristic of high-spin iron(III) complexes. Both colored forms dissolve in concentrated potassium hydroxide solution to give the dark red-orange potassium salt, $K_3[Fe(PhC({-}S){=}N({-}O))_3]$, which, upon careful neutralization, gives back the green form of the neutral complex . Both the tris(benzohydroxamato) iron(III) and its trisodium salt were prepared as described earlier.[12]

The tris(thiobenzohydroxamato)iron(III) was resolved by the precipitation of the double salt of its trianion with Λ or Δ-tris(ethylenediamine)cobalt(III) iodide, $[Co(en)_3]I_3$, from strongly basic solution. The neutral chelate was then extracted

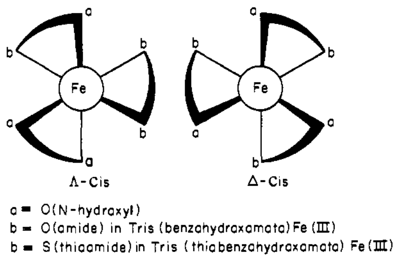


Figure 1. Λ and Δ optical isomers of *cis*-tris(benzohydroxamato)iron(III) and tris(thiobenzohydroxamato)iron(III).

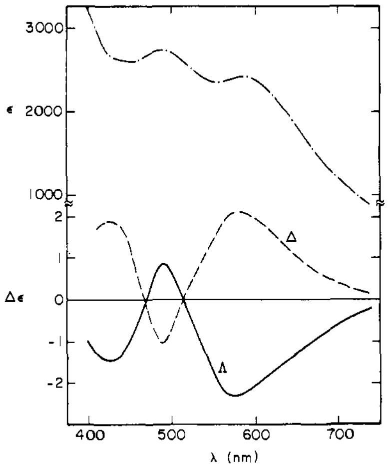
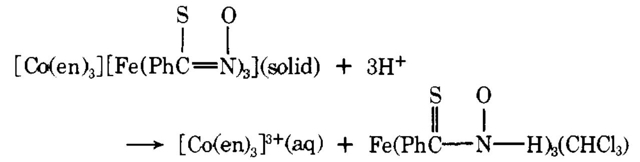


Figure 2. Visible absorption spectrum (-·-·-) and circular dichroism spectra of Δ (- - -) and Λ (—) tris(thiobenzohydroxamato)iron(III) in chloroform solution.

into chloroform after the protonation of its anion in the double salt via the reaction:



$$[\mathrm{Co(en)_3}][\mathrm{Fe(Ph\overset{\overset{\displaystyle S}{|}}{C}{=}\overset{\overset{\displaystyle O}{|}}{N})_3}](\text{solid}) + 3\mathrm{H^+} \longrightarrow [\mathrm{Co(en)_3}]^{3+}(\text{aq}) + \mathrm{Fe(Ph\overset{\overset{\displaystyle S}{\|}}{C}{-}\overset{\overset{\displaystyle O}{|}}{N}{-}H)_3(CHCl_3)}$$

The tris(benzohydroxamato)iron(III) was resolved by dissolving its trisodium salt and the resolving agent, Λ- or Δ-$[\mathrm{Co(en)_3}]\mathrm{I_3}$, in a minimum amount of water. The double salt was then precipitated by the addition of a few milliliters of methanol. Since the tris(benzohydroxamato)iron(III) chelate recemizes immediately in weakly acidic aqueous solutions, excess sodium acetate was added to the aqueous suspension of the double salt prior to the careful neutralization of its anion.

The tris(thiobenzohydroxamato)iron(III) chelate is unstable in chloroform solutions. A greenish product begins precipitating within several hours. The half-time of racemization is estimated to be greater than 10 h in chloroform solution.[5] The metal chelate is more stable in acetone solution, where the half-time of racemization is 18-22 h at room temperature. The tris(benzohydroxamato)iron(III) complex is very stable in acetone solution—greater than 95% of its optical activity was retained after 1 week in acetone solution at room temperature! However, both metal chelates racemize immediately in weakly acidic alcoholic solutions. Shaking an ethereal solution of tris(thiobenzohydroxamato)iron(III) with very dilute aqueous HCl solution effects an immediate loss of all optical activity.

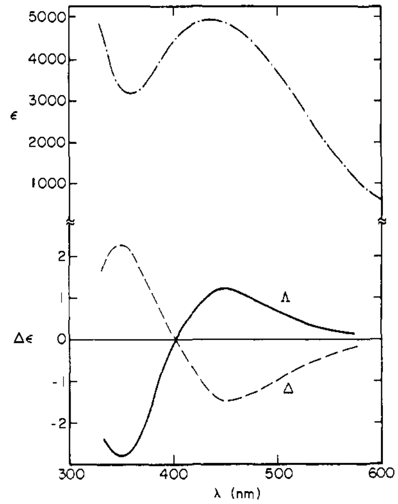


Figure 3. Visible absorption spectrum (-·-·-) and circular dichroism spectra of Δ (- - -) and Λ(—) tris(benzohydroxamato)iron(III) acetone solution.

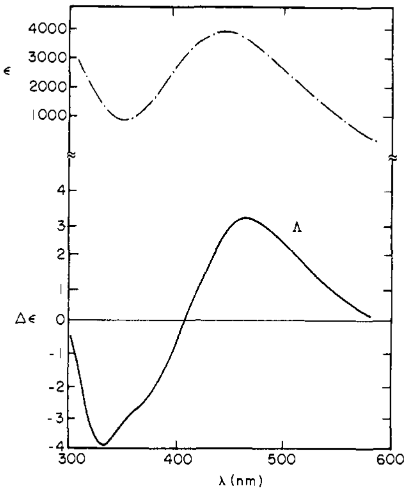


Figure 4. Visible absorption (-·-·-) and circular dichroism (—) spectra of ferrichrome A in aqueous solution.

The absorption and circular dichroism spectra of the resolved ferric chelates are shown in Figures 2 and 3. The assignments of the configuration about the metal ions are based on the assignments of the configurations for the tris(thiobenzohydroxamato)chromium(III) and -cobalt(III) complexes[5] and on the sign of the CD band for the tris(benzohydroxamato)iron(III) and ferrichrome A (see below) at ~460-465 nm. The absorption and the circular dichroism spectra of ferrichrome A are shown in Figure 4.

Ferrichrome A, which is a trihydroxamate iron(III) complex, crystallizes in the Λ-cis form,[13] and has a positive CD band at 465 nm (in the region of the strong absorption at 440 nm, see Figure 4). Consequently we assign a Λ configuration to the isomer of tris(benzohydroxamato)iron(III), which shows a positive CD band at 455 nm (the absorption band is at 435 nm). Since the ferric ion in these metal chelates is in the high-spin state, the d-d transitions are spin-forbidden, and their visible-UV and CD absorptions must be due to charge transfer and ligand transitions.

In summary, the precipitation of the diastereomeric salts of $[\mathrm{Fe(PhC(S){=}N(O))_3}]^{3-}$ or $[\mathrm{Fe(PhC(O){=}N(O))_3}]^{3-}$ with Δ- or Λ-$[\mathrm{Co(en)_3}]^{3+}$, followed by neutralization and solvent extraction of the tris(hydroxamato)- and tris(thiohydroxamato)iron(III) complexes, results in the resolution of these high-spin complexes.[14] The solution stability of the optical activity of these complexes is unprecedented.

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Polar Peroxidic Intermediates in Low Temperature Photooxygenation of *N*-Methylindoles[1]

Sir:

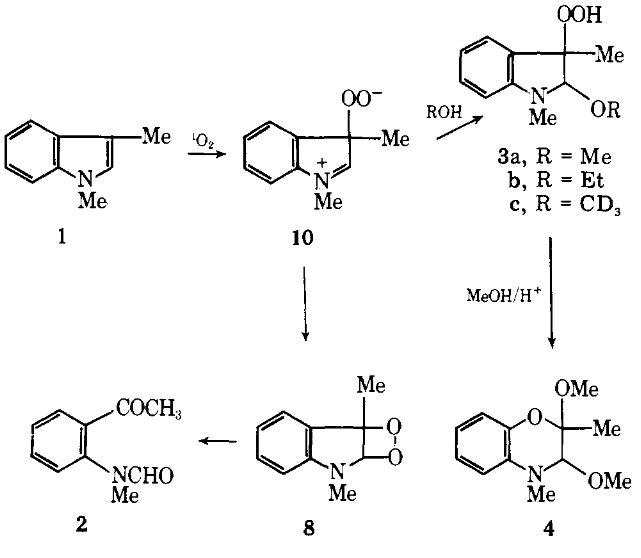
The reaction of singlet oxygen with enamines is of special interest in view of wide-spread involvement of the enamine grouping in many heterocyclic compounds.[2] Enamines are well known to react readily with singlet oxygen to form dioxetanes which can subsequently cleave to carbonyl and amide fragments.[3,4] The 1,2-cycloaddition of singlet oxygen with electron-rich olefins like enol ethers or enamines had been assumed to be a concerted $({}_{\pi}2_{s} + {}_{\pi}2_{s})$ or $({}_{\pi}2_{s} + {}_{\pi}2_{a})$ process.[5] However, recent theoretical calculations[6] have predicted that the enamine-singlet oxygen reaction is a nonconcerted process involving a zwitterion as an initial intermediate, whereas the experimental evidence for the intermediacy of such dipolar peroxides is lacking.[7] We now wish to report that low temperature photooxygenation of *N*-methylindoles gives a polar peroxide which is efficiently intercepted inter- and intramolecularly by alcohols and secondary amines, and that the trapping reactions show a remarkable temperature dependency.

We previously reported that dye-sensitized photooxygenation of 3- or 2,3-substituted *N*-methylindoles such as 1,3-dimethylindole (**1**) at room temperature gives the normal C_2–C_3 ring cleavage products, **2**, in nearly quantitative yield.[7c,8] However, rose bengal-sensitized photooxygenation[9] of **1** (5 mM) at −70 °C in methanol led to a slower but clean formation of the unstable 3-hydroperoxyindoline (**3a**) (97%) with a half-life of ca. 20 min at 30 °C in $CDCl_3$.[10] The structure of **3a**[11] was assigned on the basis of spectral data[12] and by converting it to benzoxazine **4**[11,13] with methanol containing HCl.[8a] Similar photooxygenation of **1** in ethanol at −70 °C gave **3b**[11,14] in quantitative yield. The overall reaction leading to **3** apparently consists of the addition of solvent alcohols to an initial intermediate, probably a polar peroxide.

Table I. Variation of the Product Distributions (**6, 7**) with Temperature and Solvents[a]

			Products (%)[b]	
Compound	Solvent	Temp (°C)	**6**	**7**
5a	Methanol	20	—[c]	**7a** (95)
	Methanol	−35	**6a** (78)	**7a** (17)
	Methanol	−70	**6a** (95)	**7a** (3)
	Acetonitrile	20	—[c]	**7a** (85)[d]
	Acetonitrile	−30	**6a** (50)	**7a** (35)
	Acetone	20	**6c** (18)	**7a** (50)[d]
	Acetone	−70	**6a** (62)	**7a** (26)
	Methylene chloride[e]	20	**6c** (37)	**7a** (45)[d]
	Methylene chloride[e]	−70	**6a** (85)	—[c]
5b	Methanol	20	**6d** (28)	**7b** (60)
	Methanol	−70	**6b** (95)	—[c]
	Acetonitrile	20	**6d** (36)	**7b** (55)
	Acetonitrile	−30	**6b** (68)	**7b** (22)
	Acetone	20	**6d** (51)	**7b** (36)[d]
	Acetone	−70	**6b** (75)[d]	—[c]
	Methylene chloride[e]	20	**6d** (32)	**7b** (35)[d]
	Methylene chloride[e]	−70	**6b** (25)[d]	—[c]

[a] Initial concentration (2 mM). Unless otherwise stated, rose bengal was used as a sensitizer ($CuCl_2$–$CaCl_2$ filter). [b] Determined by NMR analysis of the reaction mixture. Yields were based on reacted **5**. [c] **6** could not be detected. [d] Appreciable amounts of polymeric materials were formed. [e] Methylene blue (potassium chromate filter) was used as a sensitizer.



Similar types of intramolecular trapping reactions have been observed with *N*-methyltryptophol (**5a**) and N_b-methoxycarbonyl-N_a-methyltryptamine (**5b**). As we reported earlier, photooxygenation of **5a** in methanol at −70 °C produces **6a** (95%) and **7a** (3%), whereas at room temperature **5a** gives **7a** exclusively.[8a] We also observed that the product ratio (**6**/**7**) is highly sensitive to the reaction temperature (Table I). The hydroperoxides **6a** and **6b** were not converted to **7a** and **7b**, respectively, under the conditions.[15] As shown in Table I, the trapping reaction to yield **6** is taking place preferentially at low temperatures in any solvent listed in table I. A similar temperature dependency has also been observed in the photooxygenation of **5b**.[16]

These results clearly indicate that the initial intermediate is a peroxide which is capable of undergoing an efficient addition reaction with alcohols or secondary amines even at low temperature. Since dioxetanes including enamine dioxetanes[4] are not known to react with nucleophiles such as alcohols or amines,[18] it seems unlikely that the dioxetanes (**8, 9**) are the intermediates.[19] The results may most reasonably be explained