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Diferric Tris(carboxylato) Complexes of Binucleating Schiff Base Ligands

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The triphenolate Robson ligand 2,6-bis{[(2-hydroxyphenyl)imino]methyl}-4-methylphenol (H_3L) and its alkylated derivatives react with ferric nitrate in the presence of sodium acetate, propionate, or benzoate to yield complexes of the type $LFe_2(O_2CR)_3$ ($R = C_6H_5, CH_2CH_3, CH_3$). These diferric complexes were characterized by Mössbauer, IR, UV–visible, and ^1H NMR spectroscopies and by cyclic voltammetry. All three benzoates appear to be coordinated to the iron centers in the solid state, and IR spectroscopic evidence indicates that they bridge the two metal centers. Upon dissolution of the complexes in pyridine, one free benzoate ion is observed by ^{13}C NMR, which suggests that it is displaced from the iron by the pyridine solvent. Varying the carboxylate ligands did not significantly affect the electronic nature of the complex; however, additional alkyl substituents on the macroligand further stabilized the iron(III) metal centers.

Introduction

Bimetallic complexes play an important catalytic role in biological systems, where they comprise the active sites of a number of enzymes.[1] Many model complexes have been developed in an attempt to mimic the activity of these binuclear metal centers or, less commonly, to facilitate catalysis unrelated to the function of the original enzyme. Since the active sites in a number of metalloproteins have been proposed or demonstrated to be (μ-oxo)dimetal units,[2] a corresponding set of model complexes has been developed which features bridging oxo, alkoxo, or phenoxo groups. The bridging oxygen atom in these species facilitates cooperativity between the two metal centers by maintaining them in close but nonbonded proximity.

Alkoxide or phenoxide bridges are particularly advantageous in these model complexes, since they can be incorporated into a larger multidentate ligand, which then inhibits dissociation of the two metal centers. Robson Schiff base ligands are one such class of phenolate-bridged, multidentate ligands which were developed to provide three chelating coordination sites per metal in their nonmacrocyclic form.[3,4] Bimetallic complexes of these ligands were initially designed for nitrogen fixation, but their ability to bind and activate a variety of small substrates was quickly recognized and exploited.[5]

Diiron complexes are particularly important enzymatic models and are attractive as synthetic catalysts due to the ubiquity and versatility of iron as a biological catalyst.[6] However, Robson's nonmacrocyclic ligands have not been generally developed into diiron complexes and a second class of ligands, designated polypodal ligands, have been utilized in modeling the diiron enzymes. These polypodal ligands are complementary analogs of Robson's ligands, wherein the imine Schiff base linkages are replaced by amine junctures, allowing incorporation of one additional donor podand per metal center (see ligand **3**). Some complexes of the polypodal ligands have been shown to be active in catalyzing oxygenation reactions.[7] Exploration of diiron complexes of Robson ligands is therefore also of interest since the reduced occupation of the metal centers by the macroligand may lead to improved or unusual reactivities.

We are developing bimetallic complexes as templates upon which to promote novel chemical transformations of small ligands. The reported reactivities of both the Robson and polypodal systems, in conjunction with the known biological activity of diiron enzymes, prompted us to synthesize diiron complexes of these ligands for examination as general catalysts. In a previous paper we described the synthesis of a new diiron polypodal complex;[8] this paper outlines the synthesis and characterization of diiron complexes of an analogous Robson ligand.

Experimental Section

General Details. All reagents and solvents were purchased from commercial sources and used as received, with the following exceptions: Methanol was distilled from calcium hydride, chloroform was distilled from calcium chloride, and dimethylformamide (DMF) was distilled from molecular sieves prior to use. 2-Hydroxy-5-methylisophthalaldehyde was synthesized by the method of Taniguchi.[9] 2,6-Bis{[(2-hydroxyphenyl)imino]methyl}-4-methylphenol and its alkylated derivatives were synthesized by the method of Robson.[4]

Melting points were determined using a Thomas capillary melting point apparatus and are uncorrected. NMR spectra were obtained in pyridine-d_5 or methanol-d_4 at 25 °C on a Bruker AC300 spectrometer.

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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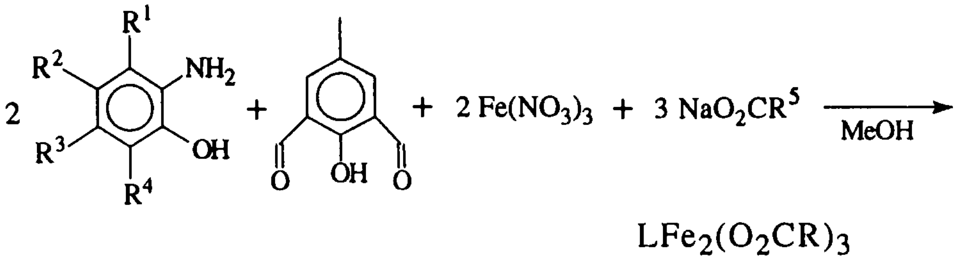
Scheme 1



2

a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^2 = CH_3$, $R^1 = R^3 = R^4 = H$
c: $R^3 = CH_3$, $R^1 = R^2 = R^4 = H$
d: $R^2 = R^4 = CH_3$, $R^1 = R^3 = H$
$R^5 = CH_3$, CH_2CH_3, C_6H_5

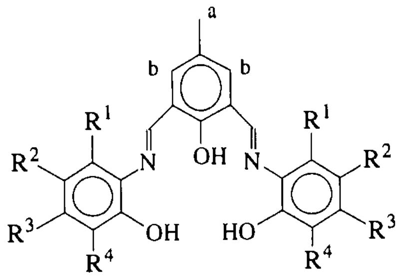
IR spectra were recorded on a Nicolet 5 DX FTIR spectrometer using KBr pellets. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in DMF solution. Cyclic voltammograms were determined in DMF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A PAR 273 potentiostat with a platinum-disk working electrode, a platinum-wire auxiliary electrode, and an SCE reference electrode were used. The ferrocenium/ferrocene couple was included as an internal standard. Mössbauer data were obtained on an Austin S-600 spectrometer and were referenced to metallic iron foil. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Solid-state ^{13}C NMR spectroscopy with MAS was performed at Montana State University, Bozeman, MT.

Tris(μ-benzoato-*O,O'*)(2,6-bis{[(2-phenoxy)imino]methyl}-4-methylphenolato)diiron(III), $LFe_2(O_2CC_6H_5)_3$ (2a). A solution containing 111 mg of 2-aminophenol (1.02 mmol) and 412 mg of $Fe(NO_3)_3{\cdot}9H_2O$ (1.02 mmol) in 5 mL of methanol was added to a warm solution of 84 mg of 2-hydroxy-5-methylisophthalaldehyde (0.51 mmol) in 5 mL of methanol. The resulting solution was maintained near the boiling point. After 15 min, 220 mg of $NaO_2CC_6H_5$ (1.53 mmol) was added, upon which a brown precipitate formed. Stirring was continued for 15 min; then the solid was filtered off and washed with methanol. Upon drying, 160 mg (35% yield) of the product was obtained; mp >210 °C. Anal. Calcd for $[LFe_2(O_2CC_6H_5)_3]{\cdot}2H_2O$, $C_{42}H_{34}Fe_2N_2O_{11}$: C, 59.04; H, 4.01. Found: C, 58.86; H, 3.96.

Identical procedures using 4-methyl-2-aminophenol, 5-methyl-2-aminophenol, and 4,6-dimethyl-2-aminophenol yielded complexes **2b-d**, respectively. Equimolar amounts of NaO_2CCH_3 or $NaO_2CCH_2CH_3$ were added in place of $NaO_2CC_6H_5$ to yield the respective carboxylate complexes. These complexes gave satisfactory elemental analyses.

Results and Discussion

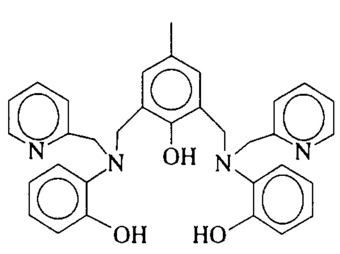
Synthesis. Ligands **1a-d** (H_3L) were conveniently synthesized *in situ* in the presence of the desired iron salt and other ligands, leading directly to the respective diferric complexes. Alternatively, ligands **1a-d** could be presynthesized, followed by reaction with the iron salt. Identical products were obtained by both methods.



1

a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^2 = CH_3$, $R^1 = R^3 = R^4 = H$
c: $R^3 = CH_3$, $R^1 = R^2 = R^4 = H$
d: $R^2 = R^4 = CH_3$, $R^1 = R^3 = H$

The complexes were routinely synthesized using $Fe(NO_3)_3$ as the iron source; however, reaction with $FeCl_2$ also gave diferric products via oxidation of both metal centers. Charged complexes of the type $[LFe_2]^{3+}3X^-$ were obtained with various counterions, X^-, which were methanol soluble for $X^- = NO_3^-$, PF_6^-, BF_4^-, and ClO_4^- and insoluble with the BPh_4^- counterion. The solubility of all complexes (**2a-d**) of the Robson ligands were greatly reduced in comparison to complexes of the analogous polypodal ligand 2,6-bis{[(2-hydroxyphenyl)(2-pyridylmethyl)amino]methyl}-4-methylphenol (**3**).[8] This general insolubility is typical of complexes of Robson ligands.[3,4]



3

Addition of sodium acetate, propionate, or benzoate to the initial reaction mixture yielded tricarboxylate complexes $LFe_2(O_2CR)_3$ (Scheme 1). These tricarboxylate complexes were isolated as stable, brown solids and have been fully characterized for $R = C_6H_5$. The solubilities of the complexes were limited in most common organic solvents, and solution studies were primarily carried out in pyridine or DMF. Repeated attempts were made to crystallize these complexes; however, X-ray-quality crystals were not obtained. Characterization of the complexes was therefore carried out by a variety of spectroscopic techniques, as detailed below.

NMR Spectroscopy. Proton resonances for the diferric complexes $LFe_2(O_2CR)_3$ (**2a-d**) were broad, with half-height line widths of 800–1400 Hz, and covered a range from +100 to −15 ppm. Spectra of this type are indicative of high-spin iron(III) complexes, with no iron(II) present.[10] Comparison of the spectra for complexes of the various methyl-substituted macroligands allowed assignment of the binucleating ligand resonances to their respective protons (Table 1). The protons at positions R^1 and R^4 and the imine protons were not observed due to their proximity to the paramagnetic centers. In general, no protons which were separated by less than four bonds from the iron centers were observed. Integration of the peaks gave areas in accord with the

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Table 1. Isotropic Proton shifts for $LFe_2(O_2CR)_3$ Complexes **2a–d** with Benzoate Ligands ($R = C_6H_5$)[a]

L	$R^2 = H$[b]	$R^3 = H$	$R^2 = CH_3$	$R^3 = CH_3$	b (H)	a (CH_3)
2a	–6.0	52			16	32
2b		51	42		16	32
2c	–7.5			–12	20	32
2d		58	43		18	32

[a] Saturated py-d_5 solutions; line widths at half-height 800–1400 Hz; units of ppm. [b] See ligand structure **1** for proton designations.

Table 2. Mössbauer Properties for $LFe_2(O_2CR)_3$ Complexes **2a–d** with Benzoate Ligands ($R = C_6H_5$)[a]

complex	δ[b]	ΔE_Q	Γ
2a	0.43	0.64	0.54
2b (R^2 = Me)	0.42	0.67	0.66
2c (R^3 = Me)	0.42	0.70	0.54
2d ($R^2 = R^4$ = Me)	0.41	0.70	0.53

[a] Solid complexes. [b] Isomer shifts relative to iron foil at room temperature; all units in mm/s.

Table 3. Electronic Spectral Data for $LFe_2(O_2CR)_3$ Complexes **2a–d** with Benozate Ligands ($R = C_6H_5$)[a]

complex	λ_{max}[b] (ϵ)[c]	complex	λ_{max}[b] (ϵ)[c]
2a	418 (29 800)	**2c** (R^3 = Me)	411 (29 900)
2b (R^2 = Me)	420 (30 800)	**2d** ($R^2 = R^4$ = Me)	412 (30 400)

[a] DMF solution at 25 °C. [b] Units of nm. [c] Units of $M^{-1}\ cm^{-1}$.

Table 4. Effect of Alkyl Substitution on the Reduction Potentials for $LFe_2(O_2CR)_3$ Complexes **2a–d** with Benzoate Ligands ($R = C_6H_5$)[a]

complex	$E_{1/2}$(I)[b]	$E_{1/2}$(II)	complex	$E_{1/2}$(I)[b]	$E_{1/2}$(II)
2a	–0.55	–1.06	**2c** (R^3 = Me)	–0.59	–1.09
2b (R^2 = Me)	–0.61	–1.10	**2d** ($R^2 = R^4$ = Me)	–0.07	–1.20

[a] In DMF. [b] Units of V (vs SCE).

Table 5. Effect of Carboxylates on the Reduction Potentials for $LFe_2(O_2CR)_3$ Complex **2c**[a]

R	$E_{1/2}$(I)[b]	$E_{1/2}$(II)
CH_3	–0.60	–1.09
CH_2CH_3	–0.60	–1.11
C_6H_5	–0.59	–1.10

[a] In DMF. [b] Units of V (vs SCE).

proposed assignments. Protons at ligand position R^2 were shielded (δ –6.0 to –7.5), while those at position R^3 were deshielded (δ 51–58). In the methyl-substituted complexes, methyl protons were deshielded at position R^2 (δ 42–43) and shielded at position R^3 (δ –12). This alternating shielding and deshielding is consistent with dominant π-type contact shifts.

Proton resonances for the benzoate ligands were obscured by solvent; however, deuterium resonances were observed for the labeled complex at 10.1, 8.2, 7.5, and 6.5 ppm. These are in good agreement with reported benzoate resonances in similar complexes.[19b]

Mössbauer. Solid state Mössbauer spectra of the benzoate complexes **2a-d** were obtained at room temperature and were essentially identical throughout the series (Table 2). Each complex exhibited a quadrupolar doublet with an isomer shift and quadrupolar splitting indicative of only one type of high-spin iron(III) center per molecule.[11] (The spectrum of **2b**, Figure S1, is available in the supplementary material as a representative example.) This agrees well with the oxidation-state assignment made by NMR.

Electronic Absorption. The UV–visible spectra of complexes **2a-d** were obtained in DMF solution and are characterized by a strong band at 415 ± 10 nm (ϵ 30 100 ± 900 $M^{-1}\ cm^{-1}$). This absorption is attributed to the imine functionality, with a possible contribution from a $\pi \rightarrow \pi^*$ ligand-to-metal charge transfer (LMCT) transition.[12,13] Absorptions for the series of benzoate complexes are shown in Table 3. As expected, alkyl substitution on the binucleating ligand does not affect the position of the absorption band.

Electrochemistry. Cyclic voltammetric measurements were performed on the diferric complexes in DMF solution with 0.1 M TBAH as the supporting electrolyte. Each compound showed two reduction couples, $E_{1/2}$(I) and $E_{1/2}$(II), corresponding to the $Fe^{III}Fe^{III}/Fe^{II}Fe^{III}$ and $Fe^{II}Fe^{III}/Fe^{II}Fe^{II}$ couples, respectively. (Potentials for the benzoate complexes are listed in Table 4.) The first couple was reversible in all cases, while the second couple was quasireversible. Reversibility was indicated by the lack of dependence of the $E_{1/2}$ values on scan rates from 25 to 200 mV/s, by the ΔE_p values being consistently about 60 mV and by the i_c/i_a ratios being close to unity.

The negative reduction potentials observed indicate that high-spin d^5 iron centers are favored in these complexes. This is due to stabilization of the iron(III) centers by the macroligand phenolates in combination with the carboxylate bridges. The same preference for forming diferric complexes was observed with the analogous polypodal ligand **3**.[8] In both cases, attempts to synthesize the complex from ferrous chloride resulted in facile oxidation of the iron(II) to form diferric products. Unlike these basic N_2O_3 and N_4O_3 macroligands, the less basic, N_6O polypodal ligand 2,6-bis{[bis(2-pyridylmethyl)amino]methyl}-4-methylphenol has been reported to facilitate the reduction of iron(III) reagents to yield mixed-valent Fe(II)–Fe(III) complexes.[14]

Addition of alkyl substituents to the terminal phenolate rings of the ligand (**2b-d** vs **2a**) stabilized the oxidized, diferric form of the complexes even further, shifting both the $Fe^{III}Fe^{III}/Fe^{II}Fe^{III}$ and $Fe^{II}Fe^{III}/Fe^{II}Fe^{II}$ couples to more negative potentials. Both potentials correlate with the pK_a's of the alkyl-substituted phenols (R^2 = 0.98 and 0.95, respectively), which indicates that the alkyl groups stabilize the diferric complex primarily via resonance through the phenolate oxygen.[15] No correlation was observed with substituent effects transmitted through the imine nitrogens. Carboxylate ligands exhibit a weaker inductive effect, and changing these ligands from benzoate to acetate or propionate did not significantly affect the reduction potentials of the complexes (Table 5).

Coordination Mode of the Benzoate Ligands. Elemental analysis supported the presence of three benzoate ligands per complex, and the general insolubility of these complexes compared to their ionic analogs, $[LFe_2]^{3+}3X^-$ ($X^- = NO_3^-, PF_6^-, BF_4^-, ClO_4^-$), suggested that all three benzoates were coordinated to the metal centers. Two bridging carboxylates are very common in diiron complexes of this type and are present in the analogous polypodal ligand complex; however, we are aware of no similar cases in which the irons are bridged by three benzoates.[16] We therefore attempted to elucidate the coordination mode of the benzoate ligands.

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(16) Diferric complexes containing two bridging carboxylates along with additional carboxylates in other binding modes have been reported. For example, see: Tolman, W. B.; Liu, S.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 152.

(a) Infrared Spectroscopy. The infrared spectra of the tribenzoate complexes **2a-d** in KBr pellets were dominated by peaks between 1300 and 1625 cm^{-1} corresponding to the stretching modes of the C=C and C=N bonds in the system. Spectra for the series of methyl-substituted complexes were essentially identical, with the primary differences occurring in the relative peak intensities.

Benzoate stretching bands ν_{asym}(COO) and ν_{sym}(COO) were identified at 1544 and at 1412 cm^{-1}, respectively. The frequency difference ($\Delta\nu$) between these bands can be correlated to the coordination mode of the carboxylato group.[17] In **2a-d**, this difference was 132 cm^{-1}, which is significantly smaller than the difference observed for sodium benzoate ($\Delta\nu$ = 160 cm^{-1}). This suggests the presence of bridging benzoates in the complexes, although it does not rule out the possibility of a chelation mode of binding. However, the formation of bridging carboxylate ligands in diiron complexes is well established,[14,18-19] while fewer examples of bidentate terminal (chelating) carboxylate ligands have been reported for iron.[20] Several other diiron complexes containing bidentate bridging benzoates have been reported,[18] and these show frequency differences in the range $\Delta\nu$ = 130–150 cm^{-1}. This further supports assignment of the carboxylates as bridging species. Resonances indicative of ionic or monodentate benzoates were not observed,[21] and monodentate bridging benzoates are unlikely given the diferric nature of these complexes.[22]

(b) NMR. Complex **2c** was synthesized using ^{13}C-labeled-carboxy benzoate ($C_6H_5{}^{13}CO_2^-$). The ^{13}C NMR spectrum of this complex showed a single sharp resonance with a shift of δ 169, while sodium benzoate in a 50:1 pyridine–water solution exhibits a corresponding peak at δ 174. This sharp peak indicates that at least one of the benzoates associated with the complex is present as an uncoordinated counterion in pyridine solution. No other resonances were observed; however, this does not rule out coordinated benzoate ligands since the proximity of their carboxy carbons to the iron centers is expected to prohibit their observation by NMR. In order to determine the number of free benzoates per complex in solution, carboxy-labeled methyl benzoate (δ 167) was synthesized and added as an internal standard. Integration of the benzoate peak versus the methyl benzoate standard indicated that approximately one free benzoate was present for each complex in pyridine solution.

The observation of uncomplexed benzoate in the NMR spectra is in direct contrast to the IR spectra, in which no ionic benzoate was observed. A reasonable explanation is that pyridine displaces one of the benzoate ligands, since the NMR spectra were obtained in pyridine solution while the IR studies were performed in the solid state. To further probe this possibility, the solid-state ^{13}C NMR spectrum of the labeled complex was obtained. A standard of labeled potassium benzoate showed a strong, sharp resonance at 173 ppm for the labeled carboxy carbon. This resonance was completely missing in the spectrum of the complex, nor were there any other resonances which could be attributed to the labeled carbon of an uncomplexed benzoate. Observation of a free benzoate ion occurred only when the complex was maintained in pyridine solution. (Solution and solid-state spectra of the labeled complex and potassium benzoate, Figures S2-S5, are available in the supplementary material.) This strongly supports a benzoate coordination mode wherein all three benzoates are bound to the iron centers in the solid state, probably in a bridging manner as indicated by IR spectroscopy, followed by displacement of at least one benzoate ligand by pyridine in solution. Geometric considerations make it likely that two of these carboxylates bridge between the diiron centers of one complex, while the third benzoate bridges between iron centers in two different complexes. This would result in a polymeric structure which would be disrupted, and therefore solubilized, upon displacement of the inter-complex bridging benzoate.

Summary

Diferric complexes of the triphenolate Robson ligands **1a-d** (H_3L) were synthesized. When the ligand or its precursors were reacted with ferric nitrate in the presence of carboxylate ligands, complexes of the type $LFe_2(O_2CR)_3$ (R = C_6H_5, CH_2CH_3, CH_3) (**2a-d**) were obtained. These complexes are analogous to the previously reported diiron complex of the polypodal ligand **3**, with the exception that **2** accommodates one extra benzoate ligand due to the lower denticity of the Robson ligand. Infrared and ^{13}C NMR evidence indicates that the benzoates are coordinated in the solid state and each bridge two metal centers. As with many related complexes, two of the carboxylates probably bridge between the diiron centers. The third carboxylate may bridge between iron centers in different complexes, leading to a polymeric structure. In pyridine solution, one free benzoate ion is observed, which suggests that it is displaced by the solvent.

Acknowledgment. The support of this research by the National Science Foundation through ROW and EPSCoR grants is gratefully acknowledged. We also thank Paul Deck (Northwestern University) for the Mössbauer spectral plot and Earle Adams (Montana State University) for the solid-state ^{13}C NMR spectra.

Supplementary Material Available: The ^{57}Fe Mössbauer spectrum of $LFe_2(O_2CC_6H_5)_3$ (**2b**) (Figure S1), solution and solid-state NMR spectra of ^{13}C-labeled $LFe_2(O_2CC_6H_5)_3$, (**2c**) (Figures S2 and S3), and solution and solid-state NMR spectra of ^{13}C-labeled potassium benzoate (Figures S4 and S5) (5 pages). Ordering information is given on any current masthead page.

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