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Stereoselectivity in Ion-Pair Formation. 3. Preferential Association of Dicarboxylate Anion with Tris(ethylenediamine)cobalt(III)

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The changes in the circular dichroism (CD) spectra of optically active tris(ethylenediamine)cobalt(III) were measured upon the addition of various dicarboxylate dianions, *o*-, *m*-, and *p*-phthalates in one group and $^-OOC(CH_2)_nCOO^-$ (n = 0–4) in the other group: oxalate, malonate, succinate, glutarate, and adipate. It was found that the shape and intensity of the CD change vary depending upon the position of the two carboxyl groups of added anions. The detailed examination of these findings suggests that the skeleton of $^-OOC–C–C–COO^-$ with two carboxyl groups adjacent to each other is favored for a stereospecific interaction with the complex ion. Furthermore the results are supported by a consideration of the association constants determined for the ion pairs between the complex ion and the dicarboxylate anions by utilizing the CD measurements. It is concluded that the CD change and the stability of ion pair are closely related to the relative position of two carboxyl groups.

Introduction

Many interesting studies have been reported on stereoselectivity in the coordination compounds. However, most of these studies are concerned with inner-sphere complexes. One of the familiar examples of this kind is a study[1] of the stereoselective production of propylenediamine–metal complexes. In contrast, few papers have been published on the stereoselectivity of ion-pair formation with chiral coordination compounds. One such study is on the difference in the interaction of L-(2*R*,3*R*)-tartrate with Λ- and Δ-$[Co(en)_3]^{3+}$ in aqueous solution. One reason for the lack of information is that the complex ion and the counterion are loosely bound to each other and so the relative positions of both the ions cannot be easily determined. We thought therefore that information on the structure of such ion pairs should be sought in order to clarify the origin of stereoselectivity in ion pair formation. From this point of view, we found from comparison of the NMR and CD spectra that a malate ion interacts with $[Co(en)_3]^{3+}$ through the carboxyl groups in aqueous solution.[2] In this paper we attempt to obtain more distinct information about the stereoselective interactions between $[Co(en)_3]^{3+}$ and dicarboxylate anions.

Circular dichroism is employed because the measurement of the CD change might serve as a powerful means of investigating an intimate interaction between the complex ion and anion in aqueous solution. For example, Mason and Norman[3] have measured the CD spectra of optically active $[Co(en)_3]^{3+}$ in the presence of PO_4^{3-} and other anions. The substantial change in the CD spectrum observed was argued in favor of substantial hydrogen bonding between PO_4^{3-} and the complex ion.

By contrast, Smith and Douglas[4] have measured the CD spectra of $[Co(en)_3]^{3+}$ and $[Co(gly)(en)_2]^{2+}$ in the presence of a variety of electrolytes. They concluded that a large CD increase in the A_2 transition is related to the preferred stereochemical orientation of the ion pair between the complex ion and a highly charged oxyanion, while small CD increases in all transitions are associated with the random interaction with a singly charged small anion. On the contrary, we found that a fumarate dianion gives a CD change pattern similar to that usually observed for a singly charged anion.[2] This fact suggests that a fumarate ion behaves as a singly charged anion[5] and interacts with the complex ion only through one of its carboxyl groups. We expect that a systematic consideration of this phenomenon will give detailed information about the interactions between the complex ion and dicarboxylate anions.

Experimental Section

Materials. $[Co(en)_3]Br_3{\cdot}3H_2O$ was prepared and resolved into enantiomers Λ- and Δ-$[Co(en)_3]Br_3{\cdot}H_2O$ by using silver L-tartrate. The purity of these complexes was checked by elemental analysis and spectroscopic methods. All other chemicals were reagent grade and were used without further purification.

Measurements. The circular dichroism (CD) spectra were recorded on a reference solution of optically active $[Co(en)_3]^{3+}$ (0.002 M) and on a sample solution of the complex ion (0.002 M) containing a dicarboxylate anion (0.0275 M). To obtain the association constant the CD intensities at 430 and 455 nm were measured for the reference solution and the sample solution containing the dicarboxylate anion ranging in concentration from 0.0025 to 0.0275 M. The ionic strength (μ) was set at 0.1 by the addition of an appropriate amount of sodium perchlorate. A JASCO J-40CS recording spectropolarimeter with a 2-cm cell was used for the CD measurements. The cell was kept at 25.0 ± 0.2 °C with a Haake circulator, Model FK. The difference CD spectra between the sample and reference solutions were measured by using the data processor (DP) compartment operating at 0.2 nm/step of processor resolution. The dicarboxylate salts used here were obtained by neutralizing the dicarboxylic acids with $LiOH{\cdot}H_2O$. The neutralized dicarboxylic acids showed a pH around 7 and so the hydrogen dicarboxylate content was negligible.

Anion–Cation Association Constants. The outer-sphere association equilibrium in our case is

$$M^{3+} + X^{2-} \rightleftarrows MX^{+}$$

if only 1:1 association is assumed, where M^{3+} and X^{2-} denote $[Co(en)_3]^{3+}$ and the dicarboxylate anion, respectively. The outer-sphere association constant K is given by

$$K = [MX^+]/[M^{3+}][X^{2-}] = C_{MX}/(C_M - C_{MX})(C_X - C_{MX}) \quad (1)$$

where C_M, C_X, and C_{MX} refer to the total concentration of M^{3+}, X^{2-}, and MX^+, respectively. The difference of circular dichroism ΔCD between the sample and reference solutions can be given by

$$\Delta CD = 2C_{MX}(\Delta\epsilon_{MX} - \Delta\epsilon_M) \quad (2)$$

where the cell length is 2 cm and $\Delta\epsilon$ denotes the molar circular dichroism of the species indicated by the subscript. Combining eq 1 and 2, we have

$$C_M(C_X - C_{MX})/(\Delta CD/2) = (C_X - C_{MX})/(\Delta\epsilon_{MX} - \Delta\epsilon_M) + 1/K(\Delta\epsilon_{MX} - \Delta\epsilon_M) \quad (3)$$

First an appropriate value of K is assumed and the values of C_{MX} obtained from eq 1 are substituted into eq 3. The plot of the values of the left-hand side of eq 3 vs. $(C_X - C_{MX})$ gives a refined association constant as (slope)/(intercept), which is again substituted into eq 1. The procedures are continued until a constant K is attained. The linearity in the plots of eq 3 supports the assumption that only 1:1 association occurs under these experimental conditions.

Results and Discussion

The CD spectra of the reference and sample solutions are shown in Figure 1. These CD spectra have an E_a component in the longer wavelength region and an A_2 component in the

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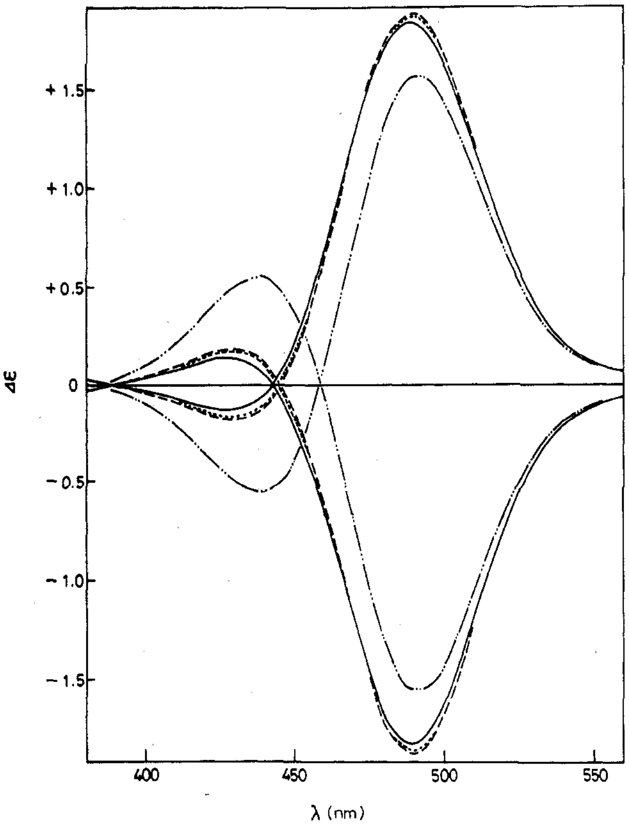


Figure 1. CD spectra of the reference (Λ- or Δ-$[Co(en)_3]^{3+}$) (—) and sample solutions containing *o*-phthalate (–··–), *m*-phthalate (– – –), and *p*-phthalate (- - -). Λ- or Δ-$[Co(en)_3]^{3+}$ and dicarboxylate concentrations were 0.002 and 0.0275 M, respectively, 25.0 °C, μ = 0.1 ($NaClO_4$).

shorter wavelength region. This figure indicates that the CD spectrum of optically active $[Co(en)_3]^{3+}$ changes upon the addition of dicarboxylate anions and the CD changes for Λ- and Δ-$[Co(en)_3]^{3+}$ are the same in magnitude. These CD changes can be observed more clearly by recording the difference CD spectra between the reference and sample solutions, which are presented in Figures 2 and 3. The dicarboxylate anions can be tentatively classified into two groups on the basis of the CD change pattern in the first absorption region of $[Co(en)_3]^{3+}$ in Figure 1. In group A the CD intensity largely increases in the A_2 component. Anions in this group strongly interact with the complex ion and behave as doubly charged anions. In group B the CD intensity slightly increases in both E_a and A_2 components. Anions in this group weakly interact with the complex ion and behave as singly charged anions. The results obtained will be discussed with this classification in mind.

Figure 2 shows the CD changes of Δ-$[Co(en)_3]^{3+}$ upon the addition of *o*-, *m*-, and *p*-phthalates. Since these anions are all doubly charged, they all interact with the complex ion to the same extent if the electrostatic force plays an important role in the interaction of this system. Of these phthalates, however, only the ortho isomer gives rise to a considerable change in the CD spectrum of the complex ion, and the other two isomers give small and similar CD changes. Furthermore the CD change patterns for doubly charged *m*- and *p*-phthalate anions are surprisingly similar to those usually observed for singly charged anions, e.g., benzoate (Figure 2). Thus *m*- and *p*-phthalate anions seem to interact with the complex ion as singly charged anions. This fact indicates that the steric factor but not the electrostatic force is important in the ion-pair formation leading to a substantial CD change. Such anions interact with the complex ion probably through the two carboxyl groups, and the relative position of these two carboxyl groups is significant for the interaction with the complex ion. From this result, it is concluded that the skeleton I is essential

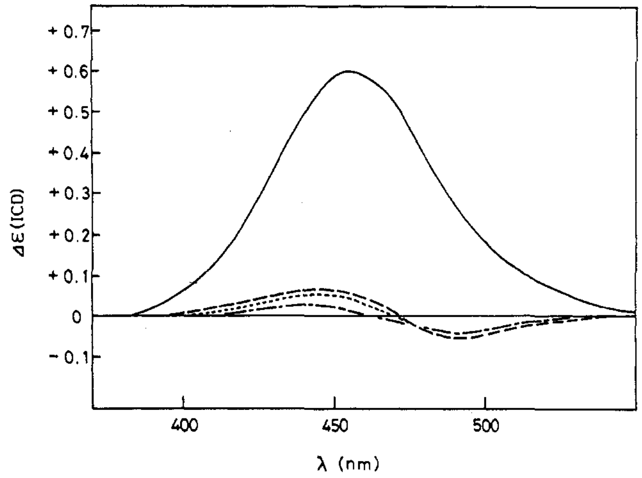


Figure 2. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon the addition of the dicarboxylate anions (0.0275 M): (—) *o*-phthalate, (– – –) *m*-phthalate, (- - -) *p*-phthalate, (–·–) benzoate at 25.0 °C and μ = 0.1 ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{ref}$.

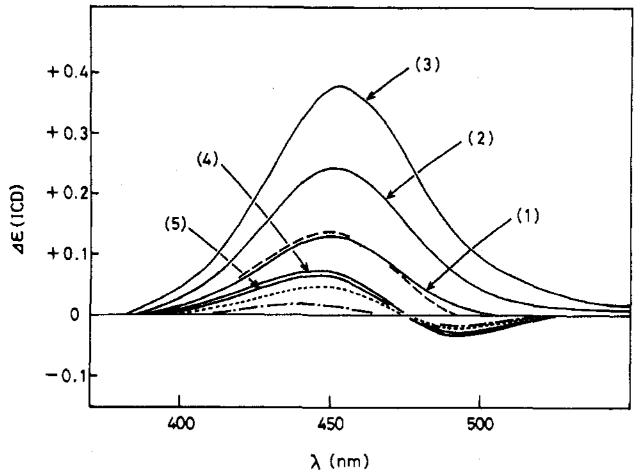
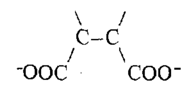


Figure 3. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon the addition of the dicarboxylate anions (0.0275 M): (—) (1) oxalate, (2) malonate, (3) maleate (the gauche form of succinate), (4) glutarate, and (5) adipate, (– – –) succinate (obsd), (- - -) fumarate (the trans form of succinate), (–·–) propionate at 25.0 °C and μ = 0.1 ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{ref}$.



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to a favorable association between the complex ion and the phthalate anion.

Figure 3 shows the CD changes for the dicarboxylate anions $^{-}OOC(CH_2)_nCOO^{-}$. As described in a previous paper,[2] malate, having the same skeleton as succinate, consists of gauche and trans rotamers with respect to the orientation of the two carboxyl groups, and their contributions to the CD change could be replaced by those of maleate and fumarate anions, respectively. This is based on the idea that maleate and fumarate are approximate stereochemical models for the gauche and trans rotamers of malate. If the same assumption is applied to the case of succinate, the CD change for the gauche rotamer of succinate should be nearly equal to that for maleate. Therefore, the CD change should be the greatest for maleate equivalent to the gauche form of succinate (n =

Table I. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)

	Wavelength, nm	*o*-Phthalate	*m*-Phthalate	*p*-Phthalate	Sulfate
Λ-$[Co(en)_3]^{3+}$	430	63.2 ± 2.2			
	455	64.3 ± 2.3			
Δ-$[Co(en)_3]^{3+}$	430	66.4 ± 2.6	7.5 ± 0.9	2.1 ± 0.3	33.8 ± 0.4
	455 (443)[a]	65.7 ± 2.6	7.9 ± 0.7	3.4 ± 0.7	33.9 ± 0.8

[a] The measurements were undertaken at 443 nm for *m*- and *p*-phthalates.

2) in Figure 3. As a result, Figure 3 implies that the CD change increases gradually with an increase in the number of carbon chains for $n < 2$ and is the greatest for $n = 2$, viz., for the gauche form of succinate, while it decreases sharply with an increase in the number of carbon chains for $n > 2$. In the case of $n = 3$ and 4, these anions give a CD change pattern similar to that for a propionate anion, which suggests that they behave as singly charged anions. These findings support the conclusion that the skeleton I is favorable for a stereospecific interaction between the complex ion and the dicarboxylate anion.

The results mentioned above are also confirmed from a consideration of the association constants in these systems. The association constants obtained here are presented in Tables I and II. In the phthalate system, only *o*-phthalate associates markedly with the complex ion like a sulfate ion. The other two isomers, *m*- and *p*-phthalates, show smaller association constants. On the other hand, in the $^{-}OOC(CH_2)_nCOO^{-}$ system, the association constants gradually increase in the order oxalate < malonate < succinate (gauche form). The association constants for glutarate and adipate are very small. Thus, it is concluded that *o*-phthalate and the gauche form of succinate, with two carboxyl groups adjacent to each other, give the greatest CD changes and associate strongly by chelating through hydrogen bonds with $[Co(en)_3]^{3+}$, while *m*- and *p*-phthalates, glutarate, and adipate, with two carboxyl groups remote from each other, associate poorly with $[Co(en)_3]^{3+}$ through a hydrogen bond with only one carboxyl group.

The results obtained here seem to be reasonably interpreted on the basis of the idea[6] that the best match of hydrogen–hydrogen distance of axial amine protons in the complex with the oxygen–oxygen distance of the anion results in a preferable association. The H–H distance of axial amine protons in $[Co(en)_3]^{3+}$ is shown in Figure 4. This distance is smaller than the N–N distance of coordinated nitrogens because of the inclination of N–H bonds. In all dicarboxylate anions examined here, the interoxygen distances in one carboxyl group are similar and are close to 2.2 Å. On the other hand, the oxygen–oxygen distance between two carboxyl groups differs for each dicarboxylate anion. The match of the latter distance with the H–H distance of amine protons can play an important role in the interactions between the complex ion and dicarboxylate anions. The oxygen–oxygen distances between two carboxyl groups are shown in Figure 5.

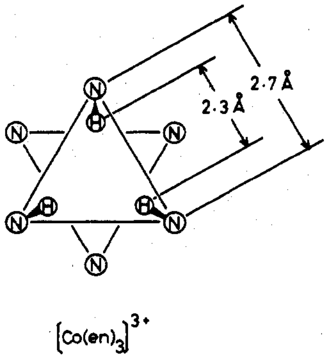
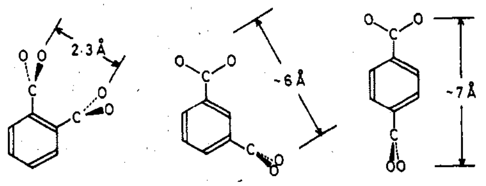
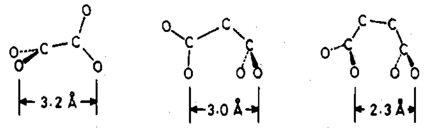


Figure 4. Schematic drawing of the structure of $[Co(en)_3]^{3+}$ along the threefold axis and H–H distance between its axial amine protons. See ref 7.



o-phthalate (A) m-phthalate (B) p-phthalate (C)



oxalate (D) malonate (E) succinate (gauche) (F)

Figure 5. Oxygen–oxygen distances between two carboxyl groups in the dicarboxylate dianions. The distances in this figure were determined on the basis of the Dreiding models. Of these distances, A, D, E, and F are the possible distances which match best the H–H distance of the axial amine protons in $[Co(en)_3]^{3+}$.

Of the phthalates, the ortho isomer can fit the H–H distance of the amine protons, and this leads to the preferential association. On the other hand, it is impossible that meta and para isomers associate with a complex ion with both carboxyl group oxygens simultaneously hydrogen bonded to amine protons. The oxygen–oxygen distance between two carboxyl groups, 6–7 Å, is too large in comparison with the H–H distance, 2.3 Å, of the axial amine protons in $[Co(en)_3]^{3+}$. These *m*- and *p*-phthalates seem to be forced to interact with a complex ion only through one carboxyl group. This leads to a CD change similar to that usually observed for a singly charged anion. Thus, the CD change is closely related to the distance between the two carboxyl groups and to their relative position.

On the other hand, in the $^{-}OOC(CH_2)_nCOO^{-}$ system, oxalate and malonate have no rotamers with different carboxylate carbon–carbon distances and the range of possible

Table II. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)

	Wavelength, nm	Oxalate	Malonate	Maleate[b]	Glutarate	Adipate
Λ-$[Co(en)_3]^{3+}$	430	17.9 ± 0.4	27.3 ± 0.2	48.8 ± 1.3		
	455	19.6 ± 1.4	26.5 ± 0.4	48.2 ± 1.3		
Δ-$[Co(en)_3]^{3+}$	430	19.4 ± 0.3	25.8 ± 0.6	47.0 ± 1.0	4.9 ± 1.3	3.5 ± 1.0
	455 (443)[a]	18.3 ± 0.3	25.8 ± 0.5	45.9 ± 0.9	6.1 ± 0.9	2.2 ± 1.5

[a] The measurements were undertaken at 443 nm for glutarate and adipate. [b] Gauche form of succinate. It is assumed that the association constant for the gauche form of succinate is equal to that for maleate.

oxygen–oxygen distances is thereby limited, while succinate has rotamers with carboxyl groups gauche and trans to each other. As described before, the interactions of gauche and trans rotamers of succinate with $[Co(en)_3]^{3+}$ could be replaced by those of maleate and fumarate, respectively. Thus the oxygen–oxygen distances between two carboxyl groups, which are the best distances matching the H–H distance of the axial amine protons in $[Co(en)_3]^{3+}$, are 3.2, 3.0, and 2.3 Å for oxalate, malonate, and the gauche form of succinate, respectively. The distance between two carboxyl groups matches better with the H–H distance of amine protons as the skeleton carbon increases. Thus, the dicarboxylates associate with the complex ion in the order oxalate < malonate < succinate (gauche form).

By contrast, glutarate and adipate can exist as several rotamers. The possible rotamers of glutarate are trans–trans (T–T), trans–gauche (T–G), and two gauche–gauche (G–G) forms. Though the CD changes for these dicarboxylates cannot be separated into the contributions from each rotamer, it is possible to tackle this problem with the aid of molecular models. According to a consideration of such molecular models, G–T and T–T rotamers contribute to the CD change only as singly charged anions would. The oxygen–oxygen distances between two carboxyl groups for these two rotamers are ~6 Å. These distances do not fit the H–H distance of amine protons in $[Co(en)_3]^{3+}$. Only a G–G rotamer can fit the complex ion and lead to a great CD change. However, the population of this rotamer seems to be small since it is electrostatically at a disadvantage due to the repulsion between two carboxyl groups.[8] Thus the sum of the contributions from these rotamers will give a small CD change, and its pattern comes to be similar to that for a singly charged anion.

Factors other than steric ones which affect the interactions between the complex ion and dicarboxylate anions will now be examined. The dipolar effect may be one of these factors. However, it is not so important because *m*-phthalate, which has a certain dipole moment, behaves as a singly charged anion. In contrast, oxalate, which has no dipole, associates with the complex ion to a great extent (Table II). This result cannot be interpreted in terms of the dipolar effect. Thus the interaction between the complex ion and the dicarboxylate anion seems to be controlled predominantly by the steric effect, though the dipolar effect cannot be ruled out.

It is concluded that the degree of the interaction between $[Co(en)_3]^{3+}$ and a dicarboxylate anion depends predominantly on the relative position of two carboxyl groups in the dicarboxylate anion. The better match of the H–H distance of axial amine protons in the complex with the oxygen–oxygen distance of the anion results in a smooth association (group A). On the other hand, the dicarboxylate anion with the greater oxygen–oxygen distance between two carboxyl groups cannot interact with $[Co(en)_3]^{3+}$ through the two carboxyl groups simultaneously and thus associates poorly with the complex ion. These anions only slightly alter the CD spectrum of $[Co(en)_3]^{3+}$ and the CD change pattern is similar to that usually observed for a singly charged anion (group B). One more noteworthy conclusion is as follows. Succinate, glutarate, and adipate have more than two rotamers. Of these, only one rotamer can interact substantially with the complex ion and give a large CD change. This rotamer, however, only gives a small CD change contribution because of its low concentration compared with the other components. Thus, the overall CD changes are relatively small for these dicarboxylate anions.

Registry No. Λ-$[Co(en)_3]^{3+}$, 27228-84-8; Δ-$[Co(en)_3]^{3+}$, 16569-46-3; *o*-phthalate, 3198-29-6; *m*-phthalate, 42966-02-9; *p*-phthalate, 3198-30-9; sulfate, 14808-79-8; oxalate, 338-70-5; malonate, 156-80-9; maleate, 142-44-9; glutarate, 56-16-6; adipate, 764-65-8; benzoate, 766-76-7; propionate, 72-03-7; fumarate, 142-42-7; succinate, 56-14-4.

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Synthesis of Electron-Deficient Biferracarboranes

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The polyhedral expansion of 3,1,2-$C_5H_5FeC_2B_9H_{11}$ produced three new electron-deficient biferracarboranes $(C_5H_5Fe)_2C_2B_9H_{11}$, $(C_5H_5Fe)_2C_2B_8H_9(OH)$, and $[C_5H_5FeC_2B_9H_{11}FeC_2B_9H_{11}]^-$. All three complexes contained formal Fe(III) atoms and were diamagnetic. The proposed structures, based on spectroscopic and crystallographic data, contain nonbonded iron atoms. These complexes constitute the first examples of long-range electron-spin coupling through a carborane polyhedron.

Ferracarboranes have been synthesized containing formal Fe(II) and Fe(III) oxidation states.[1] Those of formula $[Fe(C_2B_nH_{n+2})_2]^{2-}$ and $[C_5H_5FeC_2B_nH_{n+2}]^-$ contain formal Fe(II) and are readily air oxidized to the stable Fe(III) complexes $[Fe(C_2B_nH_{n+2})_2]^-$ and $C_5H_5FeC_2B_nH_{n+2}$. These latter iron(III) metallocarboranes can be viewed as two-carbon carboranes in which a $\{C_5H_5Fe\}$ vertex has replaced a $\{BH\}$ vertex. Because $\{C_5H_5Fe^{II}\}$ is formally "isoelectronic" with $\{BH\}$, the Fe(III) complexes represent polyhedra containing one electron less than the required $2n + 2$ framework electrons.[2] A result of this electron deficiency is that polyhedral rearrangements have not yet been observed in this class of metallocarboranes. Crystallographic studies[1d] have shown that these iron(III) metallocarboranes possess regular closo-polyhedral geometries, indicating that one-electron deficiency has little or no effect upon polyhedral structure.

Prior to this work, only one electron-deficient biferracarborane had been reported,[3] the two-electron deficient species $(C_5H_5Fe^{III})_2C_2B_6H_8$ prepared by polyhedral expansion of 4,5-$C_2B_7H_9$. This curious compound was initially obtained in a paramagnetic ($\mu_{eff} = 3.05\ \mu_B$) form presumably containing two unpaired electrons. It underwent a slow transformation to a diamagnetic species and a crystal structure[3] of the diamagnetic complex showed a unique 10-vertex closo-

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