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Oxidation-Reduction Properties of Peroxo- and Superoxo-Bridged Cobalt Complexes^{1,2}

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Kinetics of reduction of a series of μ -peroxo-bridged cobalt complexes $[\text{Co}(\text{en})_2(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{en})_2]^{3+}$, $[\text{Co}(\text{dien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{dien})]^{3+}$, $[\text{Co}(\text{trien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{trien})]^{3+}$, and $[\text{Co}(\text{tep})(\mu\text{-}\text{O}_2)\text{Co}(\text{tep})]^{4+}$ by Fe^{2+} were studied, where en is ethylenediamine, dien is diethylenetriamine, trien is triethylenetetramine, and tep is tetraethylenepentamine. The rate is first order in both oxidant and reductant, with second-order rate constants $k_{2(\text{en})} = 400 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$, $k_{2(\text{dien})} = 140 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$, $k_{2(\text{trien})} = 25 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$, $k_{2(\text{tep})} = 3.0 \pm 0.5 \text{ M}^{-1} \text{ s}^{-1}$. The data are explained in terms of an inner-sphere mechanism and compared with results previously obtained for μ -amino- μ -peroxo systems. For the corresponding μ -superoxo complexes $[\text{Co}(\text{en})_2\text{O}_2\text{Co}(\text{en})_2]^{5+}$, $[\text{Co}(\text{trien})\text{O}_2\text{Co}(\text{trien})]^{5+}$, and $[\text{Co}(\text{tep})\text{O}_2\text{Co}(\text{tep})]^{5+}$, $k_2'(\text{en}) > 8000 \text{ M}^{-1} \text{ s}^{-1}$, $k_2'(\text{trien}) = 430 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$, and $k_2'(\text{tep}) = 380 \text{ M}^{-1} \text{ s}^{-1}$.

Introduction

The nature of the bonding and reactivity of metal-dioxygen complexes has recently been the subject of intensive investigation.^{4,5} Although factors influencing the thermodynamics⁶ and kinetics^{4d,7} of oxygen complexation are becoming better understood, the reactivities of such complexes, particularly the dioxygen moiety, remain to be elucidated. Recently Sykes⁸ has reported a detailed study of the reduction of $[\text{Co}(\text{en})_2(\mu\text{-}\text{O}_2,\text{NH}_2)\text{Co}(\text{en})_2]^{3+}$ by Cr^{2+} and V^{2+} where en is ethylenediamine. This work is a progression from earlier studies of Taube⁹ and Sykes and co-workers¹⁰⁻¹² on reduction of superoxo and peroxo oxygen complexes. However, no consistent series of complexes has been examined for the superoxo- nor peroxo-bridged complexes.

Since the superoxo complex is thought to be reduced by an outer-sphere mechanism^{8,10-12} whereas an inner-sphere mechanism has been proposed for the reduction of the peroxo-bridged complex, it was felt that the study of a homologous series of compounds might shed some light on mechanistic details. Furthermore, in order to use the information gained from model compound studies in furthering our understanding of oxidase enzymes,¹³ detailed knowledge of their redox chemistry is of fundamental importance. Thus we have examined the reduction by Fe^{2+} of the following μ -peroxo complexes: $[\text{Co}(\text{en})_2(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{en})_2]^{3+}$, $[\text{Co}(\text{dien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{dien})]^{3+}$, $[\text{Co}(\text{trien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{trien})]^{3+}$, and $[\text{Co}(\text{tep})(\mu\text{-}\text{O}_2)\text{Co}(\text{tep})]^{4+}$, where dien is diethylenetriamine, trien is triethylenetetramine, and tep is tetraethylenepentamine.

In addition, reactivity of these compounds toward acid decomposition (i.e., charge transfer with concomitant protonation of the amine leading to aquation) has been examined, as well as the 1 e reduction of the corresponding μ -superoxo complexes $[\text{Co}(\text{en})_2(\mu\text{-}\text{O}_2)\text{Co}(\text{en})_2]^{5+}$, $[\text{Co}(\text{trien})(\mu\text{-}\text{O}_2)\text{Co}(\text{trien})]^{5+}$, and $[\text{Co}(\text{tep})(\mu\text{-}\text{O}_2)\text{Co}(\text{tep})]^{5+}$.

Experimental Section

Acid salts of polyamine ligands ethylenediamine dihydrochloride, diethylenetriamine trihydrochloride, triethylenetetramine disulfate, and tetraethylenepentamine 2.5-sulfate were obtained from commercial sources and used without further purification. The tetrahydrochloride salt of triaminotriethylamine (tren) was prepared by the method of Mann and Pope.¹⁴

Solutions of the oxygen complexes containing these ligands were prepared by mixing standard aliquots of cobalt nitrate solution

Table I. Rate of Reduction of Cobalt-Oxygen Complexes by Ferrous Ion ($\mu = 0.2 \text{ M}$ (KNO_3); $T = 25^\circ \text{C}$)

Complex	$k_2, \text{M}^{-1} \text{s}^{-1}$	$\log k_{\text{O}_2}$	E^\ddagger , kcal mol ⁻¹
$[\text{Co}(\text{en})_2(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{en})_2]^{3+}$	400 ± 20	8.0 ± 0.1	4.2
$[\text{Co}(\text{dien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{dien})]^{3+}$	140 ± 10	1.1 ± 0.1	7.0
$[\text{Co}(\text{trien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{trien})]^{3+}$	25 ± 3	8.0 ± 0.1	
$[\text{Co}(\text{tep})(\mu\text{-}\text{O}_2)\text{Co}(\text{tep})]^{4+}$	3 ± 0.5	15.0 ± 0.1	

(standardized by EDTA titration with murexide indicator) with stoichiometric amounts of ligand (2:1 for en; 1:1 for all other ligands) adding the stoichiometric quantity of KOH required to reach the potentiometric end point, thus ensuring complete formation of the single μ -peroxo or μ -peroxo- μ -hydroxo species.^{6,15} Ionic strength was adjusted to 0.2 M with KNO_3 in most cases, although NaClO_4 was used in some runs to check for a possible specific ion effect. Ferrous ammonium sulfate solutions were prepared immediately before use. Such solutions were always used within 30 min of preparation.

In a typical experiment, solutions of ferrous salt and of the cobalt-oxygen complex were mixed in a Durrum Jasco D-150 stopped-flow spectrophotometer and the change in absorbance at 360 nm (corresponding to λ_{max} for the oxygen complex) was monitored. The concentration of ferrous ion was made up in large excess of that of the cobalt-dioxygen complex, so that pseudo-first-order kinetics were observed, as indicated in Figure 1. Duplicate runs were performed at each concentration on two separately prepared solutions, for a total of four runs per concentration. Five different concentrations were investigated for each complex. Concentration of $\text{Fe}(\text{II})$ ranged from 1×10^{-3} to $5 \times 10^{-2} \text{ M}$; $\text{Co}(\text{II})$ concentration ranged from 1×10^{-4} to $5 \times 10^{-3} \text{ M}$. Temperature-dependence studies on the $[\text{Co}(\text{en})_2(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{en})_2]$ and $[\text{Co}(\text{dien})(\mu\text{-}(\text{O}_2,\text{OH}))\text{Co}(\text{dien})]$ systems were performed over the range 20–45 °C in order to test the validity of the relative rates. Activation parameters were obtained using a standard Arrhenius plot.

For experiments involving cobalt-superoxo complexes, decrease in absorbance at 710 nm, corresponding to λ_{max} for the superoxo complex, and increase in absorbance at 360 nm (λ_{max} of peroxo-cobalt product) were followed with identical results.

Spectral characterization of the intermediate in the reduction of the peroxo product was afforded by repeated kinetic runs at 5-nm intervals over the range 700–330 nm, after the method of Sykes.⁸

Results and Discussion

The second-order rate constants for ferrous ion reduction of some μ -peroxo bis(cobalt chelates) are given in Table I. It was initially suspected that the rate might depend in some simple manner on the degree of $\text{Co}(\text{III})$ character at the metal

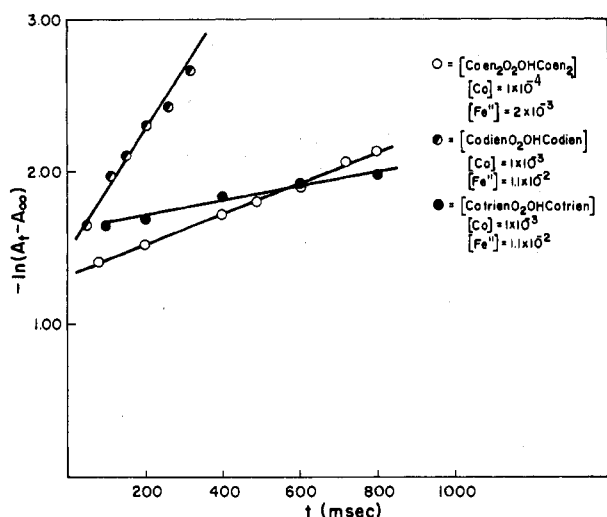
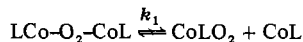


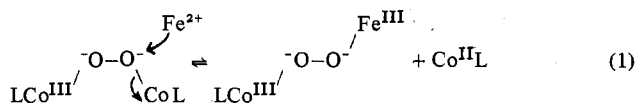
Figure 1. Pseudo-first-order dependence of the reduction of binuclear μ -hydroxo- μ -dioxygen-cobalt(II) complexes by ferrous ion.

center as reflected in the equilibrium constant for the oxygenation reaction. (An increased value of K_{O_2} is believed to be related to the degree of Co(III) character of the complex.^{5,6}) It is readily apparent from Table I, however, that no such correlation exists. Rather, the trend exhibited by the rates might imply operation of a simple inner-sphere mechanism, as the rates of reduction parallel those for substitution, i.e., $(\text{en})_2 > \text{dien} > \text{trien} > \text{tep}$.

While the observed rates are quite high relative to the simple acid hydrolysis rates of these complexes, they are not totally out of the range expected for an inner-sphere process, particularly if approach of the ferrous ion labilizes the cobalt-oxygen bond. Furthermore, the rate of spontaneous oxygen bond cleavage



is rather rapid for these complexes ($k_1 \approx 0.01 \text{ s}^{-1}$ for $\text{L} = (\text{en})_2$).⁴⁹ Earlier work by Sykes⁸ has indicated that in the initial reduction step of the related $[\text{Co}(\text{en})_2(\text{O}_2\text{NH}_2)]^{3+}$ complex by Cr^{2+} , no chromic ion is released into solution, consistent with an inner-sphere reaction. Thus, the rate-determining step in the initial reaction of the reductant (in this case, ferrous ion) with the oxygen complex is thought to be attack by the reductant at the peroxo bridge with concomitant labilization of the cobalt-oxygen bond due to electron transfer, resulting in the release of 1 equiv of cobaltous chelate (eq 1).



While our results are consistent with an inner-sphere mechanism, such a result might also be expected in an outer-sphere reaction, if the steric differences between the complexes are large. In fact, we have found such an effect in the reduction of the corresponding superoxo complexes.

In an attempt to better characterize the reaction pathway, therefore, we have examined the nature of the intermediate formed on initial reduction of the peroxo complex, using repeated stopped-flow scans as outlined in the Experimental Section. The resultant spectrum obtained is given in Figure 2. Several points relevant to the reaction are immediately discernible. First, the strong resemblance of the two spectra (reactant and intermediate) is striking. The presence of the Co^{III} chromophore at $\sim 500 \text{ nm}$ is maintained in the in-

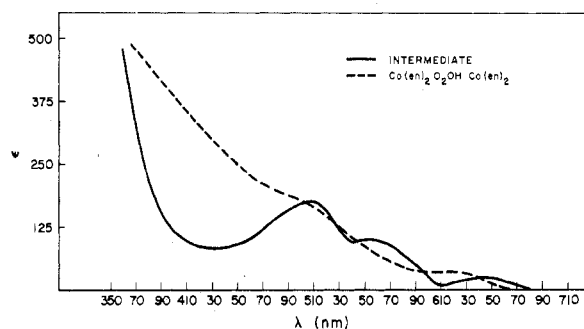


Figure 2. Electronic spectrum of initial intermediate formed on reduction of the bis(ethylenediamine)- μ -hydroxo- μ -dioxygen-cobalt(II) complex by ferrous ion.

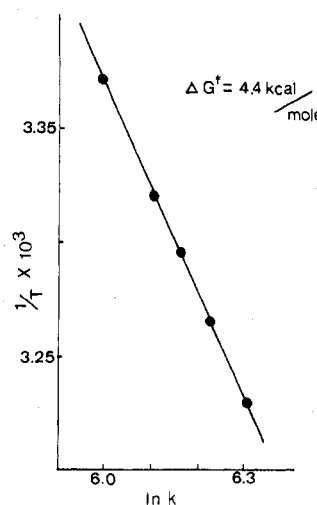


Figure 3. Arrhenius plot for the reduction of $[\text{Co}(\text{en})_2(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{en})_2]^{3+}$ by Fe^{2+} at $\mu = 0.2 \text{ M}$ (KNO_3).

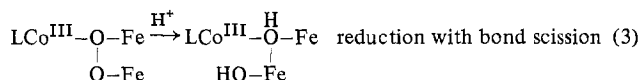
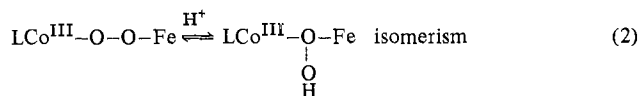
intermediate spectrum, implying retention of a formally cobalt(III) moiety in the intermediate, as proposed in eq 1. Equally interesting is the high-intensity band growing in below 370 nm, which might most logically be assigned to an $\text{L} \rightarrow \text{M}$ charge transfer, as in the simple bis-cobalt system.^{4a} The small shift of this band implies the surprising result that the electron distribution in the cobalt-iron hybrid peroxo complex is only slightly perturbed relative to the initial reactant. Such a situation might occur if the energy difference between the metal and $\pi^* \text{O}_2$ orbitals was large, so that any perturbation of the metal orbitals would only slightly affect the overall energy of transition. Such an explanation would also explain the relative insensitivity of the charge-transfer band in the bis-cobalt μ -peroxo complexes, which for a wide variety of ligands remains in the 350–360-nm range. A disturbing feature of this explanation is that such a large separation should tend to destabilize the complex in that effective overlap between orbitals of highly disparate energies would be decreased.

It may be noted that a peroxo \rightarrow iron(III) transition might occur in such a complex at an energy similar to the $\text{O}_2 \rightarrow \text{Co}(\text{III})$ transition. The intermediate spectrum is qualitatively similar to that observed by Sykes for a proposed $\text{Co-O}_2^{2-}\text{-Cr}$ complex.⁸

In addition, the temperature dependences of the reductions of $[\text{Co}(\text{en})_2(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{en})_2]^{3+}$ and $[\text{Co}(\text{dien})(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{dien})]^{3+}$ were examined. Over the temperature range 20–45 $^\circ\text{C}$, excellent linearity in the Arrhenius plot is obtained. If the reaction proceeded by dual pathways (inner sphere and outer sphere) and activation parameters for the pathways were different, as would be expected, linearity would

not be expected. In addition, the relative magnitudes of the reduction rates of the en and dien complexes are maintained throughout the temperature range investigated.

Assuming a mechanism similar to that proposed by Sykes,⁸ eq 2 and 3 may occur. Such processes, however, were not



observed in our own study, due to complications of acid decomposition.

While the μ -amido- μ -peroxo bis-cobalt systems studied by Weil,⁵ Sykes,¹² and others are quite stable in strong acid (although isomerizing in very strongly acidic solutions), the μ -hydroxo- μ -peroxo systems studied herein undergo relatively rapid acid hydrolysis to regenerate Co(II) and molecular oxygen, as with the pentaammine system studied by Taube.⁹ Thus, for the slower secondary reduction and isomerization reactions, the hydrolysis rates became strongly competitive and could not easily be separated out.

In the initial reaction step reported here, the rate of hydrolysis was at least tenfold slower than reduction for all of the complexes reported and thus could easily be corrected. (For several other systems investigated, including $[\text{Co}(\text{EDDA})(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{EDDA})]^-$ and $[\text{Co}(\text{DTMA})(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{DTMA})]^+$, the rate of hydrolysis was competitive with ferrous ion reduction, so that useful data could not be obtained.) Qualitatively, the hydrolysis rates followed the same order found for reduction, $\text{Co}(\text{en})_2 > \text{Co}(\text{dien}) > \text{Co}(\text{trien}) > \text{Co}(\text{tep})$.

Thus, there was the possibility that acid concentration could affect the observed redox rates in another manner, either by setting up an equilibrium between peroxo and hydroperoxo species⁵ or by simple hydrolysis of the hydroxo bridge leading to a different stereochemistry of the reacting species. We therefore checked the effect of acid concentration on the rate of ferrous reduction of the $[\text{Co}(\text{en})_2(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{en})_2]^{3+}$ and $[\text{Co}(\text{dien})(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{dien})]^{3+}$ complexes and found that over the range investigated ($[\text{H}^+] = 0.01\text{--}0.03 \text{ M}$) the rate was absolutely independent of acid concentration.

It is therefore believed that the reason for the observed identical ordering of hydrolysis rates and redox rates for the complexes lies in their similar processes of bond breaking from the cobalt center, which in the redox reaction may be assisted by the ferrous ion, being consistent with a simple inner-sphere process and involving no special protonated forms, as evidenced by the acid independence of the redox reaction.

Such a finding does not contradict the invocation by Sykes⁸ of protonated forms of the oxygen complex with differing kinetic properties but merely implies that for these complexes under the conditions investigated, such protonated forms, if they exist, are in vanishingly small concentration, so that their effect is negligible. Alternatively, such forms do not lie on a favorable pathway for reduction.

The reasons for the kinetic inertness of the μ -amido complex relative to the μ -hydroxo are not immediately obvious, as NH_2^- is a stronger base than OH^- and might thus be expected to more readily protonate with subsequent decomposition of the complex. The most reasonable explanation, pointed out by a reviewer, is that in the μ -amido complex no lone pairs are available as a protonation site to initiate decomposition, whereas in the μ -hydroxo complex such a site is available.

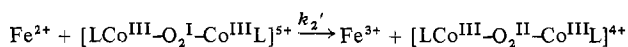
To afford a direct comparison of the relative reactivity of the μ -amido- and μ -hydroxo-bridged μ -peroxo systems, we have briefly examined the reaction of $(\text{Co}(\text{trien}))_2\text{NH}_2\text{O}_2$ with

Table II. One-Electron Ferrous Reduction of Some μ -Superoxo Complexes

Complex	k_2' , $\text{M}^{-1} \text{ s}^{-1}$
$[\text{Co}(\text{en})_2(\mu-\text{O}_2)\text{Co}(\text{en})_2]^{5+}$	>8000
$[\text{Co}(\text{trien})(\mu-\text{O}_2)\text{Co}(\text{trien})]^{5+}$	430 ± 10
$[\text{Co}(\text{tep})(\mu-\text{O}_2)\text{Co}(\text{tep})]^{5+}$	380 ± 5

Fe(II). For this complex $k_2 = 15 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$ compared with $k_2 = 30 \text{ M}^{-1} \text{ s}^{-1}$ for the hydroxo-bridged complex. For this system then, the hydroxo-bridged species appears to be slightly more reactive, although little may be made of such a small difference. More data, however, are required to determine if this difference is a general trend and what factors contribute to the differing reactivities of these complexes. We are undertaking such a general study.

Finally, we have briefly examined the rates of reduction by Fe(II) of several μ -superoxo species at $\mu = 0.2$, 25°C , with the rather surprising results given in Table II for the reaction



The results are identical within experimental error regardless of whether product formation (measured by absorbance increase at 360 nm, resulting from the μ -peroxo complex formed in the 1 e reduction) or disappearance of reactant (at 710 nm) was measured. Since the reaction was fast relative to subsequent reduction (cf. Table I), correction for the second reaction was easily handled.

While these data are only preliminary in nature, several features of interest are apparent. First of all, the initial reduction of the superoxo complex is much faster than that of the peroxo complex perhaps due to the unfilled π^* orbital of the superoxo complex (in agreement with the relative stabilities of the complexes). Of more interest is the curious parallelism in relative rates for the μ -peroxo and μ -superoxo systems. While the rate trend might naively suggest an inner-sphere mechanism is operative for the superoxo species as well as for the peroxo, the rates observed are much too fast to be accommodated in terms of any bond cleavage at the cobalt center. Furthermore, the product is unmistakably the μ -peroxo complex, in which all of the bonds present in the superoxo complex have remained intact. While a wide series of μ -superoxo complexes have been examined elsewhere,⁸ no evidence for an inner-sphere pathway has ever been found. Therefore, an outer-sphere mechanism must be operative here, as has been proposed elsewhere¹⁰⁻¹² for superoxide complex reduction. Thus, the possible explanation for the observed rate trend could encompass any of the following. First, simple steric factors could be operative, with the larger ligands inhibiting approach of the ferrous ion for effective orbital overlap. A second, related possibility would be the increased "back strain" of the larger complexes. As in-plane bending would tend to increase accessibility of the bridging oxygen to the approaching reductant, thus increasing the likelihood of reaction, the reduced capacity of the more hindered complexes to bend would lead to effective shielding of the dioxygen. Finally, as the larger ions would be less effectively solvated, the effective positive charge at the metal center seen by the approaching ion would be greater, and simple electrostatic repulsion would prevent close approach, thus decreasing reaction rate.

While, as mentioned, such considerations might also apply to the μ -peroxo complexes, their slower reaction rates and intermediate spectra coupled with the ion-exchange data of Sykes⁸ lead us to assign an inner-sphere mechanism for the reduction of the μ -peroxo complexes.

Further investigations in this area, utilizing a wider range of reductants and substrates, are in progress.

Registry No. $[\text{Co}(\text{en})_2(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{en})_2]^{3+}$, 36885-26-4; $[\text{Co}(\text{dien})(\mu-(\text{O}_2, \text{OH}))\text{Co}(\text{dien})]^{3+}$, 60306-17-4; $[\text{Co}(\text{trien})(\mu-$

(O₂,OH)Co(trien)]³⁺, 36431-46-6; [Co(tep)(μ-O₂)Co(tep)]⁴⁺, 36883-61-1; [Co(en)₂(μ-O₂)Co(en)]⁵⁺, 60325-91-9; [Co(trien)(μ-O₂)Co(trien)]⁵⁺, 60325-90-8; [Co(tep)(μ-O₂)Co(tep)]⁵⁺, 59200-72-5; Fe²⁺, 15438-31-0.

References and Notes

- (1) Abstracted in part from a dissertation submitted by G.M. to the faculty of Texas A&M University in partial fulfillment for the degree of Doctor of Philosophy.
- (2) This research was supported by a research grant, No. A-259, from the Robert A. Welch Foundation.
- (3) Texas A&M University Health Fellow.
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Theoretical Study of the Electromagnetic Properties of Bis(fulvalene)diiron in Its Three Oxidation States

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An iterative extended Hückel molecular orbital calculation is used to obtain wave functions for the ground state of biferrocenylene [bis(fulvalene)diiron] and several low-lying states of the mono- and dioxidized cations. The molecular orbitals are compared to those calculated for ferrocene and to those obtained from a previous study of ferrocene and the ferrocenium ion. The calculated electron distributions are used to determine the electric field gradient at each iron nucleus for bis(fulvalene)diiron and ferrocene. A large quadrupole splitting, comparable to that calculated for ferrocene, is obtained for both compounds in agreement with experiment. The ground state of monooxidized bis(fulvalene)diiron is obtained by removal of an electron from an e_{2g} type orbital delocalized over the two ferrocene moieties due to d-orbital relaxation effects similar to those observed for the ferrocenium ion. For the monovalent cation, the electric field gradient at the iron nuclei and g values are calculated. The values are in agreement with experiment. A possible assignment of the electronic spectral transitions unique to the mixed-valence state is made. Such d-orbital relaxation effects are not observed for the dioxidized species. The ground state of the divalent cation is obtained by removal of two electrons from the highest occupied molecular orbital of the neutral species, a delocalized carbon π orbital with substantial metal-metal antibonding character. The calculated diamagnetic ground state is the basis for a consistent explanation of the unexpectedly large quadrupole splitting and other observed spectroscopic properties. Removal of electrons from a_{1g} or degenerate e_{2g} type d orbitals yields excited configurations which do not account for the observed behavior of dioxidized bis(fulvalene)diiron.

Introduction

Organometallic mixed-valence compounds form systems in which two or more atoms of the same metal exist in different formal oxidation states within one molecule. Recently there has been a growing interest in such compounds because, in contrast to the polymeric inorganic mixed-valence systems, they offer the possibility of studying on an intramolecular basis the unusual phenomena associated with the coexistence of differing valence sites in a given system. Inorganic and organometallic systems alike show a large variation in the degree of interaction between the differing sites. The range spans from firmly trapped valences, in which the properties of the compound are merely those of the component parts with little or no interaction, to complete delocalization and non-integral valences.¹ For these latter compounds, the magnetic and spectroscopic properties do not resemble those of the constituent parts of the molecule.² Various theories have been advanced in an attempt to explain the observed behavior of these compounds.^{1,3}

The two structurally related systems, biferrocenylene [bis(fulvalene)diiron, BFD] (Ia) and biferrocene (IIa), appear to be at opposite ends of the scale. The properties of the mixed-valence compound biferrocene(2,3) picrate (IIb) can be attributed to the constituent ferrocene and ferrocenium moieties⁴⁻⁸ and those of the fully oxidized biferrocene(3,3) salt (IIc) to two ferrocenium units.⁴ Although the structure of

neutral BFD was determined several years ago,⁹ only recently a new and more efficient synthesis¹⁰ allowed preparation of the mono- (Ib) and dioxidized (Ic) salts and thus made possible an experimental investigation of the properties of this compound in all of its oxidation states.¹⁰ BFD(2,3) and BFD(3,3) were found to exhibit properties distinctly different from those of ferrocene or the ferrocenium ion.^{4,10}

The Mössbauer spectrum of unoxidized BFD(2,2) resembles that of ferrocene and biferrocene(2,2).¹⁰ The spectrum of biferrocene(2,3) salts is a composite of separate ferrocene and ferrocenium transitions¹¹ with some recent evidence⁴ for an additional low-energy equivalent iron atom component as well. On the other hand, Mössbauer results for the BFD monovalent cations indicate totally equivalent iron atoms with a spectrum resembling that of neither ferrocene nor the ferrocenium ion.¹⁰ Mössbauer studies alone cannot determine if the apparent equivalence is due to rapid oscillation of a "trapped" valence electron between inequivalent iron(II) and iron(III) sites which exchange at a rate greater than 10⁸ s⁻¹ (the reciprocal of the lifetime of the Mössbauer excited state) or actual delocalization of the odd electron over two iron sites made equivalent by either a metal-metal or a metal-ligand-metal interaction, resulting in a fractional valence state. The equivalence of the iron atoms in BFD(2,3) is confirmed however by x-ray photoelectron spectroscopy (ESCA).¹⁰

Both the Mössbauer and ESCA studies on BFD(2,3) refute prior speculation that the compound exhibited trapped valency. This suggestion was supported by an initial electronic spectroscopy study where an absorption in the near-infrared

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