to the spectra in pyridine solution. These results suggest that there is some coordination of THF to this complex but not to the other complexes. The electron-withdrawing Cl may decrease the coordinating ability of the salicylaldimine sufficiently that formation of a 5-coordinate species becomes more favorable.

Conclusions

The EPR spectra of these Cu(salen-NO) and Cu(salpn-NO) derivatives indicate that exchange interactions through saturated linkages are strongly dependent upon the detailed molecular conformation. Thus, they can be useful probes of structural changes and weak molecular interactions.

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Registry No. I, 88730-14-7; II, 88730-15-8; III, 88730-16-9; IV, 88730-17-0; V, 88730-18-1; VI, 88730-19-2; Cu(salen-NO), 88730-20-5; Cu(4-OMe-salen-NO), 88730-21-6; Cu(salpn-NO), 88730-22-7; Cu(3-OEt-salpn-NO), 88730-23-8; Cu(4-OMe-salpn-NO), 88730-24-9; Cu(4,6-$(OMe)_2$-salpn-NO), 88730-25-0; Cu(5-Cl-salpn-NO), 88730-26-1; diaminopropionic acid hydrochloride, 6018-55-9; *S*-ethyl trifluorothioacetate, 383-64-2; 2,4-diaminobutyric acid dihydrochloride, 6970-28-1; 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, 14691-88-4; salicylaldehyde, 90-02-8; 2-hydroxy-*p*-anisaldehyde, 673-22-3; 3-ethoxysalicylaldehyde, 492-88-6; 4,6-dimethoxysalicylaldehyde, 708-76-9; 5-chlorosalicylaldehyde, 635-93-8.

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Structure of the Iron Pentacarbonyl Anion

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Full structure calculations using an atom superposition and electron delocalization molecular orbital theory show the form of the (square-pyramidal) iron pentacarbonyl anion where the bent apical carbonyl ligand eclipses a basal one has a slight edge in stability over the staggered conformation. The bending is dominated by the singly occupied molecular orbital that is mainly of apical carbonyl π^* character. On bending, an iron 4p orbital is allowed by symmetry to mix in and stabilize this orbital, an effect not noted in a Walsh analysis by Hoffmann et al. The angle of bending, 121–125°, is supported by an EPR study by Fairhurst et al. We also find the basal carbonyl ligands bend down 5–15° to maximize d–π^* stabilization.

Introduction

There are excellent reasons to believe the apical carbonyl ligand will bend in the iron pentacarbonyl anion, on the basis of a Walsh diagram and analysis by Hoffmann et al.[1] and the recent EPR study of Fairhurst et al.[2] for $Fe(CO)_5^-$ in a $Cr(CO)_6$ matrix. The direction of this bending has not been explored in the model theoretical study and was not resolved by EPR. The nature of the singly occupied molecular orbital is unclear in that according to the Walsh analysis of ref 1 it appears to have d_{yz} metal character (coordinates are defined in Figure 1) while Fairhurst et al. favor d_{z^2}.

We have completed full structure predictions for $Fe(CO)_5^-$ for two orientations. We also find the basal ligands bend down a few degrees. In this paper we examine these and other properties of $Fe(CO)_5^-$ within the framework of molecular orbital theory.

Method

We use an atom superposition and electron delocalization molecular orbital (ASED–MO) technique. This theory uses the electrostatic theorem[3] for forces on nuclei in molecules within a molecular electronic charge density partitioning model. The density is broken into rigid free-atom parts and an electron delocalization bond charge part. As atoms bond together to form a molecule, the forces on the nuclei are integrated, yielding a repulsive energy due to the rigid-atom densities and the atomic nuclei and an attractive energy due to electron delocalization.[4a] The sum is exactly the molecular binding energy. The atom superposition component is evaluated from the atomic density functions. At equilibrium, the Laplacian of this component contains harmonic, cubic, and quartic stretching force constants to good accuracy.[4b] The electron delocalization energy has been found to be well approximated by a one-electron molecular orbital energy. A Hamiltonian similar in form to that of extended Hückel is used.[4c] The ASED–MO theory has been used for numerous predictions of structures, force constants, and electronic properties of molecules, surfaces, and solids. The parameters used in the present study were also used in an earlier analysis of the structure and bonding in (cyclobutadiene)iron tricarbonyl.[5] They are given in Table I.

Results and Discussion

Our fully optimized eclipsed and staggered iron pentacarbonyl anion structures may be seen in Figure 2. The energies are practically identical, with the eclipsed form only 0.03 eV more stable. The orbitals and bonding analysis are found to be the same for both conformations, so we will treat only the eclipsed one, except to note the slight differences in other structure parameters of the two forms. The apical Fe–C–O angle is 121° for the eclipsed and 125° for the staggered conformation, both supporting the estimate of 119° by Fairhust et al. based on their EPR data. The basal CO–Fe–CO angles are 152 and 159° for the eclipsed and 155° for the staggered form, close to the typical value of 150° quoted by Rossi and Hoffmann.[6] We find ligand-kinking distortions are destabilizing.

For each orientation, the apical CO bond length is 0.10 Å longer than the basal CO lengths, an indication that the unpaired electron in this d^9 anion is described by a molecular orbital with apical CO π^* character. It may also be noted in Figure 2 that the distance between Fe and C of the apical CO is 0.10–0.12 Å longer than the others. This suggests the

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Table I. Parameters Used in the Calculations: Principal Quantum Numbers, Ionization Potentials, and Slater Exponents[a]

	s			p			d					
atom	n	IP, eV	ζ	n	IP, eV	ζ	n	IP, eV	ζ_1	C_1	ζ_2	C_2
Fe	4	9.37	1.7	4	5.37	1.4	3	10.5	5.35	0.5366	1.8	0.6678
C	2	20.0	1.658	2	11.26	1.618						
O	2	28.48	2.246	2	13.62	2.227						

[a] Double-ζ d's include linear coefficients.

Table II. Coefficients of Fe Atomic Orbitals for the Radical Orbital

	s	p_x	p_y	p_z	$d_{x^2-y^2}$	d_{z^2}	d_{xy}	d_{xz}	d_{yz}
coeff	−0.028	−0.027	0	−0.120	0.026	−0.037	0	−0.164	0

Table III. Calculated Spin Densities for Eclipsed and Staggered Iron Pentacarbonyl Anions[a]

	C_1	O_1	C_2	O_2	C_3	O_3	C_4	O_4	C_5	O_5	Fe
eclipsed	0.094	0.056	0.040	0.023	0.005	0.002	0.040	0.023	0.460	0.193	0.065
staggered	0.080	0.046	0.007	0.003	0.007	0.003	0.080	0.046	0.466	0.191	0.070

[a] See Figure 1 for the numbering scheme.

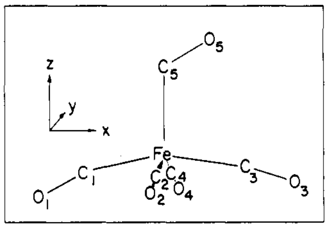

Figure 1. Coordinate system used to discuss the iron pentacarbonyl anion. The form where the apical CO eclipses a basal CO is shown. The staggered form (see Table III) has the apical CO between C_2 and C_3.

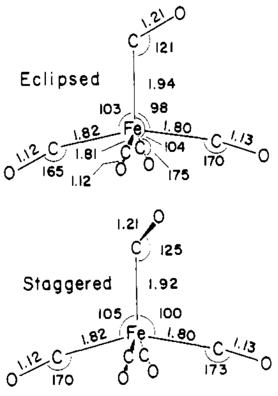

Figure 2. Calculated structures for eclipsed and staggered iron pentacarbonyl anions.

presence of antibonding character in one or more molecular orbitals.

The unpaired electron is indeed described by a molecular orbital that is antibonding between the apical CO π^*_x orbital and the Fe d_{xz} orbital, as shown in Figure 3. This contributes to the lengthening of the corresponding Fe–C bond; the other ligands show no similar antibonding interaction, rather all Fe d and CO π^* interactions are bonding. The bending of the apical CO may be seen to result from the mixing in of an Fe p_z orbital, which becomes symmetry allowed, in a bonding way. The resulting stabilization of the singly occupied molecular orbital energy level accounts for about 80% of the total stabilization gained on bending. Our energy level correlation diagram is qualitatively different from the Walsh diagram displayed by Hoffmann et al. in ref 1 in that the d_{xz} rather than the d_{z^2} orbital is stabilized the most on bending because of the Fe $4p_z$ mixing. The reason for this difference is the basal ligands used in ref 1 were model ones that omitted π^* orbitals.

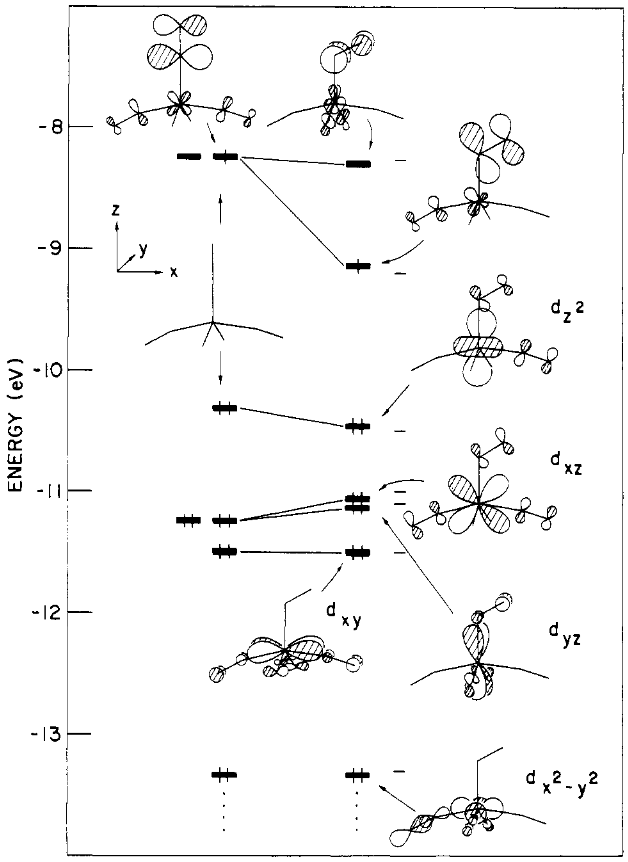

Figure 3. Molecular orbital correlation diagram for linear to bent apical CO in the iron pentacarbonyl anion. The structure was not optimized for the linear form at left. Lightly drawn levels indicate orbital energies prior to bending basal ligands down.

We also predict bending of 5–15° down for the basal CO ligands (Figure 2). As shown in Figure 3, when this bending is removed, the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ orbitals are destabilized a bit, overcoming the slight stabilization of the singly occupied orbital and the d_{z^2} orbital (d_{xy} is unshifted). X-ray studies of metal carbonyls commonly show such bends.

It may be seen in Figure 3 that all the metal d_{z^2}, d_{xy}, d_{xz}, and d_{yz} orbitals are dominated by mixing with ligand π^* orbitals in a bonding way. These orbitals also have Fe d–CO π antibonding character, but the accepting ability of the higher lying CO π^* orbitals is stronger. The lowest orbital shown and one nearly degenerate but not shown have basal CO 5σ

orbitals overlaping with the Fe $d_{x^2-y^2}$ orbital in a σ-donation bonding fashion.

The coefficients of the iron atomic orbitals in the radical molecular orbital shown in Table II show the dominance of d_{xz} in our calculation. Contributions to spin density are these coefficients squared. The p_z contribution is significant, but EPR atomic parameters are unavailable for the p orbitals. Using s and d atomic parameters from the literature,[7] we have found a mixture of d_{xz}, d_{z^2}, and s spin density that reproduces the principal values of the ^{57}Fe hyperfine tensor from Fairhurst et al.[2] with signs as follows: $a_{zz} = 20.1$, $a_{yy} = -9.5$, and $a_{xx} = 13.6$. Other signs are inconsistent with d_{xz} dominance (the signs are not experimentally measurable). The spin density distribution is then $0.28d_{xz}$, $0.07d_{z^2}$, and 0.01s. These numbers must be ascribed some uncertainty because p-orbital contributions are not included. The spin density distributions from our molecular orbital calculations show, by using a Mulliken partitioning of the overlap regions, an unpaired electron density on Fe of only ~0.07, as may be seen in Table III. This underestimate results from our using an approximate non-self-consistent theory, which in this case appears to be overestimating the charge transfer to the apical CO. Fairhurst et al.[2] estimate a spin density of 0.24 on the apical carbon, about half of our calculated value. The orbital distribution on the Fe center based on the hyperfine tensor fitting and the molecular orbital calculation is $d_{xz} >> d_{z^2} > s$. The hyperfine splittings for the carbon atoms in the basal ligands run ~80 and 90% less than the apical splitting, in qualitative agreement with the calculated values in Table III.

It may be noted that the calculated oxygen atom spin densities are less (about half) than those of their neighboring carbon atoms. This is because the π^* orbitals are polarized toward carbon.

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Registry No. $Fe(CO)_5^-$, 55472-73-6.

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Notes

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Self-Exchange Rate for the Cu(II)/Cu(I) Couple Complexed to TAAB, an N_4 Macrocycle

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A number of copper proteins that are believed to function as electron transferases have been isolated and subjected to detailed kinetic studies in vitro.[1-3] Electron-transfer rates have been measured for reactions between these proteins and a variety of small molecules[4-8] as well as other metalloproteins,[9] and more recently, some self-exchange rates have been reported.[10,11] The results are generally interpreted in terms of the Marcus theory for outer-sphere electron-transfer phenomena,[12] which, in its simplest form, relates the rate of an electron-transfer reaction to the equilibrium constant for the overall reaction and the self-exchange rate constant for each couple involved. Unfortunately, few self-exchange rates are available from relevant copper complexes so that the theory can be applied only in a restricted way. In fact, although self-exchange rates for several copper complexes have been estimated with use of Marcus theory,[13-17] the only directly measured value has been obtained in aqueous hydrochloric acid[18]—and there the reaction may occur via an inner-sphere mechanism.[5,13] In general the problem with these measurements is that the Cu(II) and Cu(I) oxidation states prefer different stereochemistries[19-22] and ligand types; hence, considerable structural reorganization is usually involved. Since both oxidation states are substitution labile, even defining species can be a problem. The proteins apparently avoid the reorganizational problems by dictating a coordination environment that is a compromise between ones that would be favored by copper(I) and copper(II).[23,24]

In an attempt to minimize the structural changes about copper attending electron transfer, we have studied the self-exchange reaction of the Cu(II)/Cu(I) couple when complexed to the relatively inflexible macrocyclic ligand tetrabenzo[*b*,*f*,*j*,*n*]-[1,5,9,13]tetraazacyclohexadecine (**1**), which is denoted TAAB. This system has been studied by Busch and coworkers, who have reported $E_{1/2} = 0.06$ V vs. SCE.[25] Although there has been some controversy regarding the proper formulation of the oxidation state of the reduced form,[25-29]

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