Figure 1. Cyclic voltammograms (I-a, II-a, III-a) at a scan rate of 100 m V s⁻¹, rotating disk electrode voltammograms (I-b, II-b, III-b–d) at an electrode rotation rate of 1000 rpm, and a scan rate of 10 mV s⁻¹ on a glassy carbon disk electrode with 0.2 M Na₂SO₄ at 25 °C. I for 1 mM Cu²⁺ complex **3** at pH 10.0. II for 1 mM Ni²⁺ complex **3** at pH > 7.0. III for 1 mM free ligand and Fe complex at pH 7.3 (Tris buffer); curve a and b for Fe²⁺ complex **3**, curve c for Fe³⁺ complex **7** (aeration product of Fe²⁺ complex **3**), curve d for free ligand **1**. No further oxidation wave was seen up to +0.5 V vs. SCE.

oxidation (to **5**) at +0.62 V; in the subsequent CV sweep the reversible *o*-quinone/catechol (**4** ⇌ **6**) wave appears at +0.14 V, as was seen with the free ligand. In view of the fact that the oxidation potential (+0.35 V) for Ni²⁺/Ni³⁺ in the phenolate-pendant cyclam complex **2**[15] is in a similar range with the present oxidation potential (+0.30 V) of the *o*-methoxyphenolate, we have attempted to determine formal charges for the initial 2e oxidized product that was obtained by applying constant potential of +0.45 V at pH 8.3.[21] Its ESR silent behavior supports nonradical structure **4**, excluding the electron-transferred semiquinone-Ni³⁺ structure. The magnetic susceptibility of **4** measured by the Evans method[22] was 2.8 μ_B, indicating a high-spin Ni²⁺ complex for **4**. The further 1e oxidized (at +0.70 V) product has structure **5** with its ESR spectrum[23] characteristic to Ni³⁺ and magnetic moment of 1.7 μ_B. This electrochemically oxidized solution showed an identical CV as those before the 1e oxidation.

The most unusual synergistic oxidation behavior was revealed by the definite 3e oxidation[24] *of Fe²⁺ complex **3** simultaneously at −0.30 V (pH 7.3 Tris buffer) on RDE* (see Figure 1-IIIb). The CV of **3** in Figure 1-IIIa shows no other redox wave up to +0.5 V!). The potential of −0.30 V is too low for the 2e oxidation of 2H⁺-, Cu²⁺-, or Ni²⁺-binding *o*-methoxyphenolate. The 1e oxidation potential for Fe²⁺/Fe³⁺ in **2** was −0.16 V.[13] We are thus tempted to conclude that Fe²⁺ is initially oxidized to Fe³⁺ **7** at the lower potential of −0.30 V under the influence of stronger σ-donor, *o*-methoxyphenolate and thereupon that Fe³⁺ catalytically drains 2e out of this ligand to a possible quinone pendant **8**.[25] All the attempts to prepare **8** in large quantity for further identification by electrochemical oxidation at −0.10 V resulted in failure, mostly due to the immediate halt of the electric current. We suspect that this is because kinetically reactive **8** undergoes immediate intramolecular (e.g., Michael addition) as well as intermolecular reactions whose unidentified products stick to the electrode surface. Mild aeration (20 min) of **3** initially oxidizes Fe²⁺ to Fe³⁺ [**7**, deep violet, λ_max 278 nm (ε 5500), 518 nm (ε 2150) at pH 7.0, in analogy to Fe³⁺ complex of **2**[13]], which undergoes further 2e oxidation to **8** at −0.30 V (curve c).

Although the final product structure **8** remains open to question, the present Fe macrocyclic complexes **3** and **7** have offered the first prototype for synergistic intramolecular redox coupling between monodentate catecholate and metal ions to render the catechol unusually vulnerable to oxidation. We are currently studying the catechol-cleaving reaction with **3**. Further modification of metal ions or macrocyclic structure with catechol pendant would find the novel redox system. Moreover, the reactivity of the remaining 6th axial position would be extremely interesting as a catalytic site.

Determination of the Charge on Carbon in a Bridging Methylene Iron Dimer with Solid-State Deuterium NMR Spectroscopy

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The chemistry of bridging methylene metal dimers and the value of the ¹³C NMR chemical shifts have been interpreted as due to a partial negative charge on the carbon atom.[2] PES yields a C₁ₛ binding energy indicative of −0.5 e charge.[3] However, for (μ-CH₂)[MnCp(CO)₂]₂, a high-resolution X-ray diffraction electron density map shows no excess charge buildup.[4] We are attempting to resolve the dilemma by using solid-state deuterium NMR techniques. In the results for *cis*-(μ-C²H₂)(μ-CO)[FeCp^d(CO)]₂ (Cp^d = 5% deuteriated cyclopentadienyl) presented here, we find no evidence for an excess negative charge on the bridging methylene carbon atom.

(21) The products **4** [λ_max 458 nm (ε 11200) and 508 nm (*sh*, ε 10700) at pH 5.3] and **5** [λ_max 279 nm (ε 6400), 441 nm (*sh*, ε 10800), 489 nm (ε 11600) at pH 5.0] reveal characteristic UV–vis absorption spectra, which differ from those of noncoordinating *o*-benzoquinone (λ_max 390 nm, ε 1800 at pH 5.0) or of the *o*-quinone-pendant cyclam (λ_max 406 nm, ε 1900 at pH 3.5).

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(23) The ESR spectrum of **5** (g_⊥ = 2.18, g_∥ = 2.01 at 77 K) is similar to those of Ni³⁺-[14]aneN₄(cyclam) (g_⊥ = 2.23, g_∥ = 2.02: Zeigerson, E.; Ginzburg, G.; Schwartz, N.; Luz, Z.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1979**, 241–243.) and of **2** (M = Ni³⁺) (g_⊥ = 2.18, g_∥ = 2.02; Kimura, E.; Koike, T., unpublished data.).

(24) The number of electrons involved were calibrated by using well-established 2e and 1e oxidation RDE wave heights of the Ni^II complex **3**, as illustrated in Figure 1-II.

(25) The 2e oxidation of another part of the ligand (e.g., the cyclam part) at this potential is very unlikely, in view of the fact that phenolate-cyclam in **2** (M = Fe³⁺) is not oxidized up to +0.9 V (Kimura, E., unpublished data.).

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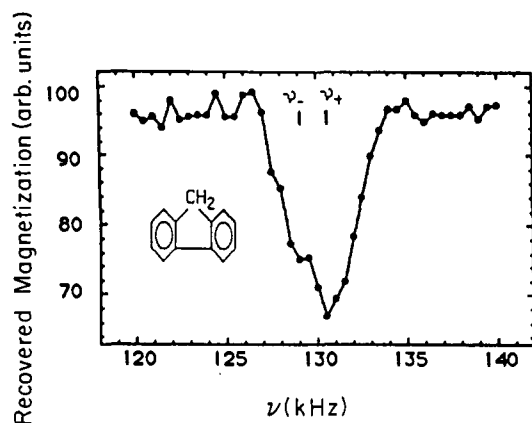
Figure 1. ADLF spectrum of $(9,9\text{-}^2H_2)$fluorene. Spectrum acquired at 77 K field cycling between 2.3 and 0 T magnetic fields. Other spectrometer parameters are: zero-field rf irradiation time of 3 s with $H_1 = 10$ mG peak and frequency increment of 0.5 kHz; high-field detection via ^1H resonance at 100 MHz sampled with Ostroff–Waugh pulse sequence of 128 echoes; high-field residence time of 120 s.
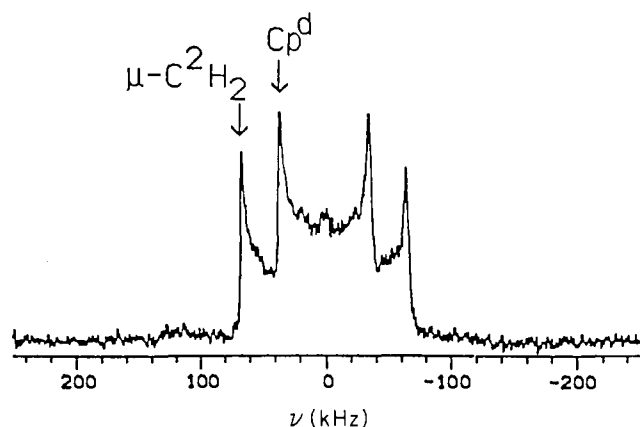
Figure 2. Solid-state NMR spectrum of cis-$(\mu\text{-}C^2H_2)(\mu\text{-}CO)[FeCp^d\text{-}(CO)]_2$ (Cp^d = 5% deuteriated cyclopentadienyl). The innermost powder pattern is due to the Cp ring deuterons; the outer powder pattern is due to the deuteriated bridging methylene unit. High-field NMR spectrometer parameters are as follows: spectrum acquired at 11.7 T; $T = 300$ K; 1416 scans; relaxation delay = 30 s; 90° ^2H pulse length = 3.0 μs; 30-μs delay between the two pulses of quad echo sequence.

In solid-state deuterium NMR[5] and adiabatic demagnetization in the laboratory frame (ADLF) spectroscopy,[6] one obtains the deuterium quadrupole coupling constant, $e^2q_{zz}Q/h$, and the asymmetry parameter, η. Q is the deuterium nuclear quadrupole moment.[7] The quantity eq_{zz} is the largest component of the traceless electric field gradient tensor in the principal axis system. The value of eq_{zz} is a sum of nuclear and electronic contributions

$$eq_{zz} = \sum_n K_n \frac{3z_n^2 - r_n^2}{r_n^5} - e\left\langle \Psi^* \Big| \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} \Big| \Psi \right\rangle \quad (1)$$

where e is the absolute value of the electronic charge, the index n is over the other atoms in the molecule with nuclear charge K_n, and the index i is over the electrons of the molecule. Additional interest in deuterium electric field gradients accrues from the absence of excited-state effects since only occupied molecular orbitals contribute to the electric field gradient.[8] The major axis
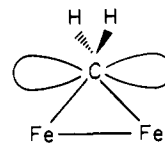
Table I. IR and Deuterium NMR Data for $(9,9\text{-}^2H_2)$Fluorene and cis-$(\mu\text{-}C^2H_2)(\mu\text{-}CO)[FeCp^d(CO)]_2$

	$(9,9\text{-}^2H_2)$-fluorene	cis-$(\mu\text{-}C^2H_2)(\mu\text{-}CO)$-$[FeCp^d(CO)]_2$
ν(C–H), cm^{-1}	2919[a]	2953, 2899[b]
C–H, Å[c]	1.1	1.1
$^1J(^1H\text{-}^{13}C)$, Hz[d]	128 (5)	138 (4), 147 (4)
solid-state deuterium NMR (300 K)		
$eq_{zz}Q/h$, kHz[e]	168 (2)	174 (2)
ADLF (77 K)		
$eq_{zz}Q/h$, kHz	173 (1)	f
η	0.02 (1)	f
Δq, electron[g]	0 (reference)	0.00 (17)[h]

^{a} ν_{CH}^{is} from spectrum of partially deuteriated fluorene. ^{b} Spectrum acquired with micro diffuse reflectance cell. Sample diluted 100-fold in dry KBr. ^{c} Distance from correlation given in ref 19a. For the iron dimer, ν_{CH}^{is} assumed to be equal to average ν(C–H) stretching frequency. ^{d} Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic Press: New York, 1980; pp 93–106. ^{e} Assumed $\eta = 0$. ^{f} Proton T_1 too short for ADLF experiment at 77 K. ^{g} Defined in eq 2. ^{h} Error limit represents assumed 0.010 Å uncertainty in C–H bond length.

of the electric field gradient tensor is directed very nearly along the C–^2H bond vector.[9,10] The value of eq_{zz} is due to charge density in the C–^2H bond and on the atom to which the deuteron is bound. We note that eq_{zz} depends on the carbon nuclear charge to the first power and the C–^2H bond distance to roughly the inverse third power.[10c]

Many models have been used to interpret quadrupole coupling constants depending on the bond to be studied: C–X (X = Cl, Br, I),[8d,11] X = O (X = C, P, S),[12] B·pyridine (B = Lewis acid),[13] and Co–L.[14] In assigning charge on carbon, our approach uses a "standard" methylene unit to provide a reference for eq_{zz} in an aliphatic C–^2H bond. We use a reference system so as to circumvent the problems, both experimental and definition,[15] associated with absolute charge measurement. Variations of the eq_{zz} about the reference value are modeled by variable occupancy of the carbon 2p-orbital perpendicular to the C–^2H bond and in the plane of the dimetallocyclopropane unit.[3b,16] Thus, we have

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$e^2 q_{zz} Q/h (\text{sample}) =$

$$e^2 q_{zz} Q/h (\text{reference}) + \frac{e^2 Q \Delta q}{a_0{}^3 h} \left\langle \Psi_p{}^* | \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} | \Psi_p \right\rangle \quad (2)$$

where Δq is the change in occupancy of the 2p-orbital relative to the reference. The field gradient expectation value is calculated by using a Slater-type orbital ($Z_C = 1.72$) and an analytical expression.[10b] Equation 2 is valid for comparisons between molecules having the same C–H bond distance; otherwise, $e^2 q_{zz} Q/h (\text{reference})$ must be scaled; errors in $e^2 q_{zz} Q/h (\text{reference})$ accumulate at the rate of 1 kHz per 0.001 Å difference in bond length.[10a,c] Also, we assume that the two C–H bond lengths are equally affected by deuterium substitution. We emphasize that the reference is used to account for the contribution to eq_{zz} from the charge distribution associated with an aliphatic C–H bond.

According to the second term of eq 2, for $d(\text{C–H}) = 1.1$ Å, an extra occupancy of the carbon 2p-orbital of –0.5 e should reduce the deuterium quadrupole coupling constant by 30.6 kHz. Small changes in $d(\text{C–H})$ matter little: for $d(\text{C–H}) = 1.09$ Å and 1.11 Å, reductions of 30.9 and 30.2 kHz, respectively, are predicted.

The reference molecule is a three-ring aromatic compound, $(9,9\text{-}^2H_2)$fluorene.[17] The C^2H_2 unit is incorporated into a relatively rigid molecule, thus, reducing the potential for motional averaging affecting the value of $e^2 q_{zz} Q/h (\text{reference})$.[18] Spectra were obtained at 38.5 MHz at 300 and 198 K with solid-state deuterium NMR and at 77 K with ADLF spectroscopy (Figure 1).

As noted above, the model is most conveniently applied when the $C\text{-}^2H$ bond distances in the reference and sample are equal. Recently, McKean has developed a linear correlation between the $\nu_{CH}{}^{is}$ stretching frequency and bond distance.[19,20] The slope of the correlation is –0.0001 Å per cm^{-1}, making possible precise, relative assessments of the C–H bond distances (Table I).

Acquisition of solid-state deuterium NMR spectra at 76.7 MHz for *cis*-$(\mu\text{-}C^2H_2)(\mu\text{-}CO)[\text{FeCp(CO)}]_2$ proved to be difficult due to an extremely long deuterium T_1. Therefore, the Cp ring positions were partially deuteriated to reduce the deuterium T_1 at the C^2H_2 unit.[21-23] The solid-state deuterium NMR spectrum of *cis*-$(\mu\text{-}C^2H_2)(\mu\text{-}CO)[\text{FeCp}^d(CO)]_2$ is shown in Figure 2.

The observed deuterium NMR parameters (Table I) are simply not compatible with the assignment of a large excess charge on carbon in this, the first application of solid-state deuterium NMR techniques to the determination of charge structure in an organometallic complex. Rather, we find that the bridging methylene carbon has zero charge relative to the reference aliphatic carbon atom within limits that we estimate to be 0.17 e based on an assumed uncertainty of 0.010 Å in the C–H bond distances.

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Chloride Ion Pairs in Water

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The study of ions in water by statistical mechanical methods has made a significant contribution to our understanding of solution chemistry and biological processes in saline solutions. Integral equation methods have been used recently by Pettitt and Rossky[1] to study solvent-averaged forces and the effective interactions or the potentials of mean force (PMF) for the alkali halides in water at infinite dilution. Integral equations revealed that the PMF's of unlike charged ions in water display clear minima in the ion-contact and solvent-separated regions. The presence of such minima and maxima is not predicted by continuum solvent theory. It is a direct result of explicitly molecular correlations.[1,2] The striking result obtained from the approximate integral equation theory for the PMF between negatively charged ions is that the ions display a stable contact minimum whereas only a modest minimum was found for positive charge pairs.[1] Of particular significance is the Cl$^-$–Cl$^-$ pair whose approximate PMF indicates the possibility of a substantial minimum at the ion-contact pair distance. A short dynamical simulation has indeed confirmed the plausibility of such a contact minimum, apparently due to the formation of bridging hydrogen bonds between water molecules and the ion pair.[3] However, no quantitative estimates of this free energy have been reported.

In this communication, we report a quantitative study of the Cl$^-$–Cl$^-$ PMF in water with use of an umbrella sampling method[4] and the same Hamiltonian as that used in the integral equation study.[1] The system studied here consists of two chloride ions and 295 water molecules in a rectangular box with periodic boundary conditions and lengths of 25.4, 18.6, and 18.6 Å in the *x,y,z* directions, respectively. Sampling was performed with microcanonical molecular dynamics, and the equations of motions were integrated by the Verlet algorithm with a time step of 1.5×10^{-15} s.[5] The water intermolecular potential employed was the rigid TIPS model of Jorgensen[6] and the SHAKE procedure was used to constrain the internal geometry of the water molecules.[5] The interactions in the system were truncated by using previously studied switching functions.[7] The water–water switch used a distance parameter of 9.3 Å and the ion–water parameter was 12.0 Å.

To facilitate sampling we chose a bias potential, U_B, such that it consisted of an approximation to the negative of the free energy surface, U_A, plus a loose harmonic constraint, U_H, used primarily for control. The use of a bias potential that approximates the negative of the PMF means that we are sampling from a nearly flat distribution and therefore only the difference between the guessed bias and the true PMF need to be explicitly calculated. For U_A we have used the negative of the PMF obtained from integral equation estimates.[1] The harmonic potential was then used to constrain the chloride ions to a certain separation region. The form of the harmonic potential used is

$$U_H(r) = \frac{1}{2} k_x (x - x_0)^2 + \frac{1}{2} k_{yz} (y^2 + z^2) \quad (1)$$

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