Proton Magnetic Resonance Determination of the Primary Solvation Number of Nickel(II) in Aqueous Solution

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Abstract: Proton magnetic resonance line widths as a function of temperature were obtained for both acidified and unacidified aqueous solutions containing nickelous ion. The treatment of these data revealed that the primary solvation number of Ni(II) could be determined near −30° by a signal integration technique, and this solvation number was found to be 6.0 ± 0.2.

The application of magnetic resonance signal integration techniques in recent years has led to the determination of definitive primary solvation numbers of metallic cations both in aqueous[2,3] and more extensively in nonaqueous[4-6] solutions. The references given to the nonaqueous solution studies represent only a fraction of the published work in that research area.

Both paramagnetic and diamagnetic ions have been studied in nonaqueous solvents, but only diamagnetic ions have yielded to direct integration methods in aqueous solution. This is principally because both the protons and the ^{17}O of coordinated water are situated close to and both interact strongly with the unpaired electrons of a paramagnetic ion. As a consequence the proton and ^{17}O magnetic resonance signals arising from water "bound" to a paramagnetic ion are quite broad and extremely difficult to integrate in a reliable manner.

Recently Connick and Fiat[7] have recorded the ^{17}O signal arising from water bound to Ni(II) in aqueous solution. While this signal could not be precisely integrated, its chemical shift with respect to bulk water could be determined. The use of this chemical shift value in conjunction with line-broadening data led the authors[7] to suggest that the coordination number of Ni(II) might be four.

The authors[7] recognized the need for an independent determination of the primary solvation number of nickelous ion in aqueous solution, and such an independent determination is the subject of the investigation reported here.

The basis for the present determination was established through a study of the proton magnetic resonance line widths of an acidified and an unacidified $Ni(NO_3)_2$ solution as outlined in the following sections.

Experimental Section

A 1.500 *M* $Ni(NO_3)_2$ solution was prepared from an analyzed stock solution of $Ni(NO_3)_2$. This solution was also made 2.000 *M* in $LiNO_3$ through the addition of the dried analytical reagent grade salt. The lithium nitrate was added in order to enable measurements to be made at temperatures near −30°. A second solution was prepared which was 1.500 *M* in $Ni(NO_3)_2$ and 3.000 *M* in HNO_3.

A single broad proton signal was observed for each of these solutions with spectra recorded on a Varian A-60A spectrometer. Temperature variation and control were achieved through use of a Varian V-6040 temperature-control unit.

All spectra were recorded with a radiofrequency power level of 0.5 mG and a filter bandwidth of 0.04 Hz. The signal/noise under these conditions is of the order of 10^3. The signals were carefully phased and were found to be Lorentzian within experimental uncertainty.

Total proton concentrations in each solution were obtained from density measurements made with a Westphal balance.

Results

A plot of T_2^{-1} *vs.* T^{-1} for both the acidified and unacidified solutions is shown in Figure 1. In the case of the two solutions studied here, T_2^{-1} is given to an excellent approximation by the experimentally observed half-width at half-maximum intensity of each absorption mode signal.

Theoretical expressions for v, the absorption mode signals arising from both the acidified and unacidified solutions, can be derived in a manner similar to that given by Swift and Connick.[8]

The modified Bloch equations appropriate to both the acidified and unacidified solutions are

$$-G_A(T_{2A}^{-1} + \tau_{AB}^{-1} - i\Delta\omega_A) + G_B\tau_{BA}^{-1} = -i\omega_1 M_0^A \qquad (1)$$

$$G_A\tau_{AB}^{-1} - G_B(T_{2B}^{-1} + \tau_{BA}^{-1} - i\Delta\omega_B) = -i\omega_1 M_0^B$$

where the notation is the same as that employed by Swift and Connick.[8] Nuclear environment B represents the primary solvation sphere of Ni^{2+}, and A represents all other proton environments.

Swift and Connick solved eq 1 under the condition that $M_0^A \gg M_0^B$. For 1.500 *M* solutions of Ni^{2+} this inequality is clearly invalid and hence an exact solution to eq 1 must be obtained and this solution is given as

$$v = \omega_2(AC - BD)/(C^2 + D^2) \qquad (2)$$

where *A*, *B*, *C*, and *D* are defined as shown below.

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[2] (a) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963); (b) *J. Am. Chem. Soc.*, **88**, 4754 (1966).

[3] T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *J. Chem. Phys.*, **46**, 406 (1967).

[4] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

[5] S. Nakamura and S. Meiboom, *J. Am. Chem. Soc.*, **89**, 1765 (1967).

[6] H. G. Glaeser, G. W. Dodgen, and J. P. Hunt, *ibid.*, **89**, 3065 (1967).

[7] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

[8] T. J. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962).

$$A = M_0^{\mathrm{A}} + \frac{(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})[M_0^{\mathrm{A}}\tau_{\mathrm{AB}}^{-1} + M_0^{\mathrm{B}}(T_{2\mathrm{A}}^{-1} + \tau_{\mathrm{AB}}^{-1} + \tau_{\mathrm{BA}}^{-1})]}{[(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{B}}^2]} + \frac{\Delta\omega_{\mathrm{B}}\Delta\omega_{\mathrm{A}}M_0^{\mathrm{B}}}{[(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{B}}^2]}$$

$$B = \frac{\Delta\omega_{\mathrm{B}}[M_0^{\mathrm{A}}\tau_{\mathrm{AB}}^{-1} + M_0^{\mathrm{B}}(T_{2\mathrm{A}}^{-1} + \tau_{\mathrm{AB}}^{-1} + \tau_{\mathrm{BA}}^{-1})]}{[(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{B}}^2]} - \frac{\Delta\omega_{\mathrm{A}}(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})M_0^{\mathrm{B}}}{[(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{B}}^2]}$$

$$C = T_{2\mathrm{A}}^{-1}\frac{\tau_{\mathrm{AB}}^{-1}(T_{2\mathrm{B}}^{-2} + T_{2\mathrm{B}}^{-1}\tau_{\mathrm{BA}}^{-1} + \Delta\omega_{\mathrm{B}}^2)}{[(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{B}}^2]}$$

$$D = \Delta\omega_{\mathrm{A}} + \frac{\tau_{\mathrm{AB}}^{-1}\tau_{\mathrm{BA}}^{-1}\Delta\omega_{\mathrm{B}}}{[(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{B}}^2]}$$

Equation 2 can be simplified through appropriate approximations based on the relative magnitudes of the parameters which appear in A, B, C, and D. Consider first the acidified solution. From the study of Swift and Stephenson[9] on the protonation of aquated cations, τ_{BA}^{-1} may be taken as temperature independent and equal to 4×10^6 sec^{-1} over the temperature range of Figure 1. The quantity $\Delta\omega_{\mathrm{B}}$ was obtained from the chemical shift study of Wayland and Rice,[10] and it varies from 2930 sec^{-1} at $-31°$ to 2140 sec^{-1} at 59°. These values together with the values of T_2^{-1} from Figure 1 lead to the following set of inequalities for the acidified solution over the temperature range of Figure 1.

$$\tau_{\mathrm{BA}}^{-2} \gg T_{2\mathrm{B}}^{-1}\tau_{\mathrm{BA}}^{-1} \gg \Delta\omega_{\mathrm{B}}^2$$
$$\tau_{\mathrm{BA}}^{-1} \gg T_{2\mathrm{A}}^{-1} \qquad (3)$$

With this set of inequalities eq 2 becomes to an excellent approximation

$$v = \omega_1 \times \frac{(M_0^{\mathrm{A}} + M_0^{\mathrm{B}})(x_{\mathrm{A}}T_{2\mathrm{A}}^{-1} + x_{\mathrm{B}}T_{2\mathrm{B}}^{-1})}{(x_{\mathrm{A}}T_{2\mathrm{A}}^{-1} + x_{\mathrm{B}}T_{2\mathrm{B}}^{-1})^2 + (x_{\mathrm{A}}\Delta\omega_{\mathrm{A}} + x_{\mathrm{B}}\Delta\omega_{\mathrm{B}})^2} \qquad (4)$$

where x_{A} and x_{B} are the respective mole fractions of protons in the environments A and B. Thus, the observed signal for the acidified solution is a "fast exchange" Lorentzian line for which $T_2^{-1} = x_{\mathrm{A}}T_{2\mathrm{A}}^{-1} + x_{\mathrm{B}}T_{2\mathrm{B}}^{-1}$ and for which the product of the peak height times the line width at half-maximum intensity is proportional to the total proton concentration in the solution at all temperatures studied. This result for the acidified solution is quite useful in the analysis of the line-broadening data obtained for the unacidified solution since it is reasonable to assume that $T_{2\mathrm{B}}$ is the same or approximately the same in both solutions at the same temperature. With this assumption the term $T_{2\mathrm{B}}^{-1}\cdot(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})$ is much greater than $\Delta\omega_{\mathrm{B}}^2$ above about 20° and even at the lower temperatures of Figure 1, $\Delta\omega_{\mathrm{B}}^2$ is always less than about 5% of $T_{2\mathrm{B}}^{-1}(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})$.

$$v = \frac{\omega_1\left\{M_0^{\mathrm{A}} + \left[\dfrac{M_0^{\mathrm{A}}\tau_{\mathrm{AB}}^{-1} + M_0^{\mathrm{B}}(T_{2\mathrm{A}}^{-1} + \tau_{\mathrm{AB}}^{-1} + \tau_{\mathrm{BA}}^{-1})}{(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})}\right]\right\}[T_{2\mathrm{A}}^{-1} + P(T_{2\mathrm{B}} + \tau_{\mathrm{BA}})^{-1}]}{[T_{2\mathrm{A}}^{-1} + P(T_{2\mathrm{B}} + \tau_{\mathrm{BA}})^{-1}]^2 + [\Delta\omega_{\mathrm{A}} + P\Delta\omega_{\mathrm{B}}(1 + \tau_{\mathrm{BA}}/T_{2\mathrm{B}})^{-2}]^2} \qquad (5)$$

It will be shown subsequently in this paper that for the purpose of the Ni(II) solvation number determination, values of τ_{BA}, $T_{2\mathrm{B}}$, and $T_{2\mathrm{A}}$ within relatively broad error limits are required at a temperature of approximately $-30°$. For this purpose $T_{2\mathrm{B}}(T_{2\mathrm{B}}^{-1} + \tau_{\mathrm{BA}}^{-1})$ may be taken as being very much greater than $\Delta\omega_{\mathrm{B}}^2$ and eq 2 is given to a suitable degree of approximation by eq 5, where the term P is defined as the concentration of B nuclei divided by the concentration of A nuclei.

Two limiting cases are of special interest here since they are approached near 60 and $-30°$, respectively. The limits and the resultant expressions for v are

$$T_{2\mathrm{B}}^{-1} \gg \tau_{\mathrm{BA}}^{-1}, \tau_{\mathrm{AB}}^{-1}, T_{2\mathrm{A}}^{-1} \qquad (\mathrm{A})$$

$$v = \frac{\omega_1 M_0^{\mathrm{A}}(T_{2\mathrm{A}}^{-1} + P\tau_{\mathrm{BA}}^{-1})}{(T_{2\mathrm{A}}^{-1} + P\tau_{\mathrm{BA}}^{-1})^2 + \Delta\omega_{\mathrm{A}}^2} \qquad (6)$$

This "slow exchange" limit corresponds to the signal from the A environment superimposed on a much broader signal from the B environment.

$$\tau_{\mathrm{BA}}^{-1} \gg T_{2\mathrm{B}}^{-1}, T_{2\mathrm{A}}^{-1} \qquad (\mathrm{B})$$

This is the same limit which applies to the acidified solution and the resultant expression for v is given as eq 4.

From eq 4 and 6 the familiar limiting expressions for T_2^{-1} are

Limit A

$$T_2^{-1} = T_{2\mathrm{A}}^{-1} + P\tau_{\mathrm{BA}}^{-1} \qquad (7)$$

Limit B

$$T_2^{-1} = x_{\mathrm{A}}T_{2\mathrm{A}}^{-1} + x_{\mathrm{B}}T_{2\mathrm{B}}^{-1} \qquad (8)$$

Also from eq 4 and 6 the product of peak height times line width at half-maximum intensity (termed I) is given in each limiting case by $I = \omega_1 M_0^{\mathrm{A}}$ for limit A and $I = \omega_1(M_0^{\mathrm{A}} + M_0^{\mathrm{B}})$ for limit B. If limit A does indeed apply to the unacidified Ni^{2+} solution near $-30°$, the primary solvation number of Ni^{2+} may be determined in a straightforward manner from a comparison of the measured I with that of a suitable standard. The question which naturally arises concerns the extent to which limit A does apply to this solution under the specified conditions.

This can only be determined from eq 2 together with known values of the quantities $T_{2\mathrm{A}}$, $T_{2\mathrm{B}}$, and τ_{BA}. Values of these quantities to a suitable approximation may be determined from the T_2 data of Figure 1 together with eq 5.

$$T_2^{-1} = T_{2\mathrm{A}}^{-1} + \left\{\frac{T_{2\mathrm{B}}}{x_{\mathrm{B}}} + \frac{\tau_{\mathrm{BA}}}{P}\right\}^{-1} \qquad (9)$$

Equation 9 may be used to fit the data of Figure 1 for the unacidified solution in order to test whether and where limits A and B apply. Lines representing $T_{2\mathrm{A}}^{-1}$, $x_{\mathrm{B}}T_{2\mathrm{B}}^{-1}$, and $P\tau_{\mathrm{BA}}^{-1}$ are shown in Figure 1, and the curve drawn through the experimental points was calculated from values taken from these lines together with eq 9.

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(9) T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, 5, 1100 (1966).

(10) B. B. Wayland and W. L. Rice, *ibid.*, 5, 54 (1966).

The shape of the lines representing $x_BT_{2B}^{-1}$ and T_{2A}^{-1} was taken as that of T_2^{-1} for the acidified solution of Figure 1. The bend near $-30°$ in the data for the unacidified solution indicates that T_{2A}^{-1} is much larger than T_{2A}^{-1} in the absence of Ni^{2+}. Such is to be expected, of course, since the value of T_{2A}^{-1} reflects sizable relaxation in the secondary solvation sphere of nickelous ions.

Both T_{2B}^{-1} and T_{2A}^{-1} are given by eq 2 of ref 7, which represents the sum of dipolar and hyperfine contributions. There is no hyperfine contribution to T_{2A}^{-1} and if the hyperfine coupling constant value determined by Wayland and Rice[10] is used, it is shown that the hyperfine contribution to T_{2B}^{-1} is negligible. Hence, both T_{2A}^{-1} and T_{2B}^{-1} are determined by dipolar contributions. A general expression for T_2^{-1} may be derived from eq 5, but it is complicated due to the relative contributions of M_0^A and M_0^B terms. A much more useful expression for fitting the data of Figure 1 is an approximation which combines the limiting expressions above for T_2^{-1} and which is a good approximation for T_2^{-1} over the entire temperature range from -30 to 60°; this is given as eq 9.

These dipolar relaxation rates are both proportional to correlation times τ_c, and in the case of both T_{2A}^{-1} and T_{2B}^{-1} it is reasonable to equate τ_c with T_{1e}, the Ni(II) electron spin-lattice relaxation time, due to the very small value of T_{1e}.[7] To the extent to which T_{1e} may be identified with τ_c of eq 2 of ref 7, the assumption concerning the shapes of the lines for $x_BT_{2B}^{-1}$, T_{2A}^{-1}, and T_2^{-1} (acidified solution) in Figure 1 is a valid one.

If the primary solvation number of Ni^{2+} is taken to be six, $P = 0.228$ for the unacidified solution and τ_{BA}^{-1} is calculated from Figure 1 to be $3 \pm 1 \times 10^4$ sec^{-1} at 298°K, in excellent agreement with the value of $3.0 \pm 0.3 \times 10^4$ sec^{-1} determined by Connick and Fiat.[7] The value of ΔH^* is 11 kcal, also in excellent agreement with the ^{17}O result. The value of ΔH^* determined by Connick and Fiat[7] is somewhat more precisely known than the value obtained from Figure 1. In addition it is reasonable to assume that this value applies to water exchange in the unacidified $Ni(NO_3)_2$-$LiNO_3$ solution studied here since water exchange should be relatively insensitive to simple changes in ionic strength. Hence the Connick and Fiat ΔH^* has been employed to obtain τ_{BA}^{-1} at -31 and 59°. The values of all other quantities were taken directly from Figure 1.

At 59°, $\tau_{BA}^{-1} = 2.1 \times 10^5$ sec^{-1}, $T_{2B}^{-1} = 4.8 \times 10^3$ sec^{-1}, and $T_{2A}^{-1} = 1.9 \times 10^2$ sec^{-1} if the primary solvation number is assumed to be six. If these numbers are substituted into eq 5, the result is a very close approximation to eq 4, and the fast exchange limit is certainly applicable. The applicability of this limit is not changed if the solvation number is assumed to be four.

At $-31°$, $\tau_{BA}^{-1} = 3.5 \times 10^2$ sec^{-1}, $T_{2A}^{-1} = 4.2 \times 10^2$ sec^{-1}, and $T_{2B}^{-1} = 1.0 \times 10^4$ sec^{-1} if the primary hydration number is six. With these values and eq 2, it is found that limit A is nearly applicable within experimental error but there is a significant deviation. The intensity I is given by the following equations for two assumed hydration numbers.

For $n = 6$

$$I = \omega_1(M_0^A + 1.17 \times 10^{-1}M_0^B) \qquad (10)$$

For $n = 4$

$$I = \omega_1(M_0^A + 1.09 \times 10^{-1}M_0^B)$$

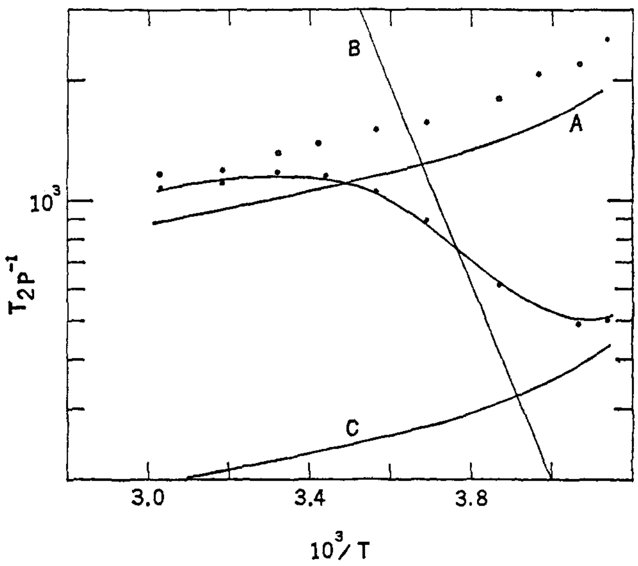

Figure 1. Plot of T_2^{-1} *vs.* $10^3/T$ for an acidified and an unacidified 1.500 *M* Ni(NO)$_3$ solution. The open circles are for unacidified solution. Line A represents $x_BT_{2B}^{-1}$; line B, $P\tau_{BA}^{-1}$; line C, T_{2A}^{-1}.

The term n is the assumed hydration number of Ni^{2+}. As is shown in eq 10, the deviation from limit A is not large and is precisely determined in terms of n. As a consequence, the primary hydration number can be determined precisely by signal integration since the observed signal is an almost completely resolved signal from the A environment. The measured hydration number will be *ca.* 10% less than the actual number and is easily related to the actual number through eq 10. In view of the approximations involved in the obtaining of values for T_{2B}^{-1}, τ_{BA}^{-1}, and τ_{AB}^{-1}, some comment must be given concerning the error limits for the coefficient of M_0^B in eq 10. The most important term in this coefficient is $T_{2A}^{-1} + \tau_{AB}^{-1}$. From eq 7, this term is nearly equal to T_2^{-1} at $-31°$, and hence the term is known within narrow error limits. The terms T_{2B}^{-1} and τ_{BA}^{-1} play relatively minor roles in the derivation of eq 10 and, even with a maximum uncertainty of ±25% in each, eq 10 is affected little.

One formidable practical problem to be solved is the selection of a suitable standard either internal or external for the signal integration. A suitable internal standard must be present in relatively high concentration and yield a well-resolved and precisely integrable signal under the same conditions employed for the recording of the water proton signal. In addition, the added substance must not interact significantly with the solvated nickelous ions. These are rather stringent requirements, and the last requirement is rather difficult to check.

The use of an external standard avoids this last difficulty but normally raises questions concerning the constancy between samples of the conditions for signal recording.

The standard chosen in the present case was an external one, the acidified nickelous ion solution described in the Experimental Section. The experimental procedure for signal recording was essentially the same as that given in the Experimental Section with the following additional features. The same sample tube filled to the same height, placed at the same depth in the probe and spinning at the same speed, was used for both the acidified and unacidified solutions. In addition both signals were recorded at the same spectrum amplitude. It was found that if these precautions were taken, the spectra were highly reproducible and quite satisfactory for the purposes of this research.

At −31° the line width of the signal from the acidified solution is approximately five times that from the unacidified solution. Hence, different sweep widths were used, but this causes no difficulty since the A-60A sweep widths can be very precisely calibrated.

Spectra were recorded for both solutions at 59 and −31°. The 59° measurements were made in order to check the suitability of the acidified solution as the standard. It was shown above that limit B and eq 4 apply to both solutions at this temperature, and hence the product of peak height times line width should be porportional to the total proton concentration in each case, and it must prove to be so experimentally if the acidified solution is to be an acceptable standard.

The integrated intensity values were converted to a value of n_e, an "effective" primary hydration number through eq 11, derived from the slow exchange limit,

$$I_u/I_a = ([H]_u - 2n_e[Ni^{2+}])/[H]_a \qquad (11)$$

where u and a refer to acidified and unacidified, and [H] is the total proton concentration. At 50°, I_u/I_a is 1.015, $[H]_a$ = 94.7 g-atom/l., $[H]_u$ = 95.6 g-atom/l., $[Ni^{2+}]$ = 1.483 g-ion/l., and n_e is calculated to be −0.2. This result is quite satisfactory and the acidified nickel solution proved to be an excellent standard.

At −31°, I_u/I_a is 0.836, $[H]_a$ = 98.7 g-atm/l., $[H]_u$ = 98.6 g-atom/l., $[Ni^{2+}]$ is 1.525 g-ion/l., and n_e is calculated from eq 11 to be 5.3. From eq 10, this corresponds to an actual hydration number of 6.0. Had the actual hydration number been 4, n_e would have been measured as 3.6.

This determination was repeated several times and the measured primary hydration number of Ni^{2+} is 6.0 ± 0.2. Twelve protons on each Ni^{2+} exchange with the bulk at the same rate, and this rate is identical within experimental error with the rate of oxygen exchange.[7]

The method employed here for hydration number determination is potentially applicable to other ions such as vanadyl.[11] However, an acidified vanadyl solution cannot be used as the external standard because T_{2B}^{-1} is much too large to permit this, and this limitation may certainly limit the application of the technique to the study of other ions.

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(11) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

Stereochemically Nonrigid Organometallic Molecules. XIV.[1] The Crystal and Molecular Structure of (1,3,5,7-Tetramethylcyclooctatetraene)diiron Pentacarbonyl[2]

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Abstract: A three-dimensional, X-ray diffraction study of the fluxional molecule $[(CH_3)_4C_8H_4]Fe_2(CO)_5$ has been completed employing the conventional sequence of Patterson maps, Fourier maps, and least-squares refinement. The crystals belong to the monoclinic system, space group $P2_1/n$, with the dimensions a = 15.126 Å, b = 13.374 Å, c = 8.587 Å, β = 101.17°. The observed density is 1.601 g cm^{-3}, that calculated assuming Z = 4 is 1.605 g cm^{-3}. The final value of the usual discrepancy index is 0.088 for 1142 independent nonzero reflections measured at 25° with a manually operated General Electric counter diffractometer. The least-squares refinement employed the full matrix and used isotropic temperature factors for all atoms except the two iron atoms, the five oxygen atoms, and the carbon atom of the bridging carbonyl group. The structure is essentially the same as that of $(C_8H_8)Fe_2(CO)_5$; the methyl groups occupy the 1 and 3 positions of the two intraannular, coordinated allyl groups. The relatively long Fe–Fe distance of 2.72 Å and the relatively long distances (2.33–2.50 Å) from the iron atoms to the nonallyl carbon atoms of the ring support the postulate that in this set of two iron atoms and two carbon atoms there are six electrons so delocalized as to provide five bonds of fractional order.

As noted in an earlier paper,[1] among the products obtained by treating the carbonyls of iron with 1,3,5,7-tetramethylcyclooctatetraene, hereafter abbreviated TMCOT, was a compound believed to be analogous to the compound $(COT)Fe_2(CO)_5$ prepared by Keller, Emerson, and Pettit[4] and formulated by them as I. $(TMCOT)Fe_2(CO)_5$ exhibits an nmr spectrum both at room temperature and at −60° consisting of only one ring proton resonance and one methyl proton resonance. Thus it appeared to be a fluxional molecule, like its COT

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(1) Part XIII: F. A. Cotton and A. Musco, *J. Am. Chem. Soc.*, 90, 1444 (1968).

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(3) National Science Foundation Summer Predoctoral Fellow.

(4) C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1390 (1965).