Although benzo[*c*]cinnoline (d) did not form a bridging complex (VI), we tried to make the cationic species VIIId using the alternative synthetic procedure. Despite variation in temperature and use of both acetone and methanol as solvent, all efforts to isolate this compound failed. We were likewise unsuccessful in extending this reaction to the acyclic azo compounds *cis*- and *trans*-azobenzene. A salmon-colored solid was isolated in each case, but it gave a variable analysis and contained no nitrogen. Further attempts to characterize it were fruitless.

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Solvent-Exchange Kinetics in Iron(II) Solutions of *N,N*-Dimethylformamide and Dimethyl Sulfoxide Studied by Nuclear Magnetic Resonance Line Broadening

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Measurements have been made of the temperature dependence of the solvent proton line broadening and shift for solutions of iron(II) perchlorate in *N,N*-dimethylformamide (DMF) and in dimethyl sulfoxide (Me_2SO) and Me_2SO–nitromethane solutions. In DMF chemical-exchange effects are observed on both line broadening and shifts and the kinetic parameters for DMF exchange were found to be $k(25\ °C) = 1.7 \times 10^6\ s^{-1}$, $\Delta H^* = 11.7 \pm 0.6$ kcal mol^{-1}, $\Delta S^* = 9.2 \pm 2$ cal mol^{-1} deg^{-1}. No exchange effects were observed in Me_2SO, but at low temperature in Me_2SO–D_3CNO_2 solution Me_2SO exchange was measurable and found to give $k(25\ °C) = 1 \times 10^6\ s^{-1}$, $\Delta H^* = 11.3 \pm 0.6$ kcal mol^{-1}, and $\Delta S^* = 6.9 \pm 2$ cal mol^{-1} deg^{-1}. No detectable effect of solvent Me_2SO concentration on the exchange rate was noted.

Introduction

Despite the wide distribution and importance of iron(II) there has been relatively little work on the substitution reactions of this ion especially when compared to cobalt(II), nickel(II), and manganese(II).[2a] The water-exchange rate on $Fe(OH_2)_6^{2+}$ was studied by Swift and Connick[2b] and the results indicate that iron(II) and cobalt(II) are of comparable lability. More recently solvent-exchange rates have been reported for iron(II) in methanol,[3] *N,N*-dimethylformamide (DMF),[4] acetonitrile,[5] and dimethyl sulfoxide (Me_2SO).[6]

A comparison of the kinetic parameters for ligand substitution and solvent exchange[7-10] is being used increasingly to test the dissociative ligand substitution mechanism[11] for first-row dipositive transition metal ions. It is hoped that this study may provide further necessary points of comparison for such tests. One problem with this type of mechanistic test is the embarrassingly large range of kinetic parameters obtained from NMR studies ostensibly on the same system. This problem might be alleviated if the variation of solvent-exchange rate with solvent and metal ion could be anticipated approximately in some way. For example, there is reference in the literature to activation enthalpies of 5.3 and 4.16 kcal mol^{-1} for solvent exchange in the Fe(II)–DMF and Fe(II)–Me_2SO systems, respectively. Comparison of these values to other solvent-exchange parameters on iron(II) and other metal ions clearly shows that these iron(II) values are peculiar. Of course, this is hardly grounds for doubting their validity in the absence of a more quantitative way of predicting the ΔH^* values but it seemed justification for a reinvestigation. With the results of the present study in hand, some attempt will be made to correlate the activation enthalpies for solvent exchange on manganese(II), iron(II), cobalt(II), and nickel(II).

Experimental Section

An excess of iron wire (99.9%) was treated with 2 M perchloric acid until hydrogen evolution ceased. The excess iron was removed by filtration and the solvent removed from the filtrate by vacuum distillation to yield crystals of hydrated ferrous perchlorate. A portion of this product was dissolved in a large excess of the required solvent, either dimethyl sulfoxide (Me_2SO) or *N,N*-dimethylformamide (DMF). The solvent was removed by vacuum distillation and the crystalline product was dissolved in the solvent in the presence of 3A Molecular Sieves and allowed to stand for at least 2 days and then the Molecular Sieves were removed by filtration. This treatment was repeated twice and the final filtrate used as a stock solution which was diluted with pure solvent for the preparation of various samples. All operations and sample preparations were carried out either in vacuo or under an argon atmosphere.

Dimethyl sulfoxide was distilled twice, the second time from Linde 3A Molecular Sieves and stored under vacuum over Molecular Sieves. Dimethylformamide was distilled first from barium oxide. The distillate was treated with silver nitrate and 3A Molecular Sieves and then distilled under vacuum twice more and stored over 3A Molecular Sieves. Nitromethane-d_3 and cyclopentane were stored under vacuum over 3A Molecular Sieves. All subsequent transfers of these solvents were by distillation on a standard vacuum line.

Each sample was checked for ferric ion by removing an aliquot with a syringe and injecting it into aqueous sodium thiocyanate. In all cases the iron(III) concentration was found to be <0.02% of the total iron. Total iron was determined by oxidation of an aliquot of the iron(II) solution with aqueous hydrogen peroxide. Then iron(III) was determined by EDTA titration with Variamine Blue B as an indicator.[12]

The solution molalities were determined by weighing known volumes of the samples and the known molar $Fe(ClO_4)_2$ concentration. In DMF five different samples were studied with concentrations in the range 0.0385–0.317 *m*. Three solutions in the 0.144–0.286 *m* range were used in Me_2SO. In all cases the line broadenings were found to depend directly on the metal ion concentration.

The NMR spectra were recorded on a Varian Associates A-56/60 spectrometer using standard temperature control and measurement methods.

Results

The solvent proton NMR line broadening caused by the paramagnetic ion can be expressed as

$$\frac{1}{T_{2p}P_M} = \frac{\pi(\Delta\nu_{obsd} - \Delta\nu_{solv})}{P_M} \tag{1}$$

where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ are the full widths at half-height of the solvent NMR resonance in the presence and absence, respectively, of the paramagnetic ion, and P_M is the ratio of the concentration of solvent bound to the paramagnetic ion to the concentration of free solvent.

The value of $(T_{2p}P_M)^{-1}$ depends on the solvent-exchange lifetime (τ_M), relaxation time of the coordinated solvent nucleus (T_{2M}), and the difference between the chemical shift of the coordinated proton and that of the ligand proton in the bulk diamagnetic environment ($\Delta\omega_M$)[2b]

$$\frac{1}{T_{2p}P_M} = \frac{1}{\tau_M}\left\{\frac{T_{2M}^{-2} + (\tau_M T_{2M})^{-1} + \Delta\omega_M^{\ 2}}{(\tau_M^{-1} + T_{2M}^{-1})^2 + \Delta\omega_M^{\ 2}}\right\} + \frac{1}{T_{2O}} \tag{2}$$

where T_{2O} is the solvent nuclear relaxation time of molecules outside the first coordination sphere of the metal ion. The temperature dependence of the individual terms is given by

$$\tau_M^{-1} = \frac{kT}{h}\exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \tag{3}$$

and[13]

$$T_{2M}^{-1} = \frac{C_M'}{T}\exp(E_M/RT) \tag{4}$$

$$T_{2O}^{-1} = \frac{C_O'}{T}\exp(E_O/RT) \tag{5}$$

$$\Delta\omega_M = -\frac{C_\omega}{T} = -\left(\frac{A}{\hbar}\right)\frac{\omega_0\mu_{eff}\beta(S(S+1))^{1/2}}{3\gamma_N kT} \tag{6}$$

The terms in the last equation[14] have their usual meaning. It should be noted that the $1/T$ preexponential factor in eq 4 and 5 has been introduced only because it is more consistent with theory as discussed elsewhere.[13] The omission of this factor does not affect the overall fit of the data and only changes the magnitude of E somewhat.

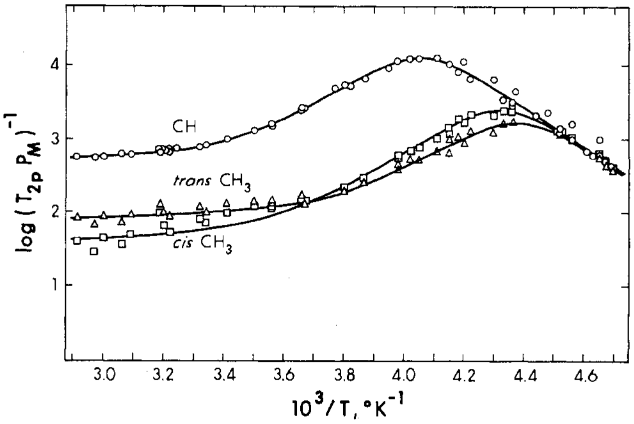

Figure 1. Temperature dependence of log $(1/T_{2p}P_M)$ for the solvent protons in iron(II) perchlorate–DMF solutions: ○, formyl or CH proton; △, trans CH_3 protons; □, cis CH_3 protons.

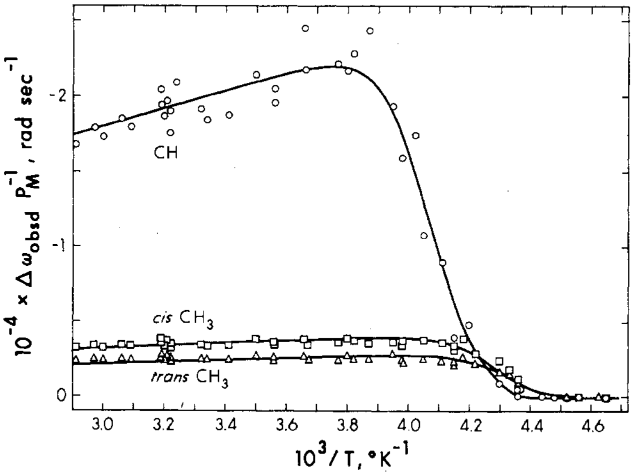

Figure 2. Temerature dependence of $\Delta\omega_{obsd}/P_M$ for the solvent protons in iron(II) perchlorate–DMF solutions: ○, formyl or CH proton; △, trans CH_3 protons; □, cis CH_3 protons.

The observed shift of the solvent proton resonance is given by[2b]

$$\frac{\Delta\omega_{obsd}}{P_M} = \frac{-\Delta\omega_M}{(1 + \tau_M/T_{2M})^2 + (\tau_M\Delta\omega_M)^2} \tag{7}$$

Iron(II) in *N,N*-Dimethylformamide. The temperature dependences of $(T_{2p}P_M)^{-1}$ and $(\Delta\omega_{obsd}/P_M)$ are shown in Figures 1 and 2. The methyl protons are assigned with the resonance at low field taken as the methyl group cis to the formyl hydrogen atom. The value of $(T_{2p}P_M)^{-1}$ is controlled by T_{2M}^{-1}, $\tau_M\Delta\omega_M^{\ 2}$, and τ_M^{-1} successively as the temperature decreases. The shift data are consistent with eq 7 in that at high temperature τ_M is small so that $(\Delta\omega_{obsd}/P_M) = -\Delta\omega_M$, and at lower temperature the observed function decreases primarily because $(\tau_M\Delta\omega_M)^2$ becomes $\gtrsim 1$. Only the outer-sphere contribution T_{2O}^{-1} is not experimentally determined and must be estimated. An upper limit on T_{2O}^{-1} has been calculated by assuming that T_{2M}^{-1} is only due to dipolar relaxation, given by[15]

$$T_{2M}^{-1} = \frac{1}{\langle r_i^6\rangle}\frac{\gamma_I^{\ 2}g^2\beta^2 S(S+1)}{15}f_D(\tau_D) \tag{8}$$

Table I. Least-Squares Best-Fit Parameters for $Fe(DMF)_6(ClO_4)_2$ in *N,N*-Dimethylformamide

Proton	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} deg^{-1}	10^{-3}-C_M', s^{-1} K	E_M, kcal mol^{-1}	C_O'/C_M'	$10^{-5}C_\omega$, rad s^{-1} K
CH	12.02	10.56	87.4	0.45[a]	0.0325[a]	60.0[a]
Trans CH_3	12.09	10.72	8.96	0.45[a]	0.56[a]	7.07[a]
Cis CH_3	11.61	8.72	3.47	0.45[a]	1.17[a]	10.4[a]
CH	11.89	10.05	89.6	0.45[a]	0[a]	60.0[a]
Trans CH_3	11.58	8.57	13.8	0.45[a]	0[a]	7.07[a]
Cis CH_3	11.31	7.53	7.47	0.45[a]	0[a]	10.4[a]
CH[b]	12.02[a]	10.77	87.4	0.45[a]		60.0
Trans CH_3[b]	12.09[a]	11.19	8.96	0.45[a]		7.07
Cis CH_3[b]	11.61[a]	8.07	3.47	0.45[a]		10.3

[a] Value held fixed at magnitude indicated by preliminary fits or calculation described in text. [b] Fits to the shift data.

and T_{2O}^{-1} is[16]

$$T_{2O}^{-1} = \frac{4.14 \times 10^{13} S(S+1)\rho}{d_O^3} \frac{S}{n} f_D(\tau_D) \qquad (9)$$

where the symbols have the usual meaning.[13] The r_i values have been estimated from the structure of $Fe(DMF)_6(ClO_4)_3$[17] after correction for the difference in ionic radii between iron(III) and iron(II). The estimated r_i values are 3.3, 5.0, and 6.0 Å for the CH, trans CH_3, and cis CH_3 protons, respectively, and $d_O \geq 6$ Å. With these estimates the ratio of eq 9 over eq 8 gives an estimate of C_O'/C_M' of 3.25×10^{-2}, 0.56, and 1.17 for the CH, trans CH_3, and cis CH_3 protons, respectively. These ratios are considered to be upper limits since the experimental value of C_M' may actually contain scalar as well as dipolar contributions and because a minimum value of d_O has been used. For these reasons the ultimate lower limit of $C_O'/C_M' = 0$ has been tested also in fitting the results.

The $(T_{2p}P_M)^{-1}$ data were first fitted with C_ω fixed at a value estimated from the high-temperature limiting shift results. These fits also gave preliminary E_M values. Since E_M must be the same for all the protons (because it is controlled by the electron spin relaxation time), the average of these preliminary E_M values was used in subsequent fits. The resulting parameters were used to fit the $(\Delta\omega_{obsd}/P_M)$ results to obtain more exact C_ω values. The latter differed by <5% from the initial estimates. Then the upper and lower limit assumptions about C_O' were tested in the fit to assess their affect on ΔH^* and ΔS^*.

The results of the various fitting procedures are summarized in Table I. It is apparent that the values of ΔH^* and ΔS^* are relatively independent of the assumptions made about $(T_{2O})^{-1}$. The various fits for the three types of protons indicate that $\Delta H^* = 11.7 \pm 0.6$ kcal mol^{-1} and $\Delta S^* = 9.2 \pm 2$ cal mol^{-1} deg^{-1} and $\tau_M^{-1} = (1.7 \pm 0.3) \times 10^6$ s^{-1} at 25 °C.

The experimental value of C_ω and the expected value of $\mu_{eff} = 5.3\ \mu_B$ can be used to calculate the scalar coupling constants $(A/\hbar)$ of 1.45×10^6, 1.80×10^5, and 2.54×10^5 rad s^{-1} for the CH, trans CH_3, and cis CH_3 protons, respectively.

If the maximum outer-sphere contribution is included, the value of $(T_{2M}^{-1} + T_{2O}^{-1})$ at 25 °C is calculated to be 647, 99, and 51 s^{-1} for the CH, trans CH_3, and cis CH_3 protons, respectively. These results are reasonably consistent with values calculated assuming a single correlation time of 5.5×10^{13} s and inner-sphere interaction distances of 3.45, 5.1, and 5.95 Å, respectively. The calculated $(T_{2M}^{-1} + T_{2O}^{-1})$ values are 676, 88, and 52 s^{-1} for the CH, trans CH_3, and cis CH_3 protons, respectively. In all cases the scalar contribution to T_{2M}^{-1} is <2% of the total value. The calculations, although rather qualitative, show that the correlation time controlling the electronic–nuclear interactions must be $<10^{-12}$ s, and since molecular rotation in DMF is much slower with a correlation time of $\sim 1.2 \times 10^{-10}$ s,[18] the correlation time for the iron(II) system must be the electron spin relaxation time. Iron(II) resembles nickel(II) in this respect.

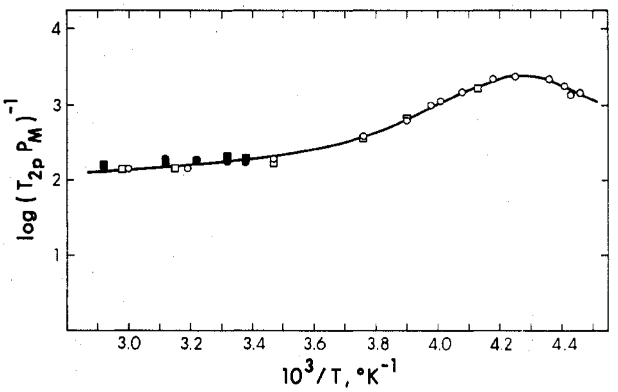

Figure 3. Temperature dependence of log $(1/T_{2p}P_M)$ for the Me_2SO protons in iron(II) perchlorate–Me_2SO–nitromethane solutions: ●, 0.144 *m* iron(II) in pure Me_2SO; ■, 0.286 *m* iron(II) in pure Me_2SO; ○, 0.281 *m* iron(II) in 2.77 *m* Me_2SO; □, 0.281 *m* iron(II) in 4.31 *m* Me_2SO.

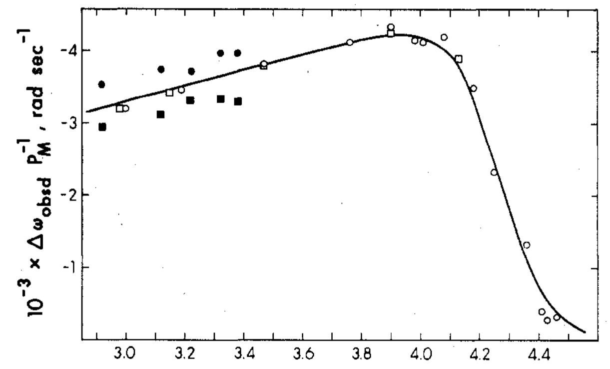

Figure 4. Temperature dependence of $\Delta\omega_{obsd}/P_M$ for the Me_2SO protons in iron(II) perchlorate–Me_2SO–nitromethane solutions: ●, 0.144 *m* iron(II) in pure Me_2SO; ■, 0.286 *m* iron(II) in pure Me_2SO; ○, 0.281 *m* iron(II) in Me_2SO diluted to 2.77 *m* Me_2SO with CD_3NO_2; □, 0.281 *m* iron(II) in Me_2SO diluted to 4.31 *m* Me_2SO with CD_3NO_2.

Iron(II) in Dimethyl Sulfoxide. The temperature dependence of $(T_{2p}P_M)^{-1}$ for iron(II) perchlorate in dimethyl sulfoxide (Me_2SO) (Figure 3) shows no indication of chemical-exchange effects. This result was not surprising in view of the results in DMF and the relatively high freezing point of Me_2SO. However, Frankel[19] has found that the liquid range of Me_2SO can be greatly extended by the addition of nitromethane. In addition it is of interest to determine if changing the concentration of Me_2SO has any effect on the rate of solvent exchange. Therefore, two solutions were prepared containing 0.281 *m* iron(II) in 2.77 and 4.31 *m* Me_2SO in nitromethane-d_3. The results of $(T_{2p}P_M)^{-1}$ and $(\Delta\omega_{obsd}/P_M)$ studies on these solutions, as well as in pure Me_2SO, are shown in Figures 3 and 4, respectively.

No outer-sphere contribution has actually been observed and an upper limit to T_{2O}^{-1} has been estimated by assuming that T_{2M} and T_{2O} are controlled by dipolar relaxation with $r_i = 5.3$ Å, estimated from models and the structure of $[FeCl_2(Me_2SO)_4](FeCl_4)$,[20] and $d_O = 6$ Å. It may be noted that eq 9 predicts that T_{2O}^{-1} depends on the exchanging solvent concentration and therefore should be different in the solutions studied. Actually $f_D(\tau_D)$ will also vary with solvent composition if the viscosity changes. If the latter effect is neglected, the slightly larger $(T_{2p}P_M)^{-1}$ in pure Me_2SO compared to that in the CD_3NO_2–Me_2SO solutions indicates that $T_{2O}^{-1} \approx 65$ s^{-1} in pure Me_2SO and 10–15 s^{-1} in the mixed solvent. Although

Table II. Least-Squares Best-Fit Parameters for $Fe(Me_2SO)_6(ClO_4)_2$ in Me_2SO and $Me_2SO-CD_3NO_2$ Mixtures

Soln[a] fitted	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	10^{-4}-C_M', s^{-1} K	E_M, kcal mol^{-1}	C_O'/C_M'	10^{-6}-C_{ω}, rad s^{-1} K
I, II	11.63	8.41	0.873	1.00^b	0	1.1^b
I, II	11.19	6.48	2.11	0.45^c	0	1.1^b
I, II	11.35	7.09	1.79	0.45^c	0.186	1.1^b
I, II, III	11.22	6.54	4.83	–0.106	0.186	1.1^b
I, II, III[d]	11.19^b	6.52	2.11^b	0.45^c		1.10
I, II, III[d]	11.35	7.19	1.79^b	0.45^c		1.10
I, II, III[d]	11.22	6.62	4.83^b	–0.106		1.10

[a] Solutions I and II contain 2.77 and 4.31 *m* Me_2SO in nitromethane-d_3, respectively, while solution III is pure Me_2SO. [b] Held constant at the value indicated. [c] Value estimated by graphical fitting and held constant in the least-squares fitting. [d] Fits of the $\Delta\omega_{obsd}/P_M$ data.

Table III. Summary of Solvent-Exchange Rate Kinetics for Iron(II)

Solvent	k(25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	Ref
DMF	$(1.7 \pm 0.3) \times 10^6$	11.7 ± 0.6	9.2 ± 2	This work
DMF	5.3×10^5	5.3	–15	4
Me_2SO	$(1.0 \pm 0.2) \times 10^6$	11.3 ± 0.6	6.9 ± 2	This work
Me_2SO	1×10^4	4.16	–28.8	6
CH_3OH	5.0×10^4	12.0	3.0	3
CH_3CN	5.5×10^5	9.7 ± 0.7	0.3 ± 2.2	5
H_2O	3.2×10^6	7.7	–3.0	2b

these estimates are quite uncertain, they are consistent with the expectation that outer-sphere effects are not significant in the mixed solvent.

After normalization by P_M the line broadening and shift measurements are found to be the same within experimental error in the two solutions containing nitromethane. The results of several fits summarized in Table II show that the solvent-exchange rate parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not very sensitive to variations in E_M and C_O and that, if $\Delta H^{\ddagger}$ is fixed, the shift and line broadening results give essentially the same $\Delta S^{\ddagger}$. From the fits tabulated plus others it seems reasonable to conclude that $\Delta H^{\ddagger} = 11.3 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = 6.9 \pm 2$ cal mol^{-1} deg^{-1}, and $\tau_M^{-1} = 1.1 \pm 0.2 \times 10^6$ s^{-1} at 25 °C.

From the chemical shift results the coupling constant $(A/\hbar)$ for the scalar interaction is calculated to be 2.67×10^5 rad s^{-1} if $\mu_{eff} = 5.3\ \mu_B$.[21]

The value of $(T_{2M}^{-1} + T_{2O}^{-1})$ is consistent with interaction distances of $r_i = 5.3$ Å and $d_0 = 6.0$ Å and a single correlation time of 1.6×10^{-12} s. This value is about 3 times larger than that estimated in DMF but is still much shorter than the expected rotational correlation time of 1.2×10^{-10} s in Me_2SO.[18] Therefore, the correlation time is assumed to be the electron spin relaxation time of $Fe(Me_2SO)_6^{2+}$.

Discussion

The available results for solvent exchange on iron(II) are summarized in Table III. As noted previously here, the earlier studies in DMF and Me_2SO seem to give unusually small activation enthalpies ($\Delta H^{\ddagger}_{ex}$) and very negative activation entropies. The results obtained in this study seem more in line with previous work on methanol, acetonitrile and water, but some question must remain as to which values, if either, are correct. Although details of the earlier work[4] in DMF have not been published, it is interesting to note that the deviation of about 6 kcal mol^{-1} from the $\Delta H^{\ddagger}_{ex}$ reported here is similar to the deviation reported with more recent studies on cobalt(II)[22] and nickel(II)[22,23] in DMF. In Me_2SO our values of $(T_{2p}P_M)^{-1}$ are 4–5 times smaller than those reported by Vigee and Ng[6] and no exchange-controlled region is observed in pure Me_2SO, nor have we observed any process with an activation energy of ~4 kcal mol^{-1}. The hyperfine coupling constant determined by Vigee and Ng (4.86×10^4 Hz) is in reasonable agreement with that found here (4.25×10^4 Hz). The presence of some iron(III) in the solutions of Vigee and Ng[6] would explain their higher $(T_{2p}P_M)^{-1}$ values and would not affect the shifts because iron(III) is in the slow-exchange region at the temperatures studied by Vigee and Ng.[6]

Unfortunately, it is difficult to quantitatively maintain the position that the results of the present study are closest to the correct values. This same problem has plagued results from NMR solvent-exchange studies for some time, perhaps the worst case being that of nickel(II) in Me_2SO, where eight independent studies have yielded $\Delta H^{\ddagger}_{ex}$ values ranging from 6.2 to 13.0 kcal mol^{-1}. Similarly for nickel(II) in water the original report of 11.6 kcal mol^{-1} [2] was revised to ~12 kcal mol^{-1},[24] and the most recent studies indicate ~14 kcal mol^{-1} for $\Delta H^{\ddagger}_{ex}$.[25] In retrospect it seems that the study yielding the largest $\Delta H^{\ddagger}_{ex}$ is likely to be most accurate. This statement can be rationalized when it is recognized that one of the commonest problems in these studies is the separation of T_{2M}^{-1} and $\tau_M \Delta\omega_M^2$ controlled regions in the $(T_{2p}P_M)^{-1}$ vs. T^{-1} curves. Since T_{2M}^{-1} has a lower apparent activation energy than τ_M, failure to separate these regions always results in too low a value for $\Delta H^{\ddagger}_{ex}$. Of course this is not to say that problems of temperature control and measurement and solvent and metal ion purity are not also important possible sources of disagreement.

The above discussion shows that it would be very helpful to have an empirical correlation of $\Delta H^{\ddagger}_{ex}$ with some extra kinetic parameter. Such a correlation could be used to point out incorrect values, to predict unmeasured values, and to indicate mechanism differences when the correlation is definitely not followed.

A correlation between water solvent exchange rates and crystal field activation energies has been examined by Basolo and Pearson[26] and refined by Companion[27] and Breitschwerdt.[28] Although apparently quite successful this type of correlation seems somewhat less attractive after the recent revisions of $\Delta H^{\ddagger}_{ex}$ in the nickel(II)–water system. This analysis also cannot be applied directly to other solvents since a larger crystal field splitting more often than not gives a smaller $\Delta H^{\ddagger}_{ex}$. The idea of adding a solvent-dependent "solvation" term was explored some time ago[29] and has been discussed qualitatively by Lincoln and West.[5] The main difficulty with this approach is the lack of 10*Dq* values for some solvents and the fact that 10*Dq* is also a function of the metal ion.

It has also been proposed[30] that solvent basicity and $\Delta H^{\ddagger}_{ex}$ may be related. The $\Delta H^{\ddagger}_{ex}$ may depend on the product of the basicity of the solvent and the acidity of the metal ion complex, and the latter may depend inversely in some way on the basicity of the nonexchanging solvent molecules. Dickert, Hoffmann, and Janjic[31] proposed such a correlation based on Gutmann's donor numbers (D_N[32]) as measures of basicity and the assumption that the acidity of the metal ion complex decreases exponentially with the D_N of the nonexchanging ligands. In the original proposal rather unlikely values of $\Delta H^{\ddagger}_{ex}$ for NH_3 (9.5 kcal mol^{-1} instead of 11 kcal mol^{-1}) and H_2O (11.6 kcal mol^{-1} instead of 14 kcal mol^{-1}) with nickel(II) were used. If the $\Delta H^{\ddagger}_{ex}$ values used here (see Table IV) are used in this correlation, the following are not well correlated (predicted $\Delta H^{\ddagger}_{ex}$ > 1 kcal from the experimental values): nickel(II) with methanol and NH_3; cobalt(II) with methanol, water, and Me_2SO; iron(II) with methanol and water.

More recently Hoffmann[7] has proposed that metal acidity (A_M) may vary linearly with the solvent ligand basicity (D_N) so that

$$A_M \propto A_O - D_N \tag{10}$$

Table IV. Correlation of $\Delta H^{\ddagger}_{ex}$[a] and Solvent Basicity

		D_N[b]	$\Delta H^{\ddagger}_{ex}$, kcal mol^{-1} Ni(II)[e]	Co(II)[e]	Fe(II)[e]	Mn(II)[e]
CH_3CN		14.1	15.0[f] (14.8)	11.4[i] (11.7)	9.7[l] (9.95)	7.25 (7.2)
CH_3OH		24[c]	15.8 (15.8)	13.8 (13.5)	12.0[m] (12.0)	6.2[k,m] (8.6)
$(CH_3)_2NCHO$		26.6	15.0 (14.8)	13.6 (13.1)	11.7[n] (11.9)	8.9[o] (8.5)
H_2O		28[c]	14.4[g] (14.0)	11.9[j] (12.8)	7.7 (11.7)	7.85[p] (8.3)
$(CH_3)_2SO$		29.8	13.0[h] (12.8)	12.2[h] (12.1)	11.3[n] (11.4)	7.4[q] (7.9)
NH_3		32[c]	11 (11.0)	11.2 (11.1)	(10.8)	8.0 (7.5)
Parameter[d]	a		1.603 ± 0.025	1.207 ± 0.035	0.9963 ± 0.045	0.7342 ± 0.039
	$10^2 b$		3.93 ± 0.096	2.69 ± 0.16	2.06 ± 0.19	1.57 ± 0.14

[a] Original references are given by C. H. Langford and V. S. Sastri, "Reaction Mechanisms in Inorganic Chemistry", M. L. Tobe, Ed., Butterworths, London, 1972, unless otherwise indicated. [b] Values taken from ref 32 unless otherwise indicated. [c] Values for H_2O and NH_3 were adjusted to give a correlation of the nickel(II) data, while that for CH_3OH was estimated from T. Ogata et al., *Bull. Chem. Soc. Jpn.*, 49, 2759 (1976). [d] Least-squares best-fit parameters to the equation $\Delta H^{\ddagger}_{ex} = aD_N - bD_N^2$; errors given are one standard deviation. [e] Calculated values in parentheses. [f] R. E. Richards et al., *Mol. Phys.*, 20, 913, 933 (1971). [g] Reference 25. [h] Reference 19. [i] R. J. West and S. F. Lincoln, *Inorg. Chem.*, 11, 1688 (1972). [j] A. H. Zeltman et al., *J. Phys. Chem.*, 73, 2689 (1969). More recently J. P. Hunt et al., *Inorg. Chem.*, 11, 1688 (1972), found a value of 10.3 kcal mol^{-1}. [k] Value not used in the least-squares analysis. [l] Reference 5. [m] Reference 3. [n] This work. [o] L. O. Morgan and T. Chen, *J. Phys. Chem.*, 76, 1973 (1972). [p] J. P. Hunt et al., *Inorg. Chem.*, 11, 2701 (1972). [q] J. Boubel and J. Delpesech, *Adv. Mol. Relaxation Processes*, 7, 209 (1975).

with the original proposals that

$$\Delta H^{\ddagger}_{ex} \propto A_M D_N \tag{11}$$

$$\Delta H^{\ddagger}_{ex} = aD_N - bD_N^2 \tag{12}$$

where a and b are parameters which will depend only on the metal ion. A plot of $\Delta H^{\ddagger}_{ex}/D_N$ vs. D_N is found to be generally linear for nickel(II) if the D_N values for H_2O and NH_3 are taken as 28 and 32, instead of 33 and 59.[32] Since these two values have been obtained from an NMR shift correlation, these changes are not so fundamental to the original D_N scale. The results of this correlation are summarized in Table IV where experimental and calculated values are compared. The correlation is considered satisfactory if agreement is within 1 kcal mol^{-1}. On this basis three systems fail to give agreement: cobalt(II) in water, iron(II) in water, and manganese(II) in methanol. In all cases the predicted values are higher than current experimental values. This is encouraging in one way, because improved measurements have often caused $\Delta H^{\ddagger}_{ex}$ to be increased in other systems.

It is perhaps worth noting that a similar correlation can be obtained using the E_B and C_B parameters of Drago as a measure of basicity. If basicity is given by $[E_B{}^2 + C_B{}^2]^{1/2}$ as suggested by Drago,[33] then for CH_3CN, Me_2SO, DMF, and NH_3 ($D_N = 32$) we find $D_N \approx 9.4[E_B{}^2 + C_B{}^2]^{1/2}$. It is unfortunate that both the D_N and E_B, C_B scales lack direct values for methanol and water.

Recently Tanaka[34] has suggested a correlation of $\Delta H^{\ddagger}_{ex}$ with solvent size and dielectric properties. The results of the present study on iron(II) are in reasonable agreement with this correlation. Tanaka's correlation works very well for cobalt(II) and iron(II) but the graphical presentation of the results tends to hide some deficiencies. For example with nickel(II) the predicted and observed $\Delta H^{\ddagger}_{ex}$ values differ by >1.5 kcal mol^{-1} except for DMF and methanol, and only the manganese(II)–acetonitrile system is predicted within the same limits. The absence of solvent dilution effects on $\Delta H^{\ddagger}_{ex}$ found here, and previously for nickel(II),[19] also seems inconsistent with a correlation in which bulk dielectric constant is an important parameter.

The observation that dilution of the exchanging solvent does not affect the exchange rate seems contrary to recent proposals by Caldin and Bennetto.[35] Similar results have been discussed recently by Langford et al.,[36] who changed the bulk solvent structure and viscosity by adding electrolytes. Added electrolyte appears to have no effect, but the $\Delta H^{\ddagger}_{ex}$ values of Langford et al. are 3–4 kcal mol^{-1} lower than what appear to be the best current values.

Finally some remarks on the mechanism of exchange can be made. Previously Frankel[19] concluded that the independence of exchange rate on solvent composition, as observed here, was evidence for an S_N1 process. However Perry, Drago, and Kildahl[37] have emphasized that preassociation is likely to invalidate such conclusions unless the solvent concentration is much lower than the 2.88 m value used here. A comparison of iron(II) and nickel(II) shows that both metal ions yield small positive $\Delta S^{\ddagger}_{ex}$ values. There is much evidence now for a dissociative substitution mechanism for nickel(II) and the $\Delta S^{\ddagger}_{ex}$ values provide a first indication that the same may be true for iron(II).

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Registry No. DMF, 68-12-2; $Fe(DMF)_6(ClO_4)_2$, 62126-15-2; $Fe(Me_2SO)_6(ClO_4)_2$, 16742-95-3; Me_2SO, 67-68-5; Ni(II), 14701-22-5; Co(II), 22541-53-3; Fe(II), 15438-31-0; Mn(II), 16397-91-4; CH_3CN, 75-05-8; CH_3OH, 67-56-1; H_2O, 7732-18-5; NH_3, 7664-41-7.

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Mössbauer Quadrupole Splitting Analysis of Iron(IV) Dithio Chelates

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A method for the analysis of temperature-dependent quadrupole splittings in iron(IV) dithio chelates is described. The method employs a general crystal field Hamiltonian including terms of octahedral, trigonal, and C_2 symmetry. The parameters derived from the analysis point to nearly identical crystal field surroundings corresponding to a geometry between the octahedral and trigonal-prismatic limits in agreement with the known structure of one of the compounds. It is suggested that the increase of quadrupole splitting at low temperatures may be used as a marker of the above molecular symmetry. The nearly identical isomer shifts at various temperatures constitute further evidence that the compounds have similar structures and bonding properties. An important conclusion of the analysis is that the electronic properties of these iron(IV) dithio chelates are successfully interpreted on the basis of a $3d^4$ electronic configuration with some covalent character present.

Introduction

The existence of synthetic iron complexes in the formal oxidation state four is now well documented by a variety of physical methods.[2-6] Apart from the diarsine complexes of the type $[Fe(diars)_2X_2](BF_4)_2$,[7] where X = Cl or Br and diars = *o*-phenylenebis(dimethylarsine), all other well-characterized iron(IV) complexes bear the FeS_6 core in which the sulfur atoms belong to a dithiocarbamate group[2] or to the 1,1-dicarboethoxy-2,2-ethylenedithiolate dianion (DED^{2-}).[3] Furthermore, there exists evidence that iron(IV) centers are present in the oxidized forms of certain peroxidases.[8,9] Thus, the study of chemical and physical properties of synthetic iron(IV) complexes is of particular importance in order to understand the action of iron(IV) in biological systems.

Magnetic susceptibility measurements on synthetic iron(IV) complexes have yielded magnetic moments in the range 2.9–3.4 μ_B consistent with a $3d^4$ configuration in an $S = 1$ ground state. Mössbauer isomer shifts have proved very useful for assigning formal oxidation states of iron. In the case of iron(IV) complexes isomer shifts fall in the range 0.1–0.2 mm/s at room temperature relative to the metal iron. They are lower than those of iron(III) compounds in agreement with the removal of one 3d electron on passing from Fe(III) (d^5) to Fe(IV) (d^4). Quadrupole splittings (QS), on the other hand, depend upon the exact symmetry at the iron and vary in general with temperature.[2]

The molecular structures reported for two Fe(IV) complexes, namely, $(BzPh_3P)_2[Fe(DED)_3]$, I,[3] and $[Fe(pyrrdtc)_3](ClO_4)$, II,[4] are severely distorted from octahedral coordination. The average projected twist angle of the two triangular faces of the FeS_6 unit can be taken as an indication of the deviation from octahedral geometry. In this way, the values of 35.9 and 38°, reported for compounds I and II, lie between the extremes of 60° corresponding to octahedral and 0° corresponding to trigonal-prismatic geometry. However, it must be emphasized that the above values represent an average over three greatly different projected twist angles each corresponding to one of the three sulfur chelating ligands. Martin and Takats have pointed out the similarity in the structures of compound I and of tetraphenylarsonium tris(benzenedithiolato)tantalate(V).[10] For the latter compound the symmetry at the tantalum atom is best described as originating from a trigonal prism which suffers individual rotations of the chelating ligands around the C_2 axis. One of these rotations, however, is more severe than the other two causing a lowering of the overall symmetry to C_2.

Recently, detailed ligand field analysis of the Mössbauer spectra of I has shown that the temperature variation of QS is well accounted for by ascribing to the complex a geometry close to a trigonal prism with an exact C_2 point symmetry.[11] In particular, the small increase of the QS at 4.2 K relative to the value at 77 K was found to be a unique feature of the above-described asymmetric type of distortion. In the present work we have extended the QS analysis to certain tris(dithiocarbamato)iron(IV) complexes with the purpose of determining whether they behave similarly to I and more particularly to correlate QS data with structural characteristics of analogous compounds.

Experimental Section

The iron(IV) perchlorates $[Fe(pyrrdtc)_3]ClO_4$, II, and $[Fe(S_2CNMe_2)_3]ClO_4$, IV, were prepared according to Golding et al.;[12] the tetrafluoroborates $[Fe(S_2CNEt_2)_3]BF_4$, III, and $[Fe(pyrrdtc)_3]BF_4$, V, were prepared following the method of Pasek and Straub[2] except that the boron trifluoride was replaced by a 48% $BF_3{\cdot}Et_2O$ solution. The products were recrystallized twice from dichloromethane–benzene. Their identity was confirmed from Mössbauer and infrared spectra. Mössbauer spectra were recorded with a conventional constant-acceleration spectrometer as described before.[13] The source was 30 mCi of ^{57}Co in an Rh matrix. The system was calibrated with an iron-foil absorber. Measurements at 4.2 K and lower temperatures were made using a liquid helium cryostat and vapor pressure techniques. The temperature range 56–300 K was covered in a liquid nitrogen cryostat either by vapor pressure techniques or by means of a heater attached to the sample holder. Relative errors within each set of QS data were ±0.004 mm/s. By repeating the room-temperature, liquid nitrogen,