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The Ion Pentacyano(dimethyl sulfoxide)ferrate(II). Synthesis, Characterization and Substitution Kinetics in Aqueous Solution

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The complex ion pentacyano(dimethyl sulfoxide)ferrate(II) has been prepared in aqueous solution and its sodium salt isolated. Infrared and nmr measurements indicate that the dimethyl sulfoxide ligand is coordinated to iron(II) through the sulfur atom. The kinetics of formation of the complex from the free ligand and aqueous pentacyanoaquoferrate(II), measured in competition with the *N*-methylpyrazinium complexation reaction, were studied by the stopped-flow technique at several temperatures with $\mu = 1.0\ M$, pH 7. A rate law of the form $d[Fe(CN)_5(CH_3)_2SO^{3-}]/dt = k_f[Fe(CN)_5H_2O^{3-}] \cdot [(CH_3)_2SO]$ was found where $k_f = 2.4 \pm 0.1 \times 10^2\ M^{-1}\ sec^{-1}$ at 25°. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were 15.4 ± 0.5 kcal/mol and 4 ± 2 cal deg^{-1} mol^{-1}, respectively. The results are interpreted as being consistent with an SN1 dissociative type of mechanism. An investigation of the kinetics of exchange of coordinated dimethyl sulfoxide for *N*-methylpyrazinium yielded rate saturation which is typical of a limiting SN1 mechanism. The limiting first-order specific rate of dissociation was found to be $7.5 \pm 0.1 \times 10^{-3}\ sec^{-1}$ with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ equal to 26 ± 0.5 kcal/mol and 11 ± 2 cal deg^{-1} mol^{-1}, respectively. From the specific rates of the formation and dissociation reactions the association quotient $K_I = 3.3 \pm 0.5 \times 10^6\ M^{-1}$ was calculated. The results are interpreted as signifying a substantial π interaction between the pentacyanoferrate(II) moiety and the sulfur atom of dimethyl sulfoxide.

Introduction

Dimethyl sulfoxide (DMSO) has found many interesting applications[1,2] in inorganic chemistry, both as a solvent and as a ligand. The complex ion pentaammine(dimethyl sulfoxide)ruthenium(II),[3] for example, contains strongly bound DMSO which is connected to Ru(II) through the sulfur atom.[4] We have found[5] that pentacyanoferrate(II) complexes of aromatic N heterocycles present spectra, electrode potentials, and substitution kinetics[6] which are similar to those of analogous complexes employing pentaammineruthenium(II).[7,8] Our desire to extend this analogy and also our cognizance of the current interest in complexes containing iron–sulfur bonds[9] has led to the characterization of the $Fe(CN)_5(CH_3)_2SO^{3-}$ ion.

While studying the visible spectra of a series of pentacyanoferrate(II) complexes of aromatic N heterocycles,[5] we observed that the deep color of the complexes disappeared within several hours after dissolution in DMSO, even if a relatively large concentration of the free heterocycle had been previously added. Subsequent experiments showed that, in dilute DMSO–water mixtures, dissociation of the heterocycle-substituted pentacyanoferrate(II) was not complete. Moreover, the displacement reaction could be reversed if a sufficient amount of the free heterocycle were introduced after an appropriate time interval. Our report of the isolation of the pentacyano(dimethyl sulfoxide)ferrate(II) complex as a crystalline sodium salt, of its infrared, nmr, and visible spectra, and of the its aqueous substitution kinetics is presented here.

Experimental Section

Synthesis. The sodium pentacyano(dimethyl sulfoxide)ferrate(II) salt was prepared according to the following procedure. Two grams of recrystallized $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ (Eastern Chemical Corp.) was dissolved in 10 ml of cold water and treated with 10 ml of dimethyl sulfoxide (Aldrich, reagent grade) at ice-bath temperature. After 20 min, ethanol was carefully added to precipitate the product. The solid was collected on a sintered-glass filter, washed with ethanol, and redissolved in 10 ml of cold water containing 1 ml of dimethyl sulfoxide. The product was reprecipitated with ethanol, collected, and stored under vacuum over anhydrous calcium chloride. *Anal.*[10] Calcd for $Na_3[Fe(CN)_5(CH_3)_2SO] \cdot 2H_2O$: C, 22.7; N, 19.0; H, 2.7. Found: C, 22.2; N, 19.0; H, 2.7.

This salt was also prepared by dissolving $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ in a saturated solution of sodium iodide at ice-bath temperature and subsequently treating the solution with dimethyl sulfoxide. Precipitation by the addition of ethanol was found to be easier under these conditions, leading to a more crystalline material. *Anal.* Calcd for $Na_3[Fe(CN)_5DMSO] \cdot 2H_2O$: C, 22.7; N, 19.0; H, 2.7. Found: C, 22.5; N, 19.3; H, 2.7. The DMSO-d_6 derivative was prepared in the same way from DMSO-d_6 in deuterium oxide solution.

N-Methylpyrazinium iodide, used in the competitive kinetic experiments, was prepared from high-purity pyrazine (Aldrich) and methyl iodide according to the procedure of Bahner and Norton.[11] *Anal.* Calcd for $C_5H_7N_2I$: C, 27.0; N, 12.6; H, 3.18; I, 57.2. Found: C, 27.1; N, 12.8; H, 3.22; I, 57.2.

Commercially available sodium pentacyanoammineferrate(II) was recrystallized several times from saturated aqueous ammonia solution at ice-bath temperature. This salt was also prepared by a conventional procedure[12] from sodium nitroprusside and purified by several recrystallizations. Both preparations gave identical results in the experiments described below.

Rate Measurements. The specific rate of formation of the pentacyano(dimethyl sulfoxide)ferrate(II) ion in aqueous solution was measured indirectly by determining the effect of added dimethyl sulfoxide upon a competing reaction between the dissolved pentacyanoammineferrate(II) salt and the *N*-methylpyrazinium ion (MPz). In a typical experiment a solution containing both of the competing ligands was mixed rapidly with a solution of the aqueous iron(II) starting material. Each of the attacking ligands was present in large excess over the total initial concentration ($10^{-5}\ M$ or less) of sodium pentacyanoammineferrate(II). The concentration of *N*-methylpyrazinium was held constant at $0.0100\ M$. Under these conditions consumption of the pentacyanoammineferrate(II) initially present was shown by spectrometry to be complete.

Rapid kinetic measurements were made using a Durrum Model D 150 stopped-flow instrument (Durrum Instrument Co., Palo Alto, Calif.) to observe the formation of the pentacyano-*N*-methylpyra-

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Table I. Vibrational Frequencies (cm^{-1}) for the Absorption Bands of Free DMSO and of Pentacyanoferrate(II) and Pentaammineruthenium(II) Complexes

Fe(II)[a]	Ru(II)[b]	DMSO	d_6 Fe(II)[a]	d_6 Ru(II)[b]	d_6 DMSO	Assignment
	3040 w		2385 w	2278 w		ν_{CH}[f] or ν_{CD}
2995 w[c]	2949 w	2998 w	2245 w (1.34)[e]	2151 w	2249 w	
2915 w	2938 w	2917 w		2143 w	2124 w	
2100 m[c]			2100 m			ν_{CN}
2070 sh[c]			2070 sh			
2060 vs[c]			2040 vs			
1415 w	1465 w	1435 w	1030 m (1.37)	1040 m	1038 w	$\delta_{d,CH}$[f] or $\delta_{d,CD}$
1405 m	1436 m	1414 m	1025 m (1.37)	1030 m	1030 m	
1365 w	1423 m	1402 m	1010 m (1.35)	1011 m	1011 m	
1315 m	1321 m	1303 m	965 m (1.36)			$\delta_{s,CH}$ or $\delta_{s,CD}$
1292 m	1309 m	1290 m				
1070 vs	1045 s	1070 s	1075 s	1056 s	1069 s	ν_{SO}
d	1023 sh		825 s	*d*	814 s	$\rho_{r,CH}$[f] or $\rho_{r,CH}$
1022 vs	1014 vs	1008 vs	765 m (1.34)	783 w	752 m	
972 m	963 m	945 m				
940 m	910 m	918 m				
680 m	692 m	661 m	630 m	635 m	605 m	ν_{CS}
560 s			560 s			δ_{MCN}
422 m	446 m	378 m	430 m	411 m	338 m	$\delta_{s,CSO}$
390 m	389 m	329 m	390 m	364 m	305 m	$\delta_{as,CSO}$
3550 s			3570 s			ν_{H_2O}
3420 s			3400 s			
1625 s			1625 s			δ_{H_2O}

[a] $Na_3[Fe(CN)_5(CH_3)_2SO]\cdot 2H_2O$. [b] $[Ru(NH_3)_5(CH_3)_2SO](PF_6)_2$ (data taken from ref 3). [c] Key: sh, shoulder band; w, weak; m, medium; s, strong; vs, very strong. [d] Peak hidden by ND or SO absorptions. [e] Numbers in parentheses refer to the frequency ratios ν_{CH}/ν_{CD} estimated to be 1.37 by simple theory. [f] Key: ν, stretching; δ, deformation; δ_d, degenerate deformation, δ_s, symmetric deformation; δ_{as}, asymmetric deformation; ρ_r, rocking.

ziniumferrate(II) complex (λ_{max} 655 nm, ϵ 1.2×10^4 M^{-1} cm^{-1}). Pseudo-first-order rate constants, k_{obsd}, were obtained by plotting $\ln [A_\infty - A_t]$ *vs.* t, where A_t is the measured absorbance at time t.

Special care was taken in the preparation of pentacyanoammineferrate(II) solutions employed in the stopped-flow experiments. Sodium pentacyanoammineferrate(II) was dissolved in solutions of appropriate ionic strength (lithium perchlorate) already at the temperature desired for the experiments. The solutions were prepared freshly for each run and stored in darkness in the reservoir syringe of the stopped-flow instrument for a maximum of 20 min to ensure thermal equilibration.

The iron(II)-containing starting material used in this study incorporates an ammonia molecule as a ligand. However, we have obtained evidence[6] (see Results and Discussion) that, under the conditions of this work, replacement of coordinated ammonia by a water molecule from the bulk solvent is complete within the time interval before mixing.

The kinetics of exchange of coordinated DMSO for MPz were carried out starting with the pentacyano(dimethyl sulfoxide)ferrate(II) complex in aqueous solution. A Cary Model 14 recording spectrophotometer was employed for these measurements. The specific rate, k_{obsd}, at which the system arrived at a new position of equilibrium after addition of a known concentration of *N*-methylpyrazinium ion was measured. To ensure pseudo-first-order conditions, the ligand concentrations ([DMSO] = 0.0500 *M*, [MPz] = 6.2×10^{-3} to 0.200 *M*) greatly exceeded the initial pentacyano(dimethyl sulfoxide)ferrate(II) concentrations (10^{-5} *M*). Both the specific formation rate and the rate of ligand exchange were studied in the 10-40° temperature range. Temperature control in the curvettes of both the stopped-flow instrument and the Cary spectrophotometer was maintained within ±0.2°.

Infrared and Nmr Measurements. Infrared spectra were recorded with Perkin-Elmer Model 457 and 337 instruments, using Nujol and Fluorolube mulls between cesium iodide plates. Nmr measurements were made in deuterium oxide solution with a Perkin-Elmer Model R10 instrument. *tert*-Butyl alcohol (methyl proton signal) was used as an internal standard.

Results and Discussion

Direct evidence for the presence of coordinated DMSO in the solid complex was provided by infrared measurements. The frequencies and our assignments of the infrared absorptions recorded for the solid sodium pentacyano(dimethyl sulfoxide)ferrate(II) complex in the 300-4000 cm^{-1} range are shown in Table I. Also presented are the bands for the dimethyl sulfoxide-d_6 substituted species as well as the data of Senoff, *et al.*,[3] for the analogous pentaammine(dimethyl sulfoxide)ruthenium(II) complex and its d_6 deuterated derivative.

The various CH_3, SO, and CS vibrational modes for coordinated DMSO in the pentacyanoferrate(II) complexes were assigned by comparing the observed spectra with previous assignments[13-17] for DMSO and DMSO-d_6 as well as with the assignments made for the pentaammineruthenium(II) complex.[3] In the 600-4000-cm^{-1} region the close correspondence among the variously assigned DMSO bands observed respectively in the iron(II) complex, the ruthenium(II) species, and the free ligands is notable.

The observation that the SO stretching frequency in the pentacyano(dimethyl sulfoxide)ferrate(II) complex remains virtually unchanged from that for free DMSO in solution is especially interesting. This observation corresponds closely to that made by Senoff and coworkers[3] in their characterization of the complex ion pentaammine(dimethyl sulfoxide)ruthenium(II). In those experiments a very small $\Delta\nu_{SO}$, where $\Delta\nu_{SO} = \nu_{SO}(DMSO) - \nu_{SO}(complex)$, was found.

Although the SO mode for DMSO and its complexes is not a pure SO stretching vibration, the quantity $\Delta\nu_{SO}$ has given in many cases a successful correlation with the nature of the donor atom (O or S). Except for the pentaammine(dimethyl sulfoxide)ruthenium(II) ion[3] and for the iron(II) complex which is the subject of this work, all known coordination compounds of DMSO give a negative $\Delta\nu_{SO}$ (a shift to higher frequency) when DMSO is bonded to the metal *via* the sulfur atom and a positive $\Delta\nu_{SO}$ when bonding occurs through oxygen. This correlation has been called the "$\Delta\nu_{SO}$ rule."[18-22]

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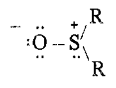
An explanation of the $\Delta\nu_{SO}$ rule is normally given in terms of the electronic structure of the sulfoxide, which can be represented as a hybrid of two resonance forms[19]



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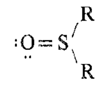

II

Coordination through the oxygen atom is postulated to stabilize structure I, with a lowering of the bond order resulting in a positive $\Delta\nu_{SO}$. Conversely, coordination *via* the sulfur atom is considered to stabilize resonance form II, yielding a negative $\Delta\nu_{SO}$.

March and Ferguson[4] explained the violation of the $\Delta\nu_{SO}$ rule by the S-bonded pentaammine(dimethyl sulfoxide)-ruthenium(II) complex in terms of $d\pi$–$d\pi$ back-donation from ruthenium(II) to sulfur. Invoking participation of empty sulfur d orbitals in the SO π bond of resonance form II, they postulated that electrons received in back-donation from Ru(II) would make those orbitals less available for interaction with the oxygen π electrons. Thus the importance of resonance form II and, consequently, the SO bond order would be decreased. The relatively small $\Delta\nu_{SO}$ was considered to be a result of competition between the back-bonding effect and the normal SO bond-strengthening influence of the metal–sulfur interaction.

In this work, $\Delta\nu_{SO} \approx 0$ for the pentacyano(dimethyl sulfoxide)ferrate(II) ion. We interpret this observation, along with the close correspondence of the other DMSO bands to those of the Ru^{II}–DMSO complex, as strong evidence that DMSO is sulfur bonded in its pentacyanoferrate(II) complex and that metal-to-ligand back-donation in part stabilizes the iron–sulfur bond.

Nmr Spectra. In Table II are presented nmr data for the pentaammine(dimethyl sulfoxide)ruthenium(II) and the pentacyano(dimethyl sulfoxide)ferrate(II) complexes in deuterium oxide solution and for free DMSO. Nearly equal downfield shifts of the methyl group absorption in the iron(II) complex and in the ruthenium(II) analog are seen.

Several investigations of ^{1}H nmr spectra of DMSO complexes and related species have recently been reported.[23-25] In those studies the methyl proton resonances of the oxygen-bonded DMSO complexes were scarcely shifted from that of the free ligand. For sulfur-bonded DMSO complexes a ~1-ppm downfield shift was observed. The somewhat smaller displacements cited in Table II are unique because the two complexes described fall into an intermediate class.

The nmr spectra of organic ligands coordinated to the pentaammineruthenium(II) substituent have been discussed recently[26,27] in terms of competing inductive, paramagnetic, and back-bonding effects. For the two complexes in Table II, the inductive (deshielding) effect predominates to almost the same extent. Although this close correspondence is probably partly fortuitous, the fact that the nmr spectrum for sulfur-bonded DMSO in the ruthenium(II) complex is virtually identical with that of DMSO in the iron(II) species is consistent with sulfur bonding in the pentacyano(dimethyl sulfoxide)ferrate(II) complex.

Table II. ^{1}H Nmr Spectra in D_2O Solution

Species	$\delta(CH_3)$	$\Delta(CH_3)^a$
DMSO	1.45^b	
$Fe(CN)_5DMSO^{3-}$	1.98^b	0.53
$Ru(NH_3)_5DMSO^{2+}$	2.01^c	0.55

^{a} $\Delta(CH_3) = \delta(CH_3)_{DMSO} - \delta(CH_3)_{complex}$. ^{b} Chemical shift quoted in ppm relative to *tert*-butyl alcohol (methyl proton signal). ^{c} δ (ref 3) corrected to refer to *tert*-butyl alcohol standard.

Visible Spectrum. Neutral aqueous solutions of the salt $Na_3[Fe(CN)_5DMSO]\cdot 2H_2O$ were found to be faintly yellow, with an absorption peak centered at 352 nm (ϵ_{max} 210 M^{-1} cm^{-1}). We characterize this band as a d–d transition. No metal-to-ligand electron-transfer bands of the type known in the pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles were observed, except for those at 220 nm and at shorter wavelengths which involve metal–cyanide electron-transfer transitions.

In the presence of a small amount (10^{-3} M) of added DMSO, the 352-nm band was stable indefinitely. Without this precaution, a very small increase in the intensity of the absorption took place after 1 day.

In d^6 pentacyano complexes of C_{4v} symmetry, for which a $^1A_1$ ground state is assumed, two visible absorptions have been usually observed.[28] The first, a relatively weak band at 500-550 nm, has been assigned[29] to the transition $^1A_2 \leftarrow {}^1A_1$. The second, a stronger band, occurs at higher energies (350-400 nm) and is assigned to the $^1E_1 \leftarrow {}^1A_1$ transition. By analogy, considering its energy and intensity, we assign the 352-nm (28.4-kK) band in the pentacyano(dimethyl sulfoxide)ferrate(II) ion to a $^1E_1 \leftarrow {}^1A_1$ transition. At very high concentrations a small shoulder, suggesting the $^1A_2 \leftarrow {}^1A_1$ transition, appears at 500 nm.

Kinetics of Complex Formation. In this work the source of aqueous pentacyanoaquoferrate(II) ion was the sodium pentacyanoammineferrate(II) salt. A previous kinetic study[6] of aqueous substitution reactions utilizing solutions of the pentacyanoammineferrate(II) ion and a number of aromatic N heterocycles yielded the following important results. First, the rates of substitution were all rapid, having half-times of the order of 10^{-1}–10^{-3} sec, depending on the ligand concentrations. Second, the specific substitution rates varied within a small interval although the basicities of the entering ligands ranged over a factor of 10^6 (see Table IV). It was concluded that loss of ammonia from the pentacyanoammineferrate(II) ion, in exchange for solvent water, must be quantitative within the interval after dissociation and before mixing, under the experimental conditions. On this basis we will refer subsequently to the pentacyanoaquoferrate(II) ion as the initial reactant in the study of kinetics of DMSO complex formation.

Two factors preclude the direct spectrophotometric measurement of the rate of the forward reaction in eq I. The first of these is that the visible–near-uv absorption spectrum

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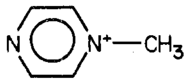
$$\mathrm{Fe(CN)_5H_2O^{3-}\,(aq) + DMSO(aq) \underset{k_r}{\overset{k_f}{\rightleftarrows}} Fe(CN)_5DMSO^{3-}(aq)} \qquad \text{(I)}$$

of the product is only slightly different from that of the reactant complex. Direct measurement of the reaction rate would therefore require the use of high concentrations of aqueous pentacyanoaquoferrate(II) ion. The second factor, as Emschwiller[30] has pointed out, is that polynuclear species such as $Fe_2(CN)_{10}{}^{6-}$ become increasingly important at high concentrations of the pentacyanoaquoferrate(II) complex. We have shown[6] that this second difficulty can be avoided by employing concentrations of $Fe(CN)_5H_2O^{3-}$ no greater than *ca.* 10^{-5} *M*. However, at low concentrations of the iron(II) complex, a direct spectrophotometric study of reaction I is impossible.

These difficulties led us to measure the forward rate constant, k_f, indirectly by determining the effect of reaction I on a competing, pseudo-first-order reaction, eq II. MPz

$$\mathrm{Fe(CN)_5H_2O^{3-}(aq) + MPz(aq) \xrightarrow{k_f'} Fe(CN)_5MPz^{2-}(aq)} \qquad \text{(II)}$$

refers to the *N*-methylpyrazinium ion



present in large excess relative to pentacyanoaquoferrate(II). Equation II was chosen as the "probe" reaction because the product is very stable, has been fully characterized,[5] and exhibits a strong electron-transfer absorption band in the visible region (λ_{max} 655 nm, log $\epsilon_{max} = 4.08$). Also, the kinetics of process II have been investigated.[6]

It has been shown (*vide infra*) that the dissociation of the products formed by reactions I and II takes place slowly compared to the forward rates. Therefore, if both DMSO and MPz are present in large excess with respect to the pentacyanoaquoferrate(II) ion, the pseudo-first-order, specific rate of formation, k_{obsd}, of the $Fe(CN)_5MPz^{2-}$ species is given by

$$k_{obsd} = k_f[\mathrm{DMSO}] + k_f'[\mathrm{MPz}] \qquad (1)$$

In Figure 1 is shown a plot of k_{obsd} measured by the stopped-flow technique (λ 655 nm, pH 7, $\mu = 1.0\,M$, 25.0°) *vs.* the DMSO concentration in the range 1.00×10^{-2} to 0.200 *M*, employing concentrations of $Fe(CN)_5H_2O^{3-}$ and MPz, *ca.* 10^{-5} and 1.00×10^{-2} *M*, respectively. From the slope was calculated the value of k_f, $(2.40 \pm 0.05) \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$. The ordinate intercept yielded a value of $k_f'[\mathrm{MPz}]$ equal to $5.6 \pm 0.1\ \mathrm{sec}^{-1}$ in agreement with the product of the previously measured k_f' [6] ($(5.5 \pm 0.1) \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$) times the MPz concentration.

Temperature Dependence. The temperature dependence of the rate of the aqueous pentacyanoaquoferrate(II)-DMSO reaction was studied between 10 and 30°. The observed rate constants at several concentrations were corrected for the contribution of the MPz complexation reaction which was measured under identical conditions but in the absence of DMSO. The results are presented in Table III.

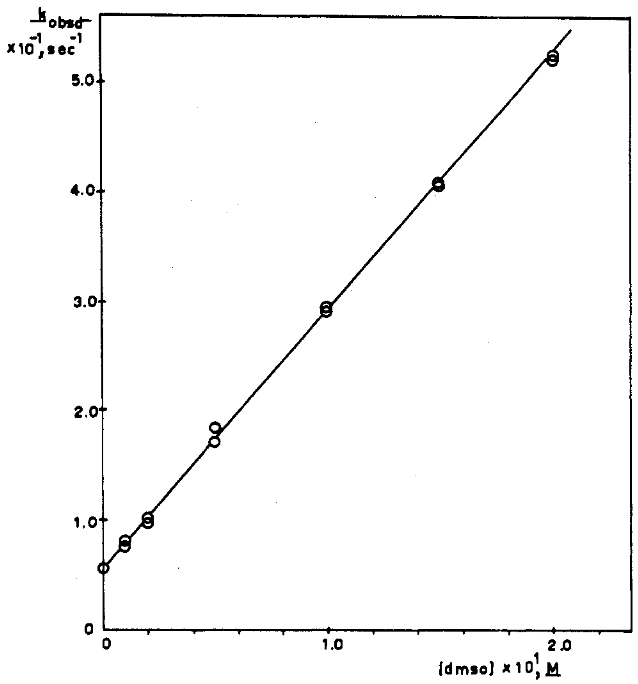


Figure 1. Observed rate constants *vs.* dimethyl sulfoxide concentration ([MPz] = 0.0100 *M*, $[Fe(CN)_5H_2O^{3-}] \approx 10^{-5}$ *M*, $\mu = 1.00$ *M* (lithium perchlorate), pH 7, 25°).

Table III. Temperature Dependence of the Formation Rate Constants[a]

Temp, °C	k_{obsd}, sec^{-1}	k_f'[MPz], sec^{-1}	k_f[DMSO], sec^{-1}	$10^{-2}k_f$, M^{-1} sec^{-1}
29.8	26.5 ± 1.5	8.3 ± 0.4	18.2 ± 1.0	3.6 ± 0.2
25.0	17.4 ± 1.0	5.5 ± 0.3	11.9 ± 0.8	2.4 ± 0.1
19.2	10.0 ± 0.5	2.7 ± 0.1	7.3 ± 0.4	1.46 ± 0.06
15.0	7.0 ± 0.3	1.80 ± 0.09	5.3 ± 0.2	1.06 ± 0.04
10.4	4.2 ± 0.2	1.20 ± 0.07	3.0 ± 0.1	0.60 ± 0.03

[a] [MPz] = 0.010 *M*, [DMSO] = 0.0500 *M*, $\mu = 1.00$ *M* (lithium perchlorate). From these data the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ relating to rate constant k_f are 15.4 ± 0.5 kcal/mol and 4 ± 2 cal deg^{-1} mol^{-1}, respectively.

Mechanism of the Substitution Process. The second-order rate constant for DMSO complexation with aqueous pentacyanoaquoferrate(II) and the activation parameters for the process are presented in Table IV. Also given in the table are similar data for reactions of substitution in $Fe(CN)_5H_2O^{3-}$ by a series of aromatic nitrogen heterocycles. We note that there is little variation among the rate constants and activation parameters for the six substitution reactions cited.

We have suggested[6] that substitution reactions of the ion $Fe(CN)_5H_2O^{3-}$ are best represented by an SN1 mechanism (eq 2, 3). By assuming a steady-state concentration of the

$$\mathrm{Fe(CN)_5H_2O^{3-}(aq) \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} Fe(CN)_5{}^{3-}(aq) + H_2O} \qquad (2)$$

$$\mathrm{Fe(CN)_5{}^{3-}(aq) + DMSO \xrightarrow{k_a} Fe(CN)_5DMSO^{3-}(aq)} \qquad (3)$$

intermediate, the rate law, eq 4, can be derived. For none of

$$\frac{d[\mathrm{Fe(CN)_5DMSO^{3-}}]}{dt} = \frac{k_d k_a[\mathrm{Fe(CN)_5H_2O^{3-}}][\mathrm{DMSO}]}{k_{-d} + k_a[\mathrm{DMSO}]} \qquad (4)$$

the ligands cited in Table IV has the rate of the complexation reaction shown other than a simple, first-order dependence upon the concentration of the attacking ligand, present in large excess. Therefore, we conclude that the k_{-d} term, which incorporates the concentration of solvent water, is substantially greater than the general k_a[L] term in the denominator, where [L] represents the concentration of the entering ligand. We note further that the reactivity of the pentacyano intermediate species appears to be quite insensitive to the nature of the attacking reagent. This would be

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Table IV. Second-Order Rate Constants for Substitution, at 25°

Ligand	$10^{-2}k_f$, M^{-1} sec^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	pK_a
4-Picoline	3.54	15.1 ± 0.5	4 ± 2	6.11[a]
Pyridine	3.65	16.1	7	5.30[a]
Isonicotinamide	2.95	15.8	6	3.65[a]
Pyrazine	3.80	15.4	5	0.6[b]
N-Methylpyrazinium	5.50	16.8	10	<0
Dimethyl sulfoxide	2.40	15.4	4	0.91[c]

[a] K. Shofield, "Hetero Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967. [b] R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience, New York, N. Y., 1967. [c] K. K. Andersen, W. H. Edmonds, J. B. Briasonni, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).

consistent with a highly reactive intermediate for which the k_a step might be diffusion controlled.

Kinetics of Ligand Exchange. To obtain information about the rate and mechanism of dissociation of the pentacyano(dimethyl sulfoxide)ferrate(II) complex, the kinetics of the ligand exchange process, eq III, were investigated. In the

$$\mathrm{Fe(CN)_5DMSO^{3-}(aq) + MPz(aq) \rightleftharpoons Fe(CN)_5MPz^{2-}(aq) + DMSO(aq)} \qquad \text{(III)}$$

experiments large excesses of both MPz and DMSO, relative to the total concentration of the pentacyanoferrate(II) species, were used to ensure pseudo-first-order conditions. The pentacyano(dimethyl sulfoxide) complex was found to be almost completely converted to the *N*-methylpyrazinium substituted species when a 20-fold excess of MPz over DMSO was used. Although the ligand-exchange reaction was observed to be reversible, the kinetics experiments were performed starting with the DMSO-substituted complex.

A plot of k_{obsd}, the measured specific rate of the substitution process, *vs.* the concentration of the *N*-methylpyrazinium ion ($10^{-3}\ M \leqslant [\text{MPz}] \leqslant 0.200\ M$, $[\text{DMSO}] = 0.0050\ M$, $\mu = 1.00$, 25°) is shown in Figure 2. The figure presents two unusual features. The first of these is that, at low concentrations of MPz, the rate of the substitution process actually *decreases* while the concentration of the attacking ligand increases. The second important feature is that, above a certain concentration of MPz, the observed rate of the ligand-exchange reaction becomes independent of the concentration of the attacking ligand. Both these striking observations can be explained employing the mechanism

$$\mathrm{Fe(CN)_5DMSO^{3-}(aq)} \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} \mathrm{Fe(CN)_5{}^{3-}(aq) + DMSO(aq)}$$

$$\mathrm{Fe(CN)_5{}^{3-}(aq) + H_2O} \overset{K}{\rightleftharpoons} \mathrm{Fe(CN)_5H_2O^{3-}(aq)}$$

$$\mathrm{Fe(CN)_5{}^{3-}(aq) + MPz(aq)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Fe(CN)_5MPz^{2-}(aq)}$$

The mechanism is analogous to one which we have previously postulated for ligand exchange in the pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles.[5] Applying the steady-state approximation to the concentration of the five coordinate intermediate species, one finds

$$\frac{-\mathrm{d}[\mathrm{Fe(CN)_5DMSO^{3-}}]}{\mathrm{d}t} = k_{\text{obsd}}\{[\mathrm{Fe(CN)_5DMSO^{3-}}]_t - [\mathrm{Fe(CN)_5DMSO^{3-}}]_\infty\}$$

where

$$k_{\text{obsd}} = \frac{k_1k_{-2}[\text{DMSO}] + k_{-1}k_2[\text{MPz}]}{k_1[\text{DMSO}] + k_2[\text{MPz}]} \qquad (5)$$

Table V. Temperature Dependence of the Saturation-Limited Rate[a]

Temp, °C	10^3k_{obsd}, sec^{-1}	Temp, °C	10^3k_{obsd}, sec^{-1}
20.0	3.6 ± 0.1	35.0	36.0 ± 0.5
25.0	7.5 ± 0.1	40.0	67 ± 1
30.0	16.4 ± 0.3		

[a] [DMSO] = 5.0 × 10^{-3} *M*, [MPz] = 0.200 *M*.

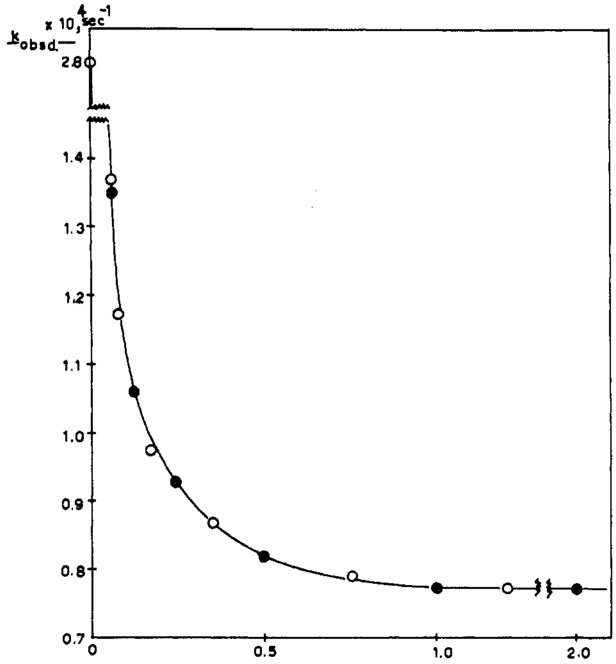

Figure 2. Plot of k_{obsd}, the specific rate of ligand exchange, *vs.* the concentration of *N*-methylpyrazinium ion. Filled circles are points determined by experiment. Open circles are points calculated using eq 5 ($[\mathrm{Fe(CN)_5DMSO^{3-}}] = 6 \times 10^{-5}\ M$, $[\text{DMSO}] = 0.0050\ M$, $\mu = 1.00\ M$, 25°).

When the *N*-methylpyrazinium ion concentration is sufficiently high, rate saturation is predicted by eq 5; *i.e.*, k_{obsd} must be reduced to k_{-1}. Similarly, as the *N*-methylpyrazinium concentration falls to zero, k_{obsd} should tend toward k_{-2}.

The specific rate, k_{-2}, referring to dissociation of the *N*-methylpyrazinium complex, has been found[5] to be 2.8×10^{-4} sec^{-1}. It is the higher value of this rate constant, relative to that for the k_{-1} step, which dictates the initial decrease seen in Figure 2. The curve in the figure can be generated (unfilled circles) by substituting in eq 5 the values given above for k_{-1} and k_{-2} and using, from Table IV, appropriate values of k_1 and k_2.

Temperature Dependence and Activation Parameters of Ligand Exchange. The temperature dependence of the rate constants for the ligand exchange (k_{-1}) process was studied in the 20-40° range, working above the kinetic saturation point in the concentration of MPz. The observed rate constants at several temperatures are shown in Table V. The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, were calculated to be 26.5 ± 0.5 kcal/mol and 11 ± 2 cal deg^{-1} mol^{-1}, respectively. The enthalpy of activation is nearly the same as that which has been measured for ligand loss in a number of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles.[5] The positive activation entropy is also consistent with a dissociative type of mechanism.

Formation Constant. From the known values of k_f and k_{-1} (or k_r) measured in this study one can calculate the association quotient for equilibrium I. Using the relationship $K_I = k_f/k_r$ we find K_I equals $(3.3 \pm 0.1) \times 10^6\ M^{-1}$.

From the activation parameters of the forward and reverse steps we find $\Delta H = -11 \pm 1$ kcal/mol and $\Delta S = -7 \pm 3$ cal deg^{-1} mol^{-1} under the experimental conditions used in this study.

The formation quotient, K_{I}, is approximately 2-10 times larger than those calculated[6] for a series of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles. In this work we have shown that the larger stability of the dimethyl sulfoxide complex is reflected in the relatively low specific rate of dissociation of the complex, rather than in a high formation rate. In view of the relatively weak basicity of dimethyl sulfoxide, its strong interaction with the pentacyanoferrate(II) group can only be explained by postulating a covalent bond between DMSO and iron(II) in the complex. The fact that complexes of oxygen bases (*e.g.*, H_2O, tetramethylene sulfone) are apparently weak and labile also suggests strongly that the bond is between iron(II) and sulfur.

Conclusion. The existence of a stable, sulfur-bonded DMSO adduct of pentacyanoferrate(II) suggests an important role for $M(d\pi)$-$S(d\pi)$ back-bonding in octahedral, low-spin iron(II) complexes. Also, in view of the similar existence of the pentaammine(dimethyl sulfoxide)ruthenium(II) ion, the analogy which has been noted[5] between complexes of pentacyanoferrate(II) and those of pentaammineruthenium(II) is further extended.

Registry No. $Na_3[Fe(CN)_5(CH_3)_2SO]$, 40548-26-3; $Na_3[Fe(CN)_5NH_3]$, 14099-05-9; $Fe(CN)_5MPz^{2-}$, 40299-79-4; $Fe(CN)_5H_2O^{3-}$, 18497-51-3; dimethyl sulfoxide, 67-68-5; *N*-methylpyrazinium iodide, 6277-35-6.

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Hydrolytic Precipitation of Iron(III) in 1 *M* (Na)NO_3 Medium

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The hydrolytic precipitation of iron(III) has been investigated at 25° in a 1 *M* $(Na^+)NO_3^-$ medium by measuring the acidity of the solutions by glass electrode potentiometry. The hydrolysis process was found to be a very slow one (equilibrium was reached after at least 4 weeks) ending in the formation of a basic precipitate of composition $Fe(OH)_2(NO_3)$. The data could be explained by assuming only the reaction $Fe^{3+} + NO_3^- + 2H_2O \rightleftharpoons Fe(OH)_2NO_3(s) + 2H^+$ with $\log K^* = 2 \log (H^+) - \log (Fe^{3+}) = -(2.20 \pm 0.03)$ where K^* is the equilibrium constant for the formation of the rather insoluble iron(III) basic nitrate.

Introduction

The hydrolytic behavior of iron(III) ions has attracted the attention of many inorganic chemists. A summary of quantitative conclusions derived from these studies up to 1964 is reported in ref 1. Work performed after 1964 is quoted in ref 2-11. One of the main features of iron(III) hydrolysis is the slowness of the equilibria, a fact recognized as early as 1936[2] when it was stated that the final product of the slow hydrolytic process was the formation of a solid phase leaving no soluble hydrolytic species in equilibrium. Due to this slowness many of the studies carried out seem to have been dealing with nonequilibrium solutions. Nevertheless valuable information has been obtained from physical techniques such as ir and visible spectrophotometry,[5] nmr,[9] esr,[11] and ultracentrifugation.[3] Potentiometric techniques (glass electrodes or redox potentials) have also yielded useful information on composition and formation constants of metastable products forming and dissociating much faster then their transformation to eventually stable products.[12,13] One of the few works dealing with equilibrium data seems to be a potentiometric study[4] of iron(III) chloride solutions. The authors of that paper have in fact applied the mass action law to their potentiometric data only when equilibrium was reached in the hydrolyzed solutions, the time required being of the order of several weeks. In this condition the only reaction required to explain the experimental data was the formation of a precipitate

$$Fe^{3+} + 2.70H_2O + 0.30Cl^- \rightleftharpoons Fe(OH)_{2.70}Cl_{0.30}(s) + 2.70H^+$$

Equilibrium data concerning the hydrolysis process seem still to be lacking for iron(III) nitrate solutions. The slowness of the equilibria has in fact prevented drawing significant conclusions from potentiometric measurements[3] recorded too soon after the starting of the hydrolytic reactions. On the other hand it was shown from ultracentrifuge, dialysis, gel filtration, and chemical analysis that the hydrolysis of ferric nitrate leads to the formation of a high molecular weight polymer, $[Fe(OH)_x(NO_3)_{3-x}]_n$ (where x lies between

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