the orders are somewhat unexpected on electronegativity grounds, particularly the result that PF_3 is comparable to $P(OCH_2)_3CC_5H_{11}$ in σ-donor capacity. It is possible, however, that "normal" basicity orders are not necessarily operative when the ligand is complexed to a transition metal.[15] If indeed $^{183}W-^{31}P$ coupling occurs through orbitals having s character, a better correlation with $\Delta\sigma$ than with $\Delta\pi$ might have been expected since increasing s character of the phosphorus lone pair in the complex should parallel its decreasing σ-donating character. The poor correlation of $^{183}W-^{31}P$ coupling with $\Delta\sigma$ could arise from the small range in $\Delta\sigma$ values for these phosphorus ligands (+0.01 to −0.34) and the large standard deviation (0.12) in the correlation compared to the acknowledged error[15] (0.12) in the $\Delta\sigma$ evaluation.

We tentatively draw the following conclusions from these studies. (a) Increases in the electronegativity of the phosphorus ligand account very well for the rise in $^{183}W-^{31}P$ coupling constants in $W(CO)_5L$ complexes. (b) Although greater ligand electronegativity is expected to raise the π-acceptor capacity of the ligand, the rise in $^{183}W-^{31}P$ coupling can be explained quite well without invoking π bonding as a coupling mechanism. (c) No significant correlation was found between tungsten–phosphorus coupling and the carbonyl stretching frequencies, force constants, and the $\Delta\sigma$ and $\Delta\pi$ quantities in the series of complexes studied.

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Axial Ligand Exchange Reactions of Ferrous Phthalocyanine. Exchange of Imidazole for Dimethyl Sulfoxide

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Ferrous phthalocyanine dissolves in dimethyl sulfoxide to give a diamagnetic blue solution. The rate of exchange of imidazole (Imid) for dimethyl sulfoxide at the axial sites to give green $FePc(Imid)_2$ obeys the rate law

$$\frac{d[FePc(Imid)_2]}{dt} = 4.17 \times 10^{13}e^{-17,900/RT}[FePc][Imid]\ M^{-1}\,sec^{-1}$$

At 25° $\Delta H^{\ddagger} = 17.3$ kcal/mole and $\Delta S^{\ddagger} = 1.8$ eu. Replacement of coordinated dimethyl sulfoxide by the first imidazole molecule is rate determining and exerts a powerful *trans* effect on the exchange of the second dimethyl sulfoxide ligand.

Introduction

One family of inorganic reactions convenient to follow experimentally involves ligand exchanges at a low-spin d^6 octahedral center. The majority of studies have been on Co(III) complexes, with a number on Rh(III) and Pt(IV) systems.[1] Ferrous complexes have biological importance, but far fewer are low-spin than is the case with Co(III), and easy oxidation to Fe(III) is an experimental complication. Work to date has been restricted to tris-diimine complexes, *e.g.*, tris(*o*-phenanthroline)iron(II) perchlorate.[2]

It has been known for 30 years that derivatives of ferrous phthalocyanine (FePc) (Figure 1) of the formula $FePc(base)_2$[3a] are low-spin[3b] d^6 complexes, and it seemed that a study of axial ligand replacement rates would be of interest. The system has a fixed geometry, with the ligands undergoing replacement *trans* to each other. The advent of a variety of dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMA), or trimethyl phosphate has removed the serious experimental disadvantage of ferrous phthalocyanine—its insolubility in common solvents. This paper describes the exchange of axially bound dimethyl sulfoxide by imidazole at a ferrous phthalocyanine center in dimethyl sulfoxide as solvent. Some preliminary results at 25° have been presented in ref 4.

Experimental Section

Purification of Materials.—(a) British Drug Houses reagent grade DMSO was purified by two methods, each of which gave samples of the same refractive index, producing the same kinetic results.

(i) The solvent was dried over solid potassium hydroxide, decanted, and then distilled at ~1.5 mm at 40°. Distillation was through a 2-ft vacuum-jacketed column packed with stainless steel gauze helices, with a nitrogen gas bleed. The middle three-fifths of the distillate was retained, treated with calcium

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[1] (a) C. H. Langford and H. B. Gray, "Ligand Replacement Reactions," W. A. Benjamin, New York, N. Y., 1965, Chapter 3; (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, Chapters 3 and 4.

[2] (a) I. M. Kolthoff, O. L. Leussing, and T. S. Lee, *J. Am. Chem. Soc.*, **70**, 2348 (1948); (b) D. W. Margerum, *ibid.*, **79**, 2728 (1957); (c) D. W. Margerum and L. P. Morgenthaler, *ibid.*, **84**, 706 (1962); (d) J. Burgess and R. H. Prince, *J. Chem. Soc.*, 4697 (1965).

[3] (a) P. A. Barrett, E. F. Bradbrook, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1820 (1939); (b) H. Senff and W. Klemm, *J. Prakt. Chem.*, **154**, 73 (1939).

[4] J. G. Jones and M. V. Twigg, *Inorg. Nucl. Chem. Letters*, **5**, 333 (1969).

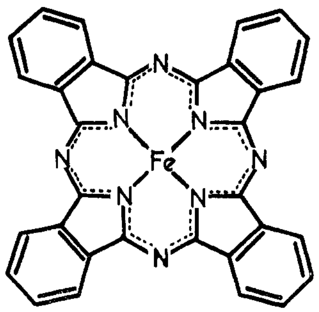

Figure 1.—Ferrous phthalocyanine, FePc. The central Pc ring is an 18-π-electron system.

hydride for 24 hr, and then distilled again at reduced pressure, the middle three-fifths again being collected and stored under dry nitrogen.

(ii) The DMSO was allowed to dry over calcium hydride and distilled as already described. It was then stood over activated molecular sieve for 2 days, decanted, and then distilled again, the middle three fifths being collected; $n^{25}\text{D}$ 1.4768, lit.[5] $n^{25}\text{D}$ 1.4760; d^{20} 1.1002 g/ml, lit.[6] d^{20} 1.1000 g/ml.

(b) Ferrous phthalocyanine was prepared by reductive cyclization of phthalodinitrile with iron pentacarbonyl,[7] giving fine blue-black needles 2 mm long, having a copper reflex. *Anal.* Calcd for $FeC_{32}H_{16}N_8$: C, 67.60; H, 2.84; N, 19.73. Found: C, 67.42; H, 2.51; N, 19.56. The measured magnetic moment of the solid sample was $\mu_{eff} = 3.92$ BM at 20° (lit. $\mu_{eff} = 3.85$,[8] 3.96[8b] BM). Dissolved in pyridine our sample had λ_{max} 655 nm, log $\epsilon_M = 5.07$; λ_{max} 592 nm, log $\epsilon_M = 4.47$ compared with literature values of 654 nm, 5.03; 593 nm, 4.47.[9]

(c) British Drug Houses reagent grade imidazole was recrystallized twice from sodium-dried benzene and was then sublimed *in vacuo* at 60°. The purified product had an uncorrected melting point of 90.5° (lit.[10] mp 90°).

(d) $FePc(Imid)_2$ was prepared by dissolving ferrous phthalocyanine in molten imidazole and then extracting the excess imidazole with ethanol, leaving the product as dark purple microcrystals,[10] which the standard Gouy method showed to be diamagnetic. *Anal.* Calcd for $FeC_{38}H_{24}N_{12}$: Fe, 7.9; C, 64.8; H, 3.4; N, 23.9. Found: Fe, 8.2; C, 64.3; H, 3.3; N, 24.2.

Magnetic Measurements (Evans' Method).[11]—Ferrous phthalocyanine was continuously extracted with DMSO in an all-glass Soxhlet apparatus *in vacuo* (with nitrogen bleed) at 40°, and after 3 days deposition of solid was noted in the blue-black extract. The extract was allowed to cool and was filtered through a No. 4 glass sinter. The precipitate was dark blue, but lighter than ferrous phthalocyanine itself, and was hygroscopic. Insufficient material was obtained for analysis. Part of the dark blue filtrate was diluted 100-fold, and using the extinction coefficient of FePc in DMSO (λ_{max} 652.5 nm; log $\epsilon_M = 4.91$) the concentration of the undiluted saturated solution was calculated to be 4×10^{-3} *M*. A portion of this solution was placed in an nmr tube with internal TMS marker (internal signal) and also in the tube was a capillary containing DMSO with TMS marker (external signal). The solution of ferrous phthalocyanine was shown to be diamagnetic, the difference between internal and external signals being $\leqslant 0.25$ cps at 33° and 60 MHz (Perkin-Elmer R10 spectrometer).

Rate Measurements and Solution Stability.—Ferrous phthalocyanine solutions ($\sim 1 \times 10^{-5}$ *M*) were made up in DMSO, under nitrogen. Solid was weighed out with a Cahn electrobalance, and solutions had λ_{max} 652.5 nm, log $\epsilon_M = 4.91$.

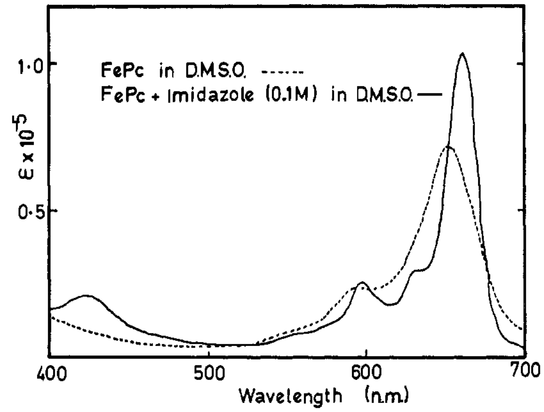

Figure 2.—Visible spectra of solutions of FePc in DMSO and DMSO + imidazole ($FePc(Imid)_2$).

Preparation was carried out under nitrogen and fresh solutions were always used for kinetic work, because ferrous phthalocyanine dissolved in dimethyl sulfoxide slowly fades. (We have found that this slow fading is due to degradation of the phthalocyanine ring by oxygen. Using pure oxygen bubbled through a solution of ferrous phthalocyanine in DMSO at 25° the color of the solution fades in a first-order manner, such that $k \cong 3 \times 10^{-6}$ sec^{-1}. Air "fades" the solution at about one-fifth the rate, and nitrogen does not fade it at all, so that it would appear that the fading rate is proportional to oxygen concentration. However, the fading rate in pure oxygen is 10,000 times slower than the rates of imidazole attack described in this paper, so fading cannot be a serious source of error.)

Imidazole dissolved freely in DMSO up to 3.0 *M*. These solutions were also prepared under nitrogen.

Kinetic runs were performed by following the reaction spectrophotometrically at a selected wavelength, using a Beckman DB spectrometer reading out through a Servoscribe 8-in. mV–time recorder.

Temperature control was *via* "Shandon Circotherm" baths and circulating units. Bath control was to ±0.05°, measured on a calorimeter thermometer.

In a typical run a DMSO reference was used and the 1-cm quartz reaction cell was half-filled with 1.2 ml of ferrous phthalocyanine solution. The lid of the cell compartment was then closed, the recorder was started, and 1.2 ml of imidazole solution was squirted into the sample cell through a $^1/_8$-in. hole in the lid, using a 5-ml syringe and an 8-in. cannula, which had been prewarmed to the temperature of the reagent solutions. Mixing occurs within 2 sec, as revealed by blank runs; the small hole in the sample compartment lid does not affect measured optical densities. The spectrophotometer readout is in per cent transmittance, with a change from 30 to 20% *T* occurring at 662 nm. Scale expansion magnified this to a space of 6 in. on the recorder chart.

Results

Experiments were carried out at 20, 25, 30, and 35° using excess imidazole concentrations of 0.0025, 0.005, 0.0075, 0.01, and 0.0125 *M* at each temperature. At each temperature and imidazole concentration, a minimum of five runs was made. The spectra at the beginning and end of the reaction are shown in Figure 2. The spectrum at the end of the reaction is identical with that of synthetic $FePc(Imid)_2$ dissolved in acetone, or $FePc(Imid)_2$ dissolved in DMSO containing a 10,000-fold excess of imidazole. [Calculations using measured equilibrium constant show that in 0.1 *M* imidazole, the iron is almost entirely in the form $FePc(Imid)_2$.] Plots of ln $[(A_\infty - A_0)/(A_\infty - A_t)]$ *vs.* *t*, using absorb-

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[5] N. B. Chapman, *et al.*, *J. Chem. Soc.*, *B*, 631 (1968).

[6] H. L. Schläfer and W. Schäffernicht, *Angew. Chem.*, **72**, 618 (1960).

[7] E. G. Meloni, L. R. Ocone, and B. P. Block, *Inorg. Chem.*, **6**, 424 (1967).

[8] A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

[9] M. Whalley, *ibid.*, 866 (1961).

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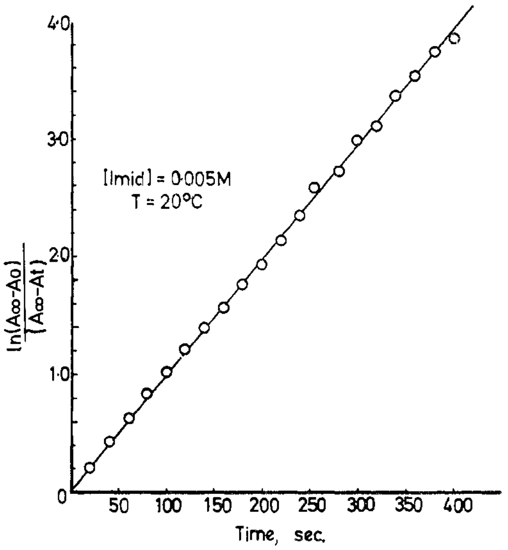


Figure 3.—Rate plot for the reaction of FePc with imidazole in DMSO.

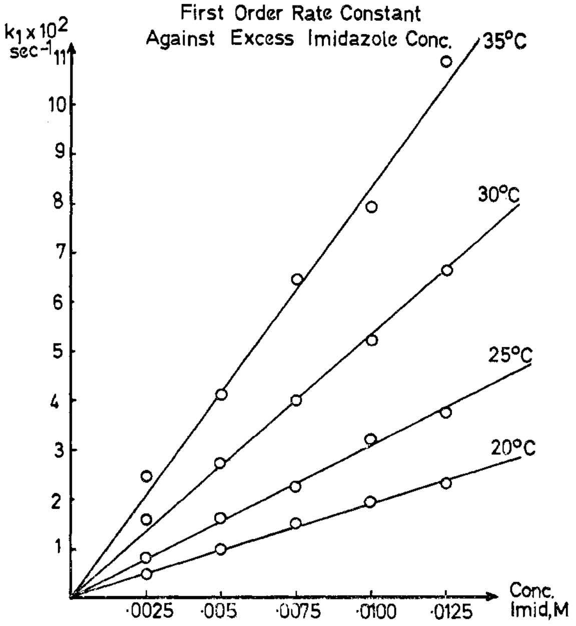


Figure 4.—Dependence of observed rate constant on imidazole concentration.

ance values at 662 nm, λ_{max} for $FePc(Imid)_2$, proved to be straight lines passing through the origin (least-mean-squares lines, Figure 3). From this it is concluded that the rate of production of $FePc(Imid)_2$ is first order with respect to ferrous phthalocyanine concentration. If the first-order rate constants are now plotted against the imidazole concentration used, straight lines passing through the origin result (Figure 4) showing that the rate is first order with respect to imidazole concentration.

An Arrhenius plot (Figure 5) gives $E_a = 17.9 \pm 0.5$ kcal/mol and $\log A = 13.6 \pm 0.5$, *i.e.*, activation parameters at 25° of $\Delta H^{\ddagger} = 17.3$ kcal/mole and $\Delta S^{\ddagger} = +1.8$ eu. Our observations are then completely described by

$$d[FePc(Imid)_2]/dt = 4.17 \times 10^{13} e^{-17,900/RT}[FePc][Imid] \quad M^{-1}\,sec^{-1} \qquad (1)$$

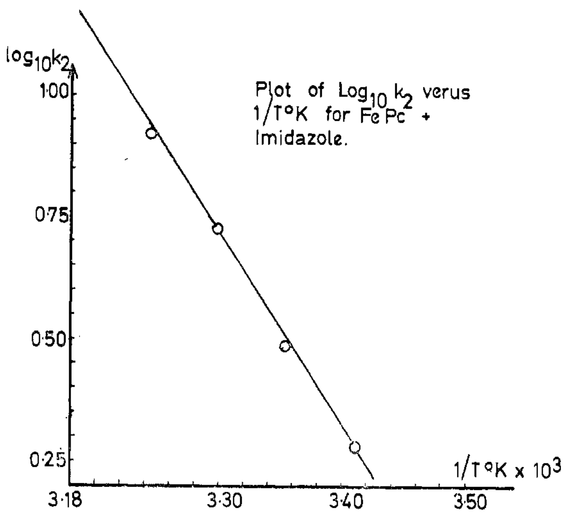


Figure 5.—Arrhenius plot, log k_2 *vs.* $1/T$°K for FePc + imidazole in DMSO.

Discussion

Dale[12] has measured the equilibria involved in addition of imidazole to ferrous phthalocyanine in DMSO and concluded that two stages were involved. Since we have found ferrous phthalocyanine to be diamagnetic in DMSO solution, it is reasonable to assume that the iron is octahedrally coordinated and so the equilibria can be represented by

$$FePc(DMSO)_2 + 2Imid \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FePc(DMSO)(Imid) + DMSO + Imid \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FePc(Imid)_2 + 2DMSO \qquad (2)$$

where $K_1 \simeq 3.5 \times 10^3\ M^{-1}$ and $K_2 \simeq 6.3 \times 10^3\ M^{-1}$.

Dale could not isolate the intermediate species, FePc-(DMSO)(Imid), and we shall assume that it has the role of a transient intermediate in the formation of $FePc(Imid)_2$. Then application of the steady-state approximation and of the assumption that the first step is rate controlling ($k_2[Imid] \gg k_{-1}$), leads to the rate expression

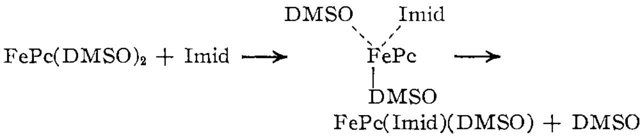
$$d[FePc(Imid)_2]/dt = k_1[Imid][FePc] - \frac{k_{-1}}{K_2}\frac{[FePc(Imid)_2]}{[Imid]} \qquad (3)$$

As $[Imid] \gg [FePc(Imid)_2]$ and as K_2 is large, we are probably justified in neglecting the second term in eq 3, which then reduces to a rate expression of the form observed. Thus we have measured the rate of the first step only; the entrance of one imidazole molecule *trans* to a DMSO ligand very much enhances the rate of replacement of that second ligand.

In replacement reactions involving ionic species, a mechanism involving prior ion-pair formation[1] has been put forward to account for kinetics of the form we have observed; both our species are neutral, and so this type of mechanism seems unlikely in our case. This

(12) B. W. Dale, Ph.D. Thesis, Oxford University, 1966.

leaves two likely alternatives for the first-step: alternative 1



which is a simple associative or SN2 mechanism, with a seven-coordinate transition state, and alternative 2

$$\mathrm{Fe(DMSO)_2} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \mathrm{Fe(DMSO)} + \mathrm{DMSO}$$

$$\mathrm{Fe(DMSO)} + \mathrm{Imid} \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} \mathrm{Fe(DMSO)(Imid)}$$

To explain the observed kinetics on the basis of this mechanism, $k_{-1}'[\mathrm{DMSO}] \gg k_2'[\mathrm{Imid}]$, and the observed second-order rate constant is $k_1 = k_2'k_1'/k_{-1}'\cdot[\mathrm{DMSO}]$. This mechanism involves the rapid, reversible formation of a five-coordinate intermediate, which may or may not distinguish between various nucleophiles.

We are currently trying to distinguish between the two mechanisms by increasing the imidazole concentration and using stopped-flow techniques. If the second mechanism applies, then at some state the condition $k_{-1}'[\mathrm{DMSO}] \gg k_2'[\mathrm{Imid}]$ may not apply, and the observed rate will become constant and equal to the rate of formation of the five-coordinate intermediate.

A comparison will now be made of our results with others relevant. First of all, ours are not quite like any yet observed for low-spin ferrous complexes. That of ferroins with hydroxide ion has a kinetic law of the form[2d]

$$\frac{-\mathrm{d}[\mathrm{ferroin}]}{\mathrm{d}t} = k_1[\mathrm{ferroin}] + k_2[\mathrm{ferroin}][\mathrm{OH}^-]$$

This is not the same as ours, though it is true that k_2 dominates the rate expression. Also, the starting material is diamagnetic and the products are paramagnetic, so that a spin change is involved, which is not the case with our reaction. The attack of cyanide on ferroin also follows a more complex rate law,[2c] though the second-order rate process dominates and there is no spin change, and the form of the rate law shows that

$$\mathrm{Fe(\mathit{o}\text{-}phen)_3^{2+}} + 2\mathrm{CN^-} \longrightarrow \mathrm{Fe(\mathit{o}\text{-}phen)_2(CN)_2}$$

$$\frac{-\mathrm{d}[\mathrm{Fe(\mathit{o}\text{-}phen)_3^{2+}}]}{\mathrm{d}t} = k_1[\mathrm{Fe(\mathit{o}\text{-}phen)_3^{2+}}] + k_2[\mathrm{CN^-}][\mathrm{Fe(\mathit{o}\text{-}phen)_3^{2+}}]$$

the attack of the first cyanide must be rate determining. However, because of steric considerations a *cis* product is almost certainly formed and so the geometry differs from that of our case.

Some parallel can be drawn with recent results of Fleischer[13] on axial ligand replacement in ferric and cobaltic hematoporphyrins, which have a similar equatorial macrocyclic ligand. In his cases a *trans* geometry is maintained, a second-order rate process applies, an oxygen donor is replaced by a nitrogen donor, and the entrance of the first nitrogen donor has a powerful accelerating effect on the entry of the second; also there is presumably no change in spin state. In the case of cyanide and thiocyanate replacing water at a cobalt center, Fleischer was able to show that a limiting SN1 process (our alternative 2) applied, but he was not able to do so in the case of ferric hematoporphyrin. He also compared his results with those of Alberty on aquocobalamin[14] and concluded that an imidazole nucleus could have a labilizing effect on water bound *trans* to it at a Co(III) center. Our results illustrate labilization by imidazole bound *trans* to an outgoing oxygen ligand at a low-spin d^6 center in a direct manner.

We are continuing work on this versatile ferrous system and related ones.

Acknowledgment.—This research was supported by Science Research Council Grant B/SR/4432. M. V. T. was supported by a Science Research Council studentship.

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