$N_2P(n\text{-}C_4H_9)_3$, 40620-73-3; $Fe_2(CO)_5C_{12}H_8N_2P(C_6H_5)_3$, 40583-29-7; $Fe_2(CO)_5C_{12}H_8N_2P(C_2H_5)(C_6H_5)_2$, 40583-30-0; $Fe_2(CO)_4C_{12}H_8N_2[P(n\text{-}C_4H_9)_3]_2$, 40583-31-1; $Fe_2(CO)_4C_{12}H_8N_2[PH(C_6H_5)_2]_2$, 40583-32-2; $Fe_2(CO)_4C_{12}H_8N_2[P(C_6H_5)_3]_2$, 40620-74-4; $Fe_2(CO)_4C_{12}H_8N_2[P(OCH_3)_3]_2$, 40583-33-3; $Fe_2(CO)_4C_{12}H_8N_2[CNC_6H_{11}]_2$, 40583-34-4; $Fe_2(CO)_6(C_{12}H_8N_2)$, 40583-35-5; $P(OPh)_3$, 101-02-0; $P(Ph)_3$, 603-35-0; $P(OMe)_3$, 121-45-9.

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Equilibria of Imidazole with Iron(III) Tetraphenylporphine

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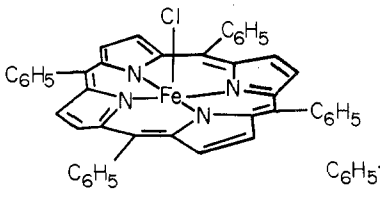
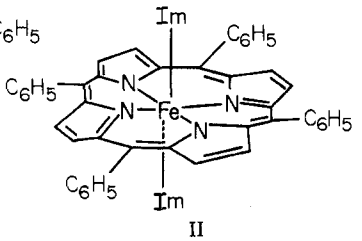
The equilibrium of imidazole with chlorotetraphenylporphinatoiron(III) has been investigated in nonpolar media. The reaction is shown to proceed by the displacement of the chloride ion by two imidazoles to give tetraphenylporphinatobis(imidazole)iron(III) chloride as a tightly bound ion pair. No evidence could be found for an intermediate six-coordinate monochloromonoimidazole complex or for an intermediate five-coordinate monoimidazole complex. The spin of the iron(III) is seen to decrease from $S = 5/2$ to $S = 1/2$ during the reaction and the absence of intermediate complexes is attributed to the high stability of the low-spin product. In all solvent studies, isosbestic points were observed indicating that only two different absorbing species are present; however, in some solvents, computed equilibrium constants showed strong dependences on imidazole concentration. In aromatic solvents computed equilibrium constants become larger with increasing solvent dielectric constant and they also depend more and more strongly on imidazole concentration. The consequences of these effects are considered.

Introduction

Iron porphyrin coordination compounds are essential constituents of a number of important biological systems including hemoglobin, the cytochromes, and the peroxidase enzymes. Many bioinorganic problems remain to be solved in these systems. Of the structural changes which may occur in the region of the iron, there is particular interest in the motion of the iron into the plane of the porphyrin as its spin state changes from high to low during a reaction. In the simplest of the iron(III) porphines, this situation is exemplified by the structures FeTPPCl,[3] I, and $FeTPPIm_2Cl$, II.[4,5] In FeTPPCl, the iron is in a high-spin, square-pyr-



I



II

amidal state about 0.3 Å above the porphine nitrogens[4] while in $FeTPPIm_2Cl$ the iron is low spin and is in an elongated tetragonal environment.[5]

(1) National Science Foundation Undergraduate Research Participant, Summer 1972.

(2) Abstracted, in part, from work performed in the partial fulfillment of the City University of New York B.A. degree.

(3) Abbreviations: TPP, tetraphenylporphine dianion; Im, imidazole; FeTPPCl, chlorotetraphenylporphinatoiron(III); $FeTPPIm_2Cl$, tetraphenylporphinatobis(imidazole)iron(III) chloride.

(4) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, 89, 1992 (1967).

(5) R. Countryman, D. M. Collins, J. L. Hoard, *J. Amer. Chem. Soc.*, 91, 5166 (1969); 94, 2066 (1972).

Spin change and the dropping of the iron into the porphine plane occur in the binding of oxygen by hemoglobin and in cytochrome reactions. As part of a program to elucidate the features of macrocyclic complexes which may influence the reactivity of their metal ions, we have been investigating the factors governing the equilibria of FeTPPCl with Im to give $FeTPPIm_2Cl$. The original work in this area is that of Davies[6] and of Cowgill and Clark.[7] These workers examined equilibria in aqueous systems of natural porphyrins; however, the presence of μ-oxo-bisiron(III) species[8] and other complexities have made it difficult to interpret their results. The work reported herein was done entirely in nonaqueous media to simplify the equilibria.

Experimental Section

Materials. $TPPH_2$ and FeTPPCl were prepared by methods developed by Adler.[9,10] The FeTPPCl was purified by converting it to μ-oxo-bis(tetraphenylporphinatoiron(III)) which was chromatographed on alumina. When samples of FeTPPCl were required, a few milligrams of the μ-oxo compound was dissolved in 100 ml of methylene chloride and a stream of dry HCl was passed through for 30 sec. After the solvent was removed, the chloro complex was dried and used within a few days.

Tetraphenylporphinatobis(imidazole)iron(III) chloride was prepared as follows. A 300-mg sample of imidazole and 60 mg of FeTPPCl were dissolved in 1000 ml of benzene. The absorption spectrum showed about a 50% conversion to $FeTPPClIm_2$. The solution was left at room temperature in the dark for several days during which lustrous purple needles formed. *Anal.* Calcd for $C_{50}H_{36}N_8FeCl\cdot 2H_2O$: C, 69.0; H, 4.56; N, 12.9; Cl, 4.05. Found: C, 69.76; H, 4.51; N, 12.58; Cl, 3.82.

Other reagents were of the highest purity readily obtainable. Solvents were stored over molecular sieves and distilled just prior to use.

Measurements. Absorption spectra were obtained with a Cary 14

(6) T. H. Davies, *J. Biol. Chem.*, 135, 597 (1940).

(7) R. W. Cowgill and W. M. Clark, *J. Biol. Chem.*, 198, 33 (1952).

(8) I. A. Cohen, *J. Amer. Chem. Soc.*, 91, 1980 (1969).

(9) A. D. Adler *et al.*, *J. Org. Chem.*, 32, 476 (1967).

(10) A. D. Adler *et al.*, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970).

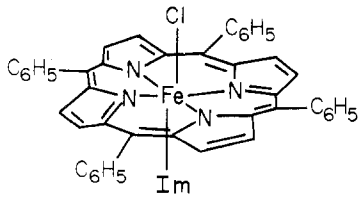
using matched cuvettes of path lengths from 0.1 to 10 cm. The cuvette holders were thermostated at 30.0 ± 0.1°.

Magnetic moment measurements were performed by the Evans method.[11] A solution of 1% hexamethyldisiloxane (HMDS) in methylene chloride was used as solvent for the metalloporphine. The chemical shift of the HMDS in this solution was compared to that of HMDS in a 1% methylene chloride solution contained in a capillary. In this part of the work the probe temperature was maintained at 30 ± 1°.

Calculations. The calculations were done by first measuring extinction coefficients at several wavelengths for both the bis-imidazole and the chloride complexes and then calculating equilibrium constants at each of the several wavelengths from spectra showing absorptions due to both species. In some of the solvents, the imidazole concentration could not be made high enough for 100% complex formation due to solubility restriction. Extinction coefficients for the bis-imidazole complex were arrived at by least squares in which the equilibrium coefficients at several wavelengths were varied to give most nearly identical equilibrium coefficients at the several wavelengths. This procedure was performed only after isosbestic points were confirmed in the system and it resulted only in small (less than 10%) changes in the constants.

Results

In methylene chloride solution, the addition of imidazole to solutions of FeTPPCl results in spectral changes summarized in Figure 1. Isosbestic points at 533 and 480 nm show that the equilibrium involves but two absorbing species, if we may exclude for the moment the unlikely possibility that there are two or more species with identical absorption spectra. The most likely interpretation is that one imidazole is binding the square-pyramidal FeTPPCl to form the octahedral FeTPPImCl, III.



III

Such a reaction could be expressed by the equilibrium constant β_{11}. When β_{11}'s are computed from the spectra as

$$\beta_{11} = [\text{FeTPPImCl}]/[\text{FeTPPCl}][\text{Im}]$$

discussed in the Experimental Section, it is found that the calculated values became greater with increasing imidazole concentration, indicating a higher order dependence on imidazole concentration. When, however, the data are interpreted by equilibrium 1, using the constant β_{21}, β_{21} is

$$2\text{Im} + \text{FeTPPCl} \rightleftharpoons \text{FeIm}_2\text{TPP}^+\text{Cl}^- \quad (1)$$

$$\beta_{21} = [\text{FeTPPIm}_2\text{Cl}]/[\text{FeTPPCl}][\text{Im}]^2$$

found to be invariant with imidazole concentration. FeTPPCl concentration was varied over a factor of 100 by varying the path length of the cell and this resulted in no significant difference in the value of β_{21}. Thus, the equilibrium constant shows that we are observing reaction 1 yielding a tightly bound ion pair, one which does not dissociate under any of the conditions we have studied. Nmr data discussed below confirm the formulation of the product as a 2:1 complex. The isosbestic points in Figure 1 were observed at all concentrations studied and this indicates that no detectable concentrations of FeTPPImCl, III, are ever achieved.

The experimental value of β_{21} is 4.8×10^5. If we assume that a 5% formation of FeTPPImCl would be detectable, then β_{11} is probably less than 1.0×10^2. Considering hypothetical constants K_1 and K_2 for the stepwise addition of the

(11) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

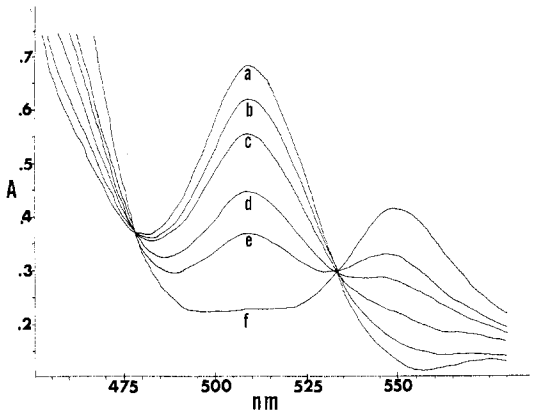


Figure 1. The absorption spectrum of 1.64×10^{-4} *M* FeTPPCl in the presence of varying amounts of imidazole: a, no imidazole; b, 6.02×10^{-4} *M* imidazole; c, 1.08×10^{-3} *M*; d, 1.57×10^{-3} *M*; e, 2.24×10^{-3} *M*; f, 6.72×10^{-3} *M*.

two imidazoles, K_1 is less than 1.0×10^2 while K_2 is greater than 4.8×10^3. Normally, stepwise constants decrease as ligands are added. Rationalization of the magnitude of K_2 with respect to K_1 is best made by hypothesizing that FeTPPImCl is high spin, as is FeTPPCl, while $\text{FeTPPIm}_2\text{Cl}$ is low spin.[12] The low-spin Fe(III) is smaller than the high-spin Fe(III) and binds the ligands more tightly than the larger high-spin Fe(III). The influence of spin change on equilibrium constants has been well-documented in simpler complexes.[13] Proof that spin change is occurring in our system comes from magnetic moment measurements.

Magnetic titrations were performed by the addition of imidazole to FeTPPCl. The chemical shift was measured between a 1% hexamethyldisiloxane (HMDS) solution in an internal capillary and 1% HMDS solutions of FeTPPCl containing varying amounts of imidazole. This shift is directly related to the bulk paramagnetism of the solution.[11] At the high concentrations of FeTPPCl necessary to produce reliable shifts, the formation of product is sufficiently favored that essentially each imidazole binds an iron until no more available iron remains. At 10^{-2} *M* FeTPPCl the shifts decrease linearly with added imidazole until the 2:1 ratio is reached and is constant thereafter. This provides further evidence for the stoichiometry in reaction 1. The shift in the absence of added imidazole is taken as 5.9 BM as is expected for a high-spin d^5 system, which can have neither orbital nor spin-orbit contributions to its observed magnetism. If this is done, the shift of the 2:1 complex is then found to be about 1.8 BM. This is adequately within experimental error of the low-spin value.

Other solvents were also studied. In some of them more complicated equilibria were observed. Data for three aromatic solvents—benzene, bromobenzene, and *o*-dichlorobenzene—appear in Figure 2. For each concentration of imidazole, β_{21}'s were computed and this was done in cells of varying path length so that the FeTPPCl concentration could be varied substantially. Once again, isosbestic points were observed in all cases and the equilibrium constants computed did not depend on total porphine concentration at a given imidazole concentration. A strong dependence of β_{21} on total imidazole concentration is, however, apparent.

Mixed-solvent systems were studied in order to determine the influence of a gradual change in solvent. Figure 3 sum-

(12) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, 6, 1729 (1967).

(13) See, for example, H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

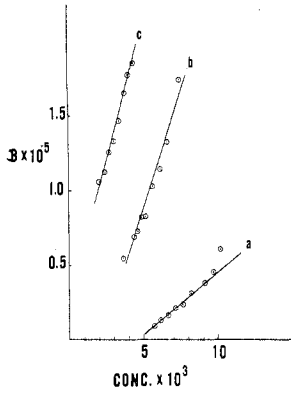


Figure 2. The dependence of calculated equilibrium constant, β_{21}, on imidazole concentration in three aromatic solvents: c, *o*-dichlorobenzene; b, bromobenzene; a, benzene.

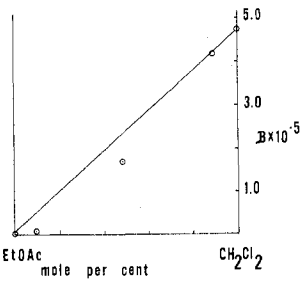


Figure 3. The dependence of calculated equilibrium constant, β_{21}, on solvent mole fraction for the binary solution ethyl acetate–methylene chloride.

marizes data for the ethyl acetate–methylene chloride system. In ethyl acetate, β_{21}'s show a strong positive dependence on imidazole concentration and so β_{21} in the figure is the interpolated value of β_{21} at equal concentrations of FeTPPCl and $FeTPPIm_2Cl$. The dependence of β_{21} on mole fraction is highly nonideal.

Discussion

Several points merit further consideration. Of initial concern is the absence of any evidence for a complex with one imidazole like FeTPPImCl. The reason FeTPPImCl is not observed is that $FeTPPIm_2Cl$ is far more stable. The reason for this is that the iron(III) in $FeTPPIm_2Cl$ is low spin while we postulate that in FeTPPImCl it is high spin as it is in FeTPPCl. Two factors may contribute to the relative stability of $FeTPPIm_2Cl$ over FeTPPImCl. First, low-spin ions should generally bind ligands better than high-spin ions because in the low-spin case there are fewer e_g electrons, which are antibonding.[12] Second, the low-spin form is smaller than the high-spin and may drop into the porphine plane so that its orbitals may better overlap with those of the porphine ring, forming stronger bonds. Thus, two factors enhance K_2 over K_1—both the change of structure and the change of spin. In hemoglobin, a spin change accompanies complexation by oxygen as high-spin iron(II) becomes diamagnetic. One author has referred to the high-spin iron(II) as being in a "poised" state. The equilibria we have studied show this to be the case for, in our system, spin change and the dropping of the iron into the porphine plane result in a considerable release of energy. Presumably, in living systems, this energy could be used directly in a subsequent reaction or used to make a conformation change in the protein.

Recently, an nmr study has been reported in which some of the data indicate the presence of substantial amounts of a third porphine species in the $FeTPPCl$–$FeTPPIm_2Cl$ system.[14]

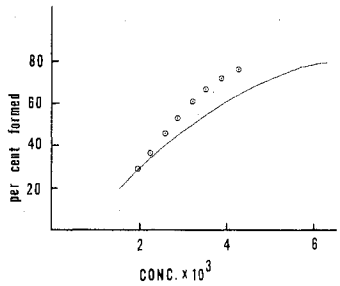


Figure 4. Per cent formation of $Im_2FeTPPCl$ *vs.* imidazole concentration in *o*-dichlorobenzene solution: circles, observed; solid line, hypothetical formation curve calculated using the observed β_{21} for 1.9×10^{-3} *M* imidazole.

The authors have tentatively suggested that this might be FeTPPImCl. In our work, the magnitude of β_{21} and the absence of detectable amounts of a third species at porphine concentrations down to 10^{-6} *M* argue against this species as a detectable component of this system at equilibrium although it is certainly possible that appreciable quantities could be present in nonequilibrium situations for kinetic reasons.

Another point of interest is the enhancement of imidazole binding constant for higher concentration of imidazole in aromatic solvents. In Figure 4, the effect is demonstrated for orthodichlorobenzene solvent. The solid line represents the per cent formation of hypothetical bis-imidazole complex using only the β_{21} observed for 2×10^{-3} *M* imidazole (30% complex formed). The experimental points show that the formation of the bis-imidazole complex is so much more efficient than that predicted by such a constant that 80% formation is achieved with about half the imidazole concentration that would be expected.

The generally higher values of β_{21} as the polarity of the solvent increases can be rationalized by hypothesizing that the ion-pair product of the reaction is more polar than the neutral reactants. The product will then be better solvated by the more polar solvents and β_{21} will increase with polarity. The interesting feature in Figure 2 is the increase of β_{21} with increasing imidazole concentration. In the benzene case, this could be the result of increasing net polarity of the solvent because of the increasing concentrations of the more polar imidazole solute. Bromobenzene and *o*-dichlorobenzene are more polar than imidazole and yet the increase of β_{21} with increasing imidazole is stronger still. Thus, changes in the net polarity of the solvent are insufficient to explain the data. Dissociation of the ion pairs likewise will not explain the increase of β_{21} with imidazole concentration. If one computes β_{21} from eq 1 but for a system where the ion pair dissociates as in (2), the computed β_{21}'s would de-

$$FeTPPCl + 2Im \rightleftharpoons FeTPPIm_2^+ + Cl^- \quad (2)$$

crease with increasing imidazole concentration. Furthermore, in the still more polar solvent acetone, β_{21} was found to be 6.6×10^5 and was independent of imidazole concentration, showing no tendency of the ion pair to dissociate in that relatively polar solvent. These data indicate that enhanced formation is probably not due to bulk dielectric constant effects. Both the solvent and the imidazole are, however, involved in the explanation of this phenomenon, as is shown by the absence of such effects in solvents like methylene chloride and acetone in contrast to the strong dependence on imidazole concentration in the aromatic sol-

(14) G. N. La Mar and F. A. Walker, *J. Amer. Chem. Soc.*, 94, 8607 (1972).

vents. Both imidazole and porphyrins are known to form aggregates of a donor-acceptor type in solution[15,16] and so the reason for the dependence of β_{21} on imidazole may be the interaction of $FeTPPIm_2Cl$ with additional imidazole. This and other possibilities are currently under consideration in our laboratory. In any event, the effect has a striking consequence in benzene. At 8.0×10^{-5} *M* in FeTPPCl, the imidazole concentration may be varied from 0.5×10^{-3} to 3×10^{-3} *M* to give spectra with isosbestic points and complete formation of the bis-imidazole complex. Solutions about 1.5×10^{-3} *M* in imidazole deposit lustrous blue crystals over several days time to become nearly clear. The crystals are the bis-imidazole complex and they may be redissolved by raising the imidazole concentration of the mother liquor to about 3.0×10^{-3} *M*, indicating the strong solvating effect of higher concentrations of the heterocycle.

(15) E. Fischer, *Ber. Bunsenges. Phys. Chem.*, **23**, 1007 (1969).
(16) D. Manzeral, *Biochemistry*, 4, 1801 (1965).

The last point of discussion is the complete absence of any detectable polymerization of FeTPPCl in any of the solvents studied. All work was carried out at several concentrations of FeTPPCl and no dependence of β_{21} on FeTPPCl could be observed. Polymerization of this porphine evidently is not a problem, possibly because of the steric requirements of the phenyl groups, which are tilted about 80° out of the porphine plane.[3-5]

Registry No. $FeTPPIm_2Cl$, 25442-52-8; FeTPPCl, 16456-81-8; imidazole, 288-32-4.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also wish to thank the National Science Foundation for partial support through Grant GY-9888. We also wish to thank Dr. Alan Adler for many helpful discussions and for a gift of very pure FeTPPCl.

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Conformational Studies of Metal Chelates. II. Stereochemistry and Conformational Analysis of the Cobalt(III) Complexes of 4,7-Diaza-5(*R*)-methyl-1,10-decanediamine

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The optically active ligand 4,7-diaza-5(*R*)-methyl-1,10-decanediamine (3.2'.3.) was prepared from previously resolved (*R*)-1,2-propanediamine. The cobalt(III) complexes *trans*-[Co(*R*-3.2'.3.)Cl_2]$^+$ and *cis*-[Co(*R*-3.2'.3.)ox]$^+$ were prepared and characterized. The methods of semiempirical conformational analysis were applied to the possible isomers of these complexes to support the structural assignments. Both conformational enthalpies and entropies were calculated using the minimization scheme of Boyd. From among the six possible trans conformers, the calculations show that the complex having the structure *trans*-(*SS*)-[Co(*R*-3.2'.3.)$\gamma\lambda\gamma Cl_2$]$^+$ is greatly favored and this structure has been assigned to the trans isomer isolated. This isomer can be converted into a cis isomer that must be either Λ-β-*cis*-(*SS*)-[Co(*R*-3.2'.3.)ox]$^+$ or Δ-α-*cis*-(*SS*)-[Co(*R*-3.2'.3)ox]$^{2+}$ if the reaction is conducted in acidic media without inversion of secondary nitrogen atoms. Based on the circular dichroism spectrum of the cis compound, it has the Λ chirality; it is Λ-β-cis-*SS*. The results of the conformational calculations support this assignment, indicating that the α-cis isomer is less stable by almost 3 kcal/mol.

Introduction

Transition metal complexes[1] of linear tetradentate ligands provide an interesting and fruitful area for observing and studying the subtle interrelations of structure, stereochemistry, and stereospecificity. Since the early work of Sargeson and coworkers[2] with triethylenetetramine, investigations have expanded in a number of directions: (a) the synthesis of linear tetradentate ligands with other donor atoms besides nitrogen (*e.g.*, N_2S_2, N_2O_2, S_4, As_2S_2, P_2S_2);[3-5] (b) the synthesis of optically active methyl-substituted triethylenetetramines;[6-9] (c) the synthesis of tetramines with different sizes of chelate rings.[10,11]

Assignment of detailed structures to conformational isomers in these systems has been achieved with difficulty, and in some cases ambiguities remain. One of the most promising tools for the assignment of conformational isomers in transition metal complexes is modern conformational analysis. The availability of large computers and efficient minimization schemes has made these semiempirical calculations feasible for systems with a large number of atoms. Calculations of the relative strain energies for different conformers

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