III, a comparison of the peaks in A at 19 K and B at 50 K (where the maximum resolution was obtained) reveal that the $d \rightarrow d$ transitions observed in the region 18 500–20 600 cm^{-1} have occurred at higher energies for A than for B. This is in agreement with the charges obtained by ESCA studies. The depletion of charge on sulfur atoms in B causes relatively less ligand field strength. In conclusion, it has become clear by now that the cation influences the charge distribution on the complex anion in B due to its proximity to the π-cloud, whereas this is not possible for the complex A.

This effect of cation on the electronic structure of the complex anion will lead to interesting observations as the system is cooled. At low temperature the thermal motions are restricted, and hence a modification of structure would occur depending upon the resultant molecular structure at that temperature. The electronic spectral studies suggested a distortion in the plane of the complex ion in B below 50 K due to a dihedral angle between the planes of the two ligands attached to the metal.[13] The splitting of EPR lines at 50 and 20 K indicate the formation of two and three magnetically distinct sites, respectively. This is possibly due to the phase transitions of the crystal lattice at these temperatures probably from triclinic (300 K) → monoclinic (50 K) → hexagonal (20 K). The feasibility of this may be found by a closer look into the unit cell dimensions of this crystal at room temperature[23] (a = 12.36 Å, b = 11.138 Å, c = 9.83 Å, α = 118.4°, β = 92.05°, γ = 91.91°). Since the angles β and γ are close to 90°, on cooling, the system can easily transform into a monoclinic cell by grouping four triclinic unit cells. The same logic may be extended to the transformation of a hexagonal cell also since α is close to 120°. However, this requires a large change in the axes b and c. These phase transition may be accompanied by a small distortion in the molecule. A comparison of the Raman spectrum at 300 K with that at 30 K reveals the peaks at 130, 182, and 505 cm^{-1} due to π(ring), δ(C–CN), and δ(C–CN) + ring deformation[25] split into two each on cooling. In addition, an overall increase in the intensity of the bands was observed. This indicates a transformation of the molecule from a centrosymmetric geometry to a noncentrosymmetric geometry. The splitting of lines at 30 K probably indicates two molecular sites. The lines below 100 cm^{-1} are usually due to lattice vibrations, which in this case show a considerable change between the spectra at 30 and 300 K. The increased resolution and the shift of the peaks to low-energy region support the idea of a lattice transformation. A consideration of the monoclinic lattice by grouping four triclinic unit cells would lead to different symmetry properties of the lattice. A minimum of C_2 symmetry exists in the lattice by which the lattice vibrations may be classified under two irreducible representations A and B; hence, considerable shift in their energies may occur. The splitting of the overlapping band structure centerd at 25 cm^{-1} at 30 K can thus be understood as due to a lattice transformation. A detailed investigation into these phase transitions is underway.

Conclusions

A systematic study of photoelectron spectroscopy with the knowledge of interatomic distances enables us to determine the charge distribution in molecules. A general equation for this purpose has been developed. This would also allow one to determine the inter- and intramolecular effects as exemplified by the fact that these studies lend support to the phase transitions observed by other techniques such as infrared, EPR, and Raman spectroscopy. A detailed study on the phase transitions of $[n\text{-}Bu_4]_2[Ni(mnt)_2]$ by a crystal structure determination and EPR studies at low temperatures will reveal the exact geometry and lattice structure of the molecule.

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Hydrolysis of a Metal-Coordinated Imine by a Proton-Containing Transition State

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Kinetic studies of the rate of disappearance of $Fe(TIM)(H_2O)_2^{2+}$ are reported. The rate law is first order in the Fe(II) complex, first order in H^+, and independent of the concentration of $Fe(H_2O)_6^{2+}$, with a second-order rate constant of 0.178 ± 0.005 M^{-1} s^{-1} at 25 °C and an ionic strength of 0.5 M. Activation parameters for the reaction were determined to be $\Delta H^* = 49.3 \pm 0.9$ kJ/mol and $\Delta S^* = -94 \pm 3$ J/(mol deg). The presence of CO or CH_3CN in the coordination shell of Fe(II) retards the reaction. This feature allows a determination of the equilibrium constant for the loss of CH_3CN from $Fe(TIM)(CH_3CN)(H_2O)^{2+}$: The value is found to be $(2.5 \pm 0.5) \times 10^{-3}$. Spectral measurements indicate that $Fe(TIM)(H_2O)_2^{2+}$ has the same electronic structure as the other iron–TIM complexes and hence is diamagnetic. The mechanism of the reaction is suggested to involve a displacement of the iron ion from the plane of the macrocyclic ring, promoted by a spin change, followed by hydrolysis of the free ligand.

In an earlier paper on the kinetics and equilibria involved in reactions of $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)(CH_3CN)(H_2O)^{2+}$ (where TIM is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) in aqueous CH_3CN solution, it was reported that solutions of the iron complex were unstable in the presence of vanadous ion.[1] Our attempt to explain this curious observation led to further investigation, which is the subject of this report. Herein we show that the mechanism of the reaction is substitution of the diaquo form of the complex ion in the ferrous oxidation state followed by hydrolysis of the imine ligand. The only need for a reducing agent is to ensure the iron ions remain dipositive. The transition state contains the complex ion and a proton. This rate law is unusual if one considers that the complex has no lone pair of electrons available for interaction with the proton. We postulate that an important step of this substitution process involves a spin change of the Fe(II) ion as it moves out of the plane of the ligand, facilitated by the association of the proton with the incipient imine lone pair. A process involving the movement of an iron ion out of the plane of a macrocyclic ligand with attendant spin change was suggested to be important in substitutions in porphyrin chemistry several

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(1) Butler, A.; Linck, R. G. *Inorg. Chem.* **1984**, *23*, 2227-2231.

years ago by Hoard and co-workers.[2]

Experimental Section

Reagents. $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ was prepared and purified as previously reported.[1] Solutions of $VO(ClO_4)_2$ were prepared by ion-exchange replacement of sulfate from commercial samples of vanadyl sulfate and were analyzed as described earlier.[3] Reduction of the vanadyl ion to vanadous was achieved with amalgamated zinc in perchloric acid. Lithium ion solutions were prepared by reaction of perchloric acid with Li_2CO_3 and were analyzed for total anion by ion-exchange techniques. All reactions were carried out under an atmosphere of N_2 or Ar in a medium 0.5 M in ionic strength.

Procedures. Spectroscopic determinations were performed on a Cary Models 14 and 15 recording spectrophotometers or on a Hewlett-Packard diode array spectrometer, Model 8452A. The NMR experiments were conducted on an IBM WP-100SY spectrometer. To carry out the reaction, a solution was made of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in appropriate ionic medium; at these low values of $[CH_3CN]$, oxidation of the iron to the Fe(III) complex quickly took place. Solutions of the Fe(III) complex stored at 0 °C were reasonably stable for several days under these conditions. Kinetic runs were performed by mixing the Fe(III) complex and appropriate amounts of acid; the samples were deoxygenated with a stream of N_2 or Ar and thermostated, and reaction was initiated by injecting a solution of V^{2+} into the sample. For experiments in which the $[CH_3CN]$ was varied, a separate injection of deoxygenated CH_3CN was added to the deoxygenated sample in order to avoid losses of CH_3CN by vaporization. All kinetic data were analyzed by a nonlinear-least-squares program. In addition to the rate constant, the value of the absorbance at "zero" time was obtained. From this value we calculated the extinction coefficient of $Fe(TIM)(H_2O)_2^{2+}$ at 650 nm as $(4.3 \pm 0.6) \times 10^3$ M^{-1} cm^{-1}, a value in reasonable agreement with that obtained from diode array spectroscopy.

Results

It was earlier found that $Fe(TIM)(CH_3CN)_2^{2+}$ is very sensitive to O_2 whenever the $[CH_3CN]$ is lowered below about 0.5 M.[1,4] Therefore, to obtain reproducible results in the determination of equilibrium constants, V^{2+} was used to react with any adventitious oxygen. This led to a slow decrease in absorptivity, which was counteracted by extrapolating the absorbance to zero time; but the nature of the decrease in absorbance was unknown. Our first experiments designed to study this process showed (1) that the solution of $Fe(TIM)(X)Y^{2+}$[5] in the presence of V^{2+} was essentially colorless after reaction was complete when corrected for the absorbance of V^{2+} and V(III) and (2) that V^{2+} was not involved in the transition state. To verify that V^{2+} was not involved kinetically or stoichiometrically, we prepared a solution of $Fe(TIM)(CH_3CN)_2^{2+}$ in deoxygenated methanol,[6] added it to a solution of deoxygenated acid, and followed the decay of the typical $Fe(TIM)(H_2O)_2^{2+}$[7] absorbance at 650 nm. This decay follows a first-order dependence on $[Fe(TIM)(H_2O)_2^{2+}]$ with a pseudo-first-order rate constant of 0.83 s^{-1} at $[H^+] = 0.47$ M and 25 °C. The progress of the reaction was identical with that found when V^{2+} was used to reduce the complex and scavenge any adventitious oxygen: $k = 0.85$ s^{-1} at $[H^+] = 0.49$ and 25 °C.[8] However, in view of the difficulty in quantitatively handling methanolic solutions of the Fe(II) complex that are low in $[CH_3CN]$, we carried out experiments with the corresponding Fe(III) complex as a source of iron and continued to use V^{2+} as a reductant to initiate the reaction, even though the V^{2+} was not involved kinetically or stoichiometrically once the Fe(II) was produced in the reaction. In order to test if ferrous ion is released from the complex prior to the transition state, several experiments were also performed with a large initial concentration of $Fe(H_2O)_6^{2+}$. Over a range of $[Fe(H_2O)_6^{2+}]$ of $(0.36–1.11) \times 10^{-2}$ M and an acidity range of 0.096–0.299M, the rate constants obtained were within experimental error of those found in the absence of ferrous ion. See Figure 1. Hence the rate law does not depend on $[Fe(H_2O)_6^{2+}]$.

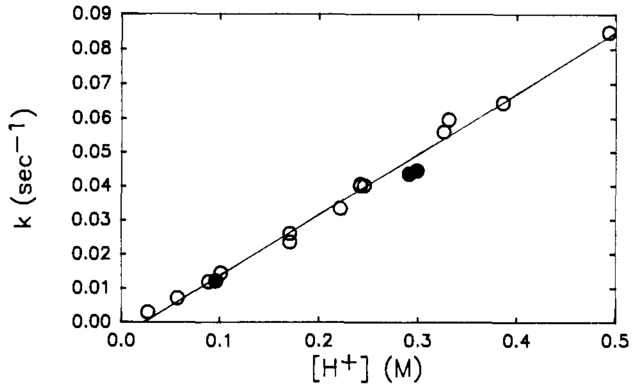

Figure 1. Observed pseudo-first-order rate constants at 25 °C and ionic strength 0.5 M (ClO_4^-) as a function of $[H^+]$. Solid circles represent experiments with $Fe(H_2O)_6^{2+}$ present. The line is the least-squares fit to all the data points.

In experiments in which the only source of CH_3CN was from the complex itself (less than[9] 6×10^{-5} M) the reaction was pseudo first order in total $[Fe(TIM)(X)Y^{2+}]$ for more than 4 half-lives. The rate constant was first order in $[H^+]$, independent of $[V^{2+}]$ over a range of $(0.43–5.1) \times 10^{-3}$ M, with a value at 25 °C and an ionic strength of 0.5 M of 0.178 ± 0.005 M^{-1} s^{-1}; the intercept in these experiments is -0.004 ± 0.001 s^{-1}. See Figure 1. Therefore, within our experimental error, all the reaction is carried through a $[H^+]$-dependent term.[10] Experiments carried out at 30.5 and 36.9 °C yielded second-order rate constants at these two temperatures of 0.27 ± 0.01 and 0.41 ± 0.02 M^{-1} s^{-1}, respectively. The three values yield the following activation parameters: $\Delta H^\ddagger = 49.3 \pm 0.9$ kJ/mol and $\Delta S^\ddagger = -94 \pm 3$ J/(mol deg).

Dependence of this reaction upon the ligands in the fifth and sixth coordination positions of the complex was also probed. Our early work with $Fe(TIM)(H_2O)CO^{2+}$ and $Fe(TIM)(CH_3CN)CO^{2+}$ demonstrated no decay over periods of days in 0.1 M acidic solutions.[1] To test the occurrence of the reaction in the presence of CH_3CN, data were obtained over a range of $[CH_3CN]$ from 3.2×10^{-3} to 2.11×10^{-2} M and of $[H^+]$ from 0.24 to 0.32 M. There are three possible species in a solution of $Fe(TIM)(X)Y^{2+}$ in aqueous CH_3CN: $Fe(TIM)(CH_3CN)_2^{2+}$, $Fe(TIM)(CH_3CN)(H_2O)^{2+}$, and $Fe(TIM)(H_2O)_2^{2+}$. Because the reaction rate is much slower when CH_3CN is present, we assumed that the rates of reaction with $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)(CH_3CN)(H_2O)^{2+}$ are both small. In terms of the total $Fe(TIM)(X)Y^{2+}$, T, these assumptions yielded

$$-d[T]/dt = kK_1K_2[T][H^+]/(K_1K_2 + K_1[CH_3CN] + [CH_3CN]^2)$$

where K_1 is the equilibrium constant for the loss of CH_3CN from $Fe(TIM)(CH_3CN)_2^{2+}$ and K_2 is the equilibrium constant for the

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(2) Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Caughey, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 2312–2319. Collins, D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066–2072. Radonovich, L. J.; Bloom, A.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2073–2078.

(3) Guenther, P.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769–3773.

(4) Flores-Arce, M.; Linck, R. G., to be submitted for publication.

(5) We use the symbol $Fe(TIM)XY^{2+}$ to indicate the complex when the fifth and sixth positions of the coordination sphere are unknown or consist of a mixture of materials.

(6) Methanol was chosen rather than water because of kinetic (and possibly thermodynamic) difficulties in dissolving $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in aqueous acid.

(7) We have no direct evidence that water occupies the fifth and sixth coordination positions, but that it does is plausible: (1) In a d^6 complex there is no known electronic reason that the coordination number would be 4 or 5 rather than 6, and (2) the spectrum of $Fe(TIM)(H_2O)_2^{2+}$ is very similar to that found when ligands that are not π acceptors, such as imidazole, occupy the fifth and sixth positions.

(8) To be certain that V^{2+} was not involved, we repeated the experiment with Eu^{2+} rather than V^{2+} as the reductant and obtained a rate constant equivalent to that with V^{2+} as the reductant when corrected for the acidity difference: With $[H^+] = 0.158$ M, $k = 0.022 \pm 0.001$ s^{-1} for Eu^{2+} as the reductant; the calculated value for V^{2+} (see below) at this $[H^+]$ is 0.024 ± 0.003 s^{-1}.

(9) Some CH_3CN is expected to be lost from the solutions during the deoxygenation process.

(10) We postulate that the negative intercept is caused by a medium effect, although a quantitative fit to a Harned type equation (Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold: New York, 1958. See also: Toppen, D. L.; Linck, R. G. *Inorg. Chem.* **1971**, *10*, 2635–2636 and references therein) yields a correction term that is unusually large.

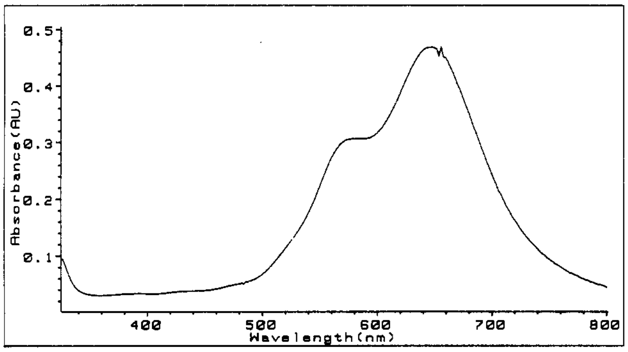

Figure 2. Calculated spectrum of Fe(TIM)$(H_2O)_2^{2+}$ as obtained from diode array spectroscopy ([Fe(II)] = 1.12×10^{-4} M; 1-cm cell). The discontinuity at 654 nm is an instrumental artifact.

loss of CH_3CN from Fe(TIM)$(CH_3CN)(H_2O)^{2+}$. The former is known to be 0.023[11] from earlier work.[1] Defining k_{obsd} as the pseudo-first-order rate constant, we can rearrange the expression for k_{obsd} and plot $[H^+]/k_{obsd}$ versus ($[CH_3CN] + [CH_3CN]^2/K_1$) to obtain a straight line from which the intercept yields a value of 0.21 ± 0.04 M^{-1} s^{-1} for k, in reasonable agreement with the value determined directly in the absence of CH_3CN.[12] The slope yields a value for K_2 of $(2.5 \pm 0.5) \times 10^{-3}$.[11] This result is consistent with our hypotheses. Therefore, we conclude that the reaction leading to disappearance of Fe(TIM)(X)Y^{2+} is effective only when CH_3CN is not in the coordination sphere of the Fe(II) ion. Combined with the qualitative observations on CO-containing complexes of Fe(II), it is clear that the presence of π-acceptor ligands inhibits the substitution and hydrolysis reaction. We further conclude that reaction is not effective in the Fe(III) form of the complex because Fe(TIM)$(H_2O)_2^{3+}$ stored in dilute acid conditions decays less than 15% in a day at 27 °C.

To demonstrate the nature of the stoichiometry of the reaction, we attempted to determine if biacetyl, the suspected hydrolysis product of the reaction, was present in spent reaction mixtures. These experiments were difficult because of the need for reasonably high concentrations of complex in order to analyze for biacetyl. Attempts to use luminescent techniques that would work at much lower concentrations of biacetyl were not quantitatively successful because of quenching of the biacetyl luminescence by the metal ions.[13] In a typical experiment a solution of Fe(TIM)$(H_2O)_2^{2+}$ was hydrolyzed under the same conditions as for the above-described kinetic experiments, the resultant acidic solution was extracted with $CDCl_3$, and the NMR spectrum was recorded. Both biacetyl and CH_3CN were found; no other peaks were present in the spectrum (1,3-diaminopropane was protonated under the experimental conditions and remained in the aqueous phase). In more quantitative experiments product mixtures were extracted with $CHCl_3$ and analyzed spectrophotometrically for biacetyl at 420 nm. The control for this experiment was a solution of biacetyl in perchloric acid that was also extracted and analyzed. We determined in two experiments that 75 and 77% of the biacetyl (predicted on the basis of the mass of original Fe complex used) were recovered. We conclude from this result that reduction of the unsaturation in the molecule is not the reaction path and that displacement of the Fe(II) and hydrolysis of the ligand is required for the overall stoichiometry.

We obtained a spectrum of Fe(TIM)$(H_2O)_2^{2+}$ by working at low $[H^+]$, extrapolating the resultant spectrum to zero time, and correcting for small amounts of Fe(TIM)$(CH_3CN)(H_2O)^{2+}$ present in the solution. This spectrum, Figure 2, shows the characteristic high-energy shoulder seen in α-diimine complexes of Fe(II).[14] Further, the spectrum is very similar to that recorded by Rose and co-workers for [Fe(TIM)$(CH_3CN)_2$]$(PF_6)_2$ dissolved in methanol.[15] On the basis of these considerations and the data of Reichgott and Rose[16] establishing that the dimethanol complex is diamagnetic, we conclude that Fe(TIM)$(H_2O)_2^{2+}$ has the same general electronic structure as the dimethanol complex, Fe(TIM)$(CH_3CN)_2^{2+}$, Fe(TIM)$(CH_3CN)(H_2O)^{2+}$, and Fe(TIM)$(CH_3CN)CO^{2+}$, and is also, like these, diamagnetic.

Discussion

The formation and hydrolysis of imines have been extensively studied by Jencks and co-workers.[17] The generally accepted mechanism is protonation of the imine nitrogen in a reversible acid/base equilibrium, attack by water at the carbon center with concomitant tautomerization of another proton to the nitrogen to form a tetrahedral intermediate at the carbon center, and, finally, breakage of the carbon–nitrogen bond with or without the assistance of a base to remove the remaining proton from the oxygen.

The transition state for the hydrolysis of Fe(TIM)$(H_2O)_2^{2+}$ involves the complex and a proton. What is curious about this rate law is that the lone pair of electrons on the nitrogen of the imine linkage is not available to act as a basic site for the proton, and there are no other "classical" lone pairs of electrons in the molecule. The conventional conclusion would be that imines complexed to metal ions are relatively stable to hydrolysis until the metal ion–imine bond breaks. The stability of metal ion–imine bonds is manifest especially in macrocyclic complexes where metal–ligand bonds break considerably more slowly than in the corresponding open-chain complexes.[18] There are therefore few references to metal ion–imine hydrolysis in aqueous solution in the literature, even in solutions reasonably high in $[H^+]$. Results of others' work illustrate the stability of complexes of TIM and related macrocyclic ligands.[19] Low-valent metal ion complexes are somewhat more reactive,[19e,20] but no evidence of hydrolysis has been presented. Using more severe conditions, Anderson and Jackels have reported that the Cu(II) complex of the diphenyl analogue of TIM is attacked by anhydrous HCl in dry CH_3CN in the presence of LiBr to yield a copper(II) halide and the tetrahydrobromide salt of the free ligands.[21] We conclude that except under such extreme circumstances the divalent Co, Ni, and Cu complexes of 14-membered macrocyclic rings are resistant to decomposition.

Whether the stability of Fe(II) is analogous to that of other divalent metal ions in 14-member macrocyclic rings is not clear. Some evidence for instability exists: Goedken, Merrell, and Busch have reported that the Fe(II) macrocyclic complex of a [14]-1,11-*trans*-tetraazadiene decomposes in 0.05 M acid with a half-life of about 40 min but did not report data on the hydrogen ion dependency of the rate.[22] This complex is very susceptible to

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(11) The standard state for equilibrium constants in this work is moles per liter.

(12) We believe the errors in this latter set of experiments are high because of the difficulty in delivering small quantities of CH_3CN accurately into the reaction system.

(13) We attempted to remove metal ions by ion-exchange chromatography, but such experiments still yielded solutions in which the biacetyl luminescence was largely quenched.

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(15) Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1977**, *99*, 1813–1818.

(16) Reichgott and Rose used Evans' magnetic susceptibility method. See: Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005, as well as ESR results.

(17) See, for instance: Jencks, W. P. *Prog. Phys. Org. Chem.* **1964**, *2*, 63–128. Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 3262–3263. Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 5637–5649. Diebler, H.; Thornley, R. N. F. *J. Am. Chem. Soc.* **1973**, *95*, 896–904. Rosenburg, S.; Silver, S. M.; Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7986–7998. Sager, J. M.; Conlon, P. *J. Am. Chem. Soc.* **1981**, *102*, 3592–3600.

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(19) (a) Rillema, D. P.; Endicott, J. F. *Inorg. Chem.* **1976**, *15*, 1459–1461. (b) Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847–857. (c) Endicott, J. F., private communication. (d) Heeg, M. J.; Endicott, J. F.; Glick, M. D.; Khalik, M. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 730–732. (e) Ferraudi, G. *Inorg. Chem.* **1985**, *24*, 281–285.

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Table I. Metal–Nitrogen Distances for TIM Complexes

complex	M–N, Å	ref
$[Fe(TIM)(CO)CH_3CN](PF_6)_2$	1.949–1.953	26
$[Fe(TIM)(CH_3CN)_2](PF_6)_2$	1.945–1.951	28
$[Co(TIM)(H_2O)_2](ClO_4)_2$	1.891, 1.904	27
$[Ni(TIM)(Imd)_2](PF_6)_2$[a]	1.96, 2.04	*b*
$[Cu(TIM)NCS](PF_6)$	1.920, 1.963	*c*
$[Cu(TIM)(Imd)](PF_6)_2$	1.984–2.000[d]	34a
$[Cu(TIM)](B(C_6H_5)_4)_2$	1.940–1.948	*e*
$[Cu(TIM)(H_2O)_2](NO_3)_2$	1.969	29

[a] Imd is imidazole. [b] Torre, L. P. Ph.D. Disseration, University of Washington, Seattle, WA, 1971. [c] Elia, A. E.; Lingafelter, E. C.; Schomaker, V. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1313–1315. [d] The Cu ion is 0.44 Å out of the plane of the imine nitrogens. [e] Elia, A. E.; Lingafelter, E. C.; Schomaker, V. *Croat. Chem. Acta* **1984**, *57*, 653–659.

conversion to the high-spin form: Upon dissolution of the bis(acetonitrile) complex in methanol with some anion present, five-coordinated high-spin complexes are isolated in which the Fe(II) ion is out of the plane of the four nitrogens.[23]

Although the 14-member macrocyclic complexes of divalent metal ions appear reasonably stable to attack by aqueous acid, there is evidence that 16-member macrocyclic complexes, especially complexes of porphyrins, do undergo acid-induced decomposition.[24] The loss of Fe(III) from porphyrin systems when Fe(II) is present has been reported.[25] This role of acid in loss of metals from porphyrin systems is presumably due to the very strongly basic character of free base porphyrins,[26] a feature not present in the imines being considered here.

None of these observations directly address several crucial questions relating to the mechanism of the substitution and hydrolysis of $Fe(TIM)(H_2O)_2^{2+}$: Where does the proton bind in the transition state for reaction of $Fe(TIM)(H_2O)_2^{2+}$? Why are $Fe(TIM)(CH_3CN)(H_2O)^{2+}$, $Fe(TIM)(CH_3CN)_2^{2+}$, and $Fe(TIM)(X)CO^{2+}$ so unreactive? Why is the ferrous complex the only one of the divalent metals between Fe and Cu to substitute rapidly from TIM in aqueous solution? To attempt to answer these questions, we examine the nature of the HOMO of $Fe(TIM)(H_2O)_2^{2+}$ and some structural data of various complexes of TIM.

$Fe(TIM)(H_2O)_2^{2+}$ presumably has D_{2h} microsymmetry, in which we choose the x axis as bisecting the α-diimine portions of the molecule. Because the diimine chelate bite is only about 81° (in $Fe(TIM)(CH_3CN)CO^{2+}$,[27] as well as other complexes of TIM[28–30]), $d_{x^2-y^2}$, a nonbonding orbital in D_{4h} symmetry, is slightly antibonding. Depending on the relative magnitudes of the π and π^* interactions with d_{xz} and d_{yz} and on the strength of the interaction of the σ orbitals with $d_{x^2-y^2}$, the HOMO will be one of these three orbitals. This analysis is similar to the ordering of levels obtained by Norman et al.[31] in their analysis of $Fe(TIM)(NCS)_2$ by the SCF–Xα–SW method, except that in the diisothiocyanato case the HOMO levels were calculated to be nonbonding (metal–ligand) levels on the axial ligands. On the basis of this analysis, we hypothesize that none of the three potential HOMO levels are suitable for attack by a proton in a frontier-orbital sense.

The structure of the TIM complexes of the divalent metals of Fe, Co, Ni, and Cu have all been determined. Table I contains the relevant metal–nitrogen bond distances for several TIM complexes. These data illustrate that the metal–nitrogen bond distances vary very little with a change in metal ion. Of the complexes examined, the Fe(II)[32] and Co(II)[28] are low spin, whereas the Ni(II) is high spin.[33] There is the usual size compression as one moves to the right in the periodic table for the Fe(II)–Co(II) pair and the Ni(II)–Cu(II) pair. The bond lengths for these complexes are normal for bonds to imines for these metals: for instance, Fe, 1.89–2.01 Å;[34] Cu(II), 1.91–2.035 Å.[35] The value for $Fe(TIM)(H_2O)_2^{2+}$ is presumably near the lower limit for Fe(II)–imine bonds. However, these length considerations change if high-spin Fe(II) complexes are examined; this phenomenon is most strikingly illustrated for those complexes in which a temperature-dependent spin change has been found; for example, Mikami et al. have studied the structural consequences of the interconversion between low- and high-spin forms in the Fe(II) complex of 2-picolylamine.[36] They found the bond lengths of the low-spin form to be about 2.002 Å for the Fe(II)–aromatic nitrogen bond and 2.024 Å for the Fe(II)–amine nitrogen bond, while the corresponding high-spin values are 2.21 and 2.18 Å, respectively. Other data on bond length changes occurring upon conversion from high- to low-spin forms indicate similar bond length variations.[37]

From these orbital and structural considerations we have formulated the following mechanism for the substitution and hydrolysis of $Fe(TIM)(H_2O)_2^{2+}$. The Fe(II) ion in $Fe(TIM)(H_2O)_2^{2+}$ undergoes a vibration that causes the metal ion to move partially out of the plane of the ring. This process lowers the energy of d_{z^2} and raises that of d_{xz} and d_{yz} as the σ electrons of the imine nitrogens begin to overlap with the lower lobe of these functions.[38] The orbital energy change causes a change in the Fe(II) spin state, resulting in an increase in effective size, a further removal from the plane of the ring, and adoption of a five-coordinate structure. MM2 calculations done by Perkovic and Endicott indicate that an ion of the size of high-spin Fe(II) will be driven from the ring of TIM (although low-spin Fe(II) is stable).[39] This activation process is similar to the net transformation observed by Goedken et al.[22,23] for the conversion of six-coordinate low-spin (high-field axial ligands) to five-coordinate

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high-spin (low-field axial ligand) [14]-diene Fe(II) complexes.[40] It was also established for Fe(II) porphyrins by Hoard and coworkers;[2] in addition, James and Stynes have suggested a similar process is important in axial substitution of the ligands on Fe(II) in some complexes.[41] What differs in our case from that of these other studies is the fate of the high-spin species. For $Fe(TIM)(H_2O)_2^{2+}$ a proton attacks the five-coordinate Fe(II) complex at the incipient lone pair on an imine nitrogen, causing the Fe(II) to be completely lost and subsequently leading to hydrolysis of the ligand.

We postulate that this process is less efficient in the other metal complexes of TIM because of their smaller size and smaller change in size upon a spin change (Co(II) and Fe(III))[42] or because of their failure to undergo a spin change that results in a dramatic increase in tetragonal plane size (Ni(II) and Cu(II)). Our spin-change-dependent mechanism is consistent with the observations that the rate of reaction is very small when π-acceptor ligands such as CH_3CN or CO are in axial positions: These ligands stabilize the d_{xz} and d_{yz} orbitals such that conversion to high spin is energetically more difficult and hence the steric drive to remove the Fe(II) from the ring is correspondingly less.

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Registry No. $Fe(TIM)(CH_3CN)(H_2O)^{2+}$, 93184-90-8; $Fe(TIM)(H_2O)_2^{2+}$, 90461-84-0; TIM, 59969-61-8.

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Equilibrium and Kinetic Studies of the Complexing of Iron(III) by 1,2-Dihydroxybenzene Derivatives

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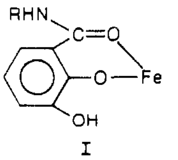
The equilibrium constants and kinetics for complexing of aqueous iron(III) by 2,3-dihdyroxybenzoic acid (DHB) and 1,2-dihydroxy-3,5-benzenedisulfonate (Tiron) have been studied in 1 M $NaClO_4$–$HClO_4$ between 0.01 and 0.7 M H^+ under conditions of [iron(III)] ≫ [ligand]. The formation constants for the reaction $Fe^{3+} + H_2L \rightleftarrows Fe{=}L + 2H^+$ are 3.15 ± 0.23 and 6.95 ± 0.60 M for Tiron and DHB, respectively. Formation constant comparisons indicate that DHB complexes in a mode analogous to that for salicylate. The reaction rate shows the $[H^+]$ dependence typical for iron(III) complexation, but there is an unusual contribution from a kinetic term second order in [iron(III)]. The kinetic results are discussed and compared to previous work on related systems.

Introduction

In plants and unicellular organisms, iron is made accessible at near neutral pH by efficient complexing of iron(III) by siderophores. The iron subsequently is released by reduction to the much less strongly complexed iron(II). For catecholate siderophores such as enterobactin, the mechanism and mode of complex formation and reduction remain controversial. The various proposals have been discussed recently by Hider et al.[1] There is a question as to whether the binding is through the salicylate mode (I) or the catecholate mode (II) and what is the site and effect of protonation of the ligand in the iron(III) complex, as well as what the ultimate iron reduction mechanism is.



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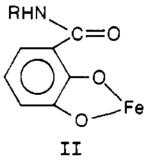
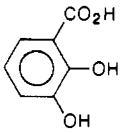
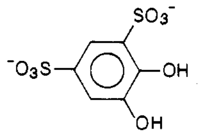


II

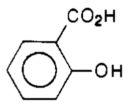
The purpose of this work is to provide some guidelines for answering the above questions by studying simple ligand model systems. The kinetics and equilibrium constants for complexing of aqueous iron(III) by 2,3-dihydroxybenzoic acid (DHB, III) and 1,2-dihydroxy-3,5-benzenesulfonate (Tiron, IV) are compared to the previously studied salicylic acid system (V).[2,3] These ligands provide a series in which the binding mode of iron(III) may be only salicylate (V), only catecholate (IV), or either (III). The presence of $-CO_2H$, $-CO_2^-$, and SO_3^- substituents may provide useful comparisons for the kinetic results.



III



IV



V

Some features of the equilibrium constants for the iron(III)–Tiron system remain uncertain despite several previous studies.[4-6] The condition of [iron(III)] ≫ [ligand] has been used here to simplify the analysis. The same conditions are used in a reexamination of the kinetics, and the acid range has been extended from that of earlier work[7] to examine ligand protonation effects.

Although DHB is a known therapeutic siderophore,[8] the iron(III)–DHB system has not been satisfactorily characterized.[9,10] The potentiometric titration results of Avdeef et al.[9] give an unusually wide variation in the formation constants, which seem

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