portion of the OEP molecule is essentially planar with all atoms within 0.05 Å of the least-squares plane. Least-squares planes were also calculated for each of the independent pyrrole rings. The results are listed in Table VI and indicate that ring 1 has smaller deviations from planarity than does ring 2. The imino hydrogen atom is bound to the nitrogen atom of ring 2 at a distance of 0.92 (2) Å. It is 0.05 Å from the least-squares plane of ring 2. The distance between the two imino hydrogen atoms across the center of the molecule is 2.36 (4) Å.

Table VII lists average bond distances and bond angles for those porphyrins whose structures have been determined completely. The values for TPP and TPrP are quite similar and have been averaged to give values representative of meso-substituted porphyrins. Also listed are the values for the common structure of free base porphyrins proposed by Codding and Tulinsky.[1] As previously indicated[1] the largest structural differences between the meso-substituted porphyrins and porphine involve the methine carbon atom. The meso porphyrins which are substituted at the methine carbon atom have C_α–C_m bond lengths which are about 0.018 Å longer than the C_α–C_m bond length found in porphine. In a similar manner, the C_α–C_m–C_α' bond angle is 1.8° smaller than the value for porphine.

OEP is substituted at the pyrrole positions and it would be expected that the largest structural difference between porphine and OEP would involve the pyrrole atoms. This appears to be the case, as the parameters in Table VII indicate. Both the C_α–C_β and the C_β–C_β' bond distances in each of the pyrrole rings are about 0.01 Å longer in OEP than in the unsubstituted porphine molecule.

The result of substitution is the same in the meso porphyrins and in OEP. Those carbon–carbon bonds closest to the site of substitution are lengthened. This lengthening of bonds is not unexpected in aromatic systems and indicates a reduction in the π-electron density at the substituted carbon atom and a subsequent transfer of π-electron density to the substituent atoms. This is supported by the observed short bond distance of 1.498 (4) Å for the average C_β–$C_{E\alpha}$ bond length.

A comparison of all the results shown in Table VII indicates that the common structure for the porphyrin macrocycle proposed by Codding and Tulinsky[1] is a good model but that substituent groups can be expected to cause significant changes in bond parameters. The naturally occurring porphyrins have pyrrole substituents and can be expected to have bond lengths and angles similar to those observed for OEP. It should be noted, however, that certain natural prophyrins have substituent groups such as vinyl groups which can conjugate with the porphyrin macrocycle and may cause additional changes in bond parameters.

Acknowledgment. We would like to thank Professor H. H. Inhoffen for his generous gift of a sample of OEP. This research was sponsored by the Advanced Research Projects Agency and the National Science Foundation through the Northwestern University Materials Research Center.

Synthesis and Reversible Ligation Studies of New Low-Spin Iron(II) Complexes Containing a Planar Cyclic Tetradentate Ligand and Other Donor Molecules Including Carbon Monoxide

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Abstract: The synthesis and characterization of three hexacoordinate low-spin Fe(II) complexes are described. All the complexes contain TIM, a 14-membered tetraimine macrocyclic ligand derived from 2,3-butanedione and 1,3-diaminopropane and all are isolated as PF_6^- salts: $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, $[Fe(TIM)(imid)_2](PF_6)_2$, and $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$. Preparative difficulties encountered in the synthesis of $[Fe(TIM)X_2](PF_6)_2$ (which are not encountered with the Ni(II) and Co(III) TIM complexes) are alleviated through the addition of stannous chloride to the reaction mixtures. In acetonitrile solutions $[Fe(TIM)(CH_3CN)_2]^{2+}$ undergoes reversible substitution reactions with both imidazole and carbon monoxide. In the case of imidazole one or more of the following three complexes are present in solution depending on the concentration of imidazole: $[Fe(TIM)(CH_3CN)_2]^{2+}$, $[Fe(TIM)(CH_3CN)(imid)]^{2+}$, and $[Fe(TIM)(imid)_2]^{2+}$. Estimates of the equilibrium constants involved in the substitution reactions show that the $[Fe(TIM)(CH_3CN)(imid)]^{2+}$ is the favored species but that the formation constant for $[Fe(TIM)(imid)_2]^{2+}$ is large enough such that no free imidazole is detectable by pmr spectroscopy when the imidazole:Fe(TIM) ratio in the system is 2. With carbon monoxide the two species present in solution are $[Fe(TIM)(CH_3CN)_2]^{2+}$ and the mixed complex $[Fe(TIM)(CH_3CN)(CO)]^{2+}$ (when $P_{CO} \leq 1$ atm).

In recent years the chemistry of synthetic complexes containing macrocyclic ligands has commanded a great deal of attention.[1] A part of the motivation for expending considerable effort in the field has come from the continuing hope that a significantly more complete understanding of the chemistry of the naturally occurring macrocycles will be forthcoming from investigations of the synthetic ones.[2,3] Included among

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(1) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 174 (1967).

studies centering on the macrocyclic complexes are those devoted to the design and synthesis of the species as well as to their spectral and redox properties.[4,5] In the case of iron macrocyclic complexes relatively little effort has been allotted to investigations of equilibria involving various ligands and those sites on the metal's coordination sphere *not* occupied by donor atoms of the macrocyclic ligand.[6]

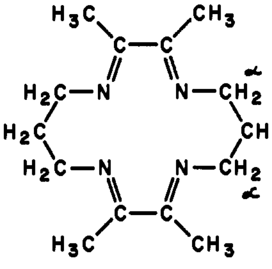
Those macrocyclic ligands which give rise to only one stereoisomeric complex and which show little or no tendency to adopt a folded configuration on the metal's coordination sphere are well suited for reversible ligation studies. For complexes of such macrocyclic ligands a single isomer exists in solution and only axial sites on the metal's coordination sphere are readily involved in substitution reactions involving various monodentate ligands (*e.g.*, CH_3CN, Cl^-, H_2O, etc.). TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) is a macrocyclic ligand having the properties just mentioned,[6a,7–10] and therefore its complexes are quite appropriate for studying axial substitution reactions.

We report here the synthesis and characterization of $[Fe(TIM)XY]^{2+}$ salts and pmr studies of equilibria involving acetonitrile, imidazole (hereafter imid), and carbon monoxide as axial ligands. The equilibria of interest are schematically represented in eq 1 and 2.

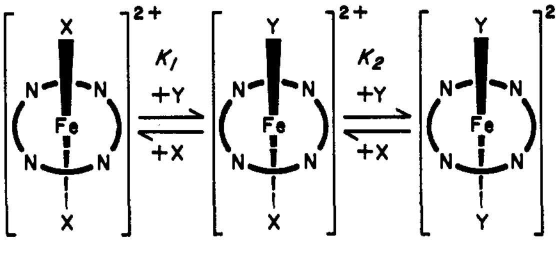
Experimental Section

The reagents used as starting materials were obtained commercially and used without further purification, unless noted.

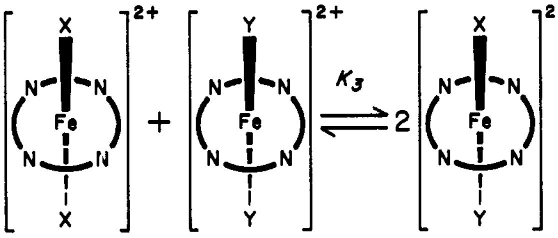
Preparation of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$. To 125 ml of methanol was added $SnCl_2 \cdot 2H_2O$ (0.5 g, 0.002 mol) and then N_2 was passed through the resulting solution for approximately 10 min. To this solution, still under N_2, was added 0.08 mol of $FeCl_2(H_2O)_x$ obtained by desiccating $FeCl_2 \cdot 4H_2O$ (15.90 g, 0.08 mol) over P_4O_{10} at room temperature for 12 hr at approximately 0.2 Torr. The resulting solution was refluxed for approximately 10 min under a nitrogen atmosphere and then set aside to cool to room temperature. Methanol (100 ml) was cooled to $-5°$ and maintained at temperatures below $+5°$ during the successive additions of 1,3-diaminopropane (13.4 ml, 0.16 mol), trifluoroacetic acid (11.9 ml, 0.16 mol), and a solution of 2,3-butanedione (14 ml, 0.16 mol) in 14 ml of methanol. The resulting clear, yellow solution was stirred and nitrogen was bubbled through it for 15 min. The pale green ferrous chloride solution containing the tin salt was added dropwise to the yellow solution under nitrogen, over a period of 30 min. The resulting solution is a deep indigo. Potassium acetate (15.6 g, 0.16 mol) was added after the first few milliliters of the ferrous chloride solution had been added. The resulting solution, still under nitrogen, was stoppered and allowed to warm to room temperature. (During a period of about 4 hr a color change to olive is observed.)



TIM



(1)



(2)

After 24 hr, glacial acetic acid (25 ml, 0.436 mol) and acetonitrile (25 ml, 0.472 mol) were added, and the nitrogen atmosphere was no longer maintained. On addition of the acetonitrile, a color change from olive to deep red is observed. The solution was filtered with suction and the volume of the filtrate was reduced by half *via* a rotary evaporator without heating the solution above room temperature. The solution was again filtered with suction and the filtrate was cooled to about 10°. A solution of ammonium hexafluorophosphate (10 g, 0.061 mol) in 80 ml of H_2O was added to the filtrate. The mixture was swirled for a few seconds, and then the microcrystalline burgundy red solid was collected. The product was washed with ethanol and then with ether and finally vacuum desiccated over P_4O_{10} at room temperature for 12 hr at approximately 0.2 Torr, yield 4.4 g (8.1%). The product was recrystallized from acetonitrile and ethanol; it may also be recrystallized from acetonitrile and water. *Anal.* Calcd for $[Fe(TIM)(CH_3CN)_2](PF_6)_2$: C, 31.97; H, 4.47; N, 12.43. Found: C, 32.17; H, 4.49; N, 12.72. The solid decomposes slowly at temperatures above 200°. Mössbauer spectrum 77°K, δ 0.62 mm/sec; ΔE_q, 1.56 mm/sec.

Preparation of $[Fe(TIM)(imid)_2](PF_6)_2$. The bis(acetonitrile) complex (0.5 g, 0.00074 mol) was dissolved in acetonitrile (8 ml) and the resulting solution was filtered. Imidazole (0.25 g, 0.0037 mol) was added, giving an immediate color change to deep blue. The addition of chloroform (40 ml) caused the precipitation of a blue powdery solid. The product was collected, washed with chloroform, and vacuum desiccated over P_4O_{10} for 12 hr at room temperature at approximately 0.2 Torr, yield 0.49 g (91%). *Anal.* Calcd for $[Fe(TIM)(imid)_2](PF_6)_2$: C, 32.89; H, 4.42; N, 15.34. Found: C, 32.46, 32.76; H, 4.29, 4.31; N, 15.45 (a), 14.54 (b), where (a) was obtained by Dumas method and (b) by a C, H, N analyzer. Mössbauer spectrum, 77°K, δ 0.58 mm/sec; ΔE_q, 1.68 mm/sec. Molecular weight: calcd, 243; found, 250 (acetonitrile, 26.77 mg sample in 10 ml of CH_3CN).

Preparation of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$. The bis(acetonitrile) complex (1.0 g, 0.00148 mol) was dissolved in 15 ml of CH_3CN. Carbon monoxide was passed through a potassium hydroxide trap and then bubbled through the solution for 30 min. A gradual color change to orange is observed. Ethanol (50 ml) was cooled to $-5°$ and added carefully to the solution over 15 min with carbon monoxide still bubbling through the solution. The mixture was cooled to $-5°$ and the microcrystalline orange product was collected, washed with ethanol then ether, and finally

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(2) G. N. Schrauzer, *Advan. Chem. Ser.*, **No. 100**, 1 (1971).

(3) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, **No. 100**, 44 (1971).

(4) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).

(5) See, for example, (a) T. J. Treux and R. H. Holm, *J. Amer. Chem. Soc.*, **94**, 4529 (1972); (b) V. L. Goedken, P. H. Merrell, and D. H. Busch, *ibid.*, **94**, 3397 (1972); (c) J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, *ibid.*, **94**, 5502 (1972).

(6) (a) R. M. Pfeiffer, N. J. Rose, and D. A. Baldwin, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. INOR-047; (b) L. Vaska and T. Yamaji, *J. Amer. Chem. Soc.*, **93**, 6673 (1971).

(7) D. A. Baldwin and N. J. Rose, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR-020.

(8) L. P. Torre, Thesis, University of Washington, 1971; L. P. Torre and E. C. Lingafelter, Program and Abstracts of American Crystallographic Association Meeting, Columbia, S. C., Jan 1971.

(9) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972).

(10) G. W. Svetich, H. W. Smith, and E. C. Lingafelter, private communication.

Table I. Characteristic Infrared Spectral Bands of $[Fe(TIM)(X)(Y)](PF_6)_2$[a]

Complex		Group associated with obsd band[b]				
X	Y	(Imid)[c,d]	CH_3CN[e-g]	CO	(TIM)	PF_6^- [h]
CH_3CN	CH_3CN		2340 w		1630 w	850 s
			2300 w		1560 w	560 s
			1040 w		1320 s	
					1295	
					1265	
					1210 s	
					1095	
					1025	
					985	
					915	
CH_3CN	CO		2340	2031 ± 1[i]	1640 w	850 s
			2300	1984 ± 1[i]	1570	560 s
			1040 w		1325	
					1280	
					1265 w	
					1210 s	
					1095	
					1025	
					990	
					915	
(imid)	(imid)	3430 s			1605	850 s
		3180 d			1320	560 s
		1540			1280	
		1505			1260	
		1170			1210 s	
		1100			1095	
		1070 s			1025	
		745			970	
		660 s			910	
		610 s				

[a] Nujol mulls. Values in cm^{-1}. [b] w = weak, s = strong, d = center of doublet. [c] Y. D. Kanaskova, I. A. Garbuzova, Y. A. Penshin and B. I. Sukhorukov, *Opt. Spectrosc.* (*USSR*), **29**, 274 (1970). [d] R. H. Carlson and T. L. Brown, *Inorg. Chem.*, **5**, 268 (1966). [e] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970). [f] Reference 5. [g] F. W. Parker, A. H. Nielson, and W. H. Fletcher, *J. Mol. Spectrosc.*, **1**, 107 (1957). [h] N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, **6**, 1924 (1967). [i] Band positions determined with Perkin-Elmer Model 225 spectrophotometer.

vacuum desiccated at room temperature over P_4O_{10} for 12 hr at approximately 0.2 Torr, yield 0.79 g (80.5%). *Anal.* Calcd for $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$: C, 30.78; H, 4.10; N, 10.56. Found: C, 30.75; H, 4.35; N, 10.79. Mössbauer spectrum, 77°K, δ 0.40 mm/sec; ΔE_q, 1.02 mm/sec.

Physical Measurements. Using KBr plates, infrared spectra were obtained as Nujol mulls with a Beckman IR-10 recording spectrophotometer in the range 4000–400 cm^{-1}. Nuclear magnetic resonance spectra were obtained on a Varian Model HA-60 (and on Varian Model HA-100 for double resonance experiments) using deuterioacetonitrile (99% D) as a solvent with 1% v/v TMS as an internal standard. Elemental analyses were performed by Chemalytics, Inc. Mössbauer spectra were taken at 77°K by the technique outlined in ref 11. Sodium nitroprusside was used as the standard. Molecular weight measurements at 37° were performed with a Mechrolab Model 301-A vapor pressure osmometer.

Results and Discussion

I. $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ and $[Fe(TIM)(imid)_2](PF_6)_2$. Following Baldwin's initial synthetic work on the preparation of $[Ni(TIM)]^{2+}$ species,[7] both Co(III)[9] and Fe(II) complexes containing TIM have been prepared. The preparation of $[Fe(TIM)X_2]^{2+}$ derivatives is similar to the preparation of the Ni(II) and Co(III) homologs, but the synthetic procedure is more involved and it gives significantly lower yields. In the case of the $[Fe(TIM)(CN_3CN)_2](PF_6)_2$ preparation the presence of stannous ion, presumably functioning as a reducing agent, has been shown to reduce the need for rigorous atmosphere control, to increase yields, and to change the nature of the reaction mixture such that the product volunteers in a crystalline form rather than as a paste (see Experimental Section). The $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ shows no indication of changing upon being exposed to the atmosphere for several weeks and has an indefinite shelf life in capped vials. The species dissolves readily in acetonitrile, and there is little or no reaction with dissolved oxygen in that solvent.

The bis(imidazole) and the bis(acetonitrile) complexes (in acetonitrile solution) are sensitive to certain bases. The bis(imidazole) complex is particularly sensitive, and color changes from deep blue to green and finally to yellow are observed when free bases are present. When strong bases such as OH^- are added to the solution, the change occurs in a matter of seconds, whereas when weak bases are present, *e.g.*, excess imidazole, the change requires 1 day or more. The nature of this reaction and its products have not been determined.

For $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ as well as for $[Co(TIM)Cl_2]PF_6$ and $[Fe(TIM)(imid)_2](PF_6)_2$ the trans structures have been definitively established *via* single-crystal X-ray diffraction studies.[8,10] The available structural data considered along with the properties observed for the TIM complexes indicate that the nitrogen atoms of this cyclic ligand must coordinate in a planar rather than a folded configuration. Thus, pmr and infrared spectra of the Ni(II)[7] and Co(III)[9] complexes as well as the spectra of the Fe(II) species (*vide infra*) reveal no multiplicity beyond that expected from a planar arrangement of the four TIM nitrogen atoms.

Both the bis(acetonitrile) and bis(imidazole) Fe(II)–(TIM) complexes are diamagnetic and their Möss-

(11) S. C. Jackels and N. J. Rose, *Inorg. Chem.*, **12**, 1232 (1973).

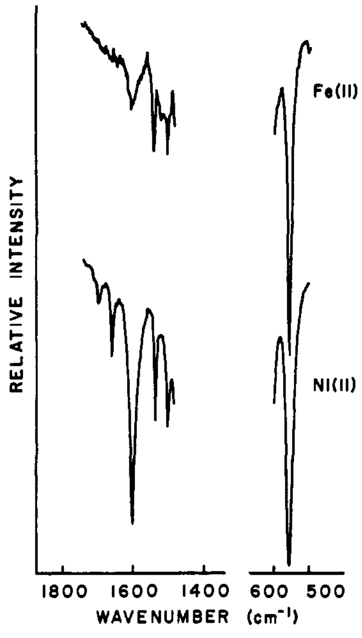

Figure 1. A portion of the infrared spectra (Nujol mull) of $[Fe(TIM)(imid)_2](PF_6)_2$ and $[Ni(TIM)(imid)_2](PF_6)_2$ showing the 1600- and 560-cm^{-1} regions for each. The band at 560 cm^{-1} is confidently assigned to a PF_6^- mode and is included to provide a relative intensity scale.

bauer spectra exhibit isomer shifts characteristic of other low spin six-coordinate Fe(II) species.[12,13] The large quadrupole splitting observed for the bis(acetonitrile) and bis(imidazole) complexes are (1) consistent with the proposed trans structures,[12] (2) comparable to those observed for bis(terimine) complexes, species thought to be significantly distorted from cubic symmetry,[14] and (3) distinctly larger than the ΔE_q values of the pseudooctahedral tris(α-diimine) complexes.[15]

In Table I are collected the characteristic infrared bands of $[Fe(TIM)XY](PF_6)_2$. This tabulation was developed in part by comparing the spectra of the $[Fe(TIM)XY](PF_6)_2$ species with each other and with spectra of the Ni(II) and Co(III) TIM complexes. There are only two major features of the spectra of $[Fe(TIM)(imid)_2](PF_6)_2$ and $[Ni(TIM)(imid)_2](PF_6)_2$ which are different. For $[Ni(TIM)(imid)_2](PF_6)_2$ (as well as for $[Co(TIM)Cl_2](PF_6)$) there is a strong band at ~1600 cm^{-1} which is assigned to the C=N stretching vibration in TIM.[9] This band is absent or very weak in all the Fe(TIM) derivatives reported here (Figures 1, 2, and 3; Table I). Such a dramatic decrease in the intensity of a band attributed to a C=N group in a low spin, pseudooctahedral Fe(II) species is not unusual and has been attributed to delocalization of the d electron density onto the ligands.[14] The other major difference in the spectrum of $[Fe(TIM)XY](PF_6)_2$ compared to the cobalt and nickel derivatives is the presence of a sharp medium-intensity band at about 980 cm^{-1}. This band is missing in spectra of $[Ni(TIM)(imid)_2](PF_6)_2$ and $[Co(TIM)Cl_2](PF_6)$. Its presence in the iron complexes may also be a consequence of the delocalization just mentioned.

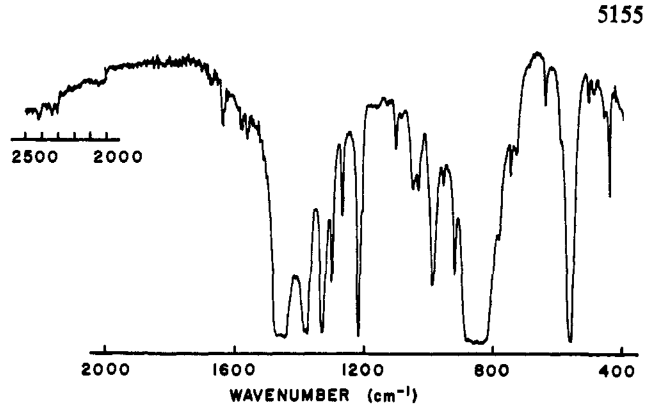

Figure 2. A portion of the infrared spectrum (Nujol mull) of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$.

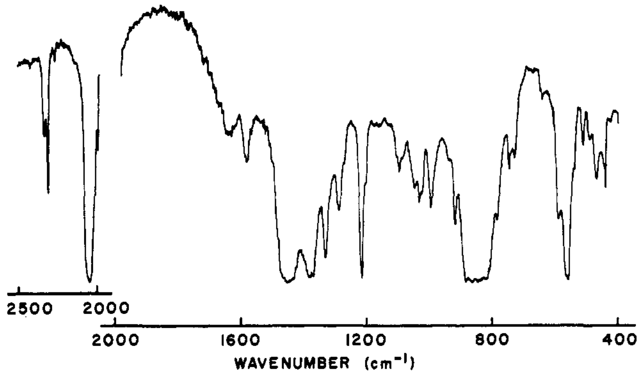

Figure 3. A portion of the infrared spectrum (Nujol mull) of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$.

A strong absorption attributable to the TIM ligand appears in the spectra at ~1210 cm^{-1} for all the TIM complexes *regardless of which metal ion is present.* This strong band, which is thought to be associated with vibrations of the five-membered chelate ring of TIM,[16] and the *metal ion dependent* band at about 980 cm^{-1} are also present in the spectrum of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ taken in acetonitrile solution (1209 and 975 cm^{-1}) and in a KBr pellet (1210 and 980 cm^{-1}). Further, the relative intensity of the two bands is the same in all three media (Nujol (Figure 2), acetonitrile, and KBr). Thus, the bands at ~1210 and 980 cm^{-1} are especially useful in characterizing new TIM complexes of Fe(II).

In the spectrum of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ only two very weak absorption bands appear in the 2300-cm^{-1} region (2300 and 2340 cm^{-1}, Figure 2). Presumably these are associated with the C≡N vibrations which give rise to the strong doublet centered at 2254 cm^{-1} in the spectrum of free acetonitrile.[17] The low intensity of the $\nu_{C\equiv N}$ band in the complex is quite striking. Significantly, a weak $\nu_{C\equiv N}$ band also occurs for another low-spin Fe(II) complex,[5b] $[Fe([14]dienN_4)(CH_3CN)_2]^{2+}$, but moderate to strong $\nu_{C\equiv N}$ bands occur for iron(III),[5b] ruthenium(II),[18] and ruthenium(III)[18] acetonitrile complexes. Upon changing the ligand trans to acetonitrile from acetonitrile to carbon monoxide (Figure 3, *vide infra*), a noticeable increase in the intensity of $\nu_{C\equiv N}$ band

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(12) G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc. A*, 956 (1970).

(13) N. E. Erickson, *Advan. Chem. Ser.*, **No. 68**, 86 (1967).

(14) P. Krumholtz, *Struct. Bonding (Berlin)*, **9**, 139 (1971).

(15) L. J. Wilson, Thesis, University of Washington, 1971.

(16) L. T. Taylor, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 7, 785 (1968).

(17) E. L. Pace and L. J. Noe, *J. Chem. Phys.*, **49**, 5317 (1968).

(18) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

Table II. Pmr Spectra of $[Fe(TIM)(X)(Y)]^{2+}$ in Deuterioacetonitrile[a]

Complex		Protons to which resonances are assigned			
X	Y	CH_3	α CH_2	β CH_2	Other
CH_3CN	CH_3CN	158.5 (12)	244[b] (7.9)	130[c]	117.5[d]
CH_3CN	CO	147.5	232[b]	125[c,g]	117.5[d]
(imid)	(imid)	167 (12)	235[b] (7.9)	96[c] (4.3)	117.5[e]
					351[f] (1.9)
					392[f] (1.8)
					412[f] (1.9)

[a] Values in Hz downfield from internal TMS. [b] Center of triplet. [c] Center of broad multiplet. [d] CH_3 of acetonitrile plus CH_xD_{3-x} resonances of solvent. [e] Center of CH_xD_{3-x} resonances of solvent. [f] Triplet, assigned to imidazole protons. [g] Estimated value; these resonances occur in the peaks attributed to protic impurities in CD_3CN.

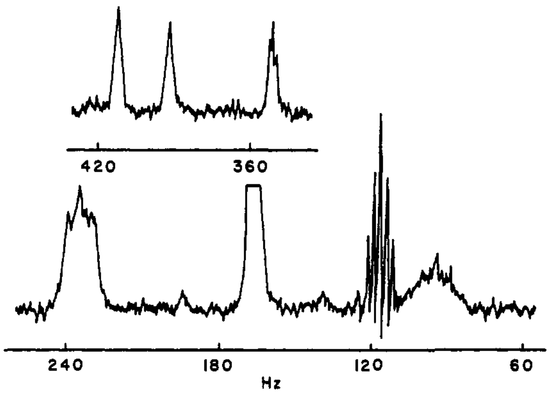

Figure 4. Pmr spectrum of $[Fe(TIM)(imid)_2](PF_6)_2$ in deuterioacetonitrile. Chemical shifts shown in Hz downfield from internal TMS.

is observed even though there is one less acetonitrile molecule per iron atom. Clearly the intensity of $\nu_{C\equiv N}$ is very sensitive to the character of the Fe-$NCCH_3$ bond which in turn must be subject to some "trans effect."

The pattern of peaks which describes the entire pmr spectrum of $[Co(TIM)(Cl)_2](PF_6)$ in deuterioacetonitrile[9] is contained within the spectra of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ and $[Fe(TIM)(imid)_2](PF_6)_2$ in that same solvent. The peak assignments for the TIM portion of the iron complexes follow those made previously[9] for $[Co(TIM)(Cl)_2]^+$ (see Figure 4 and Table II). Since the arguments supporting the assignments for TIM proton resonances have already been developed in detail, only the following summarizing comments are required here: (1) the diazapropane ring is "flexing" rapidly on the nmr time scale, (2) there is homoallylic coupling ($J \sim 2$ Hz) between the methyl protons and α protons, (3) the α protons and β protons give rise to a triplet and a broad multiplet, respectively, instead of a very complicated, many-peak pattern expected if the six-membered ring were in a fixed conformation[19] on the nmr time scale, (4) the components of the triplet of the α protons are broad, and (5) the methyl proton resonance is a very closely spaced triplet due to homoallylic coupling. For $[Fe(TIM)(CH_3CN)_2]^{2+}$ this coupling has been definitively established by double resonance experiments.

In the $[Fe(TIM)(imid)_2]^{2+}$ spectrum (Figure 4) the imidazole protons give rise to three equally intense resonances showing some multiplet character. These three resonances are assigned to the C-H protons of the imidazole and the multiplet nature of the peaks is ascribed to H-H coupling within the imidazole moiety. The fourth resonance expected (that for the N-H proton) is not found and presumably it is a very broad peak caused by the quadrupole moment of the nitrogen nucleus.[20] Imidazole alone in deuterioacetonitrile gives rise to a distinctly different pattern which is simply three peaks of relative area 2:1:1 (425, 462, and 516 Hz, respectively). A rapidly established tautomeric equilibrium accounts for the observed relative intensities instead of the 1:1:1:1 intensity ratio expected if imidazole had the bonding character represented by a unique valence bond structure featuring isolated double bonds. Neither the pattern of "free" imidazole nor of $[Fe(TIM)(imid)_2]^{2+}$ is changed in spectra arising from solutions containing both added imidazole and $[Fe(TIM)(imid)_2](PF_6)_2$. We conclude that the tautomeric equilibrium of imidazole is distinctly blocked upon coordination, and that, qualitatively speaking, the exchange of free and bound imidazole is "slow" on the nmr time scale.

For $[Fe(TIM)(CH_3CN)_2]^{2+}$ in deuterioacetonitrile the situation concerning the axial ligands is definitely different from that just discussed for $[Fe(TIM)(imid)_2]^{2+}$. The acetonitrile protons give rise to a resonance (117.5 Hz) which is superimposed upon those of the protonic impurities in the solvent (see Table II, and note that Figure 4 shows the nature of the resonances from the protonic impurities). Enrichment experiments have shown that the peak at 117.5 Hz in spectra of $[Fe(TIM)(CH_3CN)_2]^{2+}$ cannot be distinguished from the resonance due to small amounts of added acetonitrile. It is also to be noted that spectra of $[Fe(TIM)(CH_3CN)_2]^{2+}$ taken approximately 1.5 min after dissolving the $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in deuterioacetonitrile are identical with those taken from spectra several hours old. Finally, the spectrum of a sample of the bis(acetonitrile) complex recrystallized from deuterioacetonitrile shows a much less intense peak at 117.5 Hz than does the bis(acetonitrile) complex prepared from CH_3CN. Since it is rather unlikely that bound and free acetonitrile would exhibit the same chemical shift, we conclude that the bound acetonitrile of $[Fe(TIM)(CH_3CN)_2]^{2+}$ and the bulk acetonitrile are exchanging rapidly on the nmr time scale.

In view of the fact that substitution reactions of the sort just mentioned would be expected to proceed predominantly through a dissociative mechanism in low spin Fe(II) complexes,[6b,14,21] we suggest that the

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(19) W. H. Elfring, Jr., Thesis, University of Washington, 1972.

(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1966.

(21) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions, 2nd ed, Wiley, New York, N. Y., 1967, p 149.

foregoing observations concerning the two complexes may indicate that the Fe–$NCCH_3$ bond is weaker than the Fe–(imid) bond.

II. Axial Ligand Substitution. Imidazole for CH_3CN. Upon addition of imidazole to acetonitrile solutions of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, there is an immediate color change from burgundy red to blue, and $[Fe(TIM)(imid)_2](PF_6)_2$ can be obtained from the resulting solution (see Experimental Section). Further, the addition of acetic acid and water to an acetonitrile solution of $[Fe(TIM)(imid)_2](PF_6)_2$ affords the PF_6^- salt of the bis(acetonitrile) complex. With a view to elucidating the nature of the imidazole–acetonitrile substitution reactions we undertook pmr studies of deuterioacetonitrile solutions containing various amounts of imidazole, $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, and $[Fe(TIM)(imid)_2](PF_6)_2$. As indicated in the discussion below, the number and the relative areas of the TIM methyl proton resonances provide the most definitive data concerning the substitution reactions.

The nature of the equilibria involving the substitution reactions is indicated by a series of spectra taken of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in deuterioacetonitrile solution to which various amounts of imidazole were succesively added. Upon the addition of a trace amount of imidazole, the 158.5-Hz peak diminishes relative to the spectrum of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ with no added imidazole, a new peak appears at 164 Hz, and the relative sharpness of the triplet centered at 244 Hz is lost However, the relative area of the resonances in the 244-Hz region retains a value of 8 (7.9) compared to 12, the number assigned to the sum of the areas of the 164- and 158.5-Hz resonances. After the addition of one imidazole per Fe(II) present, the spectrum may be described as follows relative to the one just mentioned. The peak at 164 Hz has increased in area, the peak at 158.5 Hz has diminished, and a shoulder on the downfield side of the 164-Hz resonance is found at about 167 Hz. The area ratio of the 158.5-Hz peak to the 164 peak (plus its shoulder) is approximately 1:9. The components of the triplet previously centered at 244 Hz have completely lost their individuality and now the peaks are centered at about 237 Hz. The ratio of the sum of the areas of the peaks at 158.5, 164, and 167 Hz to the area of the broad resonance centered at 237 Hz is close to the expected 12:8 (found 12:7.5). Three new peaks are present in the spectrum at 350, 392, and 413 Hz.

Upon addition of 2 mol of imidazole per mol of Fe(II) present, the spectrum observed is essentially identical with that of the bis(imidazole) complex as depicted in Figure 4, except for the former there is a greater magnitude for the peak at 117.5 Hz (assigned to free acetonitrile and superimposed upon the resonances of the protonic impurities in the solvent; *vide supra*). Finally, after addition of excess imidazole the characteristic resonances of free imidazole are observed in addition to the spectrum shown in Figure 4.[22]

From the foregoing data it can be concluded that a diamagnetic complex, most likely $[Fe(TIM)(imid)(CH_3CN)]^{2+}$, but conceivably $[Fe(TIM)(imid)]^{2+}$, is present in the system along with $[Fe(TIM)(CH_3CN)_2]^{2+}$ and $[Fe(TIM)(imid)_2]^{2+}$. This new species, which is in equilibrium with the other two, exhibits resonances at 164 Hz (methyl protons of TIM), about 237 Hz (α protons), and, 350, 392, and 413 Hz (imidazole C–H protons). The β protons have a very broad resonance centered between 90 and 140 Hz and occurring in the region with the protonic impurities of the solvent. The reactions involved in the proposed equilibria are represented in eq 1, where X = acetonitrile and Y = imidazole. No quantitative data are available concerning the *rates* of the various reactions, forward and reverse, but they all must be reasonably rapid, in view of the observations that the systems reach equilibrium in the time required to prepare the solutions and to take the first pmr spectrum.

In order to determine the relative tendency of the proposed $[Fe(TIM)(imid)(CH_3CN)]^{2+}$ to form *vs.* that of $[Fe(TIM)(imid)_2]^{2+}$, K_3 was calculated from the known amounts of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ and $[Fe(TIM)(imid)_2](PF_6)_2$ used to prepare a specified volume of an acetonitrile solution and from the relative area of the 158.5-Hz peak to that of the sum of the 164- and 167-Hz peaks (see eq 2).

$$K_3 = 7 \pm 1 = K_1/K_2$$

It is seen that the tendency to form the mixed complex is greater than that to form $[Fe(TIM)(imid)_2]^{2+}$ by approximately one order of magnitude. However, it must also be noted that *both* K_1 and K_2 are large because free imidazole is not seen in the system until the imid : Fe ratio is greater than 2.

III. $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$. When carbon monoxide is bubbled through an acetonitrile solution of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ a color change from burgundy red to orange is observed and the salt, $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$, is obtained upon the addition of ethanol to the orange solution. The formation of this carbonyl complex must be a reversible reaction, as is indicated by the facts that acetonitrile solutions of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ left exposed to the atmosphere for about 18 hr change color from orange to burgundy red, and that $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ is readily obtained fom the red solution by adding ethanol. The reversible binding of CO is also characteristic of other Fe(II) complexes including three quite diverse species, one of which contains aminotroponimine,[23] one of which is derived from an aliphatic pentaamine,[24] and one of which contains diphenylglyoxime.[6b] Contrary to its behavior in acetonitrile solutions, solid samples of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ do not lose carbon monoxide upon standing (even at about 0.2 Torr for 12 hr) and have indefinitely long shelf lives.

The infrared spectrum of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ exhibits bands characteristic of the TIM ligand and of bound acetonitrile As can be seen in Figure

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(22) It was previously noted that the presence of free imidazole promotes some, as yet, uncharacterized reaction of $[Fe(TIM)(imid)_2](PF_6)_2$ in acetonitrile solution. The solution used for the pmr study, as described in the sentence beginning, "Finally, after. . ." shows no change for 24 hr. Thus, at least for the first 24 hr, we feel that the system's characteristics are determined solely by the reactions shown in eq 1 and 2. Spectra obtained from solutions made from 1:1 mole ratios of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ and $[Fe(TIM)(imid)_2](PF_6)_2$ are identical with those obtained from solutions containing 1:1 mole ratios of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ and imidazole and are time independent for at least 4 months.

(23) W. R. McClellan and R. E. Benson, *J. Amer. Chem. Soc.*, **88**, 5165 (1966).

(24) L. R. Melby, *Inorg. Chem.*, **9**, 2186 (1970).

3, there are two bands present in addition to those attributed to the TIM ligand, acetonitrile, and PF_6^-. These two bands (2031 and 1984 cm^{-1}) are also present in spectra taken of the complex dissolved in acetonitrile but the 1984-cm^{-1} absorption is a shoulder on the 2031-cm^{-1} peak rather than a distinct maximum as in Figure 3. The 2031- and 1984-cm^{-1} absorptions are assigned to a C≡O stretching motion[6b,23,24] with the lower energy, lower intensity band attributed to a $\nu_{^{13}C\equiv O}$ satellite.[25]

The Mössbauer spectrum of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ exhibits isomer shift and ΔE_q values well within the ranges expected for low spin Fe(II) complexes (*vide supra*). The fact that the isomer shift of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ is 0.40 mm/sec, whereas that of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ is 0.62 mm/sec, would seem to indicate that more d-π delocalization onto the ligands is occurring in the former complex. However, the relatively high C≡O stretching frequency suggests that the Fe–CO bond in $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ has considerably less π character than is observed in many other carbonyl complexes (*e.g.*, $[Cr(dien)(CO)_3]$).[26] In fact, 2031 cm^{-1} is higher than $\nu_{C\equiv O}$ for the three Fe^{II}–CO complexes mentioned above.[6b,23,24]

The similarity of the pmr spectrum of deuterionitromethane solutions of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ to those of other TIM complexes (*i.e.*, $[Ni(TIM)]^{2+}$, $[Co(TIM)(Cl)_2]^+$, and $[Fe(TIM)(CH_3CN)_2]^{2+}$) makes the assignment and interpretation of the spectrum quite straightforward: TIM methyl protons, 156 Hz; TIM α protons, 244 Hz; TIM β protons, 136 Hz (broad); acetonitrile methyl, 136 Hz (sharp). The ratio of the relative area of the α-proton resonances to the area of all the other proton peaks is found to be within experimental errror of the expected 8:19. The spectrum remains unchanged for solutions retained in capped nmr tubes up to at least 7 days and there are no "extra" peaks to be found in the spectrum. In particular, it is to be noted that the peaks of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ dissolved in deuterionitromethane are absent. We conclude that $[Fe(TIM)(CH_3CN)(CO)]^{2+}$ is the only complex present in deuterionitromethane.

In contrast to the behavior just noted, the pmr spectrum of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ in deuterioacetonitrile clearly shows the presence of two Fe(TIM) complexes. The spectrum of the complex in this solvent (prepared from the salt as rapidly as possible, placed in an nmr tube, and capped) exhibits the resonances listed in the second row of Table II, the two most intense resonances of the bis(acetonitrile) complex and a peak at 132 Hz. Because the ratio of the relative area of the TIM methyl peak at 147.5 Hz to the peak at 158.5 Hz is about 5:1, it must be concluded that the 147.5-Hz peak (Table II) is due to the mixed-ligand complex, rather than to $[Fe(TIM)(CO)_2]^{2+}$.

Spectra taken over a period of hours of the $[Fe(TIM)(CH_3CN)(CO)]^{2+}$ solution contained in the capped nmr tube show relatively small changes except for the 132-Hz peak. Over a period of 1 hr it steadily diminishes in intensity and finally vanishes, whereas, concomitantly, the resonance at 117.5 Hz (ascribed to free acetonitrile and located among the peaks due to protonic impurities in deuterioacetonitrile) grows and finally remains unchanged. We assign the 132-Hz peak to the protons of *bound* acetonitrile of $[Fe(TIM)(CH_3CN)(CO)]^{2+}$ and account for the intensity changes by postulating a "slow" exchange of bound for free acetonitrile in the deuterioacetonitrile solution. Our assignment is supported by observations made with $[Fe(TIM)(CD_3CN)(CO)](PF_6)_2$: pmr spectra of this deuterioacetonitrile complex *do not* exhibit the 132-Hz peak nor the growth of the 117.5-Hz peak. In light of (1) the "rapid" dissociation of acetonitrile from $[Fe(TIM)(CH_3CN)_2]^{2+}$ compared to the "slow" dissociation of acetonitrile from $[Fe(TIM)(CH_3CN)(CO)]^{2+}$ and (2) the very weak $\nu_{C\equiv N}$ bands in the infrared spectrum of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ compared to the moderate intensity bands of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$, we conclude that significant differences related to the "trans" effect exist in the Fe–$NCCH_3$ linkages of these two complexes.

The reversible character of the CH_3CN–CO substitution reactions is readily demonstrated using pmr and infrared spectroscopy. If a sample tube containing a deuterioacetonitrile solution of $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ is purged with nitrogen for several minutes, there is then a distinct drop in the intensity of the 147.5-Hz peak in the pmr spectrum and a concomitant increase in the 158.5-Hz resonance. As expected, repeating the process results in further diminishing and growth of the two peaks, respectively. It seems clear that these results and those mentioned earlier are consistent with an equilibrium reaction of the sort shown in eq 3.

$$CH_3CN + [Fe(TIM)(CH_3CN)(CO)]^{2+} \rightleftharpoons CO + [Fe(TIM)(CH_3CN)_2]^{2+} \quad (3)$$

Infrared spectra of acetonitrile solutions containing $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ and various amounts of carbon monoxide also are readily interpreted in terms of eq 3. Thus, when solutions (of the bis(acetonitrile) complex) through which carbon monoxide has been bubbled are exposed to the atmosphere and then spectra are taken at various time intervals, the peak at 2031 cm^{-1} is seen to diminish monotonically with time and finally to vanish altogether.

The reversible character of the acetonitrile–carbon monoxide substitution reactions taken with the clear evidence that a substantial "trans" effect is operating in the complexes suggests that the Fe(TIM) moiety is a specially suitable vehicle for studying the detailed kinetics and thermodynamics of axial ligation reactions involving carbon monoxide and/or a variety of Lewis bases. We anticipate further work in this realm.

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(25) The $\nu_{^{13}CO}/\nu_{^{12}CO}$ ratio observed in the Nujol mull spectrum is 0.977 ± 0.001, a value consistent with that reported by G. Bor, *Inorg. Chim. Acta*, 3, 191 (1969).

(26) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972.