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Kinetics of Reversible Binding of Carbon Monoxide and Benzyl Isocyanide to Ferrous Dimethylglyoxime Complexes

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Substitution reactions of ferrous dimethylglyoxime complexes $L_2Fe(DMGH)_2$, L = methylimidazole, pyridine, carbon monoxide, and benzyl isocyanide, proceed by a dissociative mechanism in nonaqueous solvents. Both carbon monoxide and benzyl isocyanide are substantially more inert in the glyoxime complexes than in corresponding porphyrin and phthalocyanine systems. The benzyl isocyanide ligand exerts a large trans-delabilizing effect on methylimidazole and pyridine, methylimidazole being 10^3 times more inert trans to BzlNC than when trans to CH_3Im. Syntheses and NMR and visible spectra are reported for the complexes. The lability of ligands in these tetragonal low-spin iron(II) complexes is shown to depend to a large extent on both the in-plane cis ligand and the axial trans ligand.

Introduction

Several years ago Williams[1,2] demonstrated that simple iron(II) glyoxime complexes mimic hemoglobin and myoglobin in their ability to reversibly bind carbon monoxide. Vaska[3] has recently reported kinetics for reversible CO binding to iron(II) diphenylglyoxime complexes in chlorobenzene solution. We have undertaken a study of the kinetics of axial ligand substitution reactions of iron(II) dimethylglyoxime complexes involving reversible binding of both CO and alkyl isocyanides for comparison with similar studies on other heme models.[4-8] These studies are designed to explore the similarities and differences between various Fe(II) complexes which mimic the heme group in order to determine those features of the porphyrin ligand which give rise to the binding characteristics of the heme group in terms of both stability (equilibria) and lability (kinetics).

Experimental Section

Materials. Iron(II) acetate[9] was prepared by refluxing iron powder (Anachemia) with glacial acetic acid (Anachemia) under nitrogen. 1-Methylimidazole (CH_3Im) (Aldrich) and pyridine (py) (Fisher) were distilled from KOH prior to use. Carbon monoxide was Matheson CP grade. Dimethylglyoxime (Analar) and benzyl isocyanide (Aldrich) were used without further purification. Toluene was freshly distilled from CaH_2 before use.

Physical Measurements. Visible spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were obtained as Nujol mulls with a Beckman IR-12. NMR spectra were obtained on a Varian HA-100 and EM-360 spectrometer using deuteriochloroform as solvent with 1% TMS as an internal standard. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz.

Syntheses. Unless stated otherwise all syntheses were carried out under a nitrogen atmosphere.

$Fe(DMGH)_2(py)_2$. Dimethylglyoxime (11 g, 0.095 mol) was dissolved in 400 ml of methanol containing pyridine (49 g, 0.62 mol). Iron(II) acetate (8 g, 0.045 mol) was added. After 10 min the solution was filtered and the brown-red solid washed with 100 ml of 10% pyridine solution in methanol (v/v) and 100 ml of 30–60 °C petroleum ether. The product was dried in vacuo; yield 16.09 g (83%). Anal. Calcd for $C_{18}H_{24}N_6O_4Fe$: C, 48.66; H, 5.44; N, 18.92. Found: C, 48.23; H, 4.34; N, 18.97. The compound was not sufficiently soluble to obtain an NMR spectrum.

$Fe(DMGH)_2(CH_3Im)_2$ was prepared by a similar procedure. Anal. Calcd for $C_{16}H_{26}N_8O_4Fe$: C, 42.68; H, 5.82; N, 24.89. Found: C, 42.34; H, 5.93; N, 24.99. The compound was not sufficiently soluble to obtain an NMR spectrum.

$Fe(DMGH)_2(py)(CO)$. $Fe(DMGH)_2(py)_2$ (1.07 g, 0.0024 mol) in 200 ml of dichloromethane was stirred 12 h under CO in the dark. The solution was concentrated to 50 ml by bubbling CO through the solution and 150 ml of petroleum ether (bp 100–120 °C) was added while the CO bubbling was maintained. The solution was filtered in air and the brown solid washed with 20 ml of methanol and 100 ml of petroleum ether (bp 30–60 °C). The product was dried in vacuo; yield 0.50 g (57%). Anal. Calcd for $C_{14}H_{19}N_5O_5Fe$: C, 42.77; H, 4.87; N, 17.81. Found: C, 42.98; H, 5.21; N, 17.76. NMR: δ 2.13 (12 H), 7.3 (2 H), 7.65 (1 H), 8.68 (2 H).

$Fe(DMGH)_2(CH_3Im)(CO)$ was prepared by a similar procedure. Anal. Calcd for $C_{13}H_{20}N_6O_5Fe$: C, 39.41; H, 5.09; N, 21.21. Found: C, 39.45; H, 5.15; N, 21.43. NMR: δ 2.14 (12 H), 3.65 (3 H), 6.76 (1 H), 7.05 (1 H), 7.54 (1 H).

$Fe(DMGH)_2(py)(BzlNC)$. $Fe(DMGH)_2(py)_2$ (1.09 g, 0.0025 mol) was added to 200 ml of dichloromethane solution containing benzyl isocyanide (0.40 g, 0.0034 mol). The solution was stirred under nitrogen for 2 h and concentrated, and petroleum ether (bp 30–60 °C) was added. After filtering the light brown solid was washed with 100 ml of 30% benzene in 30–60 °C petroleum ether (v/v) and dried in vacuo; yield 0.97 g (81%). Anal. Calcd for $C_{21}H_{26}N_6O_4Fe$: C, 52.30; H, 5.43; N, 17.42. Found: C, 52.49; H, 5.36; N, 16.88, NMR: δ 2.14 (12 H), 4.67 (2 H), 7.1–7.4 (~7 H), 7.56 (1 H), 8.68 (2 H).

$Fe(DMGH)_2(CH_3Im)(BzlNC)$ was prepared by a similar procedure. NMR: δ 2.16 (12 H), 3.57 (3 H), 4.78 (2 H), 6.66 (1 H), 7.0–7.5 (~7 H).

$Fe(DMGH)_2(BzlNC)_2$. $Fe(DMGH)_2(py)(BzlNC)$ (0.31 g, 0.000 64 mol) was added to 100 ml of chloroform solution of benzyl isocyanide (0.15 g, 0.0013 mol). The solution was refluxed for 23 h under nitrogen and evaporated to dryness, and the residue was recrystallized from benzene. The crystals were washed with 30% benzene in 30–60 °C petroleum ether (v/v) and dried in vacuo; yield 0.25 g (75%). Anal. Calcd for $C_{24}H_{28}N_6O_4Fe$: C, 55.39; H, 5.42; N, 16.15. Found: C, 55.26; H, 5.51; N, 16.27. NMR: δ 2.13 (12 H), 4.71 (4 H), 7.1–7.4 (~10 H).

Kinetics. Reactions were carried out under N_2 in thermostated 1-cm quartz or Pyrex optical cells and followed with a Cary 14 spectrophotometer.

For the reactions of $Fe(DMGH)_2(L)_2$, L = CH_3Im or py, with CO or benzyl isocyanide, 0.1 ml of a concentrated solution of the complex ($\sim 5 \times 10^{-3}$ M) was quickly prepared and syringed into a serum-capped chloroform solution (3 ml) over 760 Torr CO or containing 10^{-1}–10^{-2} M benzyl isocyanide. Substitution reactions of $Fe(DMGH)_2(L)(X)$, L = CH_3Im or py and X = CO or BzlNC, and of $Fe(DMGH)_2(BzlNC)_2$ with amines (CH_3Im or py) were carried out in neat amine solution by syringing ~0.1 ml of a concentrated amine solution of $Fe(DMGH)_2(L)(X)$ ($\sim 5 \times 10^{-3}$ M) into 3 ml of the thermostated solvent in the spectral cell.

The reaction of $Fe(DMGH)_2(L)(BzlNC)$, L = CH_3Im or py, with BzlNC was carried out by dissolving the complex in a toluene solution containing benzyl isocyanide (10^{-1}–10^{-2} M).

Results

Complexes and assumed intermediates in the dissociative reactions in the $Fe(DMGH)_2$ system are summarized in Figure 1. All of the iron(II) glyoxime complexes prepared in this work have intense absorption in the visible region (Table I).[10] The py derivatives typically show two maxima while the CH_3Im derivatives give only a single maximum in the visible region. The complexes are all stable in the solid state. In chloroform solution $Fe(DMGH)_2(py)_2$ and $Fe(DMGH)_2(CH_3Im)_2$ are oxidized rapidly, the rate of oxidation being slowed significantly in the presence of excess ligand. The air

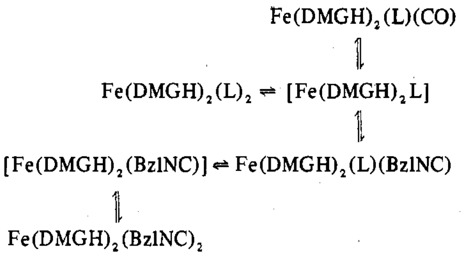

Figure 1. Reaction scheme.

Table I. Visible Spectral Data for Iron(II) Dimethylglyoxime Complexes

	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})
Fe(DMGH)$_2$(py)$_2$[a]	508 (6.9), 417 (6.3)
Fe(DMGH)$_2$(CH$_3$Im)$_2$[b]	531 (6.9)
Fe(DMGH)$_2$(py)(CO)[c]	389 (3.8), 350 (3.4)
Fe(DMGH)$_2$(CH$_3$Im)(CO)[c]	385 (4.0)
Fe(DMGH)$_2$(py)(BzlNC)[c]	444 (6.1), 345 (4.5)
Fe(DMGH)$_2$(CH$_3$Im)(BzlNC)[c]	445 (5.9)
Fe(DMGH)$_2$(BzlNC)$_2$[d]	392 (6.0)

[a] Pyridine solution. [b] 1% 1-methylimidazole solution in chloroform. [c] Chloroform solution. [d] Toluene solution.

stability of the complexes in chloroform solution is in the order Fe(DMGH)$_2$(L)$_2$ < Fe(DMGH)$_2$(L)(CO) < Fe(DMGH)$_2$(L)(BzlNC) < Fe(DMGH)$_2$(BzlNC)$_2$. The product of oxidation under the conditions of the kinetics experiments shows no absorption maximum in the visible region.

The carbonyl and isocyanide complexes are all photosensitive. Solutions of the complexes containing excess amine display a form of photochromism described previously for benzyl isocyanide complexes of ferrous phthalocyanine.[6] The rate of substitution of the isocyanide or CO by amines is markedly increased in the presence of visible light and adequate precautions were exercised in kinetic experiments. The facile photosubstitution reactions proved convenient in some cases as a means of driving the reactions to completion.

Amine Dissociation from the Fe(DMGH)$_2$(L)$_2$ Complexes. The reactions of the (L)$_2$Fe(DMGH)$_2$ complexes, L = CH$_3$Im and py, were carried out in chloroform solution owing to the insolubility of the complexes in toluene and chlorobenzene used in previous studies on other systems.[3,5] Typical spectral changes on addition of benzyl isocyanide to a solution of Fe(DMGH)$_2$(CH$_3$Im)$_2$ are given in Figure 2. Problems due to oxidation are minimal for degassed fresh solutions. The reactions proceed cleanly to completion. Analysis of the absorbance data at the maximum of the Fe(DMGH)$_2$(CH$_3$Im)$_2$ complex (530 nm) or at the maximum of the Fe(DMGH)$_2$(CH$_3$Im)(BzlNC) complex (445 nm) gives linear log plots over 3 half-lives and $k_{obsd} = 6.6 \times 10^{-4}$ s^{-1}. The corresponding reaction of the CH$_3$Im complex with CO also proceeds smoothly with a decrease in absorbance at 530 nm and a corresponding increase in absorbance at 385 nm. Again analysis at the two wavelengths is in good agreement and the value of $k_{obsd} = 7.2 \times 10^{-4}$ s^{-1} is within experimental error of that obtained from the displacement with BzlNC. The independence of the rate constant with respect to the nature of the entering reagent is good evidence for the limiting dissociative mechanism assumed for this system and therefore the two values of k_{obsd} were averaged to give the rate constant in Table II taken as the dissociative rate constant for loss of CH$_3$Im from the Fe(DMGH)$_2$(CH$_3$Im)$_2$ complex.

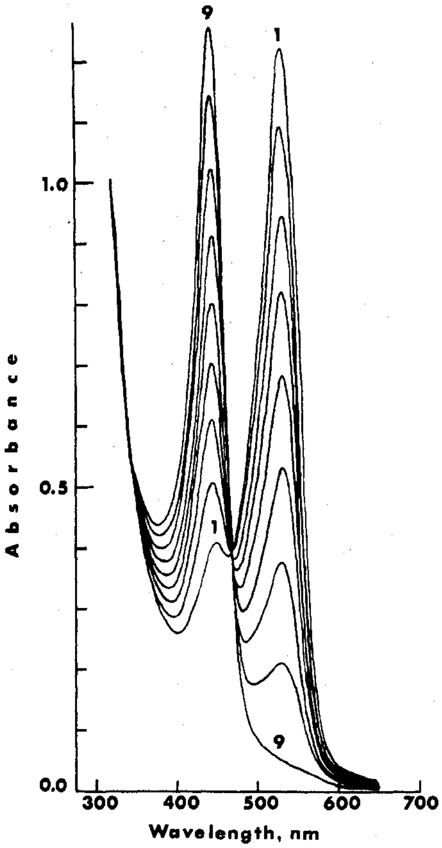

Figure 2. Spectral changes with time for the reaction Fe(DMGH)$_2$(CH$_3$Im)$_2$ + BzlNC = Fe(DMGH)$_2$(CH$_3$Im)(BzlNC) + CH$_3$Im in CHCl$_3$ at 10 °C.

The rates of the corresponding reactions of Fe(DMGH)$_2$(py)$_2$ complex are too fast for the spectra to be scanned at 10 °C and were therefore followed by the decrease in absorbance at 510 nm due to the Fe(DMGH)$_2$(py)$_2$ complex. Log plots linear over 3 half-lives were obtained and the derived rate constants for CO, $k_{obsd} = 6.8 \times 10^{-3}$ s^{-1}, and for BzlNC displacement, $k_{obsd} = 7.2 \times 10^{-3}$ s^{-1}, were averaged to give the value of the rate of dissociation of pyridine from the Fe(DMGH)$_2$(py)$_2$ complex. To verify that these reactions proceed cleanly, in one case the reaction with BzlNC was carried out at 0 °C where the spectrum could be scanned

Table II. Kinetic Data for the Reactions of Iron(II) Dimethylglyoxime Complexes[a]

	10^4k, s^{-1}							
	10 °C	45 °C	55 °C	65 °C	75 °C	85 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Fe(DMGH)$_2$(py)py[b]	70							
Fe(DMGH)$_2$(CH$_3$Im)CH$_3$Im[b]	6.9							
Fe(DMGH)$_2$(py)CO[c]		2.7	9.2	34 (2)	140		29 (2)	16 (7)
Fe(DMGH)$_2$(CH$_3$Im)CO[d]			2.5	9.3 (5)	30	85	28 (1)	10 (3)
Fe(DMGH)$_2$(py)BzlNC[c]				4.6 (9)				
Fe(DMGH)$_2$(CH$_3$Im)BzlNC[d]				3.1 (3)				
Fe(DMGH)$_2$(BzlNC)py[e]				3.41 (7)	12.4	38.2	28 (1)	9 (3)
Fe(DMGH)$_2$(BzlNC)CH$_3$Im[e]				0.199 (4)	0.718	2.82	31 (2)	12 (7)
Fe(DMGH)$_2$(BzlNC)BzlNC[d]				0.03 (1)				

[a] Leaving ligands without parentheses. [b] Chloroform solution. [c] Pyridine solution. [d] 1-Methylimidazole solution. [e] Toluene solution.

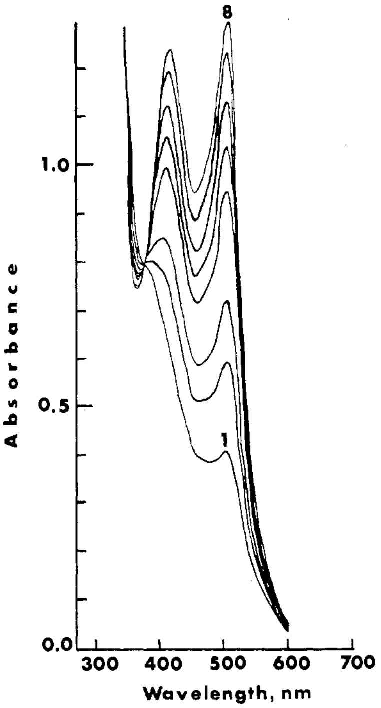

Figure 3. Spectral changes with time for the reaction $Fe(DMGH)_2(py)(CO) + py = Fe(DMGH)_2(py)_2 + CO$ in pyridine at 45 °C.

between 550 and 350 nm. In this case three excellent isosbestic points were observed and the reaction was characterized by a decrease in absorbance at 510 and 420 nm and an increase in absorbance at 440 nm, consistent with the assumed reaction.

Carbon Monoxide Dissociation from the $Fe(DMGH)_2(L)(CO)$ Complexes. Limiting rates of CO dissociation from the complexes were conveniently carried out in neat 1-methylimidazole or pyridine as solvent. Typical spectral changes are given in Figure 3. The corresponding reaction of the 1-methylimidazole complex also proceeds smoothly with an isosbestic point at 428 nm. In all cases the reactions proceed to completion and log plots were linear over 3 half-lives. The rate constants are given in Table II along with activation parameters obtained from Arrhenius plots.

Benzyl Isocyanide Dissociation from the $Fe(DMGH)_2(L)(BzlNC)$ Complexes. As with CO dissociation, dissociation of BzlNC from the complexes was followed in neat pyridine or 1-methylimidazole. Owing to the much slower reactions of the isocyanide complexes, problems due to the slow oxidation of the products $Fe(DMGH)_2(L)_2$ become important here and the interpretation of the spectral data is not straightforward.

In the case of 1-methylimidazole, while the decrease in absorbance at 445 nm due to the $Fe(DMGH)_2(CH_3Im)(BzlNC)$ proceeds smoothly, the expected corresponding increase in absorbance at 530 nm due to $Fe(DMGH)_2(CH_3Im)_2$ was observed only in the first half-life of the reaction after which an eventual decrease in absorbance at this wavelength was observed. These spectral changes are consistent with initial formation of $Fe(DMGH)_2(CH_3Im)_2$ which subsequently oxidizes in a side reaction at a rate comparable to the rate of the substitution reaction. Analysis of the spectral data at 445 nm gives excellent linear log plots over more than 2 half-lives. Since the oxidized species and the $Fe(DMGH)_2(CH_3Im)_2$ product have similar small absorbances at the 445-nm wavelength, the subsequent oxidation side reaction does not seriously affect the 445-nm analysis. These interpretations were further verified by making use of the ready photodissociation of the benzyl isocyanide ligand. Placing a 1-methylimidazole solution of the $Fe(DMGH)_2(CH_3Im)(BzlNC)$ complex in strong light results in a complete conversion of the complex to the $Fe(DMGH)_2(CH_3Im)_2$ within minutes. This solution also undergoes oxidation on standing at 65 °C at a rate comparable to the thermal substitution reaction.

For the pyridine case, analysis at 445 nm was not possible since the $Fe(DMGH)_2(py)_2$ has a peak in this region. Furthermore in the case of pyridine, the thermal reaction clearly proceeds to only ~80% completion at 65 °C under the conditions of the kinetics. Analysis of the spectral data was therefore carried out at 510 nm by using known extinction coefficients for the product. Data were plotted only for the first half-life where contributions from oxidation and back-reaction were small.

Amine Dissociation from the $Fe(DMGH)_2(L)(BzlNC)$ Complexes. Rates of L dissociation from the $Fe(DMGH)_2(L)(BzlNC)$ complex were measured in toluene solution by displacement with excess benzyl isocyanide to give the $Fe(DMGH)_2(BzlNC)_2$ complex. Clean isosbestic points and linear log plots were obtained. There is no significant oxidation of the isocyanide complexes even at elevated temperatures under the conditions of the experiment. The derived rate constants from analysis at 445 or 390 nm in both the pyridine and 1-methylimidazole cases are in good agreement and the rate constants and activation parameters are given in Table II.

Benzyl Isocyanide Dissociation from the $Fe(DMGH)_2(BzlNC)_2$ Complex. Reaction of the $Fe(DMGH)_2(BzlNC)_2$ complex in neat pyridine or 1-methylimidazole was found to be exceedingly slow in the dark. In the case of 1-methylimidazole, reaction at 65 °C is much slower than the corresponding rate of reaction of the $Fe(DMGH)_2(CH_3Im)(BzlNC)$ complex. The half-life for the reaction is of the order of 3 days. Spectra of solutions of the complex in 1-methylimidazole showed no evidence for formation of either $Fe(DMGH)_2(CH_3Im)(BzlNC)$ as evidenced by the absorbance at 445 nm or $Fe(DMGH)_2(CH_3Im)_2$ as evidenced by absorbance at 530 nm. Under the conditions of the experiment, these complexes would be expected to be oxidized. If we assume that the rate-determining step in the oxidation is the rate of dissociation of BzlNC from the diisocyanide complex, then analysis of the decrease in absorbance at 390 nm will correspond to the rate of loss of this complex. Analysis at 390 nm gives a very rough straight line over 1 half-life from which k_{obsd} is estimated to be $3 \times 10^{-6}\ s^{-1}$. Both of the expected products are detected at room temperature and at 65 °C on photochemical reaction of the complex.

Discussion

Spectral Data. The visible spectral data are collected in Table I. The assignments of the bands for the amine complexes were reported previously.[2,11,12] The longer wavelength band was assigned to charge transfer from iron to glyoxime and the shorter wavelength band to charge transfer from iron to pyridine. The methylimidazole complexes do not show the second band presumably because charge transfer to imidazole occurs at higher energy, in the UV. The band at 530 nm in the $(CH_3Im)_2Fe(DMGH)_2$ is consistent with methylimidazole being a better σ donor than pyridine. On replacement of the σ donor by a π acceptor (CO or BzlNC) the long-wavelength band shifts to higher energy as expected. The shift is greater with CO than with BzlNC consistent with the idea that CO is a better π acceptor than BzlNC.[13] It is seen that two isocyanide ligands have roughly the effect of one CO.

The NMR data for the complexes given in the Experimental Section are surprisingly insensitive to the nature of the complex. The positions of the methyl resonances of the glyoxime ligand are essentially the same in all complexes. The positions of the resonances due to axial ligands are virtually

Table III. CO and NC Stretching Frequencies

	ν(CO), cm^{-1}		ν(NC) cm^{-1}		
L trans	CH_3Im	py	CH_3Im	py	BzlNC
Fe(DMGH)$_2$[a]	1978	1985	2141	2145	2167
Fe(DPGH)$_2$[b]		1996			
FePc	1995[c]	1995[c]	2160[d]		2180[d]
Fe(por)	(1970)[e]		(2149)[f]		

[a] This work. [b] Reference 3. [c] Unpublished results in $CHCl_3$ solution. [d] Reference 7. [e] Protoheme; J. H. Wang, A. Nakahara, and E. B. Fleischer, *J. Am. Chem. Soc.*, 80, 1109 (1958). [f] Unpublished results; L = piperidine, tetraphenylporphyrin.

the same as those for the free ligands. This result stands in sharp contrast to corresponding NMR spectra of porphyrin, phthalocyanine,[14] TIM,[15,16] and TAAB[17] systems where a marked upfield shift of axial ligand resonances occurs on coordination and in TIM and TAAB where the in-plane resonances shift markedly with changes in the axial ligands. The insensitivity of the glyoxime system resonances suggests that there is little or no ring current effect here and that changes at iron brought about by axial ligands are not transmitted to the methyl groups of the glyoxime ligand.

Infrared stretching frequencies for CO and BzlNC complexes in the DMGH system and analogous systems are given in Table III. If we take the position of the CO stretch as indicative of the ability of different systems to π bond to axial ligands, the DMGH system is seen to be slightly poorer than a porphyrin but considerably better than the phthalocyanine system. The CO and NC stretches in the imidazole complexes occur at lower wavenumber than those for the corresponding pyridine complexes, consistent with the better trans σ donor enhancing back-donation to CO or BzlNC. In all systems reported, the Fe(BzlNC)$_2$ complex absorbs at higher wavenumber than the free ligand while in the LFe(BzlNC) complexes the band occurs at lower wavenumber than the free ligand. It is generally true that when BzlNC acts as a σ donor, ν_{NC} is shifted to higher wavenumber (the lone pair is in a weakly antibonding orbital) while π back-donation results in the opposite effect.[18] One expects the importance of the π bonding to decrease when the two BzlNC ligands are trans to each other.

Kinetics and Mechanism. Vaska has previously shown that the reactions of pyridine complexes of diphenylglyoxime, (py)$_2$Fe(DPGH)$_2$, in chlorobenzene with CO proceed by a dissociative mechanism. The invariance of the rates of the reactions

$$L_2Fe(DMGH)_2 + X = LFe(DMGH)_2X + L \qquad X = CO \text{ or } BzlNC$$

to both the concentration and nature of the entering group is strong evidence for a dissociative mechanism present in the DMGH system as well. Rates of reaction of CO and BzlNC complexes were carried out in pure pyridine or methylimidazole. Thus it was not possible to vary the concentration of the entering group in these cases. The DMGH and DPGH systems were investigated in different solvents. The differences between the data for the two systems are small. If we ignore solvent effects, we conclude that the DMGH system has a more labile pyridine and a more inert CO compared to the DPGH system. This is the expected order based on the greater inductive effect of methyl compared to that of phenyl. The more basic DMGH system would bind bases more poorly and π-acid ligands better. The CO stretching frequencies for the two systems are in agreement with greater π back-bonding to CO in the DMGH system.

It is seen from the rate constants in the DMGH systems that the inertness of axial ligands trans to an amine increases in the order py < CH_3Im < CO < BzlNC. In this system CO is approximately 3 times more labile than BzlNC. This result may be compared with phthalocyanine where CO is 10^3 times more labile than BzlNC and hemoglobin where CO is one-tenth as labile as ethyl isocyanide. These results are fully consistent with the IR data which indicate a π-bonding ability of porphyrin > DMGH ≫ Pc. Thus the relative inertness of isocyanides vs. CO may be understood in terms of the ability of the in-plane ligand to modify the axial π bonding of the iron. The above order also correlates well with the qualitative ease of oxidation of the three systems, the porphyrins being extremely air sensitive, the phthalocyanines stable in air, and the DMGH intermediate. Since it has been shown that the ability of metal complexes to reversibly bind O_2 also correlates with the redox potential,[19] we propose that the above order for CO binding will also reflect at least qualitatively the O_2 binding ability of these systems.

Trans Effects. The relative trans effect of pyridine and methylimidazole on BzlNC and CO lability is similar (both CO and BzlNC are more inert trans to CH_3Im) but the effect is larger in the CO case. These results are similar to those for the phthalocyanine system.[5-7] The enhanced binding of CO and BzlNC trans to methylimidazole compared with pyridine is also reminiscent of enhanced binding of O_2 trans to these ligands in cobalt[20,21] and iron porphyrins,[22] despite the fact that O_2 binding is thought to involve formal oxidation of the metal while CO does not. Factors favoring π back-donation should also favor electron transfer from metal to ligand. The differences are primarily a matter of extent. Basolo et al.[23] reported O_2 approximately 4 times more inert trans to methylimidazole compared to pyridine in an iron porphyrin system. In the Pc and DMGH systems CO is about 4 times more inert trans to CH_3Im compared to pyridine.

The most remarkable effects observed in the DMGH system are the trans effects of BzlNC. π-Acceptor ligands are generally considered strong trans directors, based on their effects in square-planar complexes proceeding by S_N2 mechanisms. In octahedral or tetragonal systems there is little evidence on the trans effect of isocyanides. Isocyanides are considered nonlabilizing groups in metal carbonyl complexes.[24] It is seen in the dimethylglyoxime system that both pyridine and methylimidazole are about 10^4 times more inert trans to BzlNC than they are in the corresponding (py)$_2$Fe(DMGH)$_2$ or (CH_3Im)$_2$Fe(DMGH)$_2$ complexes. Similarly BzlNC is also more inert trans to BzlNC than it is trans to CH_3Im or pyridine. A trans effect order BzlNC ≪ CH_3Im < py is observed.

This trans effect order stands in sharp contrast to the phthalocyanine system where CH_3Im is 10 times *more* labile in the CH_3ImFePcBzlNC complex than it is in the (CH_3Im)$_2$FePc complex and where BzlNC is destabilized trans to BzlNC by a factor of 1000. According to the definitions of Pearson, the DMGH system behaves symbiotically while the Pc system behaves antisymbiotically.[25] While this provides a classification of the two systems, it provides no explanation for the phenomena. The sensitivity of the trans effect to the cis ligand suggests that axial and in-plane bonding are intimately connected in these systems. The opposite effects in the DMGH and Pc systems may be due to the relative stability of the two five-coordinate transition states LFe vs. FeCNR, the former being stabilized in the DMGH systems and the latter in the Pc system. This preference could manifest itself in the ground state of LFeBzlNC in a preferred orientation of the iron with respect to the planar tetradentate ligand with the iron out of the plane toward the BzlNC in the Pc system but out in the opposite direction toward L in the DMGH system. Fleischer has previously pointed out that such a motion would lie along the reaction coordinate for an axial ligand dissociation.[26] For the few known structures of complexes of this type with two different axial ligands, the metal does normally lie slightly out of the plane toward either the more hindered ligand or the π-acceptor ligand.[27-30] An out-of-plane motion toward a π acceptor would increase axial π bonding but decrease the in-plane π bonding. The changes in the in-plane and axial bonding on movement out of the plane in five-coordinate complexes has been discussed by Hoffmann.[31] Unfortunately, it is difficult to decide which of the many factors is most important in a given system. Additional data on these and other systems are required before an adequate understanding of the opposite effects in these two systems is possible.

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Registry No. $Fe(DMGH)_2(py)py$, 24828-75-9; $Fe(DMGH)_2(CH_3Im)CH_3Im$, 57804-36-1; $Fe(DMGH)_2(py)CO$, 54691-99-5; $Fe(DMGH)_2(CH_3Im)CO$, 61395-33-3; $Fe(DMGH)_2(py)BzlNC$, 61395-34-4; $Fe(DMGH)_2(CH_3Im)BzlNC$, 59575-74-5; $Fe(DMGH)_2(BzlNC)BzlNC$, 59575-75-6; $FePc(CH_3Im)CO$, 61395-35-5; $FePc(py)CO$, 61395-36-6; Fe(por)(piperdine)BzlNC, 61395-37-7.

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Synthesis and Variable-Temperature Magnetochemical and Mössbauer Spectroscopy Studies of Tris(monothiocarbamato)iron(III) Complexes. A New $^2T \rightleftarrows {}^6A$ Spin-Equilibrium System Containing the FeS_3O_3 Core

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Five new tris(*N*,*N*-disubstituted-monothiocarbamato)iron(III) complexes, Fe $(N,N\text{-}R_2mtc)_3$, with R = methyl, ethyl, *n*-propyl, pyrrolidyl, and piperidyl, have been synthesized and their electronic structures in the solid state examined by variable-temperature (77–300 K) magnetochemical and ^{57}Fe Mössbauer spectroscopy studies. The R = pyrrolidyl derivative remains a high-spin $S = {}^5/_2$ compound over the entire temperature range studied, whereas the other four derivatives show anomalous magnetic behavior arising from ^2T(low spin, $S = {}^1/_2$) $\rightleftarrows$ ^6A(high spin, $S = {}^5/_2$) spin-equilibrium processes. Thus, the $Fe(mtc)_3$'s with their FeS_3O_3 core are electronically and structurally related to the tris(*N*,*N*-disubstituted-dithiocarbamato)iron(III) complexes ($Fe(dtc)_3$'s; FeS_6 core) and the tris(monothio-β-diketonato)iron(III) complexes ($Fe(mtk)_3$'s; FeS_3O_3 core) in that all three series are variable-spin $^2T \rightleftarrows {}^6A$ systems. From a comparative analysis of the Mössbauer spectral patterns of the three spin-equilibrium systems, it has been concluded that the rates of spin interconversion (k's) for the $^2T \rightleftarrows {}^6A$ (k_1, k_{-1}) processes in the solid state are $\geq 10^7$ s^{-1} for the $Fe(mtc)_3$ and $Fe(dtc)_3$ complexes but $< 10^7$ s^{-1} for the $Fe(mtk)_3$'s and all other known iron(III) $^2T \rightleftarrows {}^6A$ processes, including that for the naturally occurring substrate-bound ferric cytochrome P_{450} camphor enzyme. It is suggested that the unusual nature of the $Fe(dtc)_3$ and $Fe(mtc)_3$ complexes, i.e., with k's $\geq 10^7$ s^{-1}, may arise from geometrical factors rather than electronic ones if the rate-determining step for spin interconversion involves the low spin $\rightleftarrows$ high spin coordination sphere rearrangement that accompanies the spin-transition process.

Introduction

Since Cambi and co-workers[3] first proposed that intermediate room-temperature magnetic moments for the iron(III) dithiocarbamates ($Fe(dtc)_3$'s) and the concomitant anomalous temperature dependency of these moments were due to an equilibrium between low-spin (^2T) and high-spin (^6A) magnetic isomers, an extensive amount of research[4-7] has been devoted to this system of iron chelates. Various physiochemical techniques such as variable-temperature Mössbauer,[8] infrared,[9] and electron paramagnetic resonance spectroscopy[9] and x-ray crystallography[10] have been utilized in attempts to fully elucidate the nature of the $^2T \rightleftarrows {}^6A$ process displayed by the FeS_6 core in these metal complexes. As a series, the $Fe(dtc)_3$'s have been of special interest, not only because they have a unique electronic structure but also because they offer conveniently synthesized models for examining Fe–S bonding, a linkage which is present in both heme[11] and nonheme[12] iron-containing metalloproteins. Furthermore, the *N*,*N*-dimethyl compound, $Fe(Me_2dtc)_3$, is of commercial interest as a powerful fungicide.[13]

Much of our recent interest in the area of spin-equilibrium chemistry has focused on the solution state where laser Raman