chemical shift difference is sufficiently large to contribute to the line width.

All of these features of the nmr spectra of cobalt(III)–diamine complexes can be explained if it is assumed that substantial spin–spin coupling occurs between ^{59}Co and the equatorial protons of the ligands and that this coupling can effectively be removed by the quadrupolar relaxation of the cobalt nucleus. A direct test of this hypothesis is to decouple the cobalt nuclear spin in a heteronuclear double-resonance experiment. We predict that the spectrum of proton H^2 in $Co(pn)_3^{2+}$ will be sharpened to a four-line multiplet and that the line width of the $Co(en)_3^{3+}$ spectrum will be substantially reduced.[10]

With this explanation of the anomalous $Co(en)_3^{3+}$ spectra all of the spectra of the $M(en)_3$ complexes can be understood with a single model. The ethylenediamine chelate rings undergo rapid inversion between δ and λ conformers with small free energy differences among the various configurations.[11] An effective chemical shift difference between axial and equatorial protons is the result of the incomplete averaging by conformational inversion of the intrinsic chemical shift difference between an axial and equatorial protons held in a fixed conformation. The intrinsic chemical shift difference varies greatly with the metal ion[5] and with the exception of Co(III) is primarily responsible for the variety of spectra observed for $M(en)_3$ complexes.

Acknowledgments.—We thank Professors Douglas, Reilley, and Sudmeier for making their results available before publication. The work was supported by a grant from the National Institutes of Health, GM 16168, by the National Science Foundation which contributed generously to the purchase of the 220-MHz spectrometer, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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The Kinetics and Mechanism of the Dissociation of Di-μ-hydroxo-octaaquodiiron(III)[1]

Sir:

There is considerable interest in the properties of hydroxy- and oxy-bridged binuclear complexes. Although many transition metal ions form such complexes,[2-7] in recent years attention has been focused on the properties of iron(III) dimers.[8-13] This report is concerned with the dimer which is present in iron(III) solutions of low acidity[11] and which is also formed in the oxidation of iron(II) by 2-equiv oxidizing agents.[12] Magnetic measurements indicate that this dimer has a dihydroxy-bridged structure.[10] Equations 1 and 2 describe the equilibria obtaining between the dimer and monomeric iron(III) in dilute perchloric acid solution. The values of K_a and K_b

$$Fe(OH)_2Fe^{4+} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} 2FeOH^{2+} \quad K_a \qquad (1)$$

$$Fe(OH)_2Fe^{4+} + H^+ \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} Fe^{3+} + FeOH^{2+} + H_2O \quad K_b \qquad (2)$$

are $(1.4 \pm 0.3) \times 10^{-3}$ M and 0.87 ± 0.42, respectively, at 25° and 1.0 M ionic strength.[14] This study is, in part, an extension of our earlier work on the kinetics of the dissociation of the dimer. We have previously shown that the dimer dissociates by parallel acid-independent and acid-dependent paths (eq 3).[12] This

$$k_{obsd} = k_a + k_b[H^+] \qquad (3)$$

rate law has been confirmed in two recent studies of the dimer dissociation.[15,16] However the values of the activation energy for the acid-dependent dissociation of the dimer reported in these studies differ by about 5 kcal mol^{-1}. Because of this discrepancy and in view of the current interest in this system we are prompted to report some additional results which we have obtained on the dimer dissociation.

Iron(III) perchlorate was purified by recrystallization from perchloric acid and a stock solution of iron(III) in perchloric acid was prepared and standardized as previously described.[17] Solutions containing the dimer in 0.010, 0.025, or 0.050 M perchloric acid were prepared by adding aliquots of the iron(III) stock solution to a solution containing the appropriate amount of perchloric acid and sufficient sodium perchlorate to adjust the ionic strength to 3.0 M. These solutions were mixed with solutions containing varying amounts of perchloric acid and sodium perchlorate (ionic strength 3.0 M) on the stopped-flow apparatus,[18] and the disappearance of the dimer was followed at 340 nm.

The values of k_{obsd} at 25° are plotted against the perchloric acid concentration in Figure 1. Each rate

[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

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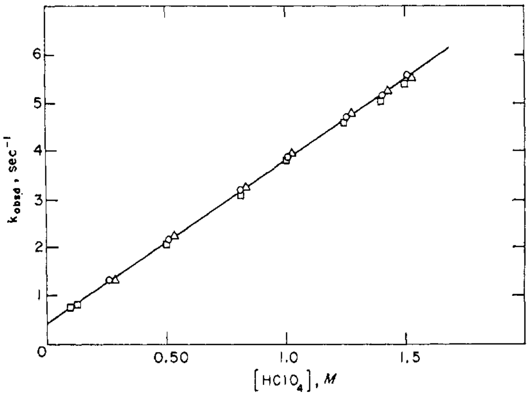

Figure 1.—Plot of k_{obsd} *vs.* $[HClO_4]$ for the dissociation of $Fe(OH)_2Fe^{4+}$ at 25° and ionic strength 3.0 *M*. The compositions of the iron(III) solutions prior to mixing were as follows: squares, $[Fe(III)] = 2.0 \times 10^{-3}$ *M* and $[HClO_4] = 0.010$ *M;* circles, $[Fe(III)] = 5.0 \times 10^{-3}$ *M* and $[HClO_4] = 0.025$ *M;* triangles, $[Fe(III)] = 10.0 \times 10^{-3}$ *M* and $[HClO_4] = 0.050$ *M*.

constant is the mean of at least five runs. Evidently the data satisfy eq 3 reasonably well. It is also apparent that the rate constants are independent of the initial iron(III) and acid concentrations over the concentration ranges used. The rate constants plotted in Figure 1 together with the rate constants at 4.8, 15.3, and 35.0° presented in Table I (44 rate constants in all) were treated by a nonlinear least-squares program to give the activation parameters presented in Table II. This table also contains the results of the other studies of this system.

TABLE I
RATE CONSTANTS FOR THE DISSOCIATION OF $Fe(OH)_2Fe^{4+}$ AT IONIC STRENGTH 3.0 M^a

$[HClO_4]$, *M*	k_{obsd}, sec^{-1} 4.8°	15.3°	35.0°	$[HClO_4]$, *M*	k_{obsd}, sec^{-1} 4.8°	15.3°	35.0°
0.26	0.30	0.65	...	1.01	0.91	1.96	7.23
0.28	...	...	2.65^b	1.03	...	...	7.21^b
0.51	0.51	1.11	...	1.26	1.04	2.37	8.73
0.53	...	...	4.16^b	1.41	1.18	2.62	9.54
0.81	0.72	1.64	...	1.51	1.31	2.78	10.1
0.83	...	...	5.98^b				

[a] Ionic strength was adjusted with sodium perchlorate. The iron(III) solution was 5.0×10^{-3} *M* in iron(III) and 2.5×10^{-2} *M* in perchloric acid before mixing. [b] The iron(III) solution used in these runs was 10.0×10^{-3} *M* in iron(III) and 5.0×10^{-2} *M* in perchloric acid before mixing.

TABLE II
KINETIC PARAMETERS AT 25.0° FOR THE DISSOCIATION OF $Fe(OH)_2Fe^{4+}$ AT IONIC STRENGTH 3.0 *M* IN $HClO_4$–$NaClO_4$ MIXTURES

	a	*b*	*c*
k_a, sec^{-1}	0.42 ± 0.01	0.4 ± 0.1	0.4 ± 0.2
k_b, M^{-1} sec^{-1}	3.33 ± 0.02	3.1 ± 0.2	3.1 ± 0.1
$\Delta H_a^{\ddagger}$, kcal mol^{-1}	12 ± 1	17 ± 2	16 ± 2
$\Delta H_b^{\ddagger}$, kcal mol^{-1}	11.2 ± 0.1	10.5 ± 0.5	6 ± 2

[a] This work. [b] Reference 15. [c] Reference 16.

Before the values of k_a and k_b are discussed, it should be noted that the observed rate constants are more generally given by eq 4, where k_d is the rate constant for the dissociation of the dimer and K_h is the hydrolysis constant of iron(III). Equation 4 allows for the fact

$$k_{obsd} = k_d\left[1 + \frac{4K_h[Fe^{3+}]_{eq}}{[1 + K_b/[H^+]]K_b[H^+]^2}\right] \qquad (4)$$

that the dissociation of the dimer may not go to completion under all the conditions used. Evidently $k_{obsd} = k_d$ when the second term on the right-hand side of eq 4 is much less than unity, a condition which is satisfied under the conditions used in this work. However, this condition was not satisfied under all the conditions used in the study reported in ref 16. At the lowest acidity used there (0.05 *M*), the second term on the right-hand side of eq 4 has a value of either 8×10^{-2} or 4×10^{-2} depending upon whether the equilibrium data at 25° and 3.0 *M* ionic strength reported by Milburn and Vosburgh ($K_h = 1.28 \times 10^{-3}$ *M* and $K_b = 0.49$)[11] or by Hedstrom ($K_h = 9 \times 10^{-4}$ *M* and $K_b = 0.74$)[19] are used. The rate constants presented in Table II have not been corrected for this factor.

It is apparent from Table II that although the values of k_a and k_b are in good agreement at 25°, the reported activation energies do not agree.[20] It is difficult to obtain a precise value of $\Delta H_a^{\ddagger}$ since it is derived from the temperature dependence of relatively small intercepts. On the other hand, the slopes of the plots of k_{obsd} *vs.* $[HClO_4]$ are known with somewhat greater precision than the intercepts, and consequently the percentage error in $\Delta H_b^{\ddagger}$ is likely to be smaller than that in $\Delta H_a^{\ddagger}$. To some extent these considerations are borne out by the results presented in Table II.

The activation parameters reported by Lutz and Wendt were determined from 11 rate constants (3 rate constants at 32°, 4 at 25°, and 4 at 15°). In view of the limited amount of data, the narrow temperature range, the narrow range of acidity (0.25–0.75 *M* at 32° and 0.25–1.0 *M* at 25 and 15°), and the relatively long extrapolations involved to obtain k_a, the uncertainty in the value of $\Delta H_a^{\ddagger}$ reported in ref 15 is almost certainly larger than the 2 kcal mol^{-1} estimated there. The study by Sommer and Margerum is somewhat more extensive than the one by Lutz and Wendt, although the temperature range covered in the former study (14.3–34.8°) is also quite small. For the reasons discussed above (and considering also the small temperature range) the uncertainty in the $\Delta H_a^{\ddagger}$ value reported in ref 16 is rather large. It is more difficult to account for the low value of $\Delta H_b^{\ddagger}$ obtained by Sommer and Margerum. The iron(III) solutions used in their study were relatively concentrated, and the iron(III) concentration was larger than the acid concentration in the solution used in most of the runs. These conditions are likely to favor the formation of trimers and perhaps even higher polymers of iron(III).[21,22]

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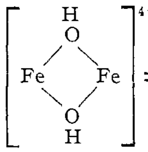
(20) Note, however, that although the values of k_a reported in ref 15 and 16 (0.8 ± 0.1 and 0.63 ± 0.04 sec^{-1}, respectively) are in good agreement at 25° and 0.5 *M* sodium perchlorate, the values of k_b (1.0 ± 0.1 and 1.95 ± 0.3 M^{-1} sec^{-1}, respectively) are not.

(21) Similar comments apply to the study made by Lutz and Wendt, since the iron(III) solution used in their work was also relatively concentrated (0.10 *M*). Unfortunately the acidity of this solution was not specified.

(22) If the iron(III) trimer is $Fe_3(OH)_3^{6+}$, then the conversion of the dimer to the trimer is described by the equation $Fe_2(OH)_2^{4+} + Fe^{3+} + H_2O \rightleftharpoons Fe_3(OH)_3^{6+} + H^+$, and it is evident that the ratio of the trimer to dimer concentration will increase as the $(Fe^{3+})/(H^+)$ ratio of the iron(III) solution increases. The highest value of the latter ratio was 0.2 in this study, but this ratio reached a value of 1.6 in the work required in ref 16.

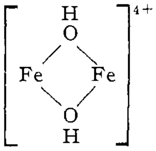
Precise temperature control is, of course, necessary in order to obtain accurate activation energies. Great pains were taken in this work to control and determine the temperature of the reaction mixtures. The solutions to be mixed were kept in a constant-temperature bath and loaded into the driving syringes through tubing and stopcocks which were surrounded by water jackets. The driving syringes were also jacketed and water was in addition circulated through the pistons of the syringes. All the connections between the driving syringes and the mixing chamber, as well as the mixing chamber and the observation tube, were thermostated. Finally, the temperature of the reaction mixture was checked by inserting one end of a thermocouple into the observation chamber.

Regardless of the exact values of the activation energies, the studies agree on the rate law for the dissociation of the dimer and on the magnitudes of k_a and k_b at 25°. The form of the rate law is consistent with the mechanism



$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{FeOHFeOH}^{4+} \qquad (5)$$

$$\mathrm{FeOHFeOH}^{4+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2\mathrm{FeOH}^{2+} \qquad (6)$$



$$+ \mathrm{H}^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{FeOHFeH_2O}^{5+} \qquad (7)$$

$$\mathrm{FeOHFeH_2O}^{5+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Fe}^{3+} + \mathrm{FeOH}^{2+} \qquad (8)$$

$$\mathrm{FeOHFeOH}^{4-} + \mathrm{H}^+ \rightleftharpoons \mathrm{FeOHFeH_2O}^{5+} \quad K \qquad (9)$$

In terms of this mechanism $K_a = k_1k_2/k_{-1}k_{-2}$, $K_b = k_1k_3K/k_{-1}k_{-3}$, and $k_4/k_{-4} = k_1K/k_{-1}$. The steady-state assumption for the concentration of the two singly bridged species gives

$$k_{\mathrm{obsd}} = \frac{k_1 + k_4[\mathrm{H}^+]}{1 + \dfrac{k_{-1} + k_{-4}K[\mathrm{H}^+]}{k_2 + k_3K[\mathrm{H}^+]}} \qquad (10)$$

Two limiting forms of eq 10 are of interest. First, if $[k_2 + k_3K[\mathrm{H}^+]] \gg [k_{-1} + k_{-4}K[\mathrm{H}^+]]$, then

$$k_{\mathrm{obsd}} = k_1 + k_4[\mathrm{H}^+] \qquad (11)$$

Under these conditions $k_a = k_1$ and $k_b = k_4$. In this case the rate-determining step in the reaction is the opening of the chelate ring, or, put somewhat differently, the slow step in the reaction is the formation of the singly bridged species. Sommer and Margerum[16] have presented mild evidence for this interpretation. Second, if $[k_2 + k_3K[\mathrm{H}^+]] \ll [k_{-1} + k_{-4}K[H^+]]$, then

$$k_{\mathrm{obsd}} = K_1k_2 + K_1Kk_3[\mathrm{H}^+] \qquad (12)$$

where $K_1 = k_1/k_{-1}$. Under these conditions $k_a = K_1k_2$ and $k_b = K_1Kk_3$. In this case equilibrium obtains between the dimer and the singly bridged intermediates and the rate-determining step is the bond rupture within the singly bridged species. Limited support for this interpretation is provided by the fact that this scheme leads to reasonable estimates of the values of the rate constants for the formation of the dimer. Substitution of the values of K_1k_2 and K_1Kk_3 in the expressions for K_a and K_b gives $k_{-2} \approx 6.4 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{-3} \approx 4.5\ M^{-1}\ \mathrm{sec}^{-1}$ at 25° and 3.0 M ionic strength when the equilibrium data reported by Hedstrom are used.[23] Although at first glance k_{-3} appears to be rather large for the replacement of a coordinated water molecule on Fe^{3+} by FeOH^{2+}[24] and the ratio k_{-3}/k_{-2} seems to be rather small, these rates can be rationalized by introducing corrections for ionic strength effects.[15] Unfortunately eq 11 does not afford estimates of the water replacement rates on FeOH^{2+} and Fe^{3+} without some additional assumptions. However it should be remembered that eq 11 and 12 are limiting forms and that there are several other ways of rationalizing the empirical rate law. Even the limiting forms are not free of ambiguities. Consider, for example, the condition required for eq 11. This condition may be satisfied with $k_2 \gg k_{-1}$ and $k_{-4} \gg k_3$ or with $k_3 \gg k_{-4}$ but with $k_{-1} \gg k_2$, with very different mechanistic implications for the two cases. Similar considerations apply to eq 12.

Finally, the rate constants for the dissociation of a number of binuclear complexes are compared in Table III. It will be seen that the rate constants for the dissociation of the oxy-bridged dimers are much more acid dependent than are the rate constants for the dissociation of the dihydroxy-bridged dimers. The enhanced acid sensitivity of the former dimers may be due, in part, to electrostatic factors and to the ease with which the oxy-bridged species are protonated.[9] If electrostatic effects are not primarily responsible for the difference in the acid sensitivity of the two classes of dimers, then under suitable conditions the acid dependence of the dissociation rate constants might be used to deter-

TABLE III

RATE CONSTANTS[a] FOR THE DISSOCIATION OF BINUCLEAR COMPLEXES AT 25°

Complex	k_a, sec^{-1}	k_b, M^{-1} sec^{-1}	k_b/k_a, M^{-1}	Ref
$(\mathrm{FeOH})_2^{4+}$	0.42	3.33	7.9	*b*
$(\mathrm{VOH})_2^{4+}$	0.03	1.54	51.3	*c*
$[(\mathrm{phen})_2\mathrm{CrOH}]_2^{4+}$		1.0×10^{-4}	>1	*d*
$[(\mathrm{en})_2\mathrm{CoOH}]_2^{4+}$	3×10^{-6}	5×10^{-4}	1.6×10^2	*e*
$[(\mathrm{NH_3})_4\mathrm{CoOH}]_2^{4+}$		(1.2×10^{-3})[f]	>1	*g*
$((\mathrm{EDTA})\mathrm{Fe})_2\mathrm{O}^{4-}$	1.2	5.0×10^8	4.2×10^8	*h*
$((\mathrm{HEDTA})\mathrm{Fe})_2\mathrm{O}^{2-}$	4.0	3.0×10^6	7.5×10^5	*h*
$((\mathrm{CyDTA})\mathrm{Fe})_2\mathrm{O}^{4-}$	9	$\sim 10^{10}$	$\sim 10^9$	*h*

[a] The observed rate constants are given by $k_{\mathrm{obsd}} = k_a + k_b[\mathrm{H}^+]$ unless otherwise noted. [b] This work. [c] Reference 2. [d] Reference 6; temperature 60°. [e] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955). [f] The observed rate constant is given by $k_{\mathrm{obsd}} = b(\mathrm{H}^+)/[1 + c(\mathrm{H}^+)]$ which reduces to $k_{\mathrm{obsd}} = b(\mathrm{H}^+)$ at low acidity. [g] Reference 4. [h] Reference 9.

(23) The values of k_{-2} and k_{-3} are 6.7×10^2 and $6.8\ M^{-1}\ \mathrm{sec}^{-1}$, respectively, if Milburn and Vosburgh's values for K_a and K_b at 25° and 3.0 M ionic strength are used.

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mine whether a particular dimer has an oxy- or a hydroxy-bridged structure.

Acknowledgment.—The authors wish to thank Drs. B. A. Sommer and D. W. Margerum for sending them a preprint of their iron(III) paper.

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Infrared Intensities of the Molecular Nitrogen and Carbonyl Stretching Vibrations in Iridium(I) Complexes

Sir:

Since the discovery of the first transition metal–molecular nitrogen compound[1] there has been a considerable amount of discussion concerning the nature of the metal–nitrogen bond.[2–5] In order to gain further insight into the nature of this bonding we have undertaken spectroscopic studies of comparable molecular nitrogen and carbonyl compounds.

We report here our initial investigation containing integrated infrared intensity data for the compounds $Ir(N_2)(P(C_6H_5)_3)_2Cl$ and $Ir(CO)(P(C_6H_5)_3)_2Cl$.

Procedure.—Chlorocarbonylbis(triphenylphosphine)iridium(I) and chloronitrogenbis(triphenylphosphine)iridium(I) were obtained from Strem Chemicals Inc. as pure crystalline compounds. This was confirmed by C, H, and N analysis and by melting point data. Spectroscopic grade chloroform was used without further treatment. Samples were prepared by weighing out the solid material on a Cahn electrobalance to ±0.01 mg. The solids were then added to volumetric flasks of appropriate size and the flasks were accurately filled with solvent. Linear Beer's law plots were observed. Spectra were obtained as soon as possible after complete dissolution of compounds, usually within 5–10 min. It was found that the nitrogen complex decomposed in solution under the conditions at which the spectra were observed to the extent of 18% during the course of a spectral measurement, whereas the carbonyl analog decomposed by only 5%. All intensity measurements reported are corrected for these effects.

Infrared spectral measurements were made on a Perkin–Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. The spectral slit width of the instrument was 1.75 cm^{-1}. Recording was at a rate of approximately 10 cm^{-1}/min on an expanded scale. Proper attention to double-beam balancing, zero transmission setting, etc., was emphasized. Sodium chloride cells (1 mm) calibrated by the interference fringe technique were employed in the measurements.

The areas under the bands were determined with a planimeter. In some cases, Simpson's rule was applied in determining the integrated absorbance which gave good agreement with values obtained by direct planimeter measurements. Intensities were determined at a number of concentrations and extrapolated to zero concentration (Figure 1). Data were analyzed by the linear least-squares method.

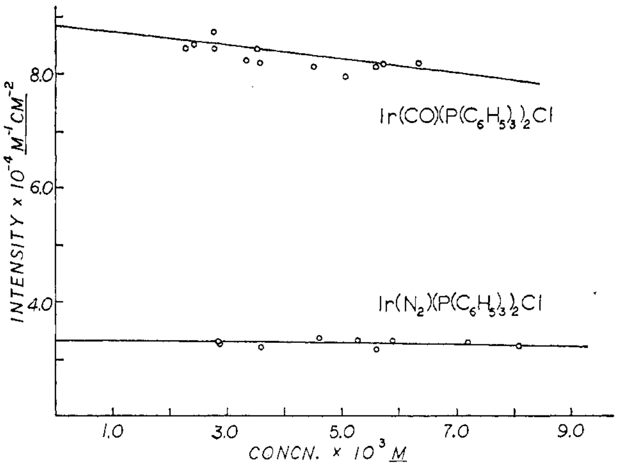

Figure 1.—Intensity *vs.* concentration for the N_2 and CO vibrational modes in the respective Ir(I) complexes.

Results and Discussion.—On the basis of infrared frequency shifts (coordinated ligand *vs.* free ligand) it is evident that the infrared frequency properties of the N_2 and CO complexes are very similar when the groups are bound to identical iridium(I) species ($\Delta\nu_{N_2} = 221$ cm^{-1} and $\Delta\nu_{CO} = 178$ cm^{-1}). Collman, *et al.*,[3] have interpreted these shifts as meaning that N_2 is a better π^* acceptor than CO. This is unexpected since the $2p\pi^*$ orbitals of N_2 are at higher energy than those of CO. Also, in CO the π^* orbital is derived from about 68% carbon 2p orbital[6,7] thereby resulting in better overlap with the metal's d orbitals than would the corresponding π^* orbitals on N_2 which employ equally populated 2p orbitals. Indeed, the difference in the metal–ligand bond is reflected in the thermal stabilities of the two complexes, the nitrogen complex being considerably more unstable.

Chatt and coworkers[4] attributed this discrepancy between infrared results and stability mainly to nitrogen's poor σ-donor property as compared with CO, since these frequency shifts are a complex function of both the σ and π properties of the ligand. Purcell concluded, on the basis of overlap populations, the π^* orbitals on N_2 are more destabilizing to the $N\equiv N$ bond than those of CO are to the $C\equiv O$ bond.[5] That is, in the instance of equal population of N_2 and CO π^* orbitals, the decrease in N_2 π overlap population will be greater than that of

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