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Notes

Contribution from the Departments of Chemistry and Physics,
University of California, Santa Barbara, California 93106

Reactions of Matrix-Isolated Iron Atoms with Dinitrogen

Marca M. Doeff,[†] Stewart F. Parker,[†] Paul H. Barrett,[‡]
and Ralph G. Pearson*[†]

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In the past, only a few binary metal–dinitrogen systems have been studied by matrix-isolation techniques.[1-4] Because these compounds are generally unstable, it is not possible to synthesize them via conventional means. However, many of the analogous metal–carbonyl complexes are well-known and exist at room temperature. Since dinitrogen and carbon monoxide share many properties (for example, they are isoelectronic), the difference between their metal-binding abilities is striking. It has been postulated that carbon monoxide is either a better σ donor than dinitrogen or a better π acceptor, or both. However, there is still considerable controversy over this matter.[5,6] Systematic studies of binary metal–dinitrogen compounds should clarify the differences between CO and N_2 as ligands.

The reaction of iron with dinitrogen is of interest not only from a theoretical standpoint but also because of its relevance to catalytic systems. It has been suggested that an iron–dinitrogen intermediate is formed as one of the steps in the conversion of dinitrogen to ammonia by the enzyme nitrogenase and in the Haber process.[7,8]

Some preliminary results have shown that such a product is indeed formed when iron is cocondensed with pure dinitrogen at 15 K.[9,10] The IR spectrum shows lines in the N–N stretching region. The Mössbauer spectrum indicates that a single product[9,10] is formed. In addition, unreacted iron atoms were observed, but no dimers, Fe_2. The latter result was also confirmed by UV–vis[2] and Raman[11] spectroscopy. This has been interpreted to mean that iron dimers and not atoms react with dinitrogen. An iron concentration study appeared to confirm this result but was based on IR data of low accuracy from a single-beam spectrometer. Although no attempts were made to determine ligand stoichiometry or structure, it was suggested that $Fe_2(N_2)_8$ is the species formed in a pure nitrogen matrix.[9,10] This is somewhat surprising since other metal–dinitrogen compounds have been found to be mononuclear and isostructural to the corresponding metal–carbonyl complexes.[3] The goal of the present study was to better characterize the product formed in the cocondensation reaction of iron with dinitrogen with regard to both metal and ligand stoichiometry. Herein, we report the results of this study, indicating that this product is indeed mononuclear and isostructural to $Fe(CO)_5$.

Details of experimental procedures have been described elsewhere.[12] Infrared spectra were obtained on a Perkin-Elmer 683. Nitrogen (99.999%) and krypton (99.995%) were obtained from Linde and used without further purification. Gaseous iron atoms were obtained by resistively heating a strip of iron foil (Johnson-Matthey) clamped between two copper electrodes. Iron atoms were cocondensed on the NaCl substrate with the matrix and reactive gases that were premixed. Different iron concentrations were obtained by changing the temperature at which the foil was heated. The concentration in the sample itself was assumed to be proportional to the weight loss of the foil during the experiment. This was low enough (less than 1%) to ensure that no significant dimer or cluster formation took place.

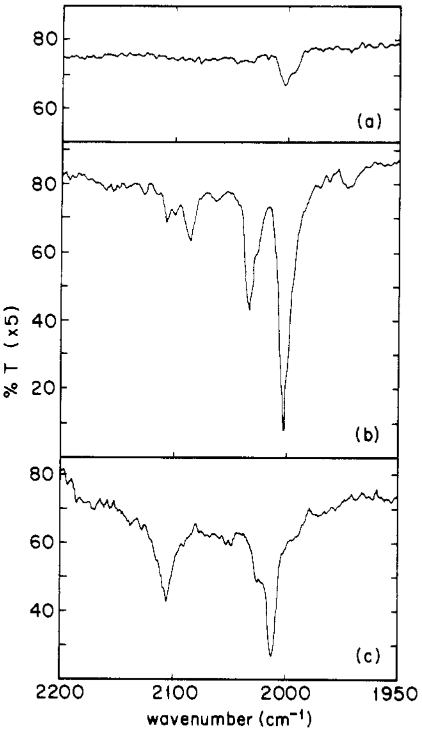

Figure 1. Infrared spectra of iron cocondensed with N_2 in Kr or N_2 matrices at 15 K in the N–N stretching region: (a) 0.3% N_2 in Kr; (b) 1.0% N_2 in Kr; (c) 100% N_2.

When iron is codeposited with pure N_2, strong lines at 2012 and 2106 cm^{-1} in the infrared appear (Figure 1). In some of the experiments a weak line at 1996 cm^{-1} is also seen. The two higher frequency bands maintain a constant intensity ratio (2012:2106 = 1.7:1) throughout a series of annealing experiments and appear with the same intensity ratio in separate experiments. This indicates that they belong to the same species, A. The band at 1996 cm^{-1} is unexplained. Annealing to 40 K causes the complex to completely disappear. No new

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[†] Department of Chemistry.
[‡] Department of Physics.

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Table I. Infrared N-N Stretching Frequencies (cm^{-1}) of the Species $Fe(N_2)_x$ (x = 0-5)

0.3% N_2	1.0% N_2	2% N_2	10% N_2	20% N_2	50% N_2	100% N_2	species^a
					2108	2106	$Fe(N_2)_5$ D_{3h}
	2108	2108	2108	2108	2108		$Fe(N_2)_4$ C_{2v}
	2098	2098	2098	2098	2098		$Fe(N_2)_4$ C_{2v}
	2086	2086	2086	2086	2086		$Fe(N_2)_4$ C_{2v}
	2062	2062					
	2032	2035	2035	2034	2036		$Fe(N_2)_3$ C_{3v}
	2026	2018	2018	2017	2018		$Fe(N_2)_2$ $D_{\infty h}$
					2010	2012	$Fe(N_2)_5$ D_{3h}
2002	2002	2002	2002	2002			$Fe(N_2)$ $C_{\infty v}$
1996 (sh)					1996 (sh)		

^{a} Assignments tentative. See text.

bands appear during warm-up, showing that the complex is thermally unstable and simply decomposes. This parallels the behavior of other known metal–nitrogen compounds.

When the metal concentration is varied in a series of experiments, it is possible to determine the stoichiometry of the iron in A. A log–log plot of the absorbances of the IR lines vs. iron concentration should yield a straight line with a slope equal to the number of metal atoms in A. When this is done for the 2106- and 2012-cm^{-1} lines, slopes very close to 1 are obtained for both, indicating that A is a monomer. When the iron content in a series of samples is held constant, but the N_2 content varied, no changes in the intensities of the lines are observed. If A were a dimer, an increase in nitrogen concentration should decrease the probability of two iron atoms encountering one another in the matrix and thus decrease the number of A molecules formed. For a monomeric species, however, a variation in N_2 pressure should not change the number of absorbers contained in the matrix. Thus, both sets of experiments confirm that A contains only one iron atom.

The presence of two lines in the N–N stretching region indicates that A has more than one bound dinitrogen, more likely three or five. The intensity ratio of nearly 3:2 is consistent with $Fe(N_2)_5$ in a D_{3h} structure. $Fe(N_2)_3$ is a C_{3v} structure is also expected to give two lines in the IR spectrum. However, this species probably would be paramagnetic, whereas magnetic measurements suggest that A is diamagnetic.[9]

Dilution experiments with nitrogen concentrations ranging from 0.30% to 50% were performed in order to distinguish between the two possibilities. The spectrum of iron cocondensed with Kr/N_2 (1.0%) is shown in the figure. At least seven new lines appear, none belonging to A. These belong to several new iron–dinitrogen species that are coordinatively unsaturated. If A contained only three nitrogens, only two new lines would be expected in the dilution experiments, one for $Fe(N_2)$ and one for $Fe(N_2)_2$. A must then have five coordinated nitrogen ligands.

When iron is condensed with Kr/N_2 (0.3%), only one IR band at 2002 cm^{-1} is seen, matching one of the lines seen for Kr/N_2 (1.0%). This probably is due to the species $Fe(N_2)$. Ozin has reported an $Fe(N_2)$ band at 2020 cm^{-1}, with the matrix not specified.[2] In experiments with higher nitrogen concentrations, the three lines at 2086, 2098, and 2108 cm^{-1} maintain a constant intensity ratio and increase as the N_2 content increases. These may belong to $Fe(N_2)_4$ in a C_{2v} structure. The remaining vibrations are due to $Fe(N_2)_2$ and $Fe(N_2)_3$. It is not possible to make definite assignments without mixed-isotope experiments. However, the complexity of the expected spectra (for example 42 lines for $Fe(N_2)_5$ and its isotopomers alone) renders such a study unfeasible. Tentative assignments can be made on the basis of experimental observations described and upon comparison to the Fe/CO system. These are summarized in Table I. In addition, a number of weak, rather broad bands appear in some of the IR spectra, ranging from about 2200 to 1950 cm^{-1}. As nitrogen content of the matrix increases, so do the intensities of these lines. This behavior would be expected if compounds of the general formula, $Fe_x(N_2)_y$ ($x > 1$) were formed in small amounts in the experiments. In a "softer" matrix (i.e., one with more nitrogen), iron atoms can diffuse more readily on deposition to form clusters.

In general, the frequencies of the N–N stretches should increase with increasing coordination number, as do the C–O stretches in the iron carbonyls.[12] This is due to decreasing π-accepting ability of the ligand as more coordination sites are occupied. For the iron system, as in many others,[5] $\Delta\nu_{N_2}$ ($\Delta\nu_{N_2} = \nu$(coordinated N_2) $- \nu$(free N_2)) is greater than that of the corresponding $\Delta\nu_{CO}$. This occurs because σ donation as well as π acceptance both lower the N–N bond strength.[13] In CO, π bonding weakens the bond, but σ donation strengthens it. Mössbauer results obtained on one iron system[14] indicate that CO is a better π acceptor than N_2, and some MO calculations support this conclusion.[6]

Finally, the Mössbauer spectrum of iron in pure nitrogen shows two overlapping quadrupole doublets. One doublet may be assigned to iron monomers, Fe_1. The other doublet must then belong to A. This has $\delta = +0.75$ mm/s and $\Delta = 1.00$ mm/s. Irradiation of the sample using a Xe lamp and a 300–350-nm band-pass filter results in the conversion of Fe_1 to A. Previously, the presence of iron atoms and the absence of dimers had been taken to mean that the dimers are the species that react with nitrogen. However, the IR evidence already described conflicts with this conclusion. It is now known that unreacted iron atoms can exist in reactive matrices such as C_2H_4 and CO.[15-18] We suggest that if iron atoms have sufficient energy to react, they bind preferentially to N_2, rather than to a second iron atom. For this reason, no dimers are seen in nitrogen. The Mössbauer isomer shift of +0.75 mm/s may be compared to that of $Fe(CO)_5$, which is −0.5 mm/s.[12] The latter value is a result of promotion of the iron from $3d^64s^2$ to $3d^8$, which gives a large positive shift, and strong π-back-bonding, which gives a negative shift.[12] The results for A, if assumed to be $Fe(N_2)_5$, show much less π bonding.

All the results presented here support the conclusion that A is a monomeric species, most likely $Fe(N_2)_5$. All of the IR stretching frequencies in dilute nitrogen matrices can be tentatively assigned to $Fe(N_2)_x$ (x = 1–4) species. There is no reason to believe that the structures of such compounds differ significantly from their iron/CO analogues. Thus, it now appears that iron does behave like other transition metals studied in its reaction with dinitrogen at low temperatures.

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Registry No. $Fe(N_2)_5$, 92763-10-5; $Fe(N_2)_4$, 92763-11-6; $Fe(N_2)_3$, 92763-12-7; $Fe(N_2)_2$, 92763-13-8; $Fe(N_2)$, 43060-89-5.

Contribution from the Department of Chemistry,
University College, Cardiff CF1 1XL, Wales, U.K.,
and School of Chemistry, Macquarie University,
North Ryde, New South Wales 2113, Australia

Chiral Metal Complexes. 17.[1] Cocrystallization of Four Diastereoisomers: A Second Example

Paul Jones,[2] Robert S. Vagg,*[3] and Peter A. Williams*[2]

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Recently the crystal structure of [Co(acac)(*R*-dqpn′)]ClO_4 was described[4] as comprising equal amounts of Δ-β and Λ-β cations with positional disorder of the pn methyl group. Another isomerism was present in that the nitrogen α or β to the asymmetric carbon could be deprotonated. Nevertheless, only two doublets due to these methyl groups were observed in the ^1H NMR spectrum of the complex and its conjugate acid, and this was interpreted as arising from a facile rearrangement of the diastereomer population in solution.

Since we have found that Co(III) complexes of the related ligand *R*-picpn (3-(*R*)-methyl-2,6-di-2-pyridyl-2,5-diazahexane) adopt a number of topologies[5] and that four diastereomers of $[Co(R,S\text{-picpn})(S\text{-alaninate})]^{2+}$ cocrystallize in the perchlorate salt as determined crystallographically,[6] we were prompted to reexamine the dqpn complex. High-resolution NMR studies show that four diastereomers persist in solution, and the original structure indeed is the second case of four cocrystallized isomers of this kind. Several other conclusions concerning related complexes may be drawn as a result.

Experimental Section

The complex [Co(acac)(*R*-dqpn′)]ClO_4 was obtained analytically pure by using previously published procedures.[4,7] In ethanol $\Delta\epsilon_{620} = +3.80\ M^{-1}\ cm^{-1}$, $\Delta\epsilon_{470} = -7.08\ M^{-1}\ cm^{-1}$, log $\epsilon_{490} = 3.52$, log $\epsilon_{307} = 3.97$, and log $\epsilon_{262} = 4.38$, in agreement with reported values.[4] NMR spectra were recorded at 360 MHz on a Bruker WM-360 spectrometer, and CD and electronic spectra were obtained on a Beckman DK 2A spectrophotometer and a CNRS Jobin-Yvon Dichrographe III. All spectra were recorded at 298 K.

Results and Discussion

The 360-MHz ^1H NMR spectra of the complex (Figure 1) shows that four diastereomers persist in $Me_2SO\text{-}d_6$ and acetone-d_6 solution. Four dqpn methyl doublets and four acac H(3) singlets are clearly resolved in both solvents. Seven acac methyl singlets are observed in $Me_2SO\text{-}d_6$, the largest comprising overlapping signals (by integration) from the most and least predominant diastereoisomers. In acetone-d_6, six such singlets are observed, the others being obscured by solvent peaks. Data are tabulated in Table I. The four diastereoisomers are present in unequal amounts, the relative concentrations being 0.17:0.78:0.49:0.55 ± 0.04 by integration. This distribution is remarkably similar to that found for "positional disorder" of the methyl groups in the solid-state structure of [Co(acac)(*R*-dqpn′)]ClO_4 (0.18:0.82:0.41:0.59). This leads to the conclusion that no reequilibration of diastereomers in solution occurs, and a consideration of the population permits assignment of signals to unique isomers.

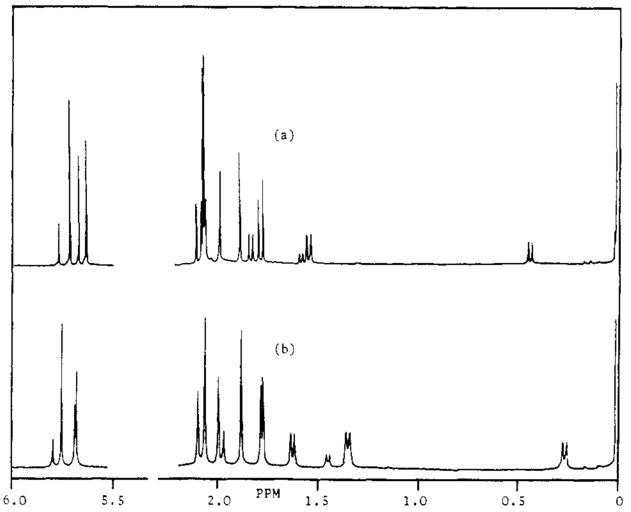

Figure 1. 360-MHz ^1H NMR spectra of the aliphatic region of Δ,Λ-β-*exo*,*endo*-[Co(acac)(*R*-dqpn′)]ClO_4 dissolved in (a) acetone-d_6 and (b) $Me_2SO\text{-}d_6$.

Since the complex must contain equal amounts of Δ and Λ species, the two with relative concentrations 0.17 and 0.78 must be of the same hand. Reference to the crystal structure shows that the methyl group in the Δ-β-endo isomer[6] is the most shielded by a quinoline ring, and we assign the highest field doublet to this species. The isomer distribution automatically indicates the resonances belonging to the Δ-β-exo complex. It was originally argued[4] that since the high-field doublet "disappears" in DCl, this signal is due to the a methyl group adjacent to the deprotonated nitrogen. This implies that *two* such signals should be present, contrary to our findings. It is however true that the trigonal nitrogen in the Δ-β isomers confers an inflexibility in the central chelate ring that forces the dqpn methyl group in the endo isomer closer to a shielding quinolyl ring. Protonation relieves this strain and is discussed below. Chemical shift differences in the Λ isomers are subtle, but the distribution of isomers in solution compared to that in the solid state is so striking that we conclude that the least concentrated Λ isomer is the endo one.

The question arises as to whether the observed isomer distribution reflects chiral discrimination energies for the various complex cations. It is possible, but we do not claim this to be true because in neither our nor the previous preparation[4] was the whole amount of complex isolated nor was it demonstrated that equilibrium was established. The cocrystallization of four diastereoisomers in the lattice of [Co(acac)(*R*-dqpn′)]ClO_4, only the second reported such phenomenon to our knowledge, may simply be due to crystal-packing effects. However, ^1H NMR results[4] on the related complexes [Co(acac)(dqen′)]ClO_4 and [Co(acac)(*R*,*R*-dqchxn′)]ClO_4, where dqen and dqchxn are the 1,2-diaminoethane and 1,2-diaminocyclohexane analogues of dqpn, indicate that certain discriminatory factors are important in complexes of this type.

When the former is dissolved in 12 M DCl, four acac methyl signals are observed. If the integrity of the coordination sphere is retained, this pattern must be generated by two diastereo-

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