

TRANSITION METAL COMPLEXES OF DINITROGEN

by

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ABSTRACT

Studies directed toward the preparation of an iron-dinitrogen system using anhydrous hydrazine and pentacyanonitrosoferrate(II) are described.

INTRODUCTION

Prior to 1965, enzymatic nitrogen fixation provided the major pathway for study of the fixation of nitrogen under relatively mild conditions (1). The results of much research have led biochemists to several general conclusions concerning biological nitrogen fixation. These findings are summarized here. The active site of the enzyme which binds the nitrogen molecule is thought to be a transition metal, probably iron and/or molybdenum (2,3). Further, the reaction requires a suitable electron carrier or reducing agent (4), and a proton source. Based on this experimental information, several theories concerning the mechanism of nitrogen fixation reactions have been proposed (5).

In 1965, Allen and Senoff (6) isolated the first stable transition metal complex with dinitrogen as a ligand. Since that time, many other complexes of dinitrogen have been reported. Some complexes have been formed directly from the air (7), others from nitrogen atmospheres only (8), while still others are formed from ammonia, hydrazine, or azide (9,10,11). Several recent reviews provide an in-depth summary of the research in the field of nitrogen fixation (5,12,13,14).

Stable dinitrogen complexes have been formed with group VIII metals that have been subjected to strong reducing conditions, as suggested from the work on biological enzyme systems. Since iron is of importance for nitrogen fixation in the enzyme systems and since stable

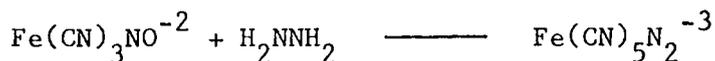
ruthenium complexes have been isolated, it was the purpose of this research to isolate an iron-dinitrogen complex.

RESULTS AND DISCUSSION

This research consisted of the attempted preparation of a pentacyanodinitrogeno iron complex. These attempts at the isolation of an iron-dinitrogen complex were centered on the reaction of tetra-n-propylammonium pentacyanonitrosoferrate with anhydrous hydrazine.

The choice of this system was guided by several general and particular considerations. In general, an iron atom was desired as the central metal in the complex since it appeared to be the site of fixation in biochemical systems. Hydrazine would provide both the source of nitrogen and the strong reducing conditions, which were observed to be necessary in enzymatic and synthetic nitrogen fixation.

The particular choice of the pentacyanonitrosoferrate anion as the substrate was made because this was the only iron nitrosyl available in the proper oxidation state. The ruthenium nitrosyl, $\text{RuClNO}(\text{das})_2\text{Cl}_2$, reacts with hydrazine to form a product initially thought to be $\text{RuN}_2\text{Cl}_2(\text{das})_2$. The iron complex should give a similar reaction:



Tetra-n-propylammonium was chosen as the cation because its size would aid in the crystallization and the ease of preparation and purification of the starting salt, tetra-n-propylammonium pentacyanonitrosoferrate.

A series of reactions with varying molar ratios of hydrazine to iron nitrosyl were conducted to find an optimum ratio for maximizing

the infrared band associated with the nitrogen-nitrogen stretching frequency of dinitrogen complexes (Table I). Previously reported bands (15,16) for N_2 had ranged from 2038 cm^{-1} for $(\text{PEt}_3)_4\text{FeN}_2$ to 1989 cm^{-1} for $[\text{FeH}_2\text{N}_2(\text{PEtPh}_2)_3]$. On this basis the band at 2000 cm^{-1} was assigned to an iron dinitrogen complex.

The 8.5:1 ratio of hydrazine to iron seems to be the best since almost all of the starting iron nitrosyl is consumed, no band associated with reduced nitrosyl (17) products is observed in the infrared spectrum, and the 2000 cm^{-1} band is maximized in comparison to the $2040\text{-}2050\text{ cm}^{-1}$ band(s) of the hydrazine by-products.

A series of reactions, conducted at the 8.5:1 ratio and room temperature and atmospheric pressure, showed the system to be extremely air- and water-sensitive, requiring the use of a dry, inert atmosphere and dried equipment at all times. To meet this requirement, a Schlenk tube system, flame-dried under vacuum, was used; nitrogen gas was passed through reduced BTS catalyst and deoxygenated; distilled solvents were necessary at all stages of the reaction. Even under these conditions, many reaction products decomposed before they could be purified.

A recurrent problem was the appearance of numerous by-products which contaminated the suspected dinitrogen complex. Many attempts were made to eliminate these by-products with varied success. A yellow hydrazine complex was found to be insoluble in dichloromethane and could usually be removed by filtrations at -78°C . The azide complex exhibited the same solubility characteristics as the dinitrogen complex

Table I. Effects of Increasing the Hydrazine/Iron Ratio.

Experiment No.	Hydrazine/Iron Ratio	Significant Frequencies (cm ⁻¹)	Functional Groups Indicated	Speculative Compounds
RS-1-21	3:2	1740(m)	-NOH	[Fe(CN) ₅ NOH] ⁻³
		1880(vs)	-NO	[Fe(CN) ₅ NO] ⁻²
		2000(w)	-N ₂	[Fe(CN) ₅ N ₂] ⁻³
		2045(vw)	-N ₃	
		2100(w)	-CN	
	5:1	2132(s)	-CN	[Fe(CN) ₅ NO] ⁻²
		1880(w)	-NO	[Fe(CN) ₅ NO] ⁻²
		2000(m)	-N ₂	[Fe(CN) ₅ N ₂] ⁻³
		2045(vs)	-N ₃	
		2100(m)	-CN	[Fe(CN) ₅ N ₂] ⁻³
RS-1-37a	8.5:1	2132(w)	-CN	[Fe(CN) ₅ NO] ⁻²
		2000(s)	-N ₂	[Fe(CN) ₅ N ₂] ⁻³
		2050(m)	-N ₃	
		2100(m)	-CN	[Fe(CN) ₅ N ₂] ⁻³
RS-1-31	11.5:1	2050(s) broad	-H ₂ NNH ₂	[Fe(CN) ₅ N ₂ H ₄] ⁻³
		2100(w)	-CN	

and could not be separated by changes in concentration, temperature, and solvents.

Under the 8.5:1 ratio and room temperature and atmospheric pressure, one reaction produced an orange crystalline material after work up. An elemental analysis of this compound showed that there were three tetra-n-propylammonium cations and five cyanides associated with the iron; however, the nitrogen analysis was too low for a compound with an empirical formula: $[(C_3H_7)_4N] [Fe(CN_5)N_2]$. The compound was very water-sensitive and the total analysis amounted to only 98.23%. This may indicate that in packaging for shipment or in the analyst's handling some dinitrogen may have been lost. Without an oxygen analysis, no firm conclusion may be drawn. This type of difficulty in the purification and low nitrogen analysis was also found in the L_4FeN_2 (L = Et₃P) system by Campbell et al. (16).

As mentioned above, several efforts were made to decrease the quantity of by-products. These efforts included a reduction in the ratio of hydrazine from 8.5 to 5:1. Under these conditions, a brick-red colored product was isolated from the reaction mixture by filtration from 2-butanone. This product had not been observed with the 8.5:1 ratio and was free of the hydrazine and azide products. Based upon its magnetic susceptibility, $\mu = 2.35$, the infrared spectrum which had an N-H stretch at 3300 cm^{-1} , and a complete elemental analysis, the material was identified as tetra-n-propylammonium amidopentacyanoferrate(III).

Various compounds related to these products were prepared to investigate their infrared spectra and physical properties. The iron compounds prepared for this purpose included: tetra-n-propylammonium hexacyanoferrate(II), tetra-n-propylammonium hexacyanoferrate(III), tetra-n-propylammonium pentacyanoaquoferate(II), tetra-n-propylammonium pentacyanonitroferate(II), tetra-n-propylammonium pentacyanoazidoferate(III), and tetra-n-propylammonium azide. None of these related compounds showed any bands in the 2000 cm^{-1} region that could account for the appearance of this band in the hydrazine pentacyanonitrosylferate reaction.

The relationship of the amido product to the reaction mechanism is difficult to state. Although its appearance at a lower hydrazine to iron nitrosyl ratio suggests that it is either an intermediate to the dinitrogen complex or more probably a product of an alternate reaction mechanism which occurs at a reduced concentration of hydrazine.

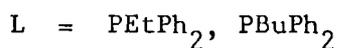
Two other series of reactions were carried out--one at high pressure and the other at low temperature. The series of reactions at high pressure (Table II) show a mixture of products in the infrared spectra of the reaction residue. In the case of a mixture of hydrogen and nitrogen gases, the products identified by their infrared frequencies included the starting nitrosyl (2100 and 1889 cm^{-1}), the reduced protonated nitrosyl complex (1740 cm^{-1}), the hydrazine and azide products (2040 - 2050 cm^{-1}), and the desired product (2000 and 2100 cm^{-1}). Again, due to the similar solubilities of these compounds, it proved impossible to isolate pure materials. The exception was the iron

Table II. High Pressure Experiments.

Experiment No.	Hydrazine/Iron Ratio	Gas (Pressure)	Time	Infrared Frequencies	Functional Groups	Speculative Compounds
RS-1-88	5:1	CO(1100psi)	3 days	2000(vs)	-CO	$[\text{Fe}(\text{CN})_4(\text{CO})_2]^{-2\text{a}}$
		N ₂ (500psi)		2100(s)	-CN	$[\text{Fe}(\text{CN})_4(\text{CO})_2]^{-2}$
RS-1-90	5:1	H ₂ (1250psi)	3 days	1740(m)	-NOH	$[\text{Fe}(\text{CN})_5\text{NOH}]^{-3}$
		N ₂ (400psi)		1880(m)	-NO	$[\text{Fe}(\text{CN})_5\text{NO}]^{-2}$
				1930(m)broad		
				2000(s)		
				2070(m)		
				2132(w)	-CN	$[\text{Fe}(\text{CN})_5\text{NO}]^{-3}$
RS-2-15	5:1	H ₂ (1350psi)	2 days	1740(m)	-NOH	$[\text{Fe}(\text{CN})_5\text{NOH}]^{-2}$
		N ₂ (400psi)		1882(m)	-NO	$[\text{Fe}(\text{CN})_5\text{NO}]^{-2}$
				2010(sh)	-N ₂	$[\text{Fe}(\text{CN})_5\text{N}_2]^{-3}$
				2048(s)	-N ₃	
				2100(m)	-CN	
				2132(w)	-CN	$[\text{Fe}(\text{CN})_5\text{NO}]^{-2}$
				RS-2-12	5:1	N ₂ (2350psi)
				2000(s)		
				2050(m)		
RS-2-3	8.5:1	N ₂ (2300psi)	20 hours	2000(s)		

a. This compound was isolated.

carbonyl complex obtained when the autoclave was charged with carbon monoxide and nitrogen. The reaction between carbon monoxide and di-nitrogen complexes is well known and has been demonstrated by several investigators (15,18).



Another series of reactions was conducted at -78°C (Table III) after it was noted that addition of hydrazine to a -78°C dichloromethane solution of the iron nitrosyl produced a change in color upon standing.

These reactions were carried out under both high and moderate ratios of hydrazine and both the absence and presence of nitrogen. Again a wide variety of compounds appeared in the infrared spectrum of the reaction product.

Table III. Low Temperature Experiments.

Experiment No.	Hydrazine/Iron Ratio	Gas	Time	Infrared Frequencies	Functional Groups	Speculative Compounds
RS-2-16	5:1	N ₂	7 days	1885(w)	-NO	[Fe(CN) ₅ NO] ⁻²
				2000(m)	-N ₂	[Fe(CN) ₅ N ₂] ⁻³
				2045(s)	-N ₃	
				2100(m)	-CN	[Fe(CN) ₅ N ₂] ⁻³
				2132(w)	-CN	[Fe(CN) ₅ NO] ⁻²
RS-2-18	1:1	N ₂	11 days	1740(w)	-NOH	[Fe(CN) ₅ NOH] ⁻³
				1882(s)	-NO	[Fe(CN) ₅ NO] ⁻²
				2000(w)	-N ₂	[Fe(CN) ₅ N ₂] ⁻³
				2100(w)	-CN	[Fe(CN) ₅ N ₂] ⁻³
				2132(s)	-CN	[Fe(CN) ₅ NO] ⁻²
RS-2-26	5:1	vacuum	10 days	1883(s)	-NO	[Fe(CN) ₅ NO] ⁻²
				2010(s)	-N ₂	[Fe(CN) ₅ N ₂] ⁻³
				2050(vs)	-N ₃	
				2100(sh)	-CN	[Fe(CN) ₅ N ₂] ⁻³
				2132(m)	-CN	[Fe(CN) ₅ NO] ⁻²

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 137, Perkin-Elmer 337, and Beckman IR-12 spectrophotometers. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colorado. All solvents used were analytical grade and were further dried and distilled. Dichloromethane (CH_2Cl_2) was distilled from phosphorous pentoxide before each use. Acetone and 2-butanone were both dried by refluxing over phosphorous pentoxide for several hours, then were distilled under nitrogen and stored in nitrogen-filled dispensers. The hydrazine (97%) was further dried by two methods: (1) calcium hydride powder and vacuum distillation and (2) refluxing over barium oxide and vacuum distillation or distillation with a nitrogen leak. The latter method was considered safer, since barium oxide left no explosive by-products or difficult to dispose of residues as did the calcium hydride. The use of a nitrogen leak reduced the possibility of an explosion due to an air leak during distillation. The tetra-n-propylammonium pentacyanonitrosferrate was prepared following the modified method of Harris (19).

Tetra-n-propylammonium Tetracyanodicarbonylferrate(II)

Anhydrous hydrazine (0.5 ml) was slowly added dropwise under a nitrogen atmosphere to a degassed solution of tetra-n-propylammonium pentacyanonitrosferrate (2 g) in dry dichloromethane (20 ml) in a

Schlenk tube maintained at -78°C . The solution was kept at -78°C under a nitrogen atmosphere for about 2 hours before being transferred, under a nitrogen blanket, to a glass-lined autoclave and charged with 1100 psi of carbon monoxide and 500 psi of nitrogen.

After three days, a red solution was decanted from a viscous yellow oil, under a nitrogen blanket, and was cooled to -78°C . A very small amount of precipitate appeared on cooling and was filtered off. The filtrate was stripped of the solvent under reduced pressure. The impurities in the residue were extracted with 2-butanone (10 ml), leaving a white powder which was filtered off and washed three times with 2-butanone (5 ml).

The white material was then dissolved in acetone (50 ml) and the solution was filtered. The volume of the solution was reduced to 20 ml and was cooled. A white powder was filtered off and dried in a vacuum over P_2O_5 for two days. The white powder (0.60 g) was identified as tetra-n-propylammonium tetracyanodicarbonylferrate(II) from its infrared spectrum, elemental analysis, and diamagnetism.

Anal. Calc. for $\text{C}_{30}\text{H}_{56}\text{FeN}_6\text{O}_2$: C, 61.25; H, 9.53; Fe, 9.49; N, 14.29; O, 5.44. Found: C, 60.79; H, 9.47; Fe, 9.48; N, 14.02; O, 6.17.

Tetra-n-propylammonium Amidopentacyanoferrate(III)

Hydrazine (0.5 ml) was slowly added dropwise with stirring under a nitrogen atmosphere to a degassed solution of tetra-n-propylammonium pentacyanonitrosoferrate (2 g) in dry dichloromethane (26 ml) in a Schlenk tube maintained at -76°C .

The solution was then allowed to warm up at room temperature for 10 min until a yellow oil began appearing. The solution was again cooled to -76°C , stirred for an additional 15 min, and then was filtered under nitrogen pressure.

The red-brown filtrate was stripped of its solvent under reduced pressure. The residue was dissolved in dry 2-butanone (25 ml) and filtered. An insoluble red powder remained behind and was washed twice with 2-butanone (25 ml).

The red powder was identified as tetra-n-propylammonium amidopentacyanoferrate(III) from its infrared spectrum, magnetic susceptibility ($\mu = 2.35$ BM), and its elemental analysis.

Anal. Calc. for $\text{C}_{43}\text{H}_{88}\text{FeN}_9\text{O}_{\frac{1}{2}}$: C, 64.84; H, 11.31; Fe, 7.01; N, 15.85; O, 1.01. Found: C, 65.89; H, 10.69; Fe, 6.78; N, 15.69; O, 1.85.

High Pressure Attempts at Tetra-n-propylammonium Pentacyanodinitrogenoferrate(II)

Several attempts were made to form tetra-n-propylammonium pentacyanodinitrogenoferrate(II) using high pressure. The conditions of pressure, types of gases used, and concentrations were varied. The reaction products were identified from the infrared spectrum of the residue.

The initial procedures were similar in each case, except for the variables indicated. In general, anhydrous hydrazine (0.5 ml) was slowly added dropwise under a nitrogen atmosphere to a dry, degassed solution of tetra-n-propylammonium pentacyanonitrosylferrate (2 g) in

dichloromethane in a Schlenk tube at -78°C . The solution was kept at -78°C under N_2 until transferred to an autoclave.

After a period of time (usually several days), the liquid was taken from the autoclave, decanted under nitrogen from the yellow oil (a hydrazine by-product), and kept at -78°C until the solvent was removed under reduced pressure. The infrared spectra taken of the residue usually showed a mixture of products that could not be separated. Table II shows a summary of conditions and results.

Low Temperature Attempts at Tetra- n -propylammonium
Pentacyanodinitrogenoferrate(II)

Several attempts were made to form tetra- n -propylammonium pentacyanodinitrogenoferrate(II) at low temperature (-78°C). The conditions were slightly varied with respect to concentration and atmosphere. The reaction products were identified from the infrared spectrum of the residue.

The initial procedures were similar in each case with about 1 mmole of tetra- n -propylammonium pentacyanonitroferrate dissolved in 20 ml of dichloromethane. The solution was cooled to -78°C and dry hydrazine was added dropwise with stirring. The reaction vessel was then sealed and kept at -78°C for varying periods of time. The solution was filtered and the filtrate was stripped of dichloromethane under reduced pressure. Infrared spectra of the filtrate residue show a mixture of inseparable products (see Table III).

Tetra-n-propylammonium Pentacyanodinitrogenoferrate(II)

Hydrazine (0.6 ml) was slowly added dropwise with stirring under a nitrogen blanket to a degassed solution of tetra-n-ammonium pentacyanonitrosylferrate (1.3 g), in 20 ml of dry, degassed dichloromethane. The system was cooled to -78°C and was purged with vacuum and nitrogen. Warmed up to room temperature, the system was stirred for 10 min. The solution was filtered and the filtrate was stripped of dichloromethane under reduced pressure. The filtrate residue was dissolved in dry acetone (10 ml) and was then filtered. The acetone was stripped off under reduced pressure. This filtrate residue was dissolved in 2-butanone (10 ml) and then filtered. The volume of 2-butanone was slightly reduced and orange-red crystals appeared which were filtered off.

Anal. Calc. for $\text{C}_{41}\text{H}_{84}\text{Fe}_1\text{N}_{10}$: C, 63.75; H, 10.88; Fe, 7.23; N, 18.14. Found: C, 64.16; H, 11.08; Fe, 7.35; N, 15.64.

Tetra-n-propylammonium Hexacyanoferrate(III)

Potassium hexacyanoferrate(III) (3.36 g) was dissolved in distilled water (10 ml) and passed through a cation exchange column (Dowex 50w - 8x). The effluent was neutralized with 10% tetra-n-propylammonium hydroxide. After removing the solvent under reduced pressure, the yellow residue was recrystallized from alcohol/ether.

The yellow material was identified as tetra-n-propylammonium hexacyanoferrate(III) monohydrate from its infrared spectrum, elemental analysis, and magnetic susceptibility, $\mu = 2.42$.

Anal. Calc. for $C_{42}H_{86}FeN_9O$: C, 63.93; H, 10.99; Fe, 7.08; N, 15.98; O, 2.03. Found: C, 64.43; H, 10.90; Fe, 7.13; N, 16.27; O (by difference), 1.4.

Tetra-n-propylammonium Azide

Sodium azide (0.59 g) dissolved in distilled water (10.5 ml) was passed through a cation exchange column (Dowex 50w - 8x) and the effluent was neutralized with tetra-n-propylammonium hydroxide. The water was removed under reduced pressure, leaving colorless crystals behind. The crystals were dried under vacuum over P_2O_5 for 24 hr. The crystals were identified as tetra-n-propylammonium azide from its infrared spectrum and elemental analysis.

Anal. Calc. for $C_{12}H_{16}N_4 \cdot 1/10 H_2O$: C, 62.61; H, 12.35, N, 24.35; O, 0.70. Found: C, 62.62; H, 11.96; N, 24.75; O, 0.73.

CONCLUSION

This system shows itself to be highly promising due to the existence of an infrared band at 2000 cm^{-1} . This infrared band is in the same region as the nitrogen-nitrogen stretching bands in other known iron-dinitrogen complexes. The absence of any such band in various related compounds to the proposed pentacyanodinitrogenoferrate(II) complex is also encouraging.

However, because of the extreme reactivity of this system and the nonseparable side products, the isolation of the dinitrogen complex or the use of the system as an enzyme model is difficult if not impossible under the methods used.

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