Studies on cyanide, amidine and related complexes

Slater, John Henry

Slater, John Henry (1969) *Studies on cyanide, amidine and related complexes*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/10013/

"STUDIES ON CYANIDE, AMIDINE AND RELATED COMPLEXES"

THESIS

presented in candidature for the
degree of
MASTER OF SCIENCE
of the
UNIVERSITY OF DURHAM
by
John Henry Slater B.Sc (London)

The work described in this thesis was performed in the Chemistry Department, Sunderland Technical College, during the period October 1964 to December 1966, under the supervision of Dr. D. Hall, Senior Lecturer in Inorganic Chemistry, and Dr. K. Wade, Lecturer in Inorganic Chemistry, University of Durham.

This thesis contains the results of some original work by the author, and no part of the material offered has been previously submitted by the candidate for a degree in this or any other University. Where use has been made of the results and conclusions of other authors in relevant studies care has been taken to ensure that the source of information is always clearly indicated, unless it is of such general nature that indication is impracticable.

AN ACKNOWLEDGEMENT

The author wishes to express his gratitude to the following:

Dr. K. Wade, Lecturer in Inorganic Chemistry, University of Durham, for general supervision during the course of this work.

Dr. D. Hall, Senior Lecturer in Inorganic Chemistry, Sunderland Technical College, for suggesting the main outlines of this work, and for his continued help during its prosecution.

Dr. E. P. Hart, Vice-Principal, Sunderland Technical College, for his encouragement.

Mr. R. R. Preston, formerly Senior Lecturer in Materials Science, Sunderland Technical College, for advice on X-ray powder technique.

Dr. B. W. Fitzsimmons, Birkbeck College, University of London and Dr. T.C. Gibb, Chemistry Department, University of Newscastle, for provision of Mossbauer measurements.

Mr. E. Lewis, and members of the laboratory staff, Sunderland Technical College, for their invaluable co-operation.

Mrs. H. Tankerville for typing the manuscript.

The Governors of the Sunderland Technical College for the award of a Research Studentship during the tenure of which this research was performed.

SUMMARY

A study has been made of some properties of ferrocyanic acid, $H_4Fe(CN)_6$, and related compounds.

The formation of a wide range of addition compounds of complex cyanide acids is reviewed, and this range extended by an experimental study of adduct formation of ferrocyanic acid with boron halides. The addition of boron halides to some molecules related to ferrocyanic acid is also reported. The infra-red spectra of the boron halide adducts are presented and interpreted. In addition some work on the thermal decomposition of ferrocyanic acid is described together with a study of its thermal decomposition products.

The preparation of amidines and related compounds from nitrile adducts has been attempted and the reaction of an amidine with some Lewis acids is described.

CONTENTS

CHAPTER 4

CHAPTER 5

CHAPTER 1

Introduction

In the following pages, a survey is made of the literature relating to complex cyanide acids $H_xM(CN)_y$ where M is a transition metal, x may be 1,2,3 or 4, and y may be 2,3,4,5,6 or 8, provided that $y > x$. Key references to these compounds, which provide a lead into the extensive literature, are the books by Williams (4) and Ford-Smith (8) and the reviews by Griffith (188) and by Chadwick and Sharpe (166). Much of the material described below has been selected from these sources, to which the reader is referred for further details.

The typical complex cyanide acids listed in Table 1 illustrate their varying stabilities and stoichiometries.

1.1 Preparation and Properties of the Acids

There are four main methods by which these acids may be prepared.

1.1.1 The HCl-ether method

This is the most important of the preparative methods in as much as it is applicable to nearly every acid. . An excess of concentrated HCl (sometimes fuming HCl) is added to a concentrated cyanide, and thus forms the complex acid in aqueous solution. The solution is cooled in ice, and the acid precipitated by the addition of ether. This solid is filtered off and washed with a mixture of HCl and ether. The solid is subsequently dissolved in absolute ethanol, filtered to remove any remaining potassium salt, and finally re-precipitated by the addition of an excess of ether. The acid is purified by repetition of the ethanol solution - ether re-precipitation cycle, and finally the ether is removed from the solid.

Table 1 - Known Complex Cyanide Acids

VI a	VII a	VIII	VIII	VIII	I b	II b
$H_3Cr(CN)_6$[5]	$H_3Mn(CN)_6$[5] $H_4Mn(CN)_6$[1]	$H_3Fe(CN)_6$[2] $H_4Fe(CN)_6$[2] $D_4Fe(CN)_6$[2]	$H_3Co(CN)_6$[1] $D_3Co(CN)_6$ $H_4Co(CN)_6$[4]	$H_2Ni(CN)_4$[5]	$H_3Cu(CN)_4$[4] $H\ Cu(CN)_2$[5]	$H_2Zn(CN)_4$[5]
$H_3Mo(CN)_8$[2] $H_4Mo(CN)_8$[1]		$H_4Ru(CN)_6$[2]	$H_3Rh(CN)_6$[1]	$H_2Pd(CN)_4$[3]	$H_2Ag(CN)_3$[6] $H\ Ag(CN)_2$[4]	$H_2Cd(CN)_4$[5]
$H_3W(CN)_8$[2] $H_4W(CN)_8$[2]	$H_3Re(CN)_8$[6]	$H_4Os(CN)_6$[2] $D_4Os(CN)_6$	$H_3Ir(CN)_6$[1] $D_3Ir(CN)_6$	$HPt(CN)_4$[1] $H_2Pt(CN)_4$[2]	$HAu(CN)_4$[1] $HAu(CN)_2$[3] $DAu(CN)_2$	$H_2Hg(CN)_4$[5]

1. Stable
2. Stable in dry air - decompose in moist air or sunlight
3. Unstable - decompose very slowly on standing
4. Extremely unstable
5. Exists only in solution
6. Doubtful existence

1.1.2 The ion-exchange method

This is essentially the same as method (a) with the exception that the aqueous solution of the acid is first formed by passing the potassium salt of the complex cyanide down an ion-exchange column in which the resin is in the hydrogen form. In the case of $KAu(CN)_2$ passing the aqueous solution down an ion-exchanger and subsequently evaporating the effluent precipitates crystals of $HAu(CN)_2$ (1).

1.1.3 Precipitation of heavy-metal salts

Addition of the calculated amount of H_2SO_4 to a solution or suspension of the barium salt of the complex acid, or treating the lead salt with H_2S, results in an aqueous solution of the complex acid, Subsequent treatment of this solution yields the free acid. Thus $H_3Fe(CN)_6$ has been prepared by treatment of the barium salt with sulphuric acid (2).

1.1.4 Addition of HCN

The pure metal cyanide is allowed to stand in an atmosphere of HCN, or covered with liquid HCN. Subsequent removal of the excess HCN leaves the complex acid. The method has been applied to the preparation of the unstable acid $HAg(CN)_2$ (3).

1.1.5 The complex cyanide acids

Octacyanomolybdic (V) acid - $H_3Mo(CN)_8.3H_2O$

Prepared by treating the silver salt with a little dilute HCl (4,5). The filtered solution is saturated with HCl at -20°C when an orange red precipitate separates. This is filtered and dried in vacuo over P_2O_5 and KOH. The acid is stable in dry air, but is decomposed by light or on warming.

Octacyanotungstic (V) acid - $H_3W(CN)_8.6H_2O$

Preparation as for octacyanomolybdic (V) acid (4) forming orange-yellow crystals with similar properties (6).

Octacyanomolybdic (IV) acid - $H_4Mo(CN)_8.8H_2O$

In addition to the octahydrate (7, 8) a hexahydrate is also reported (4, 9). This acid is produced by the HCl - ether method (4, 8, 9) or by the ion-exchange method (10). The hydrated acid is stable, and is a yellow orange in colour.

Octacyanotungstic (IV) acid - $H_4W(CN)_8.6H_2O$

Prepared by the HCl - ether method (4, 8) the ether~~er~~ate separates as an oil which crystallises on cooling to 0°C. It may also be prepared from the silver salt by adding a small excess of hydrochloric acid diluted with water, filtering and saturating the filtrate with HCl below 0°C (4).

It is dried in an atmosphere of CO_2 and finally over KOH (11). The acid crystallises in yellow needles, which are deliquescent and decompose in water at 60°C.

Hexacyanomanganic (III) acid - $H_3Mn(CN)_6$

The acid exists only in solution (12, 13) where it exhibits the properties of a strong tribasic acid (8, 13).

Hexacyanomanganic (II) acid - $H_4Mn(CN)_6$

Prepared by decomposing the lead or barium salt with H_2SO_4 or H_2S (7, 4, 14). It is only slightly soluble in alcohol and decomposes in solution.

Octacyanorhenic (V) acid - $H_3Re(CN)_8$

Preparation by the use of an ion-exchange resin has been claimed for this acid (15), but its existence is doubtful since the salt $K_3Re(CN)_8$ hydrolyses rapidly in aqueous solution (16).

Hexacyanochromic (III) acid - $H_3Cr(CN)_6$

Exists only in solution (8, 13). It is prepared by bubbling H_2S through a suspension of the lead or barium salt (17), or by the addition of tartaric acid to a solution of the potassium salt (4).

It is a strong tribasic acid (7, 13, 18, 19). According to Williams evaporating the solution in vacuo yields reddish-brown crystals of the acid (4), whereas Jones suggests that this is the metal cyanide $Cr(CN)_3$. The acid readily loses HCN on boiling its aqueous solution. (5).

Hexacyanoferric (III) acid - $H_3Fe(CN)_6$

Can be prepared by the HCl - ether method (20, 21) It can also be formed by treating the lead or barium salt with H_2SO_4 (2), by adding hydrochloric acid to the suspension of the silver salt in water (4), or by the ion-exchange method. (22).

The acid, as prepared by the HCl - ether method is pale-yellow at first but becomes chocolate-brown on drying (12). However if its solution is evaporated gently in vacuo, it is obtained as red-brown crystals (4). It is a very strong acid with dissociation constants equal to those of HCl (23, 24), is decomposed in moist air, and rapidly loses HCN on warming. By analysis it is shown to be not exactly the composition required by $H_3Fe(CN)_6$ (13), and probably contains some ferrous iron (12).

Hexacyanoferric (II) acid - $H_4Fe(CN)_6$

This acid will be considered in detail in a later section.

Hexacyanoruthenic (II) acid - $H_4Ru(CN)_6$

Prepared by the HCl - ether method (7, 4, 25, 26). It is slowly decomposed by heating at 100°C, and turns blue in moist air (12).

Hexacyano-osmic (II) acid - $H_4Os(CN)_6$

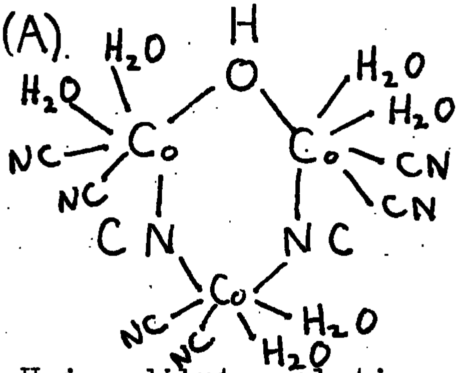
Prepared by the HCl - ether method (4, 27) its properties are similar to those of hexacyanoruthenic acid (12).

Hexacyanocobaltic (III) acid - $H_3Co(CN)_6.5H_2O$

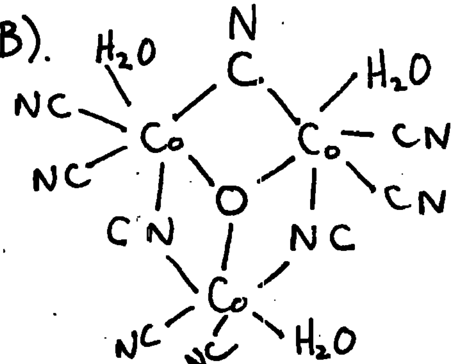
Prepared by the HCl - ether method (12, 18, 21, 28 - 31), or by using a cation-exchange resin (10, 21). It has been obtained as the pentahydrate and as $H_3Co(CN)_6.0.5H_2O$ (28). It is a strong tribasic acid (13, 18, 30, 32) and is very slowly decomposed by boiling in water (30). This decomposition was studied by HOLZL who obtained an insoluble red precipitate on prolonged boiling of the solution, and for which he postulated a cyclic polymeric structure (A) based on the results of volumetric and gravimetric analysis.

On further heating a second isomer was obtained for which the structure was suggested as:(B).

(A).



(B).



Using dilute solutions of the acid a third product was obtained for which he proposed the structure:

$$(CN)_2(H_2O)_2\,Co^{III}(CN)_2\,Co^{III}(CN)_2(H_2O)_2$$

Hexacyanocobaltic (II) acid - $H_4Co(CN)_6$

Prepared by the action of H_2S on the lead salt, or dilute H_2SO_4 on a solution of the barium salt (4). The solution is filtered and the acid precipitated by the addition of alcohol. It is very unstable.

Hexacyanorhodic (III) acid - $H_3Rh(CN)_6$

Prepared by the HCl - ether method (12), it is stable in air and on heating.

Hexacyanoiridic (III) acid - $H_3Ir(CN)_6$

Prepared by the action of dilute H_2SO_4 on the barium salt, and precipitating the acid by the addition of ether

(12, 27). It is stable in dry air, but decomposes at 300°C with evolution of HCN.

Tetracyanonickel (II) acid - $H_2Ni(CN)_4$

Exists only in solution (12), and potentiometric titration indicates that it behaves as a strong dibasic acid (8, 13).

Tetracyanopalladic (II) acid - $H_2Pd(CN)_4$

Prepared by the HCl - ether method (12), it is stable only in the presence of an excess of HCN according to Feigl (33).

Tetracyanoplatinic (III) acid - $HPt(CN)_4.2H_2O$

Formed when a solution of $H_2Pt(CN)_4$ is oxidised with H_2O_2 (4, 8). Evaporation of the solution leaves a green mass of composition $HPt(CN)_4.2H_2O$. The acid is decomposed on heating to 120°C, forming yellow $Pt(CN)_3$ (4, 7, 8).

Tetracyanoplatinic (II) acid - $H_2Pt(CN)_4$

Prepared by the HCl - ether method and evaporation of the ethereal solution (8, 12). It is also obtained by the action of H_2SO_4 on the barium or H_2S on the copper or lead salt (4, 12, 34).

The colour of the acid depends on the amount of water of crystallisation. In the anhydrous form it is yellow (12). The pentahydrate produced by the slow evaporation of the ethereal solution is red (8). Other hydrates varying in colour, are postulated by Levy (35). The acid is noticably hygroscopic (12), loses HCN slowly at room temperature, and is decomposed on heating to 140°C.

Tetracyanocupric (I) acid - $H_3Cu(CN)_4$

Prepared by the ion-exchange method (10), it is extremely unstable, decomposing to CuCN and HCN (8). Potentiometric titration of $K_3Cu(CN)_4$ with acid indicates that it is a strong tribasic acid (10, 13, 36).

Dicyanocupric (I) acid - $HCu(CN)_2$

Produced in dilute aqueous solution by dissolving CuCN in aqueous HCN (8, 37), the acid exists only in solution (12).

Tricyanoargentic (I) acid - $H_2Ag(CN)_3$

This acid has been reported (8).

Dicyanoargentic (I) acid - $HAg(CN)_2$

Prepared by the action of HCN on $[Ag_2SiO_3]n$ or $[AgSi_2O_5]n$ (8, 38), or by the action of liquid HCN on AgCN (3). It is very unstable (8), and in solution is a strong acid (13). According to Jones (12) its existence is doubtful.

Tetracyanoauric (III) acid - $HAu(CN)_4.3H_2O$

Prepared by the interaction of HCN and $HAuCl_4$ (4, 39), it has also been obtained by decomposing the silver salt with HCl, or the barium salt with H_2SO_4 (4). The acid is soluble in ether and melts at 50°C. It decomposes on heating, evolving HCN and $(CN)_2$, leaving a residue of metallic gold.

Dicyanoauric (I) acid - $HAu(CN)_2$

Prepared by passing a solution of $KAu(CN)_2$ in KCN through the acid form of a cation-exchange resin, and evaporating the effluent solution to dryness (1).

It can also be prepared by the HCl - ether method (12).

Reported to be the only acid which exists in the macro-crystalline state (1, 12) it is a strong acid in solution (1,13, 40), but appears to be largely unionised in the solid (1). It has been suggested that the acid is dimerised in solution (41, 42, 43). On heating it decomposes yielding AuCN (8).

Tetracyanozinc (II) acid - $H_2Zn(CN)_4$

This acid exists only in solution (12) and has not been isolated (8, 13). Potentiometric titration studies on $K_2Zn(CN)_4$ with acid gave no results, due to the insolubility of $Zn(CN)_2$ (8, 13).

Tetracyanocadmic (II) acid - $H_2Cd(CN)_4$

The acid exists only in solution (12), and is very unstable (8). It is probably a strong dibasic acid (13, 40). Acidification causes precipitation of $Cd(CN)_2$ (8).

Tetracyanomercuric (II) acid - $H_2Hg(CN)_4$

The acid exists only in solution (12). The addition of acids to solutions of $K_2Hg(CN)_4$ causes immediate formation of $Hg(CN)_3^-$, $Hg(CN)_2$, $HgCN^+$, and Hg^{2+} (13, 40).

Deutero - acids (12)

Two principal methods have been employed in the preparation of the isotopically substituted acids. One is by the interaction of DCl with the respective anhydrous potassium salt, and the second by repeated exchange with D_2O. $D_3Co(CN)_6$, $D_3Ir(CN)_6$, $D_4Fe(CN)_6$, $D_4Ru(CN)_6$, $D_4Os(CN)_6$, and $DAu(CN)_2$ have been prepared using these methods.

1.2 Infrared Spectra and Structure

Until very recently very little had been presented in the literature on either the infrared spectra or the structure of the complex cyanide acids. The infrared spectrum of $HAu(CN)_2$ was used to show that the acid is largely unionised in the solid state (1), and the same author examined the X-ray powder photograph but no attempt was made to determine the structure. However, recently Jones (12, 44) and Beck (45) published infrared studies on the acids in general, and Ginsberg and Koubek (46) on $H_4Fe(CN)_6$, $H_4Ru(CN)_6$, and $H_4Os(CN)_6$ in particular. The paper by Ginsberg and Koubek represents the most detailed study of ferrocyanic acid yet presented, and has been of great assistance in interpreting the results of this work. The Ginsberg results together with those of Beck on $H_4Fe(CN)_6$ will be discussed in detail in a later section.

Jones investigated the infrared spectra of most of the stable acids, and used the interpretation of the spectra in suggesting structures for some of the acids. He prepared several stable acids and compared their spectra, the recorded frequencies being given in Table 2. As a result of this study the acids were divided into two classes, one in which the number of protons is equal to half the number of cyanide groups, i.e. with formula $H_xM(CN)_{2x}$, and the other class in which the number of protons does not equal half the number of cyanide groups. In the first class the spectra of $H_3Co(CN)_6$, $H_3Rh(CN)_6$, $H_3Ir(CN)_6$, $H_2Pd(CN)_4$, and

Table 2 - I.R. Spectra of various complex cyanide acids, according to Jones (12)

Acid	$\nu(C\equiv N)$ cm^{-1}	$\nu(M-C)$ cm^{-1}	Other recorded frequencies (cm^{-1})
$H_2Pd(CN)_4$	2202	448	600-900 (br,s) max 820 Sh's at 1010 (w), 1134 (s), 1600 (w)
$H_2Pt(CN)_4$	2203	485	' ' ' ' 780 ' ' 1012 (w), 1136 (s), 1605 (w)
$H_3Co(CN)_6$	2202	550	' ' ' ' 720 ' ' 1075 (w), 1149 (s), 1610 (w)
$H_3Rh(CN)_6$	2208	507	' ' ' ' 719 ' ' 1101 (w), 1176 (s), 1613 (w)
$H_3Ir(CN)_6$	2203	510	' ' ' ' 725 ' ' 1099 (w), 1174 (s), 1623 (w)
$H\ Au(CN)_2$	2212	-	1120 (br), 1400 (br)
$H_4Fe(CN)_6$	2106 2086	583	444 (m), 678 (s), 875 (s), 1626 (br,s) 2200-3500 (br,s)
$H_4Ru(CN)_6$	2105 2080	541	476 (br), 658 (br), 877 (s), 1590 (br,s) 2200-3500 (br,s)
$H_4Os(CN)_6$	2096 2070	544	485 (br,s) 602 (br,s) 885 (s), 1613 (br,s) 2300-3500 (br,s)

$\nu(C\equiv N)$ - cyanide stretch frequency: br - broad, s - strong,
m - medium, w - weak

$\nu(M-C)$ - metal-carbon stretch frequency: max - maximum, sh - shoulder

$H_2Pt(CN)_4$ were very similar, and suggested the presence of strong symmetric hydrogen bonds. Reasonable structures for these acids were put forward on the basis of symmetric N-H-N bonds. These structures, shown in Figure 1 give infinite chains for $HAu(CN)_2$, infinite sheets for $H_2Pd(CN)_4$ and $H_2Pt(CN)_4$, and a three dimensional lattice based on linked octahedra for $H_3Co(CN)_6$, $H_3Rh(CN)_6$, and $H_3\ Ir(CN)_6$. In the second class the spectra of $H_4Fe(CN)_6$, $H_4Ru(CN)_6$, and $H_4Os(CN)_6$ were almost identical, but quite different in detail from those of the first class. The spectra indicated the presence of strong asymmetric hydrogen bonds. However no attempt to formulate a structure for these acids was made. Beck (45) recorded the spectra of $H_3Fe(CN)_6$, $H_3Co(CN)_6$, $H_4Fe(CN)_6$, $H_4Ru(CN)_6$, $H_4Os(CN)_6$, the recorded frequencies being given in Table 3. He endorsed the structure suggested by Jones for $H_3Co(CN)_6$, and considered $H_3Fe(CN)_6$ to have the same structure. Beck also suggested a structure for $H_4Fe(CN)_6$ and this will be discussed in a later section.

1.3 Adducts of the complex cyanide acids

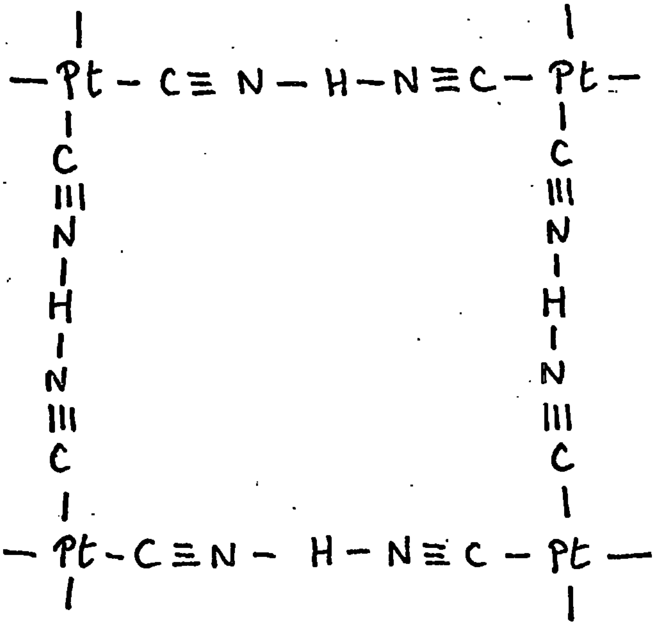
The complex cyanide acids should be capable of

FIGURE 1.

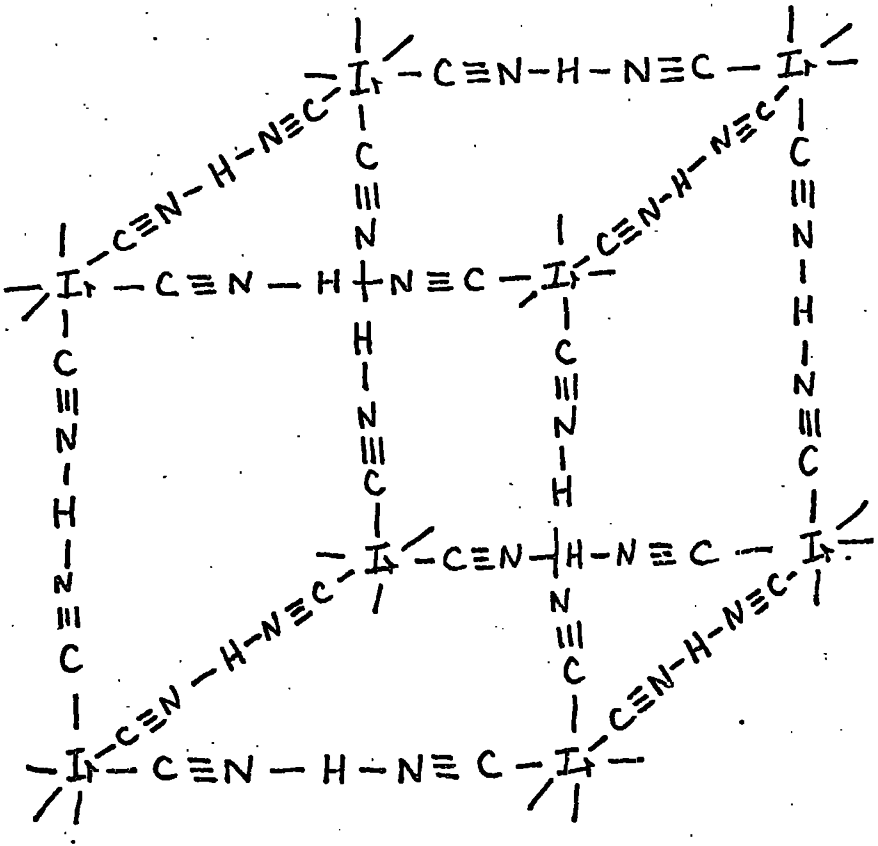
$HAu(CN)_2$ - INFINITE CHAINS

$$-C\equiv N-H-N\equiv C-Au-C\equiv N-H-N\equiv C-Au-$$

$H_2Pt(CN)_4$, $H_2Pd(CN)_4$ - INFINITE SHEETS.



$H_3Ir(CN)_6$, $H_3Rh(CN)_6$, $H_3Co(CN)_6$ - LINKED OCTAHEDRA.



I.R. Spectra of various complex cyanide acids, according to Beck (45)

$H_4Fe(CN)_6$	$H_4Ru(CN)_6$	$H_4Os(CN)_6$	Assignment
416 (s)	360 (s)	372 (s)	ν(M–C)
448 (s)	422 (m)	-	ν(M–C)
585 (s)	538 (s)	543 (s)	δ(M–C≡N)
684 (ms)	675 (m)	663 (s)	δ(N–H)?
880 (s)	890 (s)	885 (s)	δ(N–H)
1600 (s)	1600 (s)	1600 (s)	δ(N–H)
2073 (s)	2076 (s)	2073 (s)	ν(C≡N)
2101 (s)	2102 (s)	2106 (s)	ν(C≡N)
2165 (sh)	-	-	-
2570 (s)	2580 (s)	2600 (s)	ν(N–H··N)
3050 (s)	3040 (s)	3080 (s)	ν(N–H)

$H_3Fe(CN)_6$	$H_3Co(CN)_6$	
426 (s)	420	ν(M–C)
580 (m)	535	δ(M–C≡N)
1600 (s)	-	δ(N–H)
2163 (s)	2218 (s)	ν(C≡N)
2200-2850 (s)	-	ν(N–H··N)

forming two types of addition compound:

(a) by addition of a Lowry-Bronsted base, e.g.

$$RNH_2 + H_xM(CN)_n \longrightarrow RNH_3^+.H_{x-1}M(CN)_n^-$$

(b) by addition of a Lewis acid, e.g.

$$y\,BX_3 + H_xM(CN)_n \longrightarrow H_xM(CN)_n \rightarrow y\,BX_3$$

The first type is well represented in the literature, and the second is the subject of the present study.

1.3.1 Reaction with bases

The compounds formed by the interaction of $H_3Fe(CN)_6$ and organic bases are listed in Tables 4 and 5, and those between $H_4Fe(CN)_6$ and bases in Tables 6 and 7.

The compounds between $H_3Fe(CN)_6$ and organic bases, described by Cumming (47), were precipitated either from freshly prepared acid solutions or by adding an alcoholic solution of the acid to an alcoholic solution of the base at -18°C (Tables 4 and 5.) Except in the case of benzylamine, phenylethylamine, and methylamine, no salts of primary amines were produced. Secondary amine salts were formed only at low temperature, and all tertiary amines used formed salts except for trimethylamine, methyldiphenylamine, dimethylamine-azobenzene, and tetramethyldiaminodiphenylmethane. The salts were stable, highly coloured, crystalline products which were sparingly soluble in water, and usually soluble in alcohol and ether.

Using an acidified solution of $K_3Fe(CN)_6$, Ray (48) formed a stable crystalline product with hexamethylenetetramine, and by mixing concentrated solutions of the hydrochloride of the base with a solution of $K_3Fe(CN)_6$ Roeder (49) produced salts with betaine, pyridine betaine and trigonelline.

$H_4Fe(CN)_6$ also reacts with many organic bases forming salts. These are listed in Tables 6 and 7. These may be prepared either by adding acid to a salt of the base and $H_4Fe(CN)_6$, or by precipitation on mixing alcoholic solutions of the components. These salts were described by many workers (4, 52 - 57) and were reinvestigated by Cumming (47, 50). By treating the base with an alcoholic solution of $H_4Fe(CN)_6$, Eisenberg (56) found that neutral salts of general composition $(Base)_4H_4Fe(CN)_6$ are formed. The salts with the alkaloids betaine, pyridine betaine, and trigonelline are formed by mixing the hydrochloride of the base with $K_4Fe(CN)_6$ (4, 49). Briggs (58) prepared quinine primary ferrocyanide, $(C_{20}H_{24}O_2N_2)_4.H_4Fe(CN)_6.20H_2O$, which in vacuo over sulphuric acid loses 19 molecules of water leaving the yellow monohydrate, and quinine secondary ferrocyanide $(C_{20}H_{24}O_2N_2)_4.H_4Fe(CN)_6.22H_2O$, which separates as a black solid and in vacuo over

Table 4

Salts of $H_3Fe(CN)_6$ (A) from acid solution (4, 47)

Base (B)	Adduct	Appearance
Monomethyl aniline	$B_2,A.\frac{1}{2}EtOH$	Lemon-yellow prisms
Dimethylaniline	$B_2.A.3EtOH$	prismatic needles
p-nitrosodimethyl aniline	$B_2.A.3EtOH$	green-brown prisms
p-bromodimethyl aniline	$B_2.A.3EtOH$	brown prisms
Pyridine	$B_2.A.2EtOH$	yellow rhombic crystals
Quinoline	$B_3.A.2EtOH$	yellow rhombohedral crystals
Isoquinoline	$B_3.A.EtOH$	yellow rhombohedral crystals
Piperazine	$B\ .A.EtOH$	brown-yellow prisms
Piperidine	$B_2.A.2EtOH$	yellow rhombic crystals
Hexamethylene tetramine	$B_2.A.2EtOH$	yellow cubic crystals
Benzidine	$B_3.A$	blue plates
Hexamethylene tetramine	$B_4.A_3.16H_2O$	light yellow crystals (4, 48)
Betaine	$B_3.A.2H_2O$	yellow leaflets (4, 49)
Pyridinebetaine	-	yellow prisms
Trigonelline	-	yellow prisms

Table 5

Salts of $H_3Fe(CN)_6$ (A) from alcoholic solution (4, 47)

Base (B)	Adduct	Appearance
Aniline	B_3.A.EtOH	white plates
o-Toluidine	B_3.A.$\frac{1}{2}$EtOH	lemon-yellow square plates
m-Toluidine	B_3.A.$\frac{1}{2}$EtOH	light-green plates
p-Toluidine	B_2.A.1$\frac{1}{2}$EtOH	green plates
o-Phenylenediamine	B_3.A.2$\frac{1}{2}$EtOH	brown plates
m-Phenylenediamine	B_2.A.1$\frac{1}{2}$EtOH	lemon-green plates
Monomethylaniline	B_3.A	light green plates
Dimethylaniline	B_2.A.EtOH	light green plates
p-bromodimethylaniline	B_2.A.EtOH	green cubic crystals
p-nitrosodimethyl aniline	B_2.A.EtOH	red amorphous
Pyridine	B_3.A.$\frac{1}{2}$EtOH	greenish-yellow needles
Quinoline	B_3.A.$\frac{1}{2}$EtOH	buff amorphous
Isoquinoline	B_3.A.$\frac{1}{2}$EtOH	yellow amorphous
B-naphthylamine	B_3.A.2EtOH	greyish-white plates
Piperazine	B_3.A.EtOH	green plates
Piperidine	B_3.A.EtOH	lemon-yellow needles
Benzylamine	B_3.A.1$\frac{1}{2}$EtOH	silvery plates
Hexamethylene tetramine	B_3.A.1$\frac{1}{2}$EtOH	green amorphous
o-anisidine	B_4.A.2EtOH	green needles
p-xylidine	B_3.A.3EtOH	green plates
Dimethylaminoazo benzene	B_2.A.2EtOH	red plates
Hydroazobenzene	B_2.A.4EtOH	white plates
o-hydroazotoluene	B.A_2.EtOH	white plates

Table 6

Salts of $H_4Fe(CN)_6$ (A) from acid solution (4, 47, 50)

Base (B)	Adduct	Appearance
Aniline	$B_2.A.2H_2O$	white rhombohedral crystals
o-toluidine	$B_2.A.H_2O$	-
p-toluidine	no adduct formed	-
m-toluidine	$B_2.A.H_2O$	dark olive-green needles
p-xylidine	$B_2.A.2H_2O$	lemon-yellow rhombohedra
α-phenylethylamine	-	white rhombohedra
α-naphthylamine	$B_4.A.H_2O$	white plates
β-naphthylamine	$B_4.A.H_2O$	needles
Benzidine	-	rhombic crystals
monomethylaniline	$B_2.A.xH_2O$	white rectangular prisms forms several hydrates
dimethylaniline	$B_2.A$	white rhombohedral prisms
trimethylamine	-	octahedra
pyridine	-	lemon-yellow rhombohedra
quinoline	$B_2.A.\frac{1}{2}H_2O$	orange-yellow rhombohedra
hexamethylentetramine	$B_4.A_3.13H_2O$	white crystals (4,51)
betaine	$B_4.A.2H_2O$	colourless powder (4,49)
pyridinebetaine	-	needles (4,49)
trigonelline	-	red prisms (4,49)

Table 7

Salts of $H_4Fe(CN)_6$, (A) from alcoholic solution (4,47,50)

Base (B)	Adduct	Appearance
Isoquinoline	$B_2.A$	lemon-yellow rhombohedra
o-anisidine	$B_2A.\frac{1}{2}EtOH$	white prisms
Benzylamine	$B_4.A$	white plates
Piperazine	$B_2.A.2EtOH$	white plates
Piperidine	$B_4.A.EtOH$	white rhombic crystals
2:4-tolylenediamine	$B_3.A.EtOH$	white rhombohedra
Tetramethyldiamino-diphenylmethane	$B_2.A.2EtOH$	white prisms
Dimethylaminoazo-benzene	B.A.EtOH	crimson plates
Hexamethylene-tetramine	$B_2.A.\frac{1}{2}EtOH$	white plates
o-phenylenediamine	$B_4.A.5EtOH$	white plates
m-phenylenediamine	$B_4.A.4EtOH$	white plates
p-phenylenediamine	$B_4.A.2EtOH$	white plates
Guanidine	-	light yellow plates
Guanylurea	-	light yellow crystals
p-thiocyanoaniline	-	crystalline

sulphuric acid loses 21½ molecules of water.

$H_4Fe(CN)_6$ has been used to separate mixtures of organic bases. The methods take advantage of the differing solubilities of the ferrocyanide salts and include separation of mixtures of alkaloids (2), separation of pyridine from its homologues (57), and the separation of diphenylamine from aniline (47, 50).

A few salts of other acids are known. Hexamethylenetetramine combines with $H_3Co(CN)_6$ to give $3H_3Co(CN)_6 \cdot 4(CH_2)_6N_4 \cdot 9H_2O$ (59). $H_4W(CN)_8$ in alcoholic solution forms crystalline salts with pyridine and quinoline (4). $H_4Ru(CN)_6$ forms salts with brucine and strychnine (4, 26), and $H_4Os(CN)_6$ with strychnine (4, 60) The base 1-phenyl-2:3-dimethyl-4amino-5-pyrazolone, and its alkyl derivatives, form compounds with $HAu(CN)_4$ (4, 61).

1.3.2 <u>Other Adducts</u>

These can be separated into well-defined and poorly-defined types but may still be considered as Lowry-Bronsted bases in that they will accept protons under certain conditions.

<u>Well defined adducts of complex cyanide acids</u>:

$H_4Fe(CN)_6$ forms a whole series of compounds with H_2SO_4 (62, 63). Compounds containing 1,5,6, and 7 molecules of sulphuric acid to each molecule of ferrocyanic acid are known, all reverting to ferrocyanic acid on standing in moist air. If a small amount of water (5% $^{v}/_{v}$) is added to a cold saturated solution of ferrocyanic acid in concentrated sulphuric acid, rhombic plates of composition $H_4Fe(CN)_6 . 7H_2SO_4$ separate on evaporating the solution (62). Using more water (12-15% $^{v}/_{v}$), the compound $H_4Fe(CN)_6 . 5H_2SO_4$ separates on cooling in vacuo as shiny needles (62). From a 2.5% solution of $K_4Fe(CN)_6$ in concentrated H_2SO_4, colourless too pale-yellow crystals of composition $H_4Fe(CN)_6 . 6H_2SO_4$ separate on heating to 60°C, and cooling slowly (63).

Other compounds are produced by warming solutions of $H_4Fe(CN)_6$ in concentrated sulphuric acid, when gas evolution occurs (4, 62). If $H_4Fe(CN)_6$ is dissolved in concentrated H_2SO_4 at 100-110°C, crystals of composition $2H_3Fe(CN)_6 . SO_3H . 7H_2SO_4$ appear on cooling. These readily lose sulphuric acid to the air, and if the resulting product is recrystallised from alcohol, the product is of composition $H_4Fe(CN)_6 . H_2SO_4$. On repeating the treatment, but using fuming sulphuric acid, needles of composition $2\ H_2Fe(CN)_6 . SO_3 . 3H_2S_2O_7$ separate. These leave on evaporation from alcohol solution, the compounds $Fe(CN)_6 . SO_2$ and $H_3Fe(CN)_6 . SO_3H$.

Adding a tertiary phosphine oxide to a solution of ferrocyanic acid in alcohol or water deposits small colourless needles of general composition $H_4Fe(CN)_6.2 R_3PO$ (64). They are mostly soluble in water, insoluble in cold alcohol, and soon turn green in the light or in contact with moist air. A similar reaction with $H_3Co(CN)_6$ again deposits small crystals (12, 65). However these contain alcohol or water of crystallisation in addition to $H_3Co(CN)_6$ and tertiary phosphine oxide.

$H_3Fe(CN)_6$ forms a series of adducts with aldehydes and ketones (66). The aldehydes used were acetaldehyde, benzaldehyde, heptanal, citral, benzylaldehyde, cinnamaldehyde, and furfural. The ketones were acetone, methylethylketone, carvone, camphor, fenchone, and menthone. These adducts decomposed when dried in vacuo over sulphuric acid and so their exact composition could not be determined.

Ferrocyanic acid also forms a series of compounds with aldehydes and ketones (66). These are listed in Table 8. They are however stable when confined in vacuo over sulphuric acid and the compounds have a definite composition.

$H_3Co(CN)_6$ has been esterified with a variety of alcohols to yield crystalline products (67 - 72). by dissolving $H_3Co(CN)_6$ in alcohol and evaporating to dryness in the absence of moisture, a crystalline derivative is formed. On dissolving this in an ethanol-sulphuric acid mixture, and treating with HCl, the compound $H_3Co(CN)_6 . (EtOH)_3$ is obtained. Using methanol gives a similar compound $H_3Co(CN)_6 . (MeOH)_3$. These adducts are crystalline, soluble in water, and titrate as free acids. On adding pyridine to the ethanol compound, $H_3Co(CN)_6 . (C_5H_5N)_3$ is formed, (70). Passing HCl into the n-propanol solution of $H_3Co(CN)_6$ produces $H_3Co(CN)_6 . (PrOH)_3$, as well as indicating the presence of $H_3Co(CN)_6 . (PrOH)_2$ and $H_3Co(CN)_6 . PrOH$ (4).

<u>Poorly defined adducts of complex cyanide acids</u>:

Certain substances, mostly ethers or alcohols, form addition compounds with ferrocyanic acid, usually of variable composition. There appears to be only a loose association between the acid and the donor molecule since the ether or alcohol is given off continuously on standing. In some cases a definite compound can be isolated.

The compound with diethyl ether can be formed in several ways. The usual method is by the addition of ether to a solution of ferrocyanic acid in alcohol (73), although it can be formed by bringing $H_4Fe(CN)_6$ into contact with ether liquid or vapour (74, 75, 76).

Table 8

Adducts of $H_4Fe(CN)_6$ (A) with aldehydes and ketones (66)

Aldehyde (B)	Adduct
Acetaldehyde	A.B
Paraldehyde	A.B
Heptanal	A.B
Benzaldehyde	A.B
Benzylaldehyde	A.B
Cinnamaldehyde	A.B
Citral	A.B
Furfural	A.B

Ketone (B)	Adduct
Acetone	$A_2.B_5$
Acetone	$A_4.B$
Methyl ethyl ketone	$A_2.B_3$
Diethyl ketone	$A.B_2$
Butyrone	$A.B_2$
Benzyl methyl ketone	$A.B_2$
Comphor	$A.B_2$
Camphor	A.B
Fenchone	A.B
Carvone	$A.B_2.2H_2O$
Carvone	$A.B_2.\frac{1}{2}H_2O$
Menthone	$A.B_2$

With the last method, the solid quickly swells up to 4 or 5 times its original volume (16), and there is a small but noticable evolution of heat (74, 77). The presence of a small amount of water seems to act as a catalyst in this reaction, since it accelerates the formation of the etherate(78). The exact composition of this compound is not clearly established, many workers giving different results. Formulae recorded are $H_4Fe(CN)_6.2.7(C_2H_5)_2O$ (31), $H_4Fe(CN)_6.2(C_2H_5)_2O$ (75, 76, 79), $H_4Fe(CN)_6.(C_2H_5)_2O$ (2), and containing between 1 and 2 molecules of ether (74). These claims were further studied by McIntosh (77), who on the basis of detailed vapour pressure measurements, showed that the ether content varied over wide limits but without the formation of definite compounds, and he regarded the system as a solid solution.

Several compounds of ferrocyanic acid containing alcohol have been isolated. If $H_4Fe(CN)_6$ is dissolved in methanol and the resulting solution cooled to - 80°C, crystals of composition $H_4Fe(CN)_6.10MeOH$ which melt sharply at -33°C separate (77). A compound of the same composition and melting at - 45°C is obtained with ethyl alcohol under similar conditions (77).

By evaporating a solution of ferrocyanic acid in ethanol, over $CaCl_2$, Baeyer obtained $H_4Fe(CN)_6.3C_2H_5OH$ (31), while from vapour pressure measurements Holzl (80) concluded that in addition to the compound with three molecules of ethanol compounds with one and two molecules also existed. When $H_4Fe(CN)_6$ is exposed to the vapour of allyl alcohol it is claimed that $H_4Fe(CN)_6.4CH_2{:}CH{\cdot}CH_2OH$ crystallises out (76).

On adding acetone to a solution of ferrocyanic acid in methanol an oil is deposited, which when treated with a further quantity of acetone deposits a solid of composition $H_4Fe(CN)_6.(CH_3)_2CO$ (31). Also by treating the methanol solution with ether the extremely unstable $H_4Fe(CN)_6CH_3OH.(C_2H_5)_2O$ is formed. McIntosh (77) disagreed with these claims, and, by using the results of vapour pressure studies, suggested that the ferrocyanic acid-acetone system was in fact another case of solid solution formation.

Chretien (76) found that ferrocyanic acid also absorbs the vapour of ethylene oxide and epichlorhydrin.

1.3.3 Reaction with Lewis Acids

No work has so far been reported on the formation of Lewis acid adducts with complex cyanide acids, and the present work is for the most part concerned with this study, in particular the adducts formed by the addition of boron halides to the iron complex cyanide acids. Adduct formation of the salts of the complex cyanides with Lewis acids have however been reported. (81). In addition to the iron complex cyanide acids we have also studied the related alkyl ferrocyanides and their adducts with Lewis acids in order to throw further light on the behaviour of the iron complex cyanide acids.

Shriver (81) performed a series of experiments on the addition of BF_3 to various complex cyanides, including $K_4Ni(CN)_4$, $K_4Fe(CN)_6$, $K_4Mo(CN)_8$, and $Fe(phen)_2(CN)_2$. He found that the addition of boron trifluoride to the cyanide complexes was slow, which he at first attributed to the high lattice energy of the complexes, but later considered to be due to the rate of diffusion of BF_3 into the lattice. In a typical experiment anhydrous $K_2Ni(CN)_4$ absorbed BF_3, at 85°C and 300 mms pressure, to form a 1:1 adduct after about 3 hours reaction time. On allowing the reactants to stand in a sealed tube for two months at room temperature the product was $K_2Ni(CN)_4 4BF_3$. When the pressure of BF_3 over the solid was observed at intervals it was found to fall continuously, indicating that the rate of adduct formation was limited by the rate of diffusion of

BF_3 into the lattice.

The compounds formed with a range of complex cyanides are indicated in Table 9, and the frequency of bands in their infrared spectra in the $C\equiv N$ stretching frequency region are given in Table 10 where they are compared with the $C\equiv N$ frequencies of the parent complexes.

The adducts were all highly moisture sensitive, and, with the exception of $Fe(phen)_2(CN)_2.2BF_3$, were insoluble in, or reacted with common solvents.
It was noted that in the compounds formed the parent cyanide was initially prepared as a hydrate, and was dehydrated prior to reaction with BF_3. The dehydration process appeared to leave the cyanide complex in a reactive form, since the addition of BF_3 to those compounds crystallising without water of crystallisation, i.e. such compounds as $K_3Fe(CN)_6$, $K_3Cr(CN)_6$, and $Pden(CN)_2$, was very slow and could not be brought to completion.

The system KCN - BF_3 was also investigated, the materials being sealed in a tube and left at room temperature for sometime. The product of this reaction was a yellow brown solid in which a simple stoichiometric ratio was not obtained. In two similar experiments 0.14 and 0.43 moles of BF_3 per mole of KCN were absorbed.

Table 9

Complex Cyanide	Lewis Acid (P)-Pressure (T)-Temperature (t)-Time	Mole Ratio Acid:Complex
$K_2Ni(CN)_4$	BF_3 >1 atmos. Room temp. 7 weeks	4
$K_4Fe(CN)_6$	BF_3 >1 atmos. Room temp. 3 weeks	6
$K_4Fe(CN)_6$	BF_3 <1 atmos. 75°C 10 weeks	6
$K_4Mo(CN)_8$	BF_3 >1 atmos. Room temp. 3 weeks	8
$K_4Mo(CN)_8$	BF_3 >1 atmos. 45°C 1 week	8
$Fe(phen)_2(CN)_2$	BF_3 <1 atmos. 40°C 1 hour	2
$Fe(phen)_2(CN)_2$	BF_3 <1 atmos. Room temp. 1 day	2
$Fe(phen)_2(CN)_2$	BH_3 <1 atmos. Room temp. 5-9 days	2

Table 10

Infrared spectra in the C≡N stretch region (Shriver)

Compound	Absorption frequency (cm $^{-1}$)
$K_2Ni(CN)_4$	2130 (s)
$K_2Ni(CN)_4.4BF_3$	2245 (s)
$K_4Fe(CN)_6$	2047 (s)*
$K_4Fe(CN)_6.6BF_3$	2155 (br,s)
$K_4Mo(CN)_8.3H_2O$	2135 (m), 2126 (s), 2123 (s), 2100 (v.s)
$K_4Mo(CN)_8.8BF_3$	2235 (br,s)
$Fe(phen)_2(CN)_2$	2079 (s), 2067 (ms)
$Fe(phen)_2(CN)_2.2BF_3$	2153 (s), 2173 (ms)
$Fe(phen)_2(CN)_2.2BH_3$	2154 (s), 2165 (ms)
$Fe(phen)_2(CN)_2.2BCl_3$	2130 (s), 2155 (ms)
$Fe(phen)_2(CN)_2.2BBr_3$	2127 (s), 2158 (ms)
$Fe(phen)_2(CN)_2.2BMe_3$	not recorded

* In the C≡N stretching frequency region $K_4Fe(CN)_6$ shown a total of six absorption maxima, and the choice of this particular frequency seems somewhat arbitrary.

As can be seen from Table 10, the addition of BF_3 causes the C≡N stretching frequency to increase in all cases, which was taken to indicate the formation of the bond system $M-C\equiv N\rightarrow BF_3$. This bridge structure was consistent with an observed frequency at around 1100 cm^{-1}, which appeared in all cases, and was assigned to the assymetric BF_3 stretch. Magnetic measurements and electronic spectra (reflectance) also indicated the retention of metal-carbon bonding. A comparison of d-d transitions in the complex cyanide and its adduct suggested that the C≡N group does not transmit large inductive effects, although this did not appear to be true for the addition of BF_3 to $Fe(phen)_2(CN)_2$.

Further investigations have produced adducts of complex cyanides with BX_3 (X = Cl, Br, H, methyl) together with adducts of other Lewis acids, MF_4 (M = Si, Ge, and Sn), (82, 83).

1.4 Ferrocyanic acid - $H_4Fe(CN)_6$

1.4.1 Preparation

In the preparation of ferrocyanic acid the one factor on which most methods depend is the insolubility of the addition compound with ether.

All of the methods of the preparation of the complex cyanide acids described earlier have been used for the preparation of ferrocyanic acid. The most commonly used method is that using alkali ferrocyanides, strong acids and ether, and in the many published accounts there are only minor variations in the method. Thus as alternatives to the common method of using concentrated HCl, fuming HCl (73) or concentrated sulphuric acid (84) have been used. Weak acids have also been used. Thus when $K_4Fe(CN)_6$ solution was mixed with an alcoholic solution of tartaric acid evaporation of the filtrate yielded small, cubic crystals of ferrocyanic acid (85). Berzelius claimed that this method gave an impure product (86), but this was contradicated by Wehrlin (87) who claimed that a pure concentrated solution of ferrocyanic acid is produced. The action of sulphuric acid on the barium salt has also been used (86, 88 - 90), as also the action of sulphuric acid or H_2S on suspensions of the lead salt (21, 86, 90 - 93). The ion-exchange method has also been used (10, 22). Hein (10) used the synthetic resin Wolfatite A with solutions of $K_4Fe(CN)_6$, the potassium being readily replaced by hydrogen at room temperature and a contact period with the resin of 15 minutes. The usual temperature used in these preparations is that of an ice bath, but Adie (94) used a solution of

$K_4Fe(CN)_6$ in concentrated sulphuric acid at 100°C under an atmosphere of carbon dioxide, whilst Aschoff (95) reacted the same materials at room temperature.

All of the above variations however yield the addition compound with ether, when the object is to obtain a solid sample of ferrocyanic acid, and one of the main differences of opinion is on the method by which the ether is removed. At room temperature the addition compound has been de-etherated in vacuo, either alone (77, 96) or over a chemical agent such as concentrated sulphuric acid (91) or P_2O_5 (94). However many workers have claimed that the ether can only be effectively removed at elevated temperatures, e.g. in vacuo at 40°C (2), at 50°C (97), or in a stream of hydrogen at 50°C (98). Even then Browning (74) suggests that even more vigorous conditions are required, and he used temperatures of 80°C and 100°C, the latter temperature being more recently adopted by Jones (12).

1.4.2 Properties

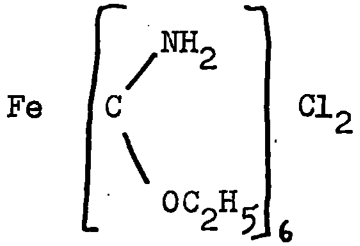
Anhydrous $H_4Fe(CN)_6$ is a white powder (96, 99), which is stable in dry air (73, 86), but turns blue in moist air (8, 99, 100), the latter effect being claimed by some workers to be due to the gradual formation of Berlin Blue (86, 91). In solution it is claimed that ferrocyanic acid slowly evolves HCN with gradual deposition of ferrous ferrocyanide, which rapidly turns blue. (4) On boiling the aqueous solution the acid is rapidly decomposed, evolving HCN, and leaving an insoluble residue of ferrous ferrocyanide. The blue colour produced in moist air is also produced by the action of light, which causes partial oxidation of the ferrous ion (101). Irradiation of solutions of ferrocyanic acid with sunlight, or with the light from a mercury discharge lamp, also produces the blue colour, and has been attributed to the reaction (102):

$$8\ H_4Fe(CN)_6 + O_2 \longrightarrow 4\ H\ Fe^{III}Fe^{II}(CN)_6 + 24\ HCN + 2\ H_2O$$

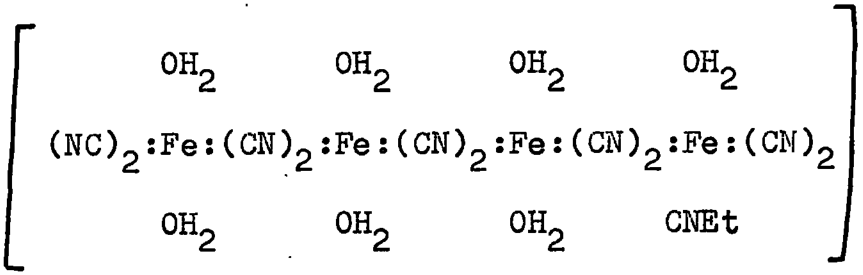
The acid is soluble in water (150 gms/litre @ 14° C) or ethanol, and insoluble in ether (4, 8, 103). The molar volume is 141 (97), and the heat of formation from its elements is -122.0 Kcals (104), and its density at 25°C, referred to water at 4°C, is 1.536. Of the four ionisation constants of $H_4Fe(CN)_6$, the first two are those of a very strong acid, whilst the third and fourth are those of much weaker acids. The dissociation constants are given as:

K_1 - as strong as HCl $>$0.1 (24)
K_2 - " " " " $>$0.1 (24)
K_3 - 10^{-3} (23) and 6×10^{-3} (24)
K_4 - 5×10^{-5} (23) 5.6×10^{-5} (105) 6.8×10^{-5} (106) 6.7×10^{-5} (24)

The hydrogen atoms in $H_4Fe(CN)_6$ can be replaced by alkyl groups to form organic derivatives of the acid. When HCl is passed through a solution of ferrocyanic acid in ethanol until saturation, crystals separate on cooling which have the general composition $H_4Fe(CN)_6.6EtOH.2HCl$ (107, 108). These crystals were formulated by Buff (107) as $(C_2H_5)_4Fe(CN)_6.2C_2H_5Cl.6H_2O$ and by Freund (108) who regarded the compound as an imino-ether,



The crystals lose water on drying over calcium oxide, forming the white compound $\left[(C_2H_5)_6Fe(CN)_6\right]Cl_2$. Similar compounds are reported to be formed by solutions of ferrocyanic acid in methanol (107, 108), propanol (31, 108), and amyl alcohol (31, 108). The results of the above reaction have been disputed by Holzl who considers that the product from ethanol solution is the alkoxonium salt $\left[Fe(CN)_6Cl_2\right](EtOH_2)_6$ which, on addition of ether, forms $\left[Fe(CN)_6\right].H.(Et_2OH)_3$ and on heating reverts to ferrocyanic acid (109). On heating ferrocyanic acid in absolute ethanol for 15 hours at 100°C, Holzl postulated that the following compound was formed:



$$\left[\begin{array}{ccccccccc} & OH_2 & & OH_2 & & OH_2 & & OH_2 & \\ (NC)_2: & Fe & :(CN)_2: & Fe & :(CN)_2: & Fe & :(CN)_2: & Fe & :(CN)_2 \\ & OH_2 & & OH_2 & & OH_2 & & CNEt & \end{array}\right]$$

The isocyano-iron derivatives, $R_4Fe(CN)_6$, are formed by other methods, and will be discussed in detail later.

Ferrocyanic acid forms a series of thio-salts with alkyl sulphides (110). They are formed from acidified ferrocyanide solution on treatment with R_2S, $R'X$, and FeX_3, and are of general formula $R_2R'SH_3.Fe(CN)_6$. They are usually insoluble in water, alcohol, and ether. The compounds produced by this method are:

Product	Reactants (ferrocyanide excluded)
$(C_2H_5)_3SH_3Fe(CN)_6$	$(C_2H_5)_2S$, C_2H_5Br, $FeBr_3$
$(C_2H_5)_2(C_4H_9)SH_3Fe(CN)_6$	$(C_2H_5)_2S$, $(CH_3)_3CCl$, $FeCl_3$
$(C_2H_5)_2(C_6H_5CH_2)SH_3Fe(CN)_6$	$(C_6H_5CH_2)_2S$, C_2H_5Br, $FeBr_3$
$(C_2H_5)(C_6H_5CH_2)_2SH_3Fe(CN)_6$	" " " "
$(C_4H_9)(C_6H_5CH_2)_2SH_3Fe(CN)_6$	$(C_6H_5CH_2)_2S$, $(CH_3)_3CCl$, $FeCl_3$
$(C_6H_5CH_2)_3SH_3Fe(CN)_6$	Passing NH_3 thro' $(C_6H_5CH_2)_3SFeCl_2$
$(C_6H_5CH_2)_2(C_6H_5CO)SH_3Fe(CN)_6$	$(C_6H_5CH_2)_2S$, C_6H_5CO, $FeCl_3$

1.4.3 Decomposition

This has been studied by many workers. Although it is clear that HCN is evolved on heating, the final product and the temperature at which decomposition begins is uncertain. The decomposition products obtained depend upon whether the material is heated in air, an inert atmosphere or in vacuo. According to early studies the decomposition was reported to yield NH_3 in addition to HCN (99), although this has not been confirmed by later work. It does appear that NH_3 is evolved when the decomposition is performed in a reducing atmosphere, e.g. a H_2/N_2 mixture (111). On heating in air Rudge (100) found that the acid was partially decomposed at 100°C, and fully decomposed at 200°C, the gaseous decomposition product being HCN. The overall reaction was expressed by the equation:

$$3\ H_4Fe(CN)_6 \longrightarrow 12\ HCN \ + \ Fe_2^{II}Fe^{II}(CN)_6$$

Browning (74) found that by heating at 100°C in the air, HCN was evolved at first forming a blue compound, but that after one day the acid was fully oxidised to Fe_2O_3, although Bodensiek (97, 98) claimed that on heating to 190°C the acid loses HCN completely, the residue being ferrous ferrocyanide, a blue-black substance. By heating in a stream of hydrogen or in vacuo different results are obtained. By gradually heating ferrocyanic acid to 230°C in a hydrogen stream, Bodensiek (98) formed brown-yellow ferrous cyanide, whilst according to Browning (74, 112) HCN evolution begins at 120°C, being still incomplete at 220°C after three hours, but that on heating for one hour at 300°C the acid is completely decomposed leaving pale yellow ferrous cyanide. On heating at 100°C in a stream of carbon dioxide it is claimed that HCN is completely removed from ferrocyanic acid, leaving a residue of white ferrous cyanide (91). These results were disputed by Deniges (113), who claimed that on heating ferrocyanic acid the first product is $H_2Fe^{II}Fe^{II}(CN)_6$, and subsequently $HFe^{II}Fe^{II}(CN)_5$. Also by heating under vacuum to 110° - 120°C it is claimed that the acid salt $H_2Fe^{II}Fe^{II}(CN)_6$ is obtained, and this is then oxidised to $HFe^{III}Fe^{II}(CN)_6$ (4, 114 - 16).

Heating above 400°C causes complete gas evolution leaving a black residue. Rammelsberg (117) considered this to be a mixture containing the elements of Fe, C, and N, which Deniges (113) considered to be iron carbide and nitride.

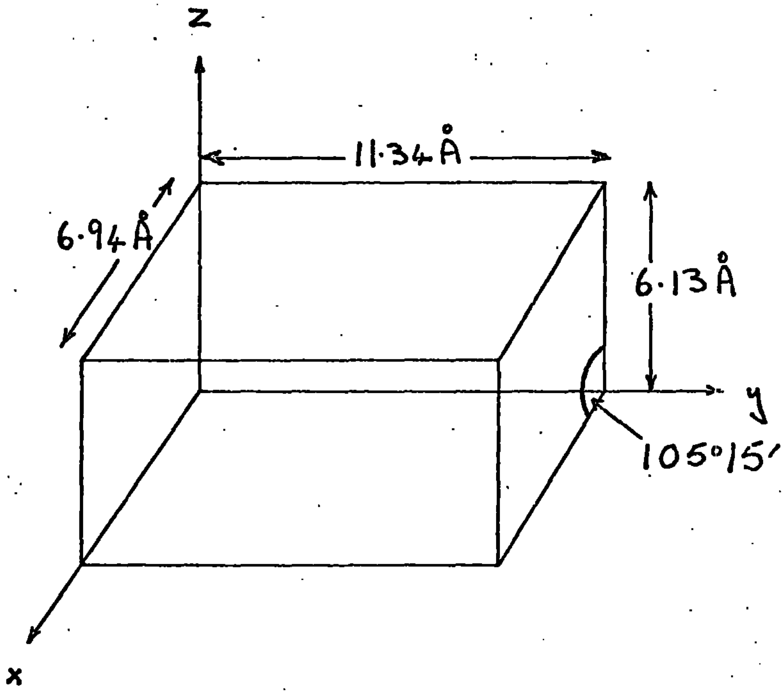
It is evident from the work reviewed that there is considerable confusion regarding the behaviour of ferrocyanic acid. On the thermal decomposition the results from vacuum treatment or in a stream of hydrogen suggest that at least up to 300°C the decomposition proceeds by loss of HCN gas, the residue being a yellow compound which contains Fe, C, and N, and shows reactions for cyanide. The nature of the residue is in dispute. X-ray powder photography (118) has been used to examine the residue and the results suggested to the author that the compound was a complex ferrous ferrocyanide rather than the simple ferrous cyanide.

1.4.4 Infrared spectrum and structure

Until recently little attempt had been made to determine the structure of ferrocyanic acid. Since preparative methods do not give a macrocrystalline structure, X-ray study has been limited to the study of powder patterns, and a preliminary report (119) gives the space group as $P2_1/a(C_{2h}^5)$, with two molecules per unit cell, the iron atoms having site symmetry Ci. The proposed unit cell is shown in Figure 2. No published details of the analysis of the powder pattern have followed the preliminary note at the time of writing.

The infrared spectrum of ferrocyanic acid has been recorded by Jones (12, 44), Beck (45), and Ginsberg (46) the latter paper being particularly detailed. The recorded frequencies of Jones are given in Table 2, and those of Beck in Table 3. The results for the strong absorption frequencies recorded by Ginsberg are shown in Table 11. All the authors are in agreement that the structure consists of $H_4Fe(CN)_6$ units, with a trans arrangement of hydrogen atoms, the units being linked by asymmetric hydrogen bonds, but of the authors only Beck is prepared to postulate a structure on the basis of the infrared evidence. The infrared spectrum results will be discussed in some detail later.

FIGURE 2.



UNIT CELL OF FERROCYANIC ACID (119)

Table 11

Strong Infrared absorption frequencies according to Ginsberg (46)

$H_4Fe(CN)_6$ Frequencies (cm^{-1})	Assignment
406 (m)	$\gamma(M-C)$
419 (m)	$\gamma(M-C)$
448 (m)	$\delta(M-C-N)$
588 (ms)	$\gamma'(M-C)+\delta(M-C\equiv N)$
668 (m)	$\pi(N-H)$
692 (m)	$\pi(N-H)$
887 (m)	$\delta(N-H)$
1650 (ms)	$\delta(N-H)$
2072 (s)	$\gamma(C\equiv N)$
2096 (s)	$\gamma(C\equiv N)$
2106 (sh)	$\gamma'(C\equiv N)$
2370 (ms)	$\nu(N-H)$
2770 (ms)	$\nu(N-H)$
3040 (vs)	$\gamma(N-H)$

CHAPTER 2

Some studies on Ferrocyanic acid

Ferrocyanic acid was chosen as the complex cyanide acid for study because more work had been previously published on this acid than any other, and yet as will be apparent from the opening chapter there is still some considerable confusion. In particular the thermal decomposition has been extensively reported, but with considerable variation in the results obtained, this being especially so in the role of the ether used in precipitation of the acid, in the temperature at which the decomposition begins and ends, and in the nature of the final decomposition product. It is well known that the decomposition of the alkyl ferrocyanides, $R_4Fe(CN)_6$, occurs by loss of the isonitrile RNC. If one can regard the alkyl ferrocyanides as members of a homologous series of which ferrocyanic acid is the parent, then it would seem reasonable to look for the tautomeric form of HCN at least as an initial product of the thermal decomposition of ferrocyanic acid. The thermal decomposition of ferrocyanic acid was therefore studied with particular attention to the following points:

1) The conditions for removal ofether from the initial precipitation product.
2) The temperature at which decomposition begins.
3) The temperature at which decomposition ceases.
4) The nature of the gases evolved.
5) The nature of the final solid decomposition product.

2.1 Preparation and purification of ferrocyanic acid

The acid was prepared by two methods, both using the action of concentrated mineral acid on potassium ferrocyanide, the particular acids used being sulphuric and hydrochloric acids.

The preparation using concentrated sulphuric acid was similar to that used by Heldt (84). 18.5 gms. of finely powdered $K_4Fe(CN)_6.3H_2O$ was added slowly with constant stirring to a mixture of 7.0 mls. of concentrated H_2SO_4, and 13.0 gms. of powdered ice. This mixture was stirred slowly for a few minutes with 92 mls. of ethanol, after which the solid residue, consisting mainly of K_2SO_4 and $KHSO_4$, was removed by filtration. The green filtrate was then treated with 100 mls. of diethyl ether, which precipitated the ferrocyanic acid etherate as a white solid, which was then separated by filtration.

The preparation using concentrated hydrochloric acid was similar to that described by King (120, 121). 20 gms. of $K_4Fe(CN)_6.3H_2O$ was dissolved in 170 mls. of water and the solution cooled in an ice bath. 60 mls. of concentrated hydrochloric acid was then added slowly, with constant stirring, the temperature being maintained at about $0^{o}C$. The addition of 25 mls. of diethyl ether resulted in the precipitation of ferrocyanic acid etherate. After filtration the solid was washed with a 1:1 mixture of concentrated HCl and ether.

The material produced by both methods was further purified in the same way. The white solid was dissolved in the minimum volume of ethanol at ice temperature, and then re-precipitated by the addition of an excess of diethyl ether, the solid being collected by filtration. The procedure was finally repeated using absolute ethanol as solvent, and sodium-dried ether for the precipitation. The diethyl ether was removed by leaving the ferrocyanic acid etherate over silica gel in a vacuum for several days. This left the ferrocyanic acid as a very fine white powder, for which analysis gave the following results:

Method	Fe(%)	C(%)	N(%)	H(%)
H_2SO_4	26.02	33.55	38.82	2.19
HCl	27.46	31.46	39.30	1.79
THEORY	25.86	33.36	38.92	1.87

After a few days in moist air, or on exposure to sunlight, the white solid rapidly turned blue. It was found that the acid could be left over silica gel in a vacuum desiccator stored in a refrigerated cabinet, and in this way the material remained as a white solid for long periods.

2.2
Action of light on Ferrocyanic Acid:

In Chapter I it was noted that ferrocyanic acid becomes blue on exposure to moist air or sunlight. In the present work it was also noted that alcoholic solutions of ferrocyanic acid rapidly deposit a blue solid on exposure to light, and in an attempt to determine whether the nature of the blue solid was influenced by the nature of the solvent, saturated solutions of ferrocyanic acid in a range of alcohols were prepared, and exposed to sunlight. After a few days a large amount of dark blue solid was precipitated in all solutions, and the solid was filtered off and dried in vacuo. The infrared spectrum of each sample of the solids was examined and found to be identical, showing absorption maxima at 1610 cm^{-1}, 2090 cm^{-1}, and 2600 - 3400 cm^{-1} (broad), together with a weak, very broad absorption at 760 - 1000 cm^{-1}.

Alcohol	Solubility
Ethanol	Readily soluble
Methanol	Readily soluble
n-propanol	Fairly soluble
iso-propanol	Practically insoluble
n-butanol	Slightly soluble
sec-butanol	Insoluble

In addition solid ferrocyanic acid was exposed to sunlight, the acid being in a vacuum desiccator over silica gel. The light blue product which resulted from this exposure was treated with alcohol, which dissolved the unchanged ferrocyanic acid (the white solid etherate could be obtained from the solution by precipitation with ether), leaving a small amount of dark blue solid. The solid was removed by filtration, and after drying in vacuo, the infrared spectrum was recorded. The spectrum was identical to that obtained for the solids deposited from alcohol solutions exposed to sunlight.

These observations are in general agreement with those of Mitra (102) who irradiated aqueous solutions of ferrocyanic acid with sunlight, obtaining a dark blue solid for which he considered the overall reaction to be;

$$8\ H_4Fe(CN)_6 + O_2 \longrightarrow 4\ HFe^{III}Fe^{II}(CN)_6 + 24\ HCN + 2\ H_2O$$

It was also noted that the action of light is much more rapid with free ferrocyanic acid than for ferrocyanic acid etherate which turns blue only very slowly. Here one may also note that the adduct of ferrocyanic acid with boron trifluoride, which will be discussed later, is still white after several months exposure to light. These results combined with those of Mitra suggest that the interaction with ether in some way inhibits the evolution of HCN.

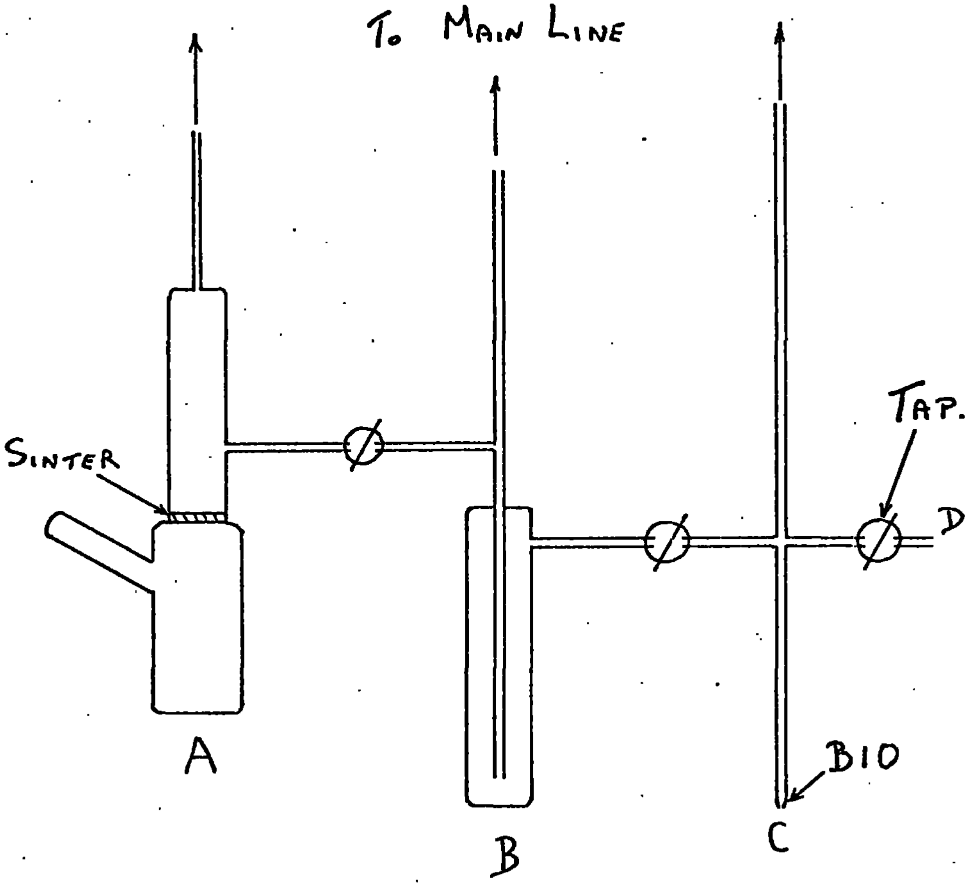
2.3 Ferrocyanic acid etherate:

The removal of ether from ferrocyanic acid etherate in order to produce pure ferrocyanic acid has been performed in a variety of ways by several authors (Chapter 1), using a wide range of temperature conditions. It was considered desirable to study this decomposition to find the most favourable condition for the removal of the ether. For this purpose the etherate was prepared by precipitation from absolute ethanol solution using sodium-dried ether. The solid was filtered and washed several times with aliquots of sodium-dried ether. Excess ether was removed by leaving the solid over silica gel under vacuum for a short time.

The study of the removal was performed in an evacuated system, a section of the vacuum line being shown in Figure 3. A sample of the etherate was placed in the vessel A, which was fitted with a sintered disc to prevent the mechanical carry-over of solid into the remainder of the apparatus, and after freezing the solid with liquid air the line was evacuated. The sample of the etherate was then allowed to warm up to room temperature, the trap B being cooled in liquid air to trap out evolved gases. After leaving the system for a sufficient period such that no further evolution of volatile material occurred the evolved gases were examined by infrared absorption and gas chromatography.

For the examination by gas chromatography a sample of the gas was transferred to a gas-chromatographic column

FIGURE 3.



by means of a sampling device not shown in Figure 3. The sampling device (122) allowed small samples of the gas mixture to be transferred quantitatively from the trap under vacuum conditions, to the chromatographic column operating at above atmospheric pressure. Examination in this way showed that the gas evolved under room temperature conditions consisted of two components. One component was shown, by comparison with the sample of sodium-dried ether used in the precipitation of the etherate, to consist of diethyl ether.

A sample of the volatiles from trap B was allowed to expand into an infrared gas cell which could be attached to the vacuum system. The infrared spectrum proved to be identical to a similar sample of the sodium-dried ether except for one peak at 720 cm $^{-1}$, which corresponds to the strongest peak in the spectrum of pure HCN. Other peaks due to HCN could not be picked out being masked by overlying peaks of diethyl ether. The results of these experiments show that under vacuum conditions at room temperature the main product from the decomposition of the etherate is diethyl ether with admixture of a small quantity of HCN.

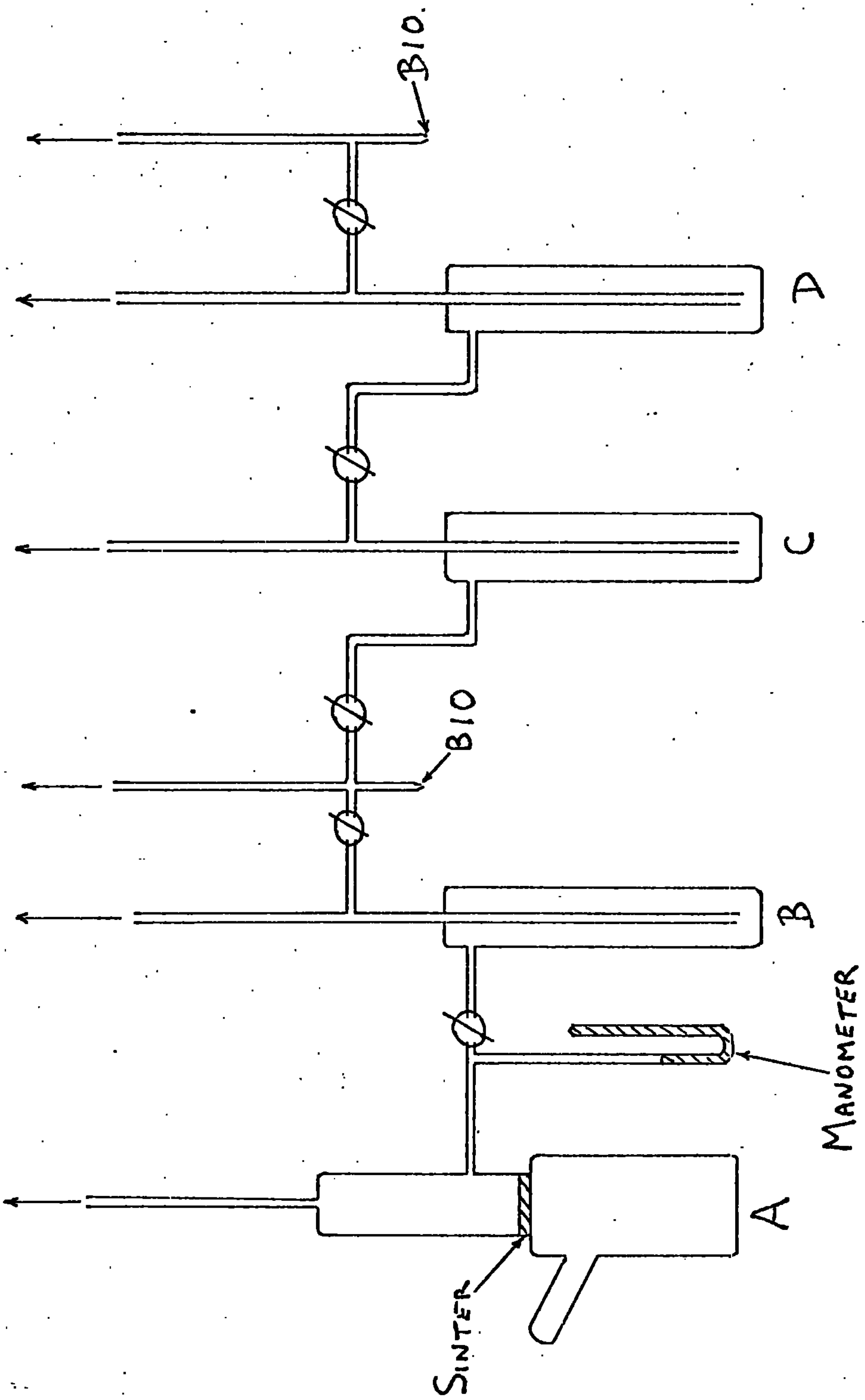
The residue in vessel A was then raised in temperature to 50°C, and volatile material again trapped out in B, which had of course been evacuated to remove the products from the previous observations. The amount of volatile material yielded from this procedure was quite small, even after several hours at 50°C. The product was identified as before to be a mixture of HCN and ether, the only difference being that the HCN : diethyl ether ratio was higher. At 80°C insufficient material was produced to allow examination by infrared absorption, but gas chromatographic observation showed the product to be again a mixture of HCN and diethyl ether with the HCN being the major constituent.

As a result of these observations we have adopted the practice of de-etheration of ferrocyanic acid by storage over silica gel under vacuum at room temperature. Whilst this practice does leave a small residue of diethyl ether it minimises the loss of HCN.

2.4 Thermal Decomposition of Ferrocyanic Acid (50 - 320°C)

The apparatus used for the decomposition is shown in Figure 4. The sample of ferrocyanic acid was contained in the vessel A, which was fitted with a sintered disc to prevent mechanical carry-over of ferrocyanic acid or its decomposition products, these all being in the form of very fine powders. Attached to the vessel A was a mercury manometer which allowed the rate of gas evolution to be followed, as well as indicating when gas evolution ceased.

FIGURE 4.



A series of traps were also attached to the vessel. The first of these (B) was used to condense out all the gaseous products evolved, and the remaining two were used for the distillative separation of the volatile products. Two B 10 cones were placed between the traps to allow for the attachment of an infrared gas cell in order to determine the nature of the separated decomposition products. The vessel A was heated up to 100°C using a water bath, from 100 - 180°C a liquid paraffin bath, and from 180 - 320°C the bath consisted of Wood's metal.

The products obtained on heating to 80°C have already been described, and the sample of ferrocyanic acid was first of all maintained at 80°C until gas evolution had sensibly ceased. On raising the temperature to 100°C the rate of gas evolution increased, although the rate was still fairly slow. After two days at this temperature the solid, which had acquired a pale blue colour during its being heated at 80°C, changed colour to Bottle Green and gas evolution still occurred but the rate of evolution was extremely slow. The spectrum of the gas collected showed it to consist of HCN and diethyl ether together with a third component.

After removal of the volatile material from the collection traps, the temperature of the bath was raised to 160°C, and maintained at this temperature for several hours until gas evolution had ceased. The solid had acquired an emerald green colour. Examination of the volatile material showed that evolution of diethyl ether had ceased, and the gas consisted largely of HCN together with a quantity of the unknown component observed at 100°C. Traces of yet another component could also be seen in the infrared spectrum.

Separation of the gases evolved at 160°C was effected. The trap B was allowed to rise to room temperature, whilst trap C was maintained at - 78°C by means of an acetone-solid CO_2 bath, and the trap D was kept at the temperature of liquid air. After a short period the spectrum of gas in each trap was observed. Only HCN was found in trap B, and the unknown component, together with some HCN was found in traps C and D. This unknown gas was thus more volatile than HCN, and its spectrum showed the following strong peaks (cm^{-1}):

1190, 1350, 1360, 1380, 1730, 1740, 2900, 2950

On raising the temperature above 160°C no gas was evolved until the temperature reached 210°C, when a slow evolution of gas began. The temperature was slowly raised with continuing gas evolution, the temperature being finally maintained for a short time at 320°C when gas evolution finally ceased. Raising the temperature still further produced no more gas evolution. The infrared spectrum of the volatile material collected showed three components, two of which were readily identified as HCN and diethyl ether. The trap B was allowed to rise to room temperature, trap C being maintained at 95°C (toluene slush bath), and trap D maintained at liquid air temperature. Since HCN has zero vapour pressure at - 95°C (123) the trap C retained all the HCN. Complete separation of the unknown component was effected in this way. The unknown component was identified as ethylene from its infrared spectrum.

The presence of ethylene was unexpected. The samples of ferrocyanic acid used in the thermal decomposition study had been prepared by use of concentrated sulphuric acid. As already noted in Chapter 1 sulphuric acid forms a series of stable adducts with ferrocyanic acid, and it was considered possible that some of the sulphuric acid used in the preparation could have remained associated with the ferrocyanic acid. Thus when the temperature was raised the sulphuric acid could bring about dehydration of ether remaining in the compound, and thus account for the presence of ethylene, i.e. (124, 125).

$$Et_2O + H_2SO_4 \longrightarrow Et_2OH^+ + HSO_4^- \longrightarrow EtOH + EtHSO_4$$

$$EtOH + H_2SO_4 \xrightarrow{160 - 170^oC} C_2H_4 + H_2O + H_2SO_4$$

In order to test this possibility further samples of ferrocyanic acid were prepared using concentrated HCl instead of H_2SO_4, and the decomposition repeated. The Decomposition was found to be the same as that already observed. The method of preparation of ferrocyanic acid does not therefore influence the nature of the decomposition products. The results of the study of the volatile products arising from the thermal decomposition are summarised in Table 12.

From the observation that the evolution of HCN appears to cease at 160°C and then restart at + 210°C with continuous gas evolution up to 320°C when all evolution of gas ceases, we are led to the conclusion that two distinct compounds at least exist. Starting from the white ferrocyanic acid continuous colour variation occurs up to 160°C when the residue has an emerald green colour, and on the recurrence of gas evolution at 210°C again continuous colour variation is observed the final product being golden-yellow. Both compounds were prepared by heating ferrocyanic acid at the appropriate temperature under vacuum conditions.

When exposed to air both compounds darken rapidly, with a small but noticeable rise in temperature, and the final dark blue colour attained is the same for both compounds. Analyses were performed on the samples exposed to air, and the following results obtained:

Product	Fe(%)	C(%)	H(%)	N(%)
A	33.7	22.2	0.93	-
B	46.0	21.32	-	23.55

A - $H_4Fe(CN)_6$ heated to 160°C and finally exposed to air
B - " " " 320°C " " " " "

From this data the following atom ratios were derived:

Product	Fe	C	H	N
A	1	3.08	1.55	-
B	1	2.15	-	2.01

The atom ratios thus correspond to the empirical formulae:

A - $H_3Fe_2(CN)_6$
B - $Fe(CN)_2$

If we disregard the hydrogen analysis result, and recall that HCN is the only major volatile thermal decomposition product, it is possible to formulate compound A as Dihydrogen iron (11) hexacyanoferrate (11),

Table 12

Summary of the decomposition of $H_4Fe(CN)_6$

Temperature	Colour of residue	Gases evolved
22°C	White	Ether, HCN
50°C	White	Ether, HCN
80°C	Pale Blue	Ether, HCN
100°C	Bottle Green	Ether, HCN, + unknown gas
160°C	Emerald Green	HCN, unknown gas, trace of C_2H_4
320°C	Golden-yellow	HCN, Ether, C_2H_4

i.e. $H_2Fe(II)\ Fe(CN)_6$. Dr. Gibb of the University of Newcastle produced a Mossbauer spectrum of this compound which certainly showed the iron atoms to have different environments, but the spectrum was complicated and further work is necessary before any definite statement can be made. At the time of writing no further work has been done on this compound.

The atom ratios for compound B admit of formulation as iron (II) hexacyanoferrate (II), i.e. $Fe_2Fe(CN)_6$. The Mossbauer spectrum was again produced by Dr. Gibb who considered the spectrum to be consistent with formulation as a ferrocyanide. However the immediate product of the thermal decomposition, the golden-yellow compound, was not examined, and our examination of the chemical properties of this compound would still appear to leave open the formulation of Bodensiek (97, 98) who regarded the compound as ferrous cyanide.

2.5 Infrared Spectra of Various Ferrocyanides

This work was undertaken in the hope that it might provide further evidence on the nature of the thermal decomposition product obtained at 320°C, i.e. the golden yellow product.

Several compounds of the form $M_2^{II}Fe(CN)_6$ were prepared by mixing aqueous solutions of ferrocyanic acid, and aqueous solutions of the appropriate metal chloride in stoichiometric ratio. The metal chlorides used were those of the divalent transition metals Mn, Co, Ni, Cu, and Zn. The precipitated ferrocyanides were filtered off, washed several times with distilled water, and dried first in a vacuum desiccator and finally in a vacuum oven at 100°C for several days. The infrared spectra of the products was observed and compared with the spectrum obtained for the product of thermal decomposition of ferrocyanic acid (320°C).

The results of the infrared observations are shown in Table 13, and apart from the characteristic $C\equiv N$ frequency at approximately 2100 cm^{-1} no attempt has been made to assign the frequencies of particular modes. All of the ferrocyanides examined showed common absorption frequencies at approximately 490 cm^{-1} (m), 600 cm^{-1} (m), 1120 cm^{-1} (w), 1410 cm^{-1} (m), 1615 cm^{-1} (m), 2100 cm^{-1} (s), and 3400 cm^{-1} (br,s). We shall have occasion later to remark on the frequency 1615 cm^{-1}. The only major difference noted between the spectra and that of the decomposition product is the existence of two $C\equiv N$ stretching frequencies for the decomposition product as against one for the transition metal ferrocyanides. We are not in a position to offer any explanation for this. The correspondence with the remaining frequencies would appear to offer support for this formulation of the decomposition product as a ferrocyanide.

However, although infrared and Mössbauer studies appear to support the ferrocyanide formulation, we should also consider the chemical behaviour of the compound.

Table 13

Infrared Spectra of Transition Metal Ferrocyanides

$Mn_2^{II}Fe(CN)_6$.	$Co_2^{II}Fe(CN)_6$.	$Ni_2^{II}Fe(CN)_6$.	$Cu_2^{II}Fe(CN)_6$.	$Zn_2^{II}Fe(CN)_6$.	$Fe_2^{II}Fe(CN)_6$?
457 (m)	-	-	-	-	460 (m)
485 (w)	480 (w)	480 (m)	497 (m)	497 (m)	485 (m)
-	505 (s)	-	-	-	-
-	522 (m)	-	-	-	-
598 (m)	602 (m)	600 (m)	597 (m)	610 (m)	617 (m)
880 (m)	-	-	-	835 (w)	-
990 (w)	990 (w)	-	-	990 (w)	-
-	1040 (w)	-	-	1040 (w)	1025 (w)
1125 (w)	1120 (w)	1120 (w)	-	1120 (w)	1120 (w)
1420 (m)	1400 (m)	1405 (m)	1400 (m)	1400 (m)	1410 (w)
1620 (m)	1615 (m)	1615 (m)	1610 (m)	1615 (m)	1615 (m)
-	-	-	-	-	2030 (s)
2065 (s)	2100 (s)	2110 (s)	2120 (s)	2110 (s)	2075 (s)
3300 (br,s)	3400 (br,s)	3400 (br,s)	3450 (br,s)	3600 (br,s)	3410 (br,s)

All absorption frequencies are expressed in wavenumbers (cm^{-1})

w - weak

m - Medium

s - Strong

br - Broad

2.6 Reactions of the Final Thermal Decomposition Product of $H_4Fe(CN)_6$

The cyanide ion shows in its compounds many similarities to the halogens. On this basis one would expect anhydrous ferrous cyanide, if it exists, to exhibit some similarity to the anhydrous ferrous halides in its behaviour. Thus a comparison of the known properties of the anhydrous ferrous halides with the final product of the thermal decomposition of ferrocyanic acid could be of assistance in determining the nature of the compound. The properties of anhydrous ferrous chloride have been studied in some detail, particularly its addition products with a variety of nitrogen compounds (126).

Ferrous chloride is said to form a series of addition compounds with ammonia:

$FeCl_2.10\ NH_3$ - is obtained, as an almost pure white powder, when NH_3 is distilled on to $FeCl_2$ at - 78°C (126, 127), and the excess of liquid ammonia is allowed to evaporate slowly. At -55°C 9.3 molecules of NH_3 per mole of $FeCl_2$ was observed.

$FeCl_2.6NH_3$ - on allowing the temperature of the 10 - ammoniate to rise to 0°C, and leaving for some time, the 6-ammoniate is obtained, (126, 127). It is also said to form when NH_3 is passed through a mixture of $FeCl_2$ and NH_4Cl, at room temperature (126, 128-130). It is a white powder, for which the dissociation pressure at various temperatures

(128, 131), and heat of formation (132) have been measured.

$FeCl_2.2NH_3$ - is readily obtained by decomposition of the hexammine, as a grey powder (126, 128, 129 132). Its dissociation pressure at various temperatures and its heat of formation have been measured (132).

$FeCl_2.NH_3$ - is obtained as a grey powder when the diammine is heated (132), and its dissociation pressures and heat of formation have been measured.

The 6-ammoniates of $FeBr_2$ (131), and FeI_2 (131, 133) have also been reported.

$FeCl_2$ also forms addition compounds with other nitrogen-containing compounds. If ~~an~~ alcoholic solutions of $FeCl_2$ and hydrazine hydrate are mixed a pale yellow powder $\left[Fe(N_2H_4)_2\right] Cl_2$ is obtained (126, 143). According to Ephraim (126, 134) the action of gaseous methylamine on $FeCl_2$ produces a solid of formula $\left[Fe(CH_3NH_2)_5\right] Cl_2$, and also products with $FeBr_2$ and FeI_2, although compound formation is disputed by Biltz (126, 132). Green crystals of $\left[Fe(N_2H_4CS)_4\right] Cl_2$ are said to result from the reaction of thiourea and ferrous chloride in alcoholic solution (126, 135). The following compounds are reported to result with pyridine and $FeCl_2$, either dry, in alcohol solution, or from aqueous solution:

$[Fe(C_5H_5N)_2]Cl_2$ - Bright yellow crystals (126, 136)
$[Fe(C_5H_5N)_3]Cl_2$ - Canary yellow crystals (126, 137-9)
$[Fe(C_5H_5N)_4]Cl_2$ - Yellow needles (126, 136, 140)

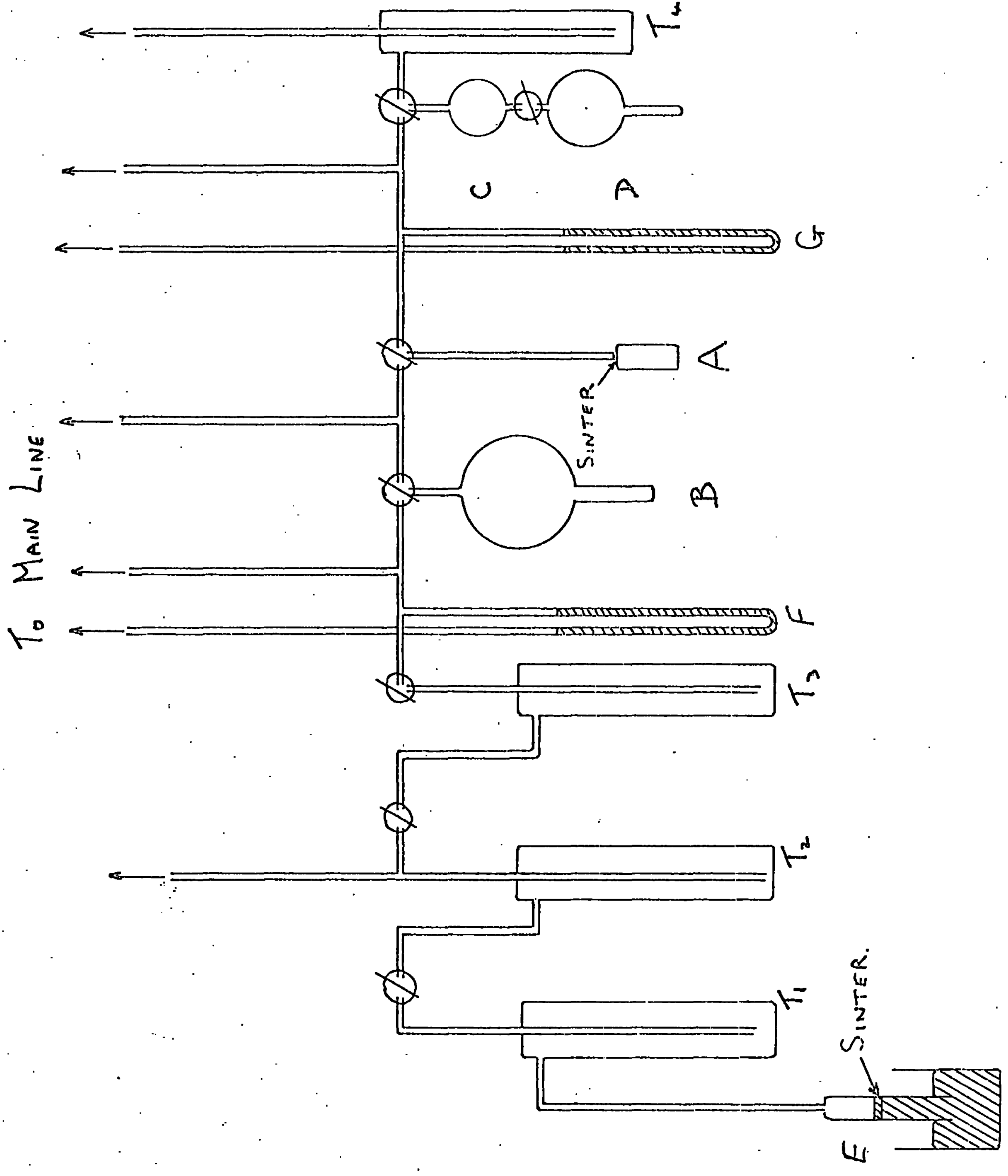
With aniline the compound $[Fe(C_6H_5NH_2)_2]Cl_2$ as yellow needles has been reported (126, 141-2)

A search for comparable behaviour in the product of the thermal decomposition of ferrocyanic acid was made.

2.6.1 Action of Ammonia

For the study of the action of ammonia the apparatus shown in Figure 5 was used. A known weight of pure ferrocyanic acid was placed in the vessel A, which was fitted with a glass sintered disc to prevent loss of solid during the decomposition and subsequent study, and the compound was decomposed at 320°C as before, the products of decomposition being collected in the trap T_4. Ammonia was immediately admitted from the calibrated bulb B, and condensed on the solid using liquid air. The ammonia had been previously admitted to the apparatus through the ventil E, and purified by trap to trap distillation using the train of traps, T_1, T_2, and T_3. The pure ammonia was then collected in the calibrated bulb B, and its pressure observed on the manometer F. The two way tap attached to B thus allowed a definite known quantity of ammonia to be isolated in B for subsequent quantitative transfer to the reaction vessel A. The amount

FIGURE 5.

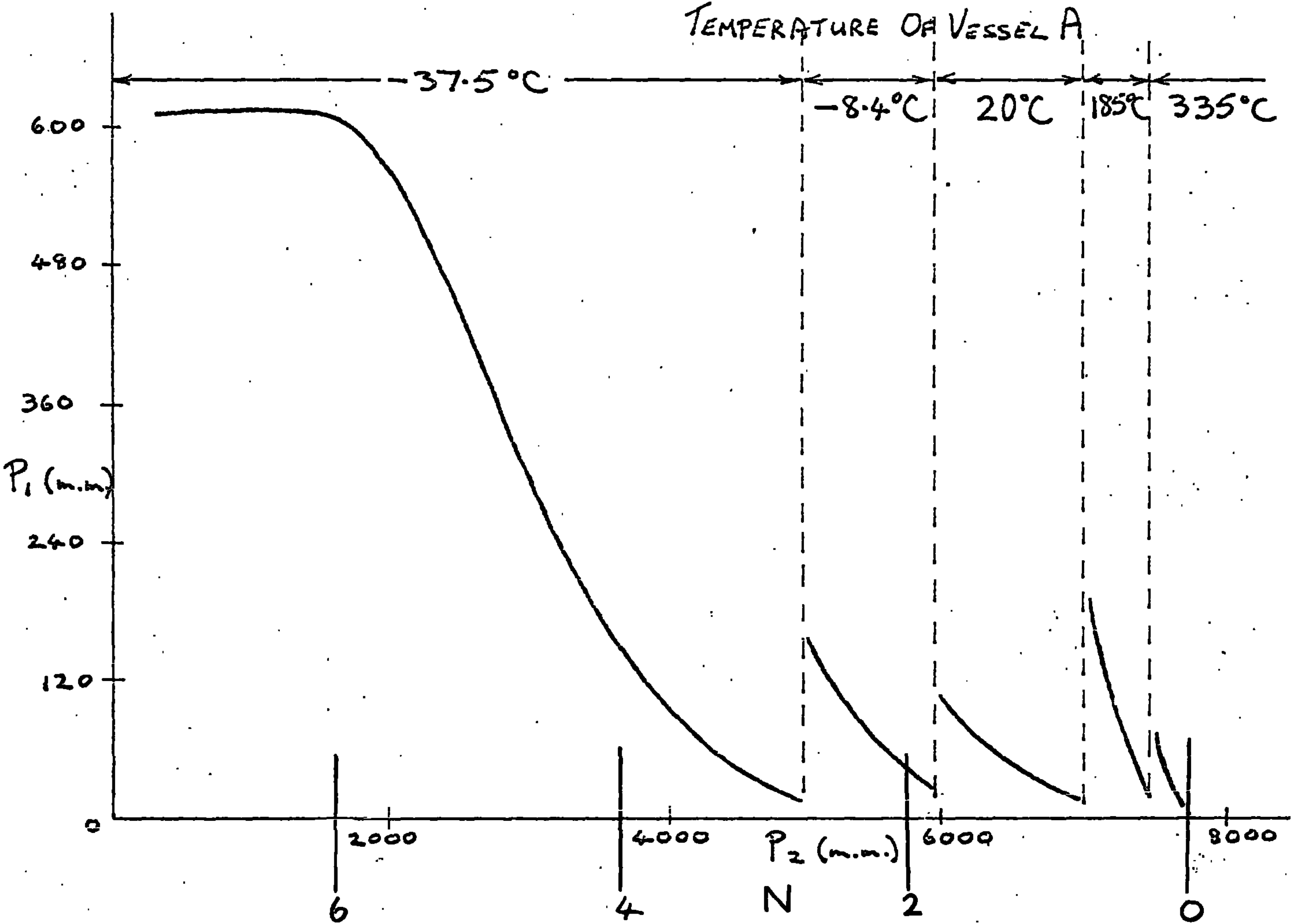


of ammonia added was determined by assuming that a 10-ammoniate would be formed, i.e. $Fe(CN)_2.10\ NH_3$, and then adding a slight excess above the calculated quantity. After condensing the ammonia on to the decomposition product using liquid air refrigerant to reduce the vapour pressure to zero, the two way tap attached to A was used to connect the reaction vessel A to the remainder of the system. The vessel A was then surrounded by a bath at - 78°C.

At the temperature of - 78°C the vessel A was exposed to the bulb system C and D. These bulbs were of exactly calibrated volume, and in conjunction with the manometer G allowed the removal of exactly known amounts of ammonia from the bulb A. The ammonia was subsequently trapped out in trap T_4. After each removal of a known amount of ammonia the pressure of the bulb A was observed until constant readings were obtained, when a further quantity of ammonia would be removed. From such data the composition of the contents of bulb A, its temperature, and the vapour pressure of ammonia over the system were known. The process was continued until the pressure fell to a small value, when a new equilibrium temperature was selected giving a suitably large vapour pressure of ammonia.

The results obtained are summarised in Figure 6 which gives the equilibrium pressure of ammonia over the system

FIGURE 6



P_1 – Equilibrium Pressure Of NH_3 Over System In Vessel A.

P_2 – Total Pressure Of NH_3 Removed From Vessel A.

N – Number Of Molecules Of $NH_3/Fe(CN)_2$ Molecule Left In Vessel A.

as a function of the total pressure of ammonia used, over various temperature ranges. The total pressure of ammonia removed from the system gives a measure of the number of moles of ammonia remaining in contact with the decomposition product. This latter is also recorded on the graph.

At the original temperature the pressure remained constant throughout. The pressure was consistent with the value of the vapour pressure of ammonia at - 78.5°C (123), the temperature of the experiment, and thus represented the pressure of excess ammonia over the system. The results showed no formation of a 10-ammoniate, and so the temperature was raised to -37.5°C in order to increase the ammonia pressure. At first the pressure remained constant, the value being again consistent with the presence of free ammonia, but at a composition corresponding to that of a 6-ammoniate the pressure decreased rapidly. From this point on the pressure of ammonia continued to decrease, eventually reaching such a low value that it was necessary to increase the temperature in order not to prolong the experiment, and eventually a temperature of 335°C was being used. Even at this final temperature it was necessary to heat for some considerable time before all the ammonia was finally removed.

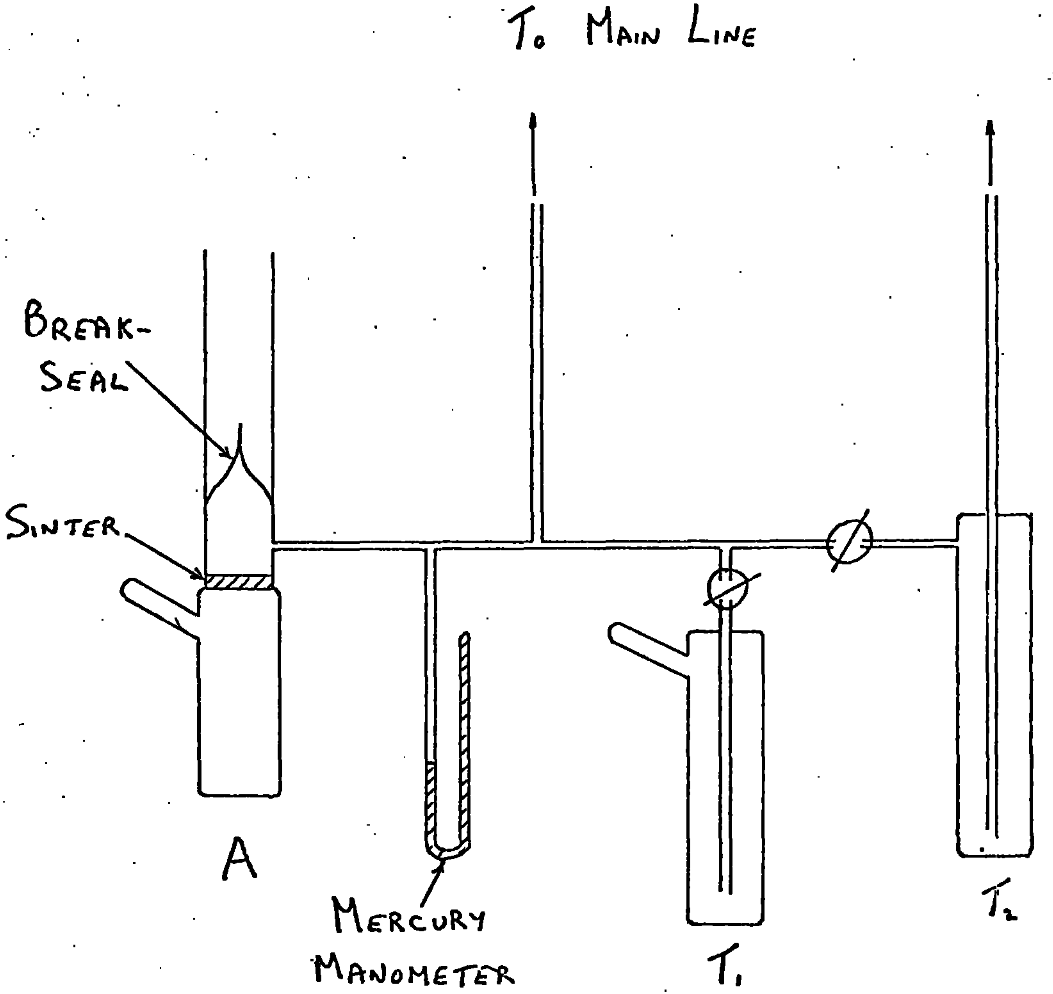
The results obtained indicate that a hexammoniate is definitely formed by the decomposition product, i.e. six moles of ammonia per formula weight of $Fe(CN)_2$. The results did not show the presence of other ammoniates, although a preliminary trial experiment with somewhat simpler apparatus had indicated the possibility of a 2-ammoniate. The results also show that the ammonia is strongly held at compositions corresponding to the lower ammoniates. The 6-ammoniate is clearly unstable in the absence of an excess of ammonia, and in such ease a study of the temperature dependence of its vapour pressure could not be used to estimate the heat of formation.

2.6.2 Action of Ethylene-Diamine

Ethylene diamine contains impurities, such as NH_3, CO_2, H_2O, together with higher boiling liquids such as diethylene triamine, and so had to be purified before use. The purification was performed by refluxing the ethylene diamine over a small amount of sodium, followed by fractional distillation in vacuo. The distilled product was transferred immediately to a vacuum line for use, as it readily absorbs carbon dioxide and water from the atmosphere.

The apparatus used is shown in Figure 7. A known amount of pure ferrocyanic acid was sealed into the

FIGURE 7.



reaction vessel A, which was fitted with a glass sintered disc and a break-seal. A known volume of the freshly purified ethylene diamine was placed in the trap T_1, and the whole system thoroughly evacuated. The tap T_1 was closed to isolate the ethylene diamine, and the ferrocyanic acid decomposed as before by heating at 320°C until no further gaseous products were evolved. Thus a known weight of the golden-yellow decomposition product remained in the apparatus. The ethylene diamine was then distilled on to the product. The reaction vessel A was then sealed at point B, and removed from the vacuum line.

No visible reaction was observed on leaving the reaction vessel at room temperature for several hours, so the tube was heated at 160°C for five hours by which time the solid had acquired a grey-green colour.

The reaction vessel was again attached to the vacuum system, and the excess of ethylene diamine condensed back into the original trap T_1. The amount of ethylene diamine recovered was noted. The grey-green solid remaining in the reaction vessel appeared to be fairly stable in air, losing ethylene diamine only very slowly on standing. From the known amount of ethylene diamine recovered, and the weight of ferrocyanic acid used, an empirical formula of $Fe(CN)_2.(en)$ was obtained. An immediate analysis of the iron content of the compound gave 33.45%, that required for $Fe(CN)_2.(en)$ being 33.33%

On warming the grey-green product in vacuo, ethylene diamine was rapidly evolved, the solid acquiring a yellow-brown colour, which turned rapidly black on exposure to oxygen. The spectrum of the grey-green additon compound showed the following frequencies (cm^{-1})

480 (w), 505 (w), 590 (m), 630 (m), 985 (m), 1020 (m), 1110 (w).
1155 (w), 1285 (w), 1335 (w), 1400 (w), 1460 (w), 1595 (m), 1635 (w).
2050 (s), 2090 (s), 2890 (w), 316) (m), 3280 - 3360 (br,m).
centred at 3300, and showing shoulders at approximately 3160, 3250, 3370 and 3480.

2.6.3. Action of Pyridine

The previous experiment was repeated using pyridine, the procedure being duplicated. No reaction occurred, even after heating the vessel at temperatures up to 200° for prolonged periods.

2.6.4. Exposure to Air

The apparatus shown in Figure 3 was used. A sample of pure ferrocyanic acid was placed in the vessel A, and the system evacuated. The sample was decomposed by heating to 320°C until gas evolution had ceased, when it was allowed to cool to room temperature. Air was then admitted to the apparatus through the tap D, with the trap B cooled in liquid air to prevent access of carbon dioxide and water. The golden-yellow solid darkened rapidly, the colour change being accompanied by a noticeable rise in temperature. The resulting dark blue, almost black, solid was left in contact with the air for some hours to ensure completion of the reaction.

Analysis: Fe: 45.05% C: 19.58% N:22.4% O: 12.97% The figure for oxygen is quoted as that required to give 100%, and we have assumed that it was the cause of reaction. These results give the following values for the atom ratios:

Fe: 1 C: 2.02 N: 1.97 O: 1.01

and these correspond to an empirical formula FeC_2N_2O.

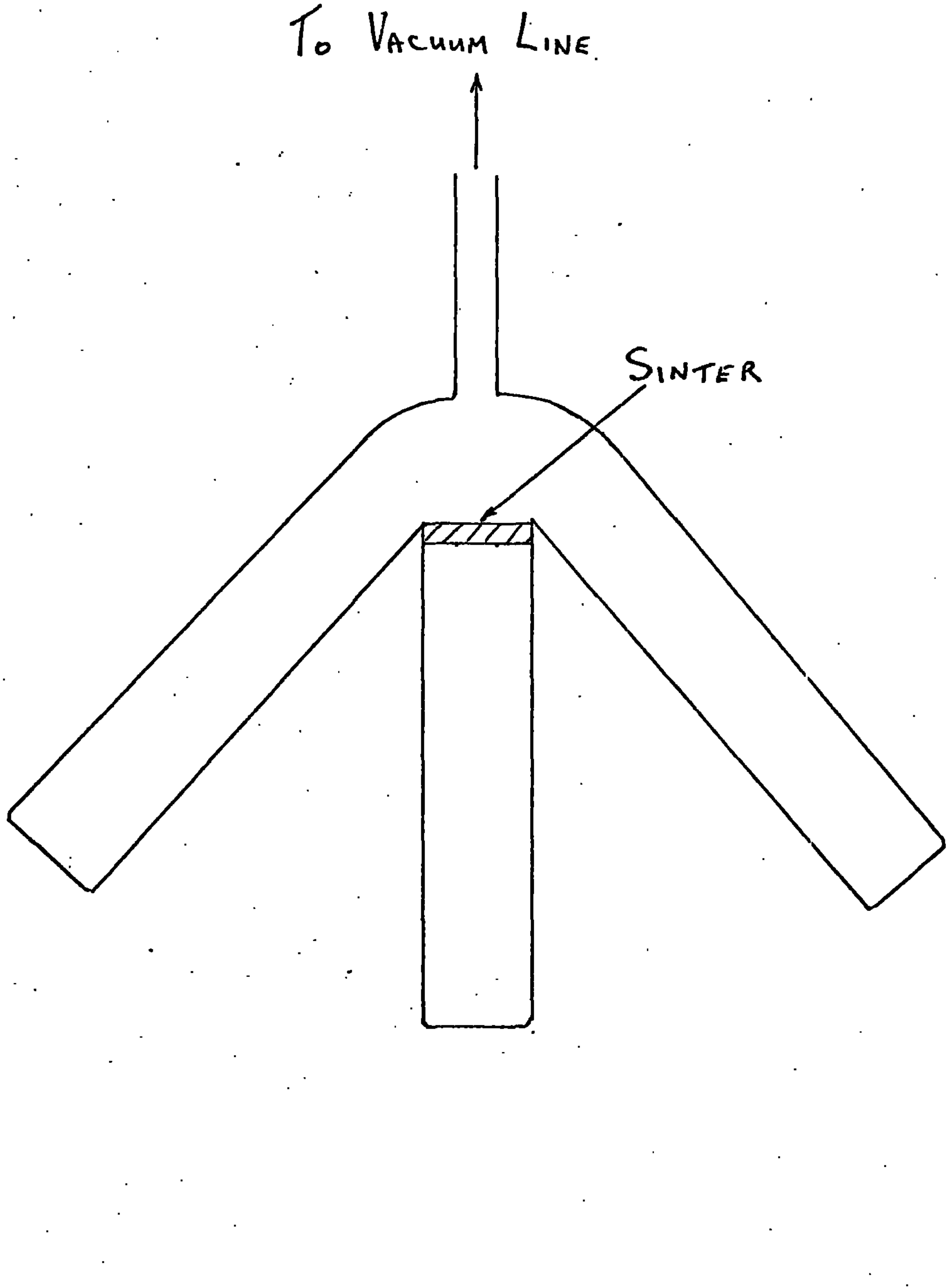
One further feature is worthy of mention here. If after the decomposition of ferrocyanic acid the golden-yellow decomposition product is allowed to stand in vacuum for some hours, a perceptible change in colour is observed, the solid acquiring a greenish hue. Under this condition exposure to air does not produce the immediate darkening observed earlier, but requires several hours for visible completion. The sample exposed to air almost immediately after preparation shows visibly complete reaction in less than a minute.

2.7 Thermal Decomposition in Carbon Monoxide

The molecules HNC and CO are isoelectronic. If on decomposing ferrocyanic acid the HNC group leaves the molecule as a unit, as appears to be the case with the isonitrile complexes which yield isonitrile, then it is possible that CO could replace the HNC in the co-ordination sphere of the iron atom. This would lead to the production of a mixed carbonyl cyanide. No compound containing carbonyl and cyanide groups only in the co-ordination sphere are known, with the exception of the carbonyl prusside ion $Fe(CN)_5CO^{3-}$, whereas the carbonyl halides are known. The fact that CN^- is classed as a psuedo-halogen suggests that these mixed carbonyl cyanides should exist. Some preliminary experiments were made to test this.

The three-limbed vessel shown in Figure 8 was used first. The central limb contained a sample of ferrocyanic acid, a second limb was filled with active charcoal, and the third limb was empty. The vessel was evacuated, the charcoal cooled in liquid air, and a large volume of carbon monoxide passed into the vessel. The charcoal under these conditions absorbed the whole of the carbon monoxide. The vessel was then sealed. The empty limb was then immersed in liquid air, the charcoal being allowed to attain room

FIGURE 8.

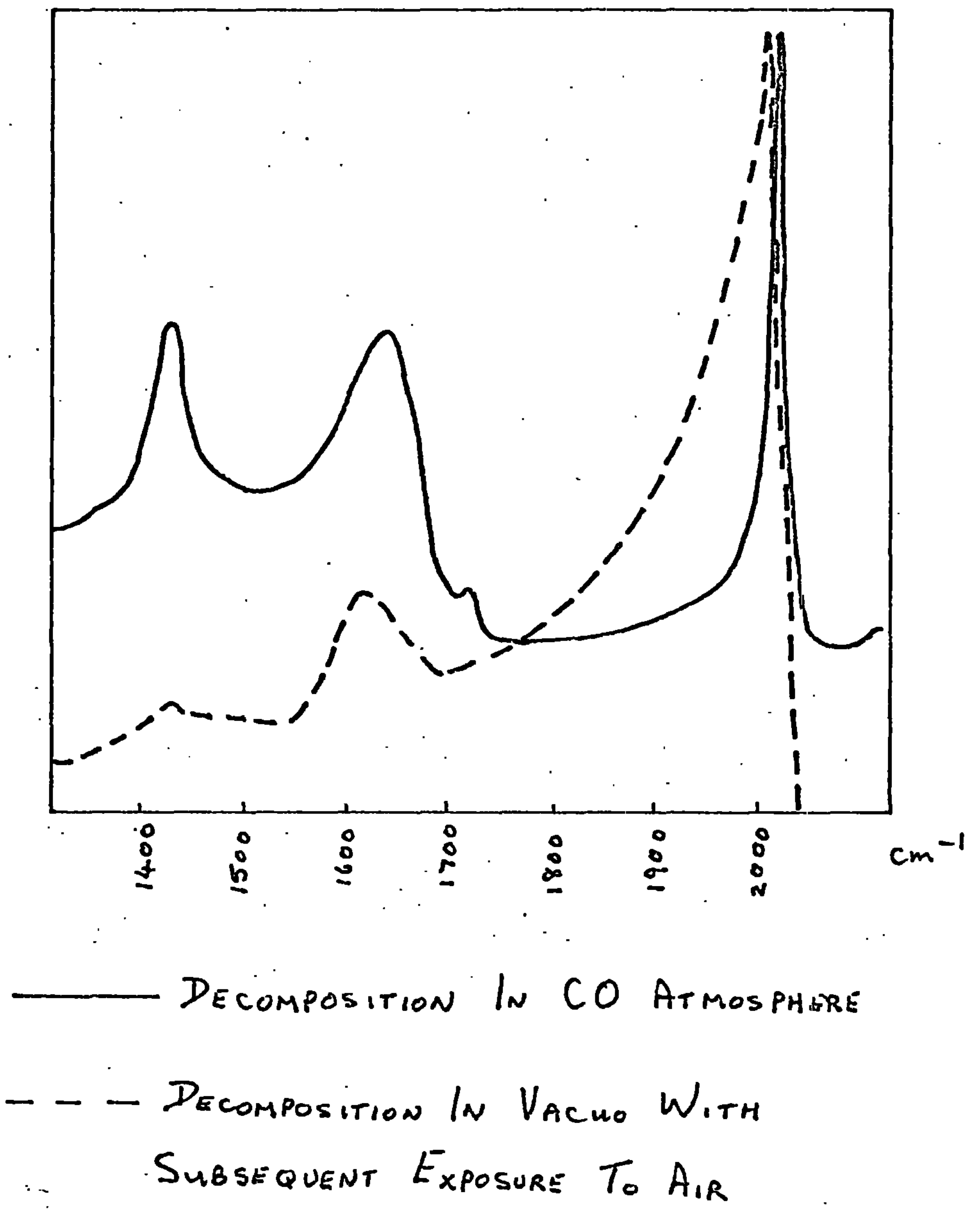


temperature with consequent desorption of the carbon monoxide. In this way the vessel was filled with an excess pressure of carbon monoxide.

The sample of ferrocyanic acid was then heated in a bath of Woods metal, only the tip of the tube being immersed so as not to provide heat to the rest of the vessel. On decomposition the ferrocyanic acid blackend, the evolved HCN being condensed in the limb cooled in liquid air to absorb the carbon monoxide, and the reaction vessel could then be opened.

The infrared spectrum of the product was found to show similar absorptions to those of the product of thermal decomposition in vacuo with subsequent exposure to air, and the spectra are compared over a limited range in Figure 9. It was not found possible to draw any definite conclusion from these observations, and the experiment was abandoned, except for one further experiment performed for us by the Billingham Laboratories of I.C.I. In this a sample of ferrocyanic acid was heated to 120^{o}C under a pressure of 500 atmospheres of CO. The dark coloured product developed a considerable pressure of gas when sealed in a tube. However the product was not homogeneous, and the infrared spectrum showed similar features to those of ferrocyanic acid, and it was concluded

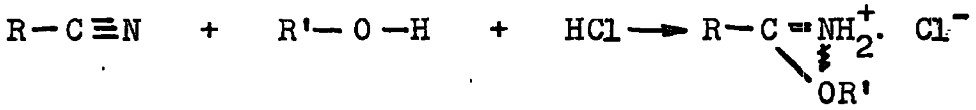
FIGURE 9


1400
1500
1600
1700
1800
1900
2000
cm^{-1}
——— Decomposition In CO Atmosphere
- - - Decomposition In Vacuo With Subsequent Exposure To Air

that decomposition was incomplete under the conditions used.

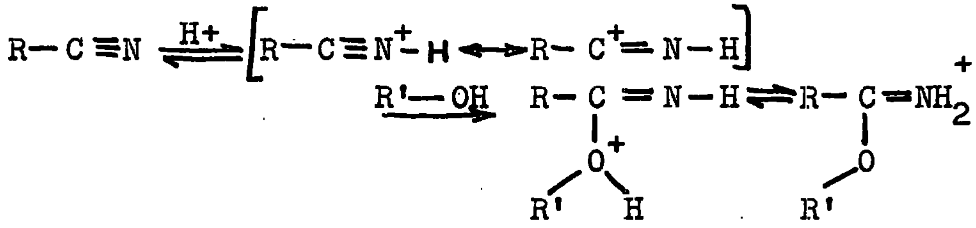
2.8 Discussion

If an organic nitrile and an alcohol are mixed in equimolar proportions in dry ether, and the solution treated with gaseous HCl, an imino-ether hydrochloride is slowly deposited (144):

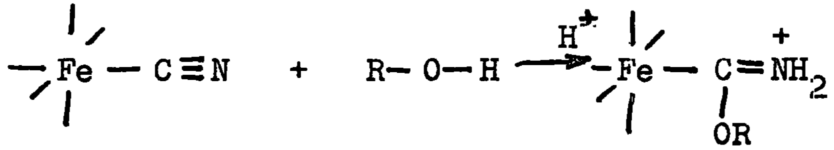


$$R-C\equiv N \;+\; R'-O-H \;+\; HCl \longrightarrow R-\underset{OR'}{C}=NH_2^{+}\cdot\ Cl^{-}$$

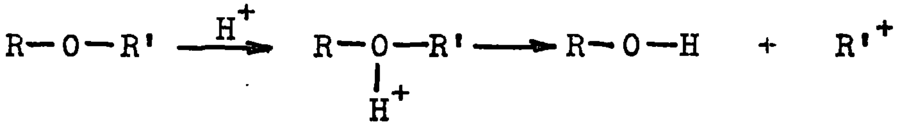
This reaction is considered to be the acid-catalysed addition of an alcohol to a nitrile (145), proceeding as follows:



Noting that the main requirement for the formation of an organic imino-ether is the presence of a strong acid to provide hydrogen ions, a similar situation might be considered to occur in the case of ferrocyanic acid. The ferrocyanic acid is a strong protonic acid and the parallel reaction would then be represented by:



In the presence of strong acids an ether readily splits in the following way:

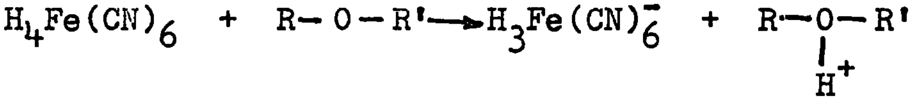


$$R-O-R' \xrightarrow{H^+} R-\underset{H^+}{O}-R' \longrightarrow R-O-H + R'^+$$

e.g. in the presence of strong sulphuric acid diethyl ether undergoes the following reactioh:

$$Et-O-Et + H_2SO_4 \longrightarrow Et-O-H + EtHSO_4 \quad (124)$$

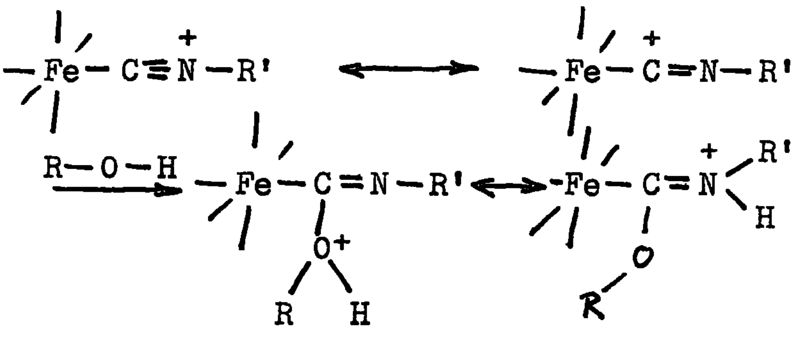
Since ferrocyanic acid is a strong acid it might cause similar cleavage of ether:



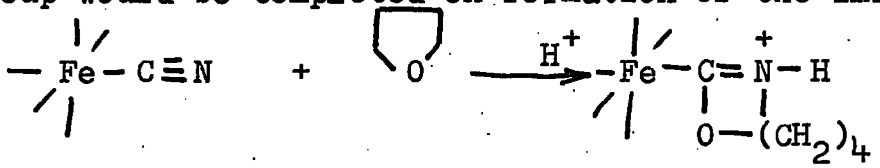
$$H_4Fe(CN)_6 + R-O-R' \longrightarrow H_3Fe(CN)_6^- + R-\underset{H^+}{O}-R'$$

$$\longrightarrow R'H_3Fe(CN)_6 + R-O-H$$

The reaction can then proceed as represented above for alcohol addition:

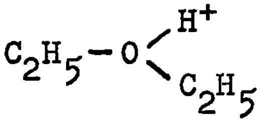


If these reactions are possible with the co-ordinated cyanide group, and there is as much reason to expect it as to doubt it, then under the conditions of preparation of ferrocyanic acid products of the type represented above could well occur. Ferrocyanic acid can also be precipitated from alcoholic solution by ring ethers, such as tetrahydrofuran, which can also undergo cleavage in the presence of strong acids, and in the particular example quoted a seven membered ring with the cyanide group would be completed on formation of the imino-ether:

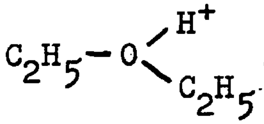


The extent of imino-ether formation with ferrocyanic acid would be dependent on the acid strength required for imino-ether formation. The first two dissociation constants of ferrocyanic acid are those of strong acids, and if these are sufficient to bring about imino-ether formation one would expect two molecules of ether to be attached for complete reaction. However the reaction is clearly one involving equilibria and therefore an overall stoichiometric composition is not to be expected, and as such could be used to account for the reported compositions of ferrocyanic acid etherate. Against this we have the observation, reported in Chaper 1, that the etherate can be formed by exposing pure solid ferrocyanic acid to ether vapour. In this case it is difficult to see how the ionisation required for imino-ether formation can occur. Again the fact that ether can be recovered unchanged at room temperature does suggest that covalent bond formation is unlikely.

A further possibility to account for formation of the etherate is that of oxonium salt formation. Ethers form a series of salts with strong acids which can be isolated as crystalline derivatives at low temperatures, e.g. diethyl oxonium hydrogen sulphate,



. HSO_4^-, and also diethyl oxonium chloride,



. Cl^-, M.Pt. - 92°C.

The strong acid character of ferrocyanic acid could then lead to the formation of an oxonium salt, such as - $C_2H_5-\underset{H}{O}-C_2H_5^+ \cdot H_3Fe(CN)_6^-$, or even further to $\left[C_2H_5-\underset{H}{O}-C_2H_5^+\right]_2 \cdot H_2Fe(CN)_6^{2-}$. Since such salts are known to be stable at low temperatures, the ready loss of ether from ferrocyanic acid would not be unexpected. Against this one has our observation that the loss of ether from the ferrocyanic acid can persist up to high temperatures.

A view that would take into account most of the observations is that of the formation of a clathrate compound when ferrocyanic acid is precipitated from its solutions by means of ether. A form of clathrate is reported to be formed by cis-dicyanotetrakis (methyl isocyano) iron (II) when it is crystallised (146). Thus 1:1 compounds are formed with such molecules as methyl cyanide and methyl alcohol. The clathrate has an open structure which favours the escape of the enclosed molecule into the surrounding atmosphere, but the escape is not isotropic, the escaping molecules leaving by those planes which are most widely spaced. Such behaviour is readily observed with the large crystals of the host lattice which can be prepared, but the micro-crystalline nature of ferrocyanic acid does not permit a comparison. If such an enclosed structure for ferrocyanic acid were accepted, then the presence of the ether, and the reversible loss of ether to the atmosphere at ordinary temperatures can be accounted for. However, it is difficult to account for the absence of alcohol when the ferrocyanic acid is precipitated from alcohol solution, or even of water when it is precipited from aqueous acid solution. The thermal decomposition products do not suggest the presence of significant quantities of alcohol or water. An explanation of the rise in temperature which is observed when the pure ferrocyanic acid is exposed to ether vapour would still be required. For this to derive from a purely clathrating process would seem to involve a lattice contraction, and yet experimental observation suggests that an increase in volume occurs.

It is possible to introduce many speculations as to the nature of the etherate of ferrocyanic acid, but the available experimental evidence does not allow a decision in favour of one or other of the suggestions. Some further exploration of the system is clearly required before the nature of the ferrocyanic etherate is understood. The most surprising observation recorded during the thermal decomposition of ferrocyanic acid was the retention of ether up to temperatures of the order of 200°C. Although the amounts involved were small by comparison with the ether lost below 80°C, it does suggest that ferrocyanic acid can never be obtained pure under the normal methods of preparation.

It may be noted here that one of the original objects of the investigation, that of looking for the tautomeric form of HCN, proved fruitless since only HCN was evolved. This of course does not imply that ferrocyanic acid contains Fe—N bonds, but merely that HNC if formed is extremely unstable, and rapidly reverts to HCN.

The study of the gases evolved in the thermal decomposition shows that decomposition of ferrocyanic acid begins at quite low temperatures. Even on removal of ether at room temperature, about 22°C, it is found that HCN is given off in trace amounts. However, the amount of HCN evolved even at 80°C is still very small, and this temperature must be maintained for several hours before any noticeable change in the solid occurs The infrared and gas chromatographic study of the gases evolved at these low temperatures clearly show a mixture of ether and HCN only, with a great preponderance of ether. At 80°C the amount of ether is small. It was found that keeping the acid under vacuumfor several hours caused almost complete removal of ether, so that the amount of ether obtained on subsequent heating to 80°C is negligibly small. These results show that the best method for producing the ferrocyanic acid from the etherate is by keeping under vacuum for several hours at room temperature, preferably in darkness. Heating to higher temperatures as described by other workers is clearly unnecessary, and would appear to bring about slight decomposition of the acid.

Chapter 3

The Isonitrile Complexes of Iron^{II} $(RNC)_4.Fe(CN)_2$

Isonitrile complexes have been generally reviewed by Malatesta (147). The isonitrile complexes of iron were originally written as $R_4.Fe(CN)_6$. However, on the addition of potassium cyanide or on heating they give off an isonitrile. They show no electrical conductance in solution and therefore must be considered as the neutral complex dicyanotetrakis alkyl isocyanide iron^{II} - $(RNC)_4.Fe(CN)_2$.

The complexes are prepared by three main methods:-

(a) by the action of an alkyl iodide on silver ferrocyanide

(b) by the action of an alkyl sulphate on potassium ferrocyanide

(c) by the action of a diazo-alkane on ferrocyanic acid

The reaction between silver ferrocyanide and methyl iodide was studied by Hartley(148). By refluxing a mixture of silver ferrocyanide and methyl iodide for sometimes an addition compound between silver iodide and hexakis methylisocyanide iron^{II} iodide is obtained.

$$Ag_4Fe(CN)_6 \quad + \quad 6CH_3I \longrightarrow (CH_3NC)_6FeI_2.4AgI$$

This addition compound is readily decomposed by a mixture of silver nitrate and dilute nitric acid.

$$(CH_3NC)_6FeI_2.4AgI \quad + \quad 2AgNO_3 \xrightarrow{HNO_3} (CN_3NC)_6Fe(NO_3)_2 +6AgI$$

Treating the nitrate with sulphuric acid forms the hydrogen sulphate which is converted to the sulphate by neutralising with barium hydroxide. $(CH_3NC)_6Fe(NO_3)_2 +2H_2SO_4 \longrightarrow (CH_3NC)_6Fe(HSO_4)_2 \quad + \quad 2HNO_3$.

In order to prepare thetetrakis methylisocyano iron^{II} this sulphate is treated with a slight excess of barium chloride, filtered and evaporated to dryness under vacuo. The solid produced is dissolved in alcohol, filtered again and the chloride precipitated by the addition of ether as a colourless solid. Drying under vacuum leaves a colourless powder.

$$(CH_3NC)_6FeSO_4 + BaCl_2 \rightarrow (CH_3NC)_6FeCl_2 + BaSO_4$$

When the chloride is heated at 130 - 150°C, under vacuum, for sometime it loses two molecules of methyl chloride and forms the isonitrile.

$$(CH_3NC)_6FeCl_2 \xrightarrow{150^{\circ}C} (CH_3NC)_4Fe(CN)_2 + 2CH_3Cl$$

The reaction between silver ferrocyanide and ethyl iodide (149) is exactly similar to that described above except that the initial reaction forms $(C_2H_5NC)_6FeI_2.4AgI$ at room temperature.

The reaction between silver ferrocyanide and n-propyl iodide was described by Holzl (150) who obtained $(C_3H_7NC)_4Fe(CN)_2$ as a white crystalline product.

The second method of preparation is by refluxing for several hours a mixture of finely divided potassium ferrocyanide and freshly distilled dimethyl sulphate (151). The mixture is filtered whilst hot and on cooling crystals of composition $(CH_3NC)_6Fe(HSO_4)_2$, (A) appear. These are filtered and the filtrate evaporated under vacuum to dryness when a solid mass is left. This contains a mixture of compounds including:

$(CH_3NC)_6Fe(CH_3SO_4)_2.2CH_3HSO_4$, (B) and $(CH_3NC)_6Fe(CH_3SO_4)_2$, (C).

Under vacuum compound B is converted slowly into compound A.

$$(CH_3NC)_6Fe(CH_3SO_4)_2.2CH_3HSO_4 \xrightarrow{\text{vacuum}} (CH_3NC)_6Fe(HSO_4)_2 + 2(CH_3)_2SO_4$$

Compound B and C are readily converted into compound A by treating their alcoholic solutions with sulphuric acid, and compound A is converted into the sulphate by neutralisation with barium hydroxide. The preparation of the isonitrile from the sulphate is performed as described in the first preparative method. According to Holzl (150) however, compounds A, B and C may all be converted immediately into the chloride by boiling their aqueous solutions with hydrochloric acid or barium chloride.

$(C_2H_5NC)_4Fe(CN)_2$ is produced similarly from potassium ferrocyanide and dimethyl sulphate.

The third method of preparation is the action of diazomethane on ferrocyanic acid (152). An ethereal solution of diazomethane is added to a suspension of ferrocyanic acid in ether, causing an extremely vigorous reaction. The product analysed as $(CH_3)_4Fe(CN)_6.H_2O$ and was formulated as $\left[(CH_3NC)_4Fe(CN).H_2O\right].CN$ a cyanide of cyanoaquotetrakis-methyl isocyanide iron^{II}.

A variation of Hartley's preparation of the isonitrile complexes again uses the $K_4Fe(CN)_6$- R_2SO_4 method (153). The mixture is refluxed for several hours and the sulphate produced exactly as before. This is dissolved in water and lithium perchlorate added to form $(RNC)_6Fe(ClO_4)_2$, the aqueous solution of which is passed down an ion-exchange column (Amberlite I.R.45) in the chloride form. The isonitrile is now formed as before by heating the chloride to about 150°C.

The isonitrile formed is a mixture of two isomers, the α- and β- forms. These were originally separated by their differing solubilities in chloroform (154). The α- form crystallises slowly from chloroform solution and the β- form appears on evaporating the chloroform solution. The modern method of separation is to chromatograph the chloroform solution on an alumina column (153). The β- form is eluted with chloroform and the α- form with a 1:1 chloroform - methanol mixture. It was suggested (155) that the two forms were cis- and trans- isomers and Powell (156) showed by X-ray studies that the β- form is the trans isomer.

Both isomers are stable pale yellow products which decompose at high temperatures without melting to RNC, $(CN)_2$ and Fe_2O_3 (152).

The isomers can be differentiated by their physical and chemical properties listed in Table 14. The most striking difference is their reaction with methyl iodide

Table 14

Properties of the isomers of dicyanotetrakis methylisocyano iron^{II}

	Cis (α) form	Trans (β) form
$CHCl_3$	Soluble (Crystals $+4CHCl_3$)	Soluble
Water	Slowly soluble Needles $+2H_2O$	Very soluble Needles $+6H_2O$
$FeCl_3$	Clear blood-red colour	Red colour
$HgCl_2$	Crystalline precipitate	Small needles
H_2PtCl_6	Yellow crystalline precipitate	Yellow crystalline precipitate
CH_3I	$(CH_3NC)_6Fe.I_2$	No reaction
$AgNO_3$ in HNO_3	Standing for a long time in concentrated solution gives an addition compound of $(CH_3NC)_6Fe.AgNO_3$	From dilute solutions gives an immediate crystalline precipitat of $(CH_3NC)_6Fe.AgNO_3$
Conductivity	None	None
Aqueous NaOH	Isonitrile smell	Isonitrile smell
HNO_3 (concentrated)	Freshly prepared no precipitate standing for a long time in a desiccator gives a slow precipitation of short needles and microscopic prisms	Slow precipitation of short needles

This will add to the α- form giving $(CH_3NC)_6FeI_2$, but shows no reaction with the β- form.

3.1 Preparation of the Starting Materials

3.1.1 Purification of Potassium Ferrocyanide

In the preparation of $(RNC)_4Fe(CN)_2$ pure potassium ferrocyanide was required in a very finely divided state and free of any water of crystallisation.

The removal of the water of crystallisation from $K_4Fe(CN)_6.3H_2O$ was studied on a Thermobalance which records loss in weight from a sample against temperature. This showed that on heating at just ~~at~~ 100°C for sometime, all water was lost from the $K_4Fe(CN)_6.3H_2O$ sample.

$K_4Fe(CN)_6.3H_2O$ crystals were dissolved in the minimum of distilled water. Ethanol was now added until the thick, light-yellow solid had all precipitated. This solid was filtered on a Buchner funnel and washed several times with alcohol. The solid was dried by leaving under vacuum at 60°C for 2 days and then increasing the temperature to about 105°C for a further 2 days. This treatment left pure, water and alcohol free potassium ferrocyanide as an extremely finely divided, light-yellow powder.

3.1.2 Purification of Dimethyl Sulphate

Commercial dimethyl sulphate contains a small quantity of sulphuric acid.

A sample of water-free barium chloride was obtained by leaving it in an oven at about 105°C for several hours. This was added to the dimethyl sulphate and the mixture refluxed for a short time when any sulphuric acid was precipitated as barium sulphate. The dimethyl sulphate was now freed from the added barium chloride and barium sulphate by distilling under vacuum. It was used immediately.

3.2 Preparation of the Complexes

3.2.1 Preparation of Dicyanotetrakis Methylisocyanide Iron^{II} $(CH_3NC)_4Fe(CN)_2$

The potassium ferrocyanide - dimethyl sulphate method was used here. 45 gm of the finely divided, purified potassium ferrocyanide was added to 200 ml of freshly distilled dimethyl sulphate in a thick walled reaction tube.

The reaction tube was completely evacuated and sealed at the neck. The tube was heated to 160°C and left at this temperature for several hours before it was opened and the contents filtered hot through a Buchner funnel, This produced a dark-brown filtrate and a light-brown solid which was nearly white on washing several times with fresh dimethyl sulphate, and probably consisted mostly of potassium methyl sulphate.

The filtrate and washings were stripped of dimethyl sulphate by distilling under vacuum, the last portion being removed very carefully to prevent charring of the residue. The solid brown residue consisting of $(CH_3NC)_6FeSO_4$ and $(CH_3HC)_6Fe(HSO_4)_2$ was dissolved in water, filtered to remove any insoluble material and a solution of barium chloride added. This precipitated barium sulphate and left the required chloride in solution.

Since the barium sulphate could not be removed by filtration, the mixture was left standing overnight and then as much liquid as possible was carefully decanted off. The remaining solid was now washed several times with distilled water, the liquid again decanted and the washings added to the main bulk of the liquid. The water was carefully distilled off under vacuum when a light-brown solid remained. This was dissolved in the minimum of alcohol andthe chloride precipitated by the addition of ether as a white solid. This solid was filtered on a Buckner funnel and dried under vacuum.

The $(CH_3NC)_6FeCl_2$ was now decomposed in a high vacuum line in the apparatus shown in Figure 1. The chloride was sealed into vessel A and heated to about 150°C for about 6 hours and the methyl chloride evolved was condensed in trap B. The remaining solid, which was now a much darker brown, was dissolved in chloroform and filtered. The solution in chloroform was passed down an alumina column and the required product was eluted with chloroform. The addition of ether to the elutant precipitated the trans isomer as a white solid which was filtered and dried under vacuum.

This white solid analysed as follows:-

	C	H	N	Fe
Found	43.87	4.33	-	20.4
Calculated for $C_{10}H_{12}FeN_6$	44.1	4.41	30.9	20.6

3.2.2 Preparation of Dicyanotetrakisethylisocyanide Iron^{II} $(C_2H_5NC)_4Fe(CN)_2$

Silver ferrocyanide, prepared by the addition of silver nitrate to potassium ferrocyanide, was heated in a sealed tube at about 60°C for 4 hours with an excess of ethyl iodide. The tube was opened and the excess of ethyl iodide filtered off. This left a very dark-brown solid which when warmed with a strong solution of silver nitrate precipitated yellow silver iodide. The solid was filtered leaving $(C_2H_5NC)_6Fe(NO_3)_2$ in solution. The filtrate was treated with a slight excess of sulphuric acid, and then an excess of barium chloride solution to precipitate barium sulphate. The chloride $(C_2H_5NC)_6FeCl_2$ remained in solution.

This solution was now treated as described in the preparation of the methyl compound, to form the trans isomer as a white powder.

This powder analysed as follows:-

	C	H
Found	51.3	6.0
Calculated for $C_{14}H_{20}FeN_6$	51.2	6.1

The original dark solid removed from the reaction tube consists mostly of $(C_2H_5NC)_6FeI_2.4AgI$. An attempt to produce the chloride directly by shaking the solid for several hours with a chloride exchange resin did not give $(C_2H_5NC)_6FeCl_2$. The product, although not identified, still contained iodine.

3.2.3 Preparation of Hexacyanoferric ^{III} acid $H_3Fe(CN)_6$ (2) (157)

The acid - ether method was used. 40 ml of saturated potassium ferrocyanide solution was cooled in ice and 40 ml of fuming hydrochloric acid added slowly with constant stirring. The mixture was stirred in an ice-bath for about an hour. The precipitated potassium chloride was filtered, and the filtrate shaken vigorously with 70 ml of ether. This resulted in the formation of three layers, a bottom aqueous layer, a middle oily layer and a top ethereal layer.

The thick, dark-brown oil was separated from the other two layers and dried under vacuum to a brown solid. After drying under vacuum for several hours the acid remained as a dark-brown solid.

Attempts to recrystallise this from absolute alcohol failed.

3.2.4 Preparation of Hexacyanocobaltic^{III} acid (157)

This was also prepared by the acid - ether method. 9 gm of potassium cobalticyanide was dissolved in 27 ml of water, and 27 gm of concentrated hydrochloric acid was added to the solution cooled in ice. The precipitated potassium chloride was filtered off and the acid precipitated from the filtrate by the addition of ether.

The acid was recrystallised several times from absolute alcohol and finally dried under vacuum to a white solid.

3.2.5 Preparation of Hexacyanoruthenic^{II} acid $H_4Ru(CN)_6$

Ruthenium metal was fused with a mixture of potassium hydroxide and potassium nitrate, and the product dissolved in water and boiled with potassium cyanide. The orange solution was decolourised with charcoal, filtered and the filtrate crystallised by evaporating the solution to small bulk. Crystals of composition $K_4Ru(CN)_6.3H_2O$ were obtained.

The potassium ruthenocyanide was converted into the acid exactly as described for hexacyanoferric^{II} acid.

3.2.6 Preparation of Deuterio-hexacyanoferric^{II} acid $D_4Fe(CN)_6$

In this preparation the operations were carried out as far as possible in a dry box.

1·8gm of anhydrous potassium ferrocyanide was mixed with

1 ml of a 50:50 mixture of 99.8% deuterio-water and deuterio-sulphuric acid. 10 ml of deuterio-ethyl alcohol (C_2H_5OD) was added and the resulting mixture filtered. The acid was precipitated by the addition of 12ml of anhydrous ether to the filtrate, filtered and de-etherated in vacuum at room temperature.

The spectrum of the product was identical to that described for $D_4Fe(CN)_6$ by Ginsberg (46).

3.3 Preparation of the boron halide adducts

All adducts were prepared by direct addition of the appropriate boron halide to the complex cyanide. The reactions were performed under vacuum in the apparatus shown in Figure 10.

The boron halide was transferred from its storage cylinder into the apparatus through a mercury bleed-in tube fitted to the B10 socket shown, and was distilled from trap to trap into bulb A. Bulb A was an exactly calibrated volume fitted with a manometer so that a known amount of boron halide could be measured and then condensed into the reaction vessel attached at the B19 socket. On completion of the reaction the amount of unreacted boron halide was measured in bulb A.

Except where otherwise stated the cyanide and boron halide were left together for one day in order to ensure

Figure 10.

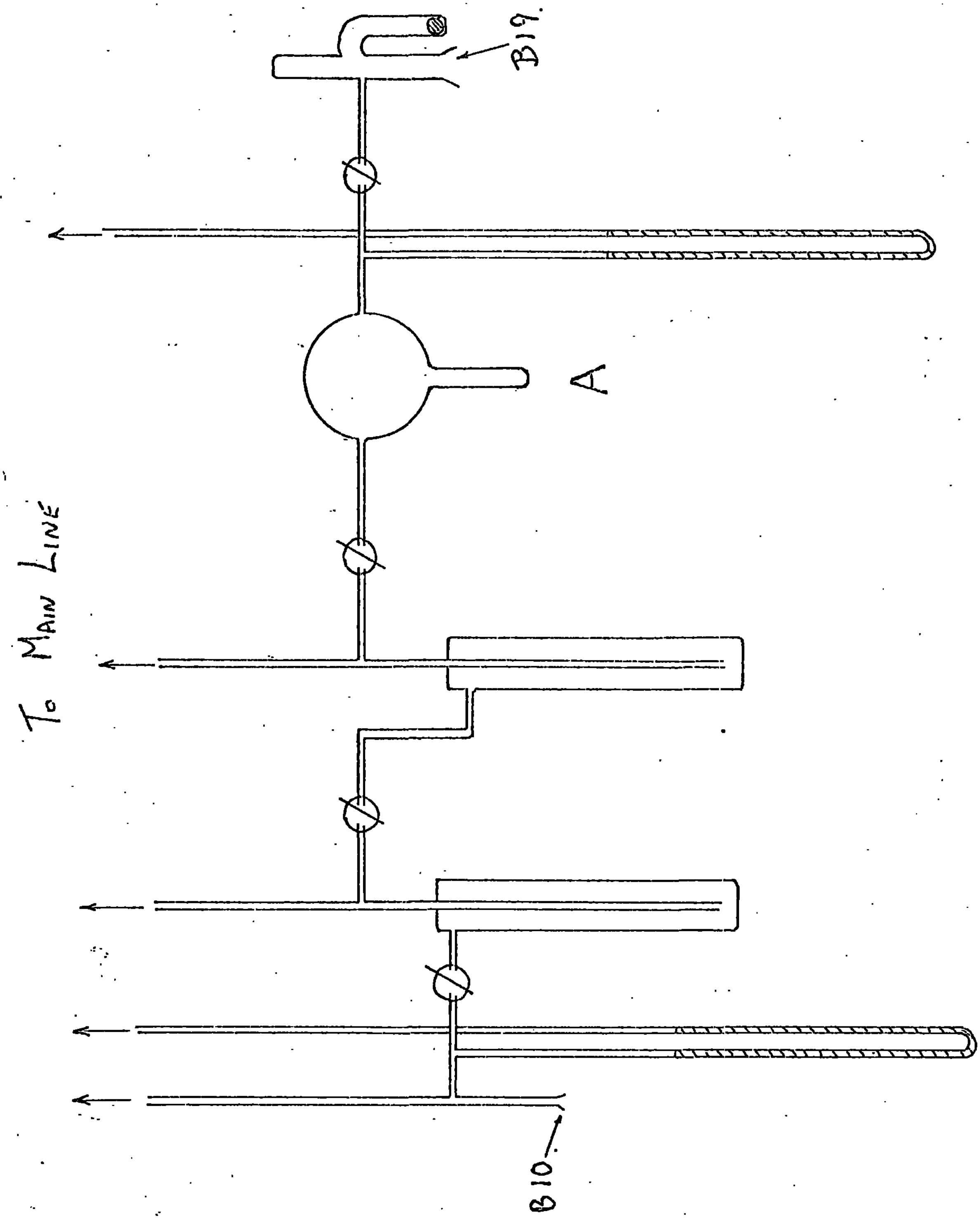


FIGURE 11(a)

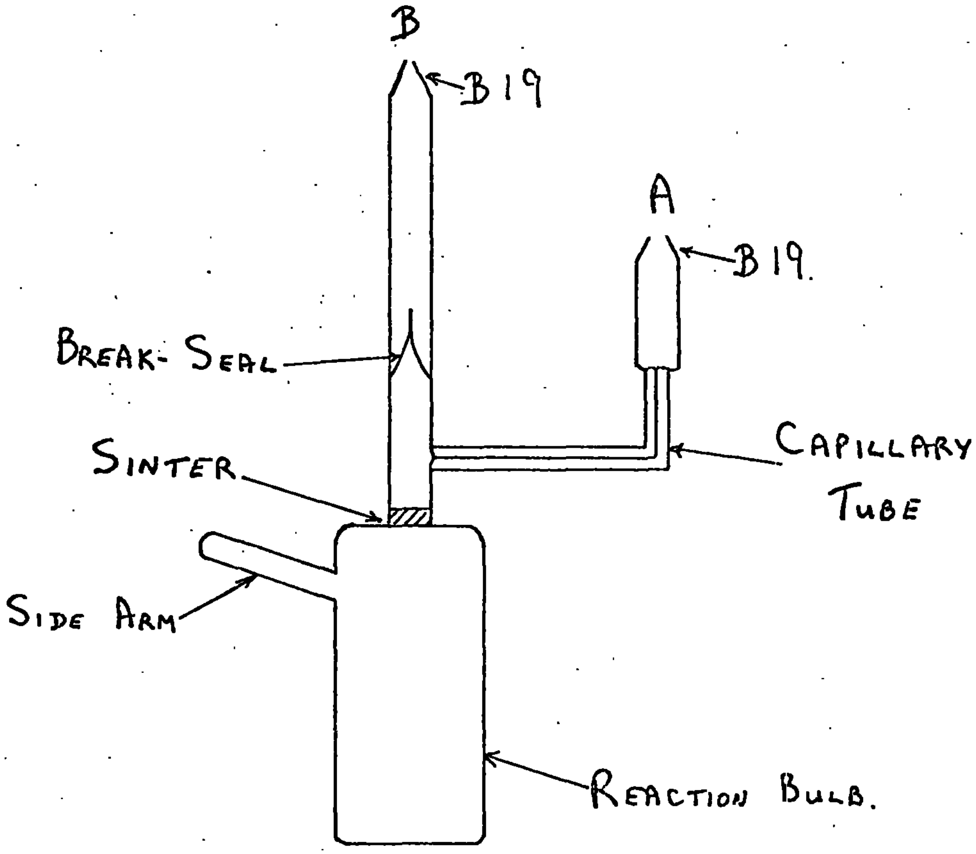
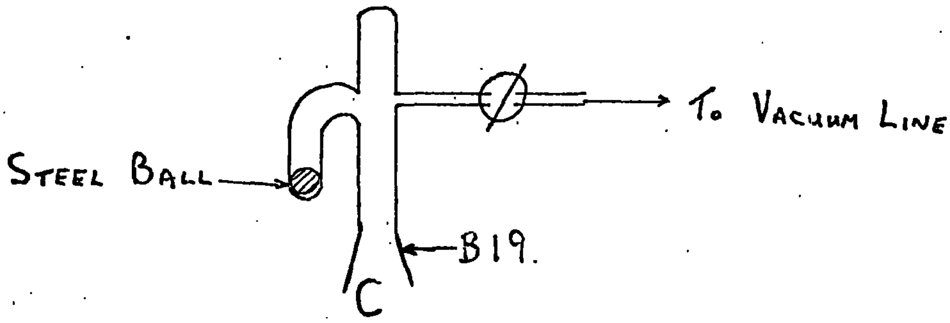


FIGURE 11(b).



complete reaction.

In some cases, for example with the alkyl ferrocyanides, the reaction with boron trifluoride was so vigorous at room temperature that the reaction product was charred. The reaction was therefore modified by holding the reactants at - 78°C for sometime before allowing room temperature to be attained, and in this way charring of the product was prevented.

3.3.1 The reaction vessel - design and method of use

The reaction vessel is shown in Figure 11a. The vessel was always used in conjunction with a special piece of apparatus fitted to the vacuum line. This is shown in Figure 11b and allows the reaction vessel to be opened under vacuum.

The sinter was included to prevent any solid escaping into the vacuum line during evacuation. The side capillary tube was used to remove the vessel from the vacuum line while retaining its vacuum by sealing with a flame, and the break-seal was to allow the vessel to be reopened under vacuum.

The reaction vessel was fitted with the required amount of sample through the side arm which was then sealed. The vessel was attached to the vacuum line by connecting A to C in Figure 11 and completely evacuated. The measured amount of boron halide was condensed into the vessel, which was then removed from the line by sealing the side capillary tube.

After reaction the vessel was attached to the vacuum line, B to C in Figure 11, and evacuated. The material in the reaction bulb was cooled in liquid air and the vessel opened by dropping the steel ball onto the break-seal using a magnet. The initial cooling in liquid air was to prevent damage to the apparatus with the sudden pressure release on breaking the seal. Any unreacted material was removed by condensing it into a trap in the base of bulb A.

This method allows an accurate measure of the amount of material added to, and removed from the sample in the reaction bulb.

3.3.2 The addition of boron halides to ferrocyanic acid

In a typical reaction 1.025 gms of boron trifluoride was condensed into the reaction vessel containing 0.89 gms. of ferrocyanic acid. After sealing the reaction vessel, and removing it from the vacuum line, the vessel was allowed to warm up to room temperature. An observable increase in volume occurred during this period corresponding to about twice the original volume on a visual estimate. Shaking the powdered product showed it to consist of individual white flakes which settled slowly, whereas the original ferrocyanic acid remained as a coagulated mass on shaking. The vessel was reopened on the vacuum line, and 0.457 gms of boron trifluoride were recovered. The boron trifluoride remaining combined with ferrocyanic acid corresponded to the stoichiometry $H_4Fe(CN)_6.2BF_3$. The white product was stable in dry air, and showed no observable vapour pressure of boron trifluoride.

In other preparations samples of ferrocyanic acid were sometimes used which had become pale blue as the result of standing in the light, and it was noted that the blue colour was discharged immediately on contact with boron trifluoride, the colour of the product being white. The product remained white on standing in the light over periods during which ferrocyanic acid itself would have changed colour. On more prolonged exposure to light the compound took on a reddish colour rather than the blue colour of the parent ferrocyanic acid.

No reaction was obtained with mixtures of boron trichloride and ferrocyanide acid, even over varied temperature ranges and contact times. Some typical experiments are noted:

(a) 0.832 gms of boron trichloride was condensed on to 0.64 gms of ferrocyanic acid, and after 24 hours contact 0.832 gms of boron trichloride were recovered.

(b) 11.93 gms of boron trichloride was condensed on to 1.857 gms of ferrocyanic acid, and left in contact for five days at 50°C. 11.85 gms of boron trichloride were recovered, and the spectrum of the solid residue was identical with that of ferrocyanic acid.

(c) 13.59 gms of boron trichloride was condensed on to 1.961 gms of ferrocyanic acid, and stored for ten weeks at -40°C, after which time 13.56 gms or boron trichloride were recovered. The only difference noted during this particular reaction was that the colour of the mixture became pale yellow, but the colour was discharged on warming to room temperature. The spectrum of the residue was again that of unchanged ferrocyanic acid. Deuterio-ferrocyanic acid showed similar behaviour to ferrocyanic acid, the only product obtained being that corresponding to the composition $D_4Fe(CN)_6.2BF_3$. Similar remarks apply to the reactions with ruthenocyanic acid, the only product obtained being that corresponding to the formula $H_4Ru(CN)_6.2BF_3$.

3.3.3 The addition of boron halides to Hexacyanoferric^{III} acid and Hexacyanocobaltic^{III} acid

Neither boron trifluoride nor boron trichloride showed any reaction with these acids.

After keeping the reactants together for one week at room temperature exactly the same amount of boron halide was removed as had been added.

3.3.4 The addition of boron halides to potassium ferrocyanide

This system has been studied by Shriver (81) and was discussed in detail in Chapter 1, section 1.3.3.

As shown in Table 9 the reaction between potassium ferrocyanide and boron trifluoride was extremely slow and was attributed by Shriver to either:

(a) the high lattice energy of the complex

or

(b) the rate of diffusion of BF_3 into the crystal lattice.

In this experiment the reaction was carried out with anhydrous, finely divided potassium ferrocyanide.

1.203 gm of boron trifluoride was condensed onto 0.92 gm of finely divided potassium ferrocyanide and after reaction 0.162 gm of boron trifluoride remained. The remaining blue powder was of composition $K_4Fe(CN)_6.6BF_3$.

This reaction was immediate showing that the second suggestion of Shriver was correct.

The infra-red absorption frequencies of the complex and the adduct are shown below, all frequencies given in wave numbers (cm^{-1}):

$K_4Fe(CN)_6$	$K_4Fe(CN)_6.6BF_3$
1981 (w)	773 (w)
2003.5 (m)	920-940 (br.s)
2022-2028.5 (br.s)	1030-1170 (v.br.s)
2037-2048 (br.s)	1304 (w)
2061 (s)	2160-2210 (v.br.s)
2071 (s)	
2091.5 (s)	

The reaction between potassium ferrocyanide and boron trichloride was not very conclusive.

1.44 gm of boron trichloride was condensed onto 0.70 gm of finely divided potassium ferrocyanide and after reaction 1.20 gm of boron trichloride remained. The product was a grey powder of composition $K_4Fe(CN)_6.BCl_3$

The infra-red spectrum of this product was identical to that of potassium ferrocyanide except for a peak at 2153-2174 (br.w).

On repeating the reaction and leaving the reactants together for ten days, the product was of composition $K_4Fe(CN)_6.0.7BCl_3$.

3.3.5 The addition of boron halides to trans dicyanotetrakismethylisocyanide iron^{II}

The reaction with boron trifluoride was extremely vigorous and resulted in some charring of the product. The reaction was therefore modified to some extent by holding the reactants at -78°C for sometime before allowing room temperature to be reached.

0.468 gm of boron trifluoride was condensed onto 0.36 gm of $(CH_3NC)_4Fe(CN)_2$ and after reaction 0.286 gm of boron trifluoride remained. The white powder which remained corresponded therefore to a composition $(CH_3NC)_4Fe(CN)_2.2BF_3$.

The infra-red absorption frequencies of the complex and the adduct are shown below, all frequencies given in wave numbers (cm^{-1}):

$(CH_3NC)_4Fe(CN)_2$	$(CH_3NC)_4Fe(CN)_2.2BF_3$
725 (w)	710 (m)
1420 (m)	724 (m)
1429 (m)	900 (s) -sh at 930
2090 (s)	1125 (s)
2190 (br.s)	1138 (s)
	1175 (m)
	1419 (w)
	2180 (br.s)
	2228 (br.s)

The reaction with boron trichloride was similar to that with boron trifluoride, although less vigorous.

0.46 gm of boron trichloride was condensed onto 0.18 gm of $(CH_3NC)_4Fe(CN)_2$ and after reaction 0.305 gm of boron trichloride remained. The white powder which remained corresponded therefore to a composition $(CH_3NC)_4Fe(CN)_2.2BCl_3$.

The infra-red absorption frequencies of the complex and the adduct are shown below:

$(CH_3NC)_4Fe(CN)_2$	$(CH_3NC)_4Fe(CN)_2.2BCl_3$
725 (w)	725 (s)
1420 (m)	869 (m)
1429 (m)	899 (w)
2090 (s)	2180 (br.s)
2190 (br.s)	2231 (br.s)

3.3.6 The addition of boron halides to trans dicyanotetrakisethylisocyanide iron^{II}

Trans $(C_2H_5NC)_4Fe(CN)_2$ reacted with boron trifluoride and boron trichloride in an exactly similar manner to trans $(CH_3NC)_4Fe(CN)_2$.

The products were white powders corresponding to the compositions, $(C_2H_5NC)_4Fe(CN)_2.2BF_3$ and $(C_2H_5NC)_4Fe(CN)_2.2BCl_3$.

The infra-red absorption frequencies of the complex and its boron trifluoride adduct are shown below:

$(C_2H_5NC)_4Fe(CN)_2$	$(C_2H_5NC)_4Fe(CN)_2.2BF_3$
740 (w)	715 (w)
810 (w)	806 (w)
854 (w)	901 (s)
1020-40 (br.w)	932 (m)
1102 (m)	1016 (w)
1143 (w)	1125 (s)
1357 (m)	1172 (m)
1372 (m)	1351 (m)
2098 (s)	1370 (w)
2165 (v.br.s)	2186 (s)
	2218 (s)

The boron trichloride adduct has the $-C\equiv N$ stretch frequencies at 2187 (s) and 2220 (s) (cm^{-1}).

3.4.1 The addition of boron trichloride - acetyl chloride mixture to hexacyanoferric^{II} acid

9.216 gm of boron trichloride and 6.02 gm of acetyl chloride were condensed onto 1.92 gm of $H_4Fe(CN)_6$ in a reaction vessel and the mixture allowed to warm slowly to room temperature. During the warming up period, the whole mass turned to a yellow viscous liquid, and the reaction vessel became warm to the touch. The liquid slowly solidified to a yellow mass with separation of a clear colourless liquid.

After standing for 24 hours the excess liquid was removed leaving 4.67 gm of dried solid, an increase of 2.75 gm on the original amount of $H_4Fe(CN)_6$.

In a second experiment there was an increase of 2.62 gm on 1.92 gm of $H_4Fe(CN)_6$.

A simultaneous analysis for iron and acetyl radical showed that the final product contained two acetyl groups per iron atom, and a boron determination showed two boron atoms per iron atom.

The spectrum of the final product, recorded on the Unicam S.P. 200 infra-red spectrometer, showed a single $-C\equiv N$ stretch frequency at 2180 cm^{-1} (s), and the following absorption frequencies. 760 (m), 870 (m) 930 (m), 1060 (w), 1195 (m) sh at 1220, 1460 (br.s), 1630 (w), 1700 (m), and 3200 (br.s).

3.4.2 The addition of acetyl chloride to hexacyanoferric^{II} acid

9.36 gm of acetyl chloride was condensed onto 1.43 gm of $H_4Fe(CN)_6$ and the mixture was left for 7 weeks, when 9.34 gm of acetyl chloride was removed. The spectrum of the residue showed it to be $H_4Fe(CN)_6$.

3.4.3 The addition of acetyl chloride to boron trichloride

3 gm of boron trichloride and 2 gm of acetyl chloride were mixed and left together for 7 weeks at room temperature. No reaction occurred, even on varying the temperature between - 40 and 50°C.

3.4.4 The addition of boron trichloride-thionyl chloride mixture to hexacyanoferric^{II} acid

An excess of boron trichloride and thionyl chloride were condensed onto a sample of $H_4Fe(CN)_6$ in a reaction vessel. There was a fairly vigorous reaction.

Sulphur dioxide and nitrosyl chloride reacted similarly, but carbonyl chloride failed to react.

3.4.5 The addition of thionyl chloride to hexacyanoferric^{II} acid

When an excess of thionyl chloride was condensed onto a sample of $H_4Fe(CN)_6$ no reaction occurred.

The same result was obtained with sulphur dioxide, nitrosyl chloride and carbonyl chloride.

3.4.6 A comparison of the spectra obtained in these reactions

In all cases the reaction was between hexacyanoferric^{II} acid, boron trichloride and a third reactant. The spectra are recorded in Table 15.

Table 15

Third reactant	CH_3COCl	$SOCl_2$	SO_2	$NOCl$
- $C\equiv N$ Stretch frequency	2180	2180	2180	2160

Other frequencies	CH_3COCl	$SOCl_2$	SO_2
	760 (m)	760 (m)	760 (m)
	870 (m)	860 (m)	700-960 (v.br)
	930 (m)	940 (m)	
	1060 (w)		
	1195 (m)	1195 (m)	1195 (m)
	1220 (sh)	1220 (sh)	1220 (sh)
	1460 (br.s)	1460 (br.s)	1440-1500 (br.s)
	1630 (w)	1610-1700 (br.w)	1620-1680 (br.w)
	1700 (m)		
	3200 (br.s)	3200 (s)	3250 (br.s)

Chapter 4.

Infra-red Spectra and Discussion.

Although the compound $H_4Fe(CN)_6$ has been known for many years it is only recently that attempts to comment on its structure have been made. The results of observation of the infra-red spectrum have been presented and discussed by Ginsberg and Koubek (46) in America, and by Beck and Smedal in Germany (45). The work of these groups shows good agreement for the observed frequencies, and the data from these two sources provide confirmation of the observations made for the same compound in this work. Both of the above-mentioned groups give detailed assignments for the observed frequencies, the assignments being particularly extensive in the work of Ginsberg and Koubek. The general conclusion is that $H_4Fe(CN)_6$ units have the trans arrangement of hydrogen atoms (D_{4h} symmetry), and are linked by asymmetric intermolecular hydrogen bonds $N-H\cdots N$.

The conclusions of the two sets of authors differ over the final structure to be assigned, Ginsberg and Koubek proposing that all hydrogen atoms are involved in asymmetric intermolecular hydrogen bonding whereas Beck and Smedal consider that only half of the hydrogen atoms are hydrogen bonded. The main point of difference is over the value to be assigned to the characteristic N—H stretching frequency. Ginsberg argues that this frequency should occur at a value similar to that observed for the molecule $H-N\equiv C$ in a solid argon matrix (i.e. at 3583 cm^{-1}) or that for the molecule $H-N=C=O$ in the gas phase (i.e. at 3531 cm^{-1}), and hence argue that since no absorption is observed in this region all N—H stretching frequencies are lowered by hydrogen bonding. In the absence of free N—H stretching frequencies the intense broad absorption observed from 2200 to 3500 cm^{-1} is then considered to result from overlapping bands due to $N-H\cdots N$, which leads to the suggestion that all hydrogen atoms in the molecule are involved in intermolecular hydrogen bonding. These authors conclude that there is insufficient evidence available to decide on a definite structure for the system. Beck and Smedal on the other hand claim that the absorption maximum at 3050 cm^{-1} is due to the free N—H stretching frequency, the remainder of the band at lower frequencies being attributed to asymmetric intermolecular hydrogen bonding. These authors base their argument on a comparison with the infra-red spectrum of $H_3Fe(CN)_6$ for which a structure involving complete intermolecular hydrogen bonding for all the hydrogen atoms in the molecule seems to be acceptable (158). A structure which involves both free N—H bonds and asymmetric intermolecular hydrogen bonds N—H···N, and preserves the 4:6 ratio of H:N atoms required by the stoichiometry is suggested (Figure 12).

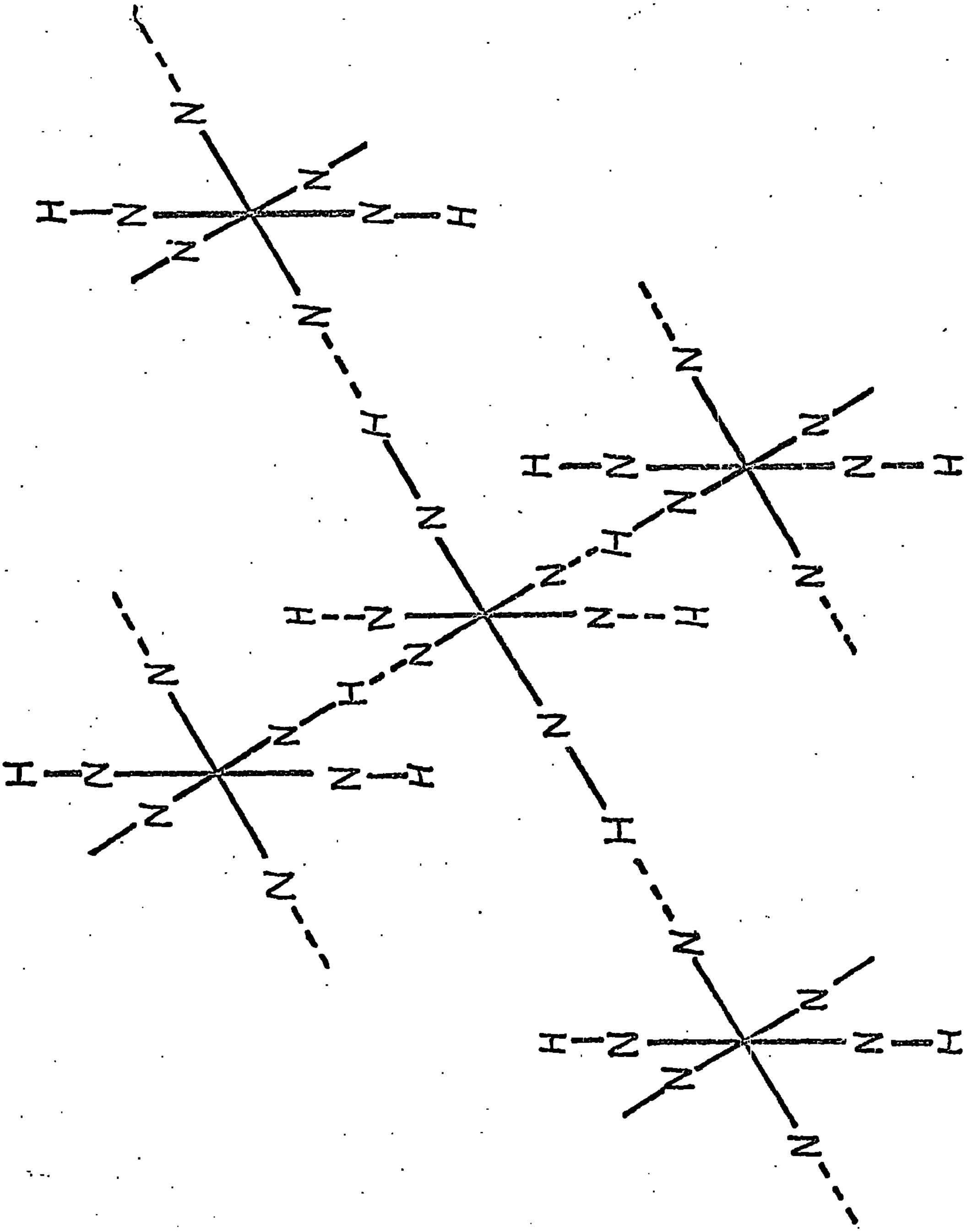
This study of the boron trifluoride adduct of ferrocyanic acid, and of the boron halide adducts of some related molecules, allows some comment to be made on these interpretations of the spectrum of ferrocyanic acid.

The present study established that ferrocyanic acid forms a bis-trifluoroboron adduct when exposed to an excess of boron trifluoride.

$$H_4Fe(CN)_6 \;+\; 2\,BF_3 \longrightarrow H_4Fe(CN)_6.2BF_3$$

The formation of the adduct is rapid, occurring with evolution of heat, and the resultant compound shows no measureable vapour pressure of boron trifluoride. On the other hand no adduct is formed when ferrocyanic acid

FIGURE 12.



is subjected to prolonged exposure to boron trichloride at a variety of temperatures in the range - 80°C to + 50°C. Parallel behaviour is observed for deuterio-ferrocyanic acid. This behaviour is in marked contrast to the observations made on the related alkyl ferrocyanide molecules $R_4Fe(CN)_6$*, ($R = CH_3$ or C_2H_5), which readily form bis-trihaloboron adducts with boron trifluoride and boron trichloride, and also in contrast to ferricyanic acid, $H_3Fe(CN)_6$, and cobalticyanic acid, $H_3Fe(CN)_6$, which give no adducts even on prolonged exposure to boron trihalides. On the basis of the work of Shriver (81), and other evidence to be cited, it is concluded that where adduct formation occurs the bond system $M-C\equiv N-BX_3$ is involved ($X = F$ or Cl). The compounds will continue to be referred to as boron halide adducts of the appropriate molecule.

The infra-red spectra of the bis-trifluoroboron adducts of ferrocyanic acid, deuterio-ferrocyanic acid, and ruthenocyanic acid are recorded in Table 16 over the range 350 cm^{-1} to 4000 cm^{-1}. This range is divided for

---

* Throughout this discussion it is convenient sometimes to refer to the dicyano tetrakis-alkylisocyano iron (II) molecules in terms of their alternative formulation as carbonium ion ferrocyanides $(R^+)_4\ (Fe(CN)_6)^{4-}$.

Table 16

Infra-red Absorption Frequencies of bis-trifluoroboron Adducts of $H_4Fe(CN)_6$, $D_4Fe(CN)_6$, and $H_4Ru(CN)_6$

$H_4Fe(CN)_6 \cdot 2BF_3$	$H_4Ru(CN)_6 \cdot 2BF_3$	$D_4Fe(CN)_6 \cdot 2BF_3$
423 w.	387 w.	420 w.
535 sh.vw.	540 sh.vw.	545 sh.vw.
592 m.	561 m.	593 m.
725 w.	720 w.	723 w.
920 s.	922 s.	938 s.
1040 sh.	1040 sh.	1040 sh.
1080 s.	1078 s.	1068 s.
1160 sh.	1150 sh.	1166 s.
1270 vw.	1270 vw.	1260 sh.vw.
1310 vw.	1310 vw.	1310 vw.
1350 vw.	1350 vw.	1350 vw.
Intermediate region masked by Nujol bands		
1685 vw.	1680 vw.	1680 w.
1725 m.	1730 m.	-
1930 sh.	1890 sh.	1990 vw.
2105 ms.	2106 ms.	2110 ms.
2193 s.	2195 s.	2200 s.
2230 sh.w.	2220 sh.w.	2220 sh.w
3280 ms.(br)	3290 ms.(br)	2350 v.w.
-	-	2580 ms.(Br)
-	-	2740 sh.vw.

convenience in discussion into the following regions:

A: 350 cm^{-1} to 650 cm^{-1} (Nujol Mull - polythene disc)
B: 650 cm^{-1} to 2000 cm^{-1}(' ' - KBr disc)
C: 2000 cm^{-1} to 2300 cm^{-1}(' ' - KBr disc)
D: 2300 cm^{-1} to 4000 cm^{-1}(hexachlorobutadiene mull)

It is apparent that over much of the range studied the spectra of these adduct molecules show a close similarity. In Table 16 no assignments have been marked for the recorded frequencies, but these will be suggested during the subsequent discussion.

4.1 Region A: (350 cm^{-1} to 650 cm^{-1}).

In this region of the infra-red spectrum metal cyanide comlexes display frequencies due to M—C stretching vibrations and M—C≡N bending vibrations (159). Table 17 records the results of our observations in this region on ferrocyanic acid, deuterio-ferrocyanic acid, and ruthenocyanic acid for the peaks assigned by Ginsberg to the M—C stretch and M—C≡N bending vibrations. The peaks were interpreted as those required under D_{4h} symmetry as ν(M—C) $[A_{2u} + E_u]$ and δ(M—C≡N)$[A_{2u} + 2\ E_u]$. Trans-dicyano tetrakis-methylisocyano iron (II), and trans-dicyano tetrakis-ethylisocyano iron (II) should also exhibit D_{4h} symmetry, and the similarity of their spectra over this region to those of the complex cyanide acids have led to the additional assignments for these molecules in Table 17.

Table 17.

M—C≡N bending and M—C stretching vibrations.

D_{4h}	δ(MCN) $A_{2u}+2E_u$			ν(MC)A_{2u}+ Eu	
$H_4Fe(CN)_6$	595 sh	583 ms	447 w	416	407
$D_4Fe(CN)_6$	605 sh	585 ms	443 w	418	406
$H_4Ru(CN)6$	550 sh	541 ms	459 w	370	362
$Me_4Fe(CN)_6$	583 ms	566 ms	498 w	403	380
$Et_4Fe(CN)_6$	588 ms	570 ms	470 w	*	*

* broad weak peak in range 400 cm^{-1} but not resolved.

Ginsberg and Koubek consider that the site symmetry does not affect the D_{4h} symmetry for M—C≡N bending and M—C stretching modes, and they assign the peaks observed at 448, 588, and approximately 600 cm^{-1} to the M—C≡N bend, and those at 406 and 419 cm^{-1} to M—C stretching modes. D_{4h} symmetry requires δ(MCN) to have three modes active in the infra-red (A_{2u} + 2 E_u) and ν(MC) to have two modes active (A_{2u} + E_u). Thus for ferrocyanic acid we assign our observed peaks as:

447, 583, 595 cm^{-1}	δ(MCN)
407, 416 cm^{-1}	ν(MC)

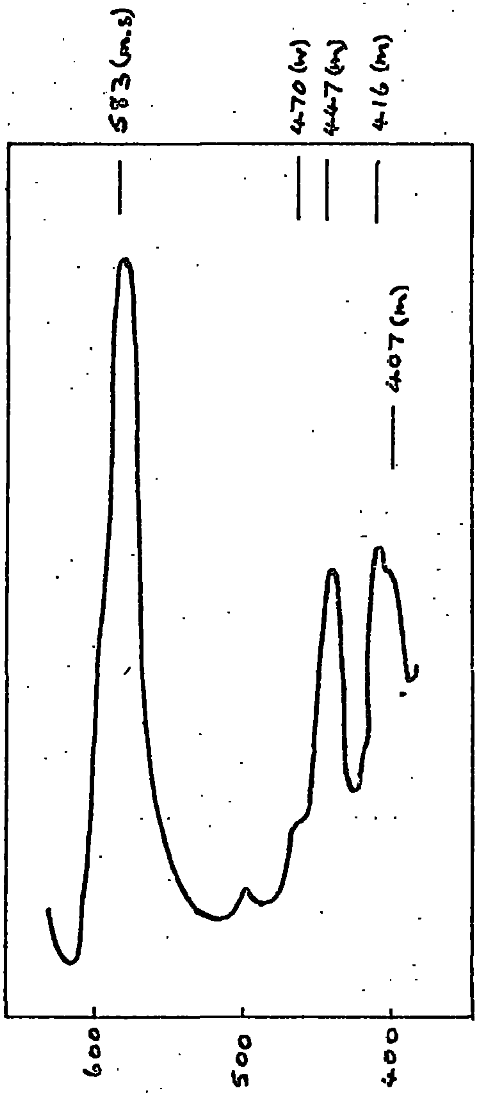
These are recorded as such in Table 17. Here we can compare assignments by Jones (160) for potassium ferrocyanide, $K_4Fe(CN)_6$, in solution:

583 cm^{-1}	$\delta(MCN)$	F_{1u}
416 cm^{-1}	$\nu(MC)$	F_{1u}

the modes being those required under O_h symmetry. Similar assignments to those of ferrocyanic acid are given by Ginsberg and Koubek for the molecules deuterioferrocyanic acid, and ruthenocyanic acid. The assignments in Table 17 for our observations on these molecules follow from those of Ginsberg and Koubek, as well as those of Beck and Smedal. The close similarity of the alkyl ferrocyanide spectra in this region to those of the complex cyanide acids has led to the assignments for these molecules in Table 17.

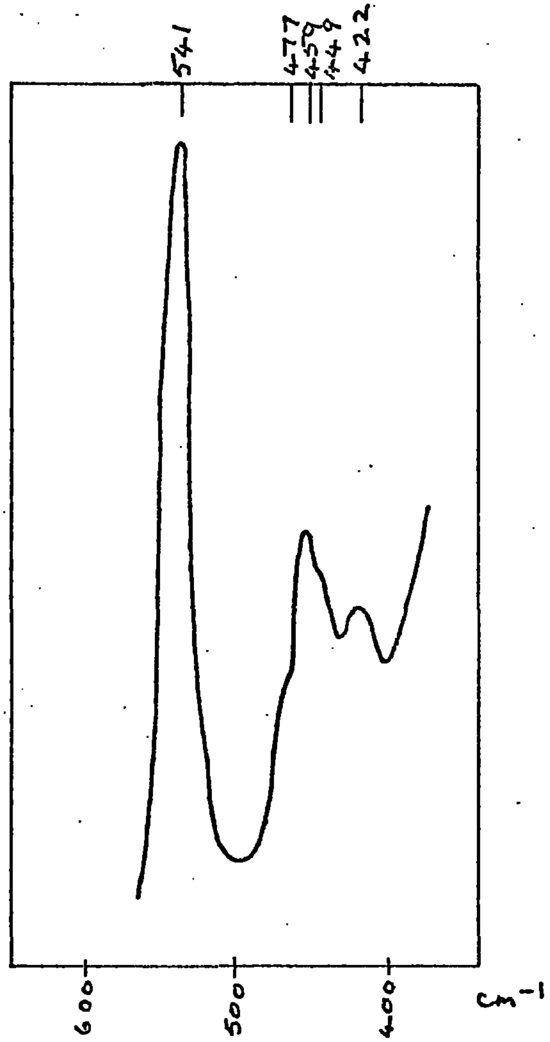
The similarity between the spectra of the alkyl ferrocyanides and those of the complex cyanide acids in this region is illustrated by Figures 13, 14, and 15. It should be noted that these figures have been reproduced from low resolution spectra in order to illustrate this similarity, and that actual measurement of frequencies recorded in Table 17 were obtained at much higher resolution. As a result these spectra at low resolution do not bring out clearly such features as the shoulder on the high frequency side of the main peak of ferrocyanic acid and

FIGURE 13



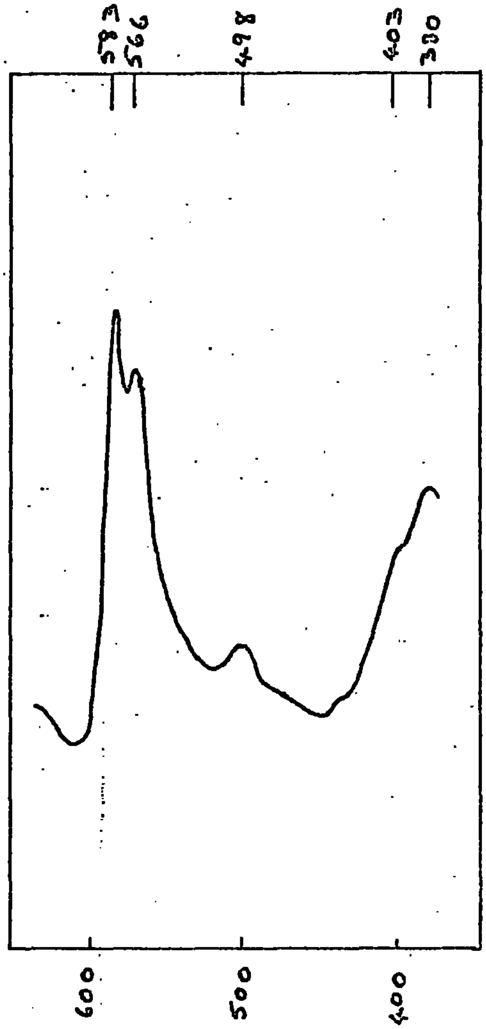
$H_4 Fe (CN)_6$.

FIGURE 14



$H_4Ru(CN)_6$

FIGURE 15

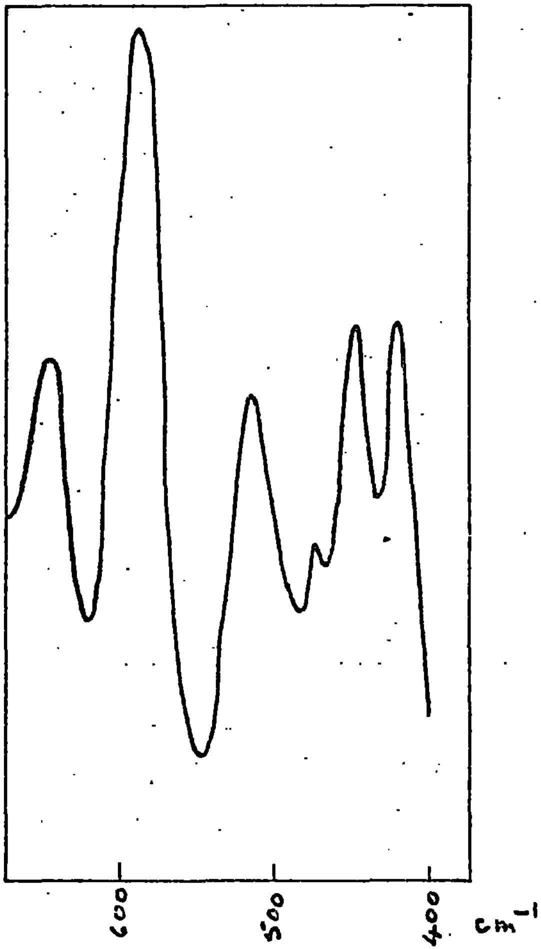


trans-$(CH_3)_4Fe(CN)_6$.

ruthenocyanic acid (Figures 13, and 14), although this is clear in the high resolution spectra. The two frequencies are not so closely associated for trans-tetramethyl ferrocyanide and are more clearly separate in Figure 15. The figure given for ruthenocyanic acid is incomplete since the M—C stretching modes for this compound lie below the lower limit of the Unicam SP100 spectrometer on which the spectrum was recorded, and in order to obtain measurements of these frequencies a Grubb-Parsons instrument was used. That the M—C stretching modes of ruthenocyanic acid lie lower than those for ferrocyanic acid is generally accepted in the literature (159). The figures serve to illustrate the broad similarity between the spectra. The spectrum of deuterio-ferrocyanic acid is more complicated in this region (Figure 16,) and the complexity can be attributed to admixture with low-lying deuterium bonded modes, a feature which will emerge in the subsequent discussion. In Figure 17 a detail of the deuterio-ferrocyanic acid spectrum recorded at somewhat higher resolution brings out the doublet structure at 406 and 418 cm^{-1} which is masked in the lower resolution spectrum of Figure 16.

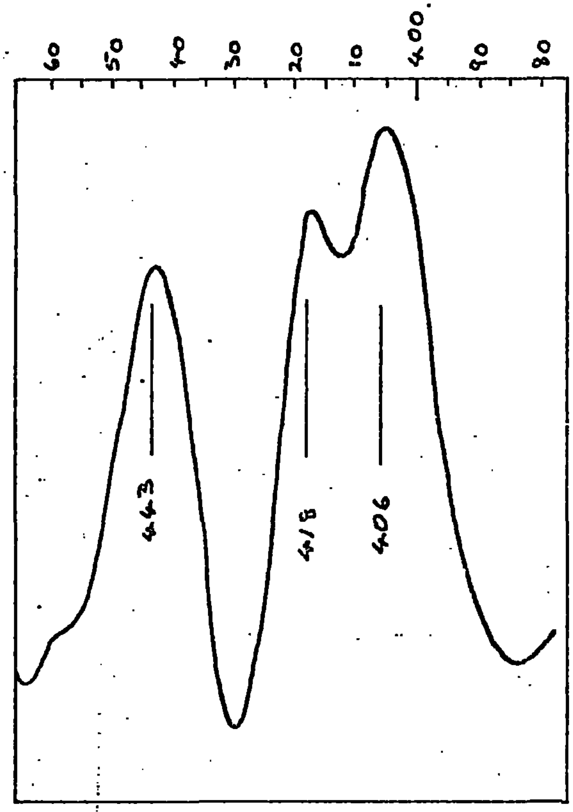
The spectra observed in the region 350 cm^{-1} to

FIGURE 16.



$D_4Fe(CN)_6$.

FIGURE 17



$D_4Fe(CN)_6$.

650 cm^{-1} for the bis-trifluoroboron adducts are given in Table 18 together with those of hexakis-methylisocyano iron (II) perchlorate, hexakis-ethylisocyano iron (II) perchlorate, potassium hexacyanoferrate (II), and its hexakis-trifluoroboron adduct. In each case the spectra show well-defined peaks in the range 590 cm^{-1} and 400 cm^{-1}, together with subsidiary peaks in the region around 520 cm^{-1}.

Table 18.

Infra-red Spectra of Trifluoroboron Adducts.

$H_4Fe(CN)_6.2BF_3$	-	592 ms		540 vw	423 m
$D_4Fe(CN)_6.2BF_3$	-	585 ms	527 vw	475 w	420 m
$H_4Ru(CN)_6.2BF_3$	-	561 ms		540 sh.vw	387 m
$Me_4Fe(CN)_6.2BF_3$	-	586 ms	524 vw	480 vw	380 m
$Et_4Fe(CN)_6.2BF_3$	-	590 ms	*		385 m
$Me_6Fe(CN)_6^{++}(ClO_4^-)_2$	625 ms	575 ms		520 sh.vw	380 m
$Et_6Fe(CN)_6^{++}(ClO_4^-)_2$	625 ms	578 ms		523 sh.vw	380 m
$K_4Fe(CN)_6.6BF_3$	-	607 ms	536 m	524 m	422 m
$K_4Fe(CN)_6$	-	588 ms			417 -

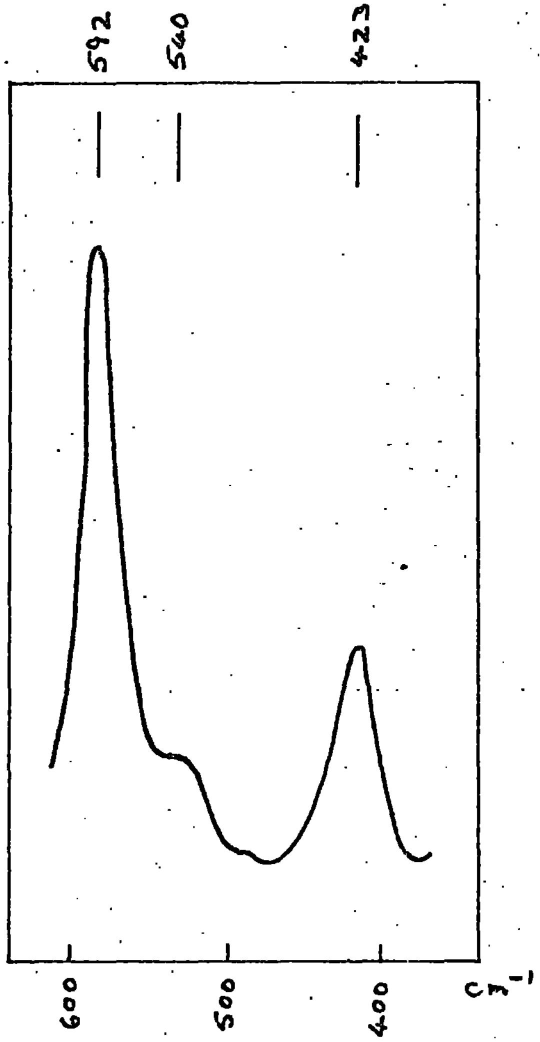
---

* main peak shows very weak shoulders above 520 cm^{-1} but not

The spectra for the bis-trifluoroboron adducts of ferrocyanic acid, ruthenocyanic acid, deuterio-ferrocyanic acid, and trans tetramethyl ferrocyanide are shown in low resolution in Figures 18, 19, 20, and 21. Actual peak frequency values have in all cases been determined from high resolution spectra, and the figures are presented to illustrate the broad features. It will be apparent, from a comparison of these figures with those presented for the parent compounds, that the spectrum has been much simplified by adduct formation. The spectra can be generally summarised as comprising two principal peaks together with weaker subsidiary peaks which occur sometimes as shoulders on the main peak. The weaker subsidiary peaks in general fall in definite regions of the spectrum at around 520 cm^{-1}.

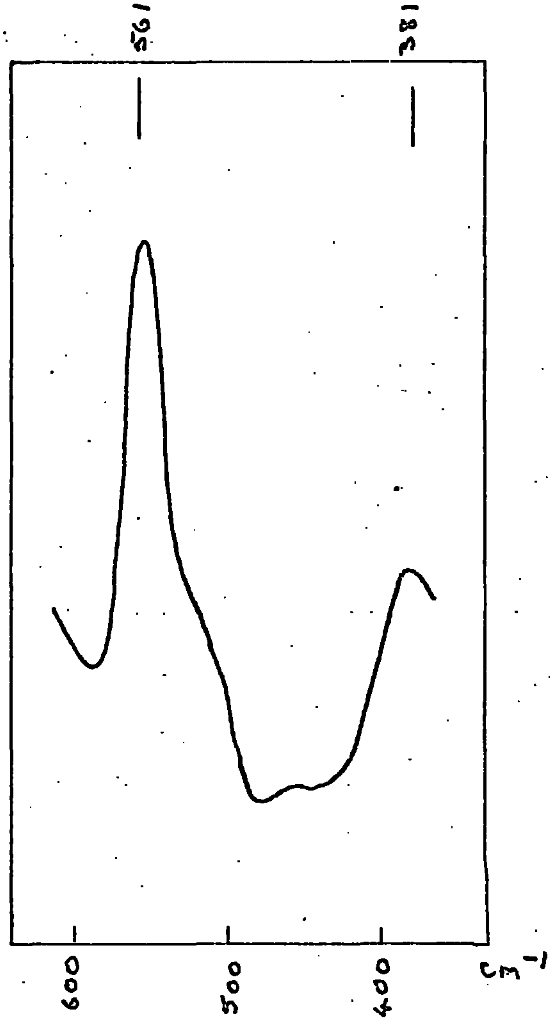
The assignments for the subsidiary peaks in the region of 520 cm^{-1} are readily made from a consideration of the infra-red spectrum of potassium ferrocyanide, and its hexakis-trifluoroboron adduct, $K_4Fe(CN)_6.6BF_3$. The hexakis-trifluoroboron adduct of potassium ferrocyanide was first described by Shriver (81), and we have prepared this material by a similar method. The spectrum of potassium ferrocyanide in this region is shown in Figure 22 and comprises two peaks, the peak recorded at 588 cm^{-1} being assigned as δ(MCN), and that at 417 cm^{-1} as ν(MC) (160). O_h symmetry requires δ(MCN) to have one mode active in the infra-red (F_{1u}), and similarly

FIGURE 18



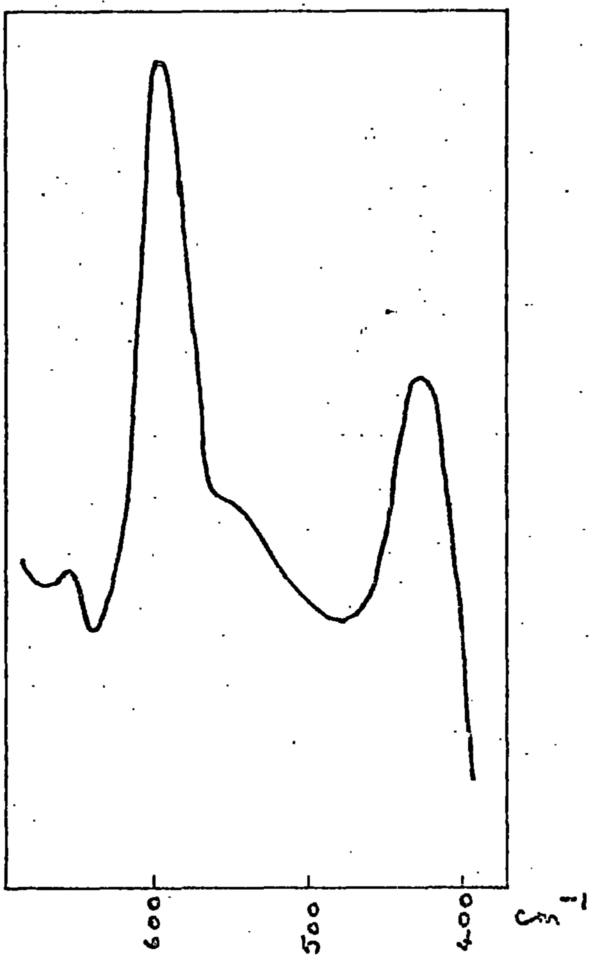
$H_4Fe(CN)_6 \cdot 2BF_3$

FIGURE 19



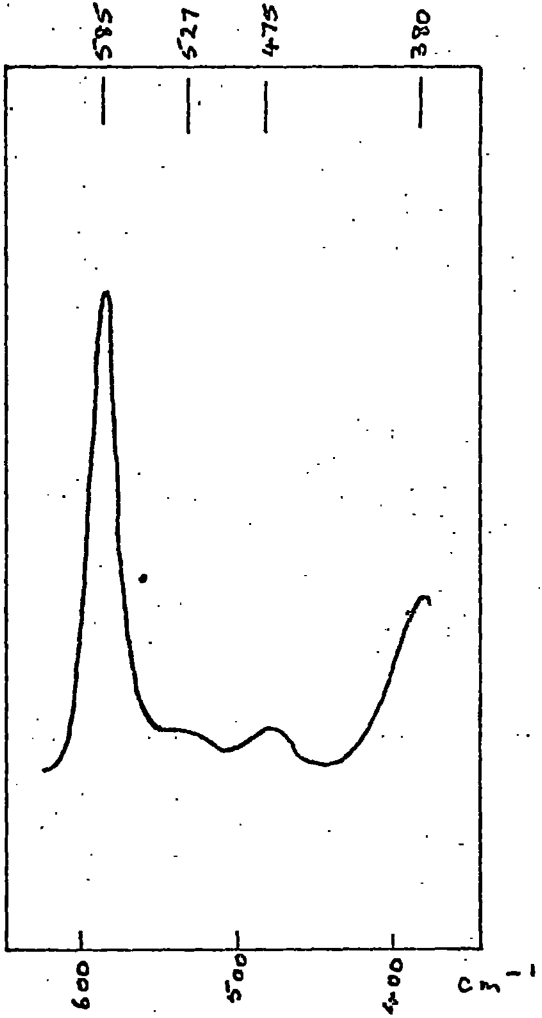
$H_4Ru(CN)_6 \cdot 2BF_3$

FIGURE 20



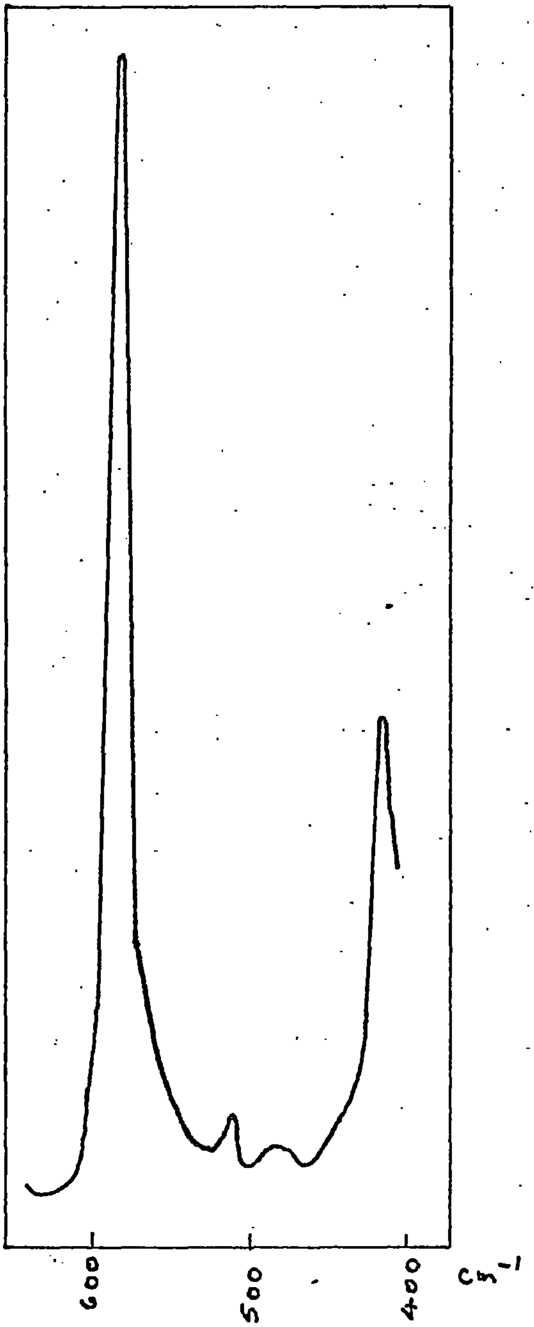
$D_4Fe(CN)_6 \cdot 2BF_3$

FIGURE 21



trans- $(CH_3)_4Fe(CN)_6 \cdot 2BF_3$

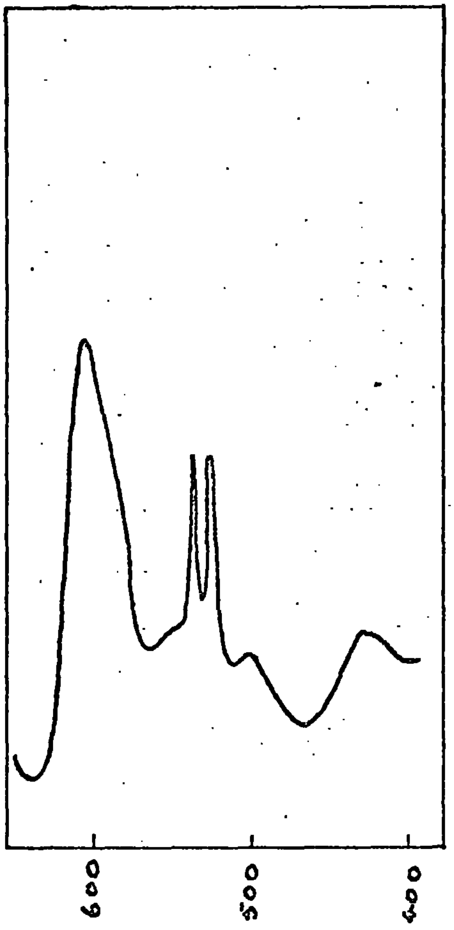
FIGURE 22



$K_4Fe(CN)_6$.

one mode active for ν(MC) (F_{1u}). The spectrum of the hexakis-trifluoroboron adduct (Figure 23) is somewhat more complicated, the two principal peaks being readily assigned to δ(MCN) and ν(MC) although shifted from their corresponding positions in the parent compound. Between these peaks there appear two sharp peaks of equal intensity at 536 cm^{-1} and 524 cm^{-1} which are superimposed on an underlying broad band of lower intensity. The two peaks correspond in range with that expected for the $\nu_4(F_2)$ vibration of BF_4^-, and could be interpreted as such the splitting being regarded as due to the change of symmetry from T_d (BF_4^-) to C_{3v} ($N—BF_3$) (161). However, a further possibility is that the splitting is due to the isotopic species $N—{}^{10}BF_3$ and $N—{}^{11}BF_3$ rather than to the symmetry effect. Such splitting has been reported by Greenwood (162) who commented on the equal intensity of the doublets despite the large difference in the isotopic abundances of ^{10}B and ^{11}B. Which of these interpretations is correct is immaterial for the purpose of our assignment, it being sufficient to note that the BF_3 asymmetric deformation vibration occurs in just this region, The underlying band of low intensity, which is also observed in potassium ferrocyanide, is not accounted for, but may be due to modes not active under the full O_h symmetry becoming

FIGURE 23



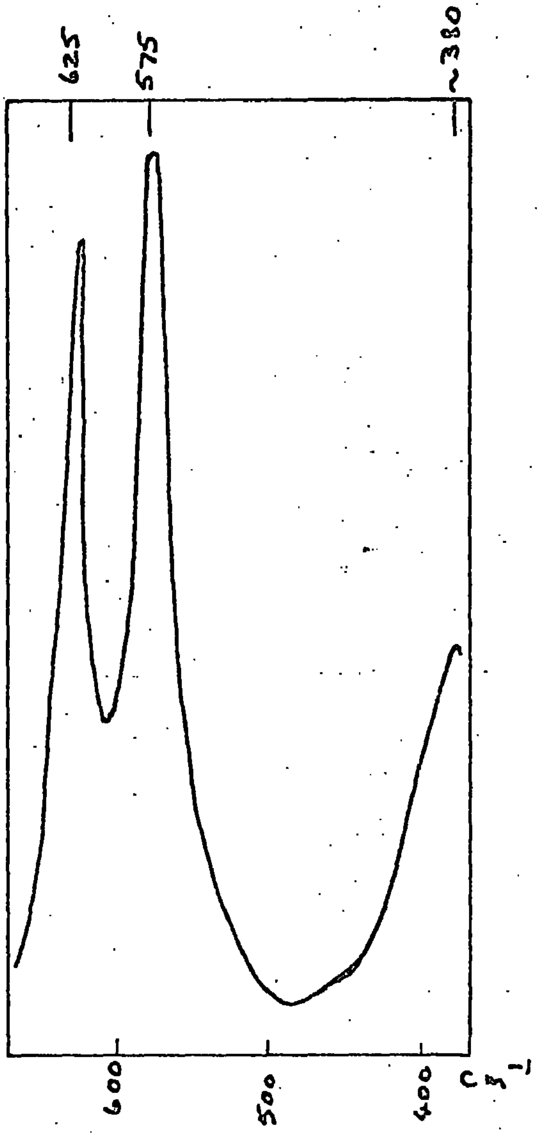
$K_4Fe(CN)_6 \cdot 6BF_3$

infra-red active under the site symmetry. The subsidiary peaks in the region above 500 cm^{-1} in the bis-trifluoroboron adducts can thus be accounted for as arising from B—F asymmetric deformation vibrations.

Figure 24 shows the spectrum of hexakis-methylisocyano iron (II) perchlorate and Figure 25 that of hexakis-ethylisocyano iron (II) perchlorate over the region 375 cm^{-1} to 650 cm^{-1}. In both cases a peak occurs at 625 cm^{-1} which is readily assigned to the ClO_4^- asymmetric bending vibration (163), and in addition a very weak broad absorption centred on 520 cm^{-1} which may arise as a result of site symmetry. The two remaining peaks are assigned as δ(MCN) and ν(MC) required under O_h symmetry.

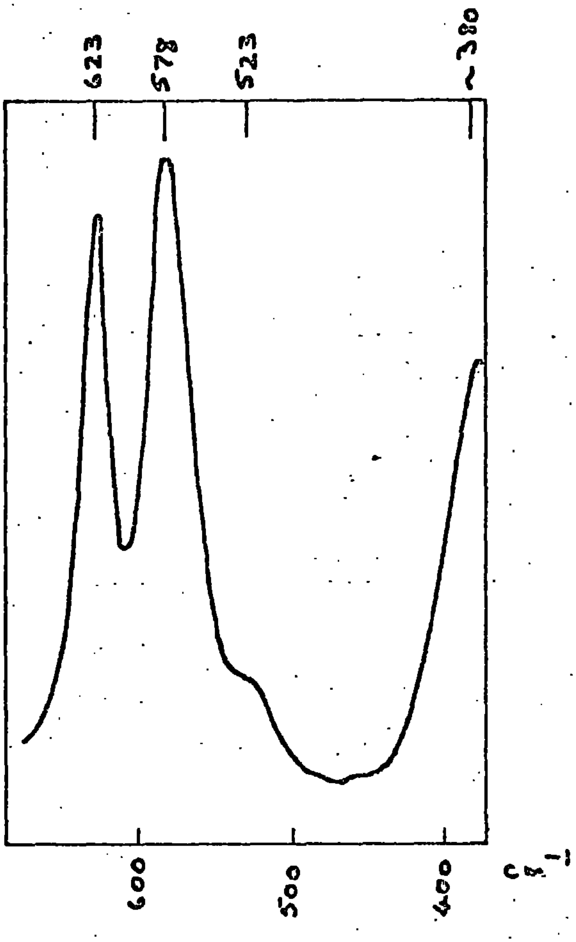
The two prominent peaks for the four molecules hexakis-methylisocyano iron (II) perchlorate, hexakis-ethylisocyano iron (II) perchlorate, potassium ferrocyanide and its hexakis-trifluoroboron adduct can thus be interpreted as those required under ~~site~~ symmetry O_h for the bending mode δ(MCN) and the stretching mode ν(MC). Comparison of these spectra with those of the bis-trifluoroboron adducts leads us to conclude that these adducts exhibit O_h local symmetry around the central metal atom. The observations of Ginsberg and Koubek, and of Beck and Smedal led them to assign D_{4h} symmetry for the complex cyanide acids $H_4M(CN)_6$, and the molecules trans-dicyano tetrakismethylisocyano iron(II)

FIGURE 24



$[(CH_3NC)_6Fe][ClO_4]_2$

FIGURE 25.



$[(C_2H_5NC)_6Fe][ClO_4]_2$

and trans-dicyano tetrakis-ethylisocyano iron (II) also exhibit the features of D_{4h} symmetry in their spectra. The formation of the bis-trifluoroboron adducts apparently leads to a change of local symmetry about the central metal atom from D_{4h} in the parent to O_h in the adduct, although the overall symmetry of the molecule must be D_{4h}. For ferrocyanic acid the change may be summarised as:-

$$\begin{array}{lllll}
 & D_{4h} & \xrightarrow{\hspace{8em}} & O_h & \\
\delta(\mathrm{MCN}) & [A_{2u} + 2\,E_u] & \left\{\begin{array}{l} 595\ \mathrm{cm}^{-1} \\ 583\ \mathrm{cm}^{-1} \\ 447\ \mathrm{cm}^{-1} \end{array}\right. \longrightarrow & [F_{1u}] & 592\ \mathrm{cm}^{-1} \\
\nu(\mathrm{MC}) & [A_{2u} + E_u] & \left\{\begin{array}{l} 416\ \mathrm{cm}^{-1} \\ 407\ \mathrm{cm}^{-1} \end{array}\right. \longrightarrow & [F_{1u}] & 423\ \mathrm{cm}^{-1}
\end{array}$$

Similarly for the other bis-trifluoroboron adducts.

Support for this interpretation of the spectrum of the bis-trifluoroboron adducts in the range 350 cm^{-1} to 650 cm^{-1} is provided by the results of Mossbauer spectra on the compounds. The results of Mossbauer observations are obtained in terms of the isomer shift (δ) which is a measure of the electron density in the immediate environment of the atom under observation, and in terms of the quadrupole splitting (ΔE) which reflects the symmetry of the electron density distribution.

For our present purpose the magnitude of the quadrupole splitting is of interest, since D_{4h} symmetry of the atom environment gives rise to quadrupole splitting whereas for the O_h environment no splitting is to be expected. The magnitude of the quadrupole splitting has been discussed by Berrett and Fitzsimmons (153).

In Table 19 values of the Mossbauer isomer shift and quadrupole splitting are recorded for compounds of interest in the present work. The results for the compounds $H_4Fe(CN)_6$, trans-$Me_4Fe(CN)_6$, and trans-$Et_4Fe(CN)_6$ show a quadrupole splitting appropriate to D_{4h} symmetry, which disappears on formation of their bis-~~alkylisocyano~~ trihaloboron adducts. No quadrupole splitting is observed for potassium ferrocyanide, and the hexakis-alkylisocyano iron (II) perchlorates where O_h symmetry is expected for the local environment of the iron atom, and the absence of the splitting in the hexakis-trifluoroboron adduct of potassium ferrocyanide indicates that the O_h local symmetry of the parent is retained on formation of its boron trifluoride adduct. These results are consistent with the results of the infra-red spectra observations, and indeed the infra-red spectra results would appear to be the more reliable in this case in reflecting the local symmetry of the iron atom when one has regard to the errors quoted on the Mossbauer

Table 19

Mossbauer Spectra

Compound	δ mm.sec^{-1}	ΔE mm.sec^{-1}
$K_4Fe(CN)_6$	+ 0.11	0.00
$K_4Fe(CN)_6.6BF_3$	+ 0.03	0.00
$H_4Fe(CN)_6$	+ 0.04	0.10
$H_4Fe(CN)_6.2BF_3$	+ 0.02	0.00
trans-$Me_4Fe(CN)_6$	0.00	0.44 *
trans-$Me_4Fe(CN)_6.2BF_3$	+ 0.07	0.00
trans-$Me_4Fe(CN)_6.2BCl_3$	+ 0.05	0.00
trans-$Et_4Fe(CN)_6$	+ 0.05	0.59 *
trans-$Et_4Fe(CN)_6.2BF_3$	+ 0.04	0.00
$(RNC)_6Fe^{++}(ClO_4^-)_2$	- 0.10	0.00

Errors for δ and ΔE = ± 0.05 mm.sec^{-1}. *

= ± 0.03 mm.sec^{-1}.

δ values are relative to Stainless Steel

* Data from Berrett and Fitzsimmons, J.Chem. Soc., 525,(1967) and the remainder from the same authors by private communication.

measurements. Such errors could well mask a residual quadrupole splitting.

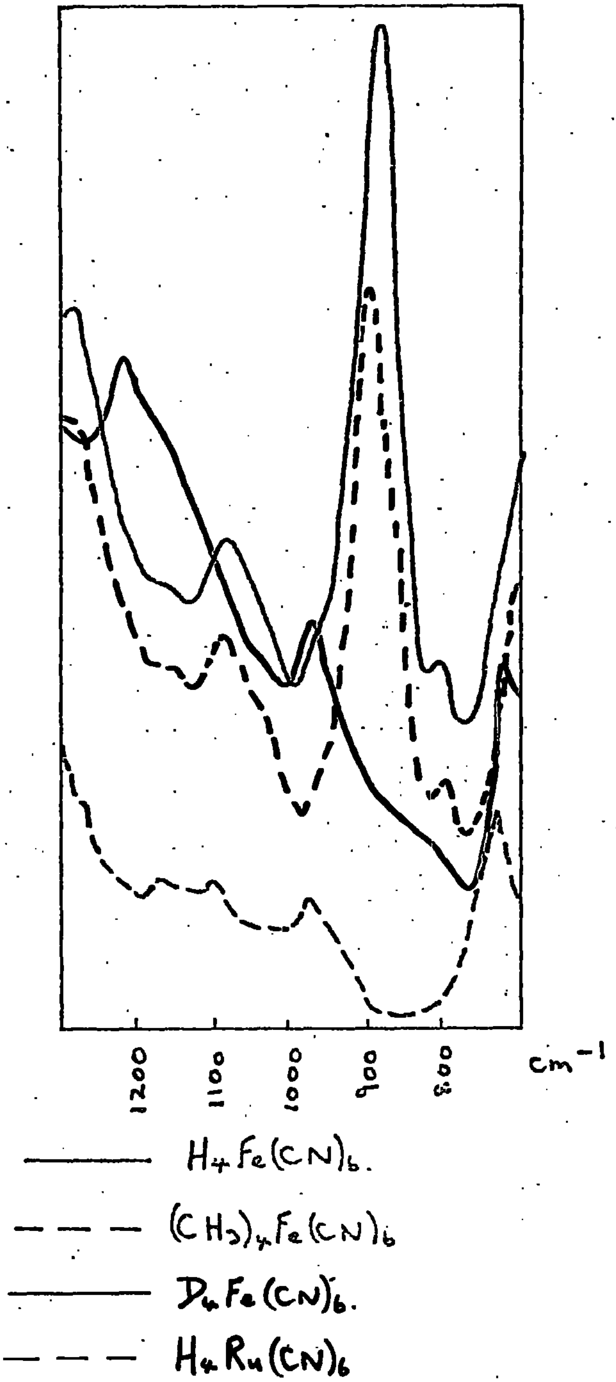
One further point emerging from the infra-red spectra results is that adduct formation brings about a small increase in the frequency for the M—C stretch, and for the M—C≡N bend.

4.2 Region B: (650 cm^{-1} to 2000 cm^{-1})

This region is the most difficult for the purpose of frequency assignments since it is expected to be composed of bending modes and combination modes in addition to the possible characteristic frequencies. No detailed discussion of this region is attempted, and remarks will be confined to features for which there are comparisons available in published work. For convenience the region is divided into two overlapping sub-regions, 650 cm^{-1} to 1300 cm^{-1}, and 1200 cm^{-1} to 2000 cm^{-1}.

Figure 26 shows the spectra of $H_4Fe(CN)_6$, $D_4Fe(CN)_6$, $H_4Ru(CN)_6$, and $Me_4Fe(CN)_6$ over the range 700 cm^{-1} to 1300 cm^{-1}, and Figure 27 their corresponding bis-trifluoroboron adducts, the spectra being presented together in order to facilitate comparisons. The four succeeding figures (28 - 31) show the spectra of the individual compounds and their adducts over the same

FIGURE 26.



1200
1100
1000
900
800
cm^{-1}
$H_4Fe(CN)_6$.
$(CH_3)_4Fe(CN)_6$
$D_4Fe(CN)_6$.
$H_4Ru(CN)_6$

FIGURE 27.


1200
1100
1000
900
800
cm⁻¹
——— $H_4Fe(CN)_6 \cdot 2BF_3$
– – – $(CH_3)_4Fe(CN)_6 \cdot 2BF_3$
——— $D_4Fe(CN)_6 \cdot 2BF_3$
– – – $H_4Ru(CN)_6 \cdot 2BF_3$

FIGURE 28.

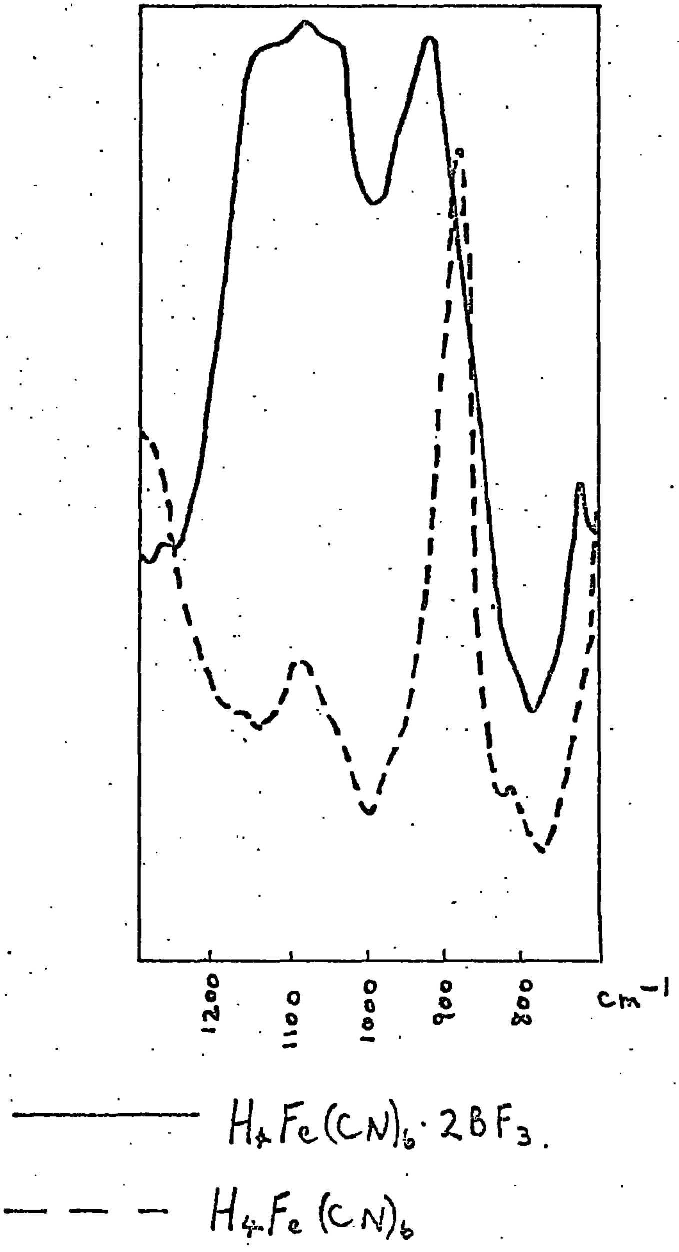


FIGURE 29

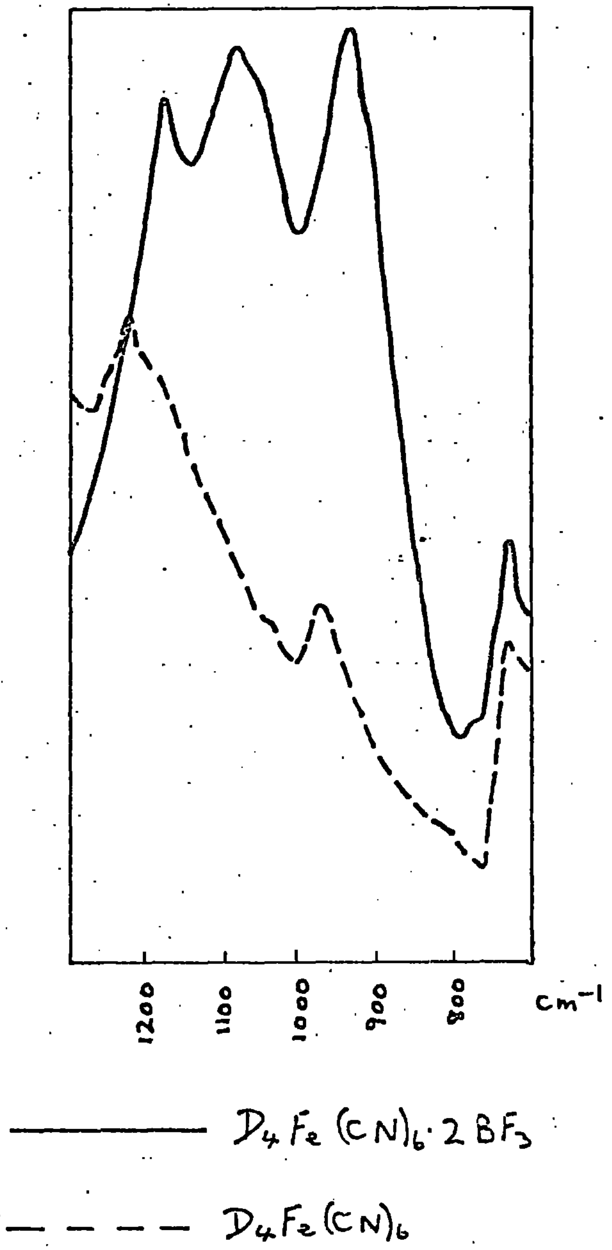


FIGURE 30

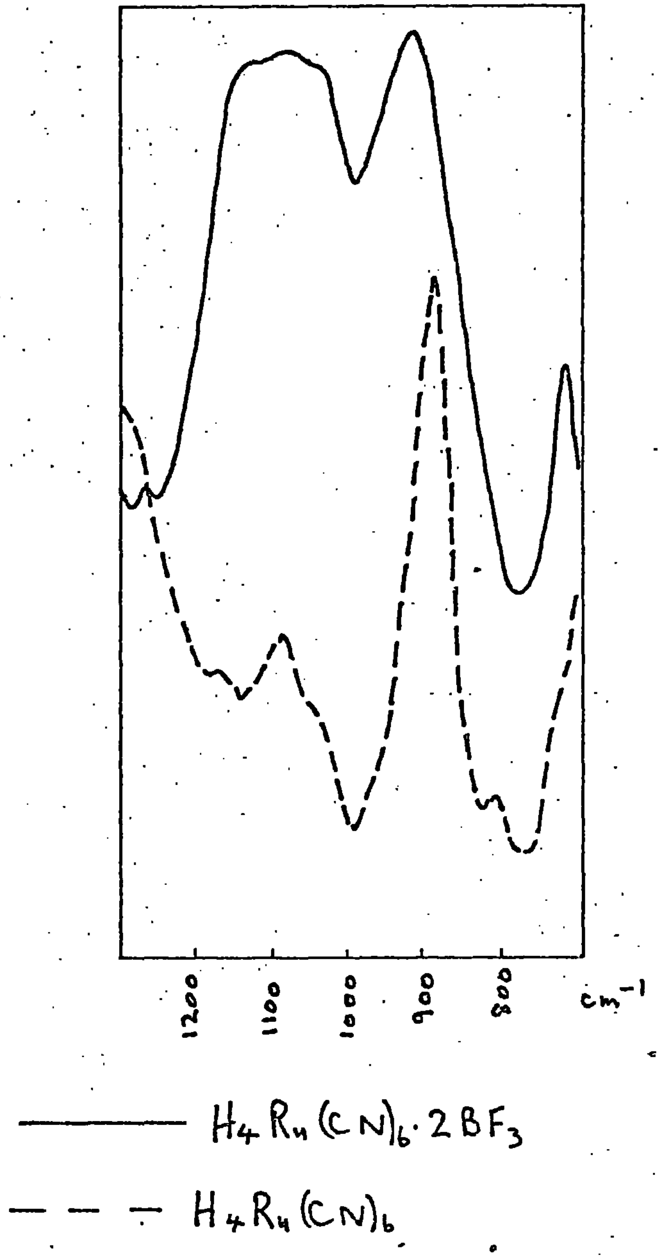
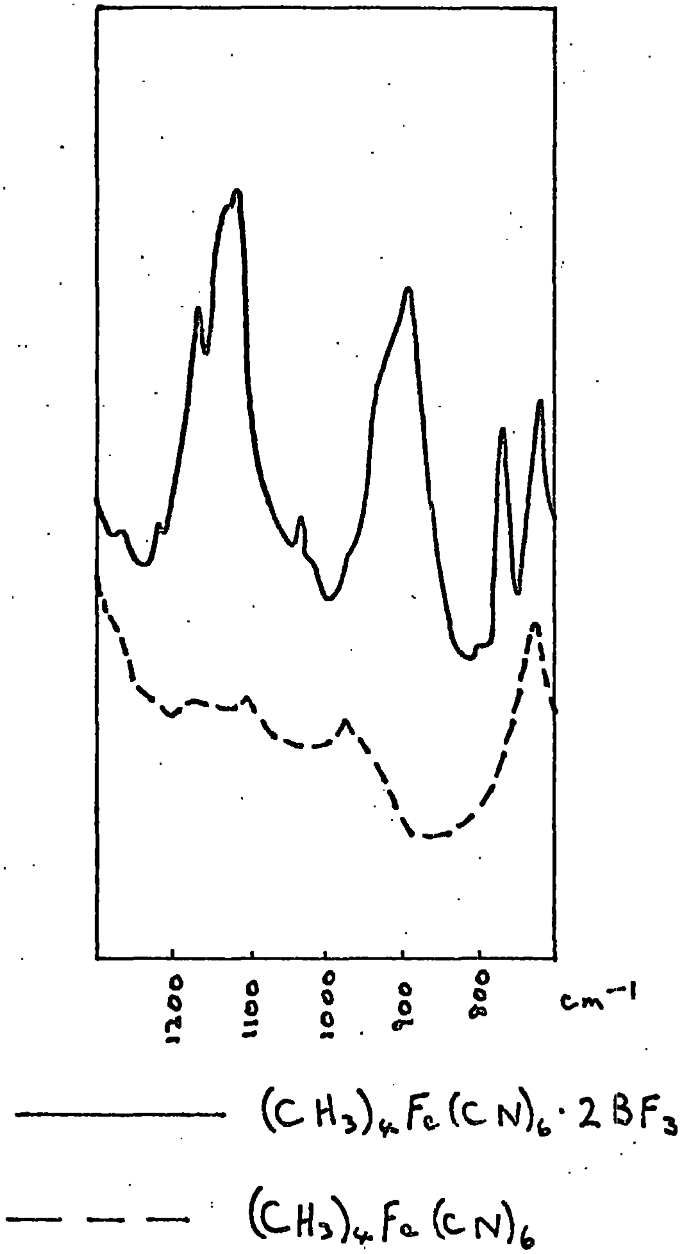


FIGURE 31



range. The spectra of $H_4Fe(CN)_6$ and $H_4Ru(CN)_6$ show marked similarity, the peak at just below 900 cm^{-1} assigned by both Ginsberg and Beck to $\delta(N-H)$, is notably absent in $D_4Fe(CN)_6$ and $Me_4Fe(CN)_6$. For the bis-trifluoroboron adducts the dominant feature is the set of strong bands lying between 920 cm^{-1} and 1700 cm^{-1}. The marked overlapping of bands makes individual assignment difficult, and the following remarks are simply based on published observations. The strong absorption at around 920 cm^{-1} is attributed to overlapping of the B—N stretching vibration (164) and the symmetric $-BF_3$ stretching mode (165). This band is also a feature of the bis-trifluoroboron adducts of trans-dicyano tetrakis-alkylisocyano iron (II) in which the asymmetry of the band is more clearly seen. In the region of 1100 cm^{-1} the absorptions have also been reported by Shriver (81) in related adducts, and are attributed to the asymmetric $-BF_3$ stretching vibration.

The remainder of the range, from 1200 cm^{-1} to 2150 cm^{-1}, is shown for $H_4Fe(CN)_6$, $D_4Fe(CN)_6$, and $H_4Ru(CN)_6$ together with their bis-trifluoroboron adducts ~~is illustrated~~ in Figures 32, 33 and 34. The lower frequency range of the spectrum is obscured in these figures by the bands due to Nujol, and no attempt has been made to examine this part of the spectrum by elimination of the Nujol bands.

FIGURE 32

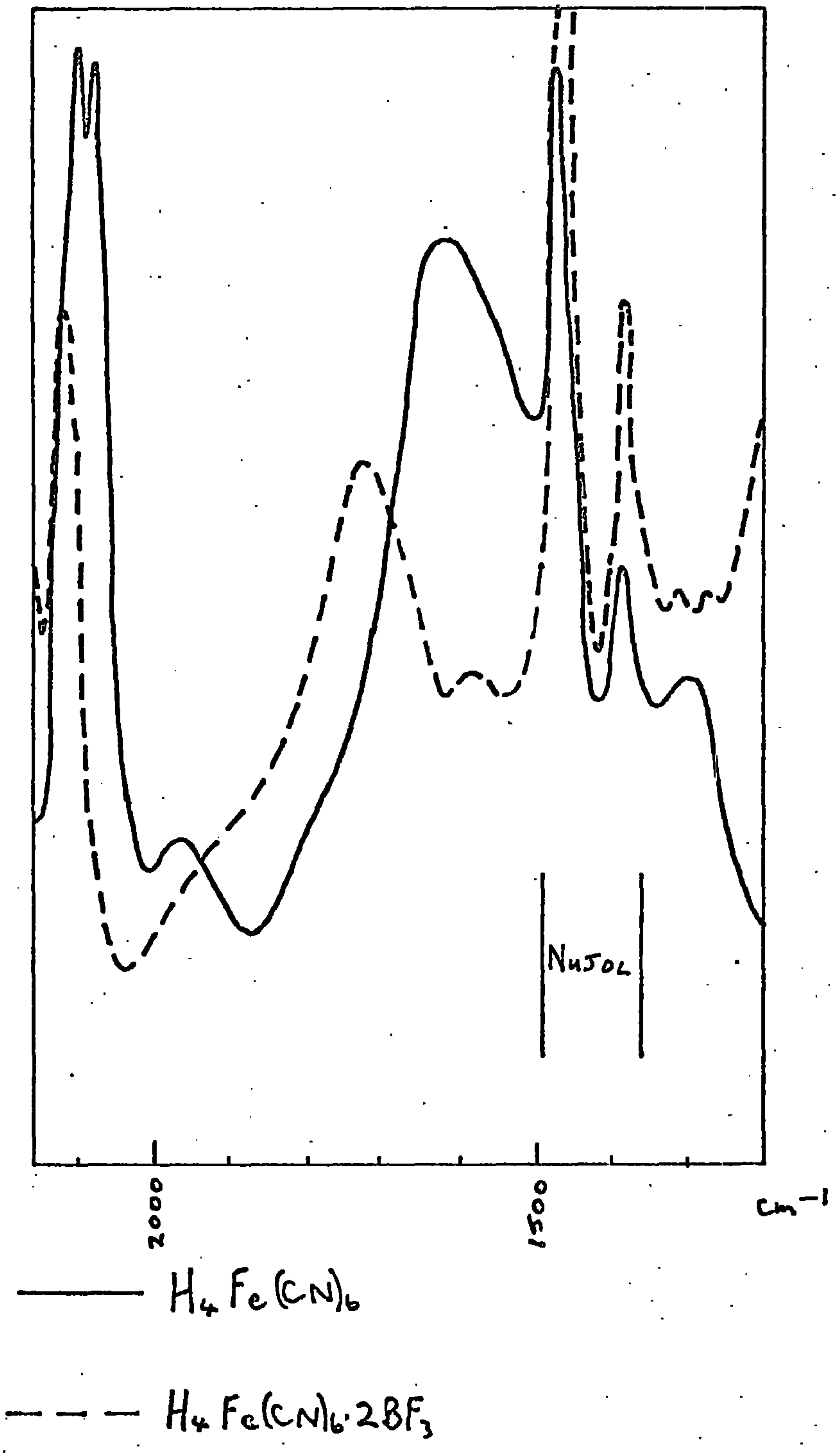


FIGURE 33.

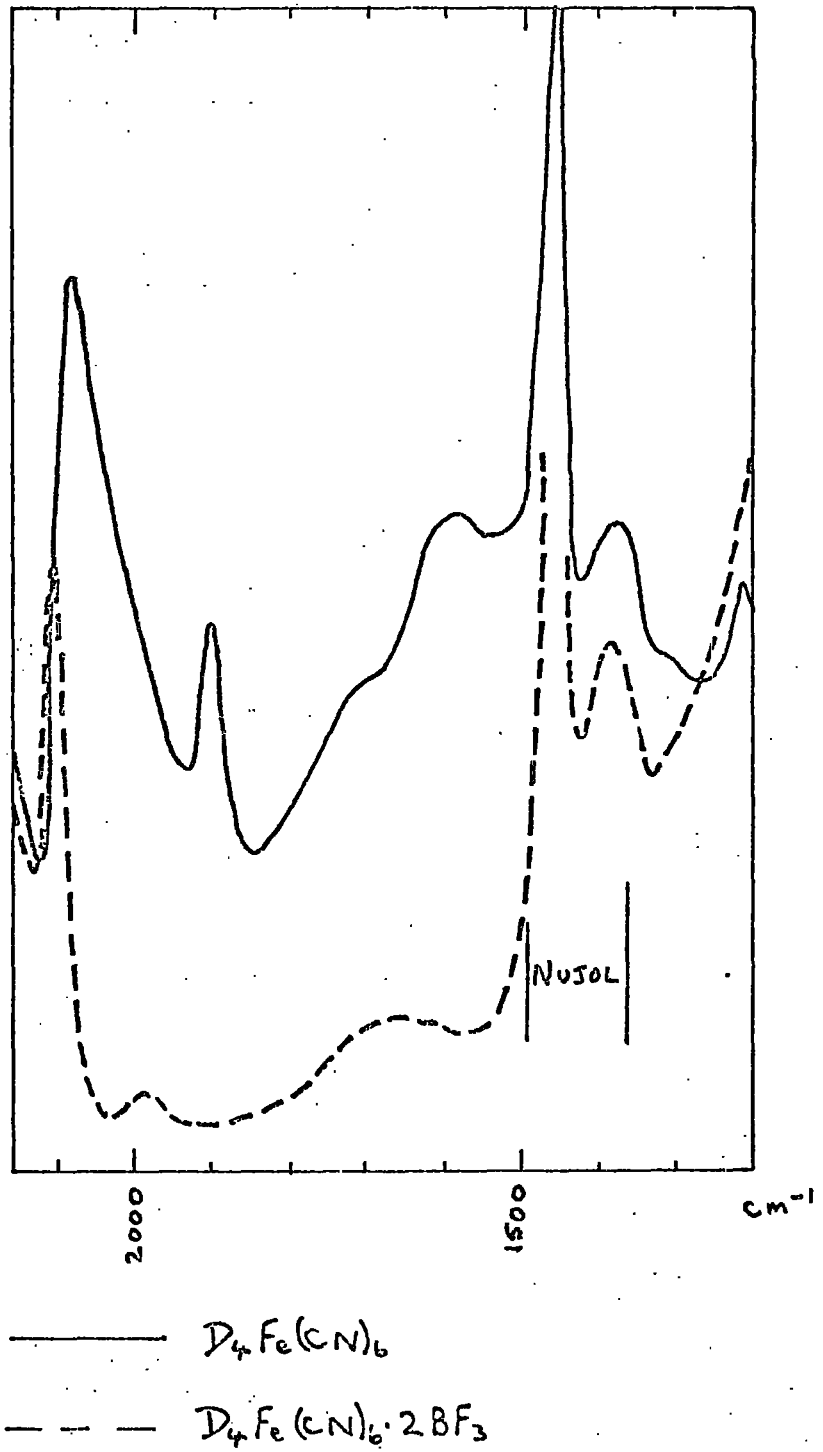
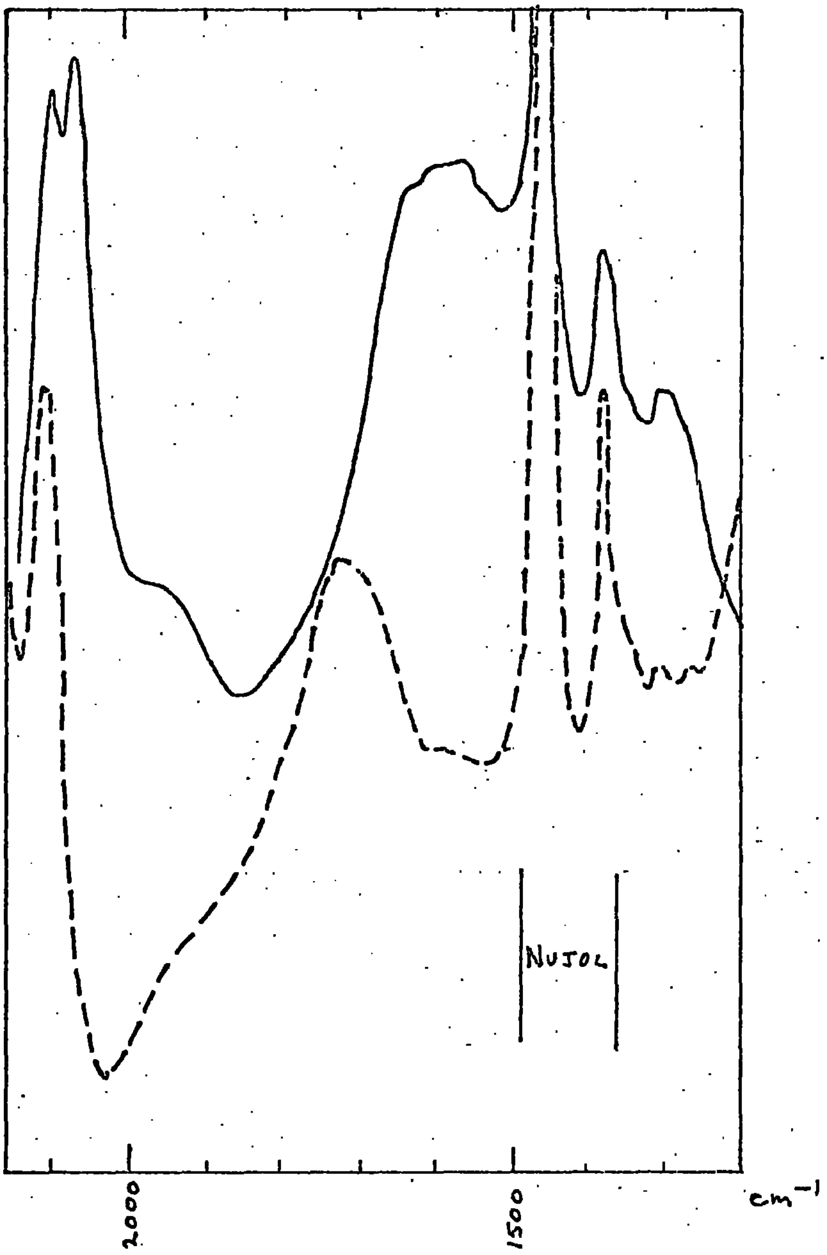


FIGURE 34



——— $H_4Ru(CN)_6$

– – – $H_4Ru(CN)_6 \cdot 2BF_3$

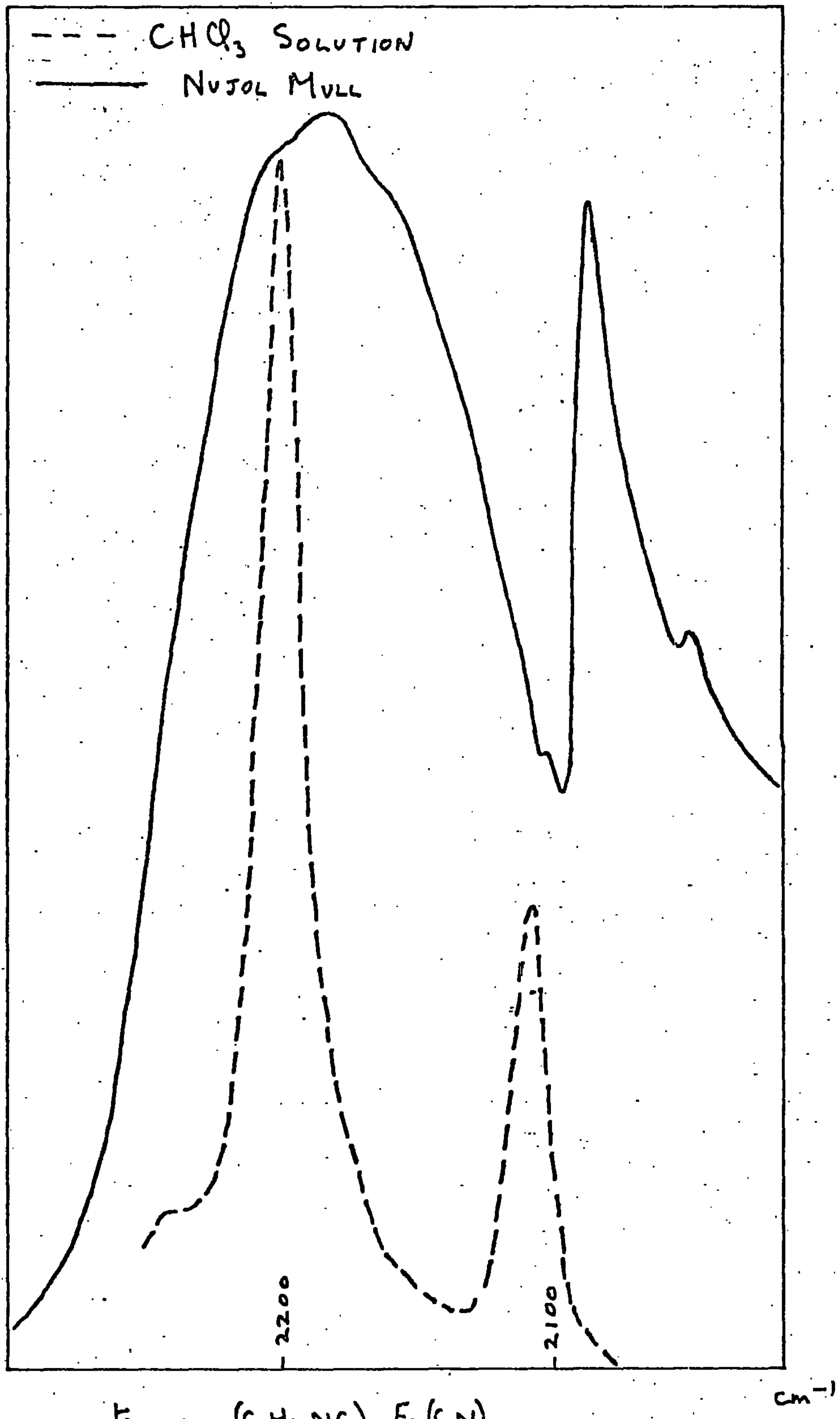
This neglect is in part due to some suspicion of adduct spectra obtained from KBr discs, but much more to the difficulty of making assignments in this range. Although the range has been discussed in much detail for the parent compounds by Ginsberg and Koubeck (46) the difficulty of assignment with any certainty is illustrated by the many reservations made in their paper over this region. Attention can be drawn to the absence in the spectra of $H_4Fe(CN)_6.2BF_3$ and $H_4Ru(CN)_6.2BF_3$ of the strong absorption at 1650 cm^{-1} which is present in the parent compounds, and attributed by Ginsberg to a hydrogen bonded N—H mode. A band of medium intensity appears around 1725 cm^{-1} which is absent in $D_4Fe(CN)_6.2BF_3$.

4.3. Region C: (2000 cm^{-1} to 2300 cm^{-1})

In this region absorptions due to C≡N stretching frequencies are observed (159). A difficulty arises in the accurate recording of peak frequencies because of the need to examine the boron halide adducts and their parent compounds as solids dispersed in a mulling agent. In solids the effect of site symmetry in increasing the number of observed C≡N frequencies is well known (166), and a good example of this is shown by the infra-red spectrum of potassium ferrocyanide. This compound gives

in the C≡N region a set of nine peaks which have been interpreted as due to the site symmetry C_i (167). The hexakis-trifluoroboron adduct, $K_4Fe(CN)_6.6BF_3$, gives only one peak which is very broad (81), and it is not possible to tell whether this broadness is due to overlapping of several peaks due to site symmetry splitting or whether it arises from other solid state effects.
In order to eliminate the effects of site symmetry compounds can be examined in solution, but in the compounds we have examined this can only be done with the trans-dicyano tetrakis-alkylisocyano iron (II) compounds. Figures 35, and 36 present a comparison of the alkyl compounds in solution and mull form. In chloroform solution trans-dicyano tetrakis-methylisocyano iron (II) exhibits the two absorption bands expected under D_{4h} symmetry at 2106 cm^{-1} (ms) and 2200 cm^{-1} (s), the peaks being generally sharp and symmetric, although the high frequency peak shows weak shoulders at both sides.
The same compound in the form of a solid dispersed in Nujol gives peaks centred on 2090 cm^{-1} (ms) and 2190 cm^{-1} (s), these being appreciably broader and no longer symmetric. It is not uncommon to observe frequency shifts for C≡N in solution and solid phase spectra, and indeed for solution spectra involving the same compound

FIGURE 35

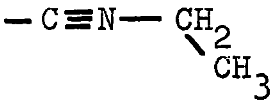


trans-$(CH_3NC)_4Fe(CN)_2$

FIGURE 36

trans-$(C_2H_5NC)_4Fe(CN)_2$

in different solvents (168), but here in addition to frequency shifts a considerable broadening of the peaks is noted. In the spectrum of trans-dicyano tetrakis-ethylisocyano iron (II) distortion of the peaks is observed in chloroform solution, and this we can attribute to the non-linear atom arrangement in the ethyl isocyano group as compared to linear* arrangement of the methylisocyano group i.e.



$-C\equiv N-CH_2-CH_3$

ethylisocyano

$-C\equiv N-CH_3$

methylisocyano.

The non-linear arrangement would be expected to reduce the symmetry from D_{4h} with splitting of the $C\equiv N$ peaks. The mull spectrum is broader, but would seem merely to reproduce the splitting displayed in chloroform solution. This leaves open the question as to whether the broadening is due to site symmetry effects or some other effect of the solid phase.

---

* methylisocyano liquid is not strictly linear the bond angle $C\equiv N-C$ being given as 167^0 (169)

The complex cyanide acids, $H_4Fe(CN)_6$, are insoluble in solvents with which they do not interact strongly, and as a result their spectra must be measured in the form of solids dispersed in a mulling agent. This is also true of their trifluoroboron adducts. In order to attempt comparisons between the systems studied it is desirable that all the compounds be examined in the same state, and hence all spectra are measured in mull form. Some uncertainty is thus introduced in the values assigned to the $C\equiv N$ frequencies as a result of broadening and frequency shift.

In Figure 37 we present the spectra of $H_4Fe(CN)_6$ and $H_4Ru(CN)_6$ in the range 2000 cm^{-1} to 2150 cm^{-1}, and in Figure 38 the spectrum of $D_4Fe(CN)_6$ in the range 1900 cm^{-1} to 2150 cm^{-1}. The frequency values are listed in Table 20 in which they are compared with the results of other observers. Comparison of these results shows reasonable agreement on the values to be assigned to the two strong absorptions, but on other peaks the disagreement is more pronounced. A number of weak and very weak absorptions are recorded on either side of the main peaks by Ginsberg (46) which are not recorded by Beck (45) or Jones (158). We have recorded a very weak shoulder at 2038 cm^{-1} in $H_4Fe(CN)_6$ and at 2034 cm^{-1} in $H_4Ru(CN)_6$.

FIGURE 37.

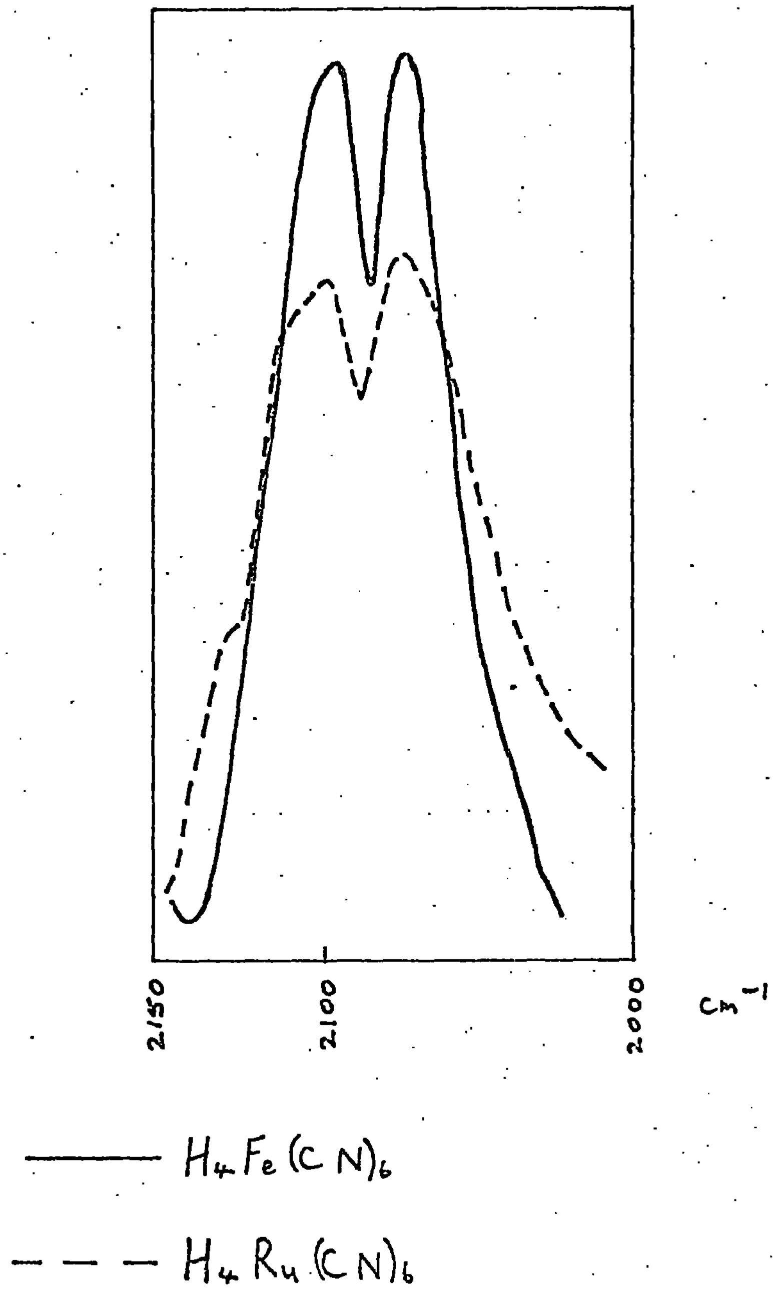


FIGURE 38

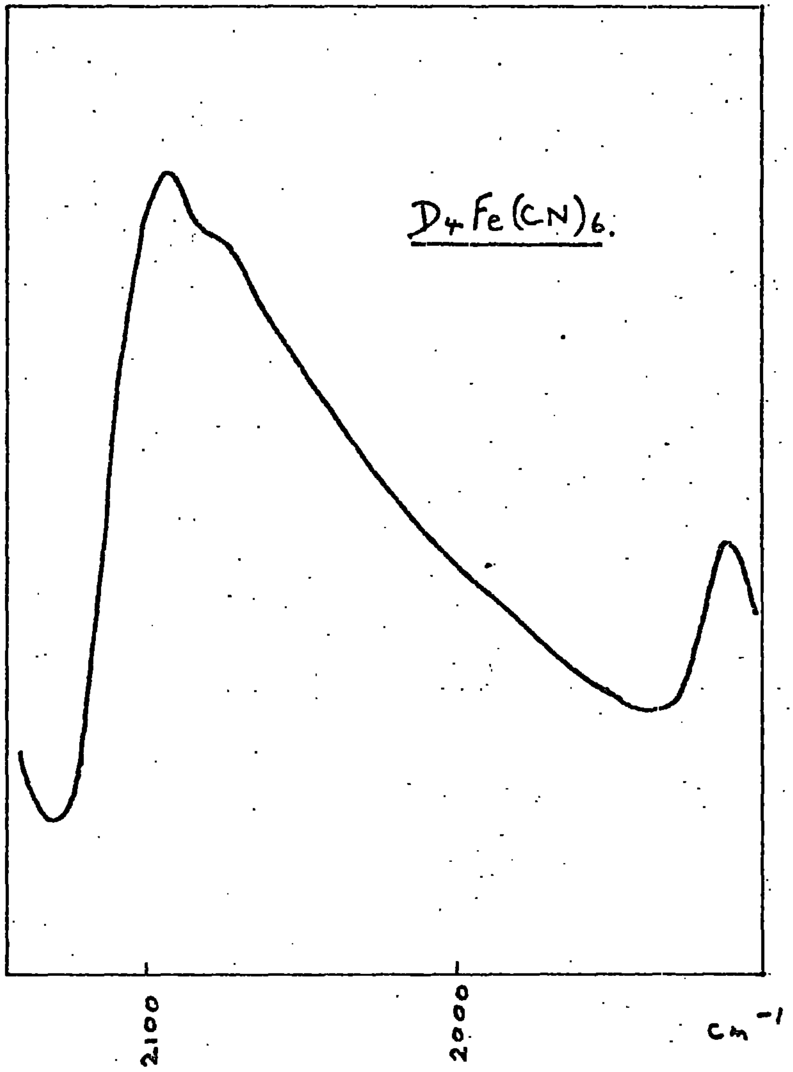


Table 20

Compound	Ginsberg	Beck	Jones	This work
$H_4Fe(CN)_6$	2134 w	-	-	-
	2125 sh.w	-	-	-
	2106 sh	2165 sh	-	2118 sh
	2096 s	2101 s	2110 s	2093 s
	2072 s	2073 s	2086 s	2070 s
	2060 sh.vw	-	-	-
	2040 sh.vw	-	-	2038 sh.vw
$H_4Ru(CN)_6$	2145 w	-	-	-
	2135 w	-	-	2131 sh
	2110 s	2102 s	2105	2097 s
	2104 sh	-	-	-
	2078 s	2076 s	2080 s	2071 s
	2062 sh.vw	-	-	-
	2045 sh.vw	-	-	2034 sh.vw
$D_4Fe(CN)_6$	1905 wm	1918 m	1908 w	1913 wm
	2100 s	2103 s	2095 s	2093 s

More serious is the lack of agreement on the value assigned to the prominent shoulder on the higher of the two strong absorptions. For $H_4Fe(CN)_6$ our recorded value (2118 cm^{-1}) is closer to that of Ginsberg (2106 cm^{-1}) than to that of Beck (2165 cm^{-1}) whilst the shoulder is not recorded at all by Jones. The lack of agreement is more marked in the case of $H_4Ru(CN)_6$ where no shoulder is observed by ~~both~~ Beck and Jones, but is observed on the low frequency side of the main peak by Ginsberg, and on the high frequency side in our work. Despite repeated attempts we have been unable to bring about agreement on this point. These differences cannot be dismissed as trivial since they represent a point of disagreement between the views of Ginsberg and Beck.

In their interpretation of the spectrum of $H_4Fe(CN)_6$ Beck and Smedal ignore the shoulder they record at 2165 cm^{-1} and regard the two strong absorptions as those required under D_{4h} symmetry (species A_{2u}, E_u). They must therefore take the view that the hydrogen-bonding interaction is not strong enough to lower the D_{4h} symmetry of the $C \equiv N$ groups. The observation that in $D_4Fe(CN)_6$ only one of the strong absorptions is shifted appreciably is considered by these authors to lend support to their views on the structure.

Using the site symmetry C_i appropriate to the recently reported space group and unit cell of $H_4Fe(CN)_6$ (119), Ginsberg and Koubek argue that the two peaks (2073, 2096 cm^{-1}) and shoulder (2106 cm^{-1}) represent the three C≡N frequencies required of D_{4h} under the site symmetry ($A_{2u} \rightarrow A_u$, $E_u \rightarrow 2A_u$). The shoulder at 2106 cm^{-1} is assigned as $\nu'(C \equiv N)\left[E_u\right]$ split by the site symmetry. On deuteration the shoulder at 2106 cm^{-1} in $H_4Fe(CN)_6$ is identified with the peak at 2100 cm^{-1} in $D_4Fe(CN)_6$, the slight shift to lower frequency being considered as due to decreased interaction with the hydrogen-bond stretching frequency. Here compare the results of Beck and Smedal where the peak considered to be unaffected by deuteration shows a slight upward shift (2101 → 2103 cm^{-1}). The deuteration shift of the doublet is not accounted for by the peak at 1905 cm^{-1} (i.e. that recorded nearest to Beck and Smedal at 1918 cm^{-1}), but is explained as follows:

"In the deuterio-acids ν(ND) should occur close to ν(CN). Since four C≡N groups per $D_4Fe(CN)_6$ are directly bound to deuterium, and since $\nu(C \equiv N)$ and ν(ND) belong to the same symmetry species, we may expect that the two ν(ND) fundamentals will interact strongly with two of the $\nu(C \equiv N)$ frequencies, while the third C≡N stretching frequency should be relatively unaffected. The spectra are consistent with this expectation. A band is observed at 2100 cm^{-1} which even under high resolution remains single, although it is asymmetric. This must be $\nu(C\equiv N)$ fundamental due to stretching of the undeuterated cyanide group. The bands at 1720 and approximately 1610 cm^{-1} may then be identified as resulting from a very strong interaction between the two remaining $\nu(C\equiv N)$ frequencies and the two N—D stretching vibrations. The strong absorptions at 2460 and 2280 cm^{-1} are the other two bands which result from this interaction".

The interpretation of Beck and Smedal has the virtue of simplicity, but has been made at the expense of ignoring a band which they have observed, and no reason is given for its exclusion. That of Ginsberg and Koubek is more attractive in that the attempt is made to include other observed bands, although by no means all of them. However both groups, in their different ways, invoke strong coupling of N—D and C$\equiv$N modes in order to account for the effects of deuteration, and this in turn must imply the existence of strong coupling between N—H and C$\equiv$N. Hadzi (170) has shown that hydrogenic stretching vibrations will, in general, be independent of other vibrations in the same molecule, and Cotton (171) has pointed out that where the bond force constant is large, as in C≡N, it is questionable whether strong coupling is to be expected, even when permitted by the symmetry.

A further feature of the argument of Ginsberg and Koubek is that the two peaks at 2072 and 2096 cm^{-1} are the result of splitting of the $\nu(C\equiv N)\ [E_u]$ mode by the site symmetry C_i. In principle it is possible to eliminate the effects of site symmetry by examination of the spectrum of a solution of the compound, but this is not possible with $H_4M(CN)_6$. The spectra of the related trans-alkyl compounds have been examined in solution (Figures 35 and 36). Firm conclusions as to the results of this study are not possible on the information available, but it would seem that peak distortions observed in solution persist in the solid phase spectra, being accentuated in the process, and the peak splitting does not occur to the extent suggested by Ginsberg and Koubek for $H_4Fe(CN)_6$.

In Table 20 we note discrepancies in the number of peaks reported by different authors. It is conceivable that the species $H_4M(CN)_6$ can act as a host lattice for the clathration of solvent molecules used in the course of its preparation. The presence of guest molecules can introduce complications in the spectrum of the host, both by virtue of the characteristic frequencies of the guest molecules, and by variation of the site symmetry. Thus the infra-red spectra of $H_2Pt(CN)_6.2EtOH$, and $H_2Pt(CN)_6.EtOH$ are almost identical with that of $H_2Pt(CN)_6$. with the addition of frequencies characteristic of ethyl alcohol (158). The etherate of $H_4Fe(CN)_6$ is reported to show only one C≡N band, (45). Variations in the degree of retention of guest molecules in the host would be expected to produce variations in the form of the observed spectrum. It might then be possible to explain the discrepancies in the observations (Table 20) as arising from varying degrees of retention of solvent molecules in the individual preparation techniques. The spectrum detail of Jones would be obtained on material prepared according to the method described (12). After preparation of the etherate of $H_4Fe(CN)_6$ Jones adopted the practice of heating at 110°C in vacuo to remove the ether. Our study of the thermal decomposition of ferrocyanic acid suggests that the ether is more safely removed at lower temperatures since at 110°C there is a risk of loss of H—C≡N from the parent compound. It will be noted that in Table 20 no subsidiary peaks or shoulders are reported by Jones, and this leads to the suspicion that subsidiary peaks may well depend upon the history of ferrocyanic acid subsequent to the precipitation of the etherate in its preparation.

Further discussion of the $H_4M(CN)_6$ species will be made after presentation of the spectra of their trifluoroboron adducts.

The frequencies observed for the boron halide adducts and their parent molecules are presented in Table 21, together with rough estimates of their relative intensities which are expressed as strong (s) and medium strong (ms). The meaning to be attached to these relative intensity descriptions should be clear from the illustrations provided. The spectra of $H_4Fe(CN)_6.2BF_3$ and $H_4Ru(CN)_6.2BF_3$ are presented over the $C\equiv N$ range in Figures 39 and 40, while in Figure 41 the spectrum of $D_4Fe(CN)_6.2BF_3$ is presented and compared with those of $H_4Fe(CN)_6.2BF_3$ and $D_4Fe(CN)_6$. The results presented in Table 21 left out such detail as shoulders on the peaks, and these are now given in Table 22.

The shoulder observed on the strong upper peak of these adducts is in the same position in each case, at least as far as a simple Gaussian resolution will allow. A suggestion as to how this shoulder might arise can be given, but in order to do so at this stage it is necessary to anticipate some of the later discussion. For reasons to be given later we assign the strong peak in the adducts as being due to the $C\equiv N$ stetch in the system

Table 21

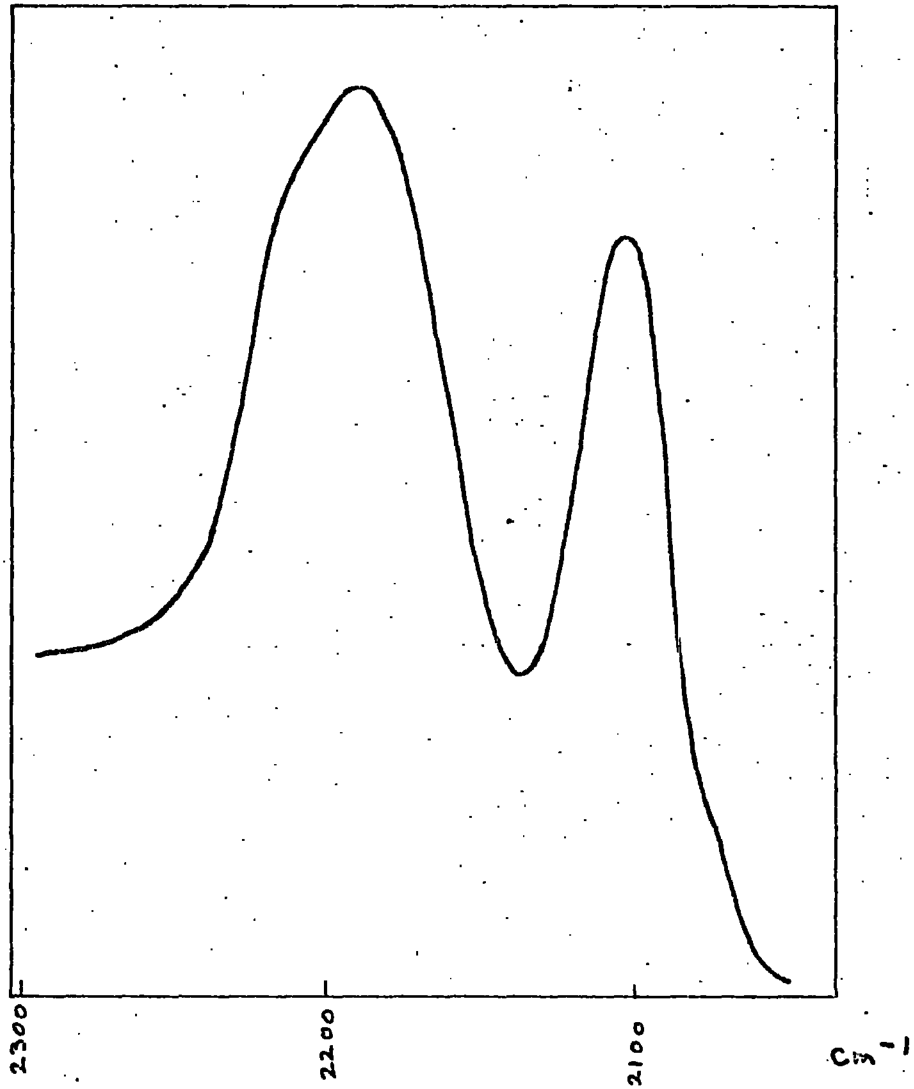
C≡N Stretching Frequencies

Compound	$\nu(C\equiv N)$ cm^{-1}	
$H_4Fe(CN)_6$	2070 ms;	2093 s.
$H_4Fe(CN)_6.2BF_3$	2105 ms;	2193 s.
$D_4Fe(CN)_6$	-	2093 s.
$D_4Fe(CN)_6.2BF_3$	2108 ms;	2198 s.
$H_4Ru(CN)_6$	2071 ms;	2097 s.
$H_4Ru(CN)_6.2BF_3$	2106 ms;	2195 s.
trans-$(CH_3NC)_4Fe(CN)_2$	2090 ms;	2190 s.
trans-$(CH_3NC)_4Fe(CN)_2.2BF_3$	2180 ms;	2228 s.
trans-$(CH_3NC)_4Fe(CN)_2.2BCl_3$	2180ms;	2231 s.
trans-$(C_2H_5NC)_4Fe(CN)_2$	2098 ms;	2165 s.
trans-$(C_2H_5NC)_4Fe(CN)_2.2BF_3$	2186 ms;	2218 s.
trans-$(C_2H_5NC)_4Fe(CN)_2.2BCl_3$	2187 ms;	2220 s.
$K_4Fe(CN)_6$	2048 *	
$K_4Fe(CN)_6.6BF_3$	2180s,v.br	
$(CH_3NC)_6Fe^{++}(ClO_4^-)_2$	2235s	
$(C_2H_5NC)_6Fe^{++}(ClO_4^-)_2$	2220s	

---

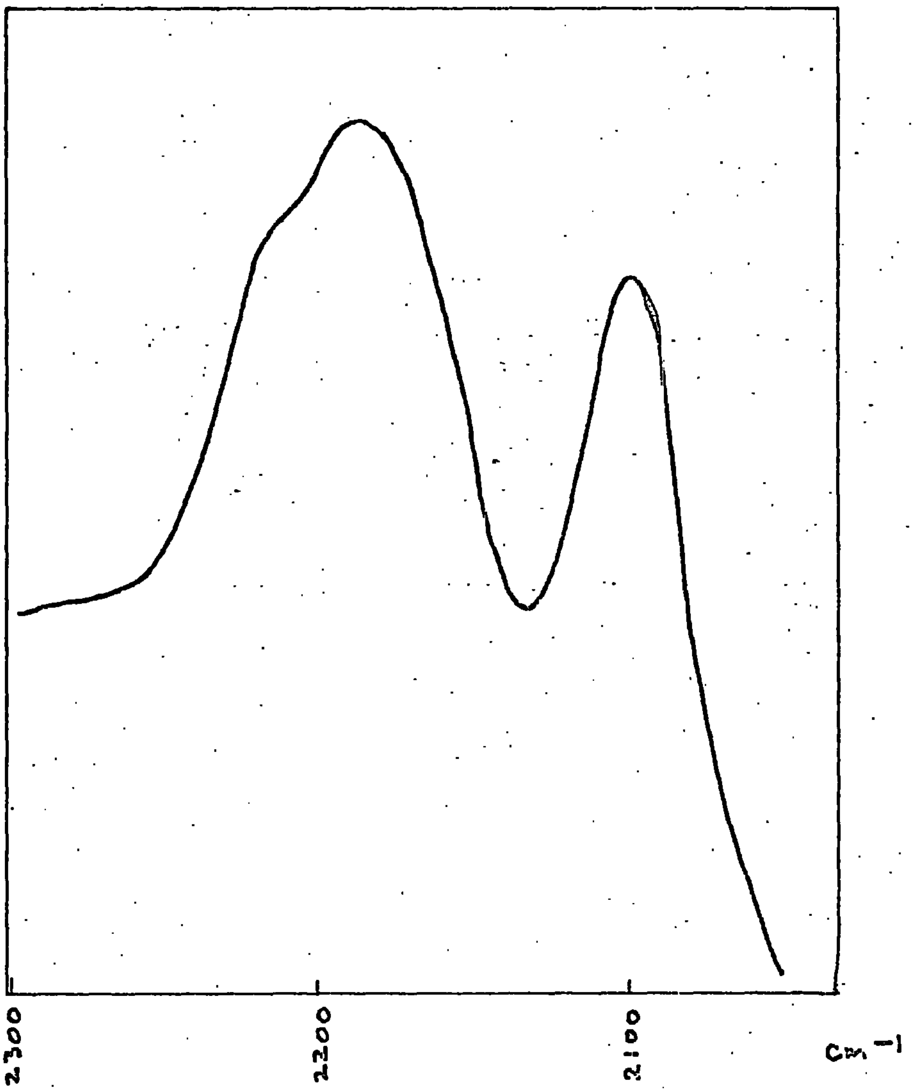
* The infra-red spectrum of $K_4Fe(CN)_6$ in the C≡N stretching region is complex (167). We have chosen the strongest band centred on 2048 cm^{-1}, in common with Shriver (81).

FIGURE 39



$H_4Fe(CN)_6 \cdot 2BF_3$

FIGURE 40.



$H_4Ru(CN)_6 \cdot 2BF_3$

FIGURE 41.

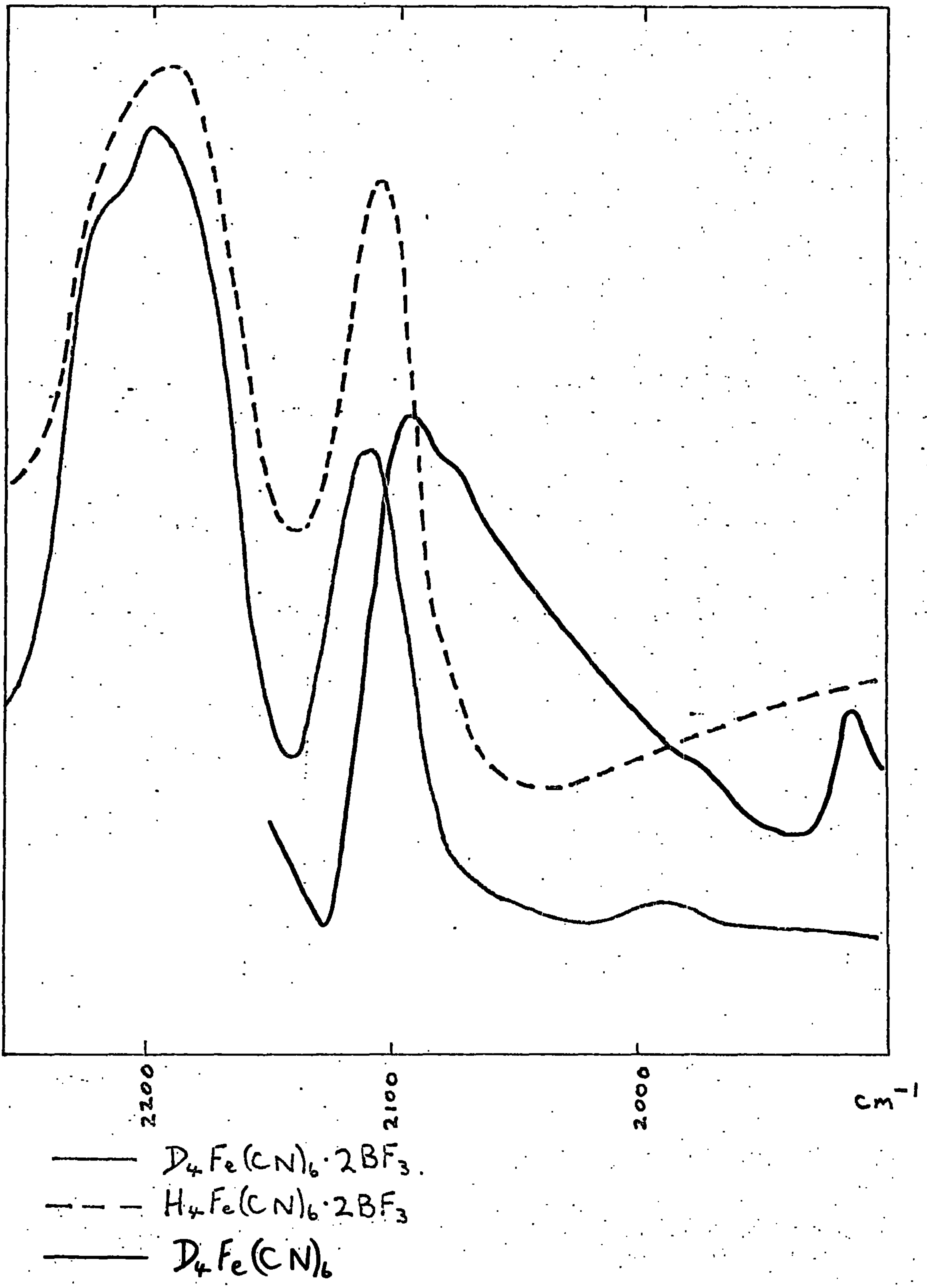

2200
2100
2000
cm^{-1}
$D_4Fe(CN)_6 \cdot 2BF_3$.
$H_4Fe(CN)_6 \cdot 2BF_3$
$D_4Fe(CN)_6$

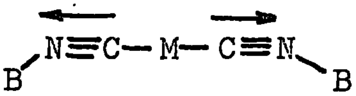
Table 22

$H_4Fe(CN)_6.2BF_3$	$H_4Ru(CN)_6.2BF_3$	$D_4Fe(CN)_6.2BF_3$
2105 ms	2106 ms	2108 ms
2193 s	2195 s	2198 s
2230 sh,vw	2230 sh.vw	2230 sh,w

$-C\equiv N-BF_3$, the two $C\equiv N$ groups involved being in the trans arrangement. If the bond system $-C\equiv N\rightarrow B$ were linear only the asymmetric $C\equiv N$ stretching frequency would be infra-red active, i.e.

$$B\rightarrow \overrightarrow{N\equiv C}-M-\overrightarrow{C\equiv N}-B$$

However, if this bond system departs from linearity, by reason of the bond angle $C\equiv N\rightarrow B$ being less than 180°, then the symmetric $C\equiv N$ stretch could become infra-red active, i.e.



That such a departure of bond angle from 180° is possible is shown by comparison with the analogous bond system $-C\equiv N-CH_3$ in trans-dicyano tetrakis-methylisocyano iron (II) in which the $C\equiv N-C$ bond angle is reported as 167° (169). Argument on the same lines could presumably be used to account for the shoulder on the upper peak of the parent molecules $H_4Fe(CN)_6$ and $H_4Ru(CN)_6$ -(see earlier discussion) - as arising from non-linearity of the hydrogen bonded hydrogen atoms attached to $C\equiv N$.

The results in Table 21 show in both parent compounds and their boron halide adducts a doublet structure in the $C\equiv N$ region of the spectrum, the lower frequency member of the doublet being the weaker. This structure is in accord with D_{4h} symmetry, i.e. $A_{2u} + E_u$. In the parent compounds we have assigned the lower frequency member of the doublet to $\nu(C\equiv N)$, i.e. free $C\equiv N$, since all the values are comparable in magnitude. The higher frequency we have assigned to the isonitrile group $\nu(C\equiv N-R)$, ($R= H$, CH_3, C_2H_5), in the parent compounds since this frequency varies with the nature of the attached group R, and in the methyl and ethyl compounds the frequency is comparable with that of the single $\nu(C\equiv N)$ observed in the hexakis-alkylisocyano iron(II) perchlorates. When cyanide groups form adducts with boron halides the value of $\nu(C\equiv N)$ is increased (81), and this is also observed in the compounds we have examined. The value assigned to the frequency shift $\Delta\nu(C\equiv N)$ which occurs on adduct formation will depend on the assignments made for the $C\equiv N$ absorption frequencies of the adducts, and there are two possibilities for making such assignments.

The two possibilities for the C≡N frequencies of the adducts can be made as follows:

A. The lower frequency member of the C≡N doublet in the adducts can be assigned to the group C≡N→BX$_3$, and the higher frequency member to the group C≡N→R (R= H, CH$_3$, or C$_2$H$_5$).

B. The lower frequency member of the C≡N doublet is assigned to C≡N—R, and the higher frequency member to the group C≡N→BX$_3$.

Each case would give rise to two different sets of values for Δν(C≡N), and the two sets are presented for comparison in Table 23.

Table 23

Shifts in characteristic C≡N frequency (cm^{-1})

Compound	Interpretation (A)		Interpretation (B)	
	Δν (C≡N)	Δν (C≡N—R)	Δν (C≡N)	Δν (C≡N—R)
$H_4Fe(CN)_6.2BF_3$	+ 35	+100	+ 123	+ 12
$H_4Ru(CN)_6.2BF_3$	+ 35	+ 98	+ 124	+ 9
$Me_4Fe(CN)_6.2BF_3$	+ 90	+ 38	+ 138	- 10
$Me_4Fe(CN)_6.2BCl_3$	+ 90	+ 41	+ 141	- 10
$Et_4Fe(CN)_6.2BF_3$	+ 84	+ 43	+ 120	+ 20
$Et_4Fe(CN)_6.2BCl_3$	+ 85	+ 45	+ 122	+ 21

In making the assignment for the C≡N frequencies in the adduct molecules we have chosen the second of these interpretations (B) since under this interpretation the values of $\Delta\nu$(C≡N) show better internal consistency than those for interpretation (A). The shift values under this interpretation are of the same order of magnitude for the individual bond types involved in each case, i.e. C≡N and C≡N—R, whereas the first interpretation gives a wide spread of values. The change $\Delta\nu$(C≡N) for the group C≡N—R is small, whilst that for the group C≡N—BX_3 is comparable in size with the shift observed for $K_4Fe(CN)_6.6BF_3$ (i.e. 135 cm^{-1}).

It seems to be generally accepted that C≡N frequency changes in isonitrile and cyanide complexes are related to changes in the σ-donor and π-acceptor characteristics of the ligands, and that changes in these characteristics would produce corresponding changes in the electronic charge density around the central atom of the complex (168, 160). The existence of an electric field gradient has been demonstrated for trans-dicyano tetrakis-methylisocyano iron (II) and trans-dicyano tetrakis-ethylisocyano iron (II) as arising from ligand inequivalences and imbalance of the electron occupation numbers of the d-orbitals (153). In trans complexes the field gradient will lie along the octahedral axis containing the free $C\equiv N$ groups, the contribution from the isonitrile groups being symmetrical in the plane normal to the axis. A change from D_{4h} to O_h local symmetry of the electronic charge distribution could be brought about by a substantial change in the axial direction, together with a relatively small change in the planar distribution. Such a change seems to be consistent with the set of frequency shifts given by interpretation (B). The alternative set of frequency shifts under interpretation (A) would correspond to significant changes in the electronic charge distribution in both the axial and planar directions, and would seem less likely to give rise to a uniform change of symmetry in the compounds.

The most certain method of distinguishing between the two possible interpretations for the frequency shift would be to have an unambiguous measure of the shift in changing from $C\equiv N$ to $C\equiv N{-}BX_3$. An opportunity for such a measurement seemed to be afforded by deuterio-ferrocyanic acid in which both Ginsberg and Beck report that the un-deuterated $C\equiv N$ group remains essentially unshifted on deuteration, whilst that of the group $C\equiv N{-}D$ was moved to another region of the spectrum. In such a case the formation of the bis-trifluoroboron adduct should result in a measureable shift which could be compared with the values for $H_4Fe(CN)_6$, it being reasonably assumed that the deuterium and hydrogen compounds would be essentially the same in this case. The result of such an experiment is represented in Figure 41 which shows the spectrum of $D_4Fe(CN)_6.2BF_3$ in the C≡N region of the infra-red spectrum, the spectra of $D_4Fe(CN)_6$ and $H_4Fe(CN)_6.2BF_3$ being also given for comparison. It is seen that the spectrum of $D_4Fe(CN)_6.2BF_3$ is essentially similar to that of $H_4Fe(CN)_6.2BF_3$, and accordingly similar to that of $H_4Ru(CN)_6.2BF_3$. The experiment does not allow us to obtain the result for which it was performed, i.e. an unambiguous measure of the shift $\Delta\nu$(C≡N), but the result is of some significance. The simplest interpretation of these results is that not only are the bis-trifluoroboron adducts of $H_4Fe(CN)_6$, $D_4Fe(CN)_6$, and $H_4Ru(CN)_6$ identical in their infra-red spectra in the C≡N region, but that the spectra of the parent compounds are also identical. "The band observed at 2100 cm^{-1} which even under high resolution remains single, although it is asymmetric" (46) must then be a doublet in which the structure is masked by some underlying band, possibly a low-lying N—D or combination mode.

Beck and Smedal claim that the absorption peak at 1905 cm^{-1} (1913 cm^{-1} in our spectrum) is $\nu(C\equiv N)$ shifted by deuteration of $H_4Fe(CN)_6$. The peak is seen to disappear on formation of the adduct $D_4Fe(CN)_6.2BF_3$, whilst the doublet structure of the strong $C\equiv N$ absorption reappears. If the reappearance of the strong doublet were due to a shift upwards of the peak at 1913 cm^{-1} then the magnitude of the shift would have to be at least of the order of 200 cm^{-1} (1913 to 2108 cm^{-1}). This would represent a very large shift indeed even for direct addition of boron halide to $C\equiv N$, and an interpretation of the peak as being due to $C\equiv N—D$ would involve the transmission of this large effect through the remainder of the molecule. It would seem therefore unlikely that the interpretation of Beck and Smedal is correct in this instance.

Ginsberg and Koubek argue that strong coupling of $N—D$ and $C\equiv N$ belonging to the same symmetry species in the system $C\equiv N—D$ results in frequency displacements in the spectrum of $D_4Fe(CN)_6$, and leaving the undeuterated $C\equiv N$ mode essentially undisplaced. The evidence of the reappearance of the doublet structure on formation of the bis-trifluoroboron adduct is not of itself sufficient to argue against this interpretation, since in the adduct spectrum the 'free' $N—D$ frequency appears to suffer an upward displacement which could lead to decoupling of the Fermi resonance. Their argument does depend of course on the interpretation of the C≡N frequencies in ferrocyanic acid. If, as we have suggested, the shoulder on the high frequency side of the C≡N doublet in the spectrum of ferrocyanic acid is due to non-linearity of the C≡N—H group (see page 177), and the principal peaks of the doublet are simply those required under D_{4h} symmetry of the C≡N system, then the alternative hypothesis, that the asymmetric C≡N peak in $D_4Fe(CN)_6$ is a doublet overlaid with a low-lying N—D mode, is also a possibility.

4.4 Region D: (2300 cm^{-1} to 4000 cm^{-1})

The bis-trifluoroboron adducts of the ferrocyanic and ruthenocyanic acids each give a single broad band centred at approximately 3300 cm^{-1} (Table 16), and their spectra are reproduced in Figures 42 and 43. Also shown in the figures is the spectrum of the parent acid over the same spectral region. The figures illustrate further the close correspondence between the compounds $H_4Fe(CN)_6.2BF_3$ and $H_4Ru(CN)_6.2BF_3$, as well as the correspondence between the parent acids $H_4Fe(CN)_6$ and $H_4Ru(CN)_6$. This close correspondence between the two sets of compounds allows the remaining discussion to be

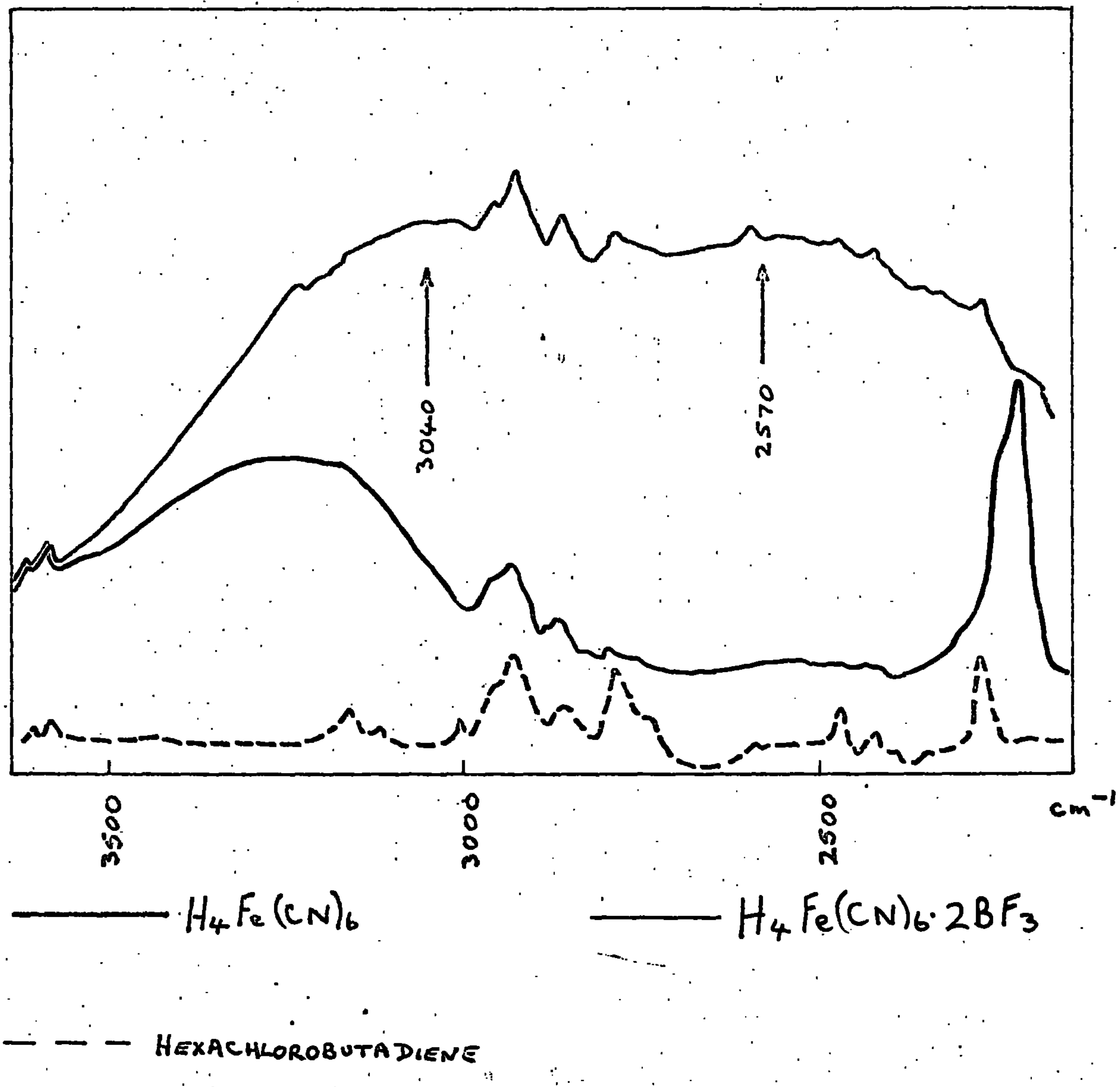
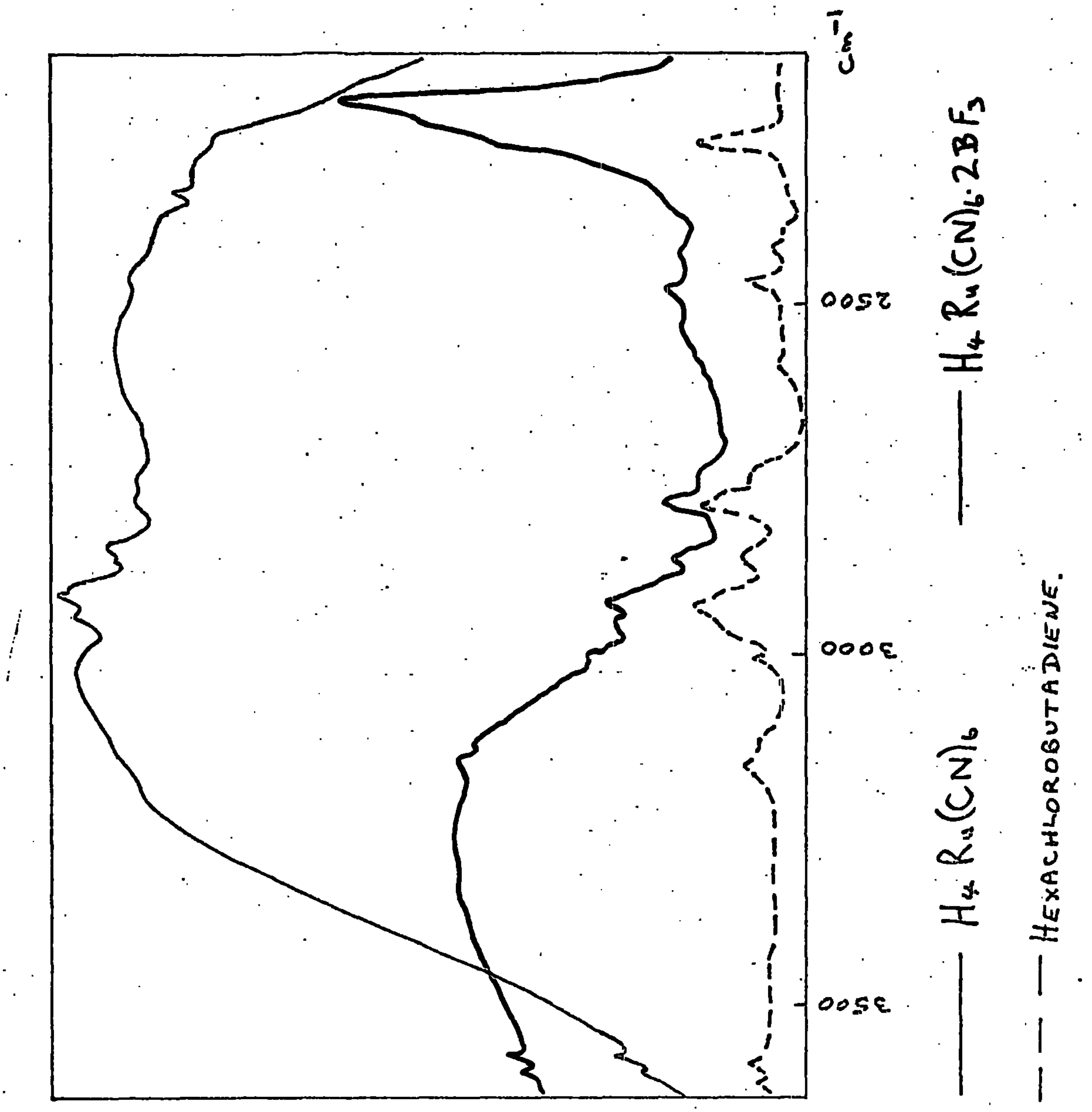

3040
2570
3500
3000
2500
cm⁻¹
H4 Fe(CN)6
H4 Fe(CN)6·2BF3
HEXACHLOROBUTADIENE

FIGURE 4.2

FIGURE 4.3.


cm⁻¹
2500
3000
3500
H4 Ru(CN)6·2BF3
H4 Ru(CN)6
HEXACHLOROBUTADIENE.

confined to one member of each set, a practice also followed by Ginsberg (46) and Beck (45). Some comment on the interpretation of the spectra of the parent acids by these authors will be useful.

Beck and Smedal (45) divide the broad absorption observed over this region into two main bands i.e.

$H_4Fe(CN)_6$	$H_4Ru(CN)_6$
3050 s.	3040 s.
2570 s.bb.	2580 s.bb.

The upper band is interpreted as due to ν(N—H), and the very broad band at lower frequency as that due to ν(N—H···N). The spectrum of $D_4Fe(CN)_6$ in which two distinct bands are clearly visible at 2490 cm^{-1} and 2306 cm^{-1} are interpreted similarly as ν(N—D) and ν(N—D···N) respectively. These authors take an essentially simple view of the spectrum as consisting of bands due to 'free' N—H stretching and asymmetric hydrogen-bonded N—H···N stretching frequencies in accord with their suggested structure of the acids (see Figure 12).

Ginsberg and Koubek (46) examined the spectrum at room temperature and at 80°K. At the lower temperature they claim that the bands are more clearly resolved, and give the component peaks as follows:

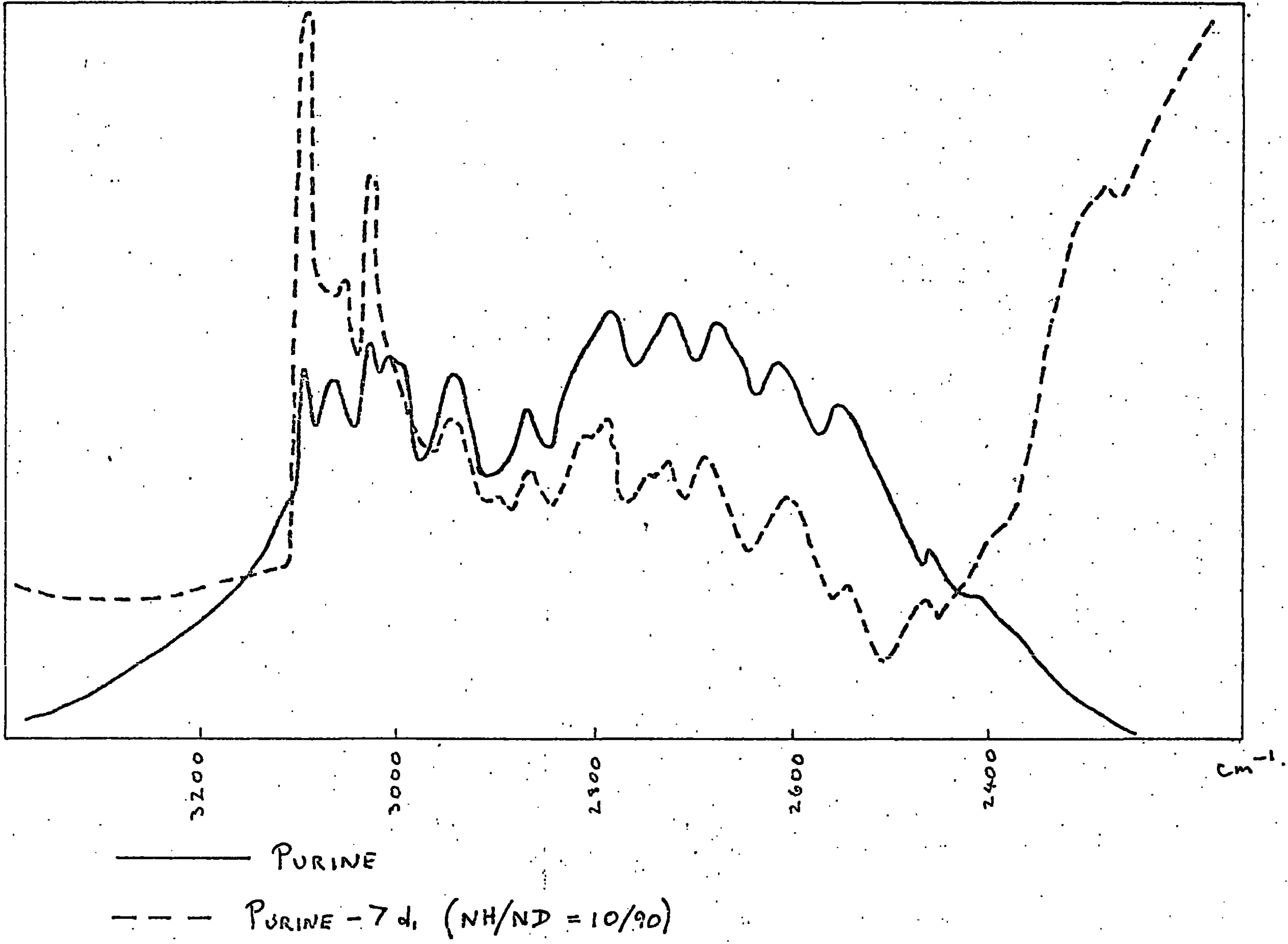
$H_4Fe(CN)_6$	$H_4Ru(CN)_6$
3200 sh.w	3200 sh.w

3040 v.s	3050 v.s
2770 ms.	2790 ms.
2630 sh.	2650 sh.
2570 s.	2580 s.
2370 ms.	2370 ms.

The bands at 3040 cm^{-1} and 2570 cm^{-1} are assigned as N—H fundamentals, and it is interesting to note that both groups are in agreement as to the position of these two main band centres. In figures 42 and 43 the position of the band centres is marked for the values given by Ginsberg. The resolution of the broad structure was made by fitting Gaussian curves into the band envelope, and it is presumed that the fitting was first made to the two main peaks, but even so there must be some considerable degree of arbitrariness in the fitting of the Gaussian components to such a broad envelope. One must therefore view with some uncertainty both the number and position of the resolved components of Ginsberg and Koubek. The 'extra' bands arising from this resolution are assigned as combination tones of N—H bending modes in Fermi resonance with the fundamentals. The authors conclude that all of the hydrogen bonds are of the asymmetrical N—H···N type, and state: "An important observation is that no absorption maxima are found between 3200 cm^{-1} and 3600 cm^{-1}, where nonhydrogen-bonded N—H would be expected to absorb. This indicates that all of the protons in the $H_4Fe(CN)_6$ acids are engaged in hydrogen-bonding". Whilst several plausible three-dimensional networks of $H_4M(CN)_6$ linked together by hydrogen bonds could be imagined by the authors, no specific structure being mentioned, they did not consider it possible to decide upon a definite structure for the acids on the information available.

Whilst there is some uncertainty as to the actual structure of the broad band envelope it is interesting to note its similarity to other N—H···N spectra, notably those of imidazole and purine which have been presented and discussed by Novak and Lautie (172). Figure 44 is a reproduction from this paper of the spectrum of purine in the region from 2,200 cm^{-1} to 3400 cm^{-1}. Of this the authors state: "The ν(N—H) absorption band of purine has its centre of gravity near 2,700 cm^{-1} and a half-width of 600 cm^{-1}. There are ten relatively well defined and strong sub-bands which disappear in the spectrum of ND substituted purine (purine-7-d_1) and are thus caused by hydrogeh-bonded NH groups. The C—H stretching fundamentals, between 3,100 and 3,000 cm^{-1}, are much narrower and can easily be distinguished from the sub-bands by deuteration". In Figure 45 we reproduce our own recorded spectra of imidazole and purine, together

FIGURE 44.



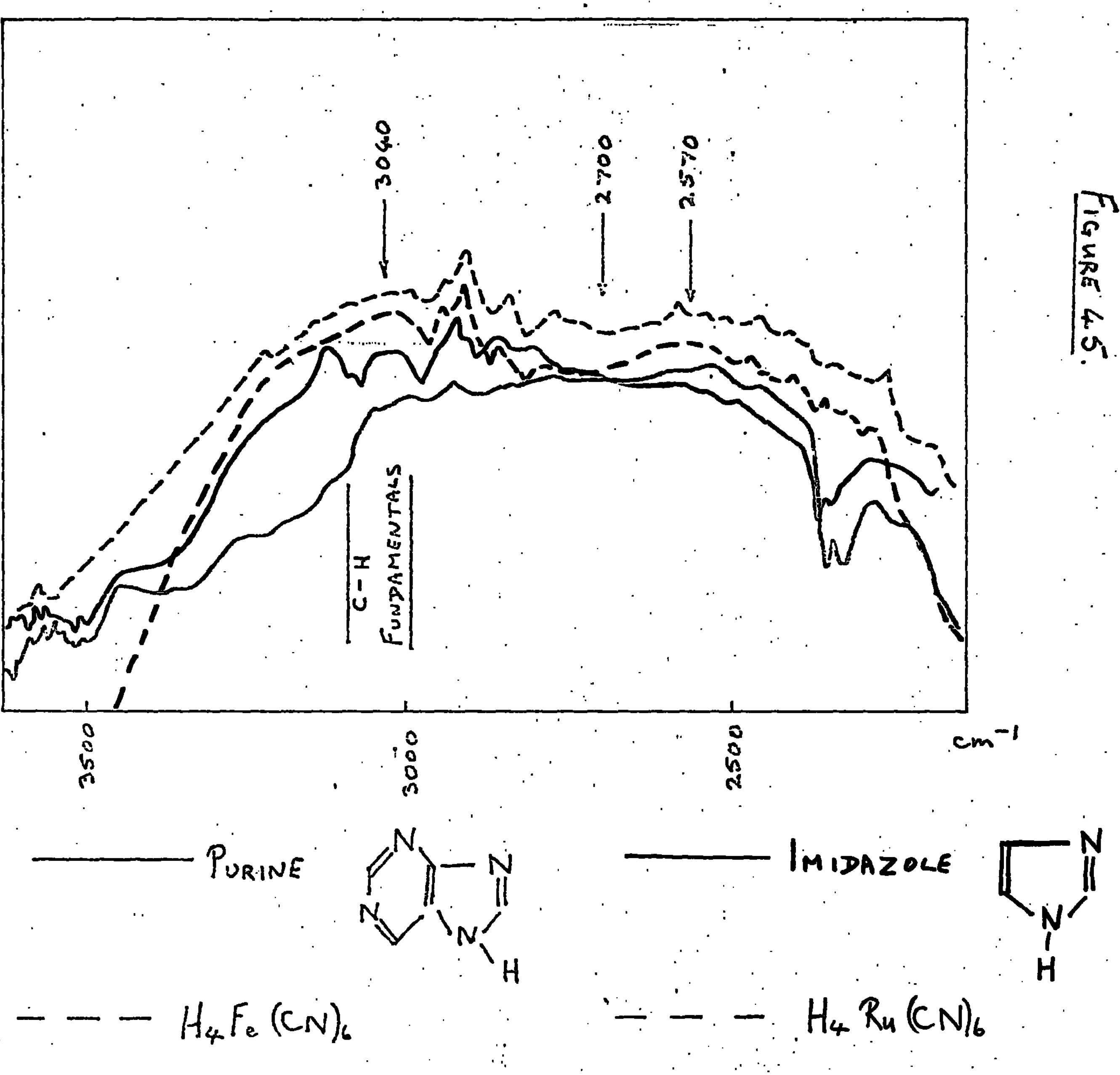

3040
2700
2570
C-H
FUNDAMENTALS
3500
3000
2500
cm⁻¹
PURINE
IMIDAZOLE
H₄Fe(CN)₆
H₄Ru(CN)₆
N
H

FIGURE 4.5.

with those of $H_4Fe(CN)_6$ and $H_4Ru(CN)_6$, and the similarity of the band envelopes is apparent, at least in the region below that assigned to the C—H fundamentals. Novak and Lautie conclude their study of the spectrum over this region with the statement: "The chief sub-maxima belong to an isolated N—H···N system. The assumption that the sub-bands are caused by the overtones and combinations of internal vibrations in Fermi resonance with the N—H stretching mode, as found for imidazole (173), seems to be the most satisfactory". The hydrogen-bond frequencies do not seem to be the decisive factor in determining the sub-band structure which contributes to the broadening of the band in this case. Such a factor as this will certainly complicate attempts to assign N—H frequencies in this region to representations of the site group, as is done by Ginsberg and Koubek. The parallel drawn between the spectra of ferrocyanic acid and purine is extended by the observation that deuteration simplifies the purine spectrum over this region, the sub-band structure disappearing, a feature which is also observed in the case of ferrocyanic acid.

The centre of gravity of the broad band in purine is located at approximately 2700 cm^{-1}, and this differs from the position of the central band of ferrocyanic acid at 2570 cm^{-1}. If Fermi resonance is used to account for the band structure such a difference is not surprising, since the position of the band centre would depend upon the degree of coupling between the frequencies involved. One can also note that the frequency value assigned to a hydrogen-bonding band is sensitive to the value of the bond lengths in the system N—H···N, (174), and it is certainly probable that these will differ between purine and ferrocyanic acid.

Ginsberg and Koubek reject the possibility of the existence of 'free' N—H frequencies on the grounds that no absorption maxima are found between 3200 cm^{-1} and 3600 cm^{-1}. They cite the N—H stretching frequencies for HNC in an argon matrix (3582 cm^{-1}) and for HNCO in the gas phase (3531 cm^{-1}) in support of this interpretation. The only recorded example for the free N—H stretching frequency in ligand HNC$\rightarrow$ is located at 3300 cm^{-1}, being that recorded for the series of compounds HNC.M(CO)$_5$ (M = Cr, Mo, or W) prepared by King (175), and this value seems a more valid basis for comparison than those quoted by Ginsberg and Koubek. The results reported by King are:

	ν(N—H)	ν(C≡N)
HNC.Cr(CO)$_5$	3360 cm^{-1}	2115 cm^{-1}
HNC.Mo(CO)$_5$	3350 "	d
HNC.W(CO)$_5$	3300 "	2130 "

The N—H stretching frequency is dependent on the nature of the metal atom in the complex. Beck and Smedal consider the free N—H frequency in ferrocyanic acid to be the absorption at 3050 cm^{-1}. In view of the values reported by King this assignment seems unlikely, although this argument does not necessarily invalidate the existence of free N—H frequencies since the band envelope in ferrocyanic acid extends beyond 3200 cm^{-1}. It is conceivable that the adoption of a different set of Gaussian components for this envelope could present the absorption at 3200 cm^{-1}, as a more intense band with the absorption at 3050 cm^{-1} appearing as a strong band because it is superimposed. The frequency shift from the values of King would be much smaller, and in a range more readily accounted for. Already we have seen a variation of 60 cm^{-1} in the compounds of King for different central atoms, and N—H frequencies are known to be sensitive to both electronic and steric effects (170). Chatt has reported on changes in N—H frequencies for ammine complexes with different attached ligands as the result of transmission of electronic effects through the central atom (176), and we have noted earlier that the electron distribution for the central atom is sensitive to changes in the ligand. Carbonyl groups are known to have strong effects on isonitrile ligands in the same co-ordination sphere (168), and the value of the N—H frequency in King's compounds must be considered subject to such effects transmitted through the C≡N group. We draw the conclusion that the value to be assigned to a possible free N—H frequency in such compounds as the $H_4M(CN)_6$ acids is very uncertain, and the question as to whether these exist are still very much open.

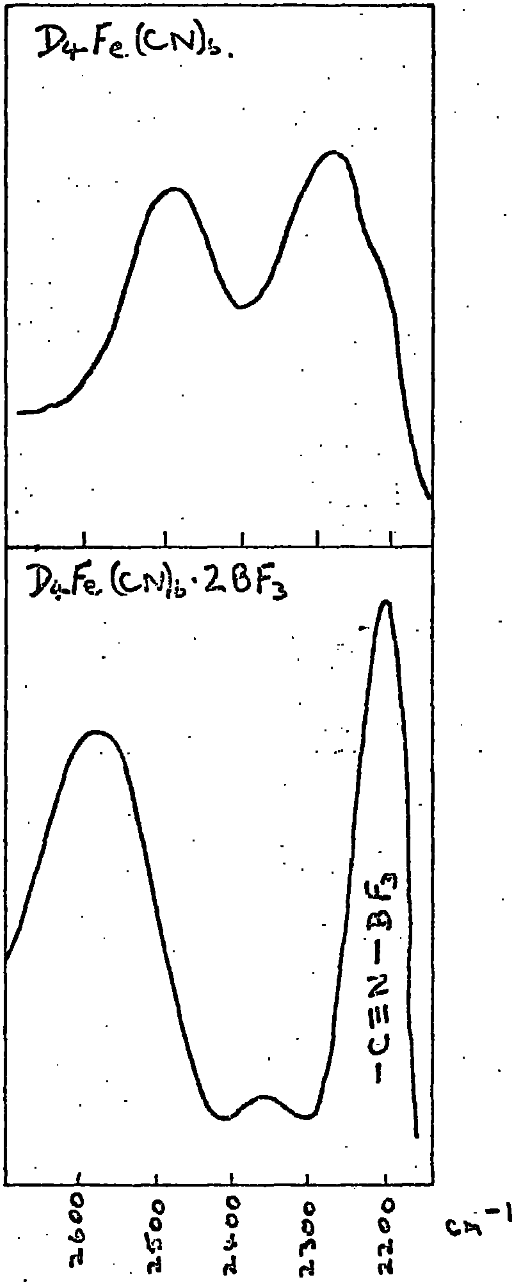
In Figure 46 we present the spectra observed for $D_4Fe(CN)_6$ and $D_4Fe(CN)_6.2BF_3$. For $D_4Fe(CN)_6$ there are two prominent absorptions, and the frequency values for these compare favourably with those of other observers:

Jones (44)	Ginsberg (46)	Beck (45)	This work
2460 cm^{-1}	2460 cm^{-1}	2490 cm^{-1}	2480 cm^{-1}
2270 cm^{-1}	2280 cm^{-1}	2306 cm^{-1}	2270 cm^{-1}

The bis-trifluoroboron adduct shows a single peak centred on 2580 cm^{-1}, accompanied by a very weak absorption at 2350 cm^{-1}. All measurements were obtained at higher resolution than that indicated in the illustration.

In the proton acids $H_4Fe(CN)_6$ the broad absorption is replaced in the bis-trifluoroboron adducts by a single band of medium intensity centred on 3300 cm^{-1}. It will be recalled that this is the value assigned by King (175) to the free N—H stretching frequency of ligand HNC→ in the compounds $HNC.M(CO)_5$. Accordingly we assign the band at 3300 cm^{-1} to the N—H stretching frequency for

FIGURE 46



$D_4Fe(CN)_6$.
$D_4Fe(CN)_6 \cdot 2BF_3$
$-C \equiv N - BF_3$
2600
2500
2400
2300
2200
cm^{-1}

the compounds $H_4M(CN)_6.2BF_3$, and the single band at 2580 cm^{-1} in $D_4Fe(CN)_6.2BF_3$ to the free N—D frequency The deuteration shift for ferrocyanic acid expressed as the ratio ν_H/ν_D has the value 1.28 as against the theoretical harmonic oscillator value in the range 1.37 to 1.41. It is interesting to note that when this value of the deuteration shift is applied to the upper band of $D_4Fe(CN)_6$ (i.e. 2480 cm^{-1}) one predicts the corresponding absorption for the proton acid to be approximately 3200 cm^{-1} (see discussion on page 194), and this would fit one of the bands resolved by Ginsberg.

It is apparent that the broad asborption band in $H_4M(CN)_6$ attributed to N—H···N modes disappear on formation of the bis-trifluoroboron adduct, and is replaced by a single absorption band centred on 3300 cm^{-1}. The result is interpreted as a break-up of the hydrogen bonding resulting in the appearance of free N—H bonds. It will be recalled (Chapter 3) that an observable increase in volume occurs on exposing the $H_4M(CN)_6$ acids to gaseous boron trifluoride, and this observation is also consistent with the removal of hydrogen bonding. For $D_4Fe(CN)_6$ the interpretation is the same with adduct formation resulting in free N—D vibrations.

4.5 $H_3Fe(CN)_6$ and $H_3Co(CN)_6$

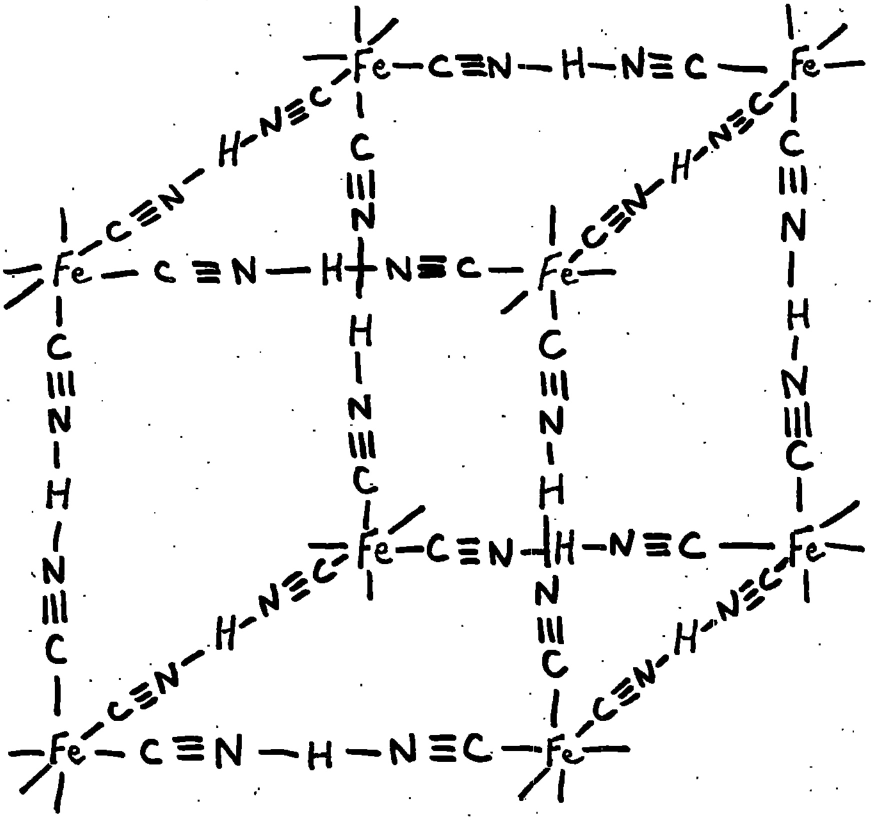
The spectra of ferricyanic acid and cobalticyanic acid have been studied by Evans (158) and by Beck (45). Both groups are agreed that the structures are the same involving all hydrogen atoms in symmetrical hydrogen-bonding of linked octahedra. We have prepared these compounds and recorded their infra-red spectra (Chapter 3). The observations compare with those recorded by Evans and Beck, e.g.

$H_3Fe(CN)_6$	Evans	Beck	This work	Assignment
	-	2163	2176	$\nu(C\equiv N)$
	-	580	585	$\delta(Fe-C\equiv N)$
	-	529	525	?
	-	426	430	$\nu(Fe-C)$
$H_3Co(CN)_6$				
	2202	2218	2198	$\nu(C\equiv N)$
	550	420	-	$\nu(Co-C)$

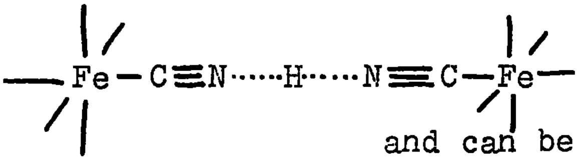
The assignments are those due to Beck (45). We found the absorptions broad and weak in the region 375 to 650 cm^{-1}, and the centres recorded above are only approximate.

The suggested structure of linked octahedra gives an open lattice (Figure 47). Evans, Jones and Wilkinson (158) suggest that the large open structure explains

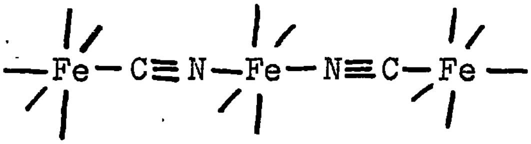
FIGURE 47



the ready formation and decomposition of the solid solutions with ether, and addition compounds with alcohol, acetone, etc., the organic molecules being located in the wide channels formed. The atom sequence in the proposed structure is:



and can be compared with the structure proposed for Berlin Green (Ferric ferricyanide) and the related compound Prussian Blue (potassium ferric ferrocyanide) in which the atom sequence is;



the distance between successive iron atoms being 5.1 Å (177). The proposed structure of ferricyanic acid differs in that the sequence N—Fe—N is replaced by N···H···N. We would thus expect the distance between successive iron atoms in ferricyanic acid to be greater than that in Berlin Green by a factor of approximately two.

The compounds $H_3Fe(CN)_6$ and Prussian Blue were examined by the X-ray powder method. The d-spacings obtained from the X-ray powder patterns were as follows:

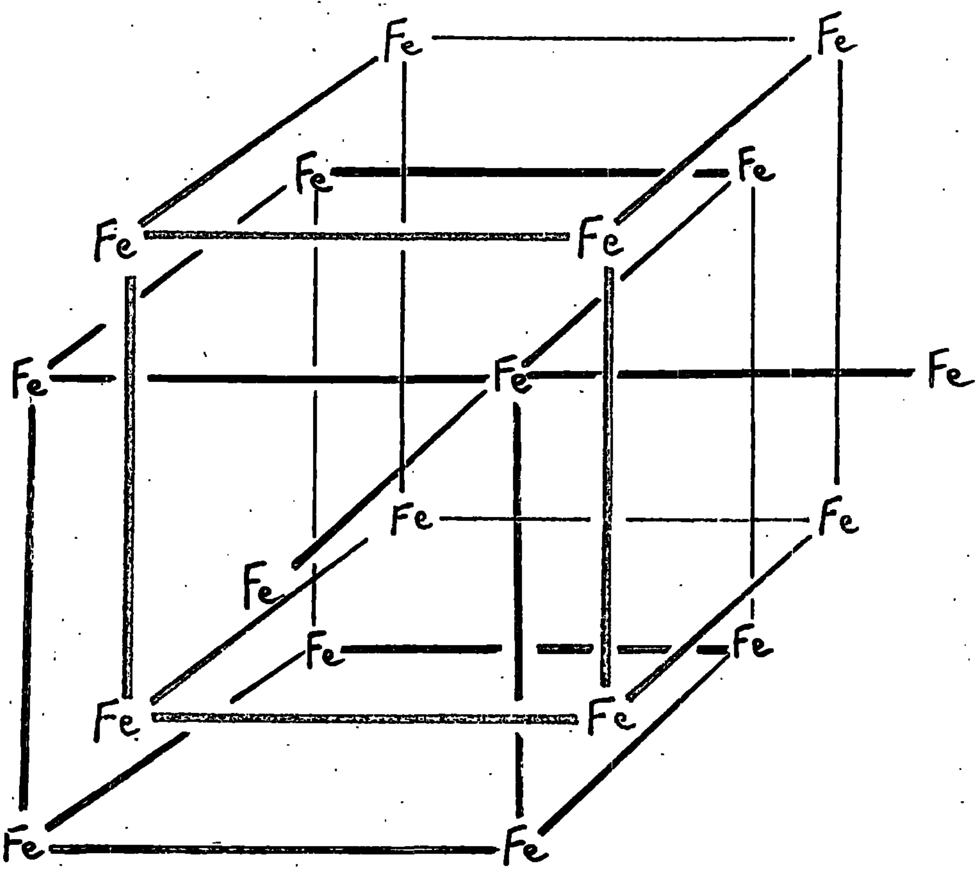
Plane	$H_3Fe(CN)_6$	$H_3Co(CN)_6$	Prussian Blue
200	5.6 Å	5.6 Å	5.1 Å
220	4.05 Å	4.0 Å	3.6 Å
400	2.82 Å	2.8 Å	2.55 Å

The X-ray powder patterns for $H_3Fe(CN)_6$ and $H_3Co(CN)_6$ were similar to Prussian Blue in that they showed the same sequence of lines with a small displacement, suggesting similar structures. A much larger interplanar spacing for the acids would be expected on the structure proposed by Evans, Jones and Wilkinson.

The small difference observed in the interplanar spacings might be reconciled by considering the structure of $H_3Fe(CN)_6$ to be formed from interpenetrating structures of the type proposed by Evans, Jones and Wilkinson, such as that illustrated in Figure 48. Such a system would satisfy the interplanar spacing requirements, and retain the symmetrical $N \cdots H \cdots N$ bonds suggested by the infra-red examination (158, 45). The interpenetrating system would still have a relatively large cage structure to admit organic molecules, as suggested by Evans et al.

When attempts were made to prepare Boron trifluoride adducts of $H_3Fe(CN)_6$ and $H_3Co(CN)_6$ no reaction was observed even after standing under an excess pressure of boron trifluoride for periods up to 48 hours.

FIGURE 4.8



In all of the examples we have studied reaction of C≡N and boron halides has occurred immediately or not at all. In the preparation of boron halide adducts of complex cyanides reported by Shriver (81), long exposures of the reactants has been the general rule, but in the one example where we have repeated his work, i.e. potassium ferrocyanide, we have found that if the material is in finely divided form reaction is immediate. That no reaction occurs when $H_3Fe(CN)_6$ and $H_3Co(CN)_6$ are exposed to boron trifluoride cannot be attributed to restricted access to the cage structure, for what ever the structure may be the cage can admit larger organic molecules. Nor can it be attributed to the higher oxidation state of the central metal atom reducing the electron availability on C≡N, for adducts have been reported by Shriver and Posner (82) with the compounds $[Fe(phen)_2(CN)_2][PF_6]$, and $Na_2Fe(CN)_5NO$ in which the iron atom is in the +3 oxidation state. The restriction must be that the C≡N groups are not available for attack by boron trifluoride.

Recalling that $H_4Fe(CN)_6$ forms a BF_3 adduct, but no adduct with BCl_3, and that hydrogen bonding in the parent compound is unsymmetrical N—H···N as against symmetrical N···H···N in $H_3Fe(CN)_6$, suggests that reaction has to do with break-up of hydrogen bonds.

A possible interpretation is that when $H_4Fe(CN)_6$ is exposed to excess boron trifluoride, the interaction with the fluorine atoms is such as to weaken the hydrogen bond to nitrogen allowing a boron trifluoride molecule to compete for the nitrogen electrons. Greenwood has suggested that formation of adducts may break up hydrogen bonds to oxygen by reducing the availability of electron pairs for hydrogen-bond formation with consequent change in the physical properties of materials (178). Since chlorine atoms form only very weak hydrogen bonds this mechanism would not be available in the case of boron trichloride, and no adduct formation can occur. The difference in behaviour of boron trifluoride and boron trichloride cannot be attributed to the reorganisation energy required to transform the BX_3 molecule from its normal ground state into a condition where it can accept a pair of electrons from the nitrogen atom. For this to occur there must be at least 18 Kcals more energy available to BF_3 than to BCl_3 (179) which could only be expected to arise mainly from the interaction $F\cdots H—N$. From the data of Coulson the energy available from such an interaction is only of the order of 5 Kcals (180). On this basis the lack of reaction of boron trifluoride with ferricyanic acid can be attributed to the greater stability of the symmetrical hydrogen bonding in this compound as against the unsymmetrical hydrogen bonding in $H_4M(CN)_6$.

In Chapter 3 we reported on reactions of ferrocyanic acid with mixtures of boron trichloride and acetyl chloride, thionyl chloride and sulphur dioxide. When the single compounds are left with ferrocyanic acid no reaction is observed, but when mixed with boron trichloride immediate reaction occurs. Qualitative analysis shows that in all cases boron trichloride is contained in the product, and that the second component is also present. In the case of the mixture with acetyl chloride a preliminary analysis showed the presence of two acetyl groups and two boron atoms per iron atom in the compound, but no confirmatory studies have yet been made. Figures 49 and 50 illustrate the infra-red spectra of these compounds, and their general similarity is apparent. Adduct formation with BCl_3 seems to be indicated by the absorption pattern between 700 cm^{-1} and 1000 cm^{-1}, and by the $C\equiv N$ peak which lies at 2180 cm^{-1} in each case. We explain the adduct formation by the solution of ferrocyanic acid in the acetyl chloride, thionyl chloride, or sulphur dioxide resulting in break up of weakening of the hydrogen bonding, which then makes available the electron pairs of the nitrogen for donation to boron trichloride.

FIGURE 49

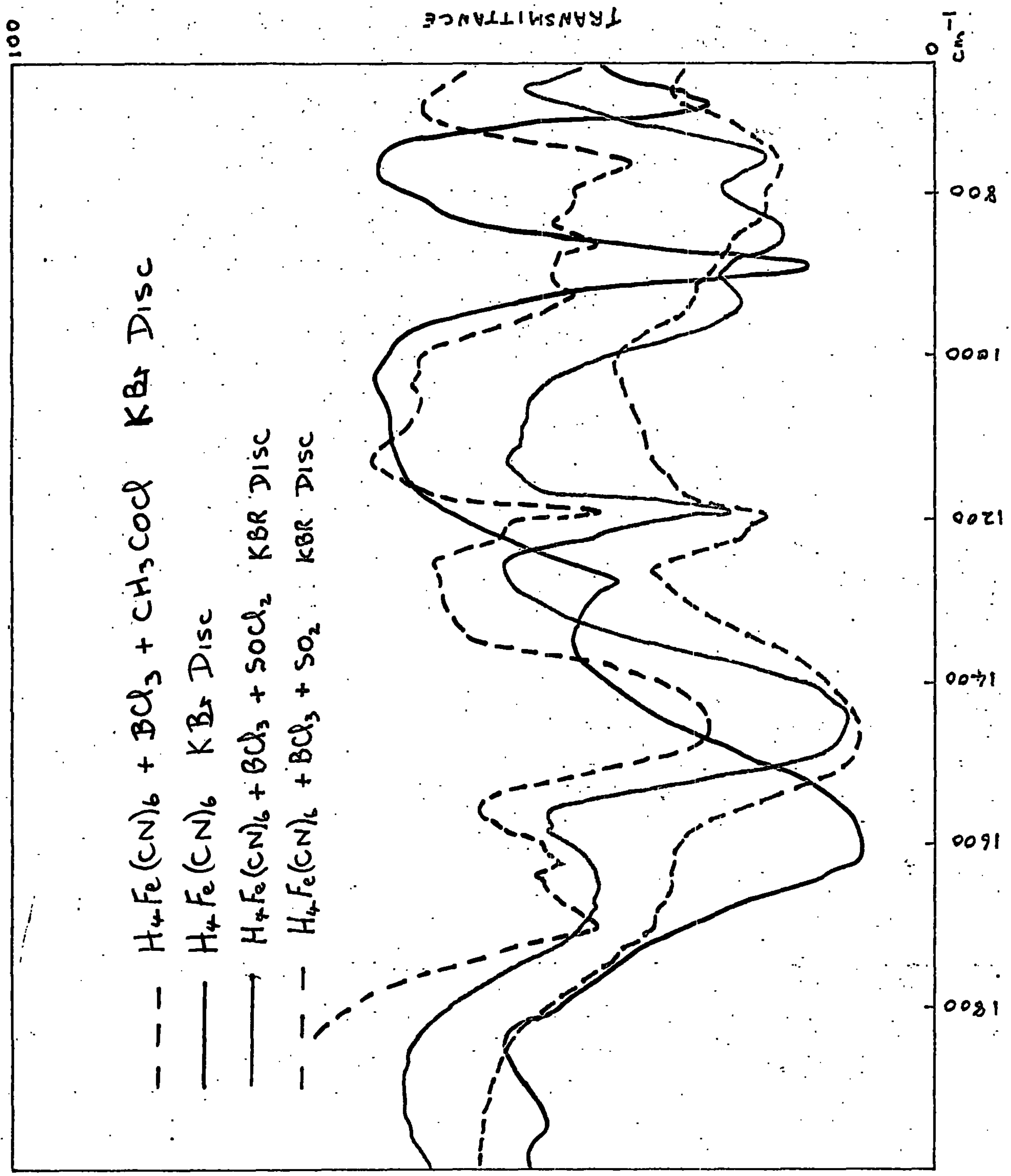
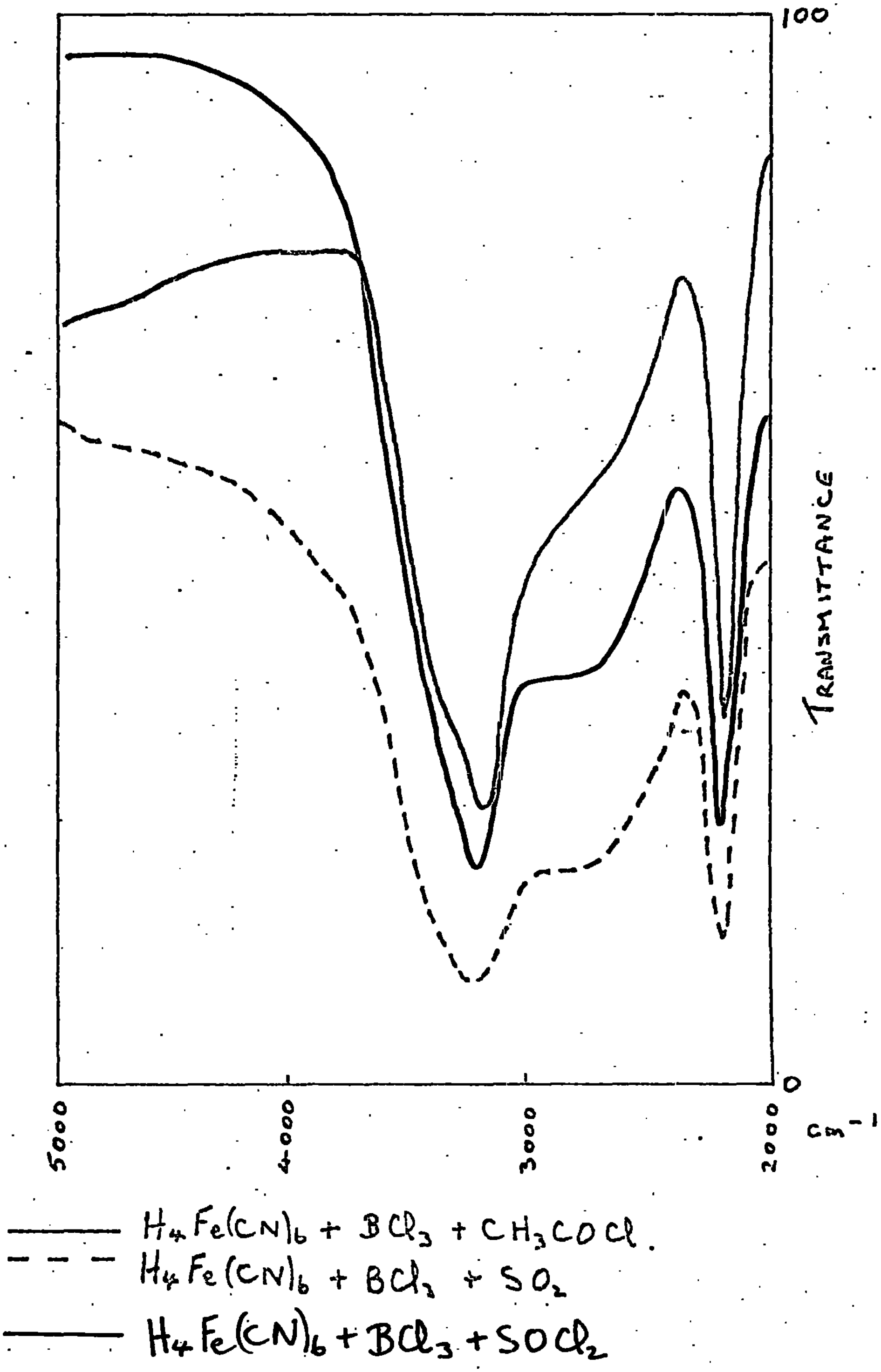

TRANSMITTANCE
100
0
cm⁻¹
800
1000
1200
1400
1600
1800
H4Fe(CN)6 + BCl3 + CH3COCl KBr Disc
H4Fe(CN)6 KBr Disc
H4Fe(CN)6 + BCl3 + SOCl2 KBR Disc
H4Fe(CN)6 + BCl3 + SO2 KBR Disc

FIGURE 50.

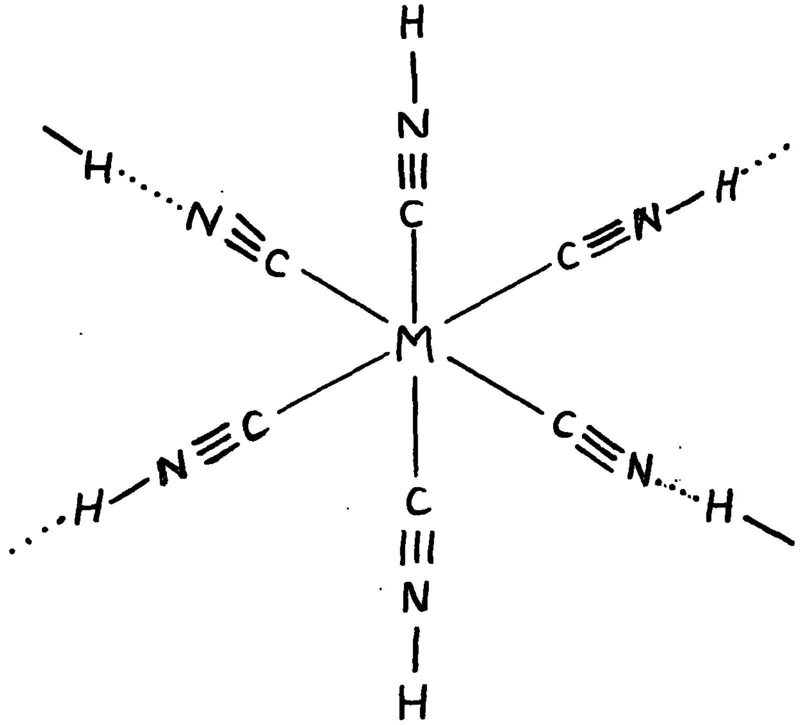


100
0
TRANSMITTANCE
5000
4000
3000
2000
cm⁻¹
$H_4Fe(CN)_6 + BCl_3 + CH_3COCl$.
$H_4Fe(CN)_6 + BCl_3 + SO_2$
$H_4Fe(CN)_6 + BCl_3 + SOCl_2$

4.6 Summary

The formation of a bis-trifluoroboron adduct as the limit of reaction of boron trifluoride with the acids $H_4M(CN)_6$ indicates that two of the $C\equiv N$ groups are different from the remaining four in these molecules. We may compare the formation of $K_4Fe(CN)_6.6BF_3$ which demonstrates the equivalence of the $C\equiv N$ groups in potassium ferrocyanide, and the formation of bis-boron trifluoride adducts with trans-dicyano tetrakis-alkyl isocyano iron (II) in which the non-equivalence of the $C\equiv N$ groups is an accepted feature of their structure. However both of the trans-dicyano tetrakis-alkylisocyano iron (II) molecules give bis-trichloroboron adducts readily by the direct action of boron trichloride, whereas the corresponding reaction with $H_4M(CN)_6$ does not yield a bis-trichloroboron adduct even under more rigorous conditions. These results clearly indicate that the $C\equiv N$ groups in the $H_4M(CN)_6$ acids are in some way restricted, and we have suggested that this restriction is due to the hydrogen bonding. Where the hydrogen bonding can be weakened by solution in non-aqueous solvents, even if the solution may only be partial, adduct formation with BCl_3 can occur. The lack of reaction of boron trifluoride with both ferricyanic and cobalticyanic acids, where symmetrical hydrogen bonding is an accepted feature of the structure, provides support for the view based on infra-red absorption studies that the hydrogen-bonding in $H_4M(CN)_6$ is of the asymmetric type N—H····N. We further suggest that the ability of boron trifluoride to react with $H_4M(CN)_6$ is due to competition between N—H····N and N--H····F resulting in the nitrogen being free to donate electrons to boron trifluoride.

We believe that this study of the adducts of $H_4M(CN)_6$ is consistent with the only firm structure proposed for the acids (45), this structure being:



Chapter 5

AMIDINE AND RELATED COMPLEXES

This section is concerned with the attempted preparation of amidines and imino-ethers from the boron halide adducts of nitriles, and the formation of some Lewis acid adducts of amidines and imino-ethers.

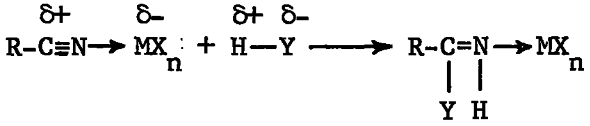
Nitrile adducts of the type R-C≡N → A, where R is an organic group, either alkyl or aryl, and A is a Lewis acid, usually a metal halide MX_n, have been described in some detail in a review by Walton (181).

With nitrile adducts two types of addition reaction seem to be possible:

(a) The charge distribution within the adduct may be represented as follows:

$$R\text{-}\overset{\delta+}{C}\equiv N \longrightarrow \overset{\delta-}{MX_n}$$

This leaves the nitrile carbon open to attack by an electronegative group



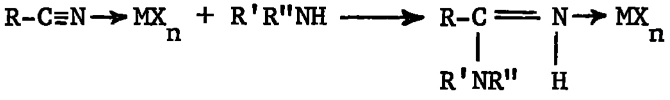
$$R\text{-}\overset{\delta+}{C}\equiv N \rightarrow \overset{\delta-}{MX_n} + \overset{\delta+}{H}\text{—}\overset{\delta-}{Y} \longrightarrow R\text{-}\underset{\underset{Y}{|}}{C}=\underset{\underset{H}{|}}{N} \rightarrow MX_n$$

where Y is the electronegative group.

(b) The formation of a nitrilium salt with an organic halide is an alternative possibility (182)

$$R\text{-}C\equiv N\rightarrow MX_n + R'X' \longrightarrow [R\text{-}C\equiv N\text{-}R']^+[MX_nX']^-$$

In reaction (a) the addition of a primary or secondary amine to the adduct would result in the formation of a complex between the Lewis acid and an amidine.



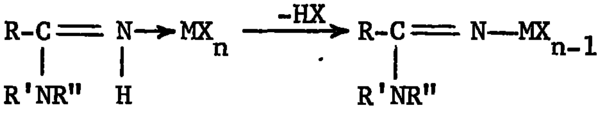
$$R\text{-}C\equiv N\rightarrow MX_n + R'R''NH \longrightarrow \underset{\substack{|\\ R'NR''}}{R\text{-}C} = \underset{\substack{|\\ H}}{N}\rightarrow MX_n$$

Amidine adduct

where R' and R" are organic groups (alkyl or aryl) or hydrogen.

Several secondary reactions are ~~are~~ now possible

(i) cleavage of HX



$$\underset{\substack{|\\ R'NR''}}{R\text{-}C} = \underset{\substack{|\\ H}}{N}\rightarrow MX_n \xrightarrow{-HX} \underset{\substack{|\\ R'NR''}}{R\text{-}C} = N\text{—}MX_{n-1}$$

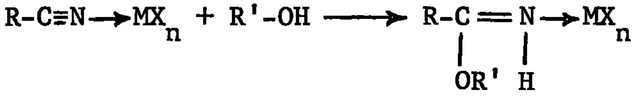
(ii) ligand displacement

$$R\text{-}C\equiv N\rightarrow MX_n + R'R''NH \longrightarrow R'R''NH\rightarrow MX_n + RCN$$

The adduct $B_{10}H_{12}\cdot 2CH_3CN$ has been shown to undergo both addition and ligand displacement. It forms an amidine with primary or secondary amines (183) or hydrazine (184) and the CH_3CN is displaced by both Et_2NCN and $(C_6H_5)_3P$ (185).

The addition reaction was studied in some detail by Oxley (186) who prepared many amidines by refluxing 1:1:1 molar ratios of nitrile, base and Lewis acid. No amidines were prepared in this manner from boron halide adducts, however.

In a similar reaction to amidine formation, the addition of an alcohol to a nitrile adduct results in the formation of an imino-ether adduct



$$\mathrm{R{-}C{\equiv}N \rightarrow MX_n + R'{-}OH \longrightarrow \underset{OR'}{R{-}C} = \underset{H}{N} \rightarrow MX_n}$$

As with amine addition, cleavage of HX and ligand displacement can occur although a further reaction is possible in this case

e.g. $$3ROH + BCl_3 \longrightarrow B(OR)_3 + 3HCl$$

5.1 Reactions between amines and boron trichloride - nitrile adducts

The nitrile and boron trichloride were mixed in equi-molar quantities in methylene dichloride in a Schlenk tube (187) and then 1 mole of amine was added.

The results are summarised in Table 24 and show that ligand displacement is the predominant reaction.

5.2 Reactions between alcohols and $MeCN,BCl_3$

The reaction was carried out as described in 5.1 except that the amine was replaced by an alcohol.

TABLE 24

The addition of various amines to nitrile adducts

Nitrile adduct	Amine	Product
$PhCN,BCl_3$	NH_3	benzamidine, BCl_3 (trace) mostly NH_4Cl
$PhCN,BCl_3$	Et_2NH	Et_2NH,BCl_3
$MeCN,BCl_3$	Et_2NH	Et_2NH,BCl_3
"	Ph_2NH	Ph_2NH,BCl_3
"	PhEtNH	$PhEtNH,BCl_3$
"	$Pr^i{}_2NH$	$Pr^i{}_2NH,BCl_3$
"	$Bu^n{}_2NH$	$Bu^n{}_2NH,BCl_3$
"	$Bu^i{}_2NH$	$Bu^i{}_2NH,BCl_3$
"	$(PhCH_2)_2NH$	$(PhCH_2)_2NH,BCl_3$
"	piperidine	$C_5H_{10}NH,BCl_3$

The reaction was studied with methanol, ethanol, propanol, butanol, tertiary butanol and amyl alcohol. In all cases there was a violent reaction with evolution of hydrogen chloride and deposition of the appropriate boron alkoxide.

5.3 The addition of Lewis acids to an amidine.

An available amidine 1,1,3,3-tetramethylguanidine, $(Me_2N)_2C{:}NH$, (referred to below as "HG"), was studied. The reactions were carried out in a Schlenk tube and melting points measured in a sealed tube.

The results are summarised in Table 25. The nature of the various products is as follows.

HG,BCl_3 - a viscous grey liquid at room temperature and a white solid at -80°C.

$GBCl_2$ - an extremely hygroscopic pale-yellow solid.

HG,HCl - a white powder

HG,HCl,BCl_3 - a white powder.

On passing dry hydrogen chloride throughga solution of 1,1,3,3-tetramethylguanidine in acetone, the hydrochloride was deposited. This reacted with BCl_3 forming an adduct of melting point 208-212°C.

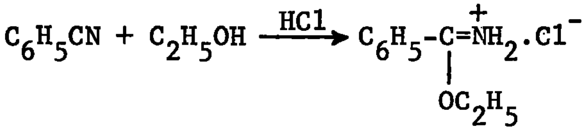
TABLE 25

Reaction of 1,1,3,3-tetramethylguanidine (HG) with boron trichloride

Mole Ratio HG:BCl_3	Temperature and solvent	Product	Melting Point
1:1	25°C CH_2Cl_2	HG,BCl_3	-
1:1	-80°C CH_2Cl_2	HG,BCl_3	-
1:1	-20°C No solvent	$GBCl_2$	118-129°C
1:1	25°C petroleum spirit	$GBCl_2$ + HG,HCl	120°C 204-6°C
1:2	25°C CH_2Cl_2	HG,HCl,BCl_3 + HG,BCl_3	215-20°C -
1:3	25°C CH_2Cl_3	HG,HCl,BCl_3 + HG,BCl_3	210-15°C -
3:1	25°C petroleum spirit	$GBCl_2$ + HG,HCl	130°C 205°C

5.4 The addition of Lewis acids to an imino-ether

N-ethylbenzimino-ether hydrochloride was prepared by refluxing a mixture of C_6H_5CN and ethanol in dry ether, while passing dry hydrogen chloride through the solution.



$$C_6H_5CN + C_2H_5OH \xrightarrow{HCl} C_6H_5-\underset{OC_2H_5}{\underset{|}{C}}=\overset{+}{N}H_2.Cl^-$$

N-ethylbenzimino-ether was deposited as a colourless oil on treating the hydrochloride with a slight excess of aqueous potassium carbonate.

The result of treating the imino-ether, and its hydrochloride, with some Lewis acids is shown in Table 26.

TABLE 26

Reaction of N-ethylbenzimino-ether (B) and its hydrochloride (B,HCl) with some Lewis acids

Reactant	Lewis acid	Product	Melting Point
B	BCl_3	$B \rightarrow BCl_3$	80-94°C
B	BF_3	$B \rightarrow BF_3$	126-7°C
B	$AlCl_3$	B,HCl	117-18°C
B,HCl	BCl_3	$B,HCl \rightarrow BCl_3$	102-4°C
B,HCl	BF_3	$B \rightarrow BF_3$	120-2°C
B,HCl	$AlCl_3$	$B \rightarrow AlCl_3$	>200°C

REFERENCES

(1) R.A. Penneman, E. Staritzky and L.H. Jones, J. Amer. Chem. Soc., 1956, 78, 62.

(2) W.M. Cumming and D.G. Brown, J. Soc. Chem. Ind. Trans., 1925, 44, 110, and 1928, 47, 84. *

(3) H. Euler, Chem. Ber., 1903, 36, 1854.

(4) H.E. Williams, 'Cyanogen Compounds', E. Arnold and Co., London, 1948.

(5) W.R. Bucknall and W. Wardlow, J. Chem. Soc., 1927, 2981.

(6) O. Olsson, Chem. Ber., 1914, 47, 917.

(7) N.V. Sidgwick, 'Chemical Elements and their Compounds', Oxford University Press, Oxford, 1950.

(8) M.H. Ford-Smith, 'The Chemistry of Complex Cyanides', H.M.S.O., London, 1964.

(9) Roseheim; Garfunkel and Kohn, Z.anorg. Chem., 1909, 63, 166.

(10) F. Hein and H. Lilie, Z. anorg. Chem., 1952, 270, 45.

(11) O. Olsson, Z. anorg. Chem., 1914, 88, 49.

(12) D. Jones, Ph.D. Thesis, Imperial College, London, 1963.

(13) J. Brigando, Bull. Soc. chim. France, 1957, 24, 503.

(14) H. Remy, 'Treatise on Inorganic Chemistry', Elsevier, London, 1956.

(15) R. Colton, R.D. Peacock and G. Wilkinson, Nature, 1958, 182, 393.

(16) Lock, Ph.D. Thesis, London, 1963.

(17) Kaiser, Ann. Suppl., 1864, 3, 171. *

(18) J. Brigando, Compt. rend., 1939, 208, 197.

(19) R. Walden, Z. phys. Chem., 1888, 2, 49.

(20) Liebig, Ann. pharm. franc., 87, 1271.

(21) G. Brauer, 'Handbuch der Praparativen Anorganischen Chemie', Enke, Stuttgart, 1954.

(22) V.L. Bogatyrev and A.I. Vulikh, Izv. Sibisk. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk. 1963, 3, 70. *

(23) B.V. Nekrassov and G.V. Zotov, J. Appl. Chem. (U.S.S.R.), 1941, 14,264.

(24) J. Jordan and G.T. Ewing, Inorg. Chem., 1962, 1, 587.

(25) Claus, Jahresb., 1855, 144. *

(26) F. Krauss and G. Schrader, Z. anorg. Chem., 1927, 165, 70.

(27) A. Martins, Annalen, 1861, 117, 361.

(28) O.K. Dobrolyubskii, J. Appl. Chem. (U.S.S.R.), 1953, 26, 1185.

(29) F. Holzl, T. Meyer and G. Tomshitz, Mh. Chem., 1944, 75, 1. *

(30) F. Holzl, Mh. Chem., 1941, 73, 1. *

(31) A.V. Baeyer and V. Villiger, Chem. Ber., 1901, 34, 2679; 1902,35,1206.

(32) B. Jaselskis and H. Diehl, Analyt. Chim. Acta, 1957, 16, 274.

(33) F. Feigl and G.B. Heisig, J. Amer. Chem. Soc., 1951, 73, 5630.

(34) Quadrat, Annalen, 1847, 63, 164.

(35) L.A. Levy, J. Chem. Soc., 1912, 1081.

(36) J. Brigando, Compt. rend., 1942, 214, 908.

(37) M.G. Vladimirov and R.A. Kakovskii, J. Appl. Chem. (U.S.S.R.), 1950, 23, 615.

(38) E. Thilo and F. Wodtcke, Z. anorg. Chem., 1958, 295, 246.

(39) M.M. Raines, Compt. rend. Acad. Sci., U.R.S.S., 1938, 18, 339.*

(40) J. Brigando and P. Job, Compt. rend., 1946, 222, 1297.

(41) I.M. Plaksin, B.N. Laskorin and G.N. Shivrin, Chem. Abst., 1962, 56, 8362.

(42) O.E. Zvyagintsev and O.I. Zakharov-Nartissov, Russ. J. Inorg. Chem., 1960, 5, 59 and 1960, 5, 63; and Chem. Abst., 1962, 56, 1002.

(43) O.E. Zvyagintsev, O.I. Zakharov-Nartissov and O.V. Ochkin, Russ. J. Inorg. Chem., 1961, 6, 1012.

(44) D. Jones and D.F. Evans, Nature, 1963, 199, 277.

(45) W. Beck and H.S. Smedal, Z. Naturforsch., 1965, 20, 109.

(46) A.P. Ginsberg and E. Koubek, Inorg. Chem., 1965, 4, 1186.

(47) W.M. Cumming, J. Chem. Soc., 1925, 1106, and J. Chem. Soc., 1924, 2541.

(48) P. Ray and P.V. Sarkar, J. Chem. Soc., 1921, 390.

(49) G. Roeder, Chem. Ber., 1913, 46, 3724.

(50) W.M. Cumming, J. Chem. Soc., 1922, 1287 and J. Chem. Soc., 1923, 2457.

(51) P. Ray and P.V. Sarkar, J. Chem. Soc., 1922, 298.

(52) Barth, Chem. Ber., 1875, 8, 1484.

(53) E. Fisher, Annalen, 1878, 190, 184.

(54) Wurster and Roser, Chem. Ber., 1879, 12, 1822.

(55) Kielmeyer, Dinglers Polytech. J., 1874, 214, 324* and Chem. Ber., 1879, 12, 2234.

(56) Eisenberg, Annalen, 1880, 205, 265.

(57) J. Mohler, Chem. Ber., 1888, 21, 1015.

(58) S.H.C. Briggs, J. Chem. Soc., 1920, 1026.

(59) P. Ray and P.V. Sarkar, J. Chem. Soc., 1921, 391.

(60) Krauss and Schrader, J. prakt. Chem., 1928, 119, 279.

(61) Brit. P., 1914, 1837.

(62) P. Chretien, Compt. rend., 1905, 141, 37.

(63) A.W. Davidson, J. Amer. Chem. Soc., 1925, 47, 974.

(64) R.H. Pickard and J. Kenyon, J. Chem. Soc., 1906, 265.

(65) R.H. Pickard and J. Kenyon, J. Chem. Soc., 1906, 202.

(66) P. Duprat, Bull. Inst. Pin., 1933, 17, 36. *

(67) F. Holzl, W. Brell and G. Schinko, Mh. Chem., 1933, 62, 349. *

(68) F. Holzl and G. Schinko, Mh. Chem., 1931, 58, 249. *

(69) F. Holzl and A. Sallmann, Mh. Chem., 1931, 58, 29.*

(70) F. Holzl, T. Meier-Mohar and F. Viditz, Mh. Chem., 1929, 53, 237. *

(71) F. Holzl, Z. Elektroch., 1937, 43, 319. *

(72) W.Z. Heldt, J. Org. Chem., 1961, 26, 3226.

(73) W.M. Cumming and D.G. Brown, J. Soc. Chem. Ind. Trans., 1928, 47, 84.*

(74) K.C. Browning, J. Chem. Soc., 1900, 1233.

(75) A. Etard and G. Bermont, Compt. rend., 1884, 99, 972.

(76) P. Chretien and Guinchant, Compt. rend., 1903, 136, 1673.

(77) D. McIntosh, J. Amer. Chem. Soc., 1908, 30, 1097.

(78) P. Chretien and Guinchant, Compt. rend., 1903, 137, 65.

(79) A. Etard and A. Vila, Compt. rend., 1910, 150, 1710.

(80) A. Holzl, Monatsh., 1929, 51, 157.

(81) D.F. Shriver, J. Amer. Chem. Soc., 1962, 84, 4610; 1963, 85, 1405.

(82) D.F. Shriver and J. Posner, J. Amer. Chem. Soc., 1966, 88, 1672.

(83) D.F. Shriver and J.J. Rupp, Abstract of Papers Presented at A.C.S. Meeting (151st) , 1966, H 37.

(84) W.Z. Heldt, J. Org. Chem., 1961, 26, 3226.

(85) P. Porrett, Schw. J., 1819, 26, 229, and Ann. Phil. Thomson, 1818, 12, 217. *

(86) J.J. Berzelius, Schw. J., 1820, 30, 44, and Ann. Chim. Phys., 1820, 15, 241. *

(87) Wehrlin, Bl. Soc. Mulh., 1874, 44, 386. *

(88) R. Porrett, Schw. J., 1816, 17, 258. *

(89) F. Kuhlmann, Compt. rend., 1858, 47, 677, and Dingl. J., 1858, 150, 418. *

(90) E. Muller, G. Wegelin and E. Kellerhof, J. prakt. Chem., 1912, 86, 91.

(91) L. Posselt, Annalen, 1842, 42, 164.

(92) S. Plesniewicz, Chem. Abst., 1935, 29, 6126.

(93) L. Playfair, Phil. Mag., 1850, 36, 200.

(94) R.H. Adie and K.C. Browning, J. Chem. Soc., 1900, 152.

(95) H. Aschoff, Arch. Pharm., 1861, 156, 258.

(96) E. Muller and W. Treadwell, J. prakt. Chem., 1909, 80, 175.

(97) W. Biltz, W.E. Eschweiler and A. Bodensiek, Z. anorg. Chem., 1928, 170, 171.

(98) A. Bodensiek, Dissert., Hanover, 1926.

(99) Robiquet, Ann. Chim. Phys., 1819, 12, 289, and Schw. J., 1820, 28, 113.*

(100) W.A.D. Rudge, Proc. Cambridge Phil. Soc., 1912, 16, 467.

(101) A. Eibner and L. Gerstaker, Chem.-Ztg., 1913, 37, 197.

(102) R.P. Mitra, D.V.S. Jain, A.K. Bannerjee and K.V. Raghavachari, Nature, 1963, 200, 163.

(103) A. Joannis, Ann. Chim. Phys., 1882, 26, 574.*

(104) M. Berthelot, Ann. Chim. Phys., 1875, 5, 464,* and Thermochimie, 1897, 2, 294.

(105) I.M. Kolthoff and W.J. Tomsicek, J. Phys. Chem., 1935, 39, 955.

(106) O.E. Lawford and S.J. Kiehl, J. Phys. Chem., 1941, 45, 300.

(107) H.L. Buff, Annalen, 1854, 91, 253.

(108) M. Freund, Chem. Ber., 1888, 21, 931.

(109) F. Holzl and J. Krakora, Monatsh., 1934, 64, 97.

(110) K.A. Hofmann and K. Ott, Chem. Ber., 1907, 40, 4935.

(111) R. Abegg, Fr. Anerbach and I. Koppel, 'Handbuch der Anorganischen Chemie', 1930, p.B 39.

(112) K.C. Browning, Proc. Chem. Soc., 1900, 16, 172.

(113) G. Deniges, Bull. Soc. chim., 1916, 19, 79.

(114) Reinman and Carius, Annalen, 1860, 113, 39.

(115) A. Etard and G. Bemont, Compt. rend., 1884, 99, 1024.

(116) Hofmann, Annalen, 1907, 352, 54.

(117) C. Rammelsberg, Annalen, 1847, 64, 299.

(118) Brill and Mark, Z. phys. Chem., 1928, 133, 443.

(119) R. Kern, Acta. Cryst., 1964, 17, 1612.

(120) J. Liebig, Annalen, 1853, 87, 127.

(121) King, Inorganic Preparations, p.101.

(122) J. Wilkinson and D. Hall, J. Chromatog., 1963, 10, 239.

(123) R.E. Dodd and P.L. Robinson, 'Experimental Inorganic Chemistry'. A Guide to Laboratory Practice', Elsevier, 1954.

(124) R.J. Gillespie and J.A. Leisten, Quart. Rev., 1954, 8, 1.

(125) I.L. Finar, 'Organic Chemistry', Vol.1, Longmans, London, 1959.

(126) R. Abegg, Fr. Auerbach and I. Koppel, 'Handbuch der Anorganischen Chemie', 1930, p.B 92.

(127) W. Biltz, Z. anorg. Chem., 1925, 148, 145.

(128) M. Giradet, Bull. Soc. chim., 1910, 7, 1028.

(129) Miller, J. Amer. Chem. Soc., 1895, 17, 578.

(130) Fowler, Chem. News, 1900, 82, 245.

(131) F. Ephraim, Z. phys. Chem., 1913, 81, 513.

(132) W. Biltz and Huttig, Z. anorg. Chem., 1920, 109, 89.
W. Biltz, Z. anorg. Chem., 1923, 130, 93.

(133) Jackson and Derby, Bull. Soc. chim., 1900, 24, 863.

(134) F. Ephraim and Linn, Chem. Ber., 1913, 46, 3742.

(135) Rosenheim and V.J. Meyer, Z. anorg. Chem., 1906, 49, 13.

(136) Weinland, Effinger and Beck, Arch. Pharm., 1927, 265, 352.

(137) Reitzenstein, Z. anorg. Chem., 1897, 15, 192.

(138) Reitzenstein, Z. anorg. Chem., 1898, 18, 253.

(139) Pfeiffer, Z. anorg. Chem., 1902, 29, 138.

(140) Costachescu and Spacu, Ann. scient. Univ. Jaissy, 1913, 7, 132.*

(141) Grossman and Hunseler, Z. anorg. Chem., 1905, 46, 361.

(142) Leeds, J. Amer. Chem. Soc., 1881, 3, 134, and J.B., 1882, 500. *

(143) Franzen and O.V. Mayer, Z. anorg. Chem., 1908, 60, 247.

(144) A.J. Hill and I. Rakinowitz, J. Amer. Chem. Soc., 1926, 48, 732.

(145) P. Sykes, 'A Guidebook to Mechanism in Organic Chemistry' Longmans, London, 1961.

(146) 'Non-Stoichiometric Compounds', Ed. L. Mandelcorn, Chapter 7, H.M. Powell, Academic Press, New York, 1964.

(147) L. Malateste, 'Progress in Inorganic Chemistry', Vol.1, Interscience Publishers, New York, 1959.

(148) E.G.J. Hartley, J. Chem. Soc., 1912, 705.

(149) E.G.J. Hartley and H.M. Powell, J. Chem. Soc., 1933, 1196.

(150) F. Holzl, W. Hauser and M. Eckmann, Monatsh., 1927, 48, 71.

(151) E.G.J. Hartley, J. Chem. Soc., 1910, 1066.

(152) J. Meyer, H. Domann and W. Muller, Z. anorg. Chem., 1937, 230, 336.

(153) R.R. Berrett and B.W. Fitzsimmons, J. Chem. Soc., 1967,A, 525.

(154) E.G.J. Hartley, J. Chem. Soc., 1913, 1196.

(155) S. Glasstone, J. Chem. Soc., 1930, 321.

(156) H.M. Powell and G.B. Stanger, J. Chem. Soc., 1939, 1105.

(157) G. Brauer, 'Handbook of Preparative Inorganic Chemistry', Vol.2, 2nd Edition, Academic Press, New York, 1965.

(158) D.F. Evans, D. Jones and G. Wilkinson, J. Chem. Soc., 1964, 3164.

(159) D.M. Adams, 'Metal Ligand and Related Vibrations', E. Arnold, London, 1967.

(160) L.H. Jones, Inorg. Chem., 1963, 2, 777.

(161) K. Nakamoto, 'Infra-Red Spectrum of Inorganic and Co-ordination Compounds', Wiley, 1963, p.103.

(162) N.N. Greenwood, J. Chem. Soc., 1959, 3811.

(163) B.J. Hathaway and A.E. Underhill, J. Chem. Soc., 1961, 3091.

(164) H.J. Coerver and C. Curran, J. Amer. Chem. Soc., 1958, 80, 3522.

(165) T.C. Waddington and F. Klanberg, J. Chem. Soc., 1960, 2339.

(166) B.M. Chadwick and A.G. Sharpe, 'Advances in Inorganic and Radiochemistry', Vol.8, Wiley, 1966, p.86.

(167) G.B. Bernino and G. Fabbri, Atti Acad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 1956, 20, 414.

(168) F.A. Cotton and F. Zingales, J. Amer. Chem. Soc., 1961, 83, 351.

(169) H.M. Powell and G.W.R. Bartindale, J. Chem. Soc., 1945, 799.

(170) D. Hadzi, 'Infra-Red Spectroscopy and Molecular Structure', Ed. M. Davies, Elsevier, 1963, p.228.

(171) F.A. Cotton, 'Modern Co-ordination Chemistry', Ed. J. Lewis and R.G. Wilkins, Interscience, 1960, p.315.

(172) A. Novak and A. Lautie, Nature, 1967, 216, 1202.

(173) A.M. Bellocq, C. Perchard, A. Novak and M.L. Josien, J. Chim. phys., 1965, 62, 1334.

(174) G.C. Pimental and A.L. McClellan, 'The Hydrogen Bond', Freeman, 1960, p.87.

(175) R.B. King, Inorg. Chem., 1967, 6, 25.

(176) J. Chatt, L.A. Duncanson, B.L. Shaw and L.M. Venanzi, Disc. Farad. Soc., 1958, 26, 131.

(177) J.F. Keggin and F.D. Miles, Nature, 1936, 137, 577.

(178) N.N. Greenwood, 'Seventh International Conference on Co-ordination Chemistry', I.U.P.A.C., Sweden, Butterworths, 1962, p.93.

(179) F.A. Cotton and J.R. Leto, J. Chem. Phys., 1959, 30, 993.

(180) C.A. Coulson, 'Valence', Oxford, 1952, p.301.

(181) R.A. Walton, Quart. Rev., 1965, 19, 126.

(182) D. Hall, P.K. Ummat and K. Wade, J. Chem. Soc.(A), 1967, 1612.

(183) M.F. Hawthorne and A.R. Pitochello, J. Amer. Chem. Soc., 1959, 81,5519.

(184) M.F. Fein, J. Bobinski, J.E. Panstian, D. Grafetein and M.S. Cohen, Inorg. Chem., 1965, 4, 422.

(185) M.F. Hawthorne and A.R. Pitochelli, J. Amer. Chem. Soc., 1958, 80, 6685.

(186) P. Oxley, M.W. Partridge and W.F. Short, J. Chem. Soc., 1947, 1110.

(187) E.O. Fischer, W. Hafner and H.O. Stahl, Z. anorg. Chem., 1955, 282, 47.

(188) W.P. Griffith, Quart. Rev., 1962, 16, 188.

* These references were obtained from the articles listed below.

(2), (17), (25), (55), (73), (130), (140) and (142) from H.E. Williams (4).

(22), (29), (30), (39), (66), (67), (68), (69), (70) and (71) from M.H. Ford-Smith (8).

(85), (86), (87), (88), (89), (99), (103) and (104) from Gmelin.