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Coordination Compound Formed by Iron Trichloride Dissolved in Liquid Hydrogen Cyanide

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After dissolving iron(III) chloride in anhydrous hydrogen cyanide at room temperature single crystals are obtained. When studied by infrared spectroscopy these crystals show that the HCN molecule is bound to the iron atom by nitrogen atom. The crystals are trigonal with $a = 10.29 \pm 0.01$ Å and $c = 6.280 \pm 0.006$ Å. A three-dimensional X-ray crystal structure analysis has shown that the unit cell contains two $FeCl_4$ tetrahedrons and one $Fe(NCH)_6$ octahedron. Inverting the full matrix and using anisotropic temperature factors, R factor based on 871 reflexions is equal to 0.07 excluding zero values. Interatomic distances computed from X-ray results show that nitrogen atom is bound to the iron atom. The color of crystals changing from yellow to green is related to the presence of iron(II) the variable amount of which leads to a linear variation of lattice constants.

Numerous experiments in recent years have shown the importance of coordination compounds in solvent–solute interaction phenomena. Liquid anhydrous hydrogen cyanide, characterized by a very high dielectric constant equal to 118, dissolves covalent halides of transition metals particularly well. As a part of the study of compounds formed in this solvent, we have isolated in the form of crystals the compound that is formed when iron trichloride is dissolved in hydrogen cyanide, and studied it by infrared absorption spectrophotometry and by X-ray diffraction.

Synthesis and Analysis

The apparatus (*1*) used for the synthesis is of Pyrex and hermetically sealed (Fig. 1). Because the synthesis must be made in a solvent as anhydrous as possible, the vessel is carefully evacuated before the reagents are brought together. These are previously purified; iron trichloride by sublimation under vacuum at 300°C and hydrogen cyanide, obtained by reaction at 0°C of 18*N* sulfuric acid on solid potassium cyanide, by two successive distillations. Hydrogen cyanide dissolves iron trichloride giving a red solution; the solubility limit is close to 300 g/liter. This solution is moved into T5 tube which is left at room temperature. After a time variable between 5 and 30 days, hexagonal prismatic crystals spontaneously appear; one can also get them by cooling down the solution. The color changes from yellow to green according to the experimental conditions. The concentration in iron trichloride for which crystals are best shaped is close to 150 g/liter. After crystallization, residual solution is transferred into T4. The last drops of liquid coating the crystals are evaporated by cooling T4 at 0°C or at an even lower temperature; T5 is then sealed off. The crystals, the decomposition of which becomes noticeable after a month, are very rapidly decomposed, however, by outside humidity.

Their composition has been determined analytically as follows. A weighed amount of crystals is dissolved in an aqueous solution of sulfuric acid, pH = 3, containing EDTA to decompose the complex, if any, formed with hydrogen cyanide. The hydrogen cyanide that is liberated is carried away by carbon dioxide and collected in a nitric acid solution of silver nitrate; the number of CN groups is then titrated in this solution. In the primary sulfuric acid solution, chloride ions are titrated by potentiometry with silver nitrate, and iron by gravimetry after precipitating Fe_2O_3. Since the color of crystals changes with experiments, the presence of iron(II) has been looked for, found, and the amount titrated with *o*-phenanthroline. Some typical results are shown in Table I.

From analysis the formula may be written as

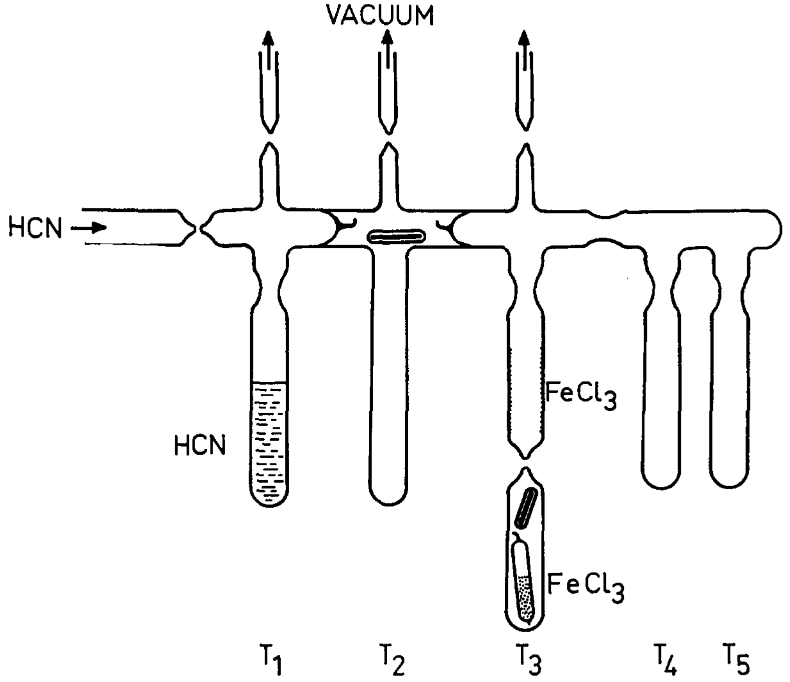

FIG. 1 Synthesis apparatus.

$Fe^{III}_{1-x}Fe^{II}_{x}Cl_{2.68}(CN)_{\lambda}$. Two remarks have to be made about x and λ.

The variable amount x of iron(II) is directly related to the time during which the reacting solution is left before crystallization, and to the color. A green solution corresponds to x close to 48% whereas a yellow solution corresponds to x close to 27%. This point is discussed below. The experimental determination of the number of CN groups gives very scattered values: λ varies between 1.5 and 3. This discrepancy has been correlated with the temperature at which T4 is set for drying crystals. A too drastic cooling (liquid nitrogen) brings about a beginning of crystal decomposition leading to a value of λ equal to 1.5; a cooling at 0°C cannot completely eliminate the mother solution and λ is found close to 3.

The correct value of λ will be determined when the crystallographic structure is known.

TABLE I

EXAMPLES OF ANALYTICAL RESULTS

Test		Ratio
Cl/Fe	1	2.71 ± 0.03
	2	2.66 ± 0.03
	3	2.77 ± 0.04
	4	2.60 ± 0.03
CN/Fe	5	2.30 ± 0.08
	6	1.66 ± 0.06
	7	2.08 ± 0.07
	8	3.2 ± 0.1

Study of Crystals by Infrared Techniques

In a glove box crystals are ground in nujol and the mixture spread out in a thin layer between two CsBr plates. The range 4000–200 cm^{-1} has been recorded with a Perkin Elmer 225 spectrometer (Fig. 2). The band assignment is shown in Table II. As a comparison bands of the deuterated compound are also shown. The latter is made starting from DCN which is prepared from KCN and D_2SO_4.

Observed frequencies related to the vibrations of the HCN coordinated group are similar to those found for addition compounds of hydrogen or deuterium cyanide with chlorides such as $HCN \cdot BCl_3$, $HCN \cdot SbCl_5$ or $2HCN \cdot TiCl_4$ (*2, 3*) (Table III). The increase of the stretching frequency of the CN triple bond with respect to free hydrogen cyanide is to be noted in every case. This displacement is related to the bonding of the CN group to the metal by the nitrogen atom. Indeed, this is observed for

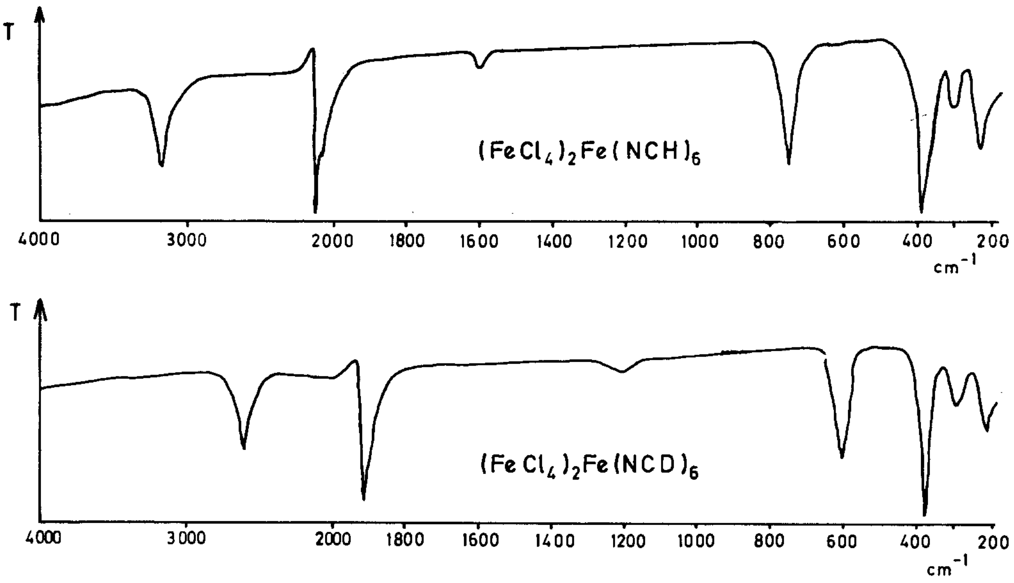

FIG. 2 Infrared spectrum.

acetonitrile of which the addition can be made only through this nitrogen atom. The stretching frequency appears at 2253 cm^{-1} for acetonitrile (*4*) and at 2270 cm^{-1} for the ion $[Fe(CH_3CN)_6]^{2+}$ (*5*). This increase of C≡N frequency when N is bound, is also clearly displayed by $W(CO)_5NCH$ and $W(CO)_5CNH$: CN frequencies are 2116 and 2095 (*6*), respectively, while it is 2097 for HCN (*7*). In the present work the stretching frequency is observed at 2131 cm^{-1} whereas it is 2096 for $H_4Fe(CN)_6$ (*8*) where the CN group is bound to the iron atom through its carbon atom. Then in the present work iron is bound to nitrogen.

TABLE II

WAVE NUMBERS OF INFRARED ABSORPTION BANDS (IN cm^{-1})

$Fe_3Cl_8(NCH)_6$	$Fe_3Cl_8(NCD)_6$	Assignment
3180 ± 2		νCH
	2584 ± 2	νC-D
2131 ± 1	1920 ± 1	νC≡N
1604 ± 2		2δ N-C-H + ? (2 × 758 = 1516)
	1208 ± 2	2δN-C-D (2 × 613 = 1226)
758 ± 2		δN-C-N
	613 ± 2	δN-C-D
375 ± 2	377 ± 1	νFe-Cl
290 ± 2 232 ± 5	291 ± 2 222 ± 2	νFe-N

Moreover, the existence in the spectrum of a C–H band at 3180 cm^{-1} shows that the molecule HCN is coordinated to the iron ion by nitrogen. At last this is confirmed by the fact that two bands are observed at 290 and 232 cm^{-1}; these vibrations have been assigned to the Fe–N stretching vibration since these frequencies are close to 298, 272, and 233 cm^{-1} found in the spectrum of $[(CH_3)_4N]_3[Fe^{III}(NCS)_6]$ (*9*). Let us point out that the frequency corresponding to Fe–C bands are close to 400 cm^{-1} since 419 and 406 cm^{-1} bands are observed for $H_4Fe(CN)_6$ (*8*).

In closing this discussion on the nature of the atom bound to iron, it should be pointed out that

TABLE III

WAVE NUMBERS OF INFRARED ABSORPTION BANDS

	νC≡N (cm^{-1})	νC–H or νC–D (cm^{-1})	References
BCl_3NCH	2189	3156	(*2*)
BCl_3NCD	1950	2607	(*2*)
$TiCl_4(NCH)_2$	2134 2135	3173	(*2*) (*3*)
HCN (sol)	2097	3135	(*7*)
DCN (sol)	1888	2550	(*7*)
$H_4Fe(CN)_6$	2096		(*8*)
CH_3CN (liq)	2253		(*4*)
$[Fe(NCCH_3)_6]^{2+}$	2270		(*5*)

ferro or ferricyanide ions have never been found when the crystals are dissolved in water. Indeed, these ions are very easy to detect, and if they existed in solid they should have been found in aqueous solution. Therefore, we conclude to the occurrence of a chain Fe–N≡C–H in the crystal and therefore HCN behaves as the nitrile of formic acid.

Crystallographic Study

The study of the unit cell is based on pictures taken following the Laue and precession methods using MoKα radiation. The single crystal has been introduced into a Lindeman glass tube in a glove box. It is a prism 0.5 mm long; its section is hexagonal and the edge is 0.1 mm. The unit cell belongs to the trigonal system and the lattice constants are $a = 10.29 \pm 0.01$ Å and $c = 6.280 \pm 0.006$ Å. Lengths are measured on films with a rule giving the $\frac{1}{100}$ mm and the film shrinkage has been corrected.

This crystal contained 38% of iron(II) (see section on Nonstoichiometry). Two space groups $P3$ and $P\bar{3}$ are possible because there are no systematically absent reflexions.

Density is very difficult to measure because of the instability of crystals when removed from the synthesis tube. Values found by pycnometry using hexadecane were in the range 1.8–1.9. Despite this scattering, these results lead to the conclusion that the unit cell contains three molecules of $FeCl_{2.68}(CN)_\lambda$.

To record intensities, the single crystal has been set on an eulerian cradle 120 mm in diameter. The used MoKα radiation was emitted by a tube supplied by a C.G.R. Theta 60 generator. Diffracted intensities have been measured with a scintillation counter associated to a pulse height analyzer.

A zirconium filter 0.1 mm thick is put in front of the counter. The distance crystal focus is 23 cm and the crystal counter is 18 cm. The aperture of the counter is a circle of 3 mm in diameter. The pulsed height analyzer centered on MoKα energy and used in a differential way cuts 10% of the incident intensity. Nine hundred twenty-two independent reflections have been recorded with a θ–2θ scan at room temperature after manual setting of the crystal. Three chosen reflections have been recorded twice a day to check the stability.

The scanning range was 1.76° in θ and symmetrical; the scanning speed was 0.35°/min in θ. The highest counting rate exceeded 7000 counts/sec for only three reflexions. The background has been measured over 100 sec at a fixed point set 0.86° before the Bragg angle of each reflexion, i.e. at the beginning of the scan. An average curve of background based upon (*hkl*) reflexions having *hkl* prime integers between them has been drawn. To substract background for each reflexion, a curve, parallel to the average background curve, is drawn starting from the fixed background point of that particular reflexion.

Absorption corrections have been applied using the method of Busing and Levy (*10*). Absorption coefficient is equal to 26.7 cm^{-1}. Corrections range from 0.60 to 0.62. Standard deviation which will be used in refinement has been computed for each reflexion (*11*).

A three-dimensional Patterson series clearly shows that the iron atoms are located on the three-fold axes. Taking into account the polar character of both space groups $P3$ and $P\bar{3}$ one iron atom has been fixed at the origin. Iron atoms are found at the center either of a tetrahedron, or of an octahedron. Considering peak heights, chlorine atoms appear to be tetrahedrally arranged around iron; for one octahedron there are two tetrahedrons $FeCl_4$ arranged head to tail. The assignment of neighbors to octahedrally surrounded iron is more difficult. Indeed there are two possibilities regarding the chemical formula: Fe–N–C or Fe–C–N; this ambiguity cannot be solved directly by X-ray. Refining by least squares (*12*) taking isotropic temperature factors and form factors as given by Cromer and Waber (*13*) leads to R factor equal to 0.13.

A three-dimensional Fourier series has been computed with observed structure factors and signs deduced from the preceding refinement. Except for the six CN groups coordinated to the iron atom, no CN group shows up which might have been in the solid as crystallization molecules. Therefore, the value of λ (number of CN groups per iron atom) is determined and the formula is $Fe^{III}_{1-x}Fe^{II}_{x}Cl_{2.68}(CN)_2$.

Final refinement has been carried out in $P3$ and $P\bar{3}$ space groups. Because of a bad stabilization of parameters in $P3$ and because of Hamilton's test (*14*) computed on the 0.005 level, the $P\bar{3}$ space groups appears the right one. This has been confirmed by using Roger's test (*15*) (Fig. 3). The final least-squares refinement based on 871 data including anisotropic temperature factors is made by inverting the full matrix and taking account of the anomalous components of form factors (*16*). It leads to an R factor equal to 0.09 including zero intensities and to 0.07 excluding zero intensities. R is taken as the ratio between the sum of differences in absolute value between observed and computed structure

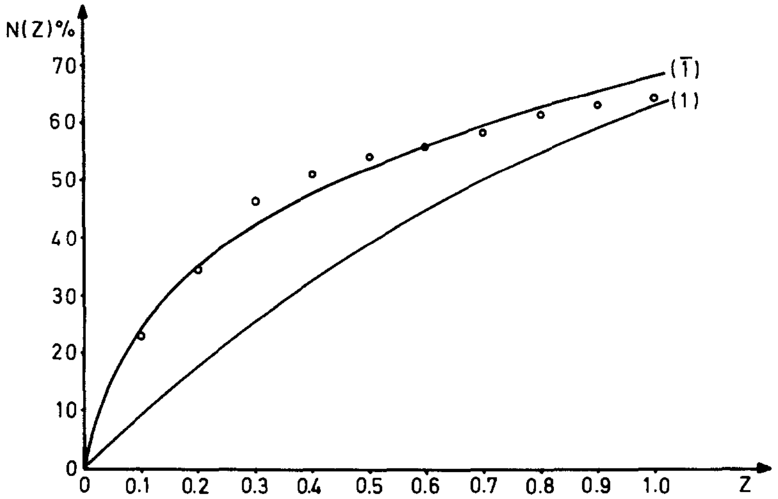

FIG. 3 Roger's test—points are experimental values. (1) is related to acentric case and ($\bar{1}$) to centric case.

factors, and the sum of observed structure factors. If observed intensities are weighed, *R* is equal to 0.09 including or excluding zero intensities. A difference series has not shown hydrogen atoms, although the accuracy on electron density is equal to $0.4e/\text{Å}^{-3}$ (*9*).

Observed and computed structure factors are shown on Table IV F(000) being equal to 1019. Atomic parameters and components of anisotropic temperature factors are gathered on Table V. The arrangement of the two $FeCl_4$ tetrahedrons and of the $Fe(NC)_6$ octahedron is drawn on Fig. 4. Interatomic distances and bond angles are shown on Fig. 5.

Discussion

Although it cannot be proved directly by X-ray what atom of the CN group is bound to the iron atom, the structural determination suggests that the

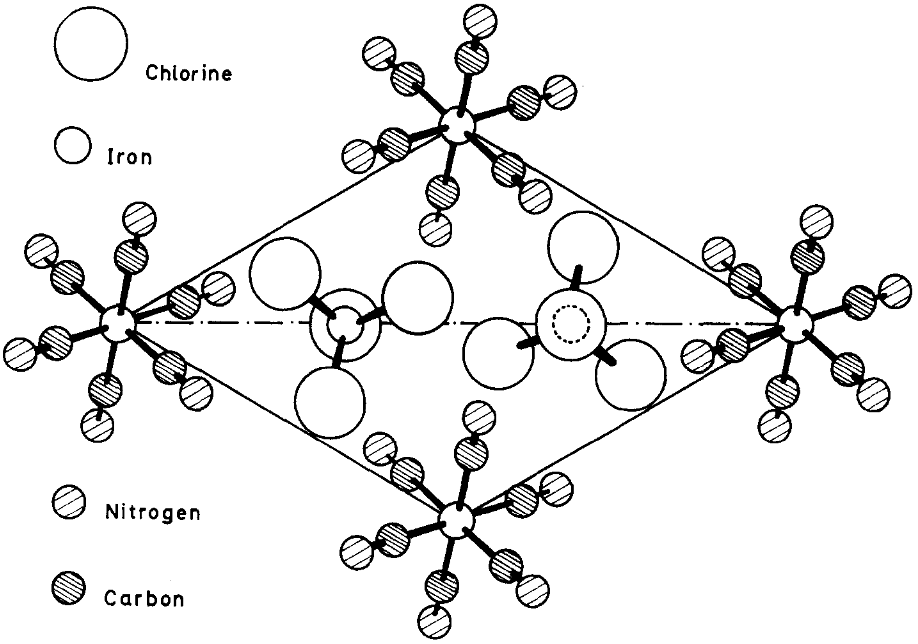

FIG. 4 Projection on (001) plane.

TABLE IV

First Column: index K; second: index L; third: F observed; fourth: F computed

H = 0

0	1	380	342
0	2	669	631
0	3	174	177
0	4	185	186
0	5	72	75
0	6	24	4
0	7	32	31
0	8	28	32
1	-7	24	26
1	-6	98	102
1	-5	78	82
1	-4	39	43
1	-3	106	107
1	-2	76	81
1	1	201	248
1	2	315	289
1	3	161	154
1	4	76	74
1	5	0	9
1	6	37	40
1	7	0	19
2	-6	71	76
2	-5	48	46
2	-4	131	135
2	-3	242	247
2	-2	194	192
2	-1	145	123
2	0	23	20
2	1	97	79
2	2	33	28
2	3	80	77
2	4	124	129
2	5	105	99
2	6	58	55
2	7	5	12
3	-7	42	41
3	-6	65	66
3	-5	14	12
3	-4	68	79
3	-3	31	35
3	-2	89	82
3	-1	178	173
3	0	297	281
3	1	284	270
3	2	24	18
3	3	140	131
3	4	25	24
3	5	80	77
3	6	51	49
3	7	8	12
4	-7	16	22
4	-6	72	70
4	-5	45	54
4	-4	28	23
4	-3	79	79
4	-2	96	100
4	-1	38	45
4	0	106	109
4	1	72	73
4	2	242	229
4	3	180	181
4	4	50	56
4	5	18	20
4	6	33	34
4	7	10	7
5	-7	17	15
5	-6	10	16
5	-5	11	17
5	-4	21	19
5	-3	61	65
5	-2	214	222
5	-1	180	187
5	0	101	102
5	1	134	131
5	2	89	84
5	3	102	100
5	4	0	12
5	5	36	37
5	6	72	68
5	7	20	20
6	-6	20	21
6	-5	32	33
6	-4	14	13
6	-3	58	61
6	-2	51	48
6	-1	124	130
6	0	239	238
6	1	129	129
6	2	1	22
6	3	58	61
6	4	19	11
6	5	36	33
6	6	34	34
7	-6	46	39
7	-5	62	64
7	-4	6	13
7	-3	22	20
7	-2	47	47
7	-1	53	54
7	1	28	29
7	2	123	124
7	3	140	139
7	4	20	21
7	5	43	37
7	6	21	15
8	-5	25	20
8	-4	43	44
8	-3	79	80
8	-2	42	42
8	-1	26	28
8	0	33	35
8	1	0	19
8	2	41	43
8	3	31	28
8	4	62	66
8	5	26	28
9	-4	6	15
9	-2	8	17
9	-1	60	61
9	0	69	66
9	1	30	33
9	2	0	3
9	3	0	19
9	4	9	9
10	-3	16	19
10	-2	6	3
10	-1	9	11
10	0	0	7
10	1	26	19
10	2	29	25
10	3	38	34
11	-2	23	27
11	-1	0	1
11	0	0	5
11	1	0	7
11	2	0	6

H = 1

0	2	90	80
0	3	115	107
0	4	42	43
0	5	82	82
0	6	105	102
0	7	28	26
1	-7	15	15
1	-6	59	64
1	-5	84	92
1	-3	169	177
1	-2	0	4
1	-1	339	335
1	0	451	419
1	2	15	12
1	3	95	87
1	4	45	45
1	5	34	35
1	6	62	63
1	7	44	40
2	-7	18	12
2	-6	29	31
2	-5	87	89
2	-4	151	159
2	-3	73	73
2	-2	166	134
2	-1	50	43
2	0	125	136
2	1	56	51
2	2	137	126
2	4	157	152
2	5	68	62
2	6	89	82
2	7	16	6
3	-7	0	2
3	-6	40	40
3	-5	47	45
3	-3	221	227
3	-2	212	215
3	-1	47	55
3	0	47	51
3	1	47	47
3	2	40	39
3	3	87	84
3	4	67	61
3	5	62	61
3	6	68	62
3	7	25	21
4	-7	23	22
4	-6	17	5
4	-5	40	44
4	-4	74	79
4	-3	82	88
4	-2	204	210
4	-1	189	188
4	0	559	552
4	1	183	178
4	2	210	211
4	3	86	84
4	4	81	83
4	5	44	43
4	6	13	6
4	7	21	22
5	-7	9	14
5	-6	58	63
5	-5	45	46
5	-4	17	14
5	-3	59	[illegible]
5	-2	49	49
5	-1	78	82
5	0	44	47
5	1	161	158
5	2	165	167
5	3	43	44
5	4	18	24
5	5	33	26
5	6	17	14
5	7	25	18
6	-6	28	31
6	-5	14	8
6	-4	60	62
6	-3	82	88
6	-2	63	66
6	-1	54	57
6	0	32	33
6	1	9	11
6	2	25	16
6	3	16	15
6	4	47	45
6	5	56	55
7	-6	38	31
7	-5	14	9
7	-4	32	29
7	-3	0	14
7	-2	26	30
7	-1	52	59
7	0	94	96
7	1	98	98
7	2	16	12
7	3	44	47
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7	5	26	29
7	6	16	23
8	-5	30	26
8	-4	0	13
8	-3	15	11
8	-2	35	29
8	-1	15	10
8	0	33	32
8	1	12	2
8	2	78	75
8	3	75	74
8	4	0	16
8	5	7	13
9	-4	17	1
9	-3	18	23
9	-2	69	67
9	-1	53	51
9	0	27	27
9	1	39	40
9	2	19	19
9	3	39	36
9	4	21	11
10	-3	19	12
10	-2	14	10
10	-1	32	32
10	0	64	57
10	1	20	23
10	2	10	9
10	3	21	6

H = 2

0	0	21	[illegible]
0	2	207	192
0	3	248	247
0	4	140	135
0	5	52	46
0	6	79	76
1	-7	20	22
1	-6	28	29
1	-5	115	127
1	-4	27	28
1	-3	445	487
1	-2	391	403
1	-1	403	411
1	0	367	349
1	1	451	430
1	2	283	266
1	3	171	154
1	4	22	21
1	5	170	167
1	6	101	95
1	7	14	8
2	-7	15	5
2	-6	40	45
2	-5	88	92
2	-4	17	19
2	-3	156	163
2	-2	21	19
2	-1	322	320
2	0	248	238
2	1	95	84
2	2	119	109
2	3	27	19
2	4	83	86
2	5	14	15
2	6	69	71
2	7	49	49
3	-6	56	58
3	-4	53	56
3	-3	88	93
3	-1	103	102
3	0	35	39
3	1	140	136
3	2	201	196
3	3	148	143
3	4	54	54
3	5	0	19
3	6	38	34
3	7	0	3
4	-7	14	14
4	-6	23	24
4	-5	9	14
4	-4	44	43
4	-3	67	74
4	-2	145	155
4	-1	134	133
4	0	28	26
4	1	65	62
4	2	33	32
4	3	50	51
4	4	29	30
4	5	52	55
4	7	14	13
5	-6	35	32
5	-5	39	41
5	-4	0	4
5	-1	136	146
5	0	228	238
5	1	98	104
5	2	47	45
5	3	46	48
5	4	0	4
5	5	25	25
5	6	33	26
6	-6	0	12
6	-4	73	74
6	-3	14	10
6	-2	65	63
6	-1	15	4
6	0	76	76
6	1	18	22
6	2	19	21
6	3	97	97
6	4	74	71
6	5	17	18
6	6	32	34
7	-5	21	24
7	-4	20	19
7	-3	89	90
7	-2	76	77
7	-1	16	2
7	0	12	18
7	1	0	9
7	2	9	13
7	3	19	11
7	4	31	26
7	5	36	32
8	-4	13	8
8	-3	9	[illegible]
8	-2	22	16
8	-1	50	51
8	0	92	92
8	1	45	[illegible]
8	2	31	17
8	3	16	14
8	4	6	8
9	-3	8	20
9	-2	16	15
9	-1	22	20
9	0	16	12
9	1	32	34
9	2	47	42
9	3	13	17
10	-1	16	15
10	0	0	5
10	1	16	2

H = 3

0	0	292	281
0	1	185	173
0	2	93	82
0	3	33	35
0	5	20	12
0	6	67	66
0	7	45	41
1	-7	1	12
1	-6	18	16
1	-5	71	72
1	-4	156	167
1	-3	89	90
1	-2	115	113
1	-1	87	89
1	0	62	64
1	1	97	87
1	2	175	161
1	3	245	235
1	4	105	107
1	5	65	63
1	6	63	65
1	7	20	11
2	-7	0	2
2	-6	54	54
2	-5	36	36
2	-4	91	95
2	-3	203	209
2	-2	155	157
2	-1	0	8
2	0	47	47
2	1	17	22
2	2	52	53
2	3	28	27
2	4	49	50
2	5	79	78
2	6	48	52
2	7	17	9
3	-7	34	32
3	-6	41	42
3	-5	14	2
3	-4	25	28
3	-3	0	2
3	-2	19	15
3	-1	52	53
3	0	223	218
3	1	257	255
3	2	11	7
3	3	129	134
3	4	19	23
3	5	68	68
3	6	41	41
3	7	4	8
4	-6	50	45
4	-4	27	30
4	-3	16	3
4	-2	19	23
4	-1	14	11
4	0	13	11
4	1	36	37
4	2	106	106
4	3	119	116
4	4	60	56
4	5	11	15
4	6	36	31
5	-6	16	14
5	-5	41	37
5	-4	29	23
5	-3	134	141
5	-2	108	116
5	-1	30	33
5	0	38	41
5	1	59	59
5	2	39	40
5	3	23	23
5	4	16	15
5	5	71	65
5	6	44	39
6	-5	44	36
6	-4	0	10
6	-3	57	59
6	-2	0	14
6	-1	110	111
6	0	73	77
6	1	29	23
6	2	40	36
6	3	20	11
6	4	31	30
6	5	0	6
7	-5	14	15
7	-4	32	25
7	-3	33	34
7	-2	11	5
7	-1	30	31
7	1	41	38
7	2	62	60
7	3	48	49
7	4	18	18
7	5	11	9
8	-4	3	15
8	-3	24	23
8	-1	28	33
8	0	19	6
8	1	14	18
8	2	0	8
8	4	16	13
9	-2	18	9
9	-1	35	26
9	0	53	54
9	1	21	26
9	2	17	11

H = 4

0	0	105	109
0	1	39	45
0	2	103	100
0	3	81	79
0	4	25	23
0	5	49	54
0	6	72	70
0	7	20	22
1	-7	21	23
1	-6	25	30
1	-5	24	32
1	-4	3	2
1	-3	46	52
1	-1	134	136
1	0	248	244
1	1	209	230
1	2	34	40
1	3	88	91
1	4	45	44
1	5	50	47
1	6	50	50
1	7	17	18
2	-7	10	3
2	-5	93	97
2	-4	13	11
2	-3	45	46
2	-2	101	101
2	-1	122	120
2	0	128	128
2	1	109	109
2	2	214	219
2	3	252	254
2	4	20	22
2	5	74	72
2	6	23	25
2	7	13	14
3	-6	48	48
3	-5	28	35
3	-4	89	91
3	-3	130	137
3	-2	39	44
3	-1	45	46
3	0	92	93
3	1	21	30
3	2	93	97
3	3	38	41
3	4	114	116
3	5	53	50
3	6	0	4
4	-6	28	32
4	-5	34	31
4	-4	29	27
4	-3	54	57
4	-2	21	30
4	-1	118	123
4	0	108	114
4	1	63	64
4	2	8	19
4	3	28	22
4	4	13	17
4	5	11	18
4	6	8	27
5	-5	29	27
5	-4	62	60
5	-3	34	33
5	-2	31	33
5	0	21	25
5	1	31	34
5	2	52	54
5	3	81	80
5	4	42	41
5	5	21	18
6	-5	8	12
6	-4	21	23
6	-3	72	74
6	-2	58	61
6	-1	8	9
6	0	26	22
6	1	26	23
6	2	18	23
6	3	14	1
6	4	4	14
6	5	37	31
7	-4	6	1
7	-2	6	4
7	-1	0	6
7	0	54	50
7	1	76	69
7	2	8	13
7	3	34	31
7	4	0	11
8	-2	17	10
8	0	0	9
8	1	9	5
8	2	41	35

H = 5

0	0	132	132
0	1	187	187
0	2	215	222
0	3	64	65
0	4	13	19
0	5	17	17
0	6	13	16
0	7	19	15
1	-7	0	2
1	-6	44	43
1	-5	30	27
1	-4	71	77
1	-3	127	137
1	-2	93	98
1	-1	60	68
1	0	31	34
1	1	48	46
1	2	33	38
1	3	40	55
1	4	77	84
1	5	53	49
1	6	27	27
1	7	15	11
2	-6	43	45
2	-5	6	7
2	-4	47	51
2	-2	44	58
2	-1	60	65
2	0	132	135
2	1	141	146
2	2	22	5
2	3	72	72
2	4	20	4
2	5	37	46
2	6	17	24
3	-6	32	31
3	-5	38	39
3	-3	22	15
3	-1	10	24
3	1	12	13
3	2	99	106
3	3	121	128
3	4	28	34
3	5	22	27
3	6	25	20
4	-5	14	6
4	-4	0	8
4	-3	59	61
4	-2	111	113
4	-1	55	53
4	0	57	54
4	1	36	37
4	2	41	42
4	3	41	41
4	4	0	13
4	5	20	23
5	-5	10	14
5	-4	13	13
5	-3	25	19
5	-1	53	49
5	0	95	98
5	1	56	59
5	2	0	0
5	4	6	6
5	5	3	10
6	-4	0	13
6	-3	0	8
6	-2	22	15
6	-1	12	1
6	0	26	20
6	1	17	7
6	2	64	58
6	3	57	54
6	4	10	8
7	-3	30	33
7	-2	0	11
7	-1	0	11
7	4	26	19
7	1	15	4
7	2	19	15
7	3	0	11
8	0	27	24

H = 6

0	0	228	230
0	1	125	130
0	2	46	48
0	3	59	61
0	5	36	33
0	6	15	21
1	-6	30	26
1	-5	55	54
1	-4	53	50
1	-3	21	5
1	-2	0	5
1	-1	30	30
1	0	12	14
1	1	7	8
1	2	69	72
1	3	131	136
1	4	70	66
1	5	23	26
1	6	38	35
2	-6	14	15
2	-5	17	29
2	-4	4	23
2	-3	101	103
2	-2	107	113
2	0	27	28
2	1	34	35
2	2	13	13
2	3	42	45
2	4	34	40
2	5	28	31
2	6	23	24
3	-5	21	17
3	-4	18	11
3	-2	33	32
3	-1	80	79
3	0	146	154
3	1	57	60
3	2	44	45
3	3	17	24
3	4	23	23
3	5	15	17
4	-5	16	12
4	-4	19	7
4	-3	43	43
4	-1	51	48
4	0	32	29
4	1	68	68
4	2	77	76
4	3	24	22
4	4	0	6
4	5	11	8
5	-4	33	27
5	-3	34	35
5	-2	30	26
5	-1	26	25
5	0	16	11
5	1	8	11
5	2	6	3
5	4	16	20
6	-2	15	13
6	-1	10	15
6	0	35	33
6	1	42	41
6	2	15	8
6	3	6	17
7	-1	11	9
7	0	9	7
7	1	0	2

H = 7

0	0	41	52
0	1	49	54
0	2	42	47
0	3	22	20
0	4	0	13
0	5	59	64
0	6	42	39
1	-6	26	26
1	-5	45	41
1	-4	26	22
1	-3	72	76
1	-2	31	31
1	-1	143	148
1	0	78	80
1	1	14	5
1	2	24	34
1	3	26	23
1	4	22	25
1	5	13	8
1	6	27	27
2	-5	17	19
2	-4	23	22
2	-3	33	37
2	-2	7	12
2	-1	35	33
2	0	0	9
2	1	51	51
2	2	60	63
2	3	49	49
2	4	15	31
2	5	11	1
3	-5	0	8
3	-4	0	11
3	-3	26	23
3	-2	62	63
3	-1	51	54
3	0	15	15
3	1	27	28
3	2	14	15
3	3	25	25
3	4	0	13
3	5	10	21
4	-4	0	3
4	-3	16	15
4	-2	0	18
4	-1	37	38
4	0	88	87
4	1	38	44
4	2	21	19
4	3	5	18
4	4	0	5
5	-3	16	1
5	-2	8	7
5	-1	13	7
5	0	0	11
5	1	21	6
5	2	25	20
5	3	22	32
6	0	0	4
6	1	0	1

H = 8

0	0	28	35
0	1	24	28
0	2	44	42
0	3	83	84
0	4	44	44
0	5	23	20
1	-5	6	12
1	-4	23	20
1	-2	64	70
1	-1	0	2
1	0	23	26
1	1	21	17
1	2	27	27
1	3	0	1
1	4	9	13
1	5	37	34
2	-3	12	6
2	-2	17	12
2	-1	30	29
2	0	93	86
2	1	70	64
2	2	0	7
2	3	28	29
3	-4	0	11
3	-3	0	1
3	-2	3	4
3	-1	10	5
3	1	14	15
3	2	34	36
3	3	41	33
3	4	24	15
4	-2	22	25
4	-1	0	6
4	0	9	1
4	2	0	3
5	0	24	23

H = 9

0	0	62	66
0	1	64	62
0	2	0	17
0	3	9	22
0	4	14	15
1	-4	0	14
1	-3	0	9
1	-1	0	5
1	0	14	14
1	1	0	4
1	2	54	53
1	3	60	56
2	-3	31	32
2	-2	8	6
2	-1	0	16
2	0	26	30
2	1	12	3
2	2	27	23
2	3	3	7
3	-2	4	8
3	-1	13	29
3	0	26	31
3	1	23	25
3	2	10	8

H = 10

0	0	0	7
0	1	14	11
0	2	0	3
0	3	15	19
1	-3	8	3
1	-2	0	12
1	-1	8	12
1	0	34	33
1	1	43	42
1	2	9	7
1	3	18	19
2	-1	11	10
2	1	0	1

H = 11

0	0	0	5
0	1	0	4
0	2	31	27

TABLE V

ATOMIC PARAMETERS AND ANISOTROPIC THERMAL VIBRATION COMPONENTS (× 10^4)[a]
$\exp[-2\pi^2(U_{11}(ha^*)^2 + U_{22}(hb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}(hka^*b^*) + 2U_{13}(hla^*c^*) + 2U_{23}(klb^*c^*))]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe 1	0	0	0	511(8)	511(8)	525(10)	256(4)	0	0
Fe 2	2/3	1/3	0.8589(2)	573(7)	573(7)	456(8)	287(3)	0	0
N	0.1904(7)	0.1472(7)	0.1950(9)	571(32)	647(35)	692(30)	296(29)	−40(25)	−56(25)
C	0.2957(10)	0.2306(11)	0.2694(15)	694(49)	981(65)	841(50)	332(48)	−63(43)	−175(46)
Cl 1	2/3	1/3	0.2073(4)	789(12)	789(12)	457(12)	394(6)	0	0
Cl 3	0.6291(3)	0.1153(2)	0.7479(3)	935(15)	692(11)	733(11)	429(11)	34(9)	−72(9)

[a] Standard deviation is given in parentheses.

group is bound by nitrogen as shown by the following discussion based upon interatomic distances.

Firstly, the length of the Fe–first-neighbor interatomic distance is equal to 2.16 Å; it is close to the 2.24 Å value observed for the distance Fe–N in the complex $[(\mathrm{HEDTA})\ \mathrm{Fe{-}O{-}Fe}\ (\mathrm{EDTAH})]^{2-}$ (*18*), while it is very different from the 1.89 value which corresponds to the Fe–C distance found in ferro- or ferricyanide compounds (*19*). Then, we conclude to a Fe–N bond.

Secondly, the bond length iron first-neighbor–iron second-neighbor is equal to 1.095 ± 0.010. This is shorter than C≡N bound in $H_4Fe(CN)_6$ equal (*19*) to 1.15 ± 0.01. The shortening in the case of our compound is to be related to the increase of the stretching frequency of the triple bond C≡N with respect to free HCN. Indeed the same thing has been observed by Duffin for $Cu(NO_3)_2 \cdot 2CH_3CN$ where the CN length is equal to 1.04 ± 0.07 (*20*) and by Ibers for $BCl_3 \cdot CH_3CN$ where it is equal to 1.122 ± 0.007 Å (*21*). It is a common statement to say that the shortening is related to the increase of the stretching force (*21, 22, 23*). This has been also observed by Kawai and Kanesaka who have attributed this effect "to a mechanical coupling between CN stretching and other vibrational mode ... (*2*). The question may be raised why this happens when the nitrogen is bound and why it does not happen when the nitrogen is bound through coordination. The following interpretation may be proposed.

Let us assume the iron–nitrogen bound in $Fe(NCH)_6$ octahedron to be a single bond; indeed its length is similar to this one found for $[(\mathrm{HEDTA})\ \mathrm{Fe{-}O{-}Fe}\ (\mathrm{EDTAH})]^{2-}$, 2.24 Å, which is among the longest Fe–N observed bonds. The covalent radius of nitrogen is equal to 0.70 Å (*24*) while that of carbon is 0.77 Å. Therefore, the length of the single bond Fe–C should be at least equal to the single bond length Fe–N. However, in $H_4Fe(CN)_6$ the interatomic CN length is 1.89 Å. This drastic shortening may be explained considering a back-coordination from the iron atom towards the carbon atom. It might be taken as a reason for the very high stability of the ferrocyanide ion. In

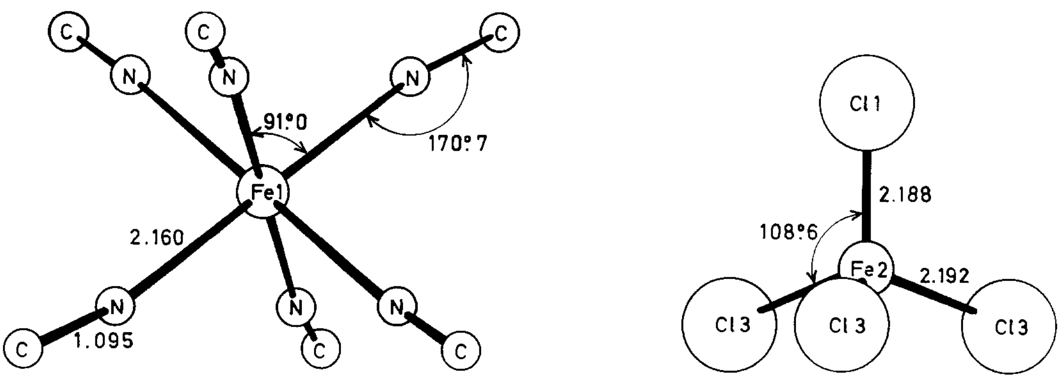

FIG. 5 Interatomic distances and bond angles.

$Fe(NCH)_6$ groups for which the chain is Fe–N–C, the iron atom does not give back any electron to nitrogen. In $Fe(CN)_6$ groups for which the chain is Fe–C–N, the backcoordination brings on the carbon atom an electronic density which pushes away triple bond electrons towards nitrogen. In a sense this may be considered as a lowering of the CN bond order. This is shown by its stretching force constant, and of its stretching frequency, and by an increase of its bond length. Therefore in the Fe–N–C–H chain, since there is no backcoordination, the N–C bond appears as a true triple bond.

It has been observed that the Fe–N–C angle is equal to $170.7 \pm 0.7°$ while it is strictly 180° for $BCl_3 \cdot CH_3CN$ (*21*) and for $Cu(NO_3)_2 \cdot 2CH_3CN$ (*20*). The departure from 180° appears significant as far as standard deviation is concerned; it is attributed to crystal packing.

Nonstoichiometry

Chemical analysis has shown that the crystals contain iron(II). The iron(II) amount is a function of the time during which the solution is left before crystallization occurs. This may be understood because of the behavior of hydrogen cyanide which reduces iron(III). Whatever the amount of iron(II) is, the unit cell is always the same. Thus, this has to be considered as a phenomenon of nonstoichiometry. The iron(II) content and the lattice constants have been measured on the same crystal. Results are shown on Fig. 6. The lowest and the highest iron(II) contents do probably not describe the phase limits since they represent the extreme compounds which it has been possible to prepare till now. In order to maintain electroneutrality, we consider that the crystal contains a variable number of hydrogen atoms, leaving or entering into the crystal as protons when the ratio Fe(II)/Fe(III) changes.

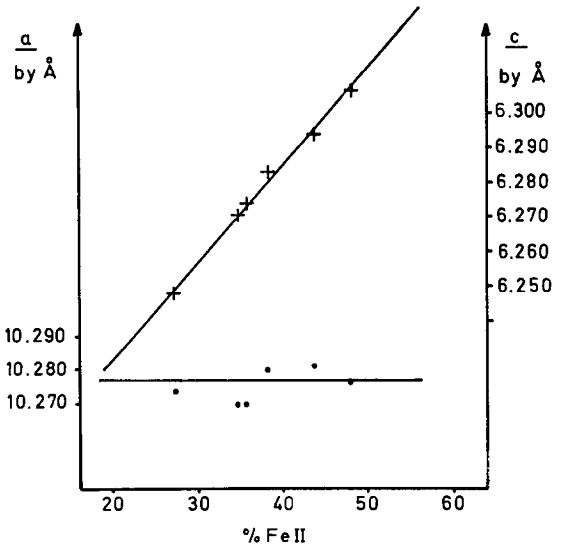

FIG. 6 Lattice constant variations as a function of the iron(II) content.

Taking account of these results, two cases are considered according to whether the iron(II) amount is higher or lower than 33%. If it is lower, it is assumed that iron(II) atoms are placed in octahedrons since $FeCl_4^{2-}$ tetrahedron is unstable (*25*). If it is higher iron(II) atoms are in octahedrons and also partially in tetrahedrons.

The single crystal we have used for crystallographic measurements contained 38% iron(II). Thus, it belongs to the second case. The Fe–Cl bond length has been found equal to 2.189 ± 0.003 Å while it is given equal to 2.162 ± 0.005 Å for $FeCl_4^-$ by Benne, Cotton, and Weaver (*26*). This change is, of course, small considering bond length measurement accuracy. However, it is in the direction of an increase. Since Fe^{III}–Cl is expected to be shorter than Fe^{II}–Cl for the same tetrahedral surrounding, this is in agreement with the above description for iron localization as long as this Fe–Cl bond length change would appear reproducible.

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