

### 209. Structure of Compounds of Ferrocyanide Type. Part I. Crystal Structure of Hexamethylisocyanidoferrous Chloride.

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The comparatively simple hexagonal structure permits a determination of the Fe-C (1.85 Å.) and C-N (1.18 Å.) distances. The former is approximately that calculated for a 50% double bond character of the link. The Fe-C-N-CH<sub>3</sub> sequence of atoms has a bend of 7° at the nitrogen atom which brings the methyl groups slightly out of line with the otherwise linear arrangement. Chloride ions and water of crystallisation molecules do not conform strictly to space-group symmetry, but adopt positions which permit a closer approach of the oppositely charged ions.

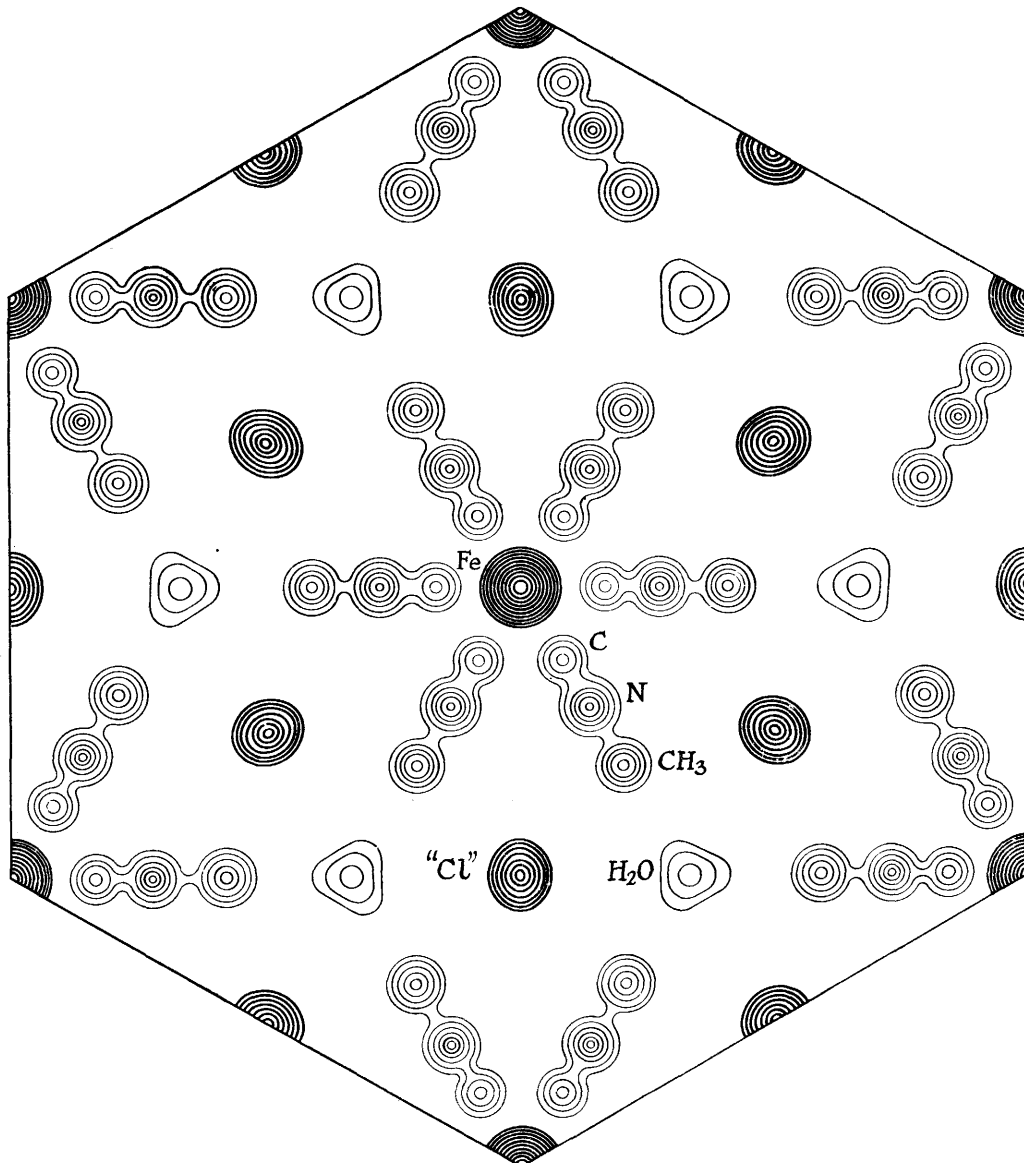
To account for the stability of complexes of the transition elements containing cyano-groups it has been suggested that these elements are capable of forming bonds, to the carbon atoms, which have in part a double-bond character (Pauling, "The Nature of the Chemical Bond," 1939). Evidence for this comes from the structures of carbonyls (Brockway and Cross, *J. Chem. Physics*, 1935, 3, 828; Crawford and Cross, *ibid.*, 1938, 6, 525; Brockway and Anderson, *Trans. Faraday Soc.*, 1937, 33, 1233; Brockway, Ewens, and Lister, *ibid.*, 1938, 34, 1350), since the metal-carbon and carbon-oxygen bond lengths observed correspond to resonance between the types M:C::O and M::C::O. That the CO group in a carbonyl can function as a ketone group is shown directly in iron enneacarbonyl (Powell and Ewens, *J.*, 1939, 286), where three such groups form bridges between iron atoms, but here of course the two carbon bonds do not link to the same iron atom. In complexes such as the ferrocyanide ion the bond may resonate between the types Fe (C $\bar{N}$ ),  $\bar{F}e:C::\bar{N}$ : and  $F\bar{e}::C::\bar{N}^-$ . The contribution of the double-bond type to the structure may be found from the iron-carbon distance, and the primary object in this series of investigations was to make an accurate determination of this distance. The normal single-bond distance would be about 2.0 Å., and double-bond character should show itself in a diminished length. Attention was first directed to tetramethyl ferrocyanide Fe(CNMe)<sub>4</sub>(CN)<sub>2</sub>. The molecule has four CNMe groups linked to iron, and in this case the two types  $F\bar{e}::C::\bar{N}_{Me}$  and  $\bar{F}e:C::\bar{N}Me$  differ in their natural stereochemical configurations in that the first bends at the nitrogen atom and the second is completely linear. In the resonance structure there might therefore be a departure from strict linearity which would reinforce the evidence from bond length. Both *cis*- and *trans*-isomers were studied, but the results, to be given later, are incomplete, and great refinement was not attempted on the discovery that the compound here dealt with had a convenient structure in which symmetry conditions made possible a more accurate determination of the required quantities.

*Hexamethylisocyanidoferrous chloride trihydrate*, Fe(CNMe)<sub>6</sub>Cl<sub>2</sub>·3H<sub>2</sub>O, was prepared from the corresponding acid sulphate by a modification of the method described by Hartley (*J.*, 1910, 97, 1725) from a specimen of his original material. The product was recrystallised from 97% alcohol, mixed with xylene to reduce the solubility of the salt; on cooling the warmed solution, faintly yellow hexagonal prisms crystallised out. The composition was established by analysis [Found: Cl (by Volhard's method), 17.1. C<sub>12</sub>H<sub>18</sub>N<sub>6</sub>Cl<sub>2</sub>Fe·3H<sub>2</sub>O requires Cl, 16.6%. C<sub>12</sub>H<sub>18</sub>N<sub>6</sub>Cl<sub>2</sub>Fe requires Cl, 19.0%], and by the molecular weight calculated from cell dimensions (see below) (Found: *M*, 426. C<sub>12</sub>H<sub>18</sub>N<sub>6</sub>Cl<sub>2</sub>Fe·3H<sub>2</sub>O requires *M*, 427). The water of crystallisation is derived from the wet alcohol, which contained ten times the amount needed for the weight of salt used. It was impossible to make a direct estimation of the water by dehydration: no loss in weight was observed when the salt was kept for some weeks over concentrated sulphuric acid under reduced pressure, and on heating the

substance at  $95^\circ$  for some days only a very slow loss took place, with gradual disintegration of the crystals. Heating to a higher temperature would have led to decomposition with loss of methyl chloride.

The crystals develop the forms  $\{10\bar{1}0\}$ ,  $\{0001\}$ , and sometimes  $\{11\bar{2}0\}$ ; they are optically uniaxial negative, show no pyroelectric effect by the liquid-air test, and have a density (floatation) of 1.394 g./c.c. Oscillation and

FIG. 1.  
Relative electron density projected on 0001.

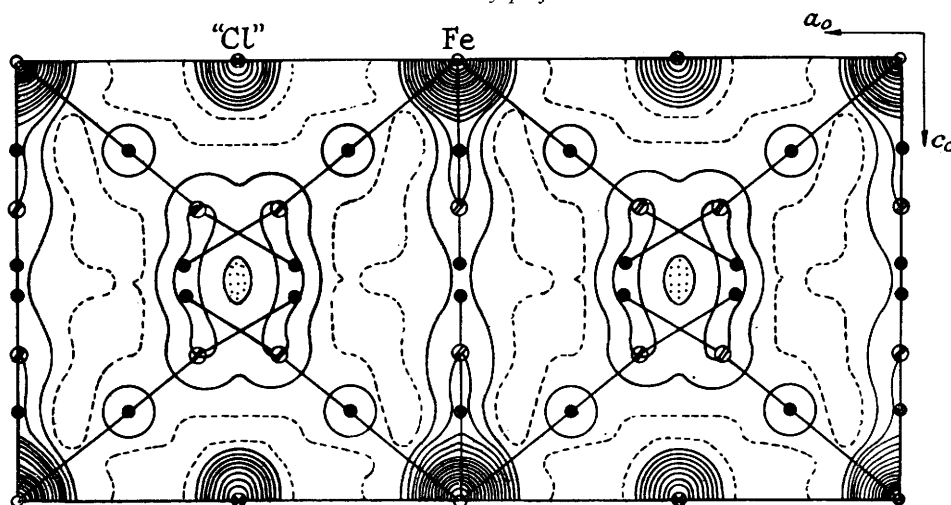


Contours are drawn at equal intervals except that for the iron and "chlorine" the interval has been doubled to avoid confusion of many lines. To preserve the effect of greater density than that given by the lighter atoms these contours at double intervals have been drawn in more heavily. The relative heights of the peaks in the arms of the octahedron, here seen lying on one of its faces, show clearly the link through the carbon atom to iron. The peak marked "Cl" represents  $\frac{2}{3}\text{Cl} + \frac{1}{3}\text{H}_2\text{O}$  as explained in the text.

Weissenberg photographs were taken about the axes  $[100]$ ,  $[001]$ , and  $[210]$  with copper radiation. From intensities estimated visually from the Weissenberg photographs relative values of the structure factors  $F_{hkt0}$  and  $F_{h\bar{h}\bar{k}l}$  were derived. The unit cell dimensions deduced are  $a = 10.45$ ,  $c = 5.304 \text{ \AA}$ , and hence the number of molecules per cell is  $0.998 \approx 1$ . Alternatively, the molecular weight calculated from the cell dimensions is 426. There are no spectra absent through space-group symmetry. Some oscillation photographs about  $[001]$

are unsymmetrical above and below the zero layer line, and therefore the possible space groups are  $C3$ ,  $C\bar{3}$ ,  $C3m$ ,  $H3m$ ,  $H32$ ,  $H\bar{3}m$ , and  $C\bar{3}m$ . Similar photographs taken with different crystals are often symmetrical, but this is due to twinning of the trigonal crystals on (0001). This twinning is of a lamellar character and is very persistent; probably no crystal obtained was entirely free from it. Crystals of the isomorphous bromide are comparatively free from this twinning and always gave unsymmetrical patterns. Intensity relations between the different reflexions show the presence of vertical planes of symmetry and this eliminates  $C3$  and  $C\bar{3}$ . Those groups without a symmetry centre were rejected in the absence of any evidence, either in the chloride or in the isomorphous bromide, of this lack of a symmetry centre. The possible groups left are  $H\bar{3}m$  and  $C\bar{3}m$ ; in both, the iron atom must lie at 000 or  $00\frac{1}{2}$ , and it is therefore possible to proceed with the Fourier electron-density synthesis without first deciding on the space-group, by giving to all structure factors the positive sign of the iron contribution, arising from iron atoms taken at 000. For the density projected on (0001) no assumptions about the space-group are necessary; it is sufficient to notice that, since there is only one iron atom per cell, its  $xy$  co-ordinates must be 00, and the further symmetry elements are brought into the resulting projection automatically from the intensity relationships. The series for electron density projected on (0001),  $(\rho)_{xy} \propto \sum \sum F_{hki0} \cos 2\pi(hx + ky)$ , was therefore summed. The resulting projection, differing but little from the final one (Fig. 1), showed the iron atom at the origin surrounded by six CNMe arms. These are located in positions very close to those required for a regular octahedral distribution around the iron atom, and show

FIG. 2.  
Relative electron density projected on  $10\bar{1}0$ .



The arms of the octahedral complex are ruled in, and those not in the line of sight show the bend at the nitrogen atom. The bend is not, however, estimated from this projection but from the accurate projected lengths obtained from Fig. 1. Two shaded areas indicate depressions. Water molecules are either included in the peak marked "Cl" (see Fig. 1) or obscured by the iron peak.

that there are vertical planes of symmetry parallel to  $(11\bar{2}0)$ , but not parallel to  $(10\bar{1}0)$ . This means that the space group is  $C\bar{3}m$ , and it is then possible to consider the distribution of the remaining atoms in accordance with this symmetry. In what follows the equivalent point positions are named according to the "Internationale Tabellen zur Bestimmung von Kristallstrukturen."

It is natural to suppose that the two chlorine ions would lie in  $(d) \frac{1}{3}\frac{2}{3}z$ , since there is no space available in the only other two-fold position  $(c) 00z$ , and that three water molecules would be located in a three-fold position  $(e)$  or  $(f)$ , with  $xy = \frac{1}{2}0, 0\frac{1}{2}, \frac{1}{2}\frac{1}{2}$ , but, although peaks are found in both these positions, the magnitude of the electron density is almost the reverse of what is expected, *i.e.*, the chlorine appears to be where the water was expected. If nevertheless it is assumed that there are two chlorine ions in  $(e)$  or  $(f)$  for the purpose of revising the signs of  $F_{hki0}$ , no appreciable alteration results on a repetition of the summation; the chlorine still appears where water is expected. Further, there are irremovable discrepancies in the calculated magnitudes of the structure factors. Thus  $F_{hki0}$  is calculated to be weak for indices when both  $h$  and  $k$  are even, whereas strong values are observed; when  $h - k = 3n$ , calculated values are strong and observed ones weak. These discrepancies are removed only if a larger contribution is made by atoms in the three-fold positions  $(e)$  or  $(f)$  and a smaller one by atoms in the two-fold position  $(d)$ . An examination of the isomorphous bromide showed these effects in an even more marked form and proved that the halogen ions must occupy the three-fold position. Since there are but two such ions per cell, there must be a random distribution of them among the three-fold positions, and of the three water molecules two must occupy the two-fold position  $(d)$  and the remaining one be distributed at random among the three-fold positions. Each

three-fold position therefore holds statistically  $\frac{2}{3}\text{Cl}$  and  $\frac{1}{3}\text{H}_2\text{O}$ . Recalculation of structure factors on this assumption gives satisfactory agreement. Three small  $F_{hki0}$ 's were found to change sign and the final summation was made with these modifications.

The basal projection is unaffected by the twinning mentioned above, but a projection on (11 $\bar{2}$ 0) cannot be obtained since with the twinned crystals it is impossible to observe  $F_{h0\bar{h}l}$  and  $F_{h0\bar{h}l}$  separately. A side view of the structure was obtained by projection on (10 $\bar{1}$ 0). The sum  $\Sigma\Sigma F_{hh^2hl} \cos 2\pi(hx' + ky)$ , where  $x'$  is the coordinate along an orthohexagonal  $b$  axis, can be evaluated, since, in this space-group,  $F_{hh^2hl} = F_{hh^2hl}$ , and the effect of twinning in superposing the two corresponding reflexions does not affect the measurement of intensities. All the signs were taken as positive, and detailed calculation from the final structure later proved these to be all correct without change of sign.

From the two projections shown in Figs. 1 and 2 the atomic positions were estimated to be as in Table I; one parameter,  $z$ , for the water molecules in ( $d$ ), could not be observed directly and this has been obtained from packing considerations.

TABLE I.

Atomic parameters.		Space-group $C\bar{3}m$ .		
Atoms.		Position.		
Fe .....	( $a$ )	000		
2Cl and 1H <sub>2</sub> O .....	( $e$ )	$\frac{1}{2}00, 0\frac{1}{2}0, \frac{1}{2}\bar{1}0$		
2H <sub>2</sub> O .....	( $d$ )	$\frac{1}{2}\frac{2}{3}z, \frac{2}{3}\frac{1}{3}z$	$z = 0.1$	
6C .....	( $i$ )	$x\bar{x}z$	$x = 0.125$	$z = 0.200$
6N .....	( $i$ )	$x\bar{x}z$	$x = 0.205$	$z = 0.330$
6C (CH <sub>3</sub> ) .....	( $i$ )	$x\bar{x}z$	$x = 0.313$	$z = 0.460$

Tables II and III show the agreement between observed and calculated structure factors; a temperature correction  $e^{-B(\sin \theta/\lambda)^2}$ , with  $B = 2$ , has been applied to the calculated values.

TABLE II.

Observed and calculated values of  $F_{hki0}$  (temperature corrected).

Indices.	$F$ , obs.	$F$ , calc.	Indices.	$F$ , obs.	$F$ , calc.	Indices.	$F$ , obs.	$F$ , calc.	Indices.	$F$ , obs.	$F$ , calc.
10 $\bar{1}$ 0	34	40	80 $\bar{8}$ 0	12	18	71 $\bar{8}$ 0	17	14	43 $\bar{7}$ 0	16	7
20 $\bar{2}$ 0	28	31	11 $\bar{2}$ 0	19	22	22 $\bar{4}$ 0	74	83	53 $\bar{8}$ 0	0	4
30 $\bar{3}$ 0	15	-7	21 $\bar{3}$ 0	16	6	32 $\bar{5}$ 0	16	18	44 $\bar{8}$ 0	41	37
40 $\bar{4}$ 0	26	23	31 $\bar{4}$ 0	9	-5	42 $\bar{6}$ 0	45	29	54 $\bar{9}$ 0	22	15
50 $\bar{5}$ 0	4	2	41 $\bar{5}$ 0	13	9	52 $\bar{7}$ 0	5	6	64 $\bar{1}$ 0	19	19
60 $\bar{6}$ 0	33	29	51 $\bar{6}$ 0	9	-4	62 $\bar{8}$ 0	36	27	55 $\bar{1}$ 0	23	22
70 $\bar{7}$ 0	8	7	61 $\bar{7}$ 0	8	6	33 $\bar{6}$ 0	33	31	66 $\bar{1}$ 20	5	14

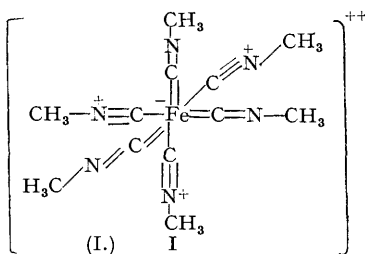
TABLE III.

Observed and calculated values of  $F_{hh^2hl}$  (temperature corrected).

Indices.	$F$ , obs.	$F$ , calc.	Indices.	$F$ , obs.	$F$ , calc.	Indices.	$F$ , obs.	$F$ , calc.	Indices.	$F$ , obs.	$F$ , calc.
11 $\bar{2}$ 0	19	22	0004	28	39	22 $\bar{4}$ 2	55	44	44 $\bar{8}$ 2	8	16
22 $\bar{4}$ 0	74	83	0005	12	21	22 $\bar{4}$ 3	58	41	44 $\bar{8}$ 3	9	17
33 $\bar{6}$ 0	33	31	0006	12	23	22 $\bar{4}$ 4	19	25	44 $\bar{8}$ 4	11	18
44 $\bar{8}$ 0	41	37	11 $\bar{2}$ 1	51	41	22 $\bar{4}$ 5	7	14	44 $\bar{8}$ 5	10	19
55 $\bar{1}$ 0	23	22	11 $\bar{2}$ 2	18	14	33 $\bar{6}$ 1	0	3	55 $\bar{1}$ 1	0	1
66 $\bar{1}$ 20	5	14	11 $\bar{2}$ 3	7	9	33 $\bar{6}$ 2	3	13	55 $\bar{1}$ 2	0	2
0001	36	39	11 $\bar{2}$ 4	6	11	33 $\bar{6}$ 3	0	3	66 $\bar{1}$ 21	10	18
0002	45	42	11 $\bar{2}$ 5	0	11	44 $\bar{8}$ 1	43	38	66 $\bar{1}$ 22	9	18
0003	42	39	22 $\bar{4}$ 1	49	38						

Fig. 1 shows the octahedral complex ion  $\text{Fe}(\text{CNMe})_6$  projected on to a plane parallel to a face of the octahedron. Measurement of the projected distance Fe-C leads to a calculated length of 1.85 Å. for the bond on the assumption of a regular octahedral arrangement of carbon atoms round the iron atom. The carbon atom is resolved in the sideways projection (Fig. 2), and its position is in good agreement with that expected for a regular octahedral distribution. When the other bond lengths are calculated from the projected lengths seen in Fig. 1, on the assumption of a linear FeCNMe arm, the C-N distance is found to be 1.18 Å., about the same as the distances in other compounds containing carbon triply bound to nitrogen, but the N-CH<sub>3</sub> length is calculated as 1.59 Å. This is much larger than the probable value for a single link, which for Pauling and Huggins's covalent radii (*Z. Krist.*, 1934, **87**, 205) would be 1.47 Å., and shows that the FeCNMe arms are not linear beyond the nitrogen atom. Bending of all the N-Me links out of the straight, so that the complex ion is flattened as a whole parallel to (0001), makes the projected length greater, and if a N-Me distance of 1.47 Å. is assumed, a bend of 7° is required to bring the projection of the methyl groups into the observed positions. Although it is less suitable for showing the detail, the (10 $\bar{1}$ 0) projection provides confirmation of the bend in the CNMe arm, particularly by the low electron density at  $xz = 0\frac{1}{2}$  where, if the arm were linear, there would be overlapping of two methyl groups with a consequent fairly high electron density.

The structure provides an accurate value for the Fe-C distance in a substance closely related to the ferrocyanides. The value 1.85 Å. agrees closely with that found in iron pentacarbonyl (Ewens and Lister, *Trans. Faraday Soc.*, 1939, 35, 681).



If the iron-carbon single and double bonds are taken as 2.00 and 1.79 Å., respectively, the interatomic distance for an intermediate bond with single bond-double bond resonance may be calculated from the expression  $R = 2.0 - (2.0 - 1.79)3x/(2x + 1)$ , where  $x$  represents the amount of double-bond character. If we use the observed value for  $R$  it is found that  $x = 0.46$ , or very nearly one-half. The complex ion may therefore be represented by the formula (I), analogous to that suggested by Pauling (*op. cit.*) for the ferrocyanide ion, the structure shown being in resonance with the similar structures obtained by interchanging the bonds.

The single-bond type places a negative charge on iron and a positive charge on the nitrogen,  $\text{Fe}::\text{C}::\text{N}^+\text{CH}_3$ , so with six single bonds there would be six positive charges on the nitrogen atoms and four negative charges on the central iron atom. The effect of double-bond formation is to displace positive charge from the nitrogen to the iron atom, both becoming neutral,  $\text{Fe}::\text{C}::\text{N}::\text{CH}_3$ , so when all the  $3d$ ,  $4s$ , and  $4p$  orbitals of the iron atom are used as in (I) there is a charge of  $-1$  on the iron and of  $+3$  divided among the six nitrogen atoms. In the single-bond form a partial ionic character may cause further neutralisation of the negative charge on the iron.

A simple qualitative explanation for the disorder effect in the structure may be given. The main architecture of the structure is determined by the shape and size of the long-armed octahedral complex ions which are packed as closely as is possible even if there were no other components of the structure, *i.e.*, the terminal methyl groups are separated in all directions at distances usual for these unlinked groups. The holes left are of sufficient size to hold the chlorine ions and water molecules. The distance from a chlorine ion to the iron at the centre of the cation is 5.2 Å. in the disordered structure, and would be increased to 6.2 Å. if the chlorine were transferred to the two-fold position occupied by part of the water, and it is natural to attribute the structure adopted to the lowering of potential energy consequent on the closer approach of the oppositely charged ions.

TABLE IV.

*Interatomic distances, bond lengths, and angles.*

Fe-C .....	1.85 Å.	C ... Cl <sup>-</sup> .....	4.08 Å.	CH <sub>3</sub> ... H <sub>2</sub> O (d) .....	3.39 and 3.73 Å.
C-N .....	1.18	C ... H <sub>2</sub> O (d) .....	5.09	CH <sub>3</sub> ... CH <sub>3</sub> .....	3.70 and 3.91
N-CH <sub>3</sub> .....	1.47	N ... Cl <sup>-</sup> .....	3.75	Cl <sup>-</sup> ... Cl <sup>-</sup> .....	5.23
Fe ... Cl <sup>-</sup> .....	5.23	N ... H <sub>2</sub> O (d) .....	4.77	Cl <sup>-</sup> ... H <sub>2</sub> O (d) .....	3.06
Fe ... H <sub>2</sub> O (e) .....	5.23	CH <sub>3</sub> ... Cl <sup>-</sup> .....	3.60	Angle C-N-CH <sub>3</sub> .....	173°
Fe ... H <sub>2</sub> O (d) .....	6.22				

Table IV gives a number of interatomic distances. The most important ones are derived directly from the Fourier analysis; those involving water molecules in position (d) are dependent on the value of  $z$  for the water molecule which is not resolved in the (1010) projection, and has been chosen from packing considerations; the N-CH<sub>3</sub> distance and the angle of bend are interdependent, since overlapping prevents an accurate direct determination of the bend which is, however, shown by both projections to be real.

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