

**2,6-DIMETHYLPHENYL (“XYLYL”) ISOCYANIDE COMPLEXES OF IRON:  
 PREPARATION AND CRYSTAL AND MOLECULAR STRUCTURES OF  
*trans*-DICHLOROTETRAKIS(XYLYL ISOCYANIDE)IRON(II),  
 $[\text{FeCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4]$  AND CHLOROPENTAKIS(XYLYL  
 ISOCYANIDE)IRON(II) TETRACHLOROFERRATE(III),  
 $[\text{FeCl}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_5][\text{FeCl}_4]$**

MICHAEL G.B. DREW,

*Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD (Great Britain)*

GEORGE H. DODD, JACQUELINE M. WILLIAMSON and GERALD R. WILLEY

*Department of Chemistry, University of Warwick, Coventry CV4 7AL (Great Britain)*

(Received April 16th, 1986)

**Summary**

The reaction of  $\text{FeCl}_2$  and xylyl isocyanide (L) ( $\text{L} = 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ ) gives two products viz. purple  $\text{FeCl}_2\text{L}_4$  (**1**) and orange  $\text{Fe}_2\text{Cl}_5\text{L}_5$  (**2**). The structural identity of these complexes has been determined by single crystal X-ray diffraction studies. Crystals of **1** are tetragonal, space group  $P4nc$ ,  $Z = 2$ , in a unit cell of dimensions  $a$  13.853(8),  $c$  8.803(8) Å. The structure has been refined to  $R$  0.068 ( $R_w$  0.071) for 613 independent reflections above background. The structure comprises octahedral  $\text{Fe}^{\text{II}}$  units with the two chlorines mutually *trans*. ( $\text{Fe}-\text{Cl}$  2.318(7), 2.288(6) Å). The four isocyanide ligands, in a *cis* arrangement around the metal, are essentially linear ( $\text{Fe}-\text{C}-\text{N}$  177.9(7),  $\text{C}-\text{N}-\text{C}$  173.8(8)°). Crystals of **2** are monoclinic, space group  $P2_1/a$ ,  $Z = 4$ , in a unit cell of dimensions  $a$  10.310(8),  $b$  20.468(17),  $c$  23.026(23) Å,  $\beta$  99.0(1)°. The structure has been refined to  $R$  0.077 ( $R_w$  0.081) for 2950 independent reflections above background. The complex is a ‘mixed’  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  species and consists of octahedral  $[\text{FeClL}_5]^+$  cations based on  $\text{Fe}^{\text{II}}$ , and tetrahedral  $[\text{FeCl}_4]^-$  anions based on  $\text{Fe}^{\text{III}}$ . For the cation, variations in  $\text{Fe}-\text{C}$  bond lengths between isocyanide ligands *trans* to one another and *trans* to chloride are discussed in terms of a *trans*-effect dominated by the strong  $\pi$ -acceptor ability of the isocyanide ligands. Further comparisons are drawn with  $\text{Fe}-\text{C}$  bond lengths observed in **1** and in similar cationic  $\text{Fe}^{\text{II}}$  systems. The  $[\text{FeCl}_4]^-$  anion has tetrahedral symmetry (mean  $\text{Fe}-\text{Cl}$  2.157 Å, mean  $\text{Cl}-\text{Fe}-\text{Cl}$  109.3°). Previous studies of the tetrahedral  $[\text{FeCl}_4]^-$  anion (high spin  $\text{Fe}^{\text{III}}$ ) show a mean  $\text{Fe}-\text{Cl}$  of 2.180 Å.

## Introduction

It has been known for sometime that alkyl isocyanides bind cooperatively to hemoglobin and hemoproteins in general [1]. Recently we have described preliminary investigations of the binding of various aryl isocyanides to hemoglobin and myoglobin in order to assess their viability as probes for distal effects within these hemoproteins [2]. There is little doubt that aryl isocyanides bind with significantly greater affinity than alkyl isocyanides to the heme iron most likely as a result of favourable metal ( $d_\pi$ )  $\rightarrow$  ligand ( $\pi^*$ ) interactions involving the delocalised  $\pi_{CN}^*$  and  $\pi_{aromatic\ ring}^*$  systems.

Allied to this study we are interested in structural parameters of related inorganic Fe  $\sim$  RNC complexes R = alkyl vs. aryl for a quantitative measure of this conjugative  $\pi$ -acceptor enhancement; in particular Fe–C–N–R dimensions and the exact conformation of bound ligands, linear vs. bent. Herein we report the isolation and crystal structure of  $FeCl_2L_4$  (**1**) and  $Fe_2Cl_5L_5$  (**2**) involving L = 2,6-dimethylphenyl isocyanide as a monodentate C-donor ligand. Compound **2** is of considerable interest in its own right as a "mixed"  $Fe^{II}/Fe^{III}$  species.

## Experimental

All reactions were carried out under nitrogen and manipulations of materials in a standard "dry box" purged with pre-purified tank nitrogen. Solvents were stored over  $CaH_2/P_2O_5$  and distilled under nitrogen prior to use. Anhydrous  $FeCl_2$  was used as obtained commercially. 2,6-Dimethylphenyl isocyanide was prepared from 2,6-dimethylphenyl amine by the phase-transfer catalysed Hoffman carbylamine reaction following the procedure of Gokel et al. [3] Routine infrared spectra were recorded on a Perkin–Elmer 580B spectrophotometer with muller samples placed between CsI plates. Proton ( $^1H$ ) NMR spectra were recorded on a Bruker WH90 instrument (90 MHz) using  $CDCl_3$  solutions doped with tetramethylsilane as internal reference.

### *Reaction of $FeCl_2$ with xylyl isocyanide*

A solution of xylyl isocyanide (1.50 g, 11.4 mmol) in methanol (20  $cm^3$ ) was added dropwise to a chilled (0°C) and mechanically stirred solution of  $FeCl_2$  (0.70 g, 5.54 mmol) in methanol (25  $cm^3$ ) maintained under a nitrogen atmosphere. On warming to room temperature the solution developed an intense purple colour. This solution was stirred at room temperature for several days and allowed to stand when purple crystals (**1**) began to form. These were collected, washed with n-hexane, and dried in vacuo. Yield 0.77 g, (42%).

The decanted solution was set aside to stand with the subsequent deposition of orange crystals (**2**) over a period of several days. These were collected and recrystallized from the minimum amount of hot methanol. Yield 0.19 g (10%). Microanalytical and spectroscopic data for **1** and **2** are listed in Table 1.

### *X-ray crystallography*

*Crystals of 1.*  $[FeCl_2L_4]$ ,  $C_{36}H_{36}N_4FeCl_2$ ,  $M = 651.5$ , tetragonal,  $a$  13.853 (8),  $c$  8.803(8) Å,  $U$  1689.5 Å<sup>3</sup>,  $Z = 2$ ,  $D_m$  1.26(3),  $D_c$  1.27 g  $cm^{-3}$ ,  $F(000) = 680$ ,  $\lambda$  0.7107 Å,  $\mu$  6.47  $cm^{-1}$ , space group  $P4nc$ .

(Continued on p. 167)

TABLE 1

MICROANALYTICAL AND SPECTROSCOPIC DATA FOR THE LIGAND AND METAL COMPLEXES

Compound	Colour	M.p. (°C)	IR <sup>a</sup>	<sup>1</sup> H NMR <sup>b</sup>	Analysis (Found (calcd.)(%))
2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC (L)	White	74–75	2117vs	2.42 7.1–7.3	C <sub>9</sub> H <sub>9</sub> N 131.17 <i>M</i> <sup>c</sup> 131
FeCl <sub>2</sub> L <sub>4</sub> (1)	Purple	138–139	2130vs 322s,br	2.65 7.2–7.5	C <sub>36</sub> H <sub>36</sub> N <sub>4</sub> FeCl <sub>2</sub> C, 66.1 (66.4) H, 5.7 (5.6) N, 8.3 (8.6) Fe, – (8.6) Cl, 10.9 (10.9)
Fe <sub>2</sub> Cl <sub>5</sub> L <sub>5</sub> (2)	Orange	168–169	2215w 2170vs 2160m 380vs,br		C <sub>45</sub> H <sub>45</sub> N <sub>5</sub> Fe <sub>2</sub> Cl <sub>5</sub> C, 56.8 (57.2) H, 4.8 (4.8) N, 7.1 (7.4) Fe, – (11.8) Cl, 18.6 (18.8)

<sup>a</sup>  $\nu$ (cm<sup>-1</sup>) in Nujol mull. <sup>b</sup>  $\delta$ (CH) (ppm) for CDCl<sub>3</sub> solutions with reference to tetramethylsilane ( $\delta$  = 0).<sup>c</sup> Mass spectrum *m/z*.

TABLE 2

ATOMIC COORDINATES ( $\times 10^4$ ) FOR 1 (with estimated standard deviations in parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Fe(1)	0	0	0
Cl(1)	0	0	–2635(8)
Cl(2)	0	0	2600(7)
C(11)	1197(4)	–646(5)	–50(15)
N(12)	1910(4)	–1062(4)	–60(14)
C(13)	2716(5)	–1653(5)	–114(14)
C(14)	3487(6)	–1342(7)	–1002(13)
C(15)	4271(8)	–1986(16)	–1044(23)
C(16)	4238(12)	–2857(15)	–388(27)
C(17)	3455(13)	–3132(8)	548(21)
C(18)	2677(8)	–2520(6)	688(15)
C(19)	3513(11)	–367(12)	–1721(19)
C(201)	1798(11)	–2798(9)	1552(18)

TABLE 3

ATOMIC COORDINATES ( $\times 10^4$ ) FOR 2 (with estimated standard deviations in parentheses)

Atom	x	y	z
Fe(2)	8654(2)	2408(1)	4401(1)
Cl(21)	9598(8)	2736(5)	3687(3)
Cl(22)	9648(9)	1548(4)	4748(4)
Cl(23)	6692(6)	2136(4)	4108(3)
Cl(24)	8845(8)	3068(4)	5146(4)
Fe(1)	6732(2)	1750(1)	1867(1)
Cl(1)	4804(3)	1142(2)	1756(2)
C(11)	7330(13)	1144(6)	1336(6)
N(12)	7595(11)	765(5)	1014(5)
C(13)	7802(17)	339(7)	585(7)
C(14)	6998(21)	348(10)	68(9)
C(15)	7161(36)	-119(17)	-366(16)
C(16)	8090(45)	-547(19)	-255(18)
C(17)	8880(31)	-584(10)	233(13)
C(18)	8839(22)	-119(9)	696(11)
C(19)	9720(23)	-115(10)	1275(12)
C(110)	5914(26)	844(15)	-57(10)
C(31)	8331(14)	2203(7)	1929(5)
N(32)	9242(11)	2478(5)	1942(5)
C(33)	10473(13)	2763(7)	1877(6)
C(34)	11335(13)	2365(9)	1694(7)
C(35)	12544(18)	2638(10)	1634(8)
C(36)	12806(16)	3263(13)	1726(9)
C(37)	11863(22)	3660(9)	1928(8)
C(38)	10669(17)	3421(8)	2020(6)
C(39)	11165(16)	1649(8)	1620(8)
C(310)	9603(17)	3814(8)	2249(9)
C(21)	5989(13)	2262(6)	1221(6)
N(22)	5533(12)	2588(5)	846(5)
C(23)	4959(15)	3052(7)	420(6)
C(24)	3771(16)	2886(9)	63(6)
C(25)	3289(20)	3407(13)	-344(7)
C(25)	3972(34)	3945(12)	-367(11)
C(27)	5109(23)	4049(10)	-31(10)
C(28)	5604(18)	3619(8)	371(7)
C(29)	6909(21)	3744(10)	737(10)
C(210)	3113(18)	2234(10)	112(9)
C(41)	7390(13)	1215(7)	2519(7)
N(42)	7742(13)	905(6)	2912(6)
C(43)	8026(21)	466(9)	3406(8)
C(44)	6953(32)	200(9)	3639(9)
C(45)	7313(37)	-207(13)	4103(12)
C(46)	8643(56)	-335(18)	4317(14)
C(47)	9613(40)	-73(13)	4080(13)
C(48)	9311(32)	362(10)	3590(9)
C(49)	5654(29)	335(13)	3395(11)
C(410)	10354(22)	663(13)	3321(12)
C(51)	6048(14)	2327(7)	2383(5)
N(52)	5556(11)	2678(5)	2659(5)
C(53)	4846(15)	3138(9)	2963(7)
C(54)	5244(23)	3756(9)	3004(8)
C(55)	4442(27)	4186(13)	3296(11)
C(56)	3366(32)	3949(17)	3488(11)

TABLE 3 (continued)

C(57)	3090(26)	3308(15)	3486(8)
C(58)	3805(18)	2873(10)	3195(7)
C(59)	6361(24)	4012(10)	2742(12)
C(510)	3438(16)	2175(12)	3147(8)

*Crystals of 2.*  $[\text{Fe}_2\text{Cl}_5\text{L}_5]$ ,  $\text{C}_{45}\text{H}_{45}\text{N}_5\text{Fe}_2\text{Cl}_5$ , monoclinic,  $M = 944.8$ ,  $a$  10.310(8),  $b$  20.468(17),  $c$  23.026(23) Å,  $\beta$  99.0(1)°,  $U$  4799.25 Å<sup>3</sup>,  $D_m$  1.27,  $D_c$  1.31 g cm<sup>-3</sup>,  $F(000) = 1948$ ,  $Z = 4$ ,  $\lambda$  0.7107 Å,  $\mu$  9.32 cm<sup>-1</sup>, space group  $P2_1/a$ .

TABLE 4

MOLECULAR DIMENSIONS IN 1 AND 2 (distances (Å), angles (°))

<i>Coordination sphere in 1</i>					
Fe(1)–Cl(1)					2.318(7)
Fe(1)–Cl(2)					2.288(6)
Fe(1)–C(11)					1.895(6)
C(11)–N(12)					1.150(8)
N(12)–C(13)					1.393(9)
Cl(1)–Fe(1)–C(11)					88.66(41)
Cl(2)–Fe(1)–C(11)					91.34(41)
Fe(1)–C(11)–N(12)					177.9(7)
C(11)–N(12)–C(13)					173.8(8)
<i>Coordination sphere in 2</i>					
Fe(1)–Cl(1)					2.371(4)
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
Fe(1)–C( $n$ 1)	1.927(14)	1.882(13)	1.915(15)	1.896(14)	1.908(14)
C( $n$ 1)–N( $n$ 2)	1.143(18)	1.135(17)	1.114(19)	1.117(19)	1.144(18)
N( $n$ 2)–C( $n$ 3)	1.366(20)	1.429(18)	1.457(18)	1.444(22)	1.461(21)
Cl(1)–Fe(2)–C( $n$ 1)	87.3(4)	88.8(4)	176.7(4)	88.2(4)	89.5(4)
C(11)–Fe(2)–C( $n$ 1)	–	90.5(5)	89.4(5)	90.2(6)	176.8(5)
C(21)–Fe(2)–C( $n$ 1)	–	–	91.6(5)	176.9(6)	89.0(5)
C(31)–Fe(2)–C( $n$ 1)	–	–	–	91.5(5)	93.9(6)
C(41)–Fe(2)–C(51)	–	–	–	–	90.2(6)
Fe(2)–C( $n$ 1)–N( $n$ 2)	174.9(12)	177.6(11)	176.9(12)	177.6(14)	174.7(11)
C( $n$ 1)–N( $n$ 2)–C( $n$ 3)	173.7(13)	173.7(13)	170.2(13)	172.3(16)	174.8(12)
<i>Anion</i>					
Fe(2)–Cl(21)					2.164(9)
Fe(2)–Cl(22)					2.150(9)
Fe(2)–Cl(23)					2.142(6)
Fe(2)–Cl(24)					2.171(8)
Cl(21)–Fe(2)–Cl(22)					106.40(39)
Cl(21)–Fe(2)–Cl(23)					112.93(29)
Cl(22)–Fe(2)–Cl(23)					106.53(35)
Cl(21)–Fe(2)–Cl(24)					113.78(35)
Cl(22)–Fe(2)–Cl(24)					104.75(34)
Cl(23)–Fe(2)–Cl(24)					111.68(32)

Precession photographs established the preliminary cell constants and space groups. Crystals were mounted to rotate around the  $a$  axes on a Stoe STADI2 diffractometer and data were collected via variable width  $\omega$ -scan. Background counts were 20 s and a scan rate of  $0.0333^\circ \text{ s}^{-1}$  was applied to a width of  $(2.0 + 0.5 \sin\mu/\tan\theta)$ . For **1** 1760 independent reflections with  $2\theta < 50^\circ$  were measured of which 613 having  $I > 3\sigma(I)$  were used in subsequent refinement. For **2** 8220 independent reflections with  $2\theta < 50^\circ$  were measured of which 2950 with  $I > 3\sigma(I)$  were used subsequently. Both structures were solved from the Patterson function. In **1** the molecule had  $C_4$  symmetry with the iron and two chlorine atoms on the rotation axis. In **2** both cations and anions were in general positions. For both structures, hydrogen atoms were included in calculated trigonal or tetrahedral positions. The methyl groups were refined as rigid groups. Non-hydrogen atoms were given anisotropic thermal parameters and both structures were refined by full-matrix least-squares. In **1** the final  $R$  value was 0.068 ( $R_w = 0.071$ ). The opposite (and rejected) enantiomorph gave  $R$  0.069. We tried refinement of a disordered model in  $P4_2/nmc$  but this was unsuccessful.

In **2** the final  $R$  value was 0.077 ( $R_w = 0.081$ ). In the final cycles of refinement, no shift/error ratio was greater than  $0.20\sigma$ . Difference Fourier maps showed no significant peaks. All calculations were carried out using SHELX-76 [4] and our own programs on the Amdahl V7A computer at the University of Reading. Final atomic coordinates are given in Tables 2 and 3. Dimensions in the coordination spheres are provided in Table 4.

## Results and discussion

Treatment of  $\text{FeCl}_2$  with xylyl isocyanide (L) in methanol under a nitrogen atmosphere yields purple crystals of  $\text{FeCl}_2\text{L}_4$  (**1**) and, subsequently, orange crystals of  $\text{Fe}_2\text{Cl}_5\text{L}_5$  (**2**). Elemental analyses obtained for these compounds are in excellent agreement with their proposed formulation (Table 1). In this regard the reaction appears to resemble previous  $\text{Fe}^{\text{II}}$ -isocyanide systems with the formation of two products, usually violet and orange in colour, which have been assigned as the octahedral *trans*- and *cis*- $\text{FeX}_2(\text{ligand})_4$  isomers, respectively [5]. Examples include both monodentate and bidentate ligands e.g.,  $\text{FeX}_2(\text{ArNC})_4$ , [6] ( $\text{Ar} = p\text{-Me.C}_6\text{H}_4$ ,  $\text{X} = \text{halogen}$ );  $\text{FeCl}_2(\text{ArNC})_4$ , [7] ( $\text{Ar} = p\text{-Me.O.C}_6\text{H}_4$ );  $\text{Fe}(\text{CN})_2(\text{MeNC})_4$ , [8,9] for which the *trans*- [10] and *cis*- [11] isomers have been confirmed by early X-ray structure determinations;  $\text{FeCl}_2(\text{t-BuDiNC})_2$ , [12] ( $\text{t-BuDiNC} = 1,2\text{-bis-(4-}t\text{-butyl-2-isocyanophenoxy)ethane}$ ) and the related unsubstituted  $\text{FeCl}_2(\text{HDiNC})_2$ , [13]. In most instances *cis*  $\rightleftharpoons$  *trans* isomerisations have been noted either by use of a catalyst e.g.,  $\text{AlCl}_3$  or directly in solution.

Confirmation of **1** as the *trans*-isomer comes from spectroscopic and X-ray structural data. The IR spectrum shows a single sharp  $\nu(\text{C}\equiv\text{N})$  band ( $2130 \text{ cm}^{-1}$ ), as expected for the *trans*-geometry, which is shifted  $+13 \text{ cm}^{-1}$  with reference to the stretching frequency of uncomplexed ligand. This shift to high energy is relatively small and can be attributed to a strong ligand ( $\sigma_{\text{NC}}^2$ )  $\rightarrow$  metal ( $d_\sigma$ ) interaction as nullified by backbonding involving metal ( $d_\pi$ )  $\rightarrow$  ligand ( $\pi^*$ ) interactions involving readily available vacant  $\pi^*$  orbitals of the aromatic ring. The superior  $\pi$ -acceptor ability aryl  $>$  alkyl isocyanides is well recognised [14]. An intense band at  $322 \text{ cm}^{-1}$  is assigned as  $\nu(\text{FeCl})$ . The proton NMR spectrum shows a singlet  $\delta$  2.65 for the

methyl protons and a multiplet for the aromatic protons  $\delta$  7.2–7.5 ppm both with slight downfield shifts.

The identity of **2** was only resolved by an X-ray structure determination. It is not the expected *cis*-isomer but, rather surprisingly, the ionic complex  $[\text{FeClL}_5]^+ [\text{FeCl}_4]^-$  based on an octahedral  $\text{Fe}^{\text{II}}$  cation and a tetrahedral  $\text{Fe}^{\text{III}}$  anion. The IR spectrum shows  $\nu(\text{C}\equiv\text{N})$  bands at 2215, 2170 and  $2160\text{ cm}^{-1}$  and a broad, intense band at  $380\text{ cm}^{-1}$  assigned as  $\nu(\text{FeCl})$  cf. the related vibration for the  $\text{FeCl}_4$  anion in  $[\text{PCl}_4][\text{FeCl}_4]$  [15]. Indeed we now find that xylyl isocyanide also reacts with  $\text{FeCl}_3$  in a redox reaction to give **2** along with other products [16]. Stone et al. [17] have reported that treatment of  $\text{Fe}^{\text{II}}$  halides in tetrahydrofuran with Na/Hg in the presence of excess xylyl isocyanide results in complete reduction to the red, five-coordinate iron ( $d^8$ ) complex  $[\text{Fe}(\text{xylyl isocyanide})_5]^0$ .

### Crystal structures

The structure of **1** consists of discrete units of  $[\text{FeCl}_2\text{L}_4]$  and the molecule is shown in Fig. 1 together with the atomic numbering scheme. Atoms Fe(1), Cl(1) and Cl(2) are coincident with the four-fold axis. The  $\text{Fe}^{\text{II}}$  ion has an approximately octahedral environment with independent dimensions of Fe(1)–Cl(1) 2.318(7), Fe(1)–Cl(2) 2.288(6), and Fe(1)–C(11) 1.895(6) Å.

The structure of **2** consists of discrete ions of formula  $[\text{FeClL}_5]^+$  and  $[\text{FeCl}_4]^-$ . It seems certain from a study of the dimensions of the ions (see below) that both are uncharged and that the cation contains  $\text{Fe}^{\text{II}}$  and the anion  $\text{Fe}^{\text{III}}$ . The cation is shown as Fig. 2 with the atomic numbering system. The  $\text{Fe}^{\text{II}}$  ion has an approximately octahedral environment with dimensions Fe(1)–Cl(1) 2.371(4) and Fe(1)–C(11) 1.927(14), 1.882(13), 1.915(15), 1.896(14), 1.908(14) Å. In comparing the structures of **1** and **2**, we note that the Fe–Cl distance in **2** is 0.068 Å longer

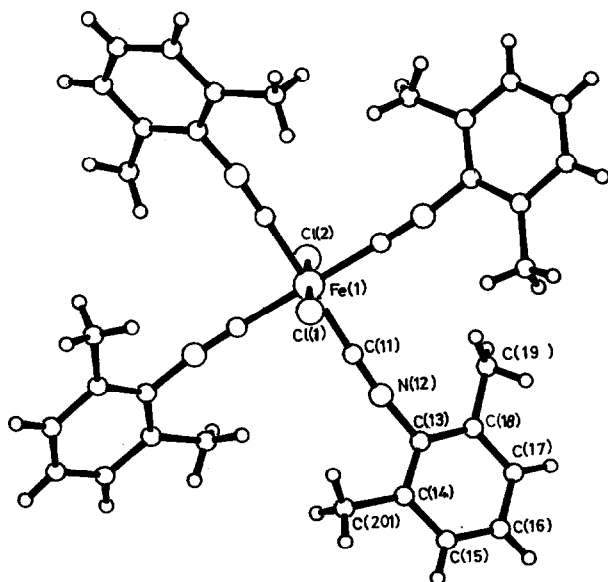


Fig. 1. Molecular structure of **1**.

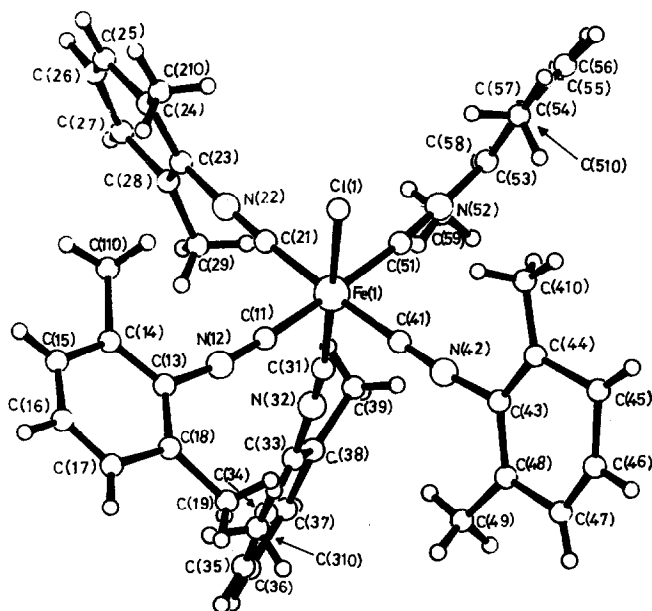


Fig. 2. Molecular structure of the cation of 2.

than the mean Fe–Cl distance in 1 and consider this to be due to the *trans* effect of the isocyanide ligand. It is interesting that the dimensions of this particular CNR ligand *trans* to Fe–Cl are no different from those of the remainder which are *cis* to Fe–Cl. This confirms that CNR is a much stronger  $\pi$ -acceptor than Cl. There are precedents for diamagnetic cationic iron(II) species of the type  $[\text{FeCl}(\text{L})_n(\text{CNR})_{5-n}]^+$  e.g.,  $[\text{FeCl}(p\text{-Me.O.C}_6\text{H}_4\text{NC})_5][\text{ClO}_4]$  [7],  $[\text{FeCl}(\text{CO})(p\text{-Me.O.C}_6\text{H}_4\text{NC})_4][\text{HgCl}_3]$  [7],  $[\text{FeCl}(\text{CNAr})_2(\text{L})_3][\text{ClO}_4]$  [18] where Ar =  $\text{C}_6\text{H}_5$ ,  $p\text{-Me.C}_6\text{H}_4$ ,  $p\text{-Me.O.C}_6\text{H}_4$ ,  $p\text{-NO}_2\text{-C}_6\text{H}_4$ ,  $\text{O-Me.C}_6\text{H}_4$ , 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; L =  $\text{PPh}(\text{OEt})_2$ , and  $[\text{FeCl}(p\text{-Me.C}_6\text{H}_4\text{NC})_3(\text{PPh}_3)_2][\text{Y}]$  [18] where Y =  $\text{ClO}_4^-$ ,  $\text{BPh}_4^-$  or  $\text{FeCl}_4^-$ . X-ray crystal structure determinations have been reported for  $[\text{FeCl}(\text{PPhF}_2)_5][\text{FeCl}_4]$  [19],  $[\text{FeCl}(\text{PPh}_3)_2(p\text{-Me.C}_6\text{H}_4\text{NC})_3][\text{FeCl}_4]$  [20] and  $[\text{FeCl}(\text{PPh}(\text{OEt})_2)_3(p\text{-Me.C}_6\text{H}_4\text{NC})_2][\text{FeCl}_4]$  [21] of which the last two are of direct relevance as both contain a chloride *trans* to an isocyanide group. Fe–Cl bond lengths are 2.338(2) Å for  $[\text{FeCl}(\text{PPh}_3)_2(p\text{-Me.C}_6\text{H}_4\text{NC})_3]^+$  (3) and 2.326(4) Å for  $[\text{FeCl}(\text{PPh}(\text{OEt})_2)_3(p\text{-Me.C}_6\text{H}_4\text{NC})_2]^+$  (4). That these Fe–Cl bond lengths are more similar to those of 1 rather than of 2 is somewhat surprising and may well be a result of the steric requirements of xylyl isocyanide ligands in close proximity. By the same token such steric requirements may be a contributing factor in the observed lengthening of the Fe–Cl bond in 2 with respect to that in 1.

A direct comparison between 1 and 2 shows Fe–C distances to be equivalent e.g. 1.895(6) Å in 1 and an averaged distance of 1.905 Å in 2. In 3 the Fe–C distances are 1.813(4) Å (*trans* to Cl) and 1.874(4), 1.860(4) Å for the mutually *trans* isocyanide ligands. In the case of 4 the Fe–C distances are appreciably shorter at 1.72(1) Å (*trans* to Cl) and 1.74(1) Å (*trans* to a diethylphenylphosphinate ligand). There are no significant differences between Fe–C distances of mutually *trans* isocyanide ligands as observed for 1, 2 and 3. However it is noticeable that in 2 the

Fe–C bond (1.915(18) Å) of the isocyanide ligand *trans* to Cl is no shorter than that of the remainder (all mutually *trans*) but is indeed somewhat longer than the comparable distance in **3** (1.813(4) Å) and particularly in **4** 1.74(1) Å. Bearing in mind the different ligand environments in **1**, **2** with respect to **3**, **4** e.g. the number and location of isocyanide ring substituents and the extra competition in a  $\pi$ -acceptor sense of the phosphine ligands in the latter, all these bond variations can be rationalised in terms of a *trans*-effect i.e. the Fe–C bonds are lengthened when the strong  $\pi$ -acceptor isocyanide ligands are *trans* to one another and shortened when the isocyanides are *trans* to weaker  $\pi$ -acceptor ligands. In **4** it is noticeable that the Fe–C  $\pi$ -interaction has a remarkable effect on the C–N bond lengths (1.23(2), 1.23(2) Å) which are significantly longer than is usually accepted for a C $\equiv$ N bond. There is no such increase in **1**, **2** or **3**.

The Fe–C–N–R linkage is essentially linear in both **1** and **2** with Fe–C–N and C–N–R angles of 177.9(7), 173.8(8) in **1** and mean values of 176.3, 172.9° in **2**. Of particular interest is the position of the phenyl rings with respect to the equatorial plane. In **1** the phenyl rings make angles of 36° with the FeC<sub>4</sub> plane. In **2** the four phenyl rings on ligands 1,2,4,5 subtend angles of 27.3, 73.0, 72.3, 74.0°, respectively with the equatorial plane whereas the unique ligand *n* = 3 (*trans* to Cl), is almost perpendicular making an angle of 88.2°. There seems to be no significant difference between the C(*n*1)–N(*n*2) bond lengths with values of 1.150(8) in **1** and (mean) 1.131 Å in **2**. However there is a correlation between N(*n*2)–C(*n*3) length and the position of the phenyl ring. Thus ligand 1 in **2** has the phenyl ring close to the equatorial plane (angle of intersection 27.3°) and an N(12)–C(13) bond (1.366(20) Å) much smaller than the rest. It may well be that this indicates some M–C–N–aryl conjugation. The remainder e.g., ligands 2–5, have phenyl rings which are almost perpendicular to the equatorial plane (and thus no possibility of overlap) and here the N(*n*2)–C(*n*3) bonds are conspicuously longer at 1.429(18), 1.457(18), 1.444(22) and 1.461(21) Å, respectively. The N(12)–C(13) distance in **1** (1.393(9) Å) is intermediate between these two extremes with an angle of intersection for the phenyl ring at 36.6°.

The [FeCl<sub>4</sub>] anion is symmetrical with tetrahedral geometry, mean Fe–Cl 2.157 Å, mean ClFeCl 109.3°, but there is quite a range of angles (104.7(3) – 113.8(3)°) which is presumably due to packing effects. A search of the Cambridge Data Centre files [22] for tetrahedral [FeCl<sub>4</sub>] complexes reveals numerous structures containing the [FeCl<sub>4</sub>]<sup>–</sup> anion but only three containing the [FeCl<sub>4</sub>]<sup>2–</sup> anion. The latter show an average Fe–Cl bond length of 2.305 Å which is considerably greater than the mean value of 2.180 Å computed for the 29 examples of the former. Differences in Fe–Cl bond lengths between tetrahedral [FeCl<sub>4</sub>]<sup>2–</sup> (high spin Fe<sup>II</sup>) and [FeCl<sub>4</sub>]<sup>–</sup> (high spin Fe<sup>III</sup>) have been discussed previously by Lauher and Ibers [23]. Clearly the present structure contains [FeCl<sub>4</sub>]<sup>–</sup> anions with a somewhat shortened Fe–Cl bond distance when compared with the mean value of previous studies.

In both structures there are no significant intermolecular distances less than the sum of Van der Waals radii.

### Acknowledgment

We thank A.W. Johans for assistance with the crystallographic investigations and SERC for funds for the diffractometer.

## References

- 1 See e.g., R.C.C. St. George and L. Pauling, *Science*, 114 (1951) 629; F.X. Cole and Q.H. Gibson, *J. Biol. Chem.*, 248 (1973) 4998; P.I. Reisberg and J.S. Olson, *J. Biol. Chem.*, 255 (1980) 4144; M.P. Mims, J.S. Olson, I.M. Russu, S. Miura, T.E. Cedel and C. Ho, *J. Biol. Chem.*, 258 (1983) 6125; T.G. Traylor and D.V. Stynes, *J. Amer. Chem. Soc.*, 102 (1980) 5938.
- 2 K. Dickinson, G.H. Dodd, M. Wood and G.R. Willey, *Biochem. J.*, submitted for publication.
- 3 G.W. Gokel, R.P. Widera and W.P. Weber, *Org. Synth.*, 55 (1976) 96.
- 4 G.M. Sheldrick, SHELX-76, Program for crystal structure determination, University of Cambridge, 1976.
- 5 For general reviews of the early studies of metal isocyanide complexes see L. Malatesta and F. Bonati (Eds.), *Isocyanide complexes of metals*, Wiley-Interscience, London, 1969 and P.M. Treichel, *Adv. Organomet. Chem.*, 11 (1973) 21. More recent coverage is given by E. Singleton and H.E. Oosthuizen, *Adv. Organomet. Chem.*, 22 (1983) 209.
- 6 L. Malatesta, A. Sacco and G. Padoa, *Ann. Chim. (Rome)*, 43 (1953) 617.
- 7 M.J. Mays and B.E. Prater, *J. Chem. Soc. (A)*, (1969) 2525.
- 8 E.G.J. Hartley, *J. Chem. Soc.*, 103 (1913) 1195.
- 9 F. Hoelzl, W. Hauser and M. Eckmann, *Monatsh. Chem.*, 48 (1927) 71.
- 10 (*trans*-isomer); R. Hulme and H.M. Powell, *J. Chem. Soc.*, (1957) 719;
- 11 (*cis*-isomer); J.B. Wilford, N.O. Smith and H.M. Powell, *J. Chem. Soc. (A)*, (1968) 1544.
- 12 D.T. Plummer and R.J. Angelici, *Inorg. Chem.*, 22 (1983) 4063.
- 13 J.A. Kargol and R.J. Angelici, *Inorg. Chim. Acta*, 68 (1983) 127.
- 14 See e.g., B.E. Bursten and R.F. Fenske, *Inorg. Chem.*, 16 (1977) 1777; J.A.S. Howell, J.-Y. Saillard, A. Le Beuze, and G. Jaouen, *J. Chem. Soc., Dalton Trans.*, (1982) 2533.
- 15 T.J. Kistenmacher and G.D. Stucky, *Inorg. Chem.*, 7 (1968) 2150.
- 16 M.G.B. Drew and G.R. Willey, unpublished data.
- 17 J.M. Bassett, D.E. Berry, G.K. Barker, M. Green, J.A.K. Howard and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1979) 1003.
- 18 G. Albertin, E. Bordignon, A.A. Orio, and G. Troilo, *Inorg. Chem.*, 14 (1975) 238.
- 19 W.S. Sheldrick and O. Stelzer, *Chem. Ber.*, 110 (1977) 3421.
- 20 G. Pelizza, G. Albertin, E. Bordignon, A.A. Orio, and S. Calogero, *Acta Cryst.*, B33 (1977) 3761.
- 21 G. Albertin, A.A. Orio, S. Calogero, L. Di Sipio, and G. Pelizza, *Acta Cryst.*, B32 (1976) 3023.
- 22 F.H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 16 (1983) 146.
- 23 J.W. Lauher and J.A. Ibers, *Inorg. Chem.*, 14 (1975) 348.