Tableau 5. *Liaisons hydrogène*

1 2 3	d_{12}	d_{23}	d_{13} (Å)	$\angle 123$ (°)
O(4)–H(5)···O(2^{iv})	0,85 (3)	1,85 (3)	2,693 (2)	174 (3)
O(4)–H(6)···O(3^{v})	0,83 (3)	1,92 (3)	2,748 (2)	177 (3)
O(5)–H(7)···O(3^{vi})	0,82 (3)	1,90 (3)	2,713 (2)	173 (3)
O(5)–H(8)···O(2^{vii})	0,68 (3)	2,01 (3)	2,687 (2)	172 (3)

Tableau 6. *Code de symétrie*

(i)	$\bar{x}$,	$\bar{y}$,	$\bar{z}$	(v)	$1-x$,	$\bar{y}$,	$\bar{z}$
(ii)	$\bar{x}$,	$1-y$,	$\bar{z}$	(vi)	$x-1$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$
(iii)	x,	$1+y$,	z	(vii)	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$
(iv)	$1-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$				

(Tableau 5). Il n'y a pas de liaison hydrogène mettant en jeu les atomes d'hydrogène de la chaîne aliphatique, les contacts possibles suivant ce mode étant supérieurs à 3,5 Å.

Le code de symétrie est explicité dans le Tableau 6.

Discussion

Cette structure est tout à fait comparable à celle de l'éthanedisulfonate-1,2 de cuivre tétrahydraté (Charbonnier, Faure & Loiseleur, 1977a). Dans ces deux structures les atomes de cuivre présentent le même entourage octaédrique et les coordinats établissent des ponts entre les atomes de métal. Les cristaux sont formés par des chaînes infinies assemblées par des liaisons hydrogène dues aux molécules d'eau.

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The Crystal Structure of Chlorobis(triphenylphosphine)tris(4-tolyl isocyanide)iron(II) Tetrachloroferrate(III)

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Crystals of the title compound are triclinic ($P\bar{1}$) with unit-cell dimensions: $a = 12 \cdot 85$ (1), $b = 19 \cdot 44$ (2), $c = 12 \cdot 45$ (1) Å, $\alpha = 92 \cdot 6$ (1), $\beta = 107 \cdot 8$ (1), $\gamma = 104 \cdot 1$ (1)°, $Z = 2$. The structure has been determined from diffractometer data by direct methods and refined by least-squares calculations to $R = 4 \cdot 2\%$ for 7530 independent reflexions. The structure consists of octahedral $[FeCl(4 CH_3C_6H_4NC)_3(PPh_3)_2]^+$ cations and tetrahedral $FeCl_4^-$ anions, held together by weak van der Waals interactions. In the cations the Fe–P bond lengths are unusually long because of the strong π-acceptor effect of the tolyl isocyanide groups.

Introduction

It has recently been found (Albertin, Bordignon, Orio & Troilo, 1975) that in the hexacoordinate Fe^{II} complexes of the type $[FeCl(CNR)_nL_{5-n}]^+$ [where $n =$

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2 or 3 and $L = PPh(OEt)_2$ or PPh_3] the number of isocyanide ligands depends on the nature of the P-containing moiety. This has been rationalized in terms of different π-bond back donation from the metal to the phosphonite or phosphine ligand. In $\{FeCl(4-CH_3C_6H_4NC)_2[PPh(OEt)_2]_3\}ClO_4$ (hereinafter compound I), whose crystal structure has recently been

determined (Albertin, Orio, Calogero, Di Sipio & Pelizzi, 1976), the Fe—P bonds are rather long compared with those usually observed in similar compounds and the Fe—C bonds indicate some double-bond character, thereby reflecting the difference in σ-donor and π-acceptor abilities of isocyanides and phosphines. In this compound the coordination around the Fe is octahedral, as shown below.

$$\text{PPh(OEt)}_2$$

$$
\begin{array}{c}
\text{Cl} \diagdown \quad\quad\quad \diagup \text{PPh(OEt)}_2 \\
\text{Fe} \\
\text{(OEt)}_2\text{PhP} \diagup \quad\quad \diagdown \text{CN}R \\
\text{CN}R
\end{array}
$$
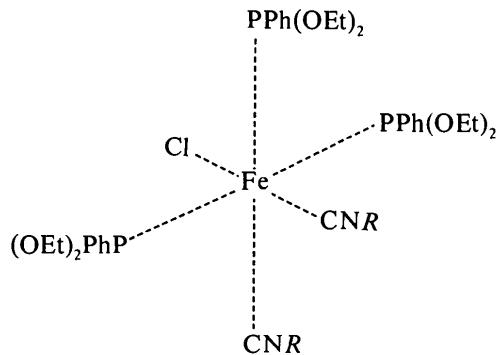
In the present paper we report the crystal structure of [FeCl(4-CH₃C₆H₄NC)₃(PPh₃)₂]FeCl₄, the preparation of which has been described earlier (Albertin, Bordignon, Orio & Troilo, 1975). This study has been carried out to understand better the extent of the $M-L$ π interaction when the nature of the P-containing ligand is changed, and to clarify its role in determining the ratio of the two different ligands in the complex. Furthermore, these X-ray data could be useful for a correlation with the Mössbauer parameters already determined for these compounds (Calogero, Albertin, Orio & Pelizzi, 1977).

Experimental

The title compound occurs as pleochroic orange crystals. Preliminary unit-cell dimensions and space-group information were obtained from rotation and Weissenberg photographs using Co $K\alpha$ radiation ($\lambda = 1.7902$ Å). The refined cell parameters and the orientation matrix for the diffractometer were determined by a least-squares fit for 20 values of θ, χ and φ, accurately measured on an automated on-line single-crystal Siemens AED diffractometer. The crystal data are in Table 1. The intensity data were collected by mounting a prismatic crystal of approximate dimen-

Table 1. *Crystal data*

C₆₀H₅₁Cl₅Fe₂N₃P₂, FW 1164·99
Triclinic, space group $P\bar{1}$
$a = 12.85$ (1), $b = 19.44$ (2), $c = 12.45$ (1) Å
$\alpha = 92.6$ (1), $\beta = 107.8$ (1), $\gamma = 104.1$ (1)°
$U = 2848$ (5) Å³, $Z = 2$, $D_c = 1.359$ g cm⁻³
μ(Mo $K\alpha$) = 8·40 cm⁻¹, $F(000) = 1198$

sions $0.10 \times 0.19 \times 0.31$ mm with the direction of maximum elongation collinear with the φ axis of the diffractometer; Mo $K\alpha$ radiation ($\lambda = 0.7108$ Å) and the $\omega-2\theta$ scanning technique were used. From 10877 independent reflexions measured in the range $2.3° < \theta < 26.0°$, with a scan speed of $2.0°$ min⁻¹, 7530 having $I > 2\sigma(I)$ were retained and used in the analysis. No decay was observed during data collection (as indicated by the intensity of a standard reflexion remeasured every 20 reflexions as a check for crystal and instrument stability). The usual Lorentz–polarization factors were applied, but no absorption correction was made.

Structure determination and refinement

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). An overall thermal parameter ($B = 3.8$ Å²) and the starting scale factor were determined by Wilson's method and used to compute normalized structure factors. The solution was based on 450 reflexions with $|E| > 2.0$; the E map calculated with the phases from the set having the highest absolute figure of merit showed four outstanding peaks which were interpreted as Fe and P atoms. All remaining non-H atoms were located from two subsequent difference Fourier maps.

In the first cycles of full-matrix least-squares refinement the aromatic rings were treated as rigid groups with D_{6h} symmetry and all atoms were allowed to vibrate isotropically ($R = 10.4\%$). A least-squares procedure using anisotropic thermal parameters for Fe, Cl, and P and isotropic for all the other atoms converged with $R = 7.7\%$. Finally, a block-diagonal cycle was carried out with anisotropic parameters for all non-H atoms and with the H atoms added in their calculated positions as a fixed contribution to the structure factors. In this way the observations/parameters ratio was 11·6/1, a ratio greater than that usually accepted for structure analysis. The final R was 4·2%. In the first stages unit weights and then the scheme $1/w = A + B|F_o| + C|F_o|^2$ were used, where the coefficients A, B, C were obtained by plotting ΔF vs $\bar{F}_o$.

Atomic scattering factors employed in the calculations were taken from Cromer & Mann (1968) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms. Final coordinates are listed in Table 2.* All calculations were performed on the Cyber 76 computer at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.

Table 2. *Fractional coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

	x	y	z		x	y	z
Fe(1)	7173 (1)	3029 (0)	5501 (1)	C(25)	5585 (3)	1406 (2)	3785 (3)
Fe(2)	2221 (1)	1802 (0)	9011 (1)	C(26)	4921 (4)	1178 (2)	2650 (4)
Cl(1)	9111 (1)	3333 (1)	5730 (1)	C(27)	3879 (4)	671 (3)	2395 (5)
Cl(2)	2934 (2)	1359 (1)	7854 (1)	C(28)	3518 (4)	382 (3)	3240 (5)
Cl(3)	3600 (1)	2437 (1)	10478 (1)	C(29)	4159 (4)	595 (2)	4350 (5)
Cl(4)	1273 (1)	2515 (1)	8148 (2)	C(30)	5193 (3)	1111 (2)	4628 (4)
Cl(5)	1094 (1)	941 (1)	9502 (1)	C(31)	7304 (3)	2298 (2)	2981 (3)
P(1)	7411 (1)	3939 (1)	6885 (1)	C(32)	8331 (3)	2288 (2)	2851 (3)
P(2)	6991 (1)	2052 (1)	4263 (1)	C(33)	8553 (4)	2491 (2)	1874 (4)
N(1)	7046 (3)	4026 (2)	3702 (3)	C(34)	7779 (4)	2701 (2)	1028 (4)
N(2)	4657 (2)	2608 (2)	4845 (3)	C(35)	6765 (4)	2731 (2)	1159 (3)
N(3)	7193 (3)	2074 (2)	7330 (3)	C(36)	6530 (4)	2541 (2)	2147 (3)
C(1)	8366 (3)	3943 (2)	8309 (3)	C(37)	7080 (3)	3644 (2)	4380 (3)
C(2)	8307 (3)	4352 (2)	9233 (3)	C(38)	7032 (4)	4448 (2)	2823 (3)
C(3)	9029 (4)	4368 (2)	10318 (3)	C(39)	6125 (3)	4257 (2)	1825 (3)
C(4)	9811 (4)	3980 (2)	10515 (3)	C(40)	6145 (3)	4664 (2)	945 (3)
C(5)	9883 (3)	3565 (2)	9609 (3)	C(41)	7034 (3)	5263 (2)	1050 (3)
C(6)	9172 (3)	3553 (2)	8510 (3)	C(42)	7019 (4)	5711 (2)	96 (4)
C(7)	6049 (3)	3865 (2)	7100 (3)	C(43)	7921 (3)	5446 (2)	2064 (3)
C(8)	5765 (3)	3470 (2)	7920 (3)	C(44)	7933 (3)	5039 (2)	2958 (3)
C(9)	4671 (4)	3329 (3)	7985 (5)	C(45)	5639 (3)	2789 (2)	5121 (3)
C(10)	3877 (4)	3581 (3)	7259 (5)	C(46)	3499 (3)	2279 (2)	4339 (3)
C(11)	4128 (4)	3971 (3)	6433 (5)	C(47)	2835 (3)	2037 (2)	5014 (3)
C(12)	5224 (3)	4110 (2)	6345 (4)	C(48)	1712 (3)	1654 (2)	4477 (4)
C(13)	7895 (3)	4873 (2)	6648 (3)	C(49)	1257 (3)	1515 (2)	3308 (4)
C(14)	7420 (4)	5400 (2)	6929 (4)	C(50)	49 (4)	1042 (3)	2729 (5)
C(15)	7839 (5)	6103 (2)	6750 (5)	C(51)	1928 (4)	1787 (2)	2669 (4)
C(16)	8714 (5)	6271 (2)	6314 (4)	C(52)	3048 (3)	2172 (2)	3180 (3)
C(17)	9206 (5)	5767 (3)	6072 (4)	C(53)	7236 (3)	2438 (2)	6640 (3)
C(18)	8786 (4)	5055 (2)	6228 (4)	C(54)	7120 (3)	1642 (2)	8185 (3)
C(19)	7840 (3)	1427 (2)	4766 (3)	C(55)	6133 (4)	1478 (2)	8460 (4)
C(20)	8738 (3)	1571 (2)	5774 (3)	C(56)	6080 (4)	1060 (2)	9315 (4)
C(21)	9306 (4)	1050 (2)	6112 (4)	C(57)	6984 (4)	811 (2)	9889 (3)
C(22)	8991 (4)	404 (2)	5456 (4)	C(58)	6911 (5)	363 (3)	10849 (4)
C(23)	8118 (4)	259 (2)	4456 (4)	C(59)	7947 (4)	974 (2)	9592 (3)
C(24)	7530 (3)	765 (2)	4101 (3)	C(60)	8035 (3)	1397 (2)	8739 (3)
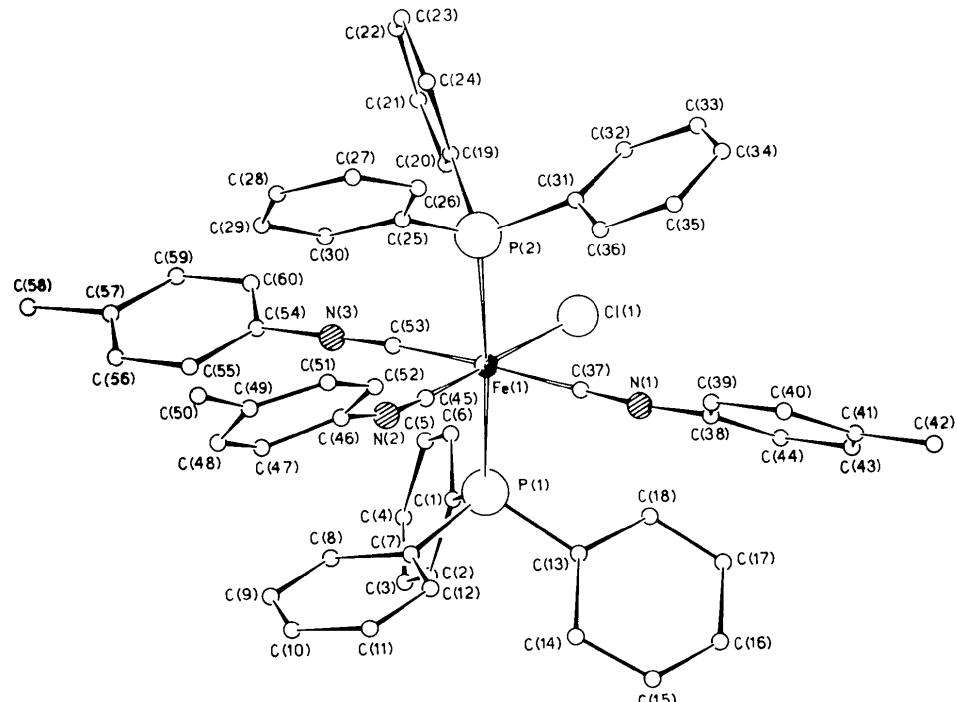
Fig. 1. Clinographic projection of $[FeCl(4\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]^+$.

Results and discussion

The crystal structure of the title compound consists of discrete [FeCl(4-CH$_3$C$_6$H$_4$NC)$_3$(PPh$_3$)$_2$]$^+$ and FeCl$_4^-$ ions which are depicted in Figs. 1 and 2 respectively. The cation has the all-*trans* structure indicated by Mössbauer studies (Calogero, Albertin, Orio & Pelizzi,

1977). The Fe atom is octahedrally surrounded by a Cl$^-$ ion, three C atoms from *p*-tolyl isocyanide groups and two P atoms from triphenylphosphine molecules. The coordination polyhedron shows some degree of distortion: of the three *trans* angles, two differ significantly from 180° [P(1)—Fe(1)—P(2) 174·2 (3); Cl(1)—Fe(1)—C(45) 172·3 (3)°], while the third is

Table 3. *Bond distances* (Å) *and angles* (°)

(a) The Fe^{II} coordination polyhedron

Fe(1)—Cl(1)	2·338 (2)	Fe(1)—C(37)	1·874 (4)		
Fe(1)—P(1)	2·309 (3)	Fe(1)—C(45)	1·813 (4)		
Fe(1)—P(2)	2·310 (3)	Fe(1)—C(53)	1·860 (4)		
Cl(1)—Fe(1)—P(1)	92·4 (2)	P(1)—Fe(1)—C(53)	86·2 (2)		
Cl(1)—Fe(1)—P(2)	86·8 (2)	P(2)—Fe(1)—C(37)	93·6 (2)		
Cl(1)—Fe(1)—C(37)	84·8 (2)	P(2)—Fe(1)—C(45)	88·6 (2)		
Cl(1)—Fe(1)—C(45)	172·3 (3)	P(2)—Fe(1)—C(53)	88·3 (2)		
Cl(1)—Fe(1)—C(53)	96·6 (2)	C(37)—Fe(1)—C(45)	89·4 (3)		
P(1)—Fe(1)—P(2)	174·2 (3)	C(37)—Fe(1)—C(53)	177·8 (4)		
P(1)—Fe(1)—C(37)	92·0 (2)	C(45)—Fe(1)—C(53)	89·4 (3)		
P(1)—Fe(1)—C(45)	92·8 (3)				

(b) The triphenylphosphine ligand

P(1)—C(1)	1·820 (4)	P(2)—C(19)	1·832 (4)
P(1)—C(7)	1·823 (4)	P(2)—C(25)	1·834 (4)
P(1)—C(13)	1·839 (3)	P(2)—C(31)	1·818 (4)
C(1)—C(2)	1·400 (6)	C(19)—C(20)	1·382 (5)
C(2)—C(3)	1·379 (5)	C(20)—C(21)	1·395 (7)
C(3)—C(4)	1·369 (7)	C(21)—C(22)	1·366 (7)
C(4)—C(5)	1·396 (7)	C(22)—C(23)	1·360 (6)
C(5)—C(6)	1·389 (5)	C(23)—C(24)	1·390 (7)
C(6)—C(1)	1·397 (6)	C(24)—C(19)	1·397 (5)
C(7)—C(8)	1·388 (6)	C(25)—C(26)	1·394 (6)
C(8)—C(9)	1·393 (7)	C(26)—C(27)	1·391 (7)
C(9)—C(10)	1·348 (8)	C(27)—C(28)	1·365 (9)
C(10)—C(11)	1·375 (9)	C(28)—C(29)	1·359 (8)
C(11)—C(12)	1·407 (7)	C(29)—C(30)	1·389 (6)
C(12)—C(7)	1·383 (6)	C(30)—C(25)	1·386 (6)
C(13)—C(14)	1·395 (7)	C(31)—C(32)	1·382 (6)
C(14)—C(15)	1·396 (6)	C(32)—C(33)	1·385 (7)
C(15)—C(16)	1·370 (9)	C(33)—C(34)	1·364 (7)
C(16)—C(17)	1·357 (9)	C(34)—C(35)	1·376 (8)
C(17)—C(18)	1·403 (7)	C(35)—C(36)	1·398 (7)
C(18)—C(13)	1·377 (7)	C(36)—C(31)	1·390 (6)

Fe(1)—P(1)—C(1)	117·8 (4)	Fe(1)—P(2)—C(19)	119·0 (4)
Fe(1)—P(1)—C(7)	108·3 (3)	Fe(1)—P(2)—C(25)	114·9 (4)
Fe(1)—P(1)—C(13)	119·2 (4)	Fe(1)—P(2)—C(31)	113·0 (3)
C(1)—P(1)—C(7)	103·4 (4)	C(19)—P(2)—C(25)	98·1 (4)
C(1)—P(1)—C(13)	101·4 (3)	C(19)—P(2)—C(31)	103·8 (4)
C(7)—P(1)—C(13)	105·0 (4)	C(25)—P(2)—C(31)	106·2 (4)
P(1)—C(1)—C(2)	119·6 (6)	P(2)—C(19)—C(20)	123·4 (6)
P(1)—C(1)—C(6)	121·8 (6)	P(2)—C(19)—C(24)	117·4 (5)
C(6)—C(1)—C(2)	118·6 (8)	C(24)—C(19)—C(20)	119·2 (7)
C(1)—C(2)—C(3)	120·6 (7)	C(19)—C(20)—C(21)	119·4 (8)
C(2)—C(3)—C(4)	120·7 (8)	C(20)—C(21)—C(22)	120·9 (9)
C(3)—C(4)—C(5)	119·8 (9)	C(21)—C(22)—C(23)	120·4 (9)
C(4)—C(5)—C(6)	120·0 (8)	C(22)—C(23)—C(24)	120·1 (9)
C(5)—C(6)—C(1)	120·3 (7)	C(23)—C(24)—C(19)	120·1 (8)
P(1)—C(7)—C(8)	120·2 (6)	P(2)—C(25)—C(26)	124·7 (7)
P(1)—C(7)—C(12)	120·3 (6)	P(2)—C(25)—C(30)	116·4 (6)
C(8)—C(7)—C(12)	118·8 (8)	C(26)—C(25)—C(30)	118·9 (8)
C(7)—C(8)—C(9)	120·5 (9)	C(25)—C(26)—C(27)	119·3 (8)
C(8)—C(9)—C(10)	120·4 (10)	C(26)—C(27)—C(28)	120·8 (10)

C(9)—C(10)—C(11)	120·6 (11)	C(27)—C(28)—C(29)	120·6 (11)
C(10)—C(11)—C(12)	119·8 (10)	C(28)—C(29)—C(30)	119·7 (9)
C(11)—C(12)—C(7)	120·0 (9)	C(29)—C(30)—C(25)	120·8 (9)
P(1)—C(13)—C(14)	121·9 (6)	P(2)—C(31)—C(32)	121·0 (6)
P(1)—C(13)—C(18)	118·3 (6)	P(2)—C(31)—C(36)	119·7 (6)
C(14)—C(13)—C(18)	119·8 (10)	C(32)—C(31)—C(36)	119·2 (6)
C(13)—C(14)—C(15)	119·2 (9)	C(31)—C(32)—C(33)	119·6 (9)
C(14)—C(15)—C(16)	120·1 (11)	C(32)—C(33)—C(34)	121·6 (9)
C(15)—C(16)—C(17)	121·1 (13)	C(33)—C(34)—C(35)	119·4 (10)
C(16)—C(17)—C(18)	119·7 (10)	C(34)—C(35)—C(36)	120·1 (10)
C(17)—C(18)—C(13)	120·0 (9)	C(35)—C(36)—C(31)	120·0 (8)

(c) The tolyl isocyanide ligand

C(37)—N(1)	1·147 (5)	C(49)—C(51)	1·375 (7)
N(1)—C(38)	1·396 (5)	C(51)—C(52)	1·381 (6)
C(38)—C(39)	1·379 (5)	C(52)—C(46)	1·365 (5)
C(39)—C(40)	1·383 (6)	C(49)—C(50)	1·528 (6)
C(40)—C(41)	1·387 (5)	C(53)—N(3)	1·143 (5)
C(41)—C(43)	1·379 (5)	N(3)—C(54)	1·397 (5)
C(43)—C(44)	1·393 (6)	C(54)—C(55)	1·381 (7)
C(44)—C(38)	1·380 (5)	C(55)—C(56)	1·376 (7)
C(41)—C(42)	1·503 (7)	C(56)—C(57)	1·376 (7)
C(45)—N(2)	1·158 (5)	C(57)—C(59)	1·367 (7)
N(2)—C(46)	1·395 (5)	C(59)—C(60)	1·387 (6)
C(46)—C(47)	1·391 (6)	C(60)—C(54)	1·375 (6)
C(47)—C(48)	1·388 (5)	C(57)—C(58)	1·523 (7)
C(48)—C(49)	1·379 (6)		

Fe(1)—C(37)—N(1)	178·6 (8)	C(47)—C(48)—C(49)	121·4 (8)
C(37)—N(1)—C(38)	175·0 (8)	C(48)—C(49)—C(51)	118·7 (9)
N(1)—C(38)—C(39)	119·2 (7)	C(48)—C(49)—C(50)	120·9 (8)
N(1)—C(38)—C(44)	119·6 (7)	C(50)—C(49)—C(51)	120·3 (8)
C(39)—C(38)—C(44)	121·2 (7)	C(49)—C(51)—C(52)	121·1 (9)
C(38)—C(39)—C(40)	118·5 (7)	C(51)—C(52)—C(46)	119·4 (7)
C(39)—C(40)—C(41)	121·9 (8)	Fe(1)—C(53)—N(3)	174·9 (8)
C(40)—C(41)—C(43)	118·2 (7)	C(53)—N(3)—C(54)	178·1 (8)
C(40)—C(41)—C(42)	121·0 (8)	N(3)—C(54)—C(55)	119·0 (8)
C(42)—C(41)—C(43)	120·8 (8)	N(3)—C(54)—C(60)	119·3 (7)
C(41)—C(43)—C(44)	121·1 (8)	C(55)—C(54)—C(60)	121·7 (9)
C(43)—C(44)—C(38)	119·0 (8)	C(54)—C(55)—C(56)	118·3 (9)
Fe(1)—C(45)—N(2)	176·8 (7)	C(55)—C(56)—C(57)	121·3 (9)
C(45)—N(2)—C(46)	167·1 (8)	C(56)—C(57)—C(59)	119·2 (9)
N(2)—C(46)—C(47)	119·9 (7)	C(56)—C(57)—C(58)	120·2 (9)
N(2)—C(46)—C(52)	119·0 (7)	C(58)—C(57)—C(59)	120·6 (10)
C(47)—C(46)—C(52)	121·1 (8)	C(57)—C(59)—C(60)	121·1 (9)
C(46)—C(47)—C(48)	118·1 (8)	C(59)—C(60)—C(54)	118·3 (8)

(d) The tetrachloroferrate ion

Fe(2)—Cl(2)	2·176 (3)	Fe(2)—Cl(4)	2·172 (3)
Fe(2)—Cl(3)	2·180 (4)	Fe(2)—Cl(5)	2·174 (3)
Cl(2)—Fe(2)—Cl(3)	109·1 (3)	Cl(3)—Fe(2)—Cl(4)	107·6 (3)
Cl(2)—Fe(2)—Cl(4)	108·7 (3)	Cl(3)—Fe(2)—Cl(5)	112·0 (3)
Cl(2)—Fe(2)—Cl(5)	109·7 (3)	Cl(4)—Fe(2)—Cl(5)	109·7 (3)
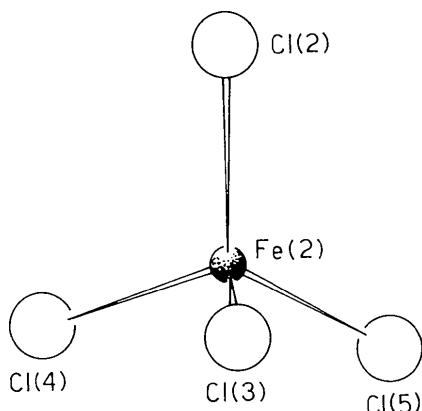
Fig. 2. Clinographic projection of $FeCl_4^-$.

close to the theoretical value [C(37)—Fe(1)—C(53) 177·8 (4)°]. On the other hand, the angle at Fe does not provide any evidence for steric hindrance involving the more bulky ligands as indicated by the average values of the Cl—Fe—P (89·6°), Cl—Fe—C (90·7°), P—Fe—C (90·2°) and C—Fe—C (89·4°) angles. From an inspection of the bond distances and angles given in Table 3, it can be observed that the Fe—P bonds [2·309 (3), 2·310 (3) Å] are among the longest distances observed in any Fe^{II}—P complex, independent of the coordination number of Fe, and are the longest of the octahedral bonds (Guggenberger, Titus, Flood, Marsh, Orio & Gray, 1972; Albertin, Orio, Calogero, Di Sipio & Pelizzi, 1976). The Fe—P distances in compound I are also rather long [2·236 (4), 2·234 (4), 2·248 (4) Å] even though they are shorter than those

Table 4. Fe—Cl *distances* (Å) *in* Fe^{II} *and* Fe^{III} *derivatives*

	Coordination number	Fe—Cl	Reference
(a) Fe^{II} compounds			
Di-μ-thio-n-butyl[bis(η-cyclopentadienyl)]-molybdenum–iron dichloride	4	2·247 (6) 2·229 (6)	Cameron & Prout (1972)
Bis(3,5-dimethyl-1,2-dithiolium) tetrachloroferrate	4	2·290 (1) 2·336 (1) [2·293 (2) 2·337 (2)]*	Freeman, Milburn, Nockolds, Mason, Robertson & Rusholme (1974)
Bis(3,5-diphenyl-1,2-dithiolium) tetrachloroferrate	4	2·301 (3) 2·337 (3) 2·275 (3) 2·305 (3) 2·303 (3) 2·314 (3) 2·337 (3) 2·287 (3)	Mason, Robertson & Rusholme (1974)
Tetramethylammonium tetrachloroferrate	4	2·290 (2) 2·296 (2) 2·289 (2)	Lauher & Ibers (1975)
Bis[chlorotri(cyclopentadienyldicarbonyliron)-antimony] tetrachloroferrate methylene chloride solvate	4	2·284 (4) 2·320 (5)	Trinh-Toan & Dahl (1971)
Chloro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)iron iodide	5	2·306 (4)	Goedken, Molin-Case & Christoph (1973)
catena-μ-Dichloro-bis(O-formamido)iron	6	2·27 (1)†	Constant, Daran & Jeannin (1971)
Bis-μ-[dicarbonyl(η-cyclopentadienylferrio-chloro]-bis{[dicarbonyl(η-cyclopentadienyl)-ferriochloro]trichloroantimony}	6	2·280 (10) 2·312 (9) 2·279 (9) 2·292 (10)	Einstein & MacGregor (1974)
Chlorotris(diethyl phenyl phosphonite)bis(4-tolyl isocyanide)iron perchlorate	6	2·326 (4)	Albertin, Orio, Calogero, Di Sipio & Pelizzi (1976)
Chlorobis(triphenylphosphine)tris(4-tolyl isocyanide)iron(II) tetrachloroferrate(III)	6	2·338 (2)	This work
(b) Fe^{III} compounds			
Tetraphenylarsonium tetrachloroferrate	4	2·19 (3)	Zarlow & Rundle (1957)
Sodium tetrachloroferrate	4	2·180 (10) 2·184 (8) 2·200 (8) 2·218 (8)	Richards & Gregory (1965)
Atrovenetin orange trimethyl ether ferrichloride	4	2·09–2·25 (⟨2·17⟩)	Paul & Sim (1965)
o-Methoxybenzenediazonium tetrachloroferrate	4	2·176 (4) 2·165 (4) 2·230 (4)	Polynova, Bokii & Poray-Koshits (1965)
α,β,γ,δ-Tetraphenylporphine diacid chloride ferrichloride	4	2·171 (9)	Stone & Fleischer (1968)
Dichlorotetra(dimethyl sulphoxide)iron(III) tetrachloroferrate(III)	4	2·162 (5)	Bennett, Cotton & Weaver (1967)
Tetrachlorophosphonium tetrachloroferrate	4	2·182 (2) 2·187 (1) 2·187 (1)	Kistenmacher & Stucky (1968)

* These values refer to two independent X-ray diffraction studies.
† A second Cl is at 2·79 Å from Fe, and both Cl are in a bridging situation.

Table 4 (*cont.*)

	Coordination number	Fe–Cl	Reference
Tris(methylthio)carbonium tetrachloroferrate	4	2·14 2·20	Atovmyan & Ponomarev (1975)
Hexakis(formonitrile)iron(II) tetrachloroferrate(III)	4	2·192 (9)	Constant, Daran & Jeannin (1970)
Hexakis(acetonitrile)iron(II) tetrachloroferrate(III)	4	2·163 (4) 2·203 (6) 2·195 (4) 2·180 (6)	Stork-Blaisse, Verschoor & Romers (1972)
Hexakis(acetonitrile)iron(II) tetrachloroferrate(III)	4	2·180 (5)	Constant, Daran & Jeannin (1972)
Chlorobis(triphenylphosphine)tris(4-tolyl isocyanide)iron(II) tetrachloroferrate(III)	4	2·176 (3) 2·180 (4) 2·172 (3) 2·174 (3)	This work
α-Chlorohaemin	5	2·218 (6)	Koenig (1965)
Chlorobis(pentane-2,4-dionato)iron	5	2·213 (8)	Lindley & Smith (1970)
Chlorobis(diethyldithiocarbamato)iron	5	2·26 (1)	Hoskins & White (1970)
Chloro[N,N-bis(salicylideneiminato)]iron nitromethane solvate	5	2·238 (4)	Gerloch & Mabbs (1967a)
Chlorobis(N,N-propylsalicylideneiminato)iron	5	2·23 (1)	Davies & Gatehouse (1972)
Chloro[N-(3-hydroxypropyl)salicylideneiminato]-iron dimer toluene solvate	5	2·226 (6)	Bertrand, Breece & Eller (1974)
Chlorobis[N-(2-phenylethyl)salicylideneiminato]-iron	5	2·251 (5) 2·262 (5)	Bertrand, Breece & Eller (1974)
Dichlorotetra(dimethyl sulphoxide)iron(III) tetrachloroferrate(III)	6	2·366 (3)	Bennett, Cotton & Weaver (1967)
Chloro-[N,N-bis(salicylidene)ethylenediamine]-iron	6	2·294 (3)	Gerloch & Mabbs (1967b)
Chloro[bis(salicylideneiminephenyl)-disulphido]iron	6	2·314 (4)	Bertrand & Breece (1974)
Aquachlorobis(α-picolinato)iron	6	2·304 (1)	Thundathil, Holt, Holt & Watson (1976)

observed in the present compound in agreement with the stronger π-acceptor ability of diethyl phenyl phosphonite in comparison with triphenylphosphine.

To our knowledge, this compound is the first, examined by X-rays, in which two Fe atoms in different oxidation states are coordinated by Cl⁻ ions. As can be seen from Table 4, in which Fe^{II}–Cl and Fe^{III}–Cl bond distances are given, the agreement between our values and those observed in compounds with a similar coordination and metal oxidation state is fairly good. If all Fe^{II}–Cl and Fe^{III}–Cl bond distances are averaged, values of 2·300 and 2·207 Å respectively are found, with the expansion of the coordination sphere upon reduction being much larger in four- and five-coordinated than in six-coordinated Fe compounds.

In the anion the Cl–Fe–Cl angles range from 107·6 to 112·0°, showing only small departures from ideal tetrahedral geometry.

The main differences between the present compound and compound I concern the Fe–C–N moieties. The Fe–C bond distances are 1·72 (1) and 1·74 (1) Å in compound I and 1·813 (4), 1·860 (4) and 1·874 (4) Å in the present compound and this significant difference can be partially explained in terms of a *trans* effect, *i.e.* these bonds are lengthened when the strong π-acceptor isocyanide ligands are *trans* to one another, as in the present compound (the shortest value of 1·813 Å refers to the isocyanide *trans* to Cl), while they are shortened when the isocyanides are *trans* to weaker π-acceptor ligands, as in (I). In the latter case there is evidence of a

very strong metal-to-ligand π back donation and this Fe–C π 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≡N bond. On the other hand, the present investigation does not support the idea of any appreciable amount of π back donation from the Fe atom to the isocyanide groups. In fact the Fe–C distances are now significantly longer and the C–N bonds are as expected for a C–N triple bond. The two Fe–C–N–C sequences involving the *trans* isocyanide groups show a small deviation from linearity, with bends ranging from 1 to 5°. The third Fe–C–N–R group is bent by 3° at C

Table 5. *The most significant van der Waals interactions* (Å)

σ is 0·005 Å for Cl···C contacts and 0·01 Å for C···C contacts.

Cl(2)···C(47)	3·806	Cl(4)···C(21^{ii})	3·581
C(4)···C(34^i)	3·38	Cl(1)···C(17^{iii})	3·778
C(56)···C(34^i)	3·55	Cl(2)···C(58^{iv})	3·806
Cl(3)···C(36^i)	3·650	C(10)···C(43^v)	3·58
Cl(3)···C(52^i)	3·679	C(3)···C(3^{vi})	3·36
Cl(4)···C(20^{ii})	3·660		

Symmetry code

(i)	x, y, z + 1	(iv)	1 – x, y, 2 – z
(ii)	x – 1, y, z	(v)	1 – x, 1 – y, 1 – z
(iii)	2 – x, 1 – y, 1 – z	(vi)	2 – x, 1 – y, 2 – z

and by 13° at N. This is a further indication of the greater double-bond character observed in the corresponding Fe—C bond as compared with the other two Fe—C bonds.

As is usually observed in metal-coordinated triphenylphosphines, the environment of the P atom is roughly tetrahedral with $M-P-C$ angles larger (ave. 115·4°) and $C-P-C$ angles smaller (ave. 103·0°) than the tetrahedral value. A very small difference between the two $P(C_6H_5)_3$ groups is that while P(2) lies practically in the plane of all the three phenyl rings, P(1) is displaced by 0·23 Å from the $C(7)\cdots C(12)$ plane and is coplanar with the other two phenyl C atoms.

Packing is due to weak van der Waals interactions; the most significant of these are given in Table 5.

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