The Crystal Structure of
Chlorotris(diethyl phenyl phosphonite)bis(4-tolyl isocyanide)iron(II) Perchlorate

By Gabriele Albertin and Angelo A. Orio

Istituto di Chimica Generale ed Inorganica, Università di Venezia, Venezia, Italy

Sandro Calogero and Lorenzo Di Sipio

Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova, Italy

and Giancarlo Pelizzi*

Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy

Crystals of the title compound are monoclinic ($P2_1/n$) with unit-cell dimensions: $a = 11\cdot926$ (4), $b = 15\cdot189$ (5), $c = 29\cdot36$ (2) Å, $\beta = 90\cdot57$ (3)°, $Z = 4$. The structure has been determined from diffractometer data (Mo $K\alpha$ radiation) by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods to an R value of 0·074 for 1273 independent reflexions. Coordination around the metal is octahedral and involves a Cl^- ion, three P atoms from diethyl phenyl phosphonite molecules and two C atoms from isocyanide groups. The Fe–P bonds (2·234, 2·236, 2·248 Å), rather long compared to those usually observed in similar compounds, and the Fe–C bonds (1·74, 1·72 Å), which indicate some double-bond character, reflect the better π-acceptor abilities of the *p*-tolyl isocyanides compared to those of the diethyl phenyl phosphonite molecules.

Introduction

The synthesis and characterization of hexacoordinate iron(II) complexes of the type $\{FeCl(CNR)_2[PPh(OEt)_2]_3\}ClO_4$ (R = substituted phenyl ring) have been recently reported (Albertin, Bordignon, Orio & Troilo, 1975); on the basis of their PMR and IR spectra in solution a *fac* structure was proposed in which the isocyanide ligands are in equatorial positions.

Crystal structures of hexacoordinate isocyanide iron(II) complexes have been reported only for $[Fe(CNMe)_6]Cl_2.3H_2O$ (Powell & Bartindale, 1945); $Fe(CNMe)_4(CN)_2$ (Hulme & Powell, 1957); $Fe(CN)_2(CNMe)_4.4CHCl_3$ (Wilford, Smith & Powell, 1968); $[Fe(CNMe)_4(C_2N_3Me_2H_2)] [PF_6]_2$ (Miller, Balch & Enemark, 1971) and therefore, to better correlate the metal–ligand electronic interactions to the relative bond lengths, more structural data would certainly be desirable, especially taking into account that all the above-mentioned structures are not sufficiently refined.

The M–$PPh(OEt)_2$ [M = Co^I, Ni^{II}, Fe^{II}] π-interaction has been discussed (Graziani, Albertin, Forsellini & Orio, 1976) in terms of tetrahedral distortion at the P atom due to the partial double-bond character of the M–P bond. The more pronounced distortion of the valency angles in $[Co(4-NO_2C_6H_4NC)_3L_2]ClO_4$ and in $Ni(CN)_2L_3$ has been attributed to a more extensive π-bond back donation from the metal to the phosphonite ligand in the d^6 Fe^{II} complex than in the d^8 Co^I and Ni^{II} complexes.

With the aim of understanding better the influence of the nature of the metal atom and of the ligands on the extent of the M–L π-interaction, we have studied the molecular structure of $\{FeCl(4-CH_3C_6H_4NC)_2[PPh(OEt)_2]_3\}ClO_4$ in which the presence of two strong π-acceptor isocyanide ligands should make the diethyl phenyl phosphonite a weaker π-acceptor than in $FeH_2[PPh(OEt)_2]_4$ (Guggenberger, Titus, Flood, Marsh, Orio & Gray, 1972).

Experimental

The title compound, prepared as previously described (Albertin, Bordignon, Orio & Troilo, 1975), occurs as yellow-orange pleochroic prismatic crystals.

Rotation and Weissenberg photographs were used for the determination of preliminary unit-cell dimensions and space group, which was assigned unambiguously as $P2_1/n$† on the basis of symmetry requirements

† Equivalent positions: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$.

Table 1. *Crystal data*

$C_{46}H_{59}Cl_2FeN_2O_{10}P_3$, F.W. 1019·7
Monoclinic, space group $P2_1/n$
$a = 11\cdot926$ (4), $b = 15\cdot189$ (5), $c = 29\cdot36$ (2) Å,‡ $\beta = 90\cdot57$ (3)°
$U = 5317\cdot5$ Å^3, $Z = 4$, $D_m = 1\cdot30$, $D_c = 1\cdot27$ g cm^{-3}
$\mu(Mo\ K\alpha) = 5\cdot4$ cm^{-1}, $F(000) = 2136$

‡ The percent differences in the e.s.d.'s of the cell constants are due to a non-homogeneous choice of reflexions considered in reciprocal space because the intensities of the reflexions with high l were rather low.

* To whom correspondence should be addressed.

and systematic absences. Refined cell parameters were obtained by least-squares calculations employing the θ values of 13 carefully centred reflexions. These param-

eters, together with other significant crystal data, are reported in Table 1.

The sample selected for data collection was mounted

Table 2. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10$ Å ^{2})
with estimated standard deviations in parentheses

Anisotropic thermal parameters are in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+2B_{33}l^2c^{*2}+B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	1719 (2)	202 (1)	1402 (2)	55 (1)	56 (1)	41 (1)	4 (1)	0 (1)	0 (1)
Cl(1)	210 (3)	350 (3)	900 (1)	70 (2)	76 (2)	58 (2)	0 (2)	10 (2)	9 (2)
Cl(2)	5844 (5)	6645 (4)	1073 (2)	107 (5)	213 (6)	245 (6)	−52 (4)	−62 (4)	55 (5)
P(1)	486 (3)	33 (3)	1964 (1)	64 (2)	68 (3)	53 (2)	9 (2)	3 (2)	2 (2)
P(2)	2822 (3)	290 (3)	793 (1)	66 (2)	68 (2)	52 (2)	11 (2)	9 (2)	1 (2)
P(3)	1906 (3)	1651 (3)	1540 (1)	62 (2)	60 (2)	54 (2)	8 (2)	6 (2)	1 (2)
O(1)	1070 (6)	−68 (6)	2447 (2)	72 (5)	104 (7)	58 (5)	9 (5)	24 (4)	9 (5)
O(2)	−371 (7)	833 (6)	2021 (3)	48 (5)	70 (5)	115 (7)	−6 (5)	9 (5)	0 (5)
O(3)	4111 (7)	331 (6)	956 (3)	74 (5)	93 (6)	57 (5)	−8 (5)	4 (4)	−32 (5)
O(4)	2529 (7)	1111 (6)	497 (3)	77 (6)	82 (6)	55 (5)	10 (5)	−1 (4)	−11 (5)
O(5)	1082 (7)	2357 (5)	1301 (3)	66 (6)	51 (5)	92 (6)	−7 (4)	−2 (5)	13 (5)
O(6)	1819 (7)	1822 (6)	2074 (3)	95 (6)	68 (6)	48 (5)	7 (5)	21 (4)	16 (4)
O(7)	6998 (13)	6284 (10)	901 (5)	196 (6)					
O(8)	5718 (15)	7600 (12)	938 (6)	223 (6)					
O(9)	5759 (15)	6743 (12)	1552 (6)	235 (7)					
O(10)	5084 (15)	6106 (12)	836 (6)	241 (7)					
N(1)	3634 (7)	−124 (7)	2024 (3)	53 (5)	77 (7)	44 (5)	9 (6)	15 (4)	−1 (5)
N(2)	1574 (9)	−1714 (7)	1206 (3)	82 (7)	85 (8)	46 (6)	5 (6)	−10 (5)	2 (6)
C(1)	−385 (9)	−929 (8)	1922 (3)	63 (7)	37 (7)	29 (6)	−11 (6)	15 (5)	−8 (5)
C(2)	−1282 (10)	−948 (10)	1615 (4)	42 (7)	109 (10)	63 (8)	−2 (8)	−5 (6)	−3 (8)
C(3)	−1902 (10)	−1742 (9)	1576 (4)	47 (8)	97 (10)	65 (8)	−39 (8)	−10 (6)	−6 (8)
C(4)	−1555 (11)	−2490 (9)	1826 (4)	84 (9)	53 (9)	77 (6)	−6 (7)	24 (7)	−11 (7)
C(5)	−725 (12)	−2492 (11)	2125 (5)	85 (11)	115 (12)	84 (10)	−17 (9)	−3 (8)	−38 (9)
C(6)	−76 (11)	−1666 (9)	2187 (5)	94 (11)	71 (10)	80 (9)	34 (8)	−16 (8)	15 (8)
C(7)	666 (11)	17 (11)	2904 (4)	90 (9)	138 (14)	48 (7)	41 (10)	1 (6)	−4 (8)
C(8)	1526 (12)	−154 (10)	3228 (4)	105 (10)	88 (11)	64 (8)	18 (9)	−4 (7)	1 (8)
C(9)	−1364 (10)	810 (12)	2311 (5)	27 (7)	155 (14)	136 (12)	−7 (9)	29 (7)	−31 (11)
C(10)	−2221 (13)	1306 (14)	2066 (7)	65 (10)	185 (19)	199 (18)	37 (12)	33 (11)	72 (15)
C(11)	2844 (11)	−626 (9)	379 (4)	72 (9)	95 (12)	56 (8)	1 (8)	6 (7)	−1 (7)
C(12)	3710 (11)	−1251 (9)	443 (4)	68 (9)	77 (10)	75 (9)	24 (8)	26 (7)	13 (8)
C(13)	3607 (14)	−2048 (11)	147 (4)	120 (13)	131 (14)	50 (9)	6 (11)	11 (8)	7 (8)
C(14)	2709 (12)	−2141 (9)	−148 (4)	106 (11)	74 (10)	61 (9)	7 (9)	16 (8)	−14 (8)
C(15)	1927 (13)	−1507 (10)	−189 (4)	137 (13)	91 (11)	48 (8)	16 (10)	−9 (8)	−13 (8)
C(16)	1849 (10)	−707 (9)	115 (4)	61 (8)	89 (10)	65 (8)	11 (7)	−13 (7)	0 (7)
C(17)	5056 (11)	578 (9)	674 (4)	77 (9)	89 (11)	80 (6)	−9 (8)	41 (7)	−8 (8)
C(18)	6124 (12)	218 (12)	961 (5)	74 (9)	127 (13)	120 (12)	8 (10)	22 (8)	18 (11)
C(19)	2927 (13)	1351 (10)	35 (4)	145 (13)	95 (11)	38 (7)	5 (10)	10 (8)	25 (7)
C(20)	1854 (14)	1737 (13)	−199 (5)	131 (14)	169 (17)	83 (11)	37 (13)	−17 (10)	16 (11)
C(21)	3158 (10)	2186 (8)	1389 (4)	60 (8)	49 (8)	68 (8)	9 (7)	18 (6)	9 (6)
C(22)	4153 (10)	2033 (8)	1676 (4)	38 (7)	65 (9)	81 (9)	12 (6)	8 (6)	−20 (7)
C(23)	5159 (12)	2466 (9)	1570 (4)	82 (10)	70 (9)	78 (10)	−5 (8)	3 (8)	−16 (8)
C(24)	5171 (11)	3023 (10)	1182 (4)	56 (8)	92 (11)	89 (10)	−35 (8)	30 (7)	−24 (8)
C(25)	4203 (14)	3158 (10)	891 (5)	124 (13)	82 (11)	92 (10)	−19 (10)	48 (9)	−1 (9)
C(26)	3264 (11)	2757 (8)	1003 (4)	69 (9)	36 (8)	79 (9)	−9 (7)	37 (7)	−6 (7)
C(27)	−114 (10)	2386 (9)	1333 (5)	38 (8)	80 (10)	111 (11)	4 (7)	−8 (7)	16 (8)
C(28)	−459 (14)	3081 (11)	991 (6)	90 (12)	91 (12)	176 (15)	14 (10)	−22 (10)	17 (12)
C(29)	1770 (13)	2724 (8)	2291 (5)	147 (13)	33 (8)	76 (9)	29 (8)	−20 (8)	−34 (7)
C(30)	1959 (14)	2499 (9)	2912 (5)	128 (12)	58 (10)	95 (10)	17 (9)	5 (9)	−23 (8)
C(31)	2832 (9)	54 (8)	1773 (4)	42 (6)	62 (9)	61 (7)	−6 (7)	14 (5)	−5 (6)
C(32)	4587 (9)	−219 (9)	2331 (4)	35 (6)	72 (8)	80 (8)	−4 (7)	0 (6)	16 (8)
C(33)	4605 (10)	209 (8)	2746 (4)	79 (8)	50 (8)	52 (7)	−11 (7)	−7 (6)	5 (7)
C(34)	5478 (11)	36 (10)	3045 (4)	81 (9)	96 (11)	75 (8)	−5 (9)	−9 (7)	36 (8)
C(35)	6351 (13)	−478 (11)	2883 (5)	107 (12)	113 (13)	110 (11)	−21 (10)	−17 (9)	40 (10)
C(36)	6294 (11)	−905 (10)	2489 (5)	71 (9)	91 (10)	90 (10)	−28 (8)	19 (7)	13 (9)
C(37)	5393 (9)	−791 (9)	2184 (5)	33 (7)	85 (10)	108 (10)	8 (7)	5 (7)	39 (8)
C(38)	7400 (12)	−532 (11)	3244 (5)	76 (10)	142 (15)	122 (8)	−28 (10)	−39 (9)	61 (11)
C(39)	1636 (10)	−918 (9)	1283 (4)	54 (7)	80 (9)	53 (8)	9 (8)	−1 (6)	−29 (7)
C(40)	1445 (11)	−2592 (9)	1047 (4)	83 (10)	69 (9)	70 (9)	−8 (8)	12 (7)	8 (7)
C(41)	2448 (14)	−3037 (9)	1008 (4)	148 (14)	77 (10)	50 (8)	8 (9)	15 (8)	22 (7)
C(42)	2281 (13)	−3952 (10)	808 (5)	110 (11)	98 (11)	77 (9)	20 (10)	17 (8)	26 (9)
C(43)	1247 (14)	−4272 (11)	679 (5)	140 (14)	88 (11)	109 (12)	0 (10)	−20 (10)	15 (9)
C(44)	274 (15)	−3779 (12)	700 (6)	133 (14)	136 (15)	106 (12)	−16 (12)	2 (10)	1 (11)
C(45)	331 (15)	−2894 (11)	883 (5)	144 (15)	115 (13)	89 (11)	−57 (12)	31 (10)	−29 (10)
C(46)	1197 (19)	−5232 (11)	456 (7)	284 (24)	39 (10)	181 (17)	−17 (14)	−14 (15)	−37 (12)

with its [001] axis parallel to the φ axis of a Siemens single-crystal automated diffractometer and all the reflexions in the 2θ range 5–46° were recorded; Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and the ω–2θ scanning technique were used. A total of 5687 independent reflexions were measured and of these only the 1273 having $I \geq 2\sigma(I)$ were used in further calculations. The intensity of a standard reflexion, $\overline{4}32$, was periodically measured after every 20 reflexions to check the stability of the instrument and of the crystal. From these measurements it was observed there was a gradual variation of the intensity, maximum value 15%, which was found to be due to a drift of the instrument. Corrections for this effect were therefore made to the measured data by means a computer program, taking the intensity of the standard reflexion as internal scaling for the data set.

The intensities were corrected for Lorentz and polarization effects, but no corrections for absorption were made. The absolute scale was determined, first by Wilson's method and then by comparison of the observed and calculated structure amplitudes.

Structure determination and refinement

The structure was solved by the heavy-atom technique; a three-dimensional Patterson map was used to locate Fe and Cl(1). Three successive structure-factor calculations and Fourier syntheses provided the positions of all remaining non-H atoms, excepting the O atoms belonging to the perchlorate group.

The refinement was carried out to $R = 10.3\%$ by means of an anisotropic block-diagonal least-squares procedure; the quantity minimized was $\sum w(\Delta F)^2$ with unit weights. At this point a difference Fourier map gave the positions of the O atoms from the ClO_4^- ion. Three additional cycles of least-squares calculations, refining isotropically the O atoms from ClO_4^-, improved R to 7.4%. In these cycles the unit weights were maintained because the usually accepted weighting schemes did not give a substantial improvement in the results. The shifts on the last cycle of refinement were less than 0.4σ for all parameters. No attempt was made to locate the H atoms. A difference Fourier synthesis carried out at the end of the refinement showed no undesirable feature.

The final values of the positional and thermal parameters are given in Table 2. The scattering factors for all the atoms were taken from the data of Cromer & Mann (1968)*. Bond lengths and angles are quoted, with their estimated standard deviations, in Table 3.

The calculations were carried out on a Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale.

Results and discussion

(i) Coordination round the metal; steric effects

The structure consists of discrete monomeric cations of formula $\{FeCl(4\text{-}CH_3C_6H_4NC)_2[PPh(OEt)_2]_3\}^+$ and ClO_4^- anions.

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

(a) In the coordination polyhedron

Fe——Cl(1)	2·326 (4)	Fe——P(1)	2·236 (4)
Fe——C(31)	1·72 (1)	Fe——P(2)	2·234 (4)
Fe——C(39)	1·74 (1)	Fe——P(3)	2·248 (5)
Cl(1)–Fe–P(1)	88·2 (1)	P(1)——Fe–C(39)	90·0 (4)
Cl(1)–Fe–P(2)	86·9 (1)	P(2)——Fe–P(3)	91·6 (2)
Cl(1)–Fe–P(3)	95·4 (1)	P(2)——Fe–C(31)	93·3 (4)
Cl(1)–Fe–C(31)	178·1 (4)	P(2)——Fe–C(39)	86·0 (4)
Cl(1)–Fe–C(39)	85·7 (4)	P(3)——Fe–C(31)	86·5 (4)
P(1)——Fe–P(2)	173·8 (1)	P(3)——Fe–C(39)	177·3 (4)
P(1)——Fe–P(3)	92·5 (1)	C(31)–Fe–C(39)	92·4 (6)
P(1)——Fe–C(31)	91·6 (4)		

(b) In the diethyl phenyl phosphonite ligand

P(1)——O(1)	1·581 (8)	C(11)–C(12)	1·41 (2)
P(1)——O(2)	1·598 (9)	C(12)–C(13)	1·49 (2)
P(1)——C(1)	1·80 (1)	C(13)–C(14)	1·38 (2)
O(1)——C(7)	1·44 (1)	C(14)–C(15)	1·35 (2)
O(2)——C(9)	1·47 (1)	C(15)–C(16)	1·51 (2)
C(7)——C(8)	1·42 (2)	C(16)–C(11)	1·42 (2)
C(9)——C(10)	1·45 (2)	P(3)——O(5)	1·611 (9)
C(1)——C(2)	1·39 (2)	P(3)——O(6)	1·593 (8)
C(2)——C(3)	1·42 (2)	P(3)——C(21)	1·76 (1)
C(3)——C(4)	1·41 (2)	O(5)——C(27)	1·43 (1)
C(4)——C(5)	1·32 (2)	O(6)——C(29)	1·51 (1)
C(5)——C(6)	1·48 (2)	C(27)–C(28)	1·51 (2)
C(6)——C(1)	1·41 (2)	C(29)–C(30)	1·58 (2)
P(2)——O(3)	1·607 (9)	C(21)–C(22)	1·47 (2)
P(2)——O(4)	1·558 (9)	C(22)–C(23)	1·41 (2)
P(2)——C(11)	1·85 (1)	C(23)–C(24)	1·42 (2)
O(3)——C(17)	1·45 (2)	C(24)–C(25)	1·44 (2)
O(4)——C(19)	1·49 (1)	C(25)–C(26)	1·32 (2)
C(17)–C(18)	1·62 (2)	C(26)–C(21)	1·43 (2)
C(19)–C(20)	1·56 (2)		
Fe——P(1)——O(1)	112·7 (3)	O(4)——C(19)–C(20)	103 (1)
Fe——P(1)——O(2)	114·6 (4)	P(2)——C(11)–C(12)	115·7 (9)
Fe——P(1)——C(1)	115·3 (4)	P(2)——C(11)–C(16)	114·1 (9)
O(1)——P(1)——O(2)	104·9 (5)	C(12)–C(11)–C(16)	128 (1)
O(1)——P(1)——C(1)	103·4 (5)	C(13)–C(12)–C(11)	114 (1)
O(2)——P(1)——C(1)	104·8 (5)	C(14)–C(13)–C(12)	120 (1)
P(1)——O(1)——C(7)	132·9 (8)	C(15)–C(14)–C(13)	121 (1)
P(1)——O(2)——C(9)	124·3 (9)	C(16)–C(15)–C(14)	125 (1)
O(1)——C(7)——C(8)	111 (1)	C(11)–C(16)–C(15)	110 (1)
O(2)——C(9)——C(10)	106 (1)	Fe——P(3)——O(5)	120·9 (4)
P(1)——C(1)——C(2)	120·1 (9)	Fe——P(3)——O(6)	109·2 (4)
P(1)——C(1)——C(6)	117·4 (9)	Fe——P(3)——C(21)	119·3 (4)
C(2)——C(1)——C(6)	122 (1)	O(5)——P(3)——O(6)	105·9 (5)
C(3)——C(2)——C(1)	118 (1)	O(5)——P(3)——C(21)	95 (7)
C(4)——C(3)——C(2)	119 (1)	O(6)——P(3)——C(21)	103·7 (5)
C(5)——C(4)——C(3)	124 (1)	P(3)——O(5)——C(27)	126·6 (8)
C(6)——C(5)——C(4)	118 (1)	P(3)——O(6)——C(29)	124·4 (7)
C(1)——C(6)——C(5)	118 (1)	O(5)——C(27)–C(28)	104 (1)
Fe——P(2)——O(3)	109·5 (3)	O(6)——C(29)–C(30)	102 (1)
Fe——P(2)——O(4)	111·3 (4)	P(3)——C(21)–C(22)	117·8 (9)
Fe——P(2)——C(11)	119·6 (4)	P(3)——C(21)–C(26)	124·1 (9)
O(3)——P(2)——O(4)	110·1 (5)	C(22)–C(21)–C(26)	118 (1)
O(3)——P(2)——C(11)	101·8 (5)	C(23)–C(22)–C(21)	119 (1)
O(4)——P(2)——C(11)	103·9 (5)	C(24)–C(23)–C(22)	118 (1)
P(2)——O(3)——C(17)	125·8 (7)	C(25)–C(24)–C(23)	123 (1)
P(2)——C(4)——C(19)	129·3 (8)	C(26)–C(25)–C(24)	118 (1)
O(3)——C(17)–C(18)	103 (1)	C(21)–C(26)–C(25)	124 (1)

Table 3 (cont.)

(c) In the tolyl isocyanide ligand

C(31)–N(1)	1·23 (1)	C(39)–N(2)	1·23 (2)
N(1)—C(32)	1·45 (1)	N(2)—C(40)	1·42 (2)
C(32)–C(33)	1·38 (2)	C(40)–C(41)	1·38 (2)
C(33)–C(34)	1·38 (2)	C(41)–C(42)	1·52 (2)
C(34)–C(35)	1·39 (2)	C(42)–C(43)	1·38 (2)
C(35)–C(36)	1·33 (2)	C(43)–C(44)	1·38 (2)
C(35)–C(38)	1·63 (2)	C(43)–C(46)	1·60 (2)
C(36)–C(37)	1·40 (2)	C(44)–C(45)	1·45 (2)
C(37)–C(32)	1·37 (2)	C(45)–C(40)	1·48 (2)

Fe——C(31)–N(1)	175 (1)	Fe——C(39)–N(2)	179 (1)
C(31)–N(1)—C(32)	173 (1)	C(39)–N(2)—C(40)	171 (1)
N(1)—C(32)–C(33)	120 (1)	N(2)—C(40)–C(41)	113 (1)
N(1)—C(32)–C(37)	115 (1)	N(2)—C(40)–C(45)	119 (1)
C(33)–C(32)–C(37)	125 (1)	C(41)–C(40)–C(45)	127 (1)
C(34)–C(33)–C(32)	118 (1)	C(42)–C(41)–C(40)	112 (1)
C(35)–C(34)–C(33)	117 (1)	C(43)–C(42)–C(41)	123 (1)
C(36)–C(35)–C(34)	123 (1)	C(44)–C(43)–C(42)	123 (1)
C(36)–C(35)–C(38)	125 (1)	C(44)–C(43)–C(46)	119 (1)
C(34)–C(35)–C(38)	112 (1)	C(42)–C(43)–C(46)	118 (1)
C(37)–C(36)–C(35)	122 (1)	C(45)–C(44)–C(43)	119 (1)
C(32)–C(37)–C(36)	114 (1)	C(40)–C(45)–C(44)	117 (1)

(d) In the perchlorate ion

Cl(2)–O(7)	1·57 (2)	Cl(2)–O(9)	1·42 (2)
Cl(2)–O(8)	1·51 (2)	Cl(2)–O(10)	1·40 (2)

O(7)—Cl(2)–O(8)	110 (1)	O(8)—Cl(2)–O(9)	99 (1)
O(7)—Cl(2)–O(9)	115 (1)	O(8)—Cl(2)–O(10)	112 (1)
O(7)—Cl(2)–O(10)	102 (1)	O(9)—Cl(2)–O(10)	120 (1)

The metal atom is six-coordinate to one Cl⁻ ion, three P atoms from the three phosphonite ligands, and two C atoms belonging to the isocyanide groups, as can be seen from the clinographic projection of Fig. 1. Bond angles in the iron environment show only small departures from the ideal octahedral values as they are in the range 85·7–95·4°. These departures are better understood by considering the equations of the three coordination planes of the octahedron (see Table 4). (a) Cl(1),P(3),C(31),C(39) are coplanar with a maximum deviation of 0·04 Å and with Fe lying in the plane; the trans angles differ very slightly from 180° [Cl(1)–Fe–C(31) = 178·1, P(3)–Fe–C(39) = 177·3°]. P(1) and P(2) are removed from that plane by −2·25 and 2·21 Å respectively. The P(1)–Fe and Fe–P(2) bonds deviate

significantly from collinearity [P(1)–Fe–P(2) = 173·8°]; (b) Cl(1),P(1),C(31),P(2) are coplanar (maximum devia-

Table 4. The equations of the least-squares coordination planes of the octahedron and atomic deviations from them (Å)

The equations of the planes are expressed in the form $AX + BY + CZ = D$, where X, Y, Z are the coordinates in Å referred to orthogonal axes.

Plane I

$A = 0·6352, B = 0·0881, C = −0·7673, D = 1·8348$
Cl(1) −0·003, P(3) 0·003, C(31) −0·038, C(39) 0·038

Plane II

$A = −0·0361, B = −0·9890, C = −0·1431, D = 0·9102$
Cl(1) −0·002, P(1) 0·017, C(31) −0·036, P(2) 0·021

Plane III

$A = −0·7673, B = 0·2051, C = −0·6075, D = 3·9412$
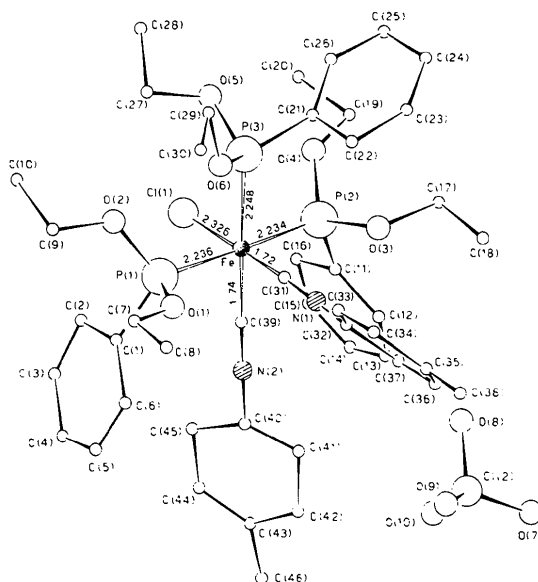P(1) 0·049, P(2) 0·053, P(3) −0·001, C(39) −0·101

Fig. 1. Clinographic projection of the structure with bond lengths in the coordination polyhedron.

Table 5. Fe–P bond distances (Å) in octahedral iron(II) compounds, with standard deviations where published

For the cyclopentadienyl derivatives the octahedral ('piano-stool') coordination is achieved by considering the C₅H₅ ligand to be tridentate.

Compound	Length	References
(π-C₅H₅)Fe[P(OC₆H₅)₃]₂ isomer I	2·15 (1), 2·15 (1)	Andrianov & Struchkov (1968a)
(π-C₅H₅)Fe[P(OC₆H₅)₃]₂ isomer II	2·14, 2·14	Andrianov & Struchkov (1968b)
(π-C₃H₅)P(C₆H₅)₃Fe(CO)₂I	2·23 (1)	Minasyants, Andrianov & Struchkov (1968)
(CO)₃FeI[P(CH₃)₂]₂IFe(CO)₃	2·293 (6), 2·312 (6)	Davies, Mais, Owston & Thompson (1968)
(π-C₅H₅)Fe(CO)[P(C₆H₅)₃](σ-C₆H₅)	2·23	Semion & Struchkov (1969a)
(π-C₅H₅)Fe(CO)[P(C₆H₅)₃](σ-COC₆H₅)	2·17	Semion & Struchkov (1969b)
(π-C₅H₅)Fe(CO)[P(C₆H₅)₃](σ-α-C₄H₃S)	2·22	Andrianov, Sergeeva, Struchkov, Anisimov, Kolobova & Beschastnov (1970)
(π-C₅H₅)Fe(CO)₂P(CF₃)₂	2·265 (3) }	
(π-C₅H₅)Fe(CO)₂PO(CF₃)₂	2·191 (3) }	Barrow, Sim, Dobbie & Mason (1974)
{FeCl(4-CH₃C₆H₄NC)₂[P(C₆H₅) (OCH₂CH₃)₂]₃}ClO₄	2·236 (4), 2·234 (4) 2·248 (5)	Present work

Table 6. *Averaged structural data (bonds in Å, angles in degrees) for the diethyl phenyl phosphonite molecule in metal complexes*

Compound	M–P	P–O	P–C	O–C	C–C	M–P–O	M–P–C	O–P–O	O–P–C	P–O–C	O–C–C	Reference
Ni(CN)₂[PPh(OEt)₂]₃	2·228 (6)	1·58 (1)	1·79 (1)	1·45 (3)	1·43 (4)	114·5 (6)	117·3 (6)	105·6 (7)	101·7 (7)	122 (1)	109 (2)	a
RuH₂[PPh(OEt)₂]₄	2·272 (3)	1·615 (3)	1·83 (1)	1·44 (1)	1·44 (3)	111·7 (3)	119·4 (4)	102·8 (2)	97·9 (2)	121·8 (5)	110 (1)	b
TcCl₂[PPh(OEt)₂]₄	2·41 (1)	1·60 (1)	1·84 (2)	1·45 (2)	1·48 (3)	116·6 (4)	119·3 (4)	–	–	123·4 (9)	109 (1)	c
{Tc(CO)₂[PPh(OEt)₂]₄}ClO₄	2·42 (1)	1·60 (2)	1·82 (2)	1·46 (3)	1·48 (4)	112·6 (4)	120·0 (7)	106·4 (8)	101·9 (9)	125 (1)	108·4 (2)	d
FeH₂[PPh(OEt)₂]₄	2·139 (2)	1·630 (2)	1·838 (3)	1·434 (7)	1·463 (9)	118·6 (1)	119·4 (1)	101·1 (2)	97·5 (2)	122·5 (3)	109·9 (4)	e
{FeCl(4-CH₃C₆H₄NC)₂[PPh(OEt)₂]₃}ClO₄	2·239 (4)	1·59 (1)	1·80 (1)	1·46 (1)	1·52 (2)	113·0 (3)	118·1 (4)	107·0 (5)	102·2 (5)	127·2 (8)	105 (1)	f

References: (*a*) Stalick & Ibers (1969). (*b*) Guggenberger (1973). (*c*) Bandoli, Clemente, Mazzi & Tondello (1974). (*d*) Biagini Cingi, Clemente, Magon & Mazzi (1975). (*e*) Guggenberger, Titus, Flood, Marsh, Orio & Gray (1972). (*f*) Present work.

tion 0·04 Å); the displacements from the least-squares planes are −0·05 for Fe, +1·68 for C(39) and −2·30 Å for P(3); (c) P(1),P(3),P(2),C(39) are slightly tetrahedrally distorted. Fe lies almost in the mean least-squares plane through them, its displacement from the plane being only 0·04 Å; Cl(1) and C(31) are removed from this plane by 2·27 and −1·76 Å respectively.

Contrary to what is usually observed in similar compounds, the increasingly bulky character of the ligands in the sequence: chlorine < p-tolyl isocyanide < diethyl phenyl phosphonite, does not seem to influence the bond angles at Fe, so that steric hindrance by the bulky PPh(OEt)₂ groups seems to be excluded.

(ii) *The* Fe–Cl *bond*

The Fe–Cl bond is worthy of some comment. To our knowledge, the only previously reported structures of octahedral Fe^{II} compounds containing Fe–Cl bonds are those of $FeCl_2$.2HCONH₂ (Constant, Daran & Jeannin, 1971) [Fe–Cl=2·27 (1); 2·79 (1) Å] and $FeCl_2$.4H₂O (Meunier-Piret & Van Meerssche, 1972) [Fe–Cl=2·256 (1) Å]. On the other hand, the number of Fe^{II}–Cl bonds with other symmetries is also rather low, apart from those in tetrahedral $FeCl_4$ anions. Some values for these bonds are: 2·284 (4), 2·320 (5) Å in {[Fe(h^5-C₅H₅) (CO)₂]₃SbCl}₂[FeCl₄].CH₂Cl₂ (Trinh-Toan & Dahl, 1971); 2·293 (2), 2·337 (2) Å in (C₇H₇S₂)₂FeCl₄ (Freeman, Milburn, Nockolds, Mason, Robertson & Rusholme, 1971); 2·275–2·337 Å in (C₁₅H₁₁S₂)₂FeCl₄ (Mason, Robertson & Rusholme, 1974); and 2·306 (4) Å in the five-coordinate [Fe(C₁₆H₃₂N₄)Cl]I (Goedken, Molin-Case & Christoph, 1973).

(iii) *The* Fe–P *bonds*

In contrast to Fe–Cl bonds, a large number of Fe–P lengths have been reported. Table 5 gives the values for octahedral Fe^{II} compounds. Inspection of the table shows that most of the compounds are phosphite or phoshine derivatives and that the Fe–P bond distances in phosphite compounds (2·14–2·15 Å) are always shorter than those in phosphine compounds (2·17–2·23 Å). This difference is consistent with the greater π-acceptor ability of P(OC₆H₅)₃ in comparison with P(C₆H₅)₃. The values found in the present compound (2·236, 2·234, 2·248 Å) lie at the upper limit of the range observed for phosphine derivatives; moreover they are surprisingly long compared with those (2·128, 2·150 Å) found in FeH₂[PPh(OEt)₂]₄ (Guggenberger *et al.*, 1972), where the arrangement of the ligands around Fe is intermediate between octahedral and tetrahedral. This lengthening can be explained by the presence of the isocyanide groups, which are strong π-acceptors and make the diethyl phenyl phosphonite molecule a weaker π-acceptor in our compound than in the dihydrido derivative. This effect can also explain the fact that the Fe–P(3) bond is longer, even if the difference is not statistically significant, than the other

two, as it involves the only phosphonite ligand which is *trans* to an isocyanide group. This last fact does not agree with PMR spectral data, from which both isocyanide groups seem to be *trans* to a phosphonite ligand (Albertin, Bordignon, Orio & Troilo, 1975).

(iv) Geometry of the [PPh(OEt)₂] ligands

The structural parameters of the diethyl phenyl phosphonite molecules are in accordance with those found for this ligand in related compounds as indicated by the values given in Table 6. The small amount of scatter about the average values for all the tabulated parameters indicates that changing the coordinated metal has little or no effect on the ligand geometry. Moreover, within a compound, the M–P–C angles are always larger (117·3–120·0°) than the M–P–O angles (111·7–118·6°) and both are always larger than the tetrahedral value; the opposite effect is observed for the O–P–O (101·1–107·0°) and O–P–C (97·5–102·2°) angles. Such a situation is typical for tetrahedral bonds in which one of them shows some double-bond character. In fact the bond angles involving the double bond are always larger than 109·5° as a consequence of repulsion effects, which are stronger for double than for single bonds. In the light of these assumptions it is of interest to compare the present compound with FeH₂[PPh(OEt)₂]₄. The above-mentioned difference between the Fe–P bonds in these two compounds, indicating a more relevant double-bond character for the dihydrido derivative, is accompanied by a different distortion of bonds at P. The values listed in Table 6 indicate a smaller distortion in our compound. The average C–O (1·46 Å) distance is comparable to, or even slightly longer than, those given in Table 6, while the average C–C (1·52 Å) bond is perceptibly longer than the corresponding ones. Departures from the tabulated values are also shown by the large P–O–C (127·2°) and by the small O–C–C (105°) angles.

(v) The phenyl isocyanide ligands

As mentioned in the introduction, only four crystal structures have been reported for octahedral isocyanide Fe^{II} complexes and, to make things worse, a detailed comparison is not possible since none of the four structures is accurate enough. The two isocyanide ligands are in a *cis* arrangement as also suggested by spectroscopic evidence (Albertin, Bordignon, Croatto & Orio, 1974; Albertin, Bordignon, Orio & Troilo, 1975). An interesting feature in the molecular geometry of the Fe–CNR system is given by the rather short (1·72, 1·74 Å) Fe–C bonds as compared to those usually found for single Fe–C bonds. This shortening indicates some double-bond character and reflects very well the strong π back donation in the Fe–CNR system, which gives rise to an increase in the bond order of the Fe–C bond. On the other hand, the shortening of the Fe–C bonds is accompanied by an appreciable lengthening of the C–N bonds (1·23, 1·23 Å), which are significantly longer than the corresponding triple-bond distance

and the distances found in isocyanide compounds (Miller, Balch & Enemark, 1971; Lewis & Lippard, 1972 and references cited therein). The N–C(phenyl) bonds (1·45 and 1·42 Å) do not deviate significantly from their normal values. The Fe–C–N–C system departs from linearity by a small amount of bending at the C atoms [5° at C(31); 1° at C(39)] and at the N atoms [7° at N(1); 9° at N(2)].

The aromatic rings are planar as expected; the average values for bond distances and angles are 1·41 Å and 120° respectively. No physical significance can be attached to the observed departures from these mean values.

(vi) The ClO₄⁻ ion

The O atoms of the perchlorate ion show either a positional disorder or, as frequently observed, an anomalous thermal effect. For this reason the values of the Cl–O distances must be considered as having poor accuracy.

The closest intermolecular contacts indicate that the structure is formed of discrete monomeric ions which interact through the O atoms of ClO₄⁻ and the phenyl rings of the cation ligands. Some of these interactions correspond to contacts that are somewhat shorter than those calculated on the basis of pure van der Waals contacts (3·7 Å): O(8)···C(12) (x, 1 + y, z) 3·29 (2), O(8)···C(3) (1 + x, 1 + y, z) 3·53 (2), O(8)···C(13) (x, 1 + y, z) 3·45 (2), O(9)···C(4) (1 + x, 1 + y, z) 3·50 (2), O(10)···C(41) (x, 1 + y, z) 3·44 (2), O(9)···C(7) (½ − x, ½ + y, ½ − z) 3·52 (2) Å.

Unfortunately, this analysis is not accurate enough (the number of observed reflexions is rather low with respect to that of possible ones) to indicate in a reliable way the influence, if any, of the negative charge of the anion on the electron distribution and consequently on bond distances and angles in the cation.

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Crystal and Molecular Structure of 3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-glucopyranose (TACEG)

BY C. FOCES-FOCES, F. H. CANO AND S. GARCÍA-BLANCO

Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain

Crystals of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-glucopyranose have hexagonal symmetry with cell dimensions $a = b = 8\cdot524$ (1) and $c = 41\cdot700$ (5) Å. Direct methods were used to solve the structure which was later refined by least-squares calculations to an R of 0·068. The cyano group was found to be *trans* or *exo* to the pyranose ring. The dioxolane ring is not planar and the pyranose ring has a skew conformation. Several criteria are presented for distinguishing between the four main conformations in six-membered rings.

Introduction

3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-glucopyranose (TACEG) was one of the two principal compounds obtained by reactions of *cis*-α-acetoxyglycopyranosyl halides with metallic cyanides (Chacon-Fuertes, 1975). The crystal structure determination was carried out in order to establish the configuration at the dioxolane-2C atom and the conformation of the pyranose ring.

Coxon & Hall (1964) have studied this compound and other 1,2-*O*-alkylidene-α-D-glucopyranoses by PMR. They said that the *cis* fusion of a 1,2-cyclic acetal ring forces the D-glucopyranose ring to depart from the expected chair conformation; this is surprising since the bulky substituents are not in predominantly equatorial orientations. From the experimental and theoretical dihedral angles they proposed a skew boat conformation for the pyranose ring which has been

confirmed by the crystal structure determination of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]-α-D-glucopyranose (Heitmann, Richards & Schroeder, 1974). On the other hand, in a similar compound Trotter & Fawcett (1966) found a flattened chair conformation for this ring. In view of this controversy we have undertaken the present study. Moreover we have attempted to describe this kind of conformation quantitatively.

Experimental

Transparent crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanolic solution. The unit-cell parameters were obtained from the θ measurements of 32 reflexions.

Crystal data

$C_{15}H_{19}O_9N$, F.W. 357·3. Hexagonal; $a = b = 8\cdot524$ (1), $c = 41\cdot700$ (5) Å, $V = 2623\cdot9$ Å^3; $D_m = 1\cdot34$, $D_x = 1\cdot36$