New polynuclear compounds of iron(II) chloride with oxygen donor ligands
Part II. Polymeric $[FeCl_2(OPMe_3)]_\infty$ and mononuclear $FeCl_2(OPMe_3)_2$. Syntheses, properties and single crystal structure determinations*

F. Albert Cotton, Rudy L. Luck** and **Kyung-Ae Son**

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843 (U.S.A.)

(Received December 12, 1990)

Abstract

A new polymeric Fe(II) chloride complex, $[FeCl_2(OPMe_3)]_\infty$ (**1**), has been synthesized from the reaction of stoichiometric quantities of $FeCl_3$, Fe and $OPMe_3$ (2:1:3) in THF. Use of a 2:1:6 ratio in the above reaction gives instead the mononuclear complex $FeCl_2(OPMe_3)_2$ (**2**). The structure of the polymer consists of infinite chains of $FeCl_2(OPMe_3)$ units, where each Fe atom is linked by four bridging chlorine atoms to two other Fe atoms. The arrangement of the four chlorine atoms and one $OPMe_3$ molecule around the iron atom results in a trigonal bipyramidal coordination geometry. Complex **2** has tetrahedral geometry. The magnitudes of the magnetic moments for **1** and **2** at room temperature are 4.90 and 5.51 BM, respectively, indicative of high spin Fe^{2+}. In **1**, two different Fe...Fe distances 3.560(0) and 3.688(0) Å alternate along the chain, the Fe–Cl bond distances are in the range 2.35–2.60 Å, the Fe–O distance is 1.954(2) Å and the P–O distance is 1.513(2) Å. In **2**, the Fe–Cl distances average to 2.291(4) Å, the average Fe–O and P–O distances are 1.994(2) and 1.504(1) Å, respectively. Crystallographic data: **1**, monoclinic, space group $P2_1/n$, $a=6.810(2)$, $b=12.943(5)$, $c=9.645(2)$ Å, $\beta=100.224(2)°$, $V=836.6(11)$ Å^3, $Z=4$, $R=0.041$ ($R_w=0.058$) for 101 parameters and 1665 unique data having $F_o^2>3\sigma(F_o^2)$. **2**, orthorhombic, space group $P2_12_12_1$, $a=11.270(3)$, $b=12.011(2)$, $c=10.811(2)$ Å, $V=1463.5(5)$ Å^3, $Z=4$, $R=0.052$ ($R_w=0.064$) for 142 parameters and 1356 unique data having $F_o^2>3\sigma(F_o^2)$.

Introduction

In Part I [1] we reported the preparation and characterization of a tetranuclear iron(II) compound, $Fe_4Cl_8(THF)_6$, by comproportionation of $FeCl_3$ and Fe in THF (tetrahydrofuran) under appropriate conditions. We have continued our study of oxo-ligand complexes of iron(II) chloride and we report here several compounds formed with trimethylphosphine oxide. In actual fact, this investigation began with attempts to prepare trimethylphosphine complexes of iron(III) chloride, by employing $FeCl_3(THF)$ [2] as starting material, but none of these were obtained. Instead, the polymeric $[FeCl_2(OPMe_3)]_\infty$ (**1**) was isolated and characterized. This result, naturally, lead to the study of the direct reaction between the THF solution of iron(II) chloride and Me_3PO. While it was found that, as expected, **1** can be obtained in this way, it was also found that $FeCl_2(OPMe_3)_2$ (**2**) can also be prepared. We report here the preparation, properties and structures of both of these compounds. Besides these there are relatively few structurally characterized oxo-ligand complexes of iron(II) chloride [3–5].

Experimental

Tetrahydrofuran was dried over Na/K alloy and then distilled under dinitrogen. $OPMe_3$ and Fe were used as purchased from Alfa and Fisher Chemical Company, respectively. Anhydrous $FeCl_3$ was used as purchased from Strem Chemical Company. All reactions were carried out under an argon atmosphere. Electronic absorption spectra were recorded on a Cary 17D spectrometer. The room temperature magnetic susceptibility measurements were recorded on a Johnson Matthey Instrument. Infrared spectra

---

*Part I is ref. 1.

**Author to whom correspondence should be addressed.

0020-1693/91/$3.50

were obtained on a Digilab FTS-60 spectrometer. Samples for infrared measurements were ground in mineral oil and placed between polished CsI plates. All manipulations for infrared measurements were completed under nitrogen. The microanalyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of $[FeCl_2(OPMe_3)]_\infty$ *(1)*

$FeCl_3$ (0.23 g, 1.44 mmol) was dissolved in 20 ml of THF and iron powder (0.04 g, 0.72 mmol) was added to the solution. The mixture was stirred and heated at reflux temperature for 4.5 h, giving a brown supernatant liquid and a small amount (*c.* 0.01 g) of grey powder. The procedure followed in the above reaction differs from that described for $FeCl_2$ by Wilkinson [6] in the amount of THF used. To the filtered brown liquid 0.199 g of $OPMe_3$ (3×0.72 mmol) was added. The reaction mixture was stirred for 18 h at room temperature, resulting in a clear yellow solution (UV–Vis: 500, 330 and 300 nm) and some yellow oily material. The solution was filtered through Celite to remove the oily substance and a layer of hexane was placed on the filtered yellow solution to effect crystallization. Several days later, diamond shaped pale pink crystals of **1** were obtained (UV–Vis, CH_2Cl_2: 355, 305 and 238 nm). These crystals were barely soluble in CH_2Cl_2, insoluble in the other common organic solvents and extremely hygroscopic. *Anal.* Calc. for $C_3H_9Cl_2FeOP$: C, 16.45; H, 4.11. Found: C, 16.19; H, 4.20%.

Preparation of $FeCl_2(OPMe_3)_2$ *(2)*

To the brown liquid, prepared as above, 0.397 g of $OPMe_3$ (6×0.72 mmol) was added. The reaction mixture was stirred for 18 h at room temperature, resulting in a pale yellow solution (UV–Vis: 500, 360(sh), 310 and 280 nm) and a yellow oily material. The solution was filtered through Celite, which removed the oily substance, and hexane was layered on the filtrate for crystallization. Irregular colorless crystals were obtained after several days (UV–Vis, CH_2Cl_2: 360, 300 and 265 nm). These crystals were also only slightly soluble in CH_2Cl_2, but more so than **1**. *Anal.* Calc. for $C_6H_{18}Cl_2FeO_2P_2$: C, 23.16; H, 5.79. Found: C, 22.65; H, 5.90%.

X-ray crystallography

The structure determinations were carried out in the normal way by employing the previously published standard methods in our laboratory. Calculations were done on a MicroVax II computer with an SDP software package. Structure solutions employed were from ref. 7. Procedural details and crystallographic information are given in Table 1. Suitable colorless crystals of complexes **1** and **2** were mounted inside Lindemann capillaries using a glove bag since the crystals were known to be hygroscopic. Accurate unit cell parameters were obtained by means of a least-squares analysis of 25 reflections in both cases. Intensity data on each compound were then collected utilizing the options specified in Table 1 and the general procedures for data collection as previously described [8]. The data for **1** were corrected for slight decay ($\sim6\%$); for **2**, three standard reflections measured every 250 reflections, showed no significant decay. Both data sets were corrected for Lorentz and polarization effects. In addition, absorption corrections were made using an empirical method [9] based on nine ψ scans ($\psi=0$–$360°$ every 10°) for χ values near 90°. The positions of the Fe atoms were determined from three-dimensional Patterson functions. The remaining non-hydrogen atoms were found by alternating least-squares full matrix cycles of refinement and difference Fourier maps. The cutoff ratio $F_o^2/\sigma(F_o^2)$ of 3 was used to define 'observed' data. For this the Enraf-Nonius SDP software was employed. The models consisting of all non-hydrogen atoms were first refined with isotropic then anisotropic thermal parameters to convergence. In both cases H atoms on the methyl groups were placed in calculated positions. In **1** thermal parameters for all of them were constrained to one value which was refined. In **2** the thermal parameters for H atoms on the same methyl group were constrained to one value which was refined. The atomic positional parameters are reported in Tables 2 and 3, and bond distances and angles are listed in Tables 4 and 5 for **1** and **2**, respectively.

Results and discussion

Syntheses

Complexes **1** and **2** can each be made by the reaction of a solution of iron(II) chloride in THF with Me_3PO. The product obtained is controlled by the quantity of Me_3PO used. The method described for the preparation of the iron(II) chloride solution is based upon that described by Wilkinson [6]. A usefully reactive solution of iron(II) chloride in THF can be obtained by treating $FeCl_3$ in THF with metallic iron. The procedure we have used for the reaction of a THF solution of $FeCl_3$ (11.5 g/l) with iron powder affords the tetranuclear compound $Fe_4Cl_8(THF)_6$, whether the $FeCl_3$ and Fe are in the stoichiometric 2:1 mole ratio or an excess of iron used [1]. This procedure differs from that described by Wilkinson [6] in the concentration of the $FeCl_3$ solution (270 g/l). Preliminary studies have shown that if we use the Wilkinson procedure a different

TABLE 1. Crystal data for **1** and **2**

Formula	$C_3H_9Cl_2FeOP$	$C_6H_{18}Cl_2FeO_2P_2$
Formula weight	218.83	310.91
Space group	$P2_1/n$	$P2_12_12_1$
Systematic absences	$h0l$, $h+l=2n+1$ $0k0$, $k=2n+1$	$h00$, $h=2n+1$ $0k0$, $k=2n+1$ $00l$, $l=2n+1$
a (Å)	6.810(2)	11.270(3)
b (Å)	12.943(5)	12.011(2)
c (Å)	9.645(2)	10.811(2)
α (°)	90	90
β (°)	100.224(2)	90
γ (°)	90	90
V (Å^3)	836.6(11)	1463.5(5)
Z	4	4
D_{calc} (g/cm^3)	1.737	1.411
Crystal size (mm)	0.45×0.40×0.30	0.5×0.5×0.3
μ(Mo Kα) (cm^{-1})	25.549	15.897
Data collection instrument	AFC5R	AFC5R
Radiation (monochromated in incident beam)	Mo Kα ($\lambda_\alpha=0.71073$ Å)	
Orientation reflections: no.; range (2θ) (°)	25, 18–21	25, 25–40
Temperature (°C)	19	21
Scan method	2θ–ω	2θ–ω
Data collection range, 2θ (°)	0–55	4–55
No. unique data, total with $F_o^2>3\sigma(F_o^2)$	2162, 1665	1926, 1356
No. parameters refined	101	142
Transmission factors: max., min. (%)	1.0000, 0.9414	1.0000, 0.8085
R[a]	0.041	0.052
R_w[b]	0.058	0.064
Quality-of-fit indicator[c]	1.442	1.36
Largest shift/e.s.d.	0.73	0.266
Largest peak (e/Å^3)	0.537	0.636

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2\{|F_o|\}$. [c] Quality-of-fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

product, containing an ionic face-sharing bioctahedral complex, $[Fe_2(\mu\text{-}Cl)_3(THF)_6]^+$, is obtained. This reaction is still under study. For convenience in the following discussion, all solutions of iron(II) chloride in THF are formally described as solutions of $FeCl_2(THF)_x$.

The reaction of an $FeCl_2(THF)_x$ solution with $OPMe_3$ gives one (or both) of two products, polymeric $[FeCl_2(OPMe_3)]_\infty$ or monomeric $FeCl_2(OPMe_3)_2$, depending on the concentration of $OPMe_3$. Monomeric $FeCl_2(OPMe_3)_2$ was obtained by reaction of $FeCl_3$, Fe and $OPMe_3$ in stoichiometric ratios 2:1:6, whereas polymeric $[FeCl_2(OPMe_3)]_\infty$ was obtained by reaction of $FeCl_3$, Fe and $OPMe_3$ in a 2:1:3 ratio. The preparative reactions for **1** and **2** can probably be described as follows.

Addition of Me_3PO to the $FeCl_2(THF)_x$ solution produces an intermediate, $FeCl_2(Me_3PO)(THF)_{x-1}$, which can either slowly polymerize by extrusion of the coordinated THF or be attacked by additional Me_3PO if an excess of the latter is present. The entire system seems to be kinetically sluggish and lacks long-term stability. However, we do not know what happens if the THF solution is simply allowed to stand. The products described here may be obtained, at least partially, by placing a layer of hexane on the THF solutions. Compounds **1** and **2** are thus obtained fairly quickly and efficiently. Neither of these products is very soluble in organic solvents and both are decomposed by water. It also appears that both of these materials may be thermodynamically unstable at room temperature since, on standing for several weeks in an inert atmosphere, they show signs of change, becoming white. The nature of the yellow oily materials that were removed by filtration through Celite is also unknown. They can be changed into solids that appear crystalline by treatment with CH_2Cl_2 but these solids seem to be mixtures, the components of which have not yet been identified.

In both **1** and **2** strong but broad absorptions were observed in the IR spectra at *c.* 1100 cm^{-1}. These may be assigned to the P–O stretching modes, downshifted from the value for Me_3PO itself, 1170 cm^{-1} [10], by coordination. Whether the broadness of these bands is entirely genuine or at least partly the result of partial hydrolysis during sample preparation is uncertain.

TABLE 2. Positional parameters and their e.s.d.s. for $[FeCl_2(OPMe_3)]_\infty$[a]

Atom	x	y	z	B (Å^2)
Fe	0.25260(4)	0.45260(3)	0.49042(3)	2.164(7)
Cl(1)	0.01288(9)	0.55413(6)	0.34611(7)	3.06(1)
Cl(2)	0.50133(9)	0.47847(6)	0.32896(6)	2.91(1)
P	0.3573(1)	0.21515(5)	0.57880(7)	2.48(1)
O	0.2698(3)	0.3021(2)	0.4824(2)	2.94(4)
C(11)	0.7417(6)	0.4043(3)	0.0186(4)	4.63(8)
C(12)	0.3192(5)	0.2348(3)	0.7542(3)	3.68(6)
C(13)	0.6191(5)	0.2013(4)	0.5839(4)	5.37(9)
H(111)	0.590(6)	0.390(3)	0.026(5)	4.3(4)*
H(112)	0.218(6)	0.577(3)	0.067(5)	4.3*
H(113)	−0.180(6)	0.468(4)	0.073(4)	4.3*
H(121)	−0.131(6)	0.304(4)	0.306(5)	4.3*
H(122)	0.192(7)	0.247(4)	0.747(5)	4.3*
H(123)	0.378(7)	0.287(3)	0.775(5)	4.3*
H(131)	−0.151(6)	0.679(3)	0.011(5)	4.3*
H(132)	0.161(6)	0.377(3)	0.139(5)	4.3*
H(133)	0.664(6)	0.281(4)	0.600(4)	4.3*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $1/3[a^2a^{*2}B_{11}+b^2b^{*2}B_{22}+c^2c^{*2}B_{33}+2ab(\cos\gamma)a^*b^*B_{12}+2ac(\cos\beta)a^*c^*B_{13}+2bc(\cos\alpha)b^*c^*B_{23}]$. Starred atoms were refined isotropically.

TABLE 3. Positional parameters and their e.s.d.s. for $FeCl_2(OPMe_3)_2$[a]

Atom	x	y	z	B (Å^2)
Fe	0.00321(9)	0.94021(8)	0.9304(1)	3.98(2)
Cl(1)	0.0881(2)	1.1130(2)	0.9234(2)	5.64(5)
Cl(2)	−0.0299(2)	0.8789(2)	1.1285(2)	5.35(5)
P(1)	−0.2512(2)	0.8531(2)	0.8410(2)	4.02(4)
P(2)	0.1801(2)	0.8408(2)	0.7257(2)	3.84(4)
O(1)	−0.1474(5)	0.9316(5)	0.8344(6)	5.2(1)
O(2)	0.1039(5)	0.8309(4)	0.8393(5)	4.9(1)
C(11)	−0.3636(9)	0.9014(9)	0.946(1)	6.5(2)
C(12)	−0.2081(8)	0.7168(7)	0.8917(9)	5.0(2)
C(13)	−0.319(1)	0.838(1)	0.692(1)	6.5(3)
C(21)	0.3128(8)	0.9175(9)	0.7570(9)	5.8(2)
C(22)	0.1044(9)	0.9090(8)	0.6016(9)	6.1(2)
C(23)	0.2216(9)	0.7076(7)	0.6709(9)	5.3(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $1/3[a^2a^{*2}B_{11}+b^2b^{*2}B_{22}+c^2c^{*2}B_{33}+2ab(\cos\gamma)a^*b^*B_{12}+2ac(\cos\beta)a^*c^*B_{13}+2bc(\cos\alpha)b^*c^*B_{23}]$.

TABLE 4. Bond distances (Å) and angles (°) and their e.s.d.s. for $[FeCl_2(OPMe_3)]_\infty$[a]

Distances	
Fe–Fe′	3.688(0)
Fe–Fe″	3.560(0)
Fe–Cl(1)	2.350(1)
Fe–Cl(1)′	2.603(1)
Fe–Cl(2)	2.518(1)
Fe–Cl(2)′	2.367(1)
Fe–O	1.954(2)
P–O	1.513(2)
P–C(11)	1.784(4)
P–C(12)	1.774(3)
P–C(13)	1.783(3)
Angles	
Cl(1)–Fe–Cl(1)′	83.88(2)
Cl(1)–Fe–Cl(2)	91.84(3)
Cl(1)–Fe–Cl(2)′	123.49(3)
Cl(1)–Fe–O	125.05(5)
Cl(1)′–Fe–Cl(2)	174.14(3)
Cl(1)′–Fe–Cl(2)′	92.52(2)
Cl(1)′–Fe–O	92.50(6)
Cl(2)–Fe–Cl(2)′	86.50(2)
Cl(2)–Fe–O	93.23(6)
Cl(2)′–Fe–O	111.43(5)
Fe–Cl(1)–Fe′	96.12(3)
Fe–Cl(2)–Fe″	93.50(2)
Fe–O–P	137.5(1)
O–P–C(11)	110.0(1)
O–P–C(12)	111.8(1)
O–P–C(13)	112.0(2)
C(11)–P–C(12)	107.7(2)
C(11)–P–C(13)	107.6(2)
C(12)–P–C(13)	107.6(2)

[a] Numbers in parentheses are e.s.d.s. in the least significant digits.

Structure and bonding for compound 1

An ORTEP drawing showing the atomic numbering scheme for **1** is presented in Fig. 1. Table 4 lists distances and angles. The polymer consists of a linear chain of trigonal planar $FeCl_2(OPMe_3)$ units arranged so that each iron atom has one of the equatorial chloride ligands on each adjacent Fe center above and the other below this unit. Thus, an overall distorted trigonal bipyramidal geometry exists at each Fe atom in the polymer. The equatorial plane is perfect, with the sum of two Cl–Fe–O angles and one Cl–Fe–Cl being 360°, but the trigonal symmetry is appreciably distorted with the individual angles being 111.4, 125.1 and 123.5°. The Cl(1)′–Fe–Cl(2) axis is nearly linear, 174.14(3)°, and deviates only a few degrees from perpendicularity to the equatorial plane. Another deviation from trigonal symmetry arises from the differences in the Fe–Cl and the Fe–O distances, with the mean Fe–Cl = 2.36(1) Å and Fe–O = 1.95 Å. Each $FeCl_2(OPMe_3)$ entity relates to its symmetry equivalents across centers of inversion, the positions of which are located at the midpoints of the adjacent Fe...Fe vectors. The infinite chains of the $[FeCl_2(OPMe_3)]_\infty$ polymeric units are arranged along the a axis of the unit cell.

The fact that the distances between adjacent iron atoms are different, 3.688(0) versus 3.560(0) Å, is related to the distorted geometry around the Fe atom. There are four different Fe–Cl distances in the Fe coordination, i.e. Fe–Cl(1) = 2.350(1) Å,

TABLE 5. Bond distances (Å) and angles (°) and their e.s.d.s. for $FeCl_2(OPMe_3)_2$[a]

Distances	
Fe–Cl(1)	2.287(2)
Fe–Cl(2)	2.295(2)
Fe–O(1)	1.992(6)
Fe–O(2)	1.995(6)
P(1)–O(1)	1.505(6)
P(1)–C(11)	1.795(11)
P(1)–C(12)	1.793(8)
P(1)–C(13)	1.788(11)
P(2)–O(2)	1.503(6)
P(2)–C(21)	1.789(9)
P(2)–C(22)	1.789(10)
P(2)–C(23)	1.769(9)
Angles	
Cl(1)–Fe–Cl(2)	113.0(1)
Cl(1)–Fe–O(1)	112.7(2)
Cl(1)–Fe–O(2)	110.1(2)
Cl(2)–Fe–O(1)	109.3(2)
Cl(2)–Fe–O(2)	110.0(2)
O(1)–Fe–O(2)	101.2(2)
O(1)–P(1)–C(11)	112.1(4)
O(1)–P(1)–C(12)	112.1(4)
O(1)–P(1)–C(13)	110.6(5)
C(11)–P(1)–C(12)	107.1(5)
C(11)–P(1)–C(13)	107.3(5)
C(12)–P(1)–C(13)	107.5(5)
O(2)–P(2)–C(21)	111.3(4)
O(2)–P(2)–C(22)	112.2(4)
O(2)–P(2)–C(23)	110.7(4)
C(21)–P(2)–C(22)	107.7(5)
C(21)–P(2)–C(23)	108.0(5)
C(22)–P(2)–C(23)	106.8(5)
Fe–O(1)–P(1)	132.1(4)
Fe–O(2)–P(2)	132.5(3)

[a] Numbers in parentheses are e.s.d.s. in the least significant digits.

Fe–Cl(2)′ = 2.367(1) Å, for the equatorial bonds and Fe–Cl(1)′ = 2.603(1) Å, Fe–Cl(2) = 2.518(1) Å for the apical bonds. The distortions from a regular trigonal bipyramidal structure are shown in detail in Fig. 2.

In the $FeCl_4^{2-}$ anion, which contains the high-spin state Fe(II) ion, the average Fe–Cl distance was found to be 2.29 Å [11]. In **1**, the Fe–Cl distances are in the range 2.35–2.60 Å. The longer Fe–Cl distances in **1** are due to the facts that the chlorine atoms are bridging rather than terminal ligands, and the coordination number of the metal atom is higher.

The Fe–O bond distance of 1.954(2) Å is shorter than the equivalent Fe–O distances found in $[FeCl_2 \cdot 2H_2O]_\infty$ (2.07 Å) and $FeCl_2 \cdot 4H_2O$ (2.09 Å). This is due, in part at least, to the lower coordination numbers of iron in the present case. The P–O distance is 1.513(2) Å, which is a normal P–O distance in phosphine oxide complexes [12]. This is considerably less than the expected single-bond distance (~1.7 Å) and suggests that there is considerable back-bonding. The angle Fe–O–P is 137.5(1)°.

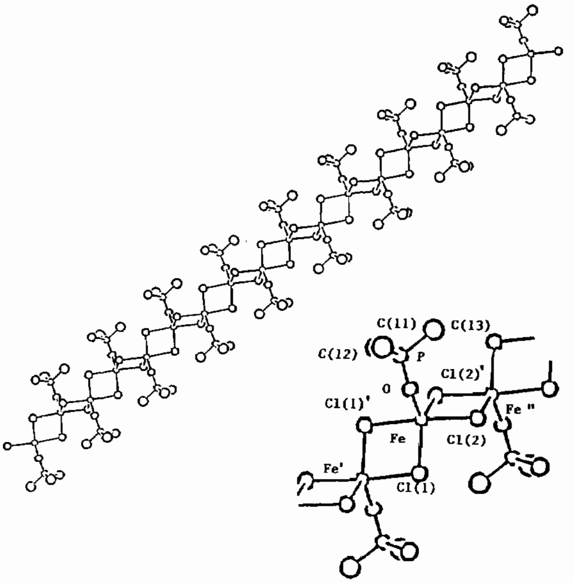

Fig. 1. ORTEP drawing of compound **1** showing the atom numbering scheme.

Compound 2

Bond distances and angles are listed in Table 5. An ORTEP drawing of the molecule is presented in Fig. 3, together with the numbering scheme used.

The structure, as shown in Fig. 3, is clearly tetrahedral. The angles defined by Cl(1)–Fe–Cl(2), Cl(1)–Fe–O(1), Cl(1)–Fe–O(2), Cl(2)–Fe–O(1) and Cl(2)–Fe–O(2) are all close to 109°. The Fe–O–P angle in **2** is 132.3(2)°. The average Fe–Cl distance is 2.291(4) Å, and the average Fe–O and P–O distances are 1.994(2) and 1.504(1) Å, respectively.

Tetrahedral geometries for Fe(II) d^6 complexes are not rare. For instance, tetrahedral structures have been found for the tetrahalogenoferrate(II) ions ($FeCl_4^{2-}$, $FeBr_4^{2-}$, FeI_4^{2-}) [11] and the tetraisothiocyanatoferrate(II) ion [13], $Fe(SCN)_4^{2-}$. Furthermore, the compounds $Fe(Ph_3P)_2X_2$, where X = Cl, Br or I, have been described and although not structurally verified by X-ray techniques it appears that these compounds also contained tetrahedrally coordinated iron(II) [14]. Complexes of the type FeL_2X_2, where L = Ph_3AsO, Ph_3PO or quinoline, and X = Cl or Br, have also been discussed [15]. The electronic spectra of these FeL_2X_2 complexes were in accord with the essentially tetrahedral structures postulated on the basis of the X-ray powder diffraction photographs. The Fe–Cl distances of the tetrachloroferrate(II) anion in various salts have been compared [16]. However, there is no previous X-ray single crystal structural analysis of any neutral four-coordinated iron(II) complex.

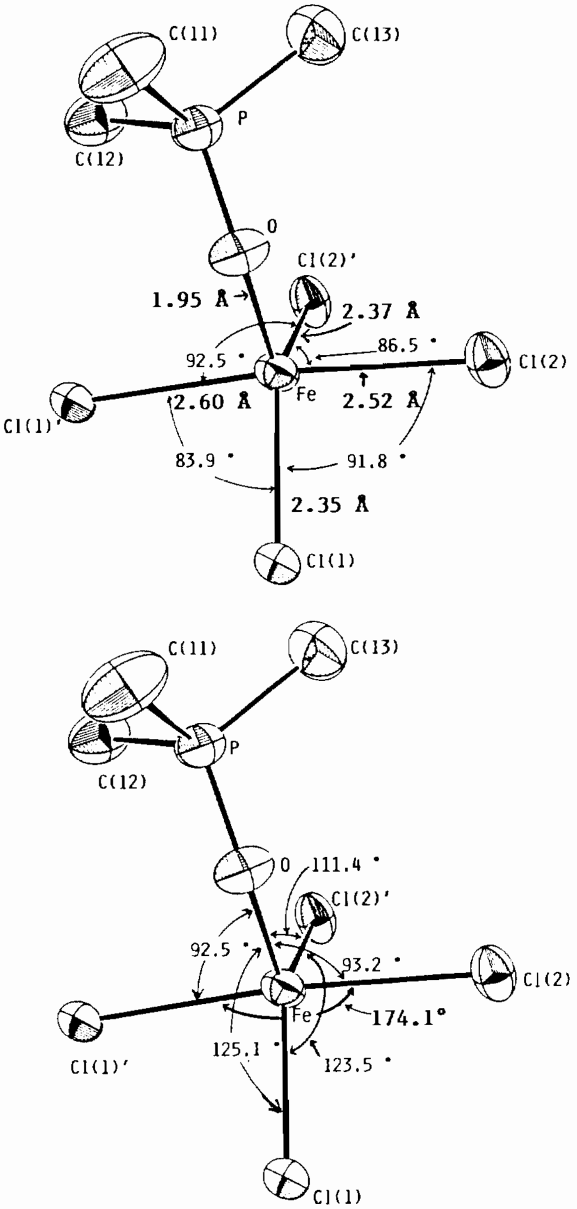

Fig. 2. Atomic environments of the iron atom in **1** with thermal ellipsoids drawn at the 50% probability level.

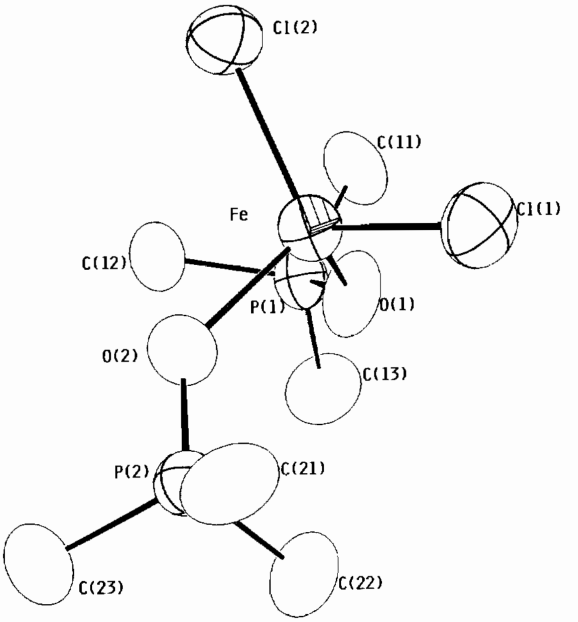

Fig. 3. ORTEP drawing of compound **2** showing the atom numbering scheme.

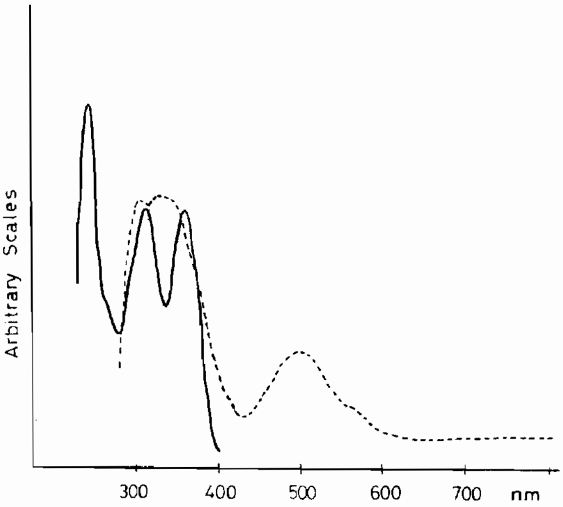

Fig. 4. Electronic absorption spectra of $[FeCl_2(OPMe_3)]_\infty$. ——, $[FeCl_2(OPMe_3)]_\infty$ (**1**) in CH_2Cl_2 solution; – – –, mother liquor in THF solution.

Magnetic properties

The magnetic susceptibilities were measured at 25 °C. The results are as follows: for **1**, $\chi_g = 43.35 \times 10^{-6}$ cgsu, $\chi_{mol} = 9.93 \times 10^{-3}$ cgsu, $\chi_{mol}^{corr} = 10.07 \times 10^{-3}$ cgsu. From this, by employing the Curie equation [17], $\mu_{eff} = 4.90$ μ_B, which is a reasonable value for high spin Fe^{2+} containing 4 unpaired electrons. For **2**, $\chi_g = 40.29 \times 10^{-6}$ cgsu, $\chi_{mol} = 12.53 \times 10^{-3}$ cgsu, $\chi_{mol}^{corr} = 12.74 \times 10^{-3}$ cgsu. Again, by employing the Curie equation, $\mu_{eff} = 5.51$ μ_B is obtained. This also is an appropriate value for high spin Fe^{2+} containing 4 unpaired electrons. The magnetic moment of **1** may be smaller than that of **2** because of either weak direct magnetic exchange between Fe atoms or superexchange interactions through the bridging Cl atoms.

Electronic absorption spectra

In the case of **1**, the spectrum for the initial clear yellow solution and that for a sample of **1** in CH_2Cl_2 are shown as the dotted and the continuous lines, respectively, in Fig. 4. In the case of **2**, the spectrum for the initial pale yellow solution and that for a sample of **2** in CH_2Cl_2 are shown as the dotted and the continuous lines, respectively, in Fig. 5. The pale

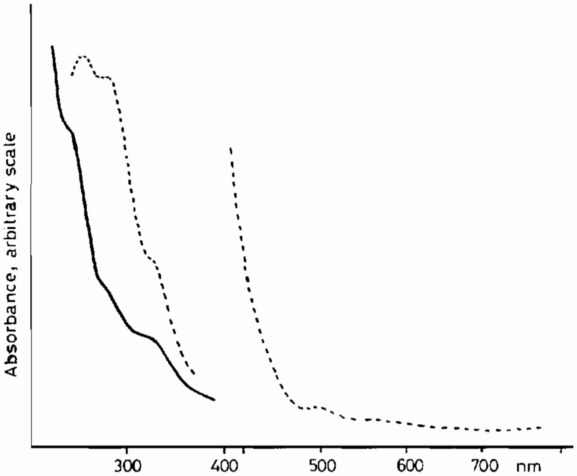

Fig. 5. Electronic absorption spectra of $FeCl_2(OPMe_3)_2$. ——, $FeCl_2(OPMe_3)_2$ (**2**) in CH_2Cl_2 solution; – – –, mother liquor in THF solution. The spectra below 400 nm are for more dilute samples since the peaks have high intensities.

color of the initial yellow solution in the syntheses of **1** and **2** may have arisen from the parity- or spin-forbidden transition of some unknown $FeCl_3$ complexes. With high-spin d^6 complexes of iron(II), there are spin-allowed transitions in the near IR region and charge transfer bands in the UV region [18]. However only charge transfer bands have been observed in each of the present cases.

Supplementary material

Lists of anisotropic thermal parameters and structure factors are available from author F.A.C.

Acknowledgement

We thank the National Science Foundation for support.

References

1 F. A. Cotton, R. L. Luck and K.-A. Son, *Inorg. Chim. Acta, 179* (1991) 11.
2 F. A. Cotton, R. L. Luck and K.-A. Son, *Acta Crystallogr., Sect. C, 46* (1990) 1424.
3 G. Wilkinson (ed.), *Comprehensive Coordination Chemistry*, Vol. IV, Pergamon, Oxford, U.K., 1987, p. 1235.
4 B. Morrison and E. J. Graeber, *J. Chem. Phys., 42* (1965) 898.
5 B. R. Penfold and J. A. Grigor, *Acta Crystallogr., 12* (1959) 850.
6 G. Wilkinson, *Org. Synth., 36* (1956) 31.
7 G. M. Sheldrick, *SHELXS-86*, Institut für Anorganische Chemie der Universität, Göttingen, F.R.G.
8 A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 18* (1979) 3558.
9 A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
10 L. W. Daasch and D. C. Smith, *J. Chem. Phys., 19* (1951) 22.
11 N. S. Gill, *J. Chem. Soc.*, (1961) 3512.
12 F. A. Cotton, R. D. Barnes and E. Bannister, *J. Chem. Soc.*, (1960) 2199.
13 D. Foster and D. M. L. Goodgame, *J. Chem. Soc.*, (1965) 268.
14 L. Naldini, *Gazzetta, 90* (1960) 391.
15 D. Foster and D. M. L. Goodgame, *J. Chem. Soc.*, (1965) 454.
16 J. W. Lauher and J. A. Ibers, *Inorg. Chem., 14* (1975) 348.
17 R. L. Carlin, *Magnetochemistry*, Springer, New York, 1989, p. 19.
18 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1968, p. 299.