New polynuclear compounds of iron(II) chloride with oxygen donor ligands
Part I. $Fe_4Cl_8(THF)_6$: synthesis and a single crystal X-ray structure determination

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 June 18, 1990)

Abstract

A new polynuclear compound of Fe(II) chloride with oxygen donor ligands has been isolated as a colorless crystalline solid, $Fe_4Cl_8(THF)_6$ (**1**), by the reaction of $FeCl_3$ and Fe in THF. **1** consists of centrosymmetric, tetranuclear molecules with two different types of Fe atoms, two (Fe(1) and Fe(1)′) in trigonal bipyramidal environments and the others (Fe(2) and Fe(2)′) in octahedral environments. Each trigonal bipyramidally coordinated iron atom is linked through doubly- and triply-shared chlorine atoms to an iron atom in an octahedral environment. The magnetic moment of **1**, per iron atom, at room temperature is 5.40 BM, which is a reasonable value for high spin Fe^{2+}. The Fe...Fe distances are 3.656(1) and 3.750(1) Å for Fe(1)...Fe(2) and Fe(2)...Fe(2)′, respectively. The order of Fe–Cl distances, Fe–(μ_3-Cl) > Fe–(μ_2-Cl) > Fe–Cl_t, is as expected. The Fe–Cl_t distance is 2.244(1) Å, the Fe–(μ_2-Cl) distances are 2.355(1)–2.488(2) Å and the Fe–(μ_3-Cl) distances are 2.506(1)–2.737(1) Å. The average Fe–O distance is 2.135(9) Å. Crystallographic data: **1**, triclinic, space group $P1$, $a = 10.607(2)$, $b = 10.993(3)$, $c = 10.038(2)$ Å, $\alpha = 111.84(3)°$, $\beta = 98.28(3)°$, $\gamma = 63.18(3)°$, $V = 969.2(6)$ Å^3, $Z = 1$, $R = 0.048$ ($R_w = 0.069$) for 188 parameters and 2616 unique data having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

With simple oxygen donor ligands, iron(II) complexes are high spin and usually easily oxidized by air to iron(III) species [1]. Some polymeric complexes of iron(II) chloride containing oxygen donor ligands were observed in the dihydrate [2] and tetrahydrate [3] forms which were characterized by single crystal X-ray determinations. The crystal structure of iron(II) chloride dihydrate consists of polymeric chains of metal and chlorine ions arranged in a near-square planar configuration with each chlorine ion shared by two metal ions; the water molecules fill the remaining octahedral positions about the metal ions [2]. The crystal structure of iron(II) chloride tetrahydrate consists of discrete $Fe(H_2O)_4Cl_2$ groups which are distorted octahedra [3]. However, the structures of polynuclear compounds of iron(II) chloride with other oxygen donor ligands such as tetrahydrofuran (THF) have not been reported previously.

We report here the preparation and the single crystal structure determination of a remarkable new polynuclear compound of iron(II) chloride with THF ligands. The point of departure for our work was the observation by Wilkinson that a usefully reactive solution of iron(II) chloride in THF could be obtained by reacting $FeCl_3$ in THF with metallic iron [4].

Experimental

Tetrahydrofuran (THF) was dried by refluxing over Na/K alloy. Anhydrous $FeCl_3$ and Fe were used as purchased from Aldrich and Strem Chemical Co., respectively. All reactions were carried out in an argon atmosphere. The electronic absorption spectrum was recorded on a Cary 17D spectrometer.

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50 © Elsevier Sequoia/Printed in Switzerland

The room temperature magnetic susceptibility measurement was recorded on a Johnson Matthey instrument.

Preparation of $Fe_4Cl_8(THF)_6$ (1)

$FeCl_3$ (0.23 g, 1.42 mmol) was dissolved in 20 ml of THF and iron powder (0.04 g, 0.72mmol) was added. The mixture was stirred and heated under argon at reflux temperature for 4.5 h. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into the filtered brown solution. These crystals were extremely hygroscopic and barely soluble in THF. UV–Vis data (THF, λ_{max}, nm): 320, 275, 255.

X-ray crystallography

The structure determination was carried out in a routine fashion by employing methods standard in our laboratory. The calculations were done on a MicroVax II computer with the SDP package software. Structure solutions employed were from ref. 5. All relevant crystallographic information is given in Table 1. A suitable colorless crystal of complex 1 was mounted inside a Lindemann capillary. Accurate unit cell parameters were obtained by means of a least-squares analysis of 25 reflections. Intensity data on each compound were then collected by utilizing the options specified in Table 1 and the general procedures for data collection as previously described [6]. The data were corrected for decay (14% decay), Lorentz, and polarization effects. In addition, an absorption correction was also made using an empirical method based on nine ψ scans (ψ = 0–360° every 10°) for χ values near 90° [7]. The heavy atoms (Fe, Cl) were located from a three-dimensional Patterson function. The remaining non-hydrogen atoms were found by alternating least-squares full matrix cycles of refinement and difference Fourier maps for a cutoff ratio $F_o^2/\sigma(F_o^2)$ of 3. For this the Enraf-Nonius SDP software was employed. All of the non-hydrogen atoms were then refined with anisotropic thermal parameters. The model was first refined with isotropic then anisotropic thermal parameters to convergence. The H atoms were placed in calculated positions and their thermal parameters constrained to one value which was refined. The

TABLE 1. Crystal data for $Fe_4Cl_8(THF)_6$

Formula	$C_{24}H_{48}Cl_8Fe_4O_6$
Formula weight	939.66
Space group	$P\bar{1}$
Systematic absences	none
a (Å)	10.607(2)
b (Å)	10.993(3)
c (Å)	10.038(2)
α (°)	111.84(3)
β (°)	98.28(3)
γ (°)	63.18(3)
V (Å^3)	969.2(6)
Z	1
D_{calc} (g/cm^3)	1.610
Crystal size (mm)	0.5×0.4×0.3
μ(Mo Kα) (cm^{-1})	20.586
Data collection instrument	AFC5R
Radiation (monochromated in incident beam)	Mo Kα ($\lambda\bar{\alpha}$ = 0.71073 Å)
Orientation reflections, no., range (2θ)	25, 20–22
Temperature (°C)	19
Scan method	2θ–ω
Data collection range, 2θ (°)	0–55
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3105, 2616
No. parameters refined	188
Transmission factors, max., min.	1.0000, 0.8716
R[a]	0.048
R_w[b]	0.069
Quality-of-fit indicator[c]	1.460
Largest shift/e.s.d., final cycle	0.008
Largest peak (e/Å^3)	0.655

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + 0.001|F_o|^2]$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

TABLE 2. Positional parameters and their e.s.d.s for $Fe_4Cl_8(THF)_6$[a]

Atom	x	y	z	B (Å^2)
Fe(1)	0.22618(6)	0.08031(6)	0.20683(6)	3.65(2)
Fe(2)	−0.08083(6)	0.18489(6)	−0.01555(6)	4.13(2)
Cl(1)	−0.0330(1)	0.0772(1)	0.1772(1)	3.35(3)
Cl(2)	0.1420(1)	0.2113(1)	0.0474(1)	4.26(4)
Cl(3)	0.3109(1)	−0.1709(1)	0.0759(1)	4.14(4)
Cl(4)	0.1956(2)	0.1843(2)	0.4462(1)	6.88(7)
O(1)	0.4345(4)	0.0656(4)	0.2061(4)	5.0(1)
O(2)	−0.1924(4)	0.4049(3)	0.1252(3)	4.7(1)
O(3)	−0.1021(4)	0.2612(4)	−0.1864(3)	4.4(1)
C(11)	0.4656(7)	0.1747(8)	0.1933(8)	7.2(3)
C(12)	0.5831(7)	0.1817(8)	0.2888(8)	7.5(3)
C(13)	0.632(1)	0.062(1)	0.340(1)	10.3(5)
C(14)	0.5495(6)	−0.0221(7)	0.2719(8)	7.3(3)
C(21)	−0.3293(6)	0.5096(6)	0.1029(6)	5.9(2)
C(22)	−0.4146(8)	0.5591(9)	0.2349(8)	8.9(3)
C(23)	−0.3107(7)	0.5205(8)	0.3482(7)	7.1(3)
C(24)	−0.1701(6)	0.4537(6)	0.2791(5)	5.7(2)
C(31)	−0.1214(8)	0.1844(6)	−0.3345(5)	6.0(2)
C(32)	−0.1733(7)	0.2927(7)	−0.4080(6)	6.3(3)
C(33)	−0.1409(9)	0.4132(7)	−0.3131(7)	7.2(3)
C(34)	−0.0707(8)	0.3740(7)	−0.1886(6)	6.9(3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $\frac{4}{3}[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

TABLE 3. Selected bond distances (Å) and angles (°) and their e.s.d.s for $Fe_4Cl_8(THF)_6$[a]

Distances (Å)		Angles (°)	
Fe(1)–Fe(2)	3.656(1)	Cl(1)–Fe(1)–Cl(2)	84.81(5)
Fe(2)–Fe(2)′	3.750(1)	Cl(1)–Fe(1)–Cl(3)	84.52(4)
Fe(1)–Cl(1)	2.737(1)	Cl(1)–Fe(1)–Cl(4)	91.67(6)
Fe(1)–Cl(2)	2.364(2)	Cl(1)–Fe(1)–O(1)	173.68(9)
Fe(1)–Cl(3)	2.355(1)	Cl(2)–Fe(1)–Cl(3)	109.76(4)
Fe(1)–Cl(4)	2.244(1)	Cl(2)–Fe(1)–Cl(4)	123.70(5)
Fe(1)–O(1)	2.142(4)	Cl(2)–Fe(1)–O(1)	93.1(1)
Fe(2)–Cl(1)	2.506(1)	Cl(3)–Fe(1)–Cl(4)	125.82(6)
Fe(2)–Cl(1)′	2.517(1)	Cl(3)–Fe(1)–O(1)	90.6(1)
Fe(2)–Cl(2)′	2.474(2)	Cl(4)–Fe(1)–O(1)	94.4(1)
Fe(2)–Cl(3)	2.488(2)	Cl(1)–Fe(2)–Cl(1)′	83.44(4)
Fe(2)–O(2)	2.145(3)	Cl(1)–Fe(2)–Cl(2)′	87.72(5)
Fe(2)–O(3)	2.117(4)	Cl(1)–Fe(2)–Cl(3)	93.61(5)
O(1)–C(11)	1.431(11)	Cl(1)′–Fe(2)–Cl(2)′	95.78(4)
O(1)–C(14)	1.426(8)	Cl(1)′–Fe(2)–Cl(3)	86.70(4)
O(2)–C(21)	1.441(6)	Cl(1)–Fe(2)–O(2)	175.1(1)
O(2)–C(24)	1.457(6)	Cl(1)–Fe(2)–O(3)	92.61(8)
O(3)–C(31)	1.449(6)	Cl(2)′–Fe(2)–Cl(3)	177.31(5)
O(3)–C(34)	1.431(11)	Cl(2)′–Fe(2)–O(2)	88.6(1)
C(11)–C(12)	1.472(10)	Cl(2)′–Fe(2)–O(3)	89.1(1)
C(12)–C(13)	1.439(15)	Cl(3)–Fe(2)–O(2)	88.9(1)
C(13)–C(14)	1.480(14)	Cl(3)–Fe(2)–O(3)	89.8(1)
C(21)–C(22)	1.494(11)	O(2)–Fe(2)–O(3)	89.6(1)
C(22)–C(23)	1.505(10)	O(2)–Fe(2)–Cl(1)′	94.7(1)
C(23)–C(24)	1.475(9)	Fe(2)–Cl(1)–Fe(2)′	96.56(4)
C(31)–C(32)	1.486(10)	Fe(1)–Cl(2)–Fe(2)′	98.11(7)
C(32)–C(33)	1.470(11)	Fe(1)–Cl(3)–Fe(2)	99.09(4)
C(33)–C(34)	1.464(10)	Fe(1)–O(1)–C(11)	124.8(3)
		Fe(1)–O(1)–C(14)	122.0(5)
		C(11)–O(1)–C(14)	109.3(5)
		Fe(2)–O(2)–C(21)	126.6(3)
		Fe(2)–O(2)–C(24)	123.3(3)
		C(21)–O(2)–C(24)	106.2(3)
		Fe(2)–O(3)–C(31)	124.2(4)
		Fe(2)–O(3)–C(34)	128.4(3)
		C(31)–O(3)–C(34)	106.1(5)

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

atomic positional parameters are reported in Table 2, and selected bond distances and angles are listed in Table 3.

Results and discussion

Synthesis

The procedure we have followed for the reaction of $FeCl_3$ with iron powder allows us to isolate the tetranuclear complex $Fe_4Cl_8(THF)_6$, whether the $FeCl_3$ and Fe are in the stoichiometric 2:1 mole ratio or an excess of iron is used. This reaction procedure differs from that described for $FeCl_2$ in ref. 4 in the amount of THF used. Preliminary studies have shown that if we use the same amount of THF as in the Wilkinson procedure a different product, which contains an ionic face-sharing bioctahedral complex, $[Fe_2(\mu\text{-}Cl_3)(THF)_6]^+$, is obtained. The counterion is still unknown and this reaction is being further studied.

Structure and bonding

An ORTEP drawing of the structure is given in Fig. 1, and the pertinent bond distances and angles are listed in Table 3. The molecule resides on a crystallographic inversion center and there is only one molecule in the unit cell.

The complexity of the structure is surprising. Presumably simpler (perhaps mononuclear) species exist in solution. The $Fe_4Cl_8(THF)_6$ molecule contains iron atoms in two quite different coordination environments. For Fe(1) and Fe(1)′ there is a trigonal bipyramid in which the equatorial plane is formed by three chlorine atoms, one terminal and two of the μ_2-Cl type, while the axial positions are occupied by a THF oxygen atom and a μ_3-Cl atom. The equatorial plane is nearly perfect, with the sum of the three Cl–Fe–Cl angles being 359.3°, but the trigonal symmetry is appreciably distorted with the individual angles being 109.8, 123.7 and 125.8°. The O(1)–Fe–Cl(1) axis is nearly linear 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 distances, two being about 2.36 Å (to μ_2-Cl atoms) and the other 2.244(1) Å (to the terminal Cl atom).

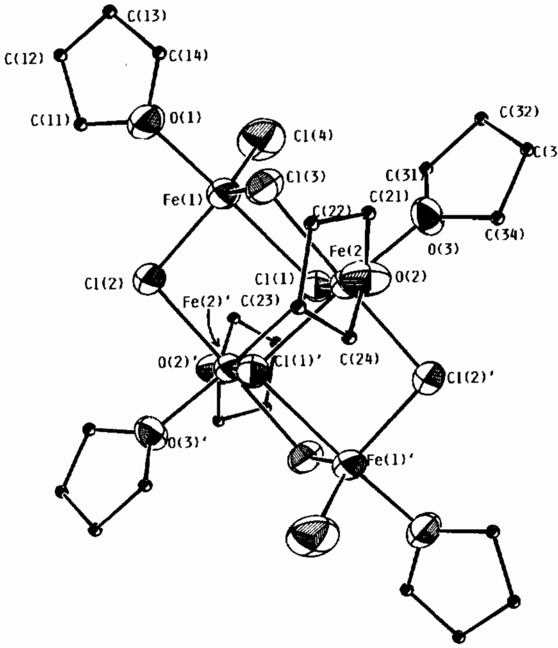
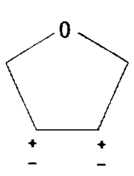


Fig. 1. An ORTEP drawing of 1. Singly primed atoms are related to unprimed atoms by an inversion center located at the mid point.

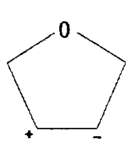
The 'octahedral' coordination about Fe(2) and Fe(2)′ is rather good in terms of angles subtended at the metal atom, all of these being within less than 5° of 90 or 180°. The distances, of course, are not equal since there are six non-equivalent ligands.

There are three types of Cl ligand: terminal, Cl_t; μ_2-Cl and μ_3-Cl. The order of Fe–Cl distances is Fe–(μ_3-Cl) > Fe–(μ_2-Cl) > Fe–Cl_t, as expected. The Fe–Cl_t distance is 2.244(1) Å, which is a normal Fe(II)–Cl_t distance. The Fe–(μ_2-Cl) distances are in the range 2.355(1)–2.488(2) Å, and the Fe–(μ_3-Cl) distances in the range 2.506(1)–2.737(1) Å. In the $FeCl_4^{2-}$ anion, which contains high-spin Fe(II), the average Fe–Cl distance is 2.29 Å.

Two common conformational geometries found for coordinated THF molecules are shown below. Type I is the envelope conformation, with four carbon atoms coplanar, and type II is the half-chair ('twist') conformation.



Type I



Type II

In **1**, all the THF rings have type I conformations. The dihedral angle between the C(11)/O(1)/C(14) plane and the C(11)/C(12)/C(13)/C(14) plane is 17(1)°. The angle between the C(21)/O(2)/C(24) plane and the C(21)/C(22)/C(23)/C(24) plane is 33.9(6)° and the angle between the C(31)/O(3)/C(34) plane and the C(31)/C(32)/C(33)/C(34) plane is 28.8(7)°.

Magnetic properties

The magnetic susceptibility of **1** was measured at 21 °C. The results are as follows: $\chi_g = 52.046 \times 10^{-6}$ cgsu, $\chi_{mol} = 48.905 \times 10^{-3}$ cgsu, and $\chi_{mol}^{cor} = 49.477 \times 10^{-3}$ cgsu. From this, by employing the Curie equation [8], $\mu_{eff} = 2.828 \times (\chi_{mol}^{cor} T)^{1/2}$, we obtain $\mu_{eff} = 10.79$ μ_B. If we assume that both types of Fe(II) have the same magnetic moment, we can calculate the value $\mu_{Fe} = 5.40$ μ_B, which is a reasonable value for high-spin Fe^{2+}.

Electronic absorption spectra

The spectrum for a sample of **1** in THF is shown in Fig. 2. With high-spin d^6 complexes of iron(II), there should be spin-allowed transitions in the near IR region and charge transfer bands in the UV region [9]. However, only charge transfer bands have been observed in this case.

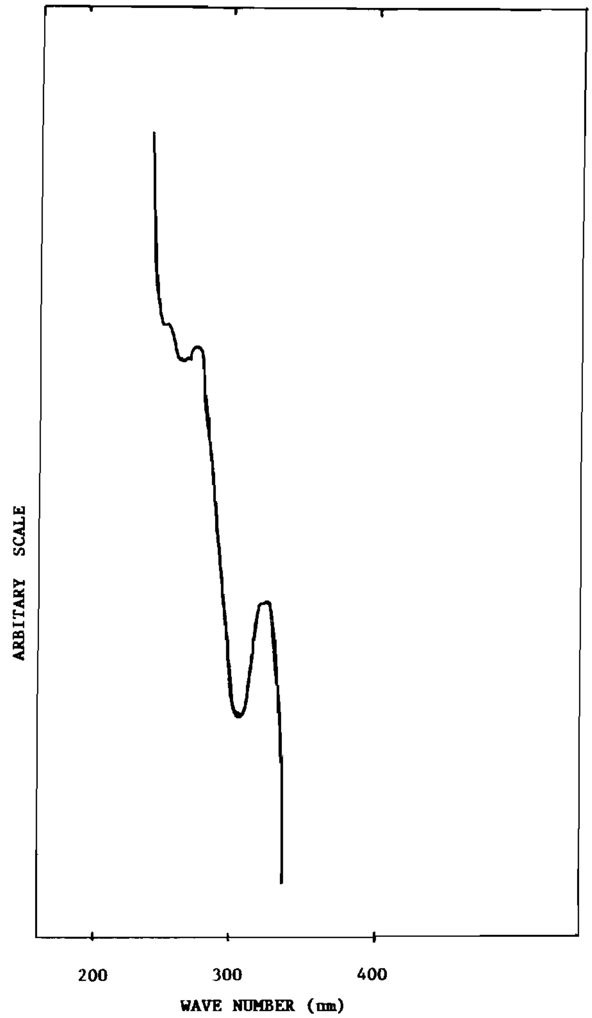


Fig. 2. Electronic absorption spectrum for **1** in THF.

Conclusions

Because of their general utility as synthetic reagents, tetrahydrofuran adducts of transition metal halides have been the subject of much study in the past. A few of them have been structurally characterized and in all cases so far they have been simple mononuclear species, either octahedral (e.g. $ScCl_3(THF)_3$, $TiCl_3(THF)_3$, $VCl_3(THF)_3$, $CrCl_3(THF)_3$, $MoCl_3(THF)_3$ and $MoI_3(THF)_3$) or tetrahedral in the case of $FeCl_3(THF)$ [10]. The $Fe_4Cl_8(THF)_6$ molecule is thus far more elaborate than previously characterized THF adducts. However, it is likely that this structure exists only in the crystalline solid.

Supplementary material

Tables of hydrogen atom positions, structure factors and anisotropic displacement parameters are available from author F.A.C.

Acknowledgement

We thank the National Science Foundation for support.

References

1 G. Wilkinson (ed.), *Comprehensive Coordination Chemistry,* Vol. 4, Pergamon, Oxford, 1987, p. 1235.
2 B. Morrison and E. J. Graeber, *J. Chem. Phys., 42* (1965) 898.
3 B. R. Penfold and J. A. Grigor, *Acta Crystallogr., 12* (1959) 850.
4 G. Wilkinson, in N. J. Leonard (ed.), *Organic Syntheses,* Vol. 36, Wiley, New York, 1956, p. 31.
5 G. M. Sheldrick, *SHELXS-86,* Institut für Anorganische Chemie der Universität, Göttingen, F.R.G.
6 A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem. 18* (1979) 3558.
7 A. C. T. North, D. C. Phillip and F. S. Matthews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
8 R. L. Carlin, *Magnetochemistry,* Springer, New York, 1989, p. 19.
9 A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, New York, 1968, p. 299.
10 (a) J. P. Fackler, Jr. (ed.), *Inorganic Syntheses,* Vol. 21, Wiley, New York, 1982, Ch. 4, p. 135; (b) F. A. Cotton, S. A. Duraj, G. L. Powell and W. J. Roth, *Inorg. Chim. Acta, 113* (1986) 81; (c) M. W. Anker, J. Chatt, G. J. Leigh and A. G. Wedd, *J. Chem. Soc., Dalton Trans.,* (1975) 2639; (d) J. R. Dilworth and J. Zubieta, in J. M. Shreeve (ed.), *Inorganic Syntheses,* Vol. 24, Wiley, New York, 1986, Ch. 4, p. 193; (e) F. A. Cotton and R. Poli, *Inorg. Chem., 26* (1987) 1514; (f) F. A. Cotton, R. L. Luck and K.-A. Son, *Acta Crystallogr., Sect. C, 46* (1990) 1424.