

Structure and Magnetic Properties of Iron(II) Chloride Tetrahydrofuranate $(2\text{FeCl}_2 \cdot 3\text{THF})_2$

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Abstract

On interacting FeCl_3 with Cp_2ReH in THF at room temperature white single crystals of the complex $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ (**I**) were obtained. The structure of (**I**) was established by total X-ray analysis. Crystals of the complex are triclinic (space group $P\bar{1}$) with the unit cell parameters: $a = 10.027(4)$, $b = 10.983(6)$, $c = 10.589(6)$ Å; $\alpha = 116.86(4)^\circ$, $\beta = 98.23(4)^\circ$, $\gamma = 68.09(4)^\circ$, $Z = 1$, $V = 964.7$ Å³. Four Fe(II) atoms in the molecule are bonded through the μ^3 -bridging Cl atoms ($\text{Fe}-\text{Cl}_{\text{av}} = 2.46$ Å), with the coordination sphere of each metal atom being supplemented by the bonding with two or one THF molecule ($\text{Fe}-\text{O}_{\text{av}} = 2.12$ Å). All the $\text{Fe} \cdots \text{Fe}$ distances in the molecule were non-bonding. The unique magnetic properties of (**I**) are shown to be specified by the co-existence of ferro- and anti-ferromagnetic exchange interactions.

Introduction

The structural chemistry of complexes of Fe(II) chloride with Lewis bases has been studied rather poorly, contrary to that of Fe(III) compounds. Typical coordination environments of the Fe atom in the former complexes are either octahedral $[\text{Cl}_4\text{L}_2]$, $[\text{Cl}_2\text{L}_4]$, or tetrahedral $[\text{Cl}_4]$. Tetrahydrofuran complexes of FeCl_2 have not been reported in the literature. That is why it was of interest to study the structure and magnetic properties of the unusual complex, $(2\text{FeCl}_2 \cdot 3\text{C}_4\text{H}_8\text{O})_2$ (**I**), which was

obtained on reduction of FeCl_3 with rhenium bis-cyclopentadienylhydride in THF.

Experimental

Synthesis of $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ (**I**)

The solution of 0.65 g (4.0 mmol) of FeCl_3 in 40 ml of THF was slowly added on mixing 30 ml of 0.04 M solution of Cp_2ReH (1.3 mmol) in THF. The resulting sediment was filtered off, and the filtrate was concentrated by evaporation up to the volume of ~10 ml. The precipitated crystals were filtered, washed with 2×5 ml of cold (0°) THF, and dried *in vacuo*. 0.47 g of white microcrystalline compound was obtained (yield 75%). Found, %: Fe 23.3; Cl 30.4. Calculated for $(2\text{FeCl}_2 \cdot 3\text{THF})_2$, %: Fe 23.8; Cl 30.2. Transparent colourless single crystals of $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ were obtained in the phase border for tetrahydrofuran–pentane under argon.

X-ray Structure Study

Recording of the single crystal of (**I**) packed in a thin-walled glass capillary was performed using 'Syntex $P\bar{1}$ ' diffractometer (Mo-K α irradiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{\text{max}} \leq 50^\circ$). 1302 reflections with $I > 2\sigma(I)$ were used for calculations, correction for extinction was neglected ($\mu_{\text{Mo}} = 20.9$ cm⁻¹). Crystals of **I** were triclinic: $a = 10.027(4)$, $b = 10.983(6)$, $c = 10.589(6)$ Å; $\alpha = 116.86(4)^\circ$, $\beta = 98.23(4)^\circ$, $\gamma = 68.09(4)^\circ$, $Z = 1$, space group $P\bar{1}$, $V = 964.7$ Å³, $\rho_{\text{calcd}} = 1.62$ g/cm³. The structure was solved by the combination of the direct method and the heavy-atom one, the hydrogen atom coordinates in the tetrahydrofuran cycles

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TABLE I. Coordinates of Atoms ($\times 10^4$),*

Atom	x	y	z
Fe(1)	4843(1)	3149(1)	4193(1)
Fe(2)	7065(2)	4196(2)	7262(2)
Cl(1)	6773(3)	4221(3)	4664(3)
Cl(2)	4236(3)	3228(3)	1897(3)
Cl(3)	5477(3)	2888(3)	6424(3)
Cl(4)	9464(3)	3154(4)	6954(4)
O(1)	3140(7)	2396(7)	3989(7)
O(2)	6249(7)	956(7)	3082(7)
O(3)	7033(8)	4343(8)	9324(7)
C(1)	3134(12)	1273(13)	4329(14)
C(2)	1874(14)	852(15)	3581(14)
C(3)	931(11)	2073(13)	3226(12)
C(4)	1646(11)	3160(12)	3783(12)
C(5)	7790(11)	449(11)	3310(11)
C(6)	8457(13)	-225(14)	1858(15)
C(7)	7325(17)	-548(15)	864(14)
C(8)	6026(12)	-118(11)	1681(12)
C(9)	7759(15)	5189(14)	10512(12)
C(10)	8375(16)	4370(19)	11335(15)
C(11)	7847(15)	3173(15)	10801(14)
C(12)	6912(14)	3269(13)	9653(12)

*Coordinates of hydrogen atoms and thermal parameters can be obtained from the authors on request.

were calculated from geometric considerations. structure refinement was carried out by the full-matrix least-squares method in the anisotropic (for hydrogen atoms isotropic) approximation up to $R = 0.038$ (no weighting scheme was used). The coordinates of the atoms are presented in Table I, and the main interatomic distances and bond angles in Table II. The structure of the molecule **I** is shown in Fig. 1.

The static magnetic susceptibility was measured by the Faraday method within the temperature range 294–79 K on a device designed at the Institute of General and Inorganic Chemistry [1]. The effective magnetic moment was calculated according to the formula $\mu_{\text{eff}} = 2.828\sqrt{\chi_M \cdot T}$, where χ_M is the molar magnetic susceptibility. The results of the investigation are presented in Fig. 2.

Discussion

Iron(II) chloride tetrahydrofuranate, $(2\text{FeCl}_2 \cdot 3\text{THF})_2$, was prepared on reduction of FeCl_3 , with rhenium biscyclopentadienyldihydrode Cp_2ReH (eqn. 1) within the THF medium.

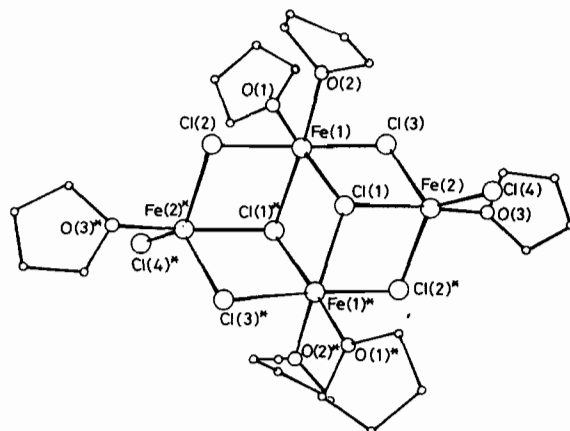
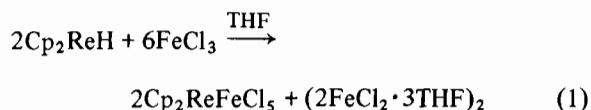


Fig. 1. Molecular structure of the complex $(2\text{FeCl}_2 \cdot 3\text{C}_4\text{H}_8 \cdot \text{O})_2$.

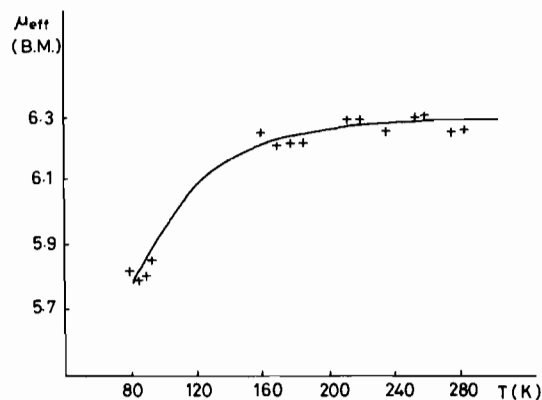


Fig. 2. Dependence of the effective magnetic moment on temperature: (----) theoretical values, (*) experimental data.

The same reaction, being carried out in a solvent of less basicity, e.g., diethyl ether, results in the complex of composition $\text{Cp}_2\text{Re}(\text{FeCl}_3)_3$ (**II**). Thus, $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ can be viewed as the product of conversion of (**II**) under the effect of the strong Lewis base.

The crystalline structure of the complex **I** is built of the centrosymmetric molecules, $(2\text{FeCl}_2 \cdot 3\text{THF})_2$, with the usual Van der Waals contacts. The molecule **I** (Fig. 1) is a four-nuclei cluster with the metal atoms being bonded through the chlorine bridges. All the distances between iron atoms (Table II) are far greater than the sum of covalent radii (~ 2.4 Å), which indicates the absence of direct metal–metal bonds within the complex.

The geometry of molecule **I** can be described as pseudocubane, in which two cubane moieties (with one apex absent) are joined with common face $\text{Fe}(1)\text{Cl}(1)\text{Fe}'(1)\text{Cl}'(1)$. Unoccupied apices are arranged symmetrically with respect to the inversion

TABLE II. Main Interatomic Distances, d (Å), and Bond Angles, ω ($^\circ$), for the Molecule $(2\text{FeCl}_2 \cdot 3\text{THF})_2$.

Distance	d	Distance	d
Fe(1)—Cl(1)	2.505(3)	Fe(1)—O(1)	2.106(8)
Fe(1)—Cl'(1)	2.519(3)	Fe(1)—O(2)	2.134(8)
Fe(1)—Cl(2)	2.477(3)	Fe(2)—O(3)	2.120(8)
Fe(1)—Cl(3)	2.473(3)	O—C mean	1.452
Fe(2)—Cl(1)	2.736(3)	C—C mean	1.472
Fe(2)—Cl(3)	2.354(3)	Fe(1)•••Fe'(1)	3.751(2)
Fe(2)—Cl'(2)	2.359(3)	Fe(1)•••Fe(2)	3.649(2)
Fe(2)—Cl(4)	2.244(4)	Fe(1)•••Fe'(2)	3.686(2)
Angle	ω	Angle	ω
Cl(1)—Fe(1)—Cl(2)	93.7(1)	Cl(3)—Fe(2)—Cl(4)	123.9(1)
Cl(1)—Fe(1)—Cl(3)	87.7(1)	Cl(3)—Fe(2)—Cl'(2)	110.1(1)
Cl(1)—Fe(1)—Cl'(1)	83.4(1)	Cl(3)—Fe(2)—O(3)	92.6(2)
Cl(1)—Fe(1)—O(1)	174.6(2)	Cl(4)—Fe(2)—Cl'(2)	125.3(1)
Cl(1)—Fe(1)—O(2)	94.5(2)	Cl(4)—Fe(2)—O(3)	95.0(2)
Cl(2)—Fe(1)—Cl(3)	177.3(1)	Fe(1)—Cl(1)—Fe'(1)	96.6(1)
Cl(2)—Fe(1)—Cl'(1)	86.7(1)	Fe(1)—Cl(1)—Fe(2)	88.1(1)
Cl(2)—Fe(1)—O(1)	89.7(2)	Fe(2)—Cl(1)—Fe'(1)	89.0(1)
Cl(2)—Fe(1)—O(2)	89.0(2)	Fe(1)—Cl(2)—Fe'(2)	99.3(1)
Cl(3)—Fe(1)—Cl'(1)	95.8(1)	Fe(1)—Cl(3)—Fe(2)	98.2(1)
Cl(3)—Fe(1)—O(1)	89.1(2)	Fe(1)—O(1)—C(1)	127.6(6)
Cl(3)—Fe(1)—O(2)	88.5(2)	Fe(1)—O(1)—C(4)	124.5(0)
Cl'(1)—Fe(1)—O(1)	92.6(2)	C—O—C mean	106.4
O(1)—Fe(1)—O(2)	89.7(2)	O—C—C mean	105.7
Cl(1)—Fe(2)—Cl(3)	84.9(1)	C—C—C mean	106.9
Cl(1)—Fe(2)—Cl(4)	91.6(1)	Fe(1)—Cl(3)—Cl'(2)	87.8(1)
Cl(1)—Fe(2)—Cl'(2)	84.3(1)	Fe(1)—Cl(2)—Cl'(3)	89.7(1)
Cl(1)—Fe(2)—O(3)	173.2(2)	Fe(2)—Cl(1)—Cl'(1)	87.9(1)

center of the molecule. Such a geometry for the iron chloride complexes has not been reported in the literature. The molecule **I** possesses two types of iron atoms which differ in their coordination environment. The Fe(1) atom, coordinating two THF molecules, is situated in the center of a slightly distorted octahedron (the Cl(2)Fe(1)Cl(3) angle is equal to 177.3°), whose bond angles (to exclude Cl(1)Fe(1)Cl'(1)) are close to 90° . At the same time the coordination number for the Fe(2) atom is 5. Its coordination polyhedron, including one THF molecule and one terminal chlorine atom, is close to trigonal bipyramid, whose axial positions are occupied by Cl(1) and O(3) atoms (the Cl(1)Fe(2)—O(3) angle is equal to 173.2°). The octahedral environment for the Fe(2) atom, which could be achieved by coordinating two THF ligands within the Cl(3)Fe(2)Cl'(2) plane, becomes impossible due to the large angle formed by these atoms (110.1°) and strong steric overcrowding.

It should be noted that the iron atom in the chlorine-containing complexes has, as a rule, an octahedral or tetrahedral (in the anion) environment [2]. The coordination number 5 for this

element is realized principally in the organometal compounds, and is quite infrequent for inorganic chemistry. Despite the different coordination numbers for the Fe(1) and Fe(2) atoms, the oxidation number for both atoms is +2, which follows from the magnetic measurements data (see below), and the Mössbauer (MB) spectroscopy evidence. On the whole, the parameters and the general view of the MB spectra are characteristic of high-spin Fe(II) compounds. However, since complex **I** possesses two inequivalent iron atoms, its MB spectrum consists of two doublets with the constants: $I_s(1) = 0.95$ mm/sec, $Q_s(1) = 2.70$ mm/sec, and $I_s(2) = 1.01$ mm/sec, $Q_s(2) = 3.24$ mm/sec; which confirms once more the correctness of the structure determination for iron chloride tetrahydrofuranate.

The doublet with the larger value of quadrupole splitting, $Q_s(2)$, refers apparently to the Fe(2) atom whose coordination number is 5, since a lower symmetry of the environment results in lower delocalization of the sixth d-electron which is responsible for the electric field gradient on the iron nucleus [3]. It should also be noted that the $Q_s(1)$ value for the Fe(1) atom is greater than is usually observed

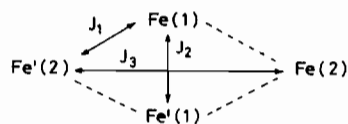
for the complexes with a slightly distorted octahedral environment (~ 2 mm/sec [3]). This can be accounted for by the fact that in the case under consideration the distortion of octahedron within the O(1)O(2)Cl(1)Cl'(1) plane is large enough ($r_{\text{Fe-O}} \sim 2.12$ Å; $r_{\text{Fe-Cl}} \sim 2.51$ Å; the Cl(1)Fe(1)Cl'(1) angle equals to 83.4° ; the O(1)Fe(1)C(2) equals to 89.7°) to result in total removal of degeneration of the low-lying d_{xy} , d_{xz} , and d_{yz} orbitals, and thus in decrease of the delocalization of the sixth d-electron.

From Fig. 1 it follows that molecule **I** possesses three types of chlorine atoms (mono-, bi-, and tridentant ones) and, correspondingly, three types of the iron-chlorine bonds, namely Fe-Cl_{term}, Fe-(μ^2 -Cl), and Fe-(μ^3 -Cl). The length of the terminal Fe-Cl bond (2.244 Å) is somewhat less than is usually observed for the tetrahedral anions $[\text{FeCl}_4]^{2-}$ (2.28–2.34 Å), and in fact it is closer to the $r_{\text{Fe-Cl}}$ for the Fe(III) containing anions $[\text{FeCl}_4]^-$ (2.16–2.22 Å) [4]. The Fe-Cl bond length in the μ^2 -bridge, 2.35–2.47 Å, is close to the Fe-Cl distance found in structures of polymeric type involving μ^2 -Cl atoms, e.g., in $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ (2.49 Å) [5]. The Fe(1)-Cl(1) and Fe(2)-Cl(1) distances for the μ^3 -bridge differ by 0.2 Å. At the same time the Fe(1)-Cl(1), Fe(1)-Cl(2), and Fe(1)-Cl(3) distances are close. The Fe-O bond length (2.11–2.13 Å) for **I** is close to the sum of covalent radii. The tetrahydrofurane cycle has the envelope conformation, with the geometric parameters (Table II) being similar to those of coordinated THF molecules for other complexes [6, 7].

The value of the magnetic moment (μ_{eff}) for the complex at 284 K is equal to 6.23 B.M., considerably higher than the value characteristic of mononuclear complexes of Fe(II) [8]. This fact indicates the presence in **I** of ferromagnetic interactions. In addition, a drop in the μ_{eff} value down to 5.82 B.M. is observed upon decrease in temperature. (Similar magnetic properties are also inherent for the complex of FeCl_2 with THF, the latter being obtained by direct dissolution of iron(II) chloride in the solvent: μ_{eff} is equal to 6.27 B.M. at 294 K, and to 6.13 B.M. at 79 K, thus indicating the equivalence of structures for both compounds).

Interpretation of the thermal dependence of the magnetic susceptibility of $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ was carried out within the framework of isotropic exchange Hamiltonian $\hat{H} = \sum_{ij} -2J_{ij}\hat{S}_i\hat{S}_j$ [9].

It follows from the X-ray structure analysis that the metal frame of $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ possesses C_{2v} symmetry, in consequence of which the exchange interactions for the compound are determined by the values of the three exchange parameters J represented below, and defining the particular type of the exchange Hamiltonian:



The values of these parameters were determined by the best fit method of theoretical χ_M^1 values to the experimental ones according to the program described in [9] (the best fit parameters are $2J_1 = 3.0$, $-2J_2 = -52.0$ cm⁻¹, $-2J_3 = 0$, mean sq. err. 3%, mon. adm. 0). The results are presented in Fig. 2.

To elucidate the reason for the large discrepancy for the exchange parameters obtained it is necessary to refer to the results of the exchange interaction theory. In the absence of direct metal-metal bonds the exchange interactions in **I** can be realized only through the bridging ligands, thus the magnetic properties of **I** can be described within the framework of the superexchange theory [10]. According to this theory $-2J_3 \sim 0$ conforms with the large length of the bridging atoms chain which connects Fe(2) and Fe'(2). The difference in sign for the two other exchange parameters is readily accounted for when taking into consideration the angular dependence of superexchange. In fact, as was established in [11], for systems with monoatomic electronegative bridging ligands (O^{2-} , F^- , Cl^-) the angular dependence of the superexchange is described by the equation

$$-2J = a \cos^2\theta + b \cos\theta + c \quad (2)$$

where θ is the M-L-M angle; $a > b > 0$, and $c < 0$.

It follows from eqn. 2 that at a certain value of the M-L-M angle ($\lesssim 90^\circ$) the change in the sign of exchange interactions from ferro- to antiferromagnetic type occurs.

According to the X-ray data the angles Fe(1)-Cl(1)Fe'(1) and Fe(1)Cl(2)Fe'(2) are equal to 96.6° and 99.3° , respectively. Hence, when passing from the exchange along the Fe(1)Cl(1)Fe'(1) chain to the exchange along the Fe(1)Cl(2)Fe'(2) a change in the type of exchange interaction from ferro- to antiferromagnetic can be expected. This is in agreement with the values obtained: $-2J_1 = 3.0$ cm⁻¹, $-2J_2 = -52$ cm⁻¹. It is worth noting that the change in the sign of $-2J$ in **I** takes place upon negligible variation in the M-L-M angle from 96.6° to 99.3° . This fact allows one to localize unambiguously the point of the change in the interaction sign for M-M through the chlorine atom near $\theta \sim 98^\circ$.

Therefore, the structure of $(2\text{FeCl}_2 \cdot 3\text{THF})_2$ specifies the unique conditions for co-existence within one molecule of ferro- and antiferromagnetic exchange interactions.

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