# Density functional theory studies on the structure, vibrational spectra of three new tetrahalogenoferrate (III) complexes

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# ABSTRACT

Three new tetrahalogenoferrate (III) complexes with the general formula (R)<sub>4</sub>N[FeCI<sub>3</sub>X]<sup>-</sup> in that (X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>) synthesized by the reaction of FeCI<sub>3</sub> with (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NF, (CH<sub>3</sub>)<sub>4</sub>NCI and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr salts in anhydrous CH<sub>3</sub>CN. These were characterized by elemental analysis, IR, UV/Visible and <sup>81</sup>Br-NMR spectroscopy. The optimized geometries and frequencies of the stationary point are calculated at the B3LYP/LANL2DZ level of theory. Harmonic vibrational frequencies and infrared intensities for FeCl<sub>3</sub>F<sup>-</sup>, FeCl<sup>-</sup><sub>4</sub> and FeCl<sub>3</sub>Br<sup>-</sup> are studied by means of theoretical and experimental methods. The calculated frequencies are in reasonable agreement with the experiment values.

**Keywords:** Tetrahalogenoferrate(III); Theoretical Study; Br-NMR; Density Functional Calculations

# **1. INTRODUCTION**

Recently, the interesting history and development of the chemistry of iron halides was reviewed [1]. A new interest steeply increasing in the last decade is caused by possibility of ferrate use as a strong oxidizing agent for environmental uses [2-5] and as a high capacity source of cathodic charge [6-8]. Furthermore it was found that some iron (III) complexes provide a useful structural and electronic model for the similarly coordinated iron (III) sites found in the heme iron enzymes [9]. The tetrahalogenoferrates (III) have been utilized in bioinorganic chemistry as reagents for synthesizing some model compounds, such as  $[Fe_2S_2Cl_4]^{2-}$  [10,11]. The investiga-

tion of the structures and properties of these compounds and their similarities are interested. In this work, we report on the synthesis and characterisation of new complexes of type  $(R)_4N[FeCl_3X]^-$  (X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>) Obtained directly from FeCl<sub>3</sub> and tetraalkylammonium salts. During this study we report the optimized geometries and infrared spectral measurements, assignments and electronic structure calculations for compounds. The structures of compounds have been optimized by the density functional theory (DFT) based method at B3LYP/ LANL2DZ levels of theory, using the Gaussian 03 package of programs [12-14]. The comparison between theory and experiment is made.

# 2. EXPERIMENTAL SECTION

#### 2.1. General

The density functional and abinitio calculation have been performed with the Gaussian program and the basis sets implemented therein [13,15-17].

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before use, thereby reducing its water content to < 4 ppm. FeCl<sub>3</sub> (Merck, p.a.) were used without further purification. Anhydrous  $Et_4N^+F^-$  and  $Me_4N^+F$  were obtained by a drying procedure of the tetrahydrate in high vacuum (d, 130°C) [18]. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. <sup>81</sup>Br-NMR were recorded on a Bruker AVA NCEDRX 500 spectrometer. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

## 2.2. Synthesis of Tetraethylammonium Fluorotrichloroferrate (III), [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][FeCl<sub>3</sub>F] (1)

To a solution of FeCl<sub>3</sub> (0.26 g, 1.6 mmol) in MeCN the solid powder tetraethtylammonium fluoride(0.26 g, 1.74mmol) was added under stirring at room temperature until yellow solid precipitate was formed. After 2 h stirring, the mixture was filtered, washed ether, and dried at room temperature. m.p. 229 - 231°C. Anal. Calc. for  $C_8H_{20}NFeCl_3F$ : C, 25.78; H, 5.37; N, 3.76. Found: C, 26.45; H, 5.89; N, 4.32%. IR (KBr) (cm<sup>-1</sup>): 3438, 3225, 3028, 2987, 2946, 2780, 2655, 2358, 1850, 1462, 1401, 1307, 1021, 792, 499, 483, 428. UV-Vis in CH<sub>3</sub>CN,  $\lambda/cm^{-1}$ : 41493, 36496, 31847, 27548.

## 2.3. Synthesis of Tetramethylammonium Tetrachloroferrate (III), [(CH<sub>3</sub>)<sub>4</sub>N][FeCl<sub>4</sub>] (2)

Solid powder tetrametylammonium chloride (0.22 g, 2 mmol) was added to a solution of FeCl<sub>3</sub> (0.29 g, 1.78 mmol) in MeCN under stirring at room temperature until yellow solid precipitate was formed. Stirring was continued for 3 h. the mixture was filtered, washed with ether, and dried at room temperature. m.p. 299 - 300°C. Anal. Calc. for C<sub>4</sub>H<sub>12</sub>NFeCl<sub>4</sub>: C, 17.65; H, 4.41; N, 5.15. Found: C, 17.96; H, 4.96; N, 5.52%. IR (KBr) (cm<sup>-1</sup>): 3421, 3225, 3017, 2980, 2960, 2780, 2655, 2477, 1850, 1484, 1411, 1283, 948, 499, 416. UV–Vis in CH<sub>3</sub>CN,  $\lambda/\text{cm}^{-1}$ : 41666, 36630, 31948, 27624.

## 2.4. Synthesis of Tetrabuthylammonium Bromotrichloroferrate (III), [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][FeCl<sub>3</sub>Br] (3)

To a solution of FeCl<sub>3</sub> (0.167 g, 1.02 mmol) in MeCN the solid powder tetrabuthtylammonium bromide (0.365 g, 1.13 mmol) was added under stirring at room temperature until dark red solid precipitate was formed. After 2 h stirring, the mixture was filtered, washed ether, and dried at room temperature. m.p. 69 - 70°C. Anal. Calc. for C<sub>16</sub>H<sub>36</sub>NFeCl<sub>3</sub>Br: C, 39.46; H, 7.43; N, 2.89. Found: C, 40.01; H, 8.21; N, 3.59%. IR(KBr) (cm<sup>-1</sup>): 3431, 3315, 3225, 3010, 2961, 2875, 2765, 2398, 1950, 1466, 1382, 1169, 1042, 531, 463, 453. UV–Vis in CH<sub>3</sub>CN,  $\lambda$ /cm<sup>-1</sup>: 42016, 36764, 31645, 27624.

#### 2.5. Computational Methods

Density functional theory (DFT) calculations were carried out at B3LYP/LANL2DZ levels of theory with the Gaussian 03 package of programs [13,19] which combines the exact Hartree-Fock exchange with Becke's and uses the Lee-Yang-Parr correlation function in order to include the most important correlation effects. The structures of the molecules were completely optimized without any symmetry in all the levels. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima [20]. Harmonic vibrational frequencies in cm<sup>-1</sup> and infrared intensities (int) in Kilometer per mole of all compounds were performed at the same level on the respective fully optimized geometries. These compounds and their data are in accordance with recent works on the formation of four coordinate intermediates.

## 3. RESULTS AND DISCUSSION

The  $(C_2H_5)_4N[FeCl_3F]$  complex was obtained by the reaction of  $(C_2H_5)_4NF$  with FeCl<sub>3</sub> in the acetonitrile solvent (reaction (1)). The reaction of FeCl<sub>3</sub> with  $(CH_3)_4NCl$  in acetonitrile solvent gave  $(CH_3)_4N[FeCl_4]$  (reaction (2)).  $(C_4H_9)_4N[FeCl_3Br]$  synthesized by the reaction of FeCl<sub>3</sub> with  $(C_4H_9)_4NBr$  in acetonitrile (reaction (3)).

 $(C_2H_5)_4NF + FeCl_3 \rightarrow (C_2H_5)_4N[FeCl_3F]$ (1)

$$(CH_3)_4NCl + FeCl_3 \rightarrow (CH_3)_4N[FeCl_4]$$
 (2)

 $(C_4H_9)_4NBr + FeCl_3 \rightarrow (C_4H_9)_4N[FeCl_3Br]$  (3)

The structures of complexes 1, 2 and 3 are shown in **Figure 1** Geometry optimization shows that symmetry for compounds 1 and 3 is  $C_{3V}$ . Geometry optimization shows that symmetry for compound 2 is  $D_{4h}$ . Selected bond distances and angles are reported in **Table 1**. We

**Table 1.** Geometrical parameters optimized of compounds1-3, bond length  $(\text{\AA})$  and angle ( $\circ$ ).

	B3LYP/LANL2DZ		
	[FeCl <sub>3</sub> F] <sup>-</sup>	[FeCl <sub>4</sub> ] <sup>-</sup>	[FeCl <sub>3</sub> Br] <sup>-</sup>
Bond lengths (Å )			
Fe1-Cl2	2.298	2.289	2.286
Fe1-Cl3	2.298	2.289	2.287
Fe1-Cl4	2.298	2.289	2.286
Fe1-X5	1.817	2.289	2.458
Bond angles (°)			
Cl2-Fe1-Cl3	109.829	109.462	109.971
Cl2-Fe1-Cl4	109.755	109.437	109.809
Cl2-Fe1-X5	109.129	109.46	109.075
Cl3-Fe1-Cl4	109.831	109.474	109.971
Cl3-Fe1-X5	108.152	109.501	109.918
Cl4-Fe1-X5	109.125	109.493	109.072



(c)

**Figure 1.** Optimized geometries of (a)  $[(C_2H_5)_4N][FeCl_3F]^-$ , (b)  $[(CH_3)_4N][FeCl_4]^-$ , (c)  $[(C_4H_9)_4N][FeCl_3Br]^-$  at B3LYP/LANL2DZ level of theory.

could not compare the calculation results given in **Table 1** with the experimental data. Because the crystal structure of the title compound is not available till now. The calculations shown that the structures of these three trichlorohaloferrate salts, are not formed dimer, trimer, or more multi nuclear structures in solid states. B3LYP/LANL2DZ results showed that the Fe-X (X = F, Cl, Br) bond length values for the [FeCl<sub>3</sub>X]<sup>-</sup> in compounds 1 - 3 are 1.817, 2.289 and 2.458 Å, respectively. Also, the Fe-Cl<sub>2</sub> bond lengths values in [FeCl<sub>3</sub>X]<sup>-</sup> are 2.298, 2.2893 and 2.286 Å, respectively. These results reveal that the bond order for Fe-X bonds decrease from com-

pounds 1 to 3, while for Fe-Cl<sub>2</sub> bonds, the bond orders increase. It can be concluded that the decrease of Fe-X bonds lengths and the increase of Fe-Cl<sub>2</sub> bond lengths in compounds 1 - 3 result from the increase of the hyper-conjugation from compounds 1 - 3 Besides, the  $\theta_{Cl2-Fe1-X5}$  bond angle values in compounds 1 - 3 are 109.129, 109.46 and 109.075, respectively (see **Table 1**). The decrease of  $\theta_{Cl2-Fe1-X5}$  bond angle values from compounds 1 to 3, could again, be explained by the increase of the hyperconjugation from compounds 1 to 3. The calculated infrared spectra of three ferrate complexes are presented in **Figure 2**. The solid-state IR spectrum for

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the complexes 1, 2 and 3 shows Fe-Cl stretching resonances (300 - 400 cm<sup>-1</sup>). The harmonic vibrational frequencies of all the stationary points at the B3LYP/LANL2DZ level along with the available experimental data [21-23] presented in **Table 2**. The compounds structure shows the presence of Fe-Cl stretching vibrations in the region  $350 - 400 \text{ cm}^{-1}$  which is the characteristic region for the ready identification of the Fe-Cl

stretching vibrations. In general the compounds Fe-Cl vibrations calculated theoretically are in good agreement with the experimentally reported values.

Zero-point energies (ZPE) and several calculated thermodynamic parameters of compounds 1 - 3, are given in **Table 3**. The total energies of compounds  $[FeCl_3F]^-$ ,  $[FeCl_4]^-$  and  $[FeCl_3Br]^-$  at 298 temperature at B3LYP/LANL2DZ methods are also presented.



**Figure 2.** Calculated infrared spectra of  $\text{FeCl}_3\text{F}^-$ ,  $\text{FeCl}_4^-$  and  $\text{FeCl}_3\text{Br}^-$  (top to bottom, frequencies in cm<sup>-1</sup>, intensities in arbitrary units).

**Table 2.** Calculated and experimental frequencies of compounds 1 - 3 (cm<sup>-1</sup>).

Compound	B3LYP/LANL2DZ	Exptl
[FeCl <sub>3</sub> F] <sup>-</sup>	125, 165, 309, 362, 630	792,483
[FeCl <sub>4</sub> ] <sup>-</sup>	119, 362	378
[FeCl <sub>3</sub> Br] <sup>-</sup>	110, 235, 325, 362	376

**Table 3.** Theoretically computed energies, zero-point vibrational energies and Gibs free energy for compounds 1 - 3.

B3LYP/LANL2DZ				
Parameters	[FeCl <sub>3</sub> F] <sup>-</sup>	[FeCl <sub>4</sub> ] <sup>-</sup>	[FeCl <sub>3</sub> Br] <sup>-</sup>	
HF energy	-268.437381	-183.540346	-181.756907	
Zero-point energy	0.005080999	0.004219585	0.003912898	
Total energy	-268.4323003	-183.536126	-181.7529941	
Gibs Free energy	-268.468259	-183.5732334	-181.7912501	

## 4. CONCLUSIONS

Three tetraalkylammonium salts of FeCl<sub>3</sub> were synthesized in one step and characterized by elemental analysis, IR, UV/Visible, and <sup>81</sup>Br-NMR techniques. Production of these compounds show the ability of tetraalkylammonium salts in halide addition to transition metal and main group elements compounds and the optimized geometry parameters calculated at B3LYP/LANL2DZ level. The optimized structures are in good agreement with the available experimental results. In the present article, the infrared spectra of the ferrate halide complexes were studied using the theoretical and experimental methods. Our theoretical infrared spectrum of compounds 1 - 3 are in very good agreement compared to our experimental spectrum.

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