Synthesis, Crystal Structure and Thermal Behaviour of a New Three-dimensional Hybrid Fluoride Framework with Mixed Valence: (Fe\textsuperscript{2+}/Fe\textsuperscript{3+})

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**Abstract**

Crystal structure of metal-organic frameworks (MOF's) compound \([Hdmta]-(Fe\textsuperscript{II}Fe\textsuperscript{III}F\textsubscript{6}(Hamtaz))\) was hydrothermally synthesized, eventually assisted via classical heating (Acid Digestion Autoclave). Crystalline structure determination is formed from single crystal X-ray diffraction data. The unit cell is orthorhombic space group Ima\textsubscript{a}m, with cell parameters \(a=15.9520(14)\ \text{Å}, b=9.4548(7)\ \text{Å}, c=9.7066(8)\ \text{Å}, V=1463.82(2)\ \text{Å}\textsuperscript{3}\) and \(Z=4\). The structure \([Hdmta]-(Fe\textsuperscript{II}Fe\textsuperscript{III}F\textsubscript{6}(Hamtaz))\) exhibits a three-dimensional inorganic network resulting from the association of \(Fe\textsuperscript{II}Fe\textsuperscript{III}F\textsubscript{6}\) planes with Hamtaz molecules in the [010] direction, as well as uncoordinated dimethylammonium cations \([Hdmta]\) which are formed by the hydrolysis of DMF solvent. The thermal analysis (TG) of the title compound shows that the decomposition undergoes two steps between 200°C and 600°C and the total experimental mass loss 63.03% assuming that the hematite \(Fe\textsubscript{2}O\textsubscript{3}\) is the final product of the decomposition.

**Keywords:** Hydrothermal synthesis; X-ray diffraction; Metal-organic frameworks; TG

**Introduction**

The synthesis of compounds containing more than one ligand using hydrothermal methods is much more difficult to control, and experimental synthesis conditions play a fundamental role. The formation of hybrid compounds is strongly determined by several factors, such as the molar ratio of reagents, pH, reaction time, solvent, reaction temperature [1,2]. The hydrothermal synthesis of crystalline inorganic-organic hybrid compounds leads to two types of hybrid networks, according to the nature of bonding interactions [3]. In class I hybrids, the organic and inorganic parts are interlinked by weak interactions (van der Waals or hydrogen bonds) that contribute to the 3D structural stability. Whereas in the Class II hybrids, the metal atoms are strongly linked by covalent or ionic-covalent bonds with the organic parts, to form metal-organic frameworks (MOFs). However, very few MOF’s built up from fluorinated inorganic frameworks have been reported in the literature [4]. The interest for hybrid fluorinated materials is associated to the application in various domains ranging from gas storage (especially hydrogen) [5], catalysis [6], ion-exchange [7], magnetism [8], luminescence [9], biomedicine [10] etc. More recently, several crystalline forms have been proposed as components for secondary batteries, used as anode or cathode in rechargeable lithium batteries [11].

At the parallel, few hybrid fluoroorer are listed. Most often, the metal fluoride species, which result from the condensation of FeA\textsubscript{B} units (A, B=N, O, F), are isolated polyanions or clusters such as FeF\textsubscript{4}, FeF\textsubscript{2}(H\textsubscript{2}O), FeF\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}. In fact, the research of inorganic 1D, 2D and 3D network structure is successful for class I and class II of hybrid fluoroorer with triazole [22]. In this study, we have paid a great deal of attention to the hybrid iron fluoride compound as the object of our investigation. The aim of the present work is to study the structure determination and the thermal analysis of the second new three-dimensional network fluoroorer with mixed valence Fe\textsuperscript{2+}/Fe\textsuperscript{3+}. We report here the results obtained by X-ray single-crystal diffraction and differential thermodiagrammetric analysis (TG).

**Experimental Section**

**Synthesis of [Hdmta]-(Fe\textsuperscript{II}Fe\textsuperscript{III}F\textsubscript{6}(Hamtaz))**

All reagents and solvents are commercially available and were used as received without further purification. The starting chemicals were FeF\textsubscript{3}, and FeF\textsubscript{2} (99.9%, Alfa Aesar), hydrofluoric acid solution 4% (prepared from 40% HF, Riedel De Haen), 3-amino-1,2,4-triazole (Hamtaz) (99%, Alfa Aesar) and dimethylformamide (DMF) (99.8%, Sigma Aldrich). The FeF\textsubscript{3}-FeF\textsubscript{2}-3-amino-1,2,4-triazole-HFaq.-DMF system was investigated and established for a constant concentration [Fe\textsuperscript{II}]\textsuperscript{1+}[Fe\textsuperscript{III}]\textsuperscript{1}=0.15 mol.L\textsuperscript{-1} and a ratio [Fe\textsuperscript{II}]\textsuperscript{1}/[Fe\textsuperscript{III}]\textsuperscript{1}=1 under solvothermal condition at 120°C under autogenously pressure (25 ml Parr Autoclave) for 72 hour. The solid product was washed with DMF and dried at room temperature.

**X-ray crystallography**

Single-crystal X-ray diffraction data was collected at room temperature on an APEX II Quazar diffractometer (4-circle Kappa goniometer, IpS microfocus source (M, K\textsubscript{α}), CCD detector). The structure was solved by direct methods which give the position of most of the atoms (iron, fluoride, nitrogen and carbon) developed by successive fourier maps and subsequent refinements using SHELXS-86 and SHELXL-97 [23-25] programs, where these last were included in WINGX package [26]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions and included as riding atoms. The structure graphics were created by the DIAMOND program [27]. Crystal data and structure refinement details for the title compound are summarized in Table 1. The final positions and equivalent isotropic thermal parameters for the new compound are shown in Tables 2 and 3, while the selected bond lengths in [Hdmta]-(Fe\textsuperscript{II}Fe\textsuperscript{III}F\textsubscript{6}(Hamtaz)) is listed in Table 4.

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5 listed the hydrogen bond distances (Å) of the new three material [Hdma]·(Fe$^{2+}$Fe$^{3+}$F$_{6}$)(Hamtazz)]. Finally, a selected bond angles are given in Table 6.

## Thermal analysis

Thermogravimetric experiments was reported for the new three-dimensional fluoroferrate with a thermoanalyzer NETZSCH STA 449 F3 under humid air atmosphere and a heating rate of 5°C.min$^{-1}$ from 25°C up to 895°C.

## Results and Discussion

### Structure description of [Hdma]·(Fe$^{2+}$Fe$^{3+}$F$_{6}$)(Hamtazz)]

Single crystal X-ray diffraction analyses, at room temperature indicate that the 3D [Hdma]·(Fe$^{2+}$Fe$^{3+}$F$_{6}$)(Hamtazz)] compounds crystallizes in the orthorhombic space group Imma. Final refinements of anisotropic displacement parameters (ADP) and secondary extinction converged to $R=0.046\%$ and $W_{R}=0.126 \%$ (1219 independent reflections and 91 parameters). Two iron atoms are located on special 4c position (Fe(2)) and general 4e position (Fe(1)). Successive Fourier analysis reflections and 91 parameters). Two iron atoms are located on special positions on several positions. In fact, the occupation of the fluoride sites was done freely at their positions, which corresponds to six fluorine atoms per unit formula. Hydrogen atoms of Hamtazz neutral were placed with HFIX options (43 for CH, NH, and 93 for NH$_{3}$).

### Table 2: Fractional atomic coordinates and equivalent isotropic displacement parameters ($U_{eq}$ for H atoms) for [Hdma]·(Fe$^{2+}$Fe$^{3+}$F$_{6}$)(Hamtazz)] material.

| Atoms  | x  | Y  | z   | $U_{eq}$ | Occ. (%) |
|--------|----|----|-----|----------|----------|
| Fe1    | 0.25 | 0.25 | 0.28355 (8) | 0.0187 (2) |
| Fe2    | 0.25 | 0.25 | 0.2837 (3) | 0.0282 (6) |
| F1     | 0.12504 (12) | 0.25 | 0.2837 (3) | 0.0282 (6) |
| F2     | 0.25 | 0.25 | 0.0891 (6) | 0.096 (4) |
| F3     | 0.0530 (5) | 0.25 | 0.2774 (10) | 0.085 (2) |
| F4     | 0.25 | 0.25 | 0.4747 (6) | 0.084 (3) |
| F5     | 0.383 (2) | 0.141 (2) | 0.083 (7) | 0.25 |
| F6     | 0.108 (3) | 0.416 (3) | 0.119 (11) | 0.25 |

### Table 1: Crystallographic data of [Hdma]·(Fe$^{2+}$Fe$^{3+}$F$_{6}$)(Hamtazz)] at room temperature.

| Crystal data Formula | C$_{x}$N$_{y}$F$_{z}$Fe$_{n}$ |
|----------------------|-------------------------------|
| Space Group          | Imma                          |
| a (Å)                | 15.9520 (14)                 |
| b (Å)                | 9.45487 (7)                  |
| c (Å)                | 9.7056 (8)                   |
| α (°)β (°)γ (°)       | 90                            |
| V (Å$^{3}$)           | 1463.8 (2)                   |
| Z                    | 4                             |
| F (000)              | 852                           |
| Formula weight (g.mol$^{-1}$) | 431.91                      |
| Dimensions (mm)      | 0.15×0.12×0.08                |
| μ (mm$^{-1}$)         | 2.06                          |
| ρ calculated (g.cm$^{-3}$) | 1.96                    |
| Temperature (K)       | 296                           |
| Radiation, (Å)       | Mo Kα, 0.71073                |
| θ pycn (°)           | 2.46 / 30.50                  |
| Limiting indices     | -22 s h ≤ 22                  |
|                       | -10 s k ≤ 13                  |
|                       | -13 l ≤ 13                    |
| Collected reflections | 7885                          |
| Reflections Unique   | 1219                          |
| Parameter refined    | 91                            |
| Goodness of fit (R$^{2}$) | 1.08                      |
| R$_{w}$ [23]         | 0.0465                        |
| WR$_{F}$             | 0.1265                        |
| ρ min/max (e Å$^{-3}$) | -0.815 / 1.176               |

From the Figure 1, we note that the arrangement of the various octahedral and organic molecules forms a tunnels with square cross section where the [Hdma] cations are located, the side of the square is equal to 6.774 Å. Thus this structure of the new material involve anionic Fe$_{2}$F$_{6}$N$_{3}$ infinite trans-chains along (100) direction. The average <C-C> and <N-C> distances of Hamtazz molecules are varied between 1.32 Å and 1.42 Å, in fact there are the same geometry than that found in the succession of guanazolium fluoroaluminates [28,29]. Dimethylammonium cations are strongly disordered, in fact two types of coordination of the iron cations are form different positions for N(4) and C(4) atoms were located with refined occupation being close to one quarter and one half, respectively, form one member of [Hdma] entity per unit formula. The formulation [Hdma]·(Fe$^{2+}$Fe$^{3+}$F$_{6}$)(Hamtazz)] was then obtained. A projection on the cb plane (Figure 1) shows that this structure contains two type of octahedral forming a Fe$^{2+}$Fe$^{3+}$F$_{6}$N$_{3}$ trimer. As a consequence, the structure presents two oxidation states for iron atoms. Every anionic Fe$^{2+}$Fe$^{3+}$F$_{6}$N$_{3}$ trimer is connected to four neutral Hamtazz molecules by four symmetry nitrogen atoms N(2) along the (110) and (110) directions. However, two types of coordination of the iron cations are observed in the new 3D fluoroferrate: (Figure 2) a distorted Fe(1)F$_{6}$ octahedral in which Fe(1) is surrounded by ten fluorine atoms while the Fe(1)-F bond length varied between 1.855(6) and 1.995(2) Å, and in the Figure 2 right of Fe(2)F$_{6}$N$_{3}$ octahedral, in which Fe(2) is coordinated to two fluorine atoms, and four nitrogen atoms from four neutral Hamtazz molecules, where the Fe(2)-F and Fe(2)-N distances equal to 2.020(2) Å and 2.278(2) Å, respectively. In fact, it must be noted that the oxidation...
Among the ten fluorine ions (Figure 3), F(1) is coordinated with two nitrogen atoms of the ligands established between Fe(2) and nitrogen atoms of the ethylamino)amine [dien] and with tris-(2-ethylamino)amine [tren], where the fluorine ions are involved in H-bonding [17-18,22].

A similar Fe-F distances for two oxidation state of iron, are found in the series of hybrid fluoroferrates with triazoles, with bis-(2-ethylamino)amine [dien] and with tris-(2-ethylamino)amine [tren], where the fluorine ions are involved in H-bonding [17-18,22].

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Among the ten fluorine ions (Figure 3), F(1) is coordinated with two iron atoms Fe(1) and Fe(2). Obviously, all fluorine atoms except F(1) are linked to only one Fe(1) atom in the centre of FeF

$$\text{Fe}^{2+}$$ octahedra and disordered FeF

$$\text{Fe}^{3+}$$ in the [Hdma]$$\big\{\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_6\text{HamtaZ})_2\big\}$$ complex. Moreover, the octahedral units of the title compound are strongly distorted with short...
In the new hybrid framework structure of \(\text{[Hdma]}\cdot\text{(Fe}^{2+}\text{Fe}^{3+}\text{F}_6\text{)(Htaz)}\), the coordination of \(M^\text{II}\) and \(M^\text{III}\) metals is identical to that found in the series of hybrid fluoroferrates with triazoles: for \(\text{FeF}_4\) clusters in \(\text{[Hdma]}\cdot\text{(Fe}^2\text{H}_2\text{O})\text{F}_3\), \(\text{[Hdma]}\cdot\text{(Fe}^2\text{H}_2\text{O})\text{F}_3\cdot0.5\text{H}_2\text{O}\) and \(\text{FeF}_4\text{Fe}_2\text{F}_3\text{(Htaz)},\) and for \(\text{FeF}_4\text{N}_4\) clusters in \(\text{[Hdma]}\cdot\text{(FeF}_4\text{H}_2\text{O})\text{(Htaz)(taz)}\) and \(\text{[Hdma]}\cdot\text{(Fe}^2\text{F}_2\text{(taz)}\text{)}\) [22].

From Figure 4, we observed the hydrogen bonds exist between fluoride anions of distorted \(\text{Fe}^1\text{F}_8\) octahedra, the primary and secondary amine group and \(\text{C-H}\) groups of eight \(\text{Fe}\text{F}_6\text{amtaz}\) molecules. The \(\text{H}^1\text{H}^1\) hydrogen atom of the secondary amine group or the \(\text{C-H}\) group, is oriented towards four fluoride anions of \(\text{Fe}^1\text{F}_8\) octahedron, such as the \(\text{H}^1\text{H}^1\text{H}^1\) length is 2.59 Å and the \(\text{N}^1\text{C}^1\text{H}^1\) angle is 112°, are indicative of weak hydrogen bonds in a new three dimensional micro porous fluoride. Furthermore, the hydrogen-bonding interactions in the structure contribute to the stability of the 3D network. The \(\text{N–H–F}\) and \(\text{C-H}\) distances are varied from 1.852(9) Å to 2.757(0) Å and close to the distances observed in fluoride metalates templated with tren (tris-(2-aminomethyl)amine) [12,13] (Table 5).

**Thermogravimetric analysis**

The TG thermal analysis in oxygen dynamic atmosphere of the title compound is given in Figure 5. During heating, it decomposes in different ways continuous at different temperature between 200°C and 600°C and it shows that the compound prepared is stable at room temperature. The weight loss is attributed to the decomposition of \(\text{[Hdma]}\cdot\text{(Fe}^2\text{Fe}^3\text{F}_6\text{)(Htaz)}\) to give the amine fluoride and HF gas. The first stage between 100°C and 350°C approximately, probably due to the release of 1.25 mol of \(\text{Htaz}\) molecule and eventually, 6 mol of hydrofluoric acid (HF), while the experimental mass loss equal to 52.12%. Moreover, the second step in the temperature range of 350°C and 550°C, approximately, is attributed to the elimination of the rest of organic moiety that corresponds to 10.91% of the experimental mass loss. In fact, the loss of HF and decomposition of \(\text{Htaz}\) molecules and the creation of \(\text{FeF}_6\) molecules make up a total experimental mass loss of 63.03%. At high temperature, above 600°C the \(\text{FeO}_2\) hematite compound is product [21-23]. The total experimental mass loss value 63.03% is in good agreement with the theoretical mass loss 63.03% assuming that the hematite \(\text{FeO}_2\) is, the final product of the oxidation.

**Conclusion**

New three-dimensional mixed valence fluoroferrate obtained from the reaction of \(\text{FeF}_2\) and \(\text{FeF}_3\) with 3-amino-1,2,4-triazole and aqueous HF in DMF solvent. The structural properties and the thermal behavior for \(\text{[Hdma]}\cdot\text{(Fe}^2\text{Fe}^3\text{F}_6\text{)(Htaz)}\) are reported. The structure exhibit \(\text{M}^\text{II}\text{F}_2\text{Fe}_2\text{F}_2\) octahedral units in which nitrogen atoms come from neutral amines, forming the infinite layers of \(\text{FeF}_6\text{Htaz}\), where the \(\text{Hdmba}\) cations are located in the cavities. This structure while being regarded the notation of Cheetham [30] leading to 3-D dimensionality with respect to both organic connectivity between metal centers (O°) and extended inorganic connectivity (I°) therefore the notation of Cheetham is I°O° (I°=inorganic and O°=organic), note that the sum of

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**Table 6:** Main bonds angles (°) for \(\text{[Hdma]}\cdot\text{(Fe}^2\text{Fe}^3\text{F}_6\text{)(Htaz)}\) material, Symmetry codes: (1) \(-x+1/2, -y+1/2, -z+1/2\); (2) \(x, y+1/2, -z+1\); (3) \(-x+1/2, -y, -z+1/2\); (4) \(x, -y, z\); (5) \(-x+1/2, y+1/2, z-1/2\). The exponents gives the overall dimensionality of the structure. The results of thermal analysis suggest that the decomposition take place in two steps and at high temperature the \(\text{FeO}_2\) hematite compounds is product.
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