Synthesis, Crystal Structure and Thermal Behaviour of a New Three-dimensional Hybrid Fluoride Framework with Mixed Valence: (Fe²⁺/Fe³⁺)

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Abstract

Crystal structure of metal-organic frameworks (MOF's) compound [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂))₂ 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 *Imma*, with cell parameters *a*=15.9520(14) Å, *b*=9.4548(7) Å, *c*=9.7056(8) Å, *V*=1463.8(2) Å³ and *Z*=4. The structure [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂))₂ exhibits a three-dimensional inorganic network resulting from the association of Fe^{II}Fe^{III}F₆N₄ planes with Hamta₂ molecules in the [010] direction, as well as uncoordinated dimethylammonium cations [Hdma] 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 Fe₂O₃ 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 (MOF's). 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 fluoroferrate are listed. Most often, the metal fluoride species, which result from the condensation of FeA_xB_y units (A, B=N, O, F), are isolated polyanions or cluster such as FeF₆³⁻, FeF₅(H₂O), FeF₄(H₂O)₂, FeF₄N₂ [12-21]. In fact, the research of inorganic 1D, 2D and 3D network structure is successful for class I and class II of hybrid fluoroferrate 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 fluoroferrate with mixed valence Fe²⁺/Fe³⁺. We report here the results obtained by X-ray single-crystal diffraction and differential thermogravimetric analysis (TG).

Experimental Section

Synthesis of [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂))₂

All reagents and solvents are commercially available and were

used as received without further purification. The starting chemicals were FeF₂ and FeF₃ (≥ 99.9%, Alfa Aesar), hydrofluoric acid solution 4% (prepared from 40% HF, Riedel De Haen), 3-amino-1,2,4-triazole (Hamta₂) (99%, Alfa Aesar) and dimethylformamide (DMF) (99.8%, Sigma Aldrich). The FeF₂-FeF₃-3-amino-1,2,4-triazole-HF_{aq}-DMF system was investigated and established for a constant concentration [Fe^{II}]+[Fe^{III}]=0.15 mol.L⁻¹ and a ratio [Fe^{II}]/[Fe^{III}]=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, IμS microfocus source (M_o, K_α), CCD detector). The structure was solved by direct methods which give the position of most of the atoms (iron, fluorine, 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 [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂))₂ is listed in Table 4. The Table

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5 listed the hydrogen bond distances (Å) of the new three material [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂)₂). 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]·(Fe²⁺Fe³⁺F₆(Hamta₂)₂)

Single crystal X-ray diffraction analyses, at room temperature indicate that the 3D [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂)₂) 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 maps and refinements allowed locating fluorine, nitrogen atoms and organic moieties. F(2), F(3) and F(4) atomic positions were statistically occupied with 0.75 site occupancy whereas for F(5) and F(6) atomic positions occupied with 0.25 site occupancy, moreover, one nitrogen atom and one carbonate atom were disordered on N(1)/C(1) sites for electronic neutrality and from distances and environment considerations. Furthermore, N(1) and C(1) atoms statistically distributed on a general position, as shown in Table 2. The fluoride atoms are randomly distributed over 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

Atoms	x	Y	z	U _{iso} */U _{eq}	Occ. (<1)
Fe1	0	0.25	0.28355 (8)	0.0187 (2)	
Fe2	0.25	0.25	0.25	0.0178 (2)	
F1	0.12504 (12)	0.25	0.2837 (3)	0.0282 (6)	
F2	0	0.25	0.0891 (6)	0.096 (4)	0.75
F3	0	0.0530 (5)	0.2774 (10)	0.085 (2)	0.75
F4	0	0.25	0.4747 (6)	0.084 (3)	0.75
F5	0	0.383 (2)	0.141 (2)	0.083 (7)	0.25
F6	0	0.108 (3)	0.416 (3)	0.119 (11)	0.25
N1/C1	0.34857 (19)	-0.0479 (5)	0.5493 (4)	0.0593 (13)	0.50/0.50
H1	0.3930 (16)	-0.082 (5)	0.575 (5)	0.071*	
N2	0.27094 (15)	-0.0816 (3)	0.5858 (2)	0.0262 (5)	
N3	0.1428 (3)	0	0.5	0.168 (6)	
H3A	0.1158	0.0536	0.4437	0.202*	0.5
H3B	0.1158	-0.0536	0.5563	0.202*	0.5
C2	0.2257 (3)	0	0.5	0.0404 (12)	
C3	0.5	0.25	0.7062 (15)	0.100 (5)	
C4	0.3483 (16)	0.25	0.771 (2)	0.084 (5)	0.5
N4	0.4357 (12)	0.2939 (16)	0.8013 (17)	0.069 (5)	0.25

Table 2: Fractional atomic coordinates and equivalent isotropic displacement parameters (U_{iso} for H atoms) for [Hdma]·(Fe₂+Fe₃+F₆(Hamta₂)₂) material.

of Hamta₂ neutral were placed with HFIX options (43 for CH, NH, and 93 for NH₂). The structure for the title compound is built up from Fe₂F₆ (Hamta₂)₂ planes connected by Hamta₂ ligands which separated by dimethylammonium cations coming from the hydrolysis of DMF solvent, resulting a second three-dimensional hybrid fluoride with 3D inorganic connectivity (Figure 1a and 1b). It is crystallizes in the same system orthorhombic with identical Centro symmetric space group *Imma*, accompanying different cell parameters, comparable to the first 3D Fe₂F₆ (Hta₂) [22].

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 Fe₂F₆N₄ infinite *trans*-chains along (100) direction. The average <C-C> and <N-C> distances of Hamta₂ 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 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]·(Fe₂F₆(Hamta₂)₂) was then obtained. A projection on the cb plane (Figure 1) shows that this structure contains two type of octahedral forming a Fe^{III}₂Fe^{II}F₆N₄ trimers. As a consequence, the structure presents two oxidation states for iron atoms. Every anionic Fe^{III}₂Fe^{II}F₆N₄ trimer is connected to four neutral Hamta₂ molecules by four symmetry nitrogen atoms N(2) along the (1̄0) and (110) directions. However, two types of coordination of the iron cations are observed in the new 3D fluoroferrate: (Figure 2 left) a distorted Fe(1)F₆ 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)F₂N₄ octahedral, in which Fe(2) is coordinated to two fluorine atoms, and four nitrogen atoms from four neutral Hamta₂ 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

Crystal data Formula	C ₆ H ₈ F ₆ Fe ₂ N ₄
Crystal System	Orthorhombic
Space Group	Imma
a (Å)	15.9520 (14)
b (Å)	9.4548 (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 pavg (°)	2.46 / 30.50
Limiting indices	-22 ≤ h ≤ 22 -10 ≤ k ≤ 13 -13 ≤ l ≤ 13
Collected reflections	7885
Reflections Unique	1219
Parameter refined	91
Goodness of fit (F ²)	1.08
R _i [I2I]	0.0465
WR ₂	0.1265
ρ min/max (e Å ⁻³)	-0.815 / 1.176

Table 1: Crystallographic data of [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta₂)₂) at room temperature.

Atoms	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
Fe1	0.0107 (3)	0.0251 (4)	0.0203 (4)	0.000	0.000	0.000
Fe2	0.0108 (3)	0.0197 (4)	0.0229 (4)	0.000	0.0017 (2)	0.000
F1	0.0126 (11)	0.0373 (15)	0.0347 (13)	0.000	0.0024 (8)	0.000
F2	0.063 (5)	0.206 (13)	0.018 (3)	0.000	0.000	0.000
F3	0.041 (3)	0.024 (2)	0.191 (8)	0.000	0.000	-0.014 (3)
F4	0.035 (3)	0.192 (11)	0.024 (3)	0.000	0.000	0.000
N1	0.0187 (13)	0.090 (3)	0.069 (2)	0.0032 (17)	-0.0011 (14)	0.057 (2)
C1	0.0187 (13)	0.090 (3)	0.069 (2)	0.0032 (17)	-0.0011 (14)	0.057 (2)
N2	0.0237 (11)	0.0273 (12)	0.0277 (11)	0.0005 (9)	-0.0004 (9)	0.0090 (9)
N3	0.020 (2)	0.230 (11)	0.256 (11)	0.000	0.000	0.217 (10)
C2	0.0185 (18)	0.045 (3)	0.058 (3)	0.000	0.000	0.029 (2)
C3	0.132 (14)	0.089 (10)	0.078 (9)	0.000	0.000	0.000
C4	0.101 (13)	0.067 (11)	0.085 (12)	0.000	-0.020 (10)	0.000
N4	0.109 (14)	0.044 (8)	0.055 (9)	-0.013 (8)	-0.012 (9)	0.000 (6)
F5	0.016 (5)	0.114 (15)	0.119 (15)	0.000	0.000	0.085 (14)
F6	0.036 (8)	0.18 (2)	0.15 (2)	0.000	0.000	0.14 (2)

Table 3: Atomic displacement parameters of [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) compound.

Selected bond distances	Distances bond (Å)	Selected bond distances	Distances bond (Å)
Fe1-F4	1.855 (6)	N1-N2	1.327 (4)
Fe1-F6	1.863 (9)	N1-H1	0.8200 (8)
Fe1-F3	1.864 (4)	N2-C2	1.345 (3)
Fe1-F5	1.871 (8)	N3-C2	1.322 (6)
Fe1-F2	1.887 (6)	N3-H3A	0.86
Fe1-F1	1.995 (2)	N3-H3B	0.86
Fe2-F1	2.020 (2)	C2-N2	1.345 (3)
Fe2-N2	2.278 (2)	C3-N4	1.44 (2)
N1-C1	1.318 (6)	C4-N4	1.48 (3)
N1-N1	1.318 (6)	N4-N4	0.83 (3)
N1-H1	0.8200 (8)	N1-N2	1.327 (4)

Table 4 : Selected bond distances (Å) in 3D hyride fluoroferrate.

Selected bond distances	Distances d(H-F) (Å)	Selected bond distances	Distances d(H-F) (Å)
N(3)-H(3A)-F(6) ⁱⁱ	1.936(3)	N(3)-H(3B)-F(3) ⁱⁱⁱ	2.453(1)
N(3)-H(3A)-F(1) ⁱ	2.425(2)	N(3)-H(3B)-F(4) ⁱⁱⁱ	2.636(5)
N(3)-H(3A)-F(3) ⁱⁱ	2.453(1)	N(1)/C(1)-H(1)-F(2) ⁱⁱⁱ	2.335(6)
N(3)-H(3A)-F(6) ⁱⁱⁱ	2.757(0)	N(1)/C(1)-H(1)-F(5) ^v	1.852(9)
N(3)-H(3A)-F(4) ⁱⁱ	2.636(5)	N(1)/C(1)-H(1)-F(1) ^{iv}	2.590(1)
N(3)-H(3B)-F(6) ⁱⁱ	2.757(0)	N(1)/C(1)-H(1)-F(3) ^{vi}	2.616(8)
N(3)-H(3B)-F(1) ⁱⁱⁱ	2.425(2)		
N(3)-H(3B)-F(6) ⁱⁱⁱ	1.936(3)		

Table 5: Hydrogen bond distances (Å) in [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) complex, Symmetry codes : (i) x, 0.5-y, z; (ii) -x, y, z; (iii) x, -y, 1-z; (iv) 0.5-x, 0.5+y, -0.5+z; (v) 0.5-x, -0.5+y, 0.5+z; (vi) 0.5-x, -y, -0.5+z.

state for Fe(1) and Fe(2) atoms are +III and +II, respectively, and the ligands established between Fe(2) and nitrogen atoms of Hamta_z molecules lead to deduce that this new fluoroferrate with mixed valence is a Class II hybrid (Figure 3).

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].

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 FeF₆ anion. Moreover, the octahedral units of the title compound are strongly distorted with short

Figure 1: Projection of the 3D [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) structure (left), and view along the [100] direction of the structure (right).

Figure 2: Representation of FeF₂N₄ octahedra and disordered FeF₆ in [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) compound.

Figure 3: View along the b axis, showing the build of fluoroferrate with Hamta_z molecules.

distances between Fe atoms and terminal fluorine atoms F(2), F(3), F(4), F(5) and F(6), medium distances between Fe atoms and bridging F(1) atoms, and long distances between Fe atoms and nitrogen atoms N(2). The Fe^{III}-F(1)-Fe^{II} angle is equal to 170.64°, whereas the both F(1)-Fe^{III}-F(1) and F(1)-Fe^{II}-F(1) angle values counterpart to 179.94° and 180°, respectively (Table 6).

In the new hybrid frameworks structure of [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) the coordination of M^{II} and M^{III} metals is identical with that found in the series of hybrid fluoroferrates with triazoles: for FeF₆ clusters in [Hdma]·(Fe₂·(H₂O)₄F₆), [Hdma]·(Fe₂·(H₂O)₄F₆)·0.5H₂O and Fe₂F₅(Htaz), and for FeF₂N₄ clusters in [Hdma]·(Fe₂F₅(H₂O)(Htaz)(taz)) and [Hdma]·(Fe₂F₅(taz)₂) [22].

From Figure 4, we observed the hydrogen bonds exist between fluorine anions of distorted Fe(1)F₆ octahedra, the primary and secondary amine group and C-H groups of eight Hamta_z molecules. The H(1) hydrogen atom of the secondary amine group or the C-H group, is oriented towards four fluorine anions of FeF₆ octahedron, such as the H(1)-F(1) length is 2.59 Å and the N(1)/C(1)-H(1)-F(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 N-H-F and C-H-F 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-aminoethyl)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 [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) 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 Hamta_z 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 moieties that corresponds to 10.91% of the experimental mass loss. In fact, the loss of HF and decomposition of Hamta_z molecules and the creation of FeF₂, make up a total experimental mass loss of 63.03%. At high temperature, above 600°C the Fe₂O₃ hematite compound is good product [21-23]. The total experimental mass loss value 63.03% is in agreement with the theoretical mass loss 63.03% assuming that the hematite Fe₂O₃, is the final product of the oxidation.

Conclusion

New three-dimensional mixed valence fluoroferrate obtained from the reaction of FeF₂ and FeF₃ with 3-amino-1,2,4-triazole and aqueous HF in DMF solvent. The structural properties and the thermal behavior for [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) are reported. The structure exhibit M^{II}N₄F₂ and M^{III}F₆ octahedral units in which nitrogen atoms come from neutral amines, forming the infinite layers of Fe₂F₆(Hamta_z)₂, where the [Hdma] 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 (Oⁿ) and extended inorganic connectivity (Iⁿ) therefore the notation of Cheetham is IⁿO³ (I=inorganic and O=organic), note that the sum of

Figure 4: Network of hydrogen bonds between amine cations and fluoride ions in the [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) structure.

Figure 5: TG heating curve of [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) material.

Selected bond angles	Degree (°)	Selected bond angles	Degree (°)
F(1)-Fe(1)-F(1) ⁶	179.94 (16)	F(3)-Fe(1)-F(5)	130.5 (11)
F(2)-Fe(1)-F(1)	90.03 (8)	F(4)-Fe(1)-F(5)	137.7 (9)
F(3)-Fe(1)-F(1)	90.00 (3)	F(6)-Fe(1)-F(5)	176.1 (14)
F(4)-Fe(1)-F(1)	89.97 (8)	F(1)-Fe(2)-N(2) ⁴	91.81 (8)
F(5)-Fe(1)-F(1)	90.02 (6)	N(2) ² -Fe(2)-N(2) ⁴	88.69 (13)
F(6)-Fe(1)-F(1)	89.98 (6)	N(2) ³ -Fe(2)-N(2) ⁴	91.31 (13)
F(3)-Fe(1)-F(2)	88.2 (3)	F(1) ¹ -Fe(2)-F(1)	180
F(4)-Fe(1)-F(2)	180.00 (1)	F(1) ¹ -Fe(2)-N(2) ²	88.19 (8)
F(6)-Fe(1)-F(2)	133.8 (11)	N(2) ⁴ -Fe(2)-N(2) ⁵	180
F(4)-Fe(1)-F(3)	91.8 (3)		

Table 6: Main bonds angles (°) for [Hdma]·(Fe²⁺Fe³⁺F₆(Hamta_z)₂) 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+1; (5) -x+1/2, y+1/2, z-1/2; (6) x, -y+1/2, z.

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 Fe₂O₃ hematite compounds is product.

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