

A new hybrid iron fluoride bipyridine with mixed valence: $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$

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Hydrothermal synthesis of iron fluoride compound, $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$, and its characterization by single crystal X-ray diffraction is reported. The compound is found to crystallize in the triclinic space group $P\bar{1}$. The monohydrate fluoroferrate of bipyridine is built up from $\text{Fe}_4\text{F}_{10}\text{N}_8$ tetrahedron connected by eight nitrogen atoms of four 2,2'-bipyridine molecules and separated by H_2O molecules. The main feature of this atomic arrangement is the coexistence of two oxidation states of iron cations and hybrid class II with 0-D dimensionality. Thermal and IR spectral analysis have been carried out for the title compound to confirm the hematite compound as residual and the presence of organic molecule, respectively. Magnetic characterization does not reveal any ferromagnetic component in the range of magnetic field from -20 kOe to 20 kOe at room temperature.

Keywords: Coordination chemistry, Hydrothermal synthesis, X-ray diffraction, Inorganic-organic hybrid compounds, Crystal structure, Hybrid compounds, Thermal analysis, Iron, Fluoroferrates, Metal organic framework

The hydrothermal synthesis of crystalline inorganic-organic hybrid materials depends on synthesis conditions such as the molar ratio of reagents, pH, solvent used, temperature and time of reaction (nature of the central metal coordination geometry)^{1,2}. Hybrid materials can be divided into two distinct classes according to the nature of bonding interactions³. Class I hybrids with weak interactions (van der Waals or hydrogen bonds) between the organic and inorganic parts are well represented in such fluorides. In class II hybrids, both parts are strongly linked by covalent or ionic-covalent bonds to form metal-organic frameworks (MOFs)⁴ or coordination polymers. A recent review article has given an exhaustive presentation of these hybrid

fluorides in terms of dimensionality, which are 0-D for isolated polyanions, 1-D chains, 2-D layers and 3-D framework structures⁵. The metal-organic frameworks represent interesting properties which lead to applications in areas such as gas storage (especially hydrogen), catalysis, ion-exchange, magnetism, luminescence and batteries⁶⁻¹¹. Numerous research works have been carried out using the hydrothermal synthesis route to prepare new fluoroferrate coordination polymers with 1,2,4-triazole to provide a new microporous and type II fluorides¹². Hydrothermal reactions with 1,2,4-triazole and DMF (dimethylformamide) as solvent, yielded a series of new hybrid fluoroferrates with various dimensionalities, i.e., 1D, 2D and 3D¹².

In the present study, the organic molecule was changed from cyclic organic molecule (1,2,4-triazole) to a bicyclic organic molecule (2,2'-bipyridine), with a view to obtain a new compound containing the maximum unoccupied space to allow insertion of lithium or in gas stocking (such as CO_2 , H_2 , etc.) Recently from the same research group, the earlier reported $[\text{FeF}_4(2,2'\text{-bipyridine})(\text{H}_2\text{O})_2]$ ²⁴ and presently reported $[\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}]$, were synthesized under the same conditions, i.e., hydrothermal with autoclave and heated at 120 °C approximately, for 72 h with the same solvent, ethanol. However, the difference is in the molar ratio of starting materials; $\text{FeF}_2/\text{FeF}_3$, 2,2'-bipyridine and HF solution. The main factor was the amount of HF solution that separated the iron and the fluoride atoms from the $\text{FeF}_2/\text{FeF}_3$ reagent entities. For the earlier reported $[\text{FeF}_4(2,2'\text{-bipyridine})(\text{H}_2\text{O})_2]$ compound²⁴, the molar ratio was $\text{FeF}_x:\text{HF}:\text{amine}::10:80:10$, where $x = 2$ or 3, while for the presently synthesized $[\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}]$, the molar ratio is $\text{FeF}_x:\text{HF}:\text{amine}::80:10:10$, where $x = 2$ or 3.

In the present work, the organic cyclic molecule has been replaced with new bicyclic molecule, while solvent used is ethanol in order to achieve a novel class II compound with new dimensionality showing mixed valence for the iron cation. Investigation of the crystal structure of the title compound, $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ shows a triclinic structure with the centrosymmetric space group $P\bar{1}$. Thermal behaviour, infrared spectroscopy

and magnetic measurements are reported for the new fluoroferrate template with 2,2'-bipyridine molecules .

Experimental

$\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ was synthesized under hydrothermal conditions at 410 K under autogenous pressure using classical heating (Autoclave) for 72 h and then cooled to room temperature. The starting materials were: $\text{FeF}_2/\text{FeF}_3$; hydrofluoric acid solution (40% HF, Riedel-de Haen), 2,2'-bipyridine and ethanol solvent, such that all reagents filled up half of the autoclave. The $\text{FeF}_2\text{-FeF}_3\text{-2,2'-bipyridine-HF}_{\text{aq.}}$ -ethanol system was investigated and established at a constant concentration of $c(\text{Fe}^{2+}) + c(\text{Fe}^{3+}) = 0.15 \text{ mol/L}$ and a molar ratio of $n(\text{Fe}^{2+})/n(\text{Fe}^{3+}) = 1$. The solid product was washed with ethanol and dried at room temperature. X-ray data collection were collected on an Oxford Diffraction Gemini S single-crystal diffractometer, using mirror-monochromated radiation. Images were collected at a 55 mm fixed crystal detector distance, using the oscillation method, with variable exposure time per image. The single crystal was carefully selected under a polarizing microscope. The structure of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ was solved by direct methods using SHELXS-97¹³ which gives the positions of most of the atoms (iron, nitrogen, fluorine atoms), and extended by Fourier maps SHELXL-97¹³, included in WINGX package¹⁴. The structure graphics were created by the DIAMOND program¹⁵.

The chemical purity of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ product was tested by EDAX measurements (Fig. 1(a)). SEM image (Fig. 1b) showing the

morphology of the compound confirmed that all non-hydrogen atoms are present, i.e., Fe, F, O, N and C. Elemental analysis for the observed atoms are C: 43.24%, N: 10.75%, O: 02.40%, F: 22.91% and Fe: 23.09%, while the calculated values are C: 44.72%, N: 10.43%, O: 02.97%, F: 17.68% and Fe: 20.79%.

A Mettler-Toledo TGA/SDTA851ELF was used for the thermal analyses in oxygen dynamic atmosphere (50 mL/min) at a heating rate of 10 °C/min. For TG analysis, 12.0836 mg of the sample was used. Infrared absorption spectrum was recorded using UV-vis-NIR Perkin Elmer Lambda 900 spectrometer in the (4000–600 cm^{-1}) frequency range. The magnetic susceptibility measurement of the powdered sample was made on a vibration sample magnetometer (VSM) on an EV9 instrument while heating from 100 K to 400 K under an applied magnetic field of strength 10 kOe ($\approx 796 \text{ kA/m}$). The magnetization as a function of the magnetic field (H), was measured using the same magnetometer in a complete cycle between $-20 \leq H/\text{kOe} \leq 20$ at room temperature. The details of data collection and refinement for the title compound are summarized in Table 1. Selected inter-atomic distances (Å) in $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ is reported in Table 2. The atomic displacement parameters and fractional atomic coordinates and equivalent isotropic displacement parameters for the new compound are given as supplementary data (Tables S1 and S2). All results of the selected bond angles and distances of organic molecules are reported in Table S3 (Supplementary data).

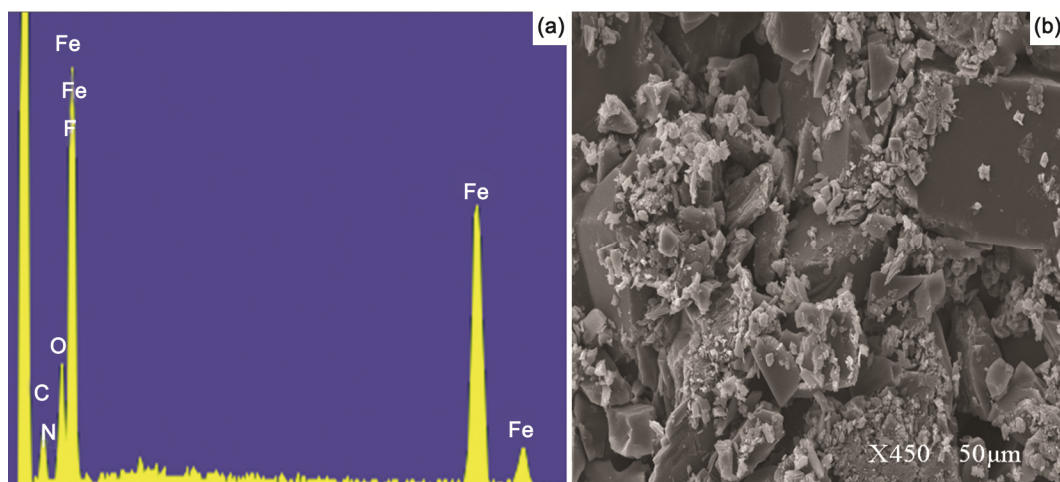


Fig. 1 — (a) EDAX spectrum of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ showing the presence of Fe, F, O, N and C, and, (b) scanning electron microscopy image of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

Table 1 — Crystallographic data of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ at room temperature

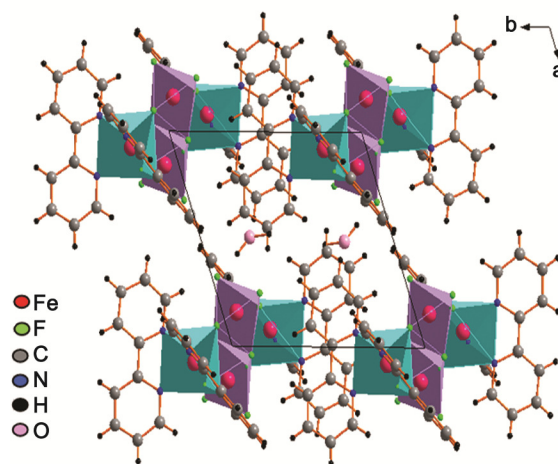
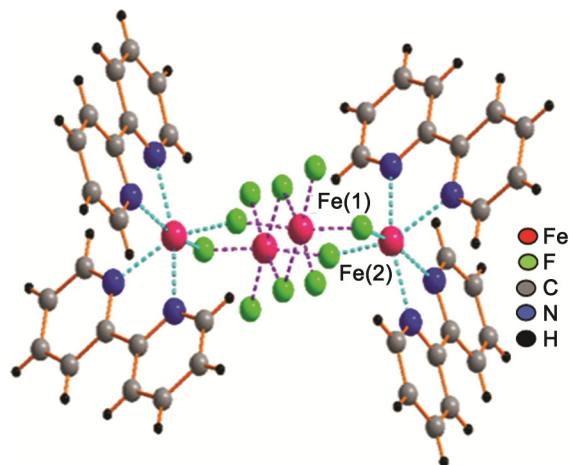
Formula	$\text{Fe}_2\text{F}_5\text{ON}_4\text{C}_{20}\text{H}_{18}$
Crystal system	Triclinic
Space group	$\text{P}\bar{1}$
a (Å)	10.0261(2)
b (Å)	10.2810(2)
c (Å)	11.5340(3)
α (°)	97.780(2)
β (°)	102.755(2)
γ (°)	107.952(2)
V (Å ³)	1076.28(4)
Z	2
F(000)	542
Formula wt (g mol ⁻¹)	537.08
Dimensions (mm)	0.3711×0.2287×0.1855
μ mm ⁻¹)	1.410
ρ_{calc} . (g cm ⁻³)	1.657
Temp. (K)	293
Radiation, λ (Å)	Mo K α , 0.71073
θ range (°)	3.27 / 31.49
Limiting indices	$-14 \leq h \leq 14$; $-14 \leq k \leq 15$; $-16 \leq l \leq 16$
Collected reflections	24454
Reflections unique	5478
Parameter refined	286
Goodness of fit (F^2)	1.078
R_1 [$I > 2\sigma I$]	0.0387
WR_2	0.1239
ρ min/max (e Å ⁻³)	-0.618/ 0.934

Results and discussion

The crystals of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ crystallize in the triclinic space group $\text{P}\bar{1}$ with unit cell parameters $a = 10.0261(2)$ Å, $b = 10.2810(2)$ Å, $c = 11.5340(3)$ Å, $\alpha = 97.780(2)^\circ$, $\beta = 102.755(2)^\circ$, $\gamma = 107.952(2)^\circ$, $V = 1076.28(4)$ Å³ and $Z = 2$. The main feature of this compound is the coexistence of two oxidation valences of iron atoms (Fe^{+2} , Fe^{+3}) in the unit cell, involving 0-D dimensionality hybrid class II. The basic structural unit is $\text{Fe}_4\text{F}_{10}\text{N}_8$ tetrahedral polyanions bonded by 2,2'-bipyridine molecules (Fig. 2). The connectivity of the tetramer is identical to that in $[\text{H}_3\text{adap}]_2 \cdot (\text{V}_4\text{O}_4\text{F}_{14}) \cdot 2\text{H}_2\text{O}$ ¹⁶. In the present case, the $\text{Fe}_4\text{F}_{10}\text{N}_8$ tetramer of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ may be regarded as a dimeric unit (Fe_2F_{10}), which is connected with two FeF_2N_4 monomers by two corner fluorine. Figure 3 shows that the Fe_2F_{10} dimers originate from the association of two FeF_6 octahedra by two fluoride

Table 2 — Selected inter-atomic distances in $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$

Bonds	Bond distance (Å)	Bonds	Bond distance (Å)
Fe(1)—F(1)	2.023(4)	Fe(2)—F(2)	2.053(9)
Fe(1)—F(2)	1.965(5)	Fe(2)—N(1)	2.179(2)
Fe(1)—F(3)	1.860(5)	Fe(2)—N(2)	2.193(5)
Fe(1)—F(4)	1.852(4)	Fe(2)—N(3)	2.188(1)
Fe(1)—F(5)	1.962(1)	Fe(2)—N(4)	2.236(2)
		Fe(2)—F(5)	2.032(6)

Fig. 2 — Projection of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ crystal structure in the (a,b) plane.Fig. 3 — Configuration of the $\text{Fe}_4\text{F}_{10}\text{N}_8$ tetramers of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

atoms with the Fe(1)-F bond length varying between 1.852(4) and 2.023(4) Å. The oxidation state is +III for Fe(1) iron atoms¹⁷. Each iron atom in FeF_2N_4 octahedron is coordinated by two fluorine atoms, (where the Fe(2)-F bond length varies between

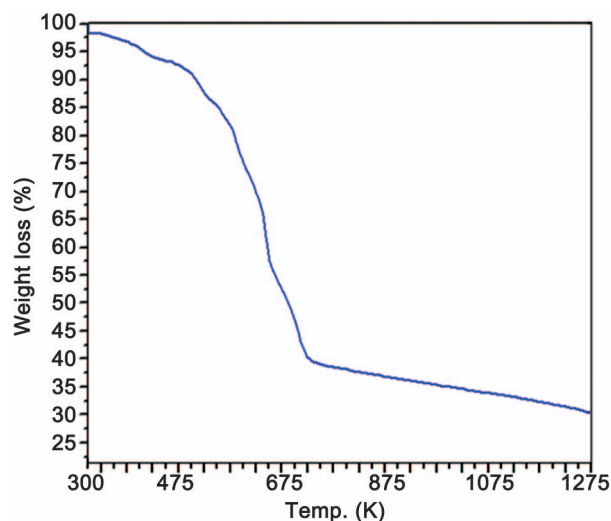


Fig. 4 — TG curve from room temperature to 1200 K, for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

2.032(6) and 2.053(9) Å), and four nitrogen atoms from 2,2'-bipyridine molecule (where the Fe(2)-N bond length varies from 2.179(2) Å to 2.236(2) Å). It is to be noted that the bonds established between Fe(2) and N(1), N(2), N(3), N(4) nitrogen atoms indicate that the title compound, $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$, is a class II hybrid. Furthermore, the hydrogen atoms of the organic molecule were placed with HFIX options (43 for CH). The O–H distances and H–O–H angles of water molecules by symmetry were found to be 1.000(2) Å and 109.2(2)°, respectively.

The TG thermal analysis of the title compound is given in Fig. 4. In the temperature range between 320 K and 450 K, the mass loss corresponds to the loss of water molecule and, eventually, of hydrofluoric acid (HF). After the dehydration process and above 470 K, the progressive elimination of bipyridine amines takes place. The decomposition of 2,2'-bipyridine molecule and the creation of FeF_2 are in the temperature range of 475–775 K. At high temperature, the iron fluoride was slightly contaminated with Fe_2O_3 ¹⁸. The total experimental mass loss value of 69.7% is in good agreement with the theoretical mass loss of 68.59%, assuming that the hematite is the final product of the oxidation.

The infrared spectrum of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ has been investigated in the frequency range of 4000–600 cm^{-1} as shown in Fig. 5. The high frequency in the 3400–3600 cm^{-1} region for the hydrated complexes is probably due to stretching vibrations of the water molecules $\nu(\text{H}_2\text{O})$ ¹⁸. The IR spectrum of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ shows strong

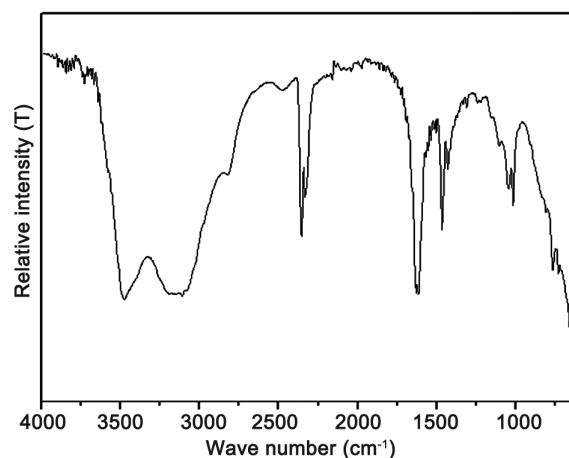


Fig. 5 — IR spectrum at room temperature for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

and broad bands for the coordinated water^{18,19}, centred at 3585 cm^{-1} , 3565 cm^{-1} and 3487 cm^{-1} . Strong absorption bands at 3111 cm^{-1} , 3081 cm^{-1} , 2976 cm^{-1} and 2826 cm^{-1} can be associated with the stretching vibration of the heterocyclic ring of C–H bonds^{20–23}. In the case of transition metal complexes of 2,2'-bipyridine, the aromatic C–H stretching modes^{23,24} can be observed at 2480 cm^{-1} , 2357 cm^{-1} and 2341 cm^{-1} . The band appearing between 1635 cm^{-1} and 1440 cm^{-1} that is shifted by approximately 30–50 cm^{-1} , should correspond to the ring stretching vibrations²³. However, the peaks observed at 1635–1616 cm^{-1} can be associated with the stretching vibration $\nu(\text{C–C})$ and $\nu(\text{C–N})$ of the heterocyclic ring. The rest of the bands are attributed to the heterocyclic ring stretching and hydrogen bending character^{20,23}. The peaks at 1313–1243 cm^{-1} may be attributed respectively, to the inter-ring stretching in 2,2'-bipyridine and ring stretching mode with hydrogen bending character^{20,23}. The absorption bands observed at 1161 cm^{-1} is related to the heterocyclic ring and –H bends²⁰. In the frequency range of 1113–1023 cm^{-1} , three absorption bands are considered to the plane hydrogen bending mode $\delta(\text{C–H})$ ^{20,23}. However, the bands at around 800–600 cm^{-1} region are due to the characteristic out-of-plane heterocyclic ring bending mode $\delta(\text{C–H})$. The strong peak at 601 cm^{-1} may be due to the stretching vibrations of iron nitrogen mode $\nu(\text{Fe–N})$, which is slightly shifted by 30 cm^{-1} as compared with that of the iron nitrates of 2,2'-bipyridine^{22,25}. The observed frequencies in the infrared spectrum of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$, their approximate intensities and probable assignments are given in Table S4.

The magnetic properties of iron fluoride complex $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$, has been examined. The specific susceptibility is evaluated from the slope of the curve representing the temperature dependence of the reciprocal molar magnetic susceptibility (χ_M^{-1}) for the compound depicted in Fig. 6.

Figure 6 also displays the evolution of specific magnetization with temperature under an applied magnetic field of 10 kOe for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ showing that the susceptibilities derivative decreases inversely with the temperature in a similar manner as established by Curie-Weiss law. The Curie constant is estimated from a fit of the temperature dependence of χ_M^{-1} , considering all the temperature ranges investigated according to the Curie-Weiss law. Further, the effective moment (Bohr magneton) for the magnetic (iron) atoms on $\text{Fe}_2\text{F}_5\text{N}_4\text{C}_{20}\text{H}_{18}\text{O}$ composition was estimated from this fitting. The value of the experimental paramagnetic effective moment, $6.83 \mu_B$, is quite close to that expected theoretically ($6.82 \mu_B$), for iron ions Fe^{2+} and Fe^{3+} (terms 5D_4 , ${}^6S_{5/2}$) assuming the mixed valence and partial quenching of the orbital angular momentum²⁷. Otherwise, the fitted parameters for the Curie-Weiss laws indicate both complex ionic states for the iron atoms. The dependence of the magnetization with the applied magnetic field at room temperature for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ compound has been represented in Fig. 7. As can be seen, the magnetization in this compound does not show any ferromagnetic component (no irreversibility in the

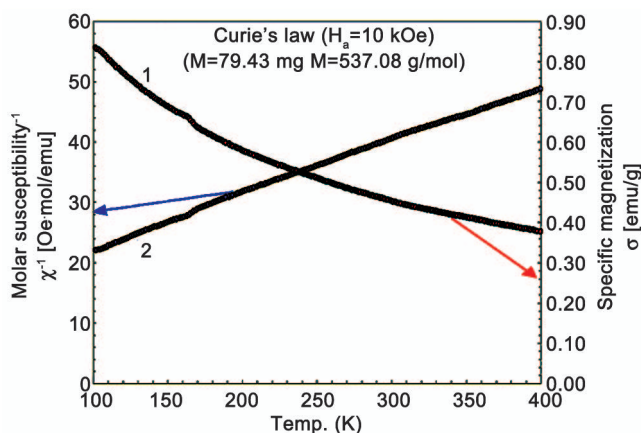


Fig. 6 — Temperature dependence of the reciprocal molar magnetic susceptibility (χ_M^{-1}), (curve-1), and $M(T)$ (curve-2), measured under applied magnetic field of 10 kOe, for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

magnetization curve $M(H)$). Furthermore, the general shape of the $M(H)$ curves, linear increase at low fields and the tendency to saturation at higher fields, is typical of the Brillouin²⁸ functions, expected in paramagnetic materials. Therefore, the magnetization curve is in good agreement with magnetic susceptibility data.

In this study, a new mixed hybrid fluoride compound was obtained with iron interacting with 2,2'-bipyridine molecules, from an ethanol solution under solvothermal conditions. This structure can be classified among the notation of Cheetham²⁶, leading to 0-D dimensionality with respect to the organic connectivity between metal centers (O^n) and extended inorganic connectivity (I^n). Therefore, the notation of Cheetham is I^0O^0 (I = inorganic and O = organic), taking into account that the sum of the exponents gives the overall dimensionality of the structure. On the other hand, and different from our recent work, some studied fluorinated compounds of triazole cations, based on DMF solvent are known with high dimensionality.

Thermal analysis of the title compound shows that the decomposition introduces a continuous and overlapping five-step processes between 370 K and 870 K. Moreover, X-ray powder diffraction analysis of the residual powder after decomposition, corresponds to Fe_2O_3 and confirms the hematite compounds as residual. IR spectroscopy proves the presence of 2,2'-bipyridine organic molecules.

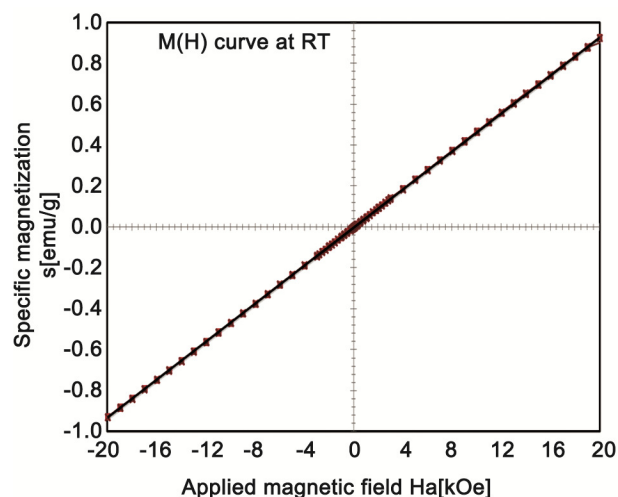


Fig.7 — Specific magnetization for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$, measured at room temperature during a close loop with maximum applied magnetic field of 20 kOe.

Supplementary data

CCDC 1484748 contains the supplementary crystallographic data of the title compound. These data can be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK or via www.ccdc.cam.ac.uk; Fax.: +44 1223 336 033, Email: deposit@ccdc-cam.ac.uk. Other supplementary data associated with this article viz., Tables S1-S3, are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_55A\(07\)810-815_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_55A(07)810-815_SupplData.pdf).

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