

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).

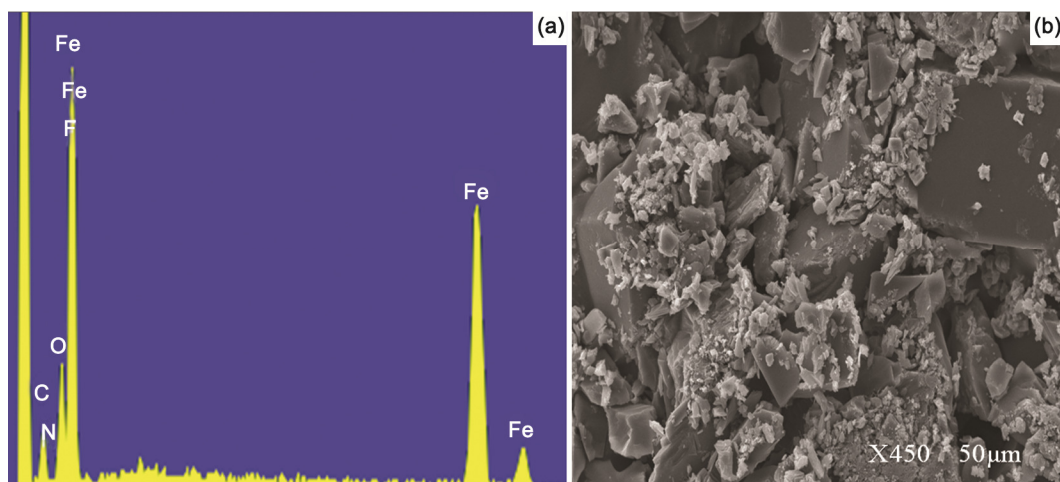


Fig. 1 — (a) EDAX spectrum of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$ showing the presence of Fe, F, O, N and C, and, (b) scanning electron microscopy image of $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

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

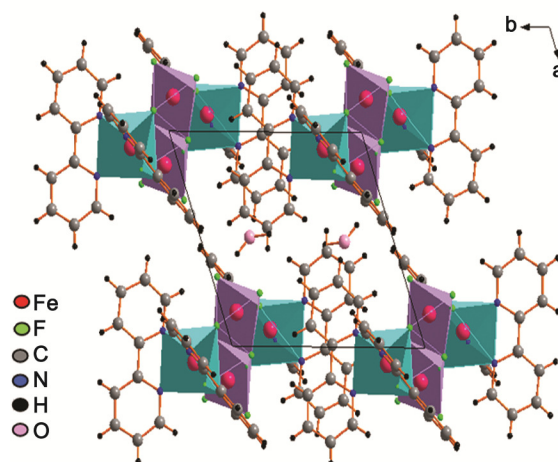
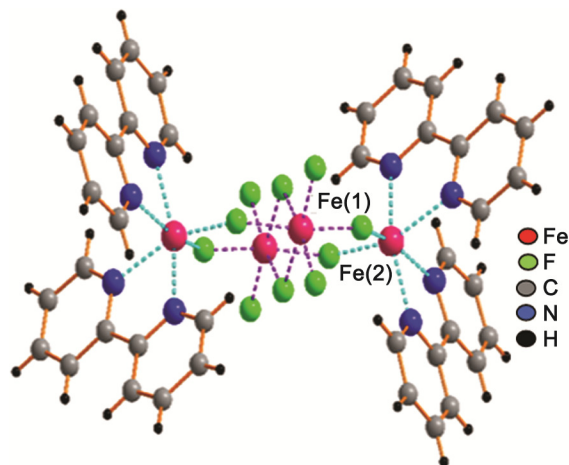
Formula	$\text{Fe}_2\text{F}_5\text{ON}_4\text{C}_{20}\text{H}_{18}$
Crystal system	Triclinic
Space group	$\text{P}\bar{1}$
a (Å)	10.0261(2)
b (Å)	10.2810(2)
c (Å)	11.5340(3)
α (°)	97.780(2)
β (°)	102.755(2)
γ (°)	107.952(2)
V (Å ³)	1076.28(4)
Z	2
F(000)	542
Formula wt (g mol ⁻¹)	537.08
Dimensions (mm)	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

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

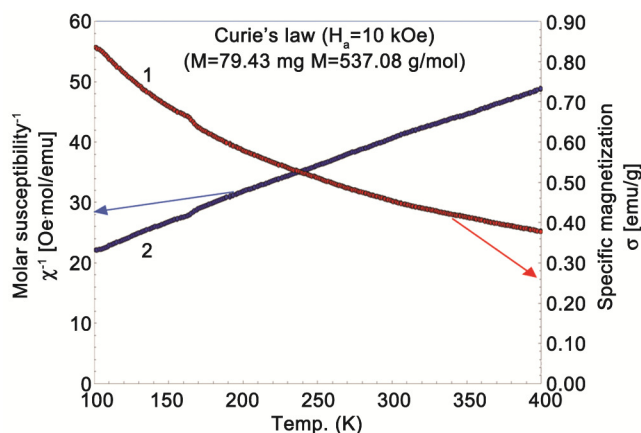


Fig. 6 — Temperature dependence of the reciprocal molar magnetic susceptibility (χ_M^{-1}), (curve-1), and $M(T)$ (curve-2), measured under applied magnetic field of 10 kOe, for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$.

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.

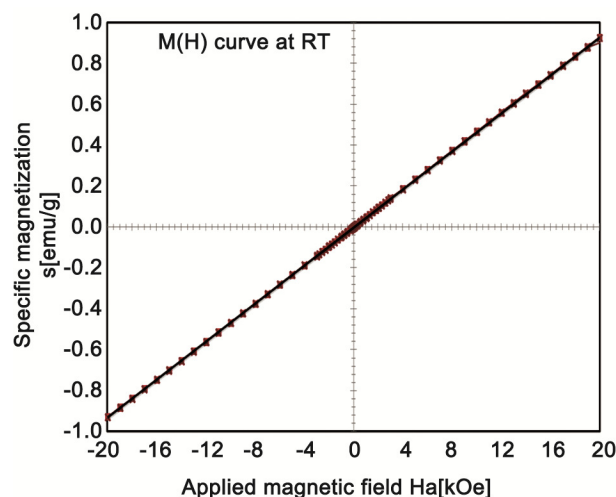


Fig.7 — Specific magnetization for $\text{Fe}_2\text{F}_5(2,2'\text{-bipyridine})_2\text{H}_2\text{O}$, measured at room temperature during a close loop with maximum applied magnetic field of 20 kOe.

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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References

- 1 Liu J Q, Wang Y Y, Zhang Y N, Liu P, Shi Q Z & Battern R, *Eur J Inorg Chem*, 1 (2009) 147.
- 2 Su Z, Fan J, Okamura T, Sun Y W & Ueyama N, *Cryst Growth Des*, 10 (2010) 3515.
- 3 Sanchez C & Ribot F, *New J Chem*, 18 (1994) 1007.
- 4 Férey G, *L'actualité chimi*, 304 (2007) 3.
- 5 Adil K, Leblanc M, Maisonneuve V & Lightfoot P, *Dalton Trans*, 39 (2010) 5983.
- 6 Collins D J & Zhou H C, *J Mater Chem*, 17 (2007) 3154.
- 7 Zou R Q, Sakurai H & Xu Q, *Angew Chem Int Ed*, 45 (2006) 2542.
- 8 Halper S R, Do L, Stork J R & Cohen S M, *J Am Chem Soc*, 128 (2006) 15255.
- 9 Qiong Y, Da-Wei F, Hang T, Ren-Gen X, Philip W H C & Songping D H, *Inorg Chem*, 47 (2008) 772.
- 10 Zhang J P, Lin Y Y, Huang X C & Chen X M, *J Am Chem Soc*, 127 (2005) 5495.
- 11 Férey G, Millange F, Morcrette M, Serre C, Doublet M, Grenèche J M & Tarascon J M, *Angew Chem*, 46 (2007) 3259.
- 12 Smida M, Lhoste J, Pimenta V, Hémon-Ribaud A, Jouffret L, Leblanc M, Dammak M, Grenèche J M & Maisonneuve V, *Dalton Trans*, 42 (2013) 15748.
- 13 Sheldrick G M, *SHELX-S-L 97, Program for the Solution of Crystal Structures*, (Univ of Göttinge, Germany), 1997.
- 14 Farrugia L J, *WinGX Suite for Small-molecule Single-Crystal Crystallography*, *J Appl Cryst*, 32 (1999) 837.
- 15 Brandenburg K & Berndt M, DIAMOND, ver. 2.1.b, Crystal impact (G R Bonn, Germany), 1999.
- 16 Aldous D W, Stephens N F & Lightfoot P, *Dalton Trans*, (2007) 2271.
- 17 Ben Ali A, Grenèche J M, Leblanc M & Maisonneuve V, *Solid State Sci*, 11 (2009) 1631.
- 18 Czakis-Sulikowska D & Katuzna-Czaplińska J, *J Therm Anal Calor*, 62 (2000) 821.
- 19 Sancak K, Er M, Unver Y, Yildirim M & Degirmencioglu I, *Trans Met Chem*, 32 (2007) 16.
- 20 Niven M L & Percy G C, *Trans Met Chem*, 3 (1978) 267.
- 21 Grupce O, Jovanovski G, Kaitner B & Naumov P, *J Struct Chem*, 42 (2001) 926.
- 22 Kumar D, Kapoor I P S, Singh G, Goel N & Singh U P, *J Therm Anal Calor*, 107 (2012) 325.
- 23 Strukl J S & Walter J L, *Spectrochim A*, 27A (1971) 223.
- 24 Smida M, Litaïem H, Dammak M & Garcia-Granda S, *Chem Res Chin Univ*, 31 (2015) 16.
- 25 Nakamoto K, *Infra-red and Raman Spectra of Inorganic and Coordination Compounds*, Wiley New York, 1978, p.259.
- 26 Cheetham A K, Rao C N R & Feller R K, *Chem Commun*, (2006) 4780.
- 27 Blundell S, *Magnetism in Condensed Matter*, (Oxford University Press UK), Vol. AA 2001, p. 196.
- 28 Blundell S, *Magnetism in Condensed Matter*, (Oxford University Press UK), Vol. C2 2001, p. 29.