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Synthesis, structure of $[H_3dien]\cdot(MF_6)\cdot H_2O$ ($M=$ Cr, Fe) and ^{57}Fe Mössbauer study of $[H_3dien]\cdot(FeF_6)\cdot H_2O$

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Abstract

Single crystals of $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**) and $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**) are obtained by solvothermal synthesis under microwave heating. **I** is orthorhombic ($Pna2_1$) with $a = 11.530(2)$ Å, $b = 6.6446(8)$ Å, $c = 13.787(3)$ Å, $V = 1056.3(2)$ Å^3 and $Z = 4$. **II** is monoclinic ($P2_1/c$) with $a = 13.706(1)$ Å, $b = 6.7606(6)$ Å, $c = 11.3181(9)$ Å, $\beta = 99.38(1)^\circ$, $V = 1034.7(1)$ Å^3 and $Z = 4$. The structure determinations, performed from single crystal X-ray diffraction data, lead to the R_1/wR_2 reliability factors 0.028/0.066 for **I** and 0.035/0.102 for **II**. The structures of **I** and **II** are built up from isolated FeF_6 or CrF_6 octahedra, water molecules and triprotonated amines. In both structures, each octahedron is connected by hydrogen bonds to six organic cations and two water molecules. The iron-based compound is also characterized by ^{57}Fe Mössbauer spectrometry: the hyperfine structure confirms the presence of Fe^{3+} in octahedral coordination and reveals the existence of paramagnetic spin fluctuations.

Keywords: Fluoride; Fluoroferrate; Fluorochromate; Microwave heating; Solvothermal synthesis; Crystal structure; Mössbauer spectrometry

1. Introduction

The search of new hybrid compounds is very active due to their potential catalytic [1–4], exchange selectivity [5,6] or electronic/magnetic properties [7,8]. During the last few years, we focused our work on several hybrid aluminium [9], zirconium and tantalum [10] fluorides in which the dimensionality of the metal fluoride entities are 0D (isolated polyanions) [11], 1D (chains) [12] or 2D (layers) [13]. Chemical systems using tris-(2-aminoethyl)amine (*tren*) or bis-(2-aminoethyl)amine (*dien*) as structure directing agents are now investigated for the crystallization of M^{3+} fluoride frameworks ($M^{3+} = Fe^{3+}$ or Cr^{3+}). In the FeF_3-*dien*-HF_{aq}-solvent system, only one phase was previously reported, $[H_3dien]\cdot(FeF_6)\cdot 2H_2O$ [14]; it is isoformular to the aluminium compound [15] but crystallizes in a different space group.

This paper describes the synthesis, the crystal structure and thermal behaviour of two isoformular fluorides templated with *dien*, $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**) and $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**). The study is completed by ^{57}Fe Mössbauer spectrometry of the iron compound in order to discuss some magnetic properties.

2. Experimental

$[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**) and $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**) were synthesized under hydrothermal conditions at $T = 190\,^\circ C$ from $Fe(OH)_3$ or $Cr(OH)_3$, bis-(2-aminoethyl)amine (*dien*) (95%), HF(40%, Riedel-de Haën) and ethanol (filling rate 50% of the autoclave). **I** was prepared from the starting materials in the molar ratio: 1/3/12/170 and microwave heating (oven MDS2100) for 1 h whereas **II** was obtained from the molar ratio 1/3/15/34 and classical

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Table 1
Crystallographic data of $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**) and $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**)

	I	**II**
Empirical formula	$FeF_6ON_3C_4H_{18}$	$CrF_6ON_3C_4H_{18}$
Formula weight ($g\,mol^{-1}$)	294.04	290.19
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$ (33)	$P2_1/c$ (14)
a (Å)	11.530(2)	13.706(1)
b (Å); β (°)	6.6446(8)	6.7606(6); 99.38(1)
c (Å)	13.787(3)	11.3181(9)
V (Å^3), Z	1056.3(2), 4	1034.7(1), 4
Four circle diffractometer/radiation	Siemens AED2/Mo$K\alpha$	
Crystal size (mm^3)	$0.30 \times 0.23 \times 0.06$	$0.70 \times 0.25 \times 0.06$
μ(Mo$K\alpha$) (mm^{-1})	1.49	1.17
$\rho_{calc.}$ ($g\,cm^{-3}$)	1.849	1.863
$\rho_{exp.}$ ($g\,cm^{-3}$)	1.84(1)	
Temperature (K)	293(2)	
2θ range (°)	2–55	2–60
($h\,k\,l$) limits	$\lvert h\rvert \leqslant 14$; $\lvert k\rvert \leqslant 8$; $\lvert l\rvert \leqslant 17$	$0 \leqslant h \leqslant 19$; $-9 \leqslant k \leqslant 0$; $-15 \leqslant l \leqslant 15$
R_{int}/R_{sigma}	0.017/0.023	–/0.025
Scan mode	ω–2θ	
Absorption correction	Gaussian	
T_{min}, T_{max}	0.713, 0.918	0.716, 0.937
Reflections measured/unique/($I > 2\sigma(I)$)	2860/2284/2003	3241/2958/2129
Number of refined parameters (on F^2)	145	150
R_1/wr_2[a]	0.028/0.066	0.035/0.102
Goodness of fit on F^2[b]	1.096	0.994
Flack parameter	0.08(2)	—
Weighting scheme ($P = [F_0^2 + 2F_c^2]/3$)	$1/[\sigma^2(F_0^2) + (0.032P)^2] + 0.22\ P]$	$1/[\sigma^2(F_0^2) + (0.062P)^2 + 0.19\ P]$
Difference Fourier residues (e Å^{-3})	0.20, −0.20	0.74, −0.49
Secondary extinction coefficient	—	1.1(2) 10^{-5}

[a] $R_1 = \Sigma||F_o - F_c||/\Sigma|F_o|$ $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w|F_o|^4]\}^{1/2}$.
[b] $Goof = S = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

heating (Parr autoclave) during 48 h. In both cases, powders and crystals, colourless for **I** and green for **II**, resulted.

The volume weight of **I** was measured with a pycnometer AccuPyc 1330 V3.03; the experimental value, $\rho_{exp} = 1.84(1)\,g\,cm^{-3}$ is consistent with the calculated value $\rho_{calc} = 1.849\,g\,cm^{-3}$.

Thermal analyses were performed with a DTA-TGA TA 2960 instrument (heating rate 10 °C/min, argon atmosphere) in the temperature range 25–650 °C. On heating, both **I** and **II** exhibit a weight loss in two steps: the first step, which occurs in the interval 80–160 °C (**I**) or 100–200 °C (**II**), is attributed to the loss (weight %) of one mole of H_2O molecules per one mole of **I** or **II** (exp./th. = 6.4/6.1 for **I** and 6.3/6.2 for **II**). The second weight loss lies in the interval 160–450 °C (**I**) or 200–550 °C (**II**) and corresponds to the decomposition of the organic molecules and the simultaneous reduction of Fe^{3+} or Cr^{3+} cations (exp./th. = 61.9/62.0 for **I** and 59.9/62.8 for **II**). The residual products are FeF_2 or CrF_2 (contaminated with a small amount of carbon graphite particles).

Mössbauer spectra were recorded with a 925 MBq γ-source of $^{57}Co/Rh$ at 300, 77 and 4.2 K using a bath cryostat; an in-field Mössbauer spectrum was recorded under 8 T at 12 K using a cryomagnetic system where the external field is applied parallel to the γ-radiation beam. The spectra were fitted using the MOSFIT program [16], the isomer shift values are referred to that of α-Fe at RT.

Crystals were carefully selected under a polarizing microscope. Data were collected on a SIEMENS AED2 four-circle diffractometer at room temperature using ω-2θ scans. Unit cell parameters were refined from least square analysis of 32 reflections in the 2θ range 30–32°. The structure determinations were performed with SHELXS-97 [17], SHELXL-97 [18] programs included in WINGX package [19]. Absorption corrections were applied using SHELX-76 software [20]. The conditions of data collection for both phases are summarized in Table 1.

3. Structure determinations of I and II

The extinction conditions led to the $Pna2_1$ noncentrosymetric space group, compatible with $Z = 4$, for **I** and $P2_1/c$ for **II**. The structures of **I** and **II** were solved using the TREF option in SHELXS-97 program. Iron and chromium atoms were first located in $4a$ and $2a$, $2c$ crystallographic sites in **I** and **II**, respectively. The remaining non-hydrogen atoms were deduced from Fourier

Table 2
Atomic coordinates, equivalent isotropic displacement parameters in $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**)[a]

Atom	x	y	z	B_{eq} (Å^2)
Fe	0.31412(3)	0.50276(7)	0.74395(4)	1.46(1)
F(1)	0.4751(2)	0.4684(3)	0.7848(2)	2.69(3)
F(2)	0.1576(2)	0.5544(3)	0.7022(2)	2.72(3)
F(3)	0.3056(2)	0.7191(3)	0.8366(2)	2.77(4)
F(4)	0.3336(2)	0.2777(3)	0.6575(2)	2.64(4)
F(5)	0.3609(2)	0.7029(3)	0.6499(2)	2.47(3)
F(6)	0.2621(2)	0.3143(3)	0.8391(2)	3.45(4)
N(1)	0.5061(2)	−0.3029(4)	0.9619(2)	2.09(4)
N(2)	0.4605(2)	0.0144(4)	0.7988(2)	2.42(5)
N(3)	0.3343(2)	−0.5121(4)	1.1688(2)	2.33(5)
C(1)	0.5653(3)	−0.1050(5)	0.9447(2)	2.48(6)
C(2)	0.4876(3)	0.0527(5)	0.9015(2)	2.54(6)
C(3)	0.4277(3)	−0.3014(4)	1.0473(2)	2.07(5)
C(4)	0.3866(3)	−0.5116(4)	1.0705(2)	2.25(5)
O_W	0.3108(2)	0.5604(4)	0.4749(2)	3.28(5)

[a] Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 637911 for (**I**) and CCDC No. 637912 for (**II**). Copies of data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 3
Atomic coordinates, equivalent isotropic displacement parameters in $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**)[a]

Atom	x	y	z	B_{eq} (Å^2)
Cr(1)	0	0	0	1.29(1)
Cr(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	1.28(1)
F(1)	0.0962(1)	0.1546(2)	−0.0589(2)	3.43(3)
F(2)	0.0774(1)	−0.0261(2)	0.1552(1)	2.82(3)
F(3)	−0.0579(1)	0.2351(2)	0.0508(1)	2.72(3)
F(4)	0.5845(1)	0.1746(2)	0.6031(1)	2.44(3)
F(5)	0.4676(1)	0.2085(2)	0.3870(1)	2.72(3)
F(6)	0.3956(1)	0.0842(2)	0.5788(1)	2.68(3)
N(1)	0.2493(1)	0.7803(3)	0.2320(2)	1.93(3)
N(2)	0.0475(2)	0.5275(3)	0.1741(2)	2.21(3)
N(3)	0.4291(2)	1.0323(3)	0.1606(2)	2.08(3)
C(1)	0.2262(2)	0.5732(4)	0.2633(2)	2.38(4)
C(2)	0.1513(2)	0.4658(3)	0.1734(2)	2.17(3)
C(3)	0.2848(2)	0.8023(3)	0.1150(2)	2.01(3)
C(4)	0.3263(2)	1.0053(3)	0.0985(2)	2.37(4)
O_W	0.2363(2)	0.1080(3)	0.3820(2)	3.93(4)

[a] Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 637911 for (**I**) and CCDC No. 637912 for (**II**). Copies of data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 4
Selected inter-atomic distances (Å) in $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**)

Fe–F(6)	1.911(2)	N(1)–C(3)	1.484(4)	C(1)–C(2)	1.501(5)
Fe–F(2)	1.925(2)	N(1)–C(1)	1.500(4)	C(3)–C(4)	1.510(4)
Fe–F(4)	1.925(2)	N(2)–C(2)	1.471(4)		
Fe–F(3)	1.926(2)	N(3)–C(4)	1.484(4)		
Fe–F(5)	1.934(2)	⟨N–C⟩	1.48		
Fe–F(1)	1.953(2)				
⟨Fe–(F)⟩	1.93				

Table 5
Selected inter-atomic distances (Å) in $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**)

Cr(1)–F(1)	2 × 1.887(1)	N(1)–C(1)	1.491(3)	C(1)–C(2)	1.508(3)
Cr(1)–F(2)	2 × 1.906(1)	N(1)–C(3)	1.492(3)	C(3)–C(4)	1.509(3)
Cr(1)–F(3)	2 × 1.907(1)	N(2)–C(2)	1.484(3)		
⟨Cr(1)–F⟩	1.90	N(3)–C(4)	1.480(3)		
		⟨N–C⟩	1.49		
Cr(2)–F(6)	2 × 1.893(1)				
Cr(2)–F(5)	2 × 1.907(1)				
Cr(2)–F(4)	2 × 1.912(1)				
⟨Cr(2)–(F)⟩	1.90				

difference calculations of the SHELXL-97 program and distinguished from distance criteria [21]. Geometrical constraints, HFIX or DFIX, were applied to localize the hydrogen atoms of organic amines and water molecules, respectively. In both structures, all the atomic positions were refined with anisotropic thermal motion except H atoms for which a common isotropic factor was used. Final refinements of anisotropic displacement parameters (ADP) and secondary extinction converged to $R_1 = 0.028$ and $wR_2 = 0.066$ (2284 independent reflections and 145 parameters) and $R_1 = 0.035$ and $wR_2 = 0.102$ (2958 independent reflections and 150 parameters) for **I** and **II**, respectively. The resulting atomic coordinates with equivalent ADP of **I** and **II** appear in Tables 2 and 3 and selected bond distances and angles are given in Tables 4 and 5, respectively.

4. Structure descriptions of I and II

In **I** and **II**, the Fe–F and Cr–F distances, 1.91–1.95 and 1.89–1.91 Å, respectively, are consistent with the sum of ionic radii of Fe^{3+} or Cr^{3+} and F^-. The M^{3+} cations are six-fold coordinated. The average ⟨C–C⟩ and ⟨N–C⟩ distances of $[H_3dien]^{3+}$ cations are equivalent and equal to 1.48 and 1.50 Å, respectively. As in $[H_3dien]\cdot(FeF_6)\cdot 2H_2O$ [14], one long $N_{central}$–$N_{terminal}$ distance (N_c–$N_t \approx 3.7$ Å) and one short distance (≈ 3.1 Å) are observed in **I** (Table 6); the $[H_3dien]^{3+}$ cations adopt a V-shape configuration, the N_t–N_c–N_t angle is 135.08(4)° (Fig. 1, left). In **II**, both N_c–N_t distances are short (≈ 3.2 Å) (Fig. 1, right) and the N_t–N_c–N_t angle increases (153.98(2)°).

In **I** and **II**, hydrogen bond networks ensure the cohesion between $(MF_6)^{3-}$ anions, H_2O molecules and $[H_3dien]^{3+}$ cations (Table 7). According to the classification of Jeffrey [22], the hydrogen bond strength is moderate (H…A bond-length, 1.5–2.2 Å, X–H…A bond angle > 130°). The MF_6 octahedra are surrounded by two water molecules and six $[H_3dien]^{3+}$ cations; the [010] projections are given in Fig. 2. In **I**, water molecules establish three hydrogen bonds with

Table 6
Distances (Å) and angles (°) between central nitrogen atom (N_c) and terminal nitrogen atoms (N_t) of $[H_3dien]^{3+}$ cations in $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**), $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**) and $[H_3dien]\cdot(FeF_6)\cdot 2H_2O$

	$d(N(1)_c–N(2)_t)$	$d(N(1)_c–N(3)_t)$	$d(N(2)_t–N(3)_t)$	$\langle N_t–N_c–N_t \rangle$
$[H_3dien]\cdot(FeF_6)\cdot H_2O$	3.127(4)	3.741(4)	6.355(4)	135.08(4)
$[H_3dien]\cdot(CrF_6)\cdot H_2O$	3.227(3)	3.206(3)	6.268(3)	153.98(2)
$[H_3dien]\cdot(FeF_6)\cdot 2H_2O$	3.15	3.75	6.87	168.4

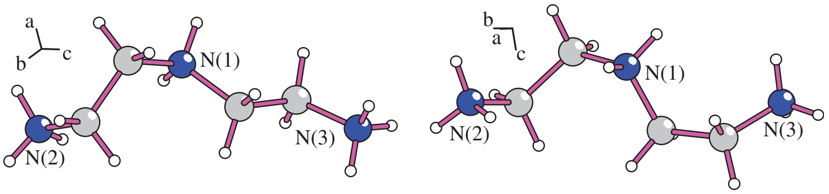

Fig. 1. Configuration of $[H_3dien]^{3+}$ cations in $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**) (left) and $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**) (right).

Table 7
X–H…A bond distances (Å) in $[H_3dien]\cdot(FeF_6)\cdot H_2O$ (**I**) and $[H_3dien]\cdot(CrF_6)\cdot H_2O$ (**II**) (X = O, N, A = F, O)

$[H_3dien]\cdot(FeF_6)\cdot H_2O$		$[H_3dien]\cdot(CrF_6)\cdot H_2O$	
X–H…A	d(*X…A*)	*X–H…A*	d(*X…A*)
O_W–H(2)…F(5)	2.655(3)	O_W–H(1)…F(1)	2.670(2)
O_W–H(1)…F(6)	2.656(3)	O_W–H(2)…F(6)	2.858(2)
N(1)–H(1)A…F(3)	2.889(3)	N(1)–H(1)A…F(2)	2.712(2)
N(1)–H(1)B…F(1)	2.898(3)	N(1)–H(1)B…F(4)	2.715(2)
N(1)–H(1)B…O_W	2.723(4)	N(1)–H(1)A…O_W	2.815(2)
N(2)–H(2)B…F(3)	2.704(3)	N(1)–H(1)B…O_W	2.815(2)
N(2)–H(2)C…F(2)	2.673(3)	N(2)–H(2)A…F(2)	2.806(2)
N(2)–H(3)A…F(4)	2.999(3)	N(2)–H(2)B…F(3)	2.699(2)
N(3)–H(3)A…F(4)	2.736(2)	N(2)–H(2)C…F(3)	3.032(2)
N(3)–H(3)B…F(1)	2.733(3)	N(3)–H(3)A…F(6)	2.766(2)
N(3)–H(3)C…F(2)	2.918(3)	N(3)–H(3)B…F(5)	2.708(2)
		N(3)–H(3)C…F(5)	2.797(2)

two FeF_6 units and one $[H_3dien]^{3+}$ cation in $_{\infty}[011]$ chains (Fig. 3, top left). In **II**, four hydrogen bonds exist between one water molecule and two CrF_6 and one $[H_3dien]^{3+}$ cation in $_{\infty}[1\,\bar{1}\,0]$ chains (Fig. 3, top right). Similar chains are found in $[H_3tren]\cdot(AlF_6)\cdot H_2O$ [15]. The $O_w…N$ distances are close to the mean distance observed for $-NH_3^+…O_w$ distances, 2.84 Å [23,24]. In the dihydrate $[H_3dien]\cdot(FeF_6)\cdot 2H_2O$, two water molecules are connected by one hydrogen bond; they are three-fold coordinated but have a different environment (Fig. 3, bottom).

According to the preparation route, the OH^-/F^- substitution cannot be excluded. Infra red spectroscopy shows that the substitution is rather weak, if any.

5. Mössbauer study of $[H_3dien]\cdot(FeF_6)\cdot H_2O$

At 300, 77 and 4.2 K, the Mössbauer spectra of $[H_3dien]\cdot(FeF_6)\cdot H_2O$ exhibit a single broad and symmetrical line that can be well fitted using a single lorentzian quadrupolar component (Fig. 4). The corresponding hyperfine data are listed in Table 8. The isomer shift value is typical of High Spin state ferric ions in octahedral coordination. In addition, the quadrupolar splitting is quite small, i.e. small electric field gradient, suggesting thus a low symmetry of Fe neighbouring. Both features are consistent with Fe^{3+} ions located in slightly distorted octahedral FeF_6 units, confirming thus the structure determination of **I**. It is important to emphasize that the isomer shift value is significantly smaller than that usually encountered in crystalline or amorphous ferric fluorides resulting from dense packing of octahedral units (~0.46–0.49 mm/s) [25–30], but remains very similar to those observed in $(NH_4)_3FeF_6$ [31,32], K_3FeF_6 [33], guanidinium [34] or diphenylguanidinium hexafluoroferrate [35], based on isolated $(FeF_6)^{3-}$ units. Such a reduction can be explained by the increase of electron density at the Fe nucleus or an increase of the covalency effects [36]. The line broadening is attributed to the presence of electronic relaxation which remains temperature independent.

This feature was further studied by the application of an external magnetic field at 12 K; the broad single line splits into a 4 line sextet (Fig. 5) which consists only of two outer and two inner lines. The absence of intermediate lines (usually labelled 2 and 5) allows to conclude that the Fe^{3+} magnetic moments are parallel to the γ-radiation, i.e. the external field. The effective field (B_{eff}) which acts at the Fe nucleus is estimated at 37 T from the in-field Mössbauer spectrum. As B_{eff} results directly here from the sum of the hyperfine field (B_{hyp}) and the external field ($B_{eff} = B_{hyp} + B_{app}$) because of their colinearity, B_{hyp} is estimated at about −45 T, taking into account that B_{hyp} is antiparallel to Fe magnetic moment ($B_{eff} = -37$ T): indeed the prevailing contribution to B_{hyp} at Fe in most of oxides and fluorides is due to the Fermi term which is negative, i.e. antiparallel to its magnetic moment. It must be noted that the hyperfine field value remains much smaller than values

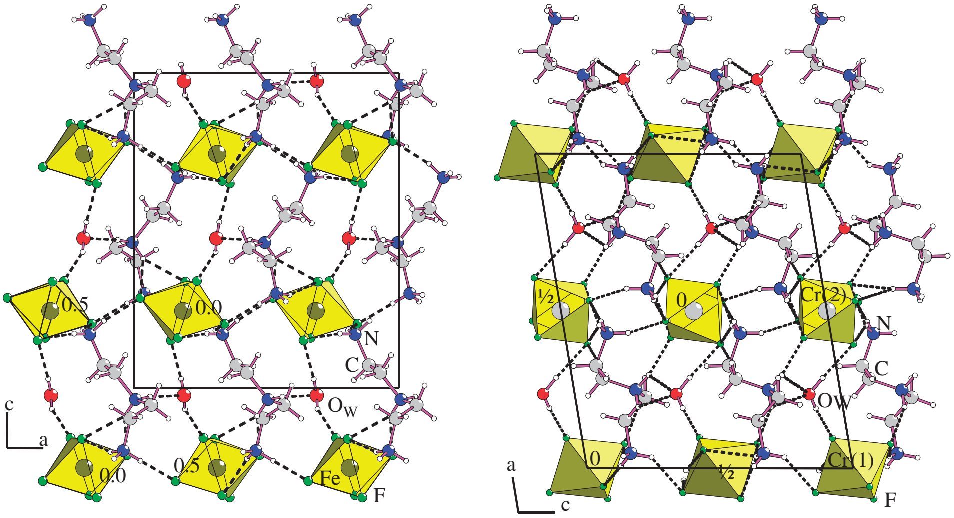

Fig. 2. [0 1 0] projections of [H_3*dien*]·(FeF_6)·H_2O (**I**) (left) and [H_3*dien*]·(CrF_6)·H_2O (**II**) (right). The atomic heights refer to Fe^{3+} (left) or Cr^{3+} (right) cations.

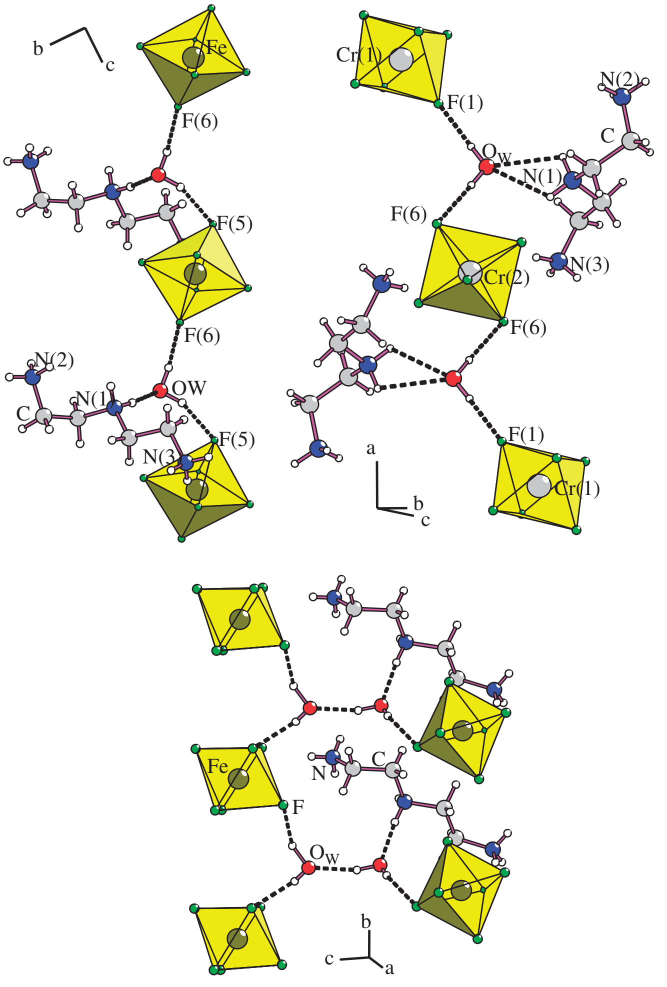

Fig. 3. Environment of H_2O molecules in [H_3*dien*]·(FeF_6)·H_2O (**I**) (top left), [H_3*dien*]·(CrF_6)·H_2O (**II**) (top right) and [H_3*dien*]·(FeF_6)·2H_2O (bottom).

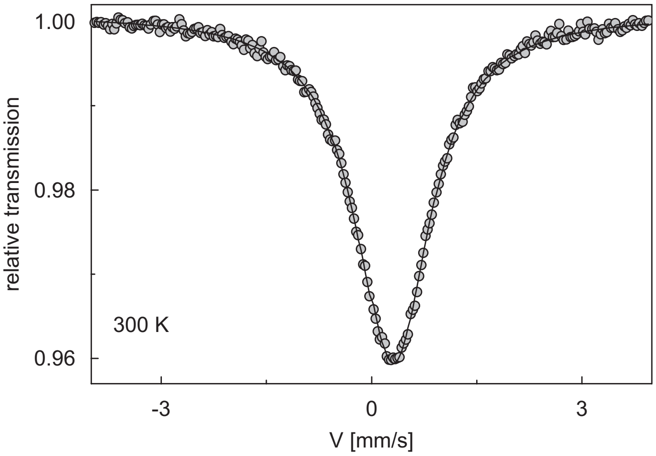

Fig. 4. Mössbauer spectrum of [H_3*dien*]·(FeF_6)·H_2O (**I**) at 300 K.

Table 8
Hyperfine Mössbauer parameters of [H_3*dien*]·(FeF_6)·H_2O

T (K)	δ (mm/s) ±0.01	Δ or 2ε(mm/s) ±0.10	Γ (mm/s) ±0.05	B_{hyp} (T) ±0.5
300	0.42	0.15	1.25	—
77	0.52	0.10	1.34	—
4.2	0.54	0.10	1.38	—
12 (8 T)	0.55	0[a]	1.38	45.0

[a] The quadrupolar shift 2ε was fixed at zero during the fitting procedure.

usually observed in ferric fluorides (ranging from 52 T up to 62 T [29]): such a reduction can be also explained by covalency effects.

On the other hand, the significant broadening of the outer lines confirms the presence of a fast relaxation of the electronic spins that are polarized in presence of the external magnetic field, providing thus a magnetic

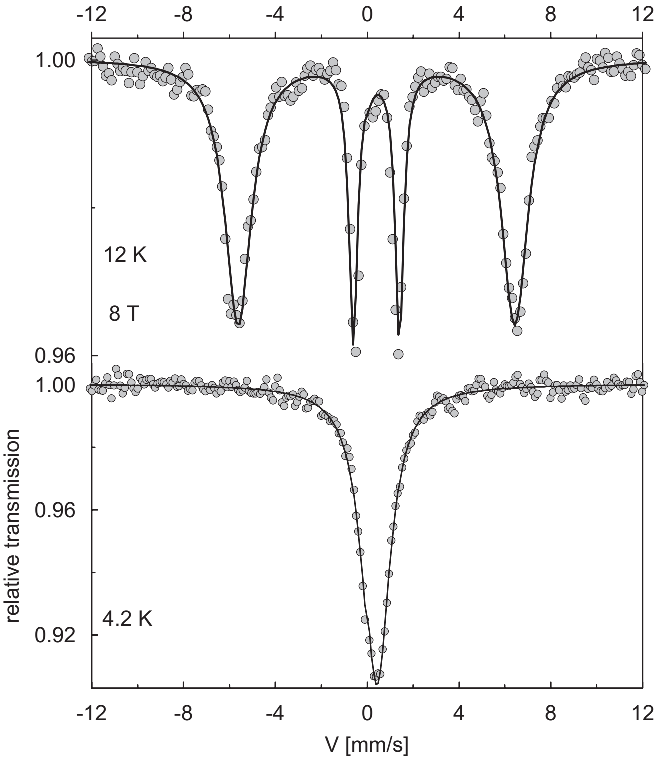

Fig. 5. Mössbauer spectra of $[H_3\textit{dien}]\cdot(FeF_6)\cdot H_2O$ (**I**) recorded at 4.2 K (bottom) and at 12 K (top) in presence of an external field of 8 T applied parallel to the γ-radiation.

hyperfine splitting [37]. A similar situation has been discussed in the case of the ammonium hexafluoroferrate [31,32]. In addition, it can be concluded to the presence of much faster spin fluctuations in $[H_3\textit{dien}]\cdot(FeF_6)\cdot H_2O$ than in $(NH_4)_3FeF_6$ [32]: indeed, the 8 T external magnetic field does not give rise to well resolved hyperfine structure as it occurs by applying a 5 T field in $(NH_4)_3FeF_6$ (see Fig. 5 of the present paper and Fig. 2 of [32]). This is probably due to the longer distances between Fe^{3+} cations in $[H_3\textit{dien}]\cdot(FeF_6)\cdot H_2O$.

6. Conclusions

The structures of $[H_3\textit{dien}]\cdot(FeF_6)\cdot H_2O$ and $[H_3\textit{dien}]\cdot(CrF_6)\cdot H_2O$, determined by X-ray diffraction, can be described from $(MF_6)^{3-}$ octahedra. $[H_3\textit{dien}]^{3+}$ cations and water molecules are connected by hydrogen bonds to the MF_6 octahedra. In both structures, water molecules are surrounded by two fluorine atoms and one nitrogen atom of secondary NH_2 group.

Mössbauer spectra of phase **I** confirm the oxidation state +III of iron cations and their octahedral coordination. The hyperfine structure shows a temperature independent line broadening which is attributed to the presence of paramagnetic spin fluctuations of Fe^{3+} located in non-interacting isolated FeF_6 units.

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