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A new organically templated gallium(III)-doped chromium(III) fluorophosphite, $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ hydrothermal synthesis, crystal structure and spectroscopic properties

Sergio Fernández-Armas,[a] José L. Mesa,[a,*] José L. Pizarro,[b] Luis Lezama,[a]
María I. Arriortua,[b] and Teófilo Rojo[a,*]

[a] *Facultad de Ciencias, Departamento de Química Inorgánica, Universidad del País Vasco, Apdo. 644, Bilbao E-48080, Spain*
[b] *Facultad de Ciencias, Departamento de Mineralogía-Petrología, Universidad del País Vasco, Apdo. 644, Bilbao E-48080, Spain*

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Abstract

A new organically templated fluoro-phosphite gallium(III)-doped chromium(III) with formula $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ has been synthesized by using mild hydrothermal conditions under autogeneous pressure. The crystal structure has been solved from X-ray single-crystal data. The compound crystallizes in the $P2_12_12_1$ orthorhombic space group, with the unit-cell parameters $a = 12.9417(7)$ Å, $b = 9.4027(6)$ Å, $c = 6.3502(4)$ Å and $Z = 4$. The final R factors were $R1 = 0.022$ (all data) and $wR2 = 0.050$. The crystal structure consists of $[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]^{2-}$ anionic chains extended along the c-axis, with the ethylenediammonium cations placed in the cavities of the structure delimited by three different chains. The IR and Raman spectra show the characteristic bands of the phosphite oxoanion. The diffuse reflectance spectroscopy allowed us to calculate the Dq and Racah parameters of the Cr(III) cations in octahedral environment. The values are $Dq = 1375\,\text{cm}^{-1}$, $B = 780\,\text{cm}^{-1}$ and $C = 3420\,\text{cm}^{-1}$. The polycrystalline ESR spectra performed at X and Q-bands show the signals belonging to the diluted Cr(III) cation in this phase. From the fit of the X-band ESR spectrum at 4.2 K, the calculated values of the axial (D) and rhombic (E) distortion parameters are 0.075 and $0.042\,\text{cm}^{-1}$, respectively, the components of the g-tensor being $g_x = 1.98$, $g_y = 1.99$ and $g_z = 1.90$.

Keywords: Hydrothermal synthesis; X-ray diffraction; IR; UV/vis and ESR spectroscopies

1. Introduction

Open-framework crystalline materials are the subjects of intense ongoing research owing to their industrial applications as catalysts, ion exchangers and in the area of gas separation [1]. The discovery of microporous aluminophosphates in the early eighties [2] spawned numerous research programs that resulted in a wealth of new inorganic open-framework materials [1]. In particular, many efforts have been devoted to the hydrothermal or solvothermal synthesis of new alumino- (AlPOs) and gallo-phosphates (GaPOs) [3–5]. Since aluminum and gallium can be non-tetrahedrally coordinated, many AlPOs and GaPOs exhibit new framework topologies that are not encountered in classical aluminosilicate zeolites. In this way, three-, two- and mono-dimensional GaPOs are known [6]. Furthermore, a number of open-framework heterobimetallic-substituted gallium phosphates (MGaPOs) [M = transition metal ion] have been synthesized under mild solvothermal conditions using organic amines or diamines as structural-directing agents [7].

It is worth mentioning the incorporation of the Zn, Co and Mn heteroatoms into framework sites of the gallophosphate molecular sieve ULM-5 by using 1,6-diaminohexane [8]. Furthermore, two organically templated layered uranium(VI) phophates have been prepared under hydrothermal conditions using either NPr_4^+ or $NHEt_3^+$ ions as structure-directing agent by O'Hare et al. [9].

Although a high number of templated phosphates are known, however, compounds of this kind with the

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*Corresponding author. Fax: +34-94-4648-500.

E-mail addresses: qipmeruj@lg.ehu.es (J.L. Mesa), qiproapt@lg.ehu.es (T. Rojo).

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phosphite, $(HPO_3)^{2-}$, oxoanion are very scarce. The possibilities of incorporating the phosphorus(III) containing pseudopyramidal $(HPO_3)^{2-}$ hydrogen-phosphite group into extended structures were shown several years ago [10]. Some organically templated phosphites with transition metal elements such as Co(II), Mn(II), Fe(III), V(III) and V(IV) cations are known [11]. Recently, a series of compounds with the general formula $(C_2H_{10}N_2)[M(HPO_3)F_3]$ [$M^{III} = V$ and Cr] has been also synthesized [11f]. The chromium(III) compound is the first example of organically templated Cr(III) in the Cr(III)–P–O system [12]. In order to extend our knowledge about these kinds of materials we here report on the new gallium(III)-doped chromium(III) phase belonging to the $(C_2H_{10}N_2)[M^{III}(HPO_3)F_3]$ family. The hydrothermal synthesis, crystal structure and spectroscopic properties of this phase are described.

2. Experimental section

2.1. Synthesis and characterization

$(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ has been synthesized by using mild hydrothermal conditions under autogeneous pressure. The reagents $Ga_2(SO_4)_3$ (1.558 mmol), $Cr(NO_3)_3 \cdot 9H_2O$ (0.062 mmol), H_3PO_3 (15.0 mmol), HF (50 mmol) and ethylenediamine (23.0 mmol) up to pH 2.0 were solved in a mixture of 27 mL water:ethanol (1.7:1). This reaction mixture was stirred up to homogeneity and sealed in a PTFE-lined stainless steel pressure vessel (fill factor 75%). After 5 days of reaction at 170°C slight green single crystals appeared, the yield was of 85%. They were isolated by filtration, washed with water and acetone and dried over P_2O_5 for 2 h.

The percentage of the elements in the $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ product was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and C,H,N elemental analysis. Fluorine content was determined using a selective electrode. Found: Ga, 25.2; Cr, 0.37; P, 11.3; C, 8.7; N, 10.2; H, 3.9; F, 21.0. $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ requires Ga, 25.5; Cr, 0.39; P, 11.5; C, 9.0; N, 10.4; H, 4.1; F, 21.2. The density, measured by flotation in a mixture of $CHCl_3/CHBr_3$, was of 2.31(1) g cm^{-3}.

The thermogravimetric analysis was carried out under air atmosphere in an SDC 2960 Simultaneous DSC-TGA TA Instrument. A crucible containing ca. 20 mg of sample was heated at 5°C min^{-1} in the temperature range 30–800°C. The decomposition curve reveals, between 250°C and 670°C, a continuous loss mass of approximately 57% with superimposed steps. This loss can be attributed to the calcination of the ethylenediammonium cation, the elimination of the fluorine anions, and chemical transformations of the inorganic residue. At 800°C an amorphous product that cannot be identified by X-ray diffraction was obtained.

2.2. Crystal structure determination

A prismatic single crystal of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ with dimensions $0.15 \times 0.15 \times 0.2\,mm^3$ was carefully selected under a polarizing microscope and mounted on a glass fiber. The diffraction data were collected at room temperature on an Oxford Diffraction XCALIBUR automated diffractometer using graphite-monochromated MoK_α radiation. Details of crystal data, intensity collection and some features of the structure refinement are reported in Table 1.

About 8003 reflections were measured in the range $3.57° \leqslant \theta \leqslant 31.61°$. A total of 2425 were independent [$Rint. = 0.0197$] and 2414 observed applying the criterion $I > 2\sigma(I)$. Corrections for Lorentz and polarization effects were done and also for absorption with the CRYSALIS program [13]. The structure was solved by direct methods (SHELXS 97 program) [14] and refined by full-matrix least-squares based on F^2, using the SHELXL 97 computer program [15]. The scattering factors were taken from Ref. [16]. The atomic coordinates and the temperature factors of the gallium and chromium cations were refined together, and their occupancy factors were fixed to the values obtained from the chemical analysis of 0.98 and 0.02 for every metal, respectively. All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms of the phosphite groups and the ethylenediammonium cations were obtained from the Fourier maps.

Table 1
Crystallographic data and details of the crystal structure refinement for the $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ compound

Chemical formula	$(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$
Formula weight (g mol^{-1})	268.38
a (Å)	12.9417(7)
b (Å)	9.4027(6)
c (Å)	6.3502(4)
V (Å^3)	772.74(8)
Z	4
Space group	$P2_12_12_1$ (no. 19)
T (°C)	293(2)
Radiation, λ (Mo$K\alpha$) (Å)	0.71073
$\rho_{obsd.}$, $\rho_{calcd.}$ (g cm^{-3})	2.31(1), 2.307
μ (Mo$K\alpha$) (mm^{-1})	3.743
Data/parameters	2425/110
$R(I > 2\sigma(I))$	$R1 = 0.021$ w$R2 = 0.050$
R (all data)	$R1 = 0.022$ w$R2 = 0.050$
GOF	1.143

$R1 = [\sum(|F_o| - |F_c|)]/\sum|F_o|$; $wR2 = \left[\sum[w(|F_o|^2 - |F_c|^2)^2\right]/\sum[w(|F_o|^2)^2]^{1/2}$; $w = 1/[\sigma^2|F_o|^2 + (xp)^2 + yp]$ where $p = [|F_o|^2 + 2|F_c|^2]/3$; $x = 0.0238$, $y = 0.3614$.

The existence of ethylediammonium cations around the chains destroys the inversion center in the crystal structure of this phase. The final R factors are $R1 = 0.022$ and $\mathrm{w}R2 = 0.050$ (all data). In the final difference synthesis, maximum and minimum peaks of 0.447, $-0.483\,\mathrm{e\,\AA^{-3}}$ were found. The CCDC depository number is 205960. A simulation based on the $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ single-crystal structure was in excellent agreement with the X-ray powder data, indicating the presence of a pure phase with high crystallinity. The drawings of the crystal structure were performed using ATOMS program [17]. Atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent temperature factors ($\mathrm{\AA}^2 \times 10^3$) for $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ (e.s.d. in parentheses)

Atom	*x*	*y*	*z*	Ueq.
Ga	1930(1)	8245(1)	1605(1)	13(1)
Cr	1930(1)	8245(1)	1605(1)	13(1)
P	2551(1)	8385(1)	6613(1)	15(1)
O(1)	1874(1)	8195(2)	4683(2)	23(1)
O(2)	1799(1)	10290(1)	1631(3)	22(1)
O(3)	1878(1)	8181(2)	−1445(2)	28(1)
F(1)	3375(1)	8174(1)	1600(2)	24(1)
F(2)	1922(1)	6186(1)	1604(2)	22(1)
F(3)	452(1)	8131(1)	1685(2)	21(1)
N(1)	10125(1)	298(2)	4892(3)	21(1)
N(2)	8819(1)	−319(2)	10051(3)	23(1)
C(1)	9628(1)	−513(2)	6606(3)	24(1)
C(2)	9413(1)	438(2)	8425(3)	23(1)

$U_{eq} = (1/3)(U_{11} + U_{22} + U_{33})$.

Table 3
Selected bond distances (Å) and angles (deg.) for $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ (e.s.d. in parentheses)

Bond distances (Å)	
GaO_3F_3 *octahedron*	
Ga–F(1)	1.871(1)
Ga–F(2)	1.936(1)
Ga–F(3)	1.916(1)
Ga–O(1)	1.956(1)
Ga–O(2)	1.931(1)
Ga–O(3)	1.939(1)
HPO_3 *tetrahedron*	
P–O(1)	1.517(1)
P–O(2)$^{\mathrm{i}}$	1.503(1)
P–O(3)$^{\mathrm{ii}}$	1.521(1)
P–H(1)	1.38(3)
Ethylenediammonium cation	
N(1)–C(1)	1.476(2)
C(1)–C(2)	1.487(1)
N(2)–C(2)	1.471(2)
Hydrogen contact distances	
N(1)–H(2)···F(3)$^{\mathrm{iii}}$	2.91(1)
N(1)–H(2)···O(2)$^{\mathrm{iii}}$	3.00(1)
N(1)–H(3)···F(1)$^{\mathrm{iv}}$	2.65(1)
N(1)–H(4)···F(3)$^{\mathrm{v}}$	2.94(1)
N(1)–H(4)···F(2)$^{\mathrm{v}}$	2.93(1)
N(2)–H(5)···F(2)$^{\mathrm{vi}}$	2.73(1)
N(2)–H(6)···F(3)$^{\mathrm{vii}}$	2.77(1)
N(2)–H(7)···F(2)$^{\mathrm{viii}}$	2.79(1)
Bond angles (deg.)	
GaO_3F_3 *octahedron*	
F(1)–Ga–O(2)	97.11(6)
F(3)–Ga–O(2)	88.17(5)
F(1)–Ga–F(2)	88.24(5)
F(3)–Ga–F(2)	86.48(5)
F(1)–Ga–O(3)	91.83(7)
F(3)–Ga–O(3)	89.45(6)
O(2)–Ga–O(3)	92.07(8)
F(2)–Ga–O(3)	88.21(7)
F(1)–Ga–O(1)	92.15(6)
F(3)–Ga–O(1)	86.29(6)
O(2)–Ga–O(1)	90.71(8)
F(2)–Ga–O(1)	88.62(7)
F(1)–Ga–F(3)	174.53(5)
O(2)–Ga–F(2)	174.63(5)
O(3)–Ga–O(1)	174.83(6)
HPO_3 *tetrahedron*	
O(2)$^{\mathrm{i}}$–P–O(1)	115.2(1)
O(2)$^{\mathrm{i}}$–P–O(3)$^{\mathrm{ii}}$	114.72(9)
O(1)–P–O(3)$^{\mathrm{ii}}$	108.05(8)
O(1)–P–H(1)	109.3(1)
O(2)$^{\mathrm{i}}$–P–H(1)	103.4(1)
O(3)$^{\mathrm{ii}}$–P–H(1)	105.5(1)
Ethylenediammonium cation	
N(1)–C(1)–C(2)	110.10(9)
N(2)–C(2)–C(1)	110.63(9)
Interpolyhedral bond angles	
P–O(1)–Ga	141.5(1)
P$^{\mathrm{x}}$–O(3)–Ga	141.8(1)
P$^{\mathrm{ix}}$–O(2)–Ga	140.92(9)

Symmetry codes: i = $-x+1/2$, $-y+2$, $z+1/2$; ii = x, y, $z+1$; iii = $x+1$, $y-1$, z; iv = $-x+3/2$, $-y+1$, $z+1/2$; v = $-x+1$, $y-1/2$, $-z+1/2$; vi = $-x+1$, $y-1/2$, $-z+3/2$; vii = $x+1$, $y-1$, $z+1$; viii = $x+1/2$, $-y+1/2$, $-z+1$; ix = $-x+1/2$, $-y+2$; $z-1/2$, x = x, y, $z-1$.

2.3. Physical measurements

The IR spectrum (KBr pellet) was obtained with a Mattson Satellite FTIR spectrophotometer in the 400–4000 cm^{-1} range. The Raman spectrum was recorded in the 200–3000 cm^{-1} range, with a Nicolet 950FT spectrophotometer equipped with a neodymium laser emitting at 1064 nm. Diffuse reflectance spectrum was registered at room temperature on a Cary 2415 spectrometer in the 210–2000 nm range. A Bruker ESP 300 spectrometer, operating at X- and Q-bands, was used to record the ESR polycrystalline spectra at room temperature and 4.2 K. The temperature was stabilized by an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter and the frequency inside the cavity was determined using a

Hewlett-Packard 5352B microwave frequency counter. The simulation of the ESR spectra was carried out with the WINEPR-SimFonia program, version 1.25, Bruker Analytische Messtechnik GmbH.

3. Results and discussion

3.1. Description of the structure

The crystal structure of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ consists of $[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]^{2-}$ anionic chains running along the [001] direction. The ethylenediammonium cations are displayed in the cavities of the structure delimited by three different chains (Fig. 1a). The organic cations establish both hydrogen bonds and ionic interactions with the anionic chains.

The $[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]^{2-}$ chains are constructed from MO_3F_3 isolated octahedra and pseudopyramidal $(HPO_3)^{2-}$ phosphite oxoanions (see Fig. 1b). The MO_3F_3 octahedra share the *trans*-O(1),O(3) atoms with the HPO_3 tetrahedra, forming an infinite chain of alternating octahedra and tetrahedra. Each octahedron also shares the O(2) atom from another HPO_3 tetrahedron belonging to a parallel identical chain, giving rise to infinite zig-zag chains as shown in Fig. 1b. A remarkable structural feature of this compound is the absence of covalent intrachain –*M*–O, F–*M*– interactions.

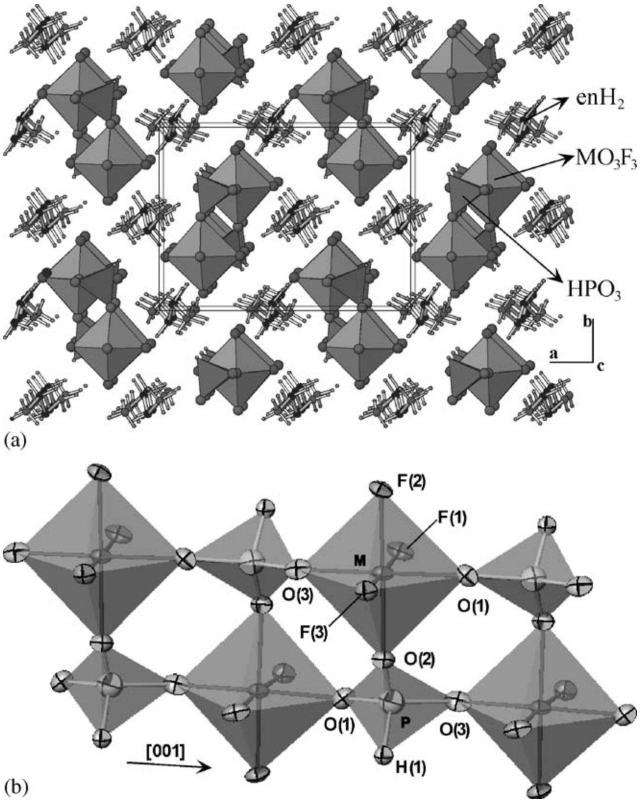

Fig. 1. Polyhedral view of: (a) the crystal structure of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$, and (b) a zig-zag chain along the *c*-axis.

Table 4
Unit-cell parameters for the $(C_2H_{10}N_2)[M(HPO_3)F_3]$ (M = V, Cr and Ga:2%Cr) compounds

Compound	Vanadium	Chromium	Gallium: 2%Cr
a (Å)	12.809(2)	12.801(2)	12.9417(7)
b (Å)	9.518(1)	9.338(1)	9.4027(6)
c (Å)	6.440(1)	6.508(1)	6.3502(4)
Z	4	4	4
V (Å)^3	785.2(2)	777.9(2)	772.74(8)
Ionic radius (Å)	0.640	0.615	0.620

The effective ionic radii were taken from Ref. [18].

The metallic cations of the MO_3F_3 octahedra in the title compound are bonded to the O(1), O(2) and O(3) oxygen atoms belonging to the HPO_3 anion, and to the F(1), F(2) and F(3) fluorine ions. The *M*–O, F bonds are in the range 1.871(1)–1.956(1) Å, whereas the *cis*-O, F–*M*–O, F angles range from 86.48(5) to 97.11(6)°, the *trans*-angles being approximately of 175°. The M^{III}–M^{III} intrachain bond distances along the *c*-axis and the zig-zag pathway are of 4.811(1) and 6.350(1) Å, respectively. The mean P–O bond distance is 1.514(8) Å. The O–P–O and H–P–O angles show values usually found in tetrahedral coordination. In this compound the ethylenediammonium cations establish strong hydrogen bonds with the oxygen atoms from the phosphite anion and the fluorine ions (see Table 3).

The title compound is isostructural with the $(C_2H_{10}N_2)[M(HPO_3)F_3]$ [M(III) = V and Cr] family of compounds [11f,12]. The variation of the unit-cell parameter of this family of compounds with different ionic radii of the metallic ions is shown in Table 4. It is to note that only the *b*-parameter of the unit-cell in this series of compounds shows a linear increase with increasing the ionic radii from the chromium(III) to vanadium(III) ions [18].

3.2. Infrared, Raman and UV–vis spectroscopies

The Infrared and Raman spectra of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ exhibit bands corresponding to the vibrations of the ethylenediammonium cation and the $(HPO_3)^{2-}$ phosphite oxoanion (Table 5). These results are similar to those found for other related phosphite compounds [11,12,19].

The diffuse reflectance spectrum of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ shows the spin allowed transitions from the fundamental state $^4A_{2g}(^4F)$ of the Cr(III) cations in octahedral geometry to the excited levels $^4T_{2g}(^4F)$, $^4T_{1g}(^4F)$ and $^4T_{1g}(^4P)$ at the frequencies 15160, 22120 and 33660 cm^{-1}. Furthermore, the spin forbidden

Table 5
Selected bands (values in cm^{-1}) from the IR and Raman spectra for the $(C_2H_{10}N_2)[Cr_{0.98}Ga_{0.02}(HPO_3)F_3]$ compound

Assignment	IR	Raman
ν (–NH$_3$)$^+$	3165 (m)	3020 (m)
ν (–CH$_2$–)	3040 (m)	2980 (m)
ν (HP)	2385 (m)	2385 (s)
δ (–NH$_3$)$^+$	1625, 1540 (m)	1620 (w)
δ (–CH$_2$–)	1480, 1455 (w)	1460, 1350 (w)
ν_{as} (PO$_3$)	1110 (s)	1100 (m)
δ (HP)	1025 (m)	1030 (m)
ν_s (PO$_3$)	1045 (s)	1065,1045 (m)
δ_s (PO$_3$)	600 (m)	585 (w)
δ_{as} (PO$_3$)	510 (w)	525 (w)

ν = stretching, δ = deformation, s = symmetric, as = asymmetric, s = strong, m = medium, w = weak.

transitions $^4A_{2g}(^4F) \rightarrow {}^2E_g(^2G)$, $^2T_{1g}(^2G)$ were observed as shoulders on the first band at 14,720 and 15,420 cm^{-1}. The Dq and Racah parameters (B and C) were calculated by fitting the experimental frequencies to the energy expressions for a d^3 ion [20a,b]. The values obtained were $Dq = 1375\,\mathrm{cm}^{-1}$, $B = 780\,\mathrm{cm}^{-1}$ and $C = 3420\,\mathrm{cm}^{-1}$. These results are similar to those found for the isostructural $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ phase [11f,12] ($Dq = 1535$, $B = 720$ and $C = 3280\,\mathrm{cm}^{-1}$) being in good agreement with those observed for the Cr(III) ion in slightly distorted octahedral environment [20c,d]. The value obtained for the B-parameter is approximately 85% of that corresponding to the Cr^{3+} free ion (918 cm^{-1}) [20a,e]. This value is higher than that obtained for the $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ phase (75%) [11f,12] indicating a less covalence character in the Cr–O, F chemical bonds probably due to the presence of Ga(III) ions in the title compound. Notwithstanding, this result should be considered with caution because the signals obtained from the reflectance diffuse spectrum for the title compound are poorer solved than in the undoped Cr(III) phase owing to the small amount of Cr(III) cations present in the compound.

3.3. Electron spin resonance spectroscopy

The powdered ESR spectra of the diluted Cr(III) cation in the $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ phase have been recorded at X- and Q-bands at ambient temperature (Fig. 2). The ESR spectra of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ performed at X-band at different temperatures are shown in Fig. 3 for comparison. As can be seen in this figure the spectra of this phase show unresolved isotropic signals centered at $g = 1.97$ in which the intensity increases with decreasing temperature.

In the case of the doped phase, the polycrystalline ESR spectra of the Cr(III) ions are formed by the whole signals corresponding to the three x, y, z directions of the applied magnetic field and some intermediate orientation ($\delta_{x,y,z}$) [21]. The splitting of the spin levels for the $^4A_{2g}(^4F)$ ground state of Cr(III) in axial symmetry, under a H_z external magnetic field applied along the z-axis, allowed us the observation of the $\Delta M_s = \pm 1$ spin allowed transitions as three signals at different values of the magnetic field.

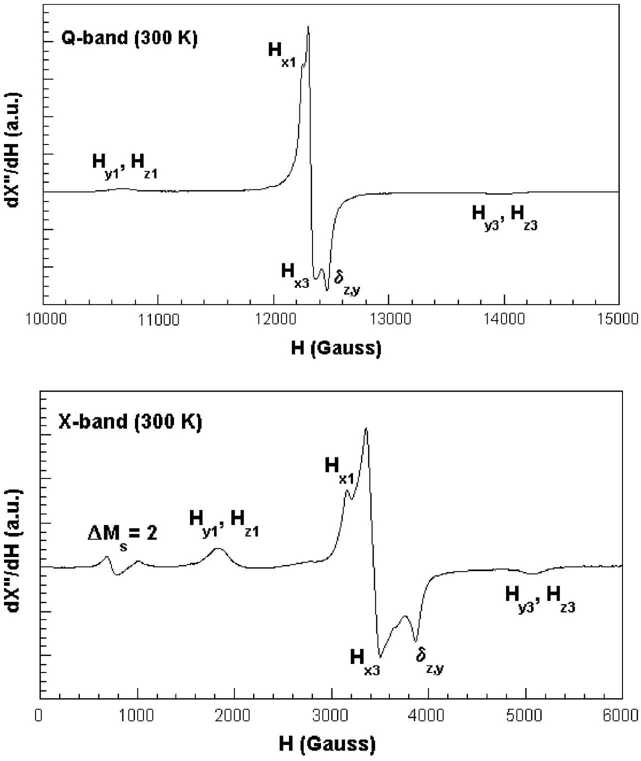

Fig. 2. ESR spectra of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ at X- and Q-bands, performed at room temperature.

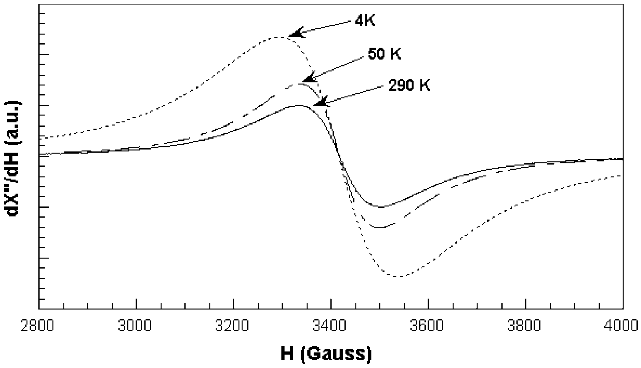

Fig. 3. ESR spectra of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ at X-band, performed at different temperatures.

The ESR spectra at X-band performed at room temperature and 4.2 K (see Fig. 4) of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ show at 800 G the forbidden $\Delta M_s = \pm 2$. This signal is not observed in the spectrum recorded at Q-band at 300 K. The rest of signals present

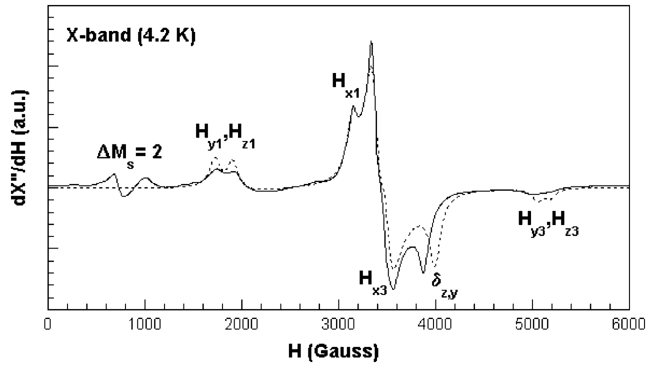

Fig. 4. Simulation (dashed line) of the ESR spectrum of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ performed at X-band at 4.2 K.

in the ESR spectra performed at X and Q-bands corresponds to the $\Delta M_s = \pm 1$ transitions. The signals due to the H_{y1}, H_{z1} at 1735, 1920; H_{x1}, H_{x3} at 3165, 3565 and H_{y3}, H_{z3} at 5000, 5165 G magnetic fields appear as three independent groups in the spectrum performed at X-band. These groups appear at 10600, 10775; 12265, 12375 and 13930, 14080 G in the spectrum recorded at Q-band. The signal at 3885 and 12470 G observed in the X- and Q-bands; respectively, can be attributed to intermediate orientations (δ_{zy}).

The ESR spin Hamiltonian parameters for $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ were estimated by comparison of the experimental spectrum at 4.2 K performed at X-band (Fig. 4) with those obtained by the computer simulation program WINEPR-SimFonia, working at the second order of the perturbation theory. The parameters were then optimized by the trial and error method. The values obtained for the g-tensor are, $g_x = 1.98$, $g_y = 1.99$ and $g_z = 1.90$. The axial and rhombic distortion parameters are $D = 0.075$ and $E = 0.024\,\text{cm}^{-1}$, respectively.

These values are in the range habitually observed for the Cr(III) cation in a slightly distorted octahedral environment [21b].

4. Concluding remarks

The hydrothermal synthesis under autogeneous pressure allowed us to obtain the $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ compound. This phase is a new member of the $(C_2H_{10}N_2)[M(HPO_3)F_3]$ [M(III) = V and Cr] family. The structure of these isostructural compounds is formed by $[M(HPO_3)F_3]^{2-}$ anionic chains. The ethylenediammonium cations compensate the charge of the chains and establish hydrogen bonds with the inorganic skeleton. The IR and Raman spectra of $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ confirm the presence of the phosphite anions. The electronic spectroscopy in the visible region is in agreement with the presence of the chromium(III) cations in slightly distorted octahedral geometry. From the ESR polycrystalline spectra, the values of the axial and rhombic distortion parameters and the g-values for the octahedrically coordinated Cr(III) cations were calculated.

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