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Tris(2-ethylamino)amine (*tren*) as template for the elaboration of fluorides: synthesis and crystal structures of $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$, $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ and $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$

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Abstract

Using tris(2-ethylamino)amine (*tren*) as a template, three new fluorides are obtained by solvothermal synthesis: $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**), $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**) and $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$ (**III**). The structure determinations are performed by single crystal technique. The structure of **I** consists of infinite spiral-like $[Zr_3F_{16}(H_2O)]^{4-}$ chains connected by tetraprotonated $[\textit{tren}H_4]^{4+}$ cations which possess a plane configuration. In **II**, isolated $[ZrF_6]$ octahedra or $[Zr_2F_{12}]$ dimers are linked to organic cations by a tridimensional hydrogen bond network. In **III**, $[TaF_7]^{2-}$ monocapped trigonal prisms and "isolated" fluoride ions are connected by hydrogen bonds to template moieties. In **II** and **III**, every organic moiety is triprotonated $[\textit{tren}H_3]^{3+}$ with a "spider" configuration. In the tantalum phase, the hydrogen bond network leads to the formation of a layered structure.

Keywords: Zirconium; Tantalum; Fluoride; Crystal structure

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1. Introduction

Zirconium fluorides have well known properties which lead to various applications; they are candidates as materials for non-linear optic (NLO), textile flame retardants or tooth enamel protectants [1]. One current area in the chemistry of fluorozirconates concerns the synthesis of templated compounds [2–4]. Numerous low dimensionality phases were obtained: $[C_2N_2H_{10}]\cdot[Zr_2F_{10}]$ (2D), $[C_4N_2H_{12}]\cdot[ZrF_6]$ (1D) [5] and $[CN_4H_8]_4\cdot[Zr_4F_{24}]\cdot 4H_2O$ (0D, tetramer) [6]. On the other hand, tantalum cation is known to build large polyanions such as $[Ta_4F_{12}O_6]^{4-}$ [7]. It is thought that high cation charge and high coordination favor the formation of large polyanions and their condensation to lead to tridimensionnal inorganic framework. Up to now, only one 3D inorganic network was evidenced in $[H_3O]\cdot[CN_3H_6]_5\cdot[ZrF_5]_6$ [8]. Consequently, our current work is devoted to the synthesis of organic–inorganic hybrid fluorides with highly charged cations.

Solvothermal method at low temperature ($T < 200\,^{\circ}C$) and low pressure ($P < 20$ bars) has proved to be effective for the synthesis of hybrid fluorides [9]. Moreover, a variation of the ratio between the inorganic (oxides or fluorides) and organic parts leads to the formation of structures with variable inorganic dimensionality [10].

Well known organic molecule, tris(2-ethylamino) amine (*tren*), was widely used in coordination chemistry. In spite of its expanded bridging ability due to the presence of three terminal amino-groups, only few

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experiments were carried out with *tren* as a structure-directing agent [11,12]. This paper describes the synthesis and the structure of three new *tren* templated fluorides: $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**), $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**) and $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$ (**III**).

2. Experimental section

$[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**), $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**) and $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$ (**III**) are obtained by solvothermal synthesis under autogenous pressure. **I** is obtained from a mixture of ZrF_4 (Alfa), HF (40%, Riedel-de Haën), *tren* (96%, Aldrich) and ethanol (96%) in the molar ratio 1:5:1:≈160, **II** from ZrF_4, *tren* and ethanol in the molar ratio 1:1:≈150 and **III** from Ta_2O_5 (Alfa), HF, *tren* and ethanol in the molar ratio 1:10:1: ≈150. Microwave heating ($T = 190\,^\circ C$, 1 h) was used for testing and for optimization of the starting mixture compositions. Selected mixtures were loaded in Teflon-lined Paar autoclaves (20 mL) and were heated at 200 °C during 96 h for **I** and at 170 °C during 3 days for **II** and **III**. For **I**, a pure powder was obtained with colorless crystals. Density was measured by flotation method in chloroform-bromoform mixture. The observed value $\rho = 2.57(5)\,g\,cm^{-3}$ is very close to the theoretical value $\rho = 2.566\,g\,cm^{-3}$. Elemental analysis led to a good agreement between experimental and calculated values (weight %): Zr, 36.4; F, 40.6; N, 7.0; C, 9.0 (exp.) and Zr, 36.7; F, 40.8; N, 7.5; C, 9.7 (calc.). For **II**, very small crystals were found among ZrF_4 powder. Several attempts to obtain larger crystals were unsuccessful. For **III**, homogeneous powder was synthesized with small crystals. The fluorine content was not estimated for **II** and **III**. Consequently, a small F/OH substitution cannot be excluded.

Thermal analyses were performed with TGA-TDA coupled analyzer TA Instruments SDT 2960 (heating rate 10 K/min, argon flow). X-ray patterns were collected on a Siemens D500 diffractometer. Thermogram of **I** shows a weight loss of 5.12% at 280 °C. This value corresponds to the departure of one H_2O and one HF molecules per formula unit. After thermal decomposition at 600 °C, crystalline ZrF_4 with a small amount of $ZrF_{3.3}O_{0.33}$ is found from the X-ray pattern. **III** undergoes a continuous weight loss in the range 200–500 °C. The X-ray analysis of the residual powder shows the presence of Ta_2O_5.

Single-crystals were selected by using an optical microscope. X-ray data were collected on a Siemens AED2 four circle diffractometer at room temperature using $\omega/2\theta$ scans. The intensities were corrected for Lorentz and polarization effects. Cell constants were determined from randomly found reflections in the 10–20° 2θ range. Orientation matrixes were refined from 32 centered reflections ranging from 27° to 32° in 2θ. The lattice parameters were refined using double-scan technique. Scattering factors and anomalous dispersion corrections for all atoms were taken from “International Tables for X-ray Crystallography” [13]. Absorption corrections were performed using SHELX-76 software

Table 1
Details of X-ray experiments and crystallographic data for **I, II** and **III** [a]

	I	**II**	**III**
Empirical formula	$Zr_3F_{16}N_4C_6H_{24}O$	$Zr_3F_{18}N_8C_{12}H_{42}$	$TaF_8N_4C_6H_{21}$
Formula weight ($g\,mol^{-1}$)	745.93	914.16	482.19
System	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$Pnma$	$P2_1/c$
a (Å)	9.2167(5)	12.326(2)	10.541(4)
b (Å)	13.983(1)	9.402(1)	8.296(1)
c (Å)	14.9809(6)	25.731(4)	15.844(3)
β (°)			108.51(4)
V (Å^3)	1930.7(2)	2982(1)	1313.9(3)
Z	4	4	4
F(0 0 0)	1440	1808	900
μ (mm^{-1})	1.75	1.16	8.46
$\rho_{calc.}$ ($g\,cm^{-3}$)	2.566	2.036	2.438
Diffractometer/Radiation	AED2 STOE/Mo K_α		
2θmax	70	50	60
Reflections unique/used	4670/4264	2795/1150	3827/2832
Refined parameters	282	160	177
Goodness of fit	1.149	1.074	1.046
R/R_w	0.038/0.134	0.085/0.276	0.052/0.142

[a] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 172932 (**I**), 172933 (**II**) and 172934 (**III**). 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).

[14] for **I** and **III**. Owing the very small size of the single-crystal, a low angular 2θ range (3–50°) was explored and no absorption correction was applied for **II**. Structure solutions were found by Patterson method and expanded using Fourier techniques (SHELXS-86 and SHELXL-97 programs [15,16]). For **I** and **III**, the non-hydrogen atom displacement parameters were refined anisotropically. For **II**, as a reason of the very small size of the single-crystal, the number of reflections (with $I > 2.5\sigma(I)$) is small. Consequently, B_{eq} of fluorine atoms are found abnormally high; isotropic displacement parameters were applied for N and C atoms in order to reduce the number of refined parameters. In all structures, hydrogen atoms were localized from geometrical constraint conditions, which imply equal distances and angles to the central atom (AFIX and DFIX options) and were refined with a common isotropic thermal parameter. To achieve the charge balance, *tren* molecules were tetraprotonated in **I** and triprotonated in **II** and **III**, in agreement with the results of difference Fourier maps and with the lengths of N(1)–F distances (2.74 Å in **I**, 3.20 Å in **II** and **III**). Structure projections were drawn with the DIAMOND program [17]. Crystallographic data and experimental details are listed in Table 1. Atomic positions and main distances are gathered in Tables 2–7.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**)

Atom	*x*	*y*	*z*	B_{eq}
Zr1	0.9871(5)	0.80957(3)	0.17724(3)	1.169(9)
Zr2	1.00171(5)	0.99598(3)	0.00589(3)	1.067(8)
Zr3	0.26376(5)	0.09837(3)	0.84497(3)	1.094(8)
F1	0.7999(4)	1.0538(4)	0.9932(3)	2.69(7)
F2	0.8822(4)	0.9356(3)	0.1149(3)	1.88(5)
F3	0.0489(5)	0.0987(3)	0.0933(3)	2.58(7)
F4	0.0950(4)	0.8706(3)	0.0532(3)	2.20(6)
F5	0.2173(4)	0.0093(3)	0.9681(3)	1.98(6)
F6	0.0232(4)	0.0879(3)	0.8950(2)	1.73(5)
F7	0.1155(5)	0.9257(3)	0.2170(3)	2.46(7)
F8	0.8477(5)	0.7517(3)	0.0915(3)	2.17(6)
F9	0.0931(4)	0.7832(2)	0.3009(2)	1.60(5)
F10	0.2485(4)	0.1979(3)	0.9422(2)	2.04(5)
F11	0.1366(5)	0.1705(3)	0.7590(3)	2.30(6)
F12	0.2017(4)	0.9693(3)	0.7985(3)	1.89(5)
F13	0.8241(4)	0.8463(3)	0.2623(3)	1.79(5)
F14	0.1406(4)	0.7204(3)	0.1341(3)	2.01(6)
F15	0.4546(4)	0.0512(3)	0.8875(3)	2.24(6)
F16	0.9288(4)	0.9036(3)	0.9129(3)	2.34(7)
O_W	0.9154(5)	0.6603(4)	0.2368(3)	1.92(6)
N1	0.5748(5)	0.0345(3)	0.1114(3)	1.36(6)
C1	0.4658(6)	0.9586(4)	0.0854(4)	1.68(7)
C2	0.5306(7)	0.8594(5)	0.0780(5)	2.3(1)
N2	0.4112(7)	0.7898(4)	0.0792(4)	2.25(8)
C3	0.5254(6)	0.1328(4)	0.0882(4)	1.50(7)
C4	0.3941(7)	0.1630(5)	0.1427(4)	2.09(9)
N3	0.3358(6)	0.2555(4)	0.1056(4)	1.82(7)
C5	0.6162(6)	0.0216(4)	0.2067(4)	1.67(7)
C6	0.7415(6)	0.0864(4)	0.2325(4)	1.74(7)
N4	0.8145(6)	0.0440(4)	0.3121(4)	1.78(7)

3. Results and discussion

In $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**), two crystallographically independent zirconium atoms Zr(1) and Zr(3) possess a eight-fold coordination and are found in a distorted square antiprism. Zr(2)F_7 polyhedron is close to a distorted pentagonal bipyramid. The coordination sphere of Zr(1) atom includes seven fluorine atoms and one oxygen atom from a water molecule whereas Zr(2) and Zr(3) coordination spheres involve only fluorine atoms. Zr–F distances lie in the range 2.063(5)–2.342(6) Å for bridging and 1.979(7)–2.034(7) Å for non-bridging fluorine atoms. Significant difference in Zr–O distance value (2.375(8) Å) additionally suggests the presence of water molecule. [Zr(1)$F_7(H_2O)$], [Zr(3)F_8] and [Zr(2)F_7] polyhedra share

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**)

Atom	*X*	*y*	*z*	B_{eq}[a]
Zr(1)	0.1006(3)	3/4	−0.1547(1)	3.05(7)
Zr(2)	0.0900(2)	3/4	−0.6921(1)	2.59(7)
Zr(3)	−0.0704(2)	3/4	−0.5542(1)	2.83(7)
F(1)	0.080(2)	3/4	−0.52557(8)	5.9(5)
F(2)	−0.130(2)	3/4	−0.4830(8)	4.9(5)
F(3)	0.217(2)	3/4	−0.102(1)	7.4(7)
F(4)	−0.059(2)	3/4	−0.722(1)	13(1)
F(5)	0.007(2)	3/4	−0.2156(9)	10(1)
F(6)	0.222(2)	3/4	−0.2082(9)	6.0(6)
F(7)	0.195(2)	3/4	−0.6316(9)	8.4(8)
F(8)	−0.216(2)	3/4	−0.5850(9)	9.2(8)
F(9)	0.240(3)	3/4	−0.725(1)	10.1(9)
F(10)	−0.007(2)	3/4	−0.626(1)	18(2)
F(11)	0.094(5)	3/4	−0.769(1)	16(2)
F(12)	−0.010(2)	3/4	−0.103(1)	17(2)
F(13)	−0.065(2)	0.544(2)	−0.5533(8)	12.2(8)
F(14)	0.093(3)	0.545(2)	−0.6932(9)	12.7(8)
F(15)	0.106(3)	0.546(2)	−0.1532(9)	15(1)
N(1)	0.122(2)	1/4	−0.044(1)	4.2(2)[a]
C(1)	0.011(4)	1/4	−0.063(2)	8.2(4)[a]
C(2)	−0.008(4)	1/4	−0.118(2)	8.2(4)[a]
N(2)	0.068(2)	1/4	−0.154(1)	4.2(2)[a]
C(3)	0.134(3)	0.373(4)	−0.012(1)	8.2(4)[a]
C(4)	0.210(3)	0.479(4)	−0.015(1)	8.2(4)[a]
N(3)	0.293(1)	0.478(2)	−0.0553(8)	4.2(2)[a]
N(4)	−0.171(2)	1/4	−0.656(1)	4.2(2)[a]
C(5)	−0.090(4)	1/4	−0.621(2)	8.2(4)[a]
C(6)	0.017(4)	1/4	−0.632(2)	8.2(4)[a]
N(5)	0.063(2)	1/4	−0.681(1)	4.2(2)[a]
C(7)	−0.240(3)	0.127(4)	−0.652(1)	8.2(4)[a]
C(8)	−0.253(3)	0.011(4)	−0.684(1)	8.2(4)[a]
N(6)	−0.191(1)	−0.002(2)	−0.7285(7)	4.2(2)[a]

[a] B_{iso}.

edges and build infinite spiral-like $[Zr_3F_{16}(H_2O)]_n$ chains along *c*-axis. Two successive trimers [Zr(1)–(F(7),F(9))–Zr(3)–(F(5),F(6))–Zr(2)–(F(2),F(4))], symmetrically connected by 2_1 axis along *c*, are almost perpendicular (Fig. 1). Similar Zr_3F_{17} chains, built up from different coordination polyhedra, were found recently in $LiCs_4Zr_3F_{17}(HF)$ [18]. All aminogroups in *tren* are protonated and the resulting organic $[tren\text{H}_4]^{4+}$ cation adopts a plane configuration (Fig. 2, left and Table 8). One template cation is linked to four inorganic chains by the system of N-H…F hydrogen bonds with H…F distances in the range 1.83–2.33 Å (Fig. 3). The central nitrogen atom N(1) is hydrogen bonded with F(1) ($d_{\text{H1A}\cdots\text{F(1)}} = 1.89$ Å). O–H…F hydrogen bonds complete the tridimensional hydrogen bond network.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$ (**III**)

Atom	*x*	*y*	*z*	B_{eq}
Ta	0.85883(3)	0.2278(4)	0.91136(2)	1.53(1)
F(1)	0.9146(8)	0.0168(8)	0.8854(6)	4.0(2)
F(2)	0.9051(7)	0.298(1)	0.0339(4)	3.5(1)
F(3)	0.9056(7)	0.4090(7)	0.8502(4)	2.8(1)
F(4)	0.7434(8)	0.0851(9)	0.9508(5)	3.4(1)
F(5)	0.7448(7)	0.1823(9)	0.7890(4)	3.1(1)
F(6)	0.7127(6)	0.3803(8)	0.9025(5)	2.9(1)
F(7)	0.0562(6)	0.2281(9)	0.9530(5)	3.1(1)
F(8)	0.0340(6)	0.2335(7)	0.7348(4)	2.07(9)
N(1)	0.64944(8)	−0.221(1)	0.1704(5)	2.0(1)
C(1)	0.5879(9)	−0.188(1)	0.2396(6)	2.2(2)
C(2)	0.660(1)	−0.271(1)	0.3265(7)	2.5(2)
N(2)	0.7985(8)	−0.2126(9)	0.3656(5)	2.0(1)
C(3)	0.62373(1)	−0.091(1)	0.1045(6)	2.1(2)
C(4)	0.708(1)	0.057(1)	0.1368(7)	2.4(2)
N(3)	0.85205(8)	0.022(1)	0.1542(5)	2.1(1)
C(5)	0.610(1)	−0.380(1)	0.1286(7)	2.1(1)
C(6)	0.716(1)	-0.452(1)	0.0938(6)	2.1(2)
N(4)	0.8403(9)	−0.48634(1)	0.1678(6)	2.2(1)

$[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**) contains three crystallographically independent zirconium atoms. Zr(1) atoms possess a distorted octahedral coordination with Zr–F distances lying in the range 1.90(2)–2.03(2) Å (Table 6). The resulting $[ZrF_6]^{3-}$ anions are isolated. Zr(2) and Zr(3) atoms are respectively seven- and six-fold coordinated. The $Zr(2)F_7$ and $Zr(3)F_6$ polyhedra are linked by a common F vertex and form $[Zr_2F_{12}]^{4-}$ dimers (Fig. 4). Zr(3)–F distances are similar to Zr(1)–F distances: 1.93(2)–2.04(2) Å for non-bridging fluorine atoms and 2.02–2.07(2) Å for bridging atoms. Contrary to Zr(1) and Zr(2) arrangement, Zr(3) environment corresponds better to octahedral geometry. Zr(2) atom is found in a distorted pentagonal bipyramid. The structure of **II** contains two types of triprotonated *tren* moieties with a "spider" conformation (Fig. 5, right). This compact shape of *tren* cations leads

Table 5
Selected distances (Å) in $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**)

Zr(1)–F8	1.989 (4)	Zr(2)–F3	1.992 (4)	Zr(3)–F15	1.984 (4)	N(1)–C(5)	1.488(7)
Zr(1)–F14	1.993 (4)	Zr(2)–F16	2.015 (4)	Zr(3)–F11	2.012 (4)	N(1)–C(3)	1.489(7)
Zr(1)–F13	2.035 (4)	Zr(2)–F1	2.037 (4)	Zr(3)–F12	2.018 (4)	N(1)–C(1)	1.513(71)
Zr(1)–F7	2.096 (4)	Zr(2)–F5	2.075 (4)	Zr(3)–F10	2.020 (4)	N(2)–C(2)	1.470(9)
Zr(1)–F9	2.126 (3)	Zr(2)–F4	2.077 (4)	Zr(3)–F9	2.218 (3)	N(3)–C(4)	1.506(8)
Zr(1)–F2	2.217 (4)	Zr(2)–F6	2.110 (3)	Zr(3)–F7	2.243 (4)	N(4)–C(6)	1.493(8)
Zr(1)–F4	2.274 (4)	Zr(2)–F2	2.143 (4)	Zr(3)–F5	2.267 (4)	C(1)–C(2)	1.514(9)
Zr(1)–O_W	2.364 (5)			Zr(3)–F6	2.345 (4)	C(3)–C(4)	1.519(8)
						C(5)–C(6)	1.518(8)

Table 6
Selected distances (Å) in $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**)

Zr(1)–F(12)	1.90(2)	Zr(2)–F(14)	1.93(2)	Zr(3)–F(13)	1.94(2)	N(1)–C(1)	1.46(3)
Zr(1)–F(15)	1.92(2)	Zr(2)–F(14)	1.93(2)	Zr(3)–F(13)	1.94(2)	N(1)–C(3)	1.46(5) × 2
Zr(1)–F(15)	1.92(2)	Zr(2)–F(11)	1.99(3)	Zr(3)–F(8)	1.96(2)	N(2)–C(2)	1.31(5)
Zr(1)–F(5)	1.95(2)	Zr(2)–F(4)	1.99(2)	Zr(3)–F(2)	1.97(2)	N(3)–C(4)	1.46(3)
Zr(1)–F(3)	1.98(2)	Zr(2)–F(7)	2.02(2)	Zr(3)–F(1)	2.00(2)	N(4)–C(5)	1.35(5)
Zr(1)–F(6)	2.03(2)	Zr(2)–F(9)	2.04(2)	Zr(3)–F(10)	2.02(2)	N(4)–C(7)	1.44(4) × 2
		Zr(2)–F(10)	2.07(2)			N(5)–C(6)	1.40(6)
						N(6)–C(8)	1.38(4)
						C(1)–C(2)	1.44(6)
						C(3)–C(4)	1.37(4)
						C(5)–C(6)	1.34(6)
						C(7)–C(8)	1.38(4)

Table 7
Selected distances (Å) in $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$ (**III**)

Ta–F(1)	1.932(7)	Ta–F(4)	1.938(7)	N(1)–C(1)	1.47(1)	N(3)–C(4)	1.49(1)
Ta–F(2)	1.935(6)	Ta–F(5)	1.966(6)	N(1)–C(3)	1.47(1)	N(4)–C(6)	1.48(1)
Ta–F(3)	1.935(6)	Ta–F(6)	1.964(6)	N(1)–C(5)	1.48(1)	C(1)–C(2)	1.51(1)
		Ta–F(7)	1.966(6)	N(2)–C(2)	1.48(1)	C(3)–C(4)	1.50(1)
						C(5)–C(6)	1.51(1)

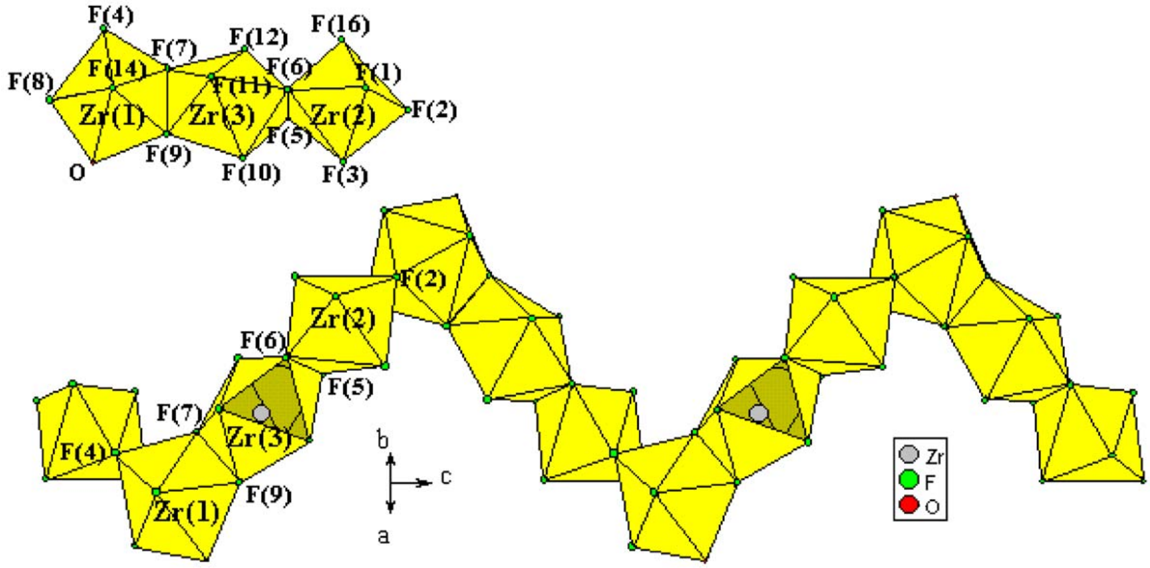

Fig. 1. Trimer of zirconium polyhedra [(Zr(1)–Zr(3)–Zr(2)] and their quasi-perpendicularly connection to form $[Zr_3F_{16}(H_2O)]^{4-}$ chain in $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**).

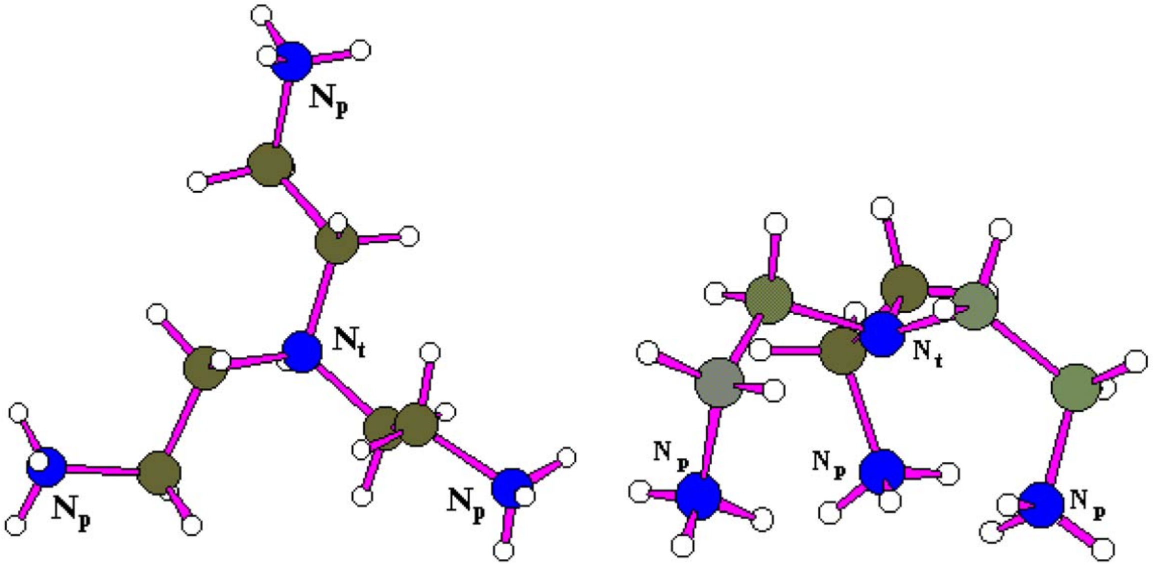

Fig. 2. Plane (left) and "spider" (right) conformations for $[tren\mathrm{H}_4]^{4+}$ (**I**) and $[tren\mathrm{H}_3]^{3+}$ (**II** and **III**) cations, respectively.

to short N_p–N_t distances between primary and tertiary amine groups (Table 8). Both independent organic moieties (central atoms N(1) and N(4)) are connected with four $[Zr_2F_{12}]$ dimers and two $[ZrF_6]$ isolated octahedra (Fig. 5). N–H…F distances lie from 1.96(2) to 2.48(2) Å.

Table 8
N–N distances (Å) in **I**, **II**, **III**

	tren cation	Conformation *tren*	N_t–N_p	N_p–N_p
I	$[\textit{tren}H_4]^{4+}$	Plane	3.73/3.77/3.80	6.15/6.22/6.56
II	$[\textit{tren}H_3]^{3+}$	"spider"	2.92/3.03 × 2	4.30/4.33 × 2
		"spider"	2.95/3.02	4.73/4.10 × 2
III	$[\textit{tren}H_3]^{3+}$	"spider"	2.99/2.99/3.01	4.01/4.07/4.23

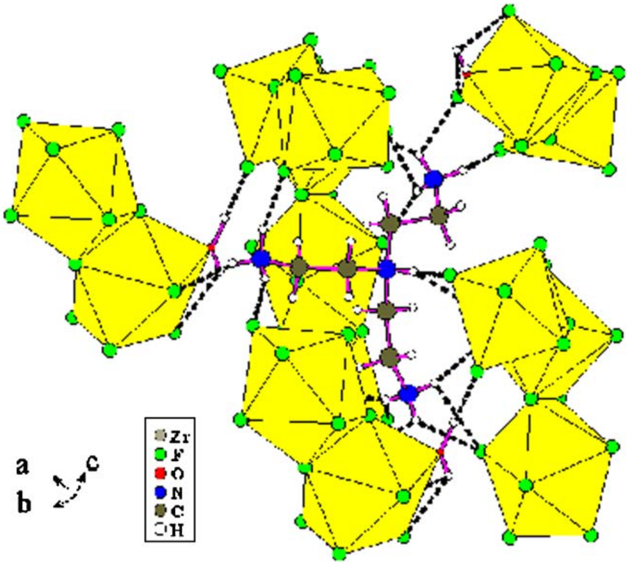

Fig. 3. Independent $[\textit{tren}H_4]^{4+}$ organic moiety linked to four $[Zr_3F_{16}(H_2O)]^{4-}$ chains by hydrogen bonds in $[(C_2H_4NH_3)_3NH]\cdot[Zr_3F_{16}(H_2O)]$ (**I**).

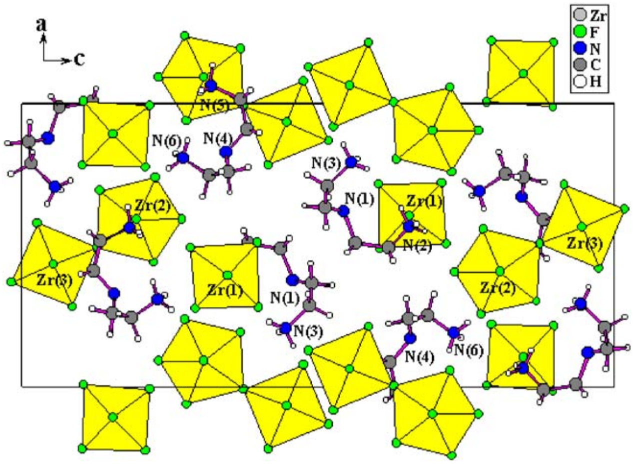

Fig. 4. Projection of $[(C_2H_4NH_3)_3N]_2\cdot[ZrF_6]\cdot[Zr_2F_{12}]$ (**II**) on the (0 1 0) plane.

In $[(C_2H_4NH_3)_3N]\cdot[TaF_7]\cdot F$ **(III),** Ta atoms are bonded to seven fluorine atoms with the formation of $[TaF_7]^{2-}$ anions (Table 7). The monocapped trigonal $[TaF_7]$ polyhedron is similar to that found in K_2TaF_7 [19]. Similarly to **II**, the *tren* molecule is triprotonated and adopts a "spider" configuration with analogous N–N distances (Table 8). Every template moiety is linked to four $[TaF_7]^{2-}$ anions (Fig. 6). In turn, the inorganic anion is connected with four organic cations. An interesting peculiarity of structure **III** is the presence of fluoride ions outside the metal coordination sphere. Similar "isolated" fluoride ions with tetrahedral coordination are found in NH_4F. Recently, a triangular coordination of such "isolated" F^- ions was observed in $[H_3N(CH_2)_6NH_3]_2\cdot M(F,OH)_6\cdot F\cdot H_2O$ (M = Al, In) [20]. In **III**, this ion, F(8), is connected with three hydrogen atoms (H(2A), H(3A) and H(4A) with distances 1.86, 1.92 and 1.82 Å, respectively) of one template moiety and with two hydrogen atoms (one short (1.95 Å) with H(3B) and one long (2.31 Å) with H(4B)) from two other moieties (Fig. 6). $[\textit{tren}H_3]^{3+}$ cations, isolated fluoride ions and $[TaF_7]^{2-}$ polyhedra build infinite (1 0 0) sheets with H…F distances in the range 2.05(1)–2.47(1) Å (Fig. 7). The shortest H…F distance between two successive layers is 2.52 Å.

4. Conclusion

Using *tren* as a template, three new compounds with 0 and 1D inorganic frameworks are synthesized. The hydrogen bond network ensures tridimensional structures in **I** and **II**, and a layered structure in **III**. In **I**, $[\textit{tren}H_4]^{4+}$ cation seems to have a dual role. On one hand, the large positive charge of the template moiety promotes the formation of strongly charged $[Zr_3F_{16}(H_2O)]^{4-}$ infinite inorganic polyanions. On the other hand, the distances between terminal aminogroups (6.15–6.56 Å), which imply large distances between inorganic parts, prevent further condensation of $[Zr_3F_{16}(H_2O)]_n$ chains towards a three-dimensional inorganic network. In **II** and **III**, the compact shape of $[\textit{tren}H_3]^{3+}$ could limit the condensation of inorganic polyhedra and led to a low dimensional inorganic framework. It must be noted that the shape of the organic cation is correlated to the number of protonated amine groups. The plane conformation is tetraprotonated $[\textit{tren}H_4]^{4+}$ whereas the "spider" conformation is triprotonated $[\textit{tren}H_3]^{3+}$. Owing to the difficulty to distinguish water molecules and isolated fluoride ions from X-ray data, this observation allowed to conclude on the final formulation of compounds. Both *tren* conformations and the related N_t–N_p distances together with the N–H…X (X = F, O) distances are in good agreement with the results of numerous *tren* structures such as $[(C_2H_4NH_3)_3N]_2\cdot[Zn_2(HPO_4)_4(H_2PO_4)_2]$ ($[\textit{tren}H_3]^{3+}$, "spider") [21] and $[(C_2H_4NH_3)_3NH]_2\cdot[UO_2(SO_4)_3]\cdot H_2O$ ($[\textit{tren}H_4]^{4+}$, plane) [22]. Moreover, it is also found that both protonation states co-exist simultaneously in a same phase [23].

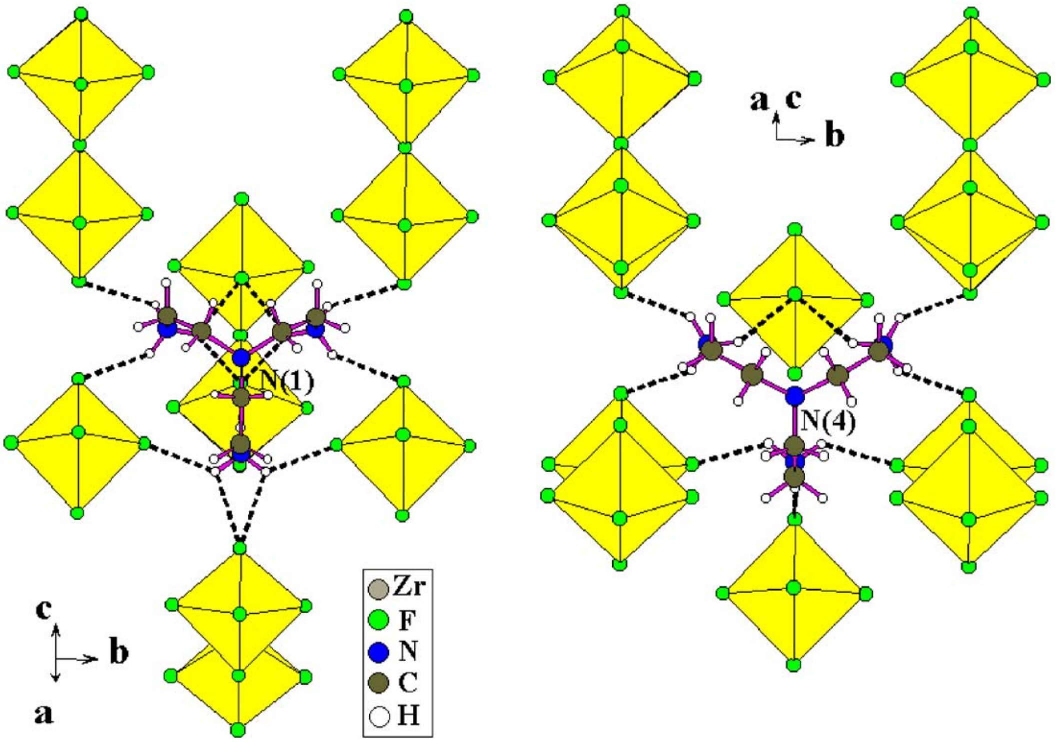

Fig. 5. Independent template moieties in $[(C_2H_4NH_3)_3N]_2 \cdot [ZrF_6] \cdot [Zr_2F_{12}]$ (**II**). Hydrogen bonds are indicated by dotted lines.

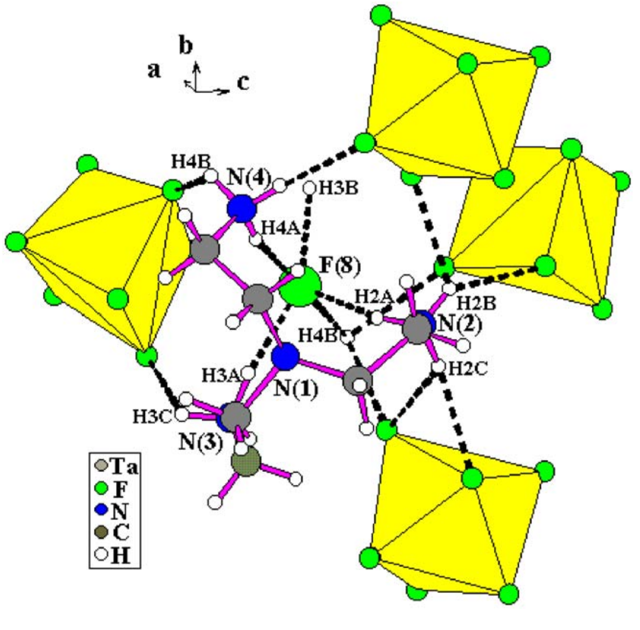

Fig. 6. Template moiety, free fluoride F(8) ion and neighboring $[TaF_7]$ polyhedra in $[(C_2H_4NH_3)_3N] \cdot [TaF_7] \cdot F$ (**III**). Hydrogen bonds are indicated by dotted lines.

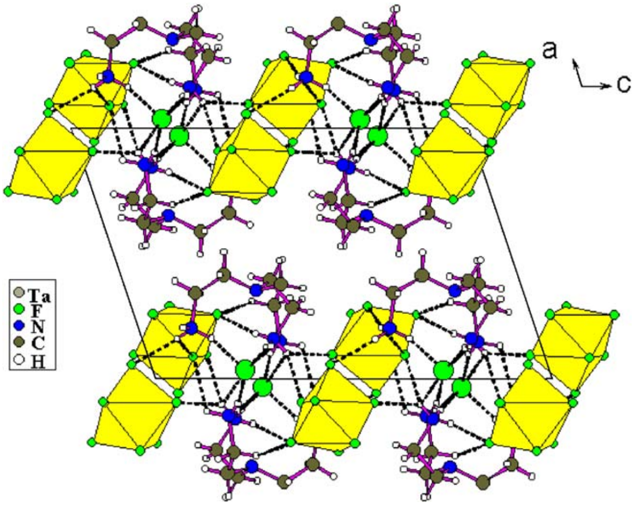

Fig. 7. Infinite sheets in $[(C_2H_4NH_3)_3N] \cdot [TaF_7] \cdot F$ (**III**). Dotted lines correspond to hydrogen bond network.

In order to precise the phase stability regions and to increase the dimensionality of the inorganic network towards open structures, the (ZrF_4,Ta_2O_5)–*tren*–HF-ethanol systems are explored by microwave heating in large concentration domains.

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