

# A new 1D hybrid fluoroaluminate templated by an original tetramine

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## Abstract

An original polyamine, 2,3 di-2-aminomethyl 1,4 diaminobut-2-ene (*ten*), characterized by single-crystal XRD analysis, has been synthesised and leads to a new hybrid fluoroaluminate  $[H_4ten] \cdot (AlF_5)_2$  by microwave heating assisted hydrothermal synthesis. The structure of  $[H_4ten] \cdot (AlF_5)_2$  is *ab initio* determined from powder data.

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## 1. Introduction

Fluoroaluminates have found application in catalysis since the discovery of  $\beta$ - $AlF_3$ , [1] active in Cl–F exchange reactions [2]. During the last decade, N-containing organic cations were used as counterions and gave access to a wide variety of structures [3], generally built up from isolated  $AlF_6$  octahedra [4]. Large polyanions  $[Al_2F_{10}]^{4-}$  [5],  $[Al_3F_{12}]^{3-}$  [6],  $[Al_4F_{18}]^{6-}$  [7,8],  $[Al_7F_{30}]^{9-}$ , together with  $(Al_7F_{29})_\infty$  [9] chains and bidimensional  $(Al_3F_{10})_\infty$  [10] layers were also observed. The thermal treatment of these hybrid aluminium fluorides led to new forms of  $AlF_3$ , [11] such as *t*- $AlF_3$  [12] obtained from  $[(CH_3)_4N] \cdot (AlF_4) \cdot H_2O$ . In this contribution, we report on the synthesis of a new polyamine, 2,3 di-2-aminomethyl 1,4 diaminobut-2-ene (*ten*), and on the structure of  $[H_4ten]Cl_4$ . A new

one dimensional hybrid fluoroaluminate  $[H_4ten] \cdot (AlF_5)_2$  is obtained in the  $Al_2O_3$ –*ten*–HF– $H_2O$  system. Its structure is determined from powder XRD data by using the direct space method (ESPOIR program [13]) and Rietveld profile refinement.

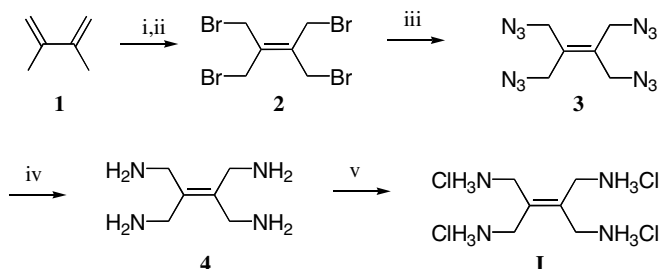
## 2. Experimental

### 2.1. Synthesis of 2,3 di-2-aminomethyl 1,4 diaminobut-2-ene $[H_4ten]Cl_4$ (I)

$NaN_3$  (1.43 g, 4.4 equiv., 22 mmol) was added to a solution of **2** (2 g, 5 mmol) in DMF (40 mL) (Scheme 1). The mixture was stirred at  $-40^\circ C$  for 24 h. At  $20^\circ C$ , after addition of water (80 mL), the aqueous phase was extracted with ether. The organic phase was dried on  $MgSO_4$  and quickly concentrated while cooling to give crystallized tetrazide **3** (1.18 g).  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 4.05 (s, 8H). To a solution of **3** (1.18 g, 4.76 mmol) in THF (5 mL) was added  $PPh_3$  (5.50 g, 4.4 equiv., 21 mmol) and  $H_2O$  (0.51 g, 6 equiv., 28.5 mmol) at  $-40^\circ C$  and the solution was stirred for 20 h at  $-40^\circ C$  and then concentrated. The solid residue was dissolved in ethyl acetate (80 mL) and after addition of  $10^{-1} N_{aq}HCl$

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Scheme 1. Reagents and conditions: (i)  $\text{Br}_2$ ,  $\text{CCl}_4$ ,  $0^\circ\text{C}$ ; (ii) NBS, 24 h, reflux, 60% (over two steps); (iii)  $\text{NaN}_3$  (4.4 equiv.), DMF,  $-40^\circ\text{C}$ , 20 h; (iv)  $\text{PPh}_3$  (4.4 equiv.),  $\text{H}_2\text{O}$  (6 equiv.), THF,  $-40^\circ\text{C}$ , 20 h; (v)  $\text{HCl}_{\text{aq}}$ , 80% (over three steps).

(210 mL, 4.4 equiv., 20.1 mmol), the solution was stirred for 1 h. The separated aqueous phase was washed with ethyl acetate (250 mL). The tetramine tetrachlorhydrate (**I**) was obtained after water removal as a solid (1.34 g, 80% yield, 4 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ),  $\delta$  (ppm, DSS): 4.05 (s, 8H), 4.78 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ): 38.0, 136.0.

## 2.2. Synthesis of $[\text{H}_4\text{ten}] \cdot (\text{AlF}_5)_2$ (**II**)

A microcrystalline powder of  $[\text{H}_4\text{ten}] \cdot (\text{AlF}_5)_2$  was prepared from  $\text{Al}_2\text{O}_3$ , *ten* (obtained after  $\text{Cl}^-/\text{OH}^-$  exchange on an anionic resin.), HF,  $\text{H}_2\text{O}$  in 1:0.5:10:515 molar ratios by microwave heating assisted hydrothermal synthesis (Fig. 1). The solid product was washed with deionised water and dried at room temperature. XRD powder patterns indicated that the  $[\text{H}_4\text{ten}] \cdot (\text{AlF}_5)_2$  (**II**) sample was contaminated with pyrochlore ( $\text{Al}_2[(\text{OH}),\text{F}]_6 \cdot \text{H}_2\text{O}$  [14]).

## 2.3. Determination of crystal structure

A single-crystal of **I**, suitable for X-ray diffraction, was selected by using an optical microscope. The crystal cell parameters were obtained from a random reflection search and X-ray diffraction data were collected on a Siemens AED2 four-circle diffractometer. Chlorine atoms were

located by direct methods using the SHELXS-86 program [15]. Nitrogen and carbon atoms were found by difference Fourier maps and the positions of hydrogen atoms were geometrically constrained (HFIX option). Structure refinements were performed using the SHELXS-97 program [16]. The positions of all non-hydrogen atoms were refined anisotropically and a unique isotropic thermal motion was used for all hydrogen atoms.

The indexation of the XRD pattern of  $[\text{H}_4\text{ten}] \cdot (\text{AlF}_5)_2$  was carried out with the McMaille [17] software from the 20 first lines. A monoclinic solution was found with satisfactory figures of merit ( $M(20) = 47$ ,  $F(20) = 75$  (0.0054,48) and was confirmed at the structure factor extraction stage using the FULLPROF program [18] (Le Bail method [19]). Direct methods failed to provide structure solutions. Calculations were then performed with Espoir, a reverse Monte Carlo program with a pseudo simulated annealing code for ab initio crystal structure determination by the direct space method. The strategy consisted of the introduction of three objects, translated and rotated randomly, until a satisfying fit to a pseudo powder pattern regenerated from the extracted structure factors was obtained: one *ten* molecule (hydrogen atoms omitted), one  $\text{AlF}_6$  octahedron and one  $\text{AlF}_4$  square plane. The geometry of *ten* was deduced from the structure of  $[\text{H}_4\text{ten}]\text{Cl}_4$ . In the first stage, the structure was determined in the non-centrosymmetric  $Pc$  space group and a model with  $(\text{AlF}_5)_\infty$  chains was obtained. This model was introduced into the Rietveld method (Fullprof) for refinement (Fig. 2). It was found that two Al atoms and the center of  $[\text{H}_4\text{ten}]^{4+}$  cations were compatible with the presence of an inversion center and consequently, the final results are given in the  $P2_1/c$  space group.

The conditions of data collection are summarized in Table 1. Atomic coordinates and main bond lengths are given in Tables 2–5.

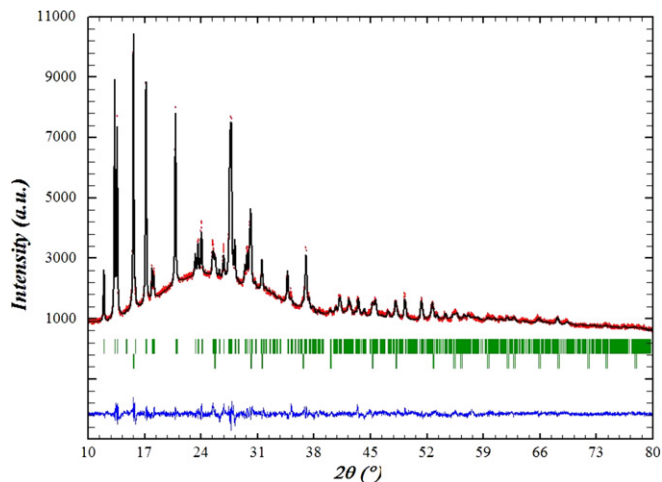


Fig. 2. Final Rietveld plot crystal structure of  $[\text{H}_4\text{ten}] \cdot (\text{AlF}_5)_2$ . The bottom sticks show the presence of  $\text{Al}_2[(\text{OH}),\text{F}]_6 \cdot \text{H}_2\text{O}$ .

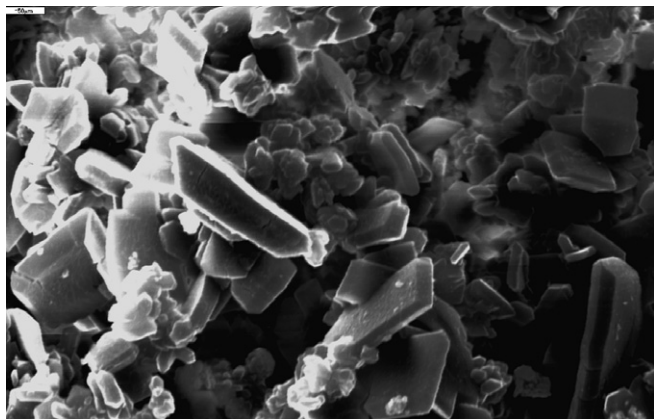


Fig. 1. Electron scanning micrograph of  $[\text{H}_4\text{ten}] \cdot (\text{AlF}_5)_2$  crystals.

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