Ternary transition-metal fluoride precursors for the fluoro lytic sol–gel route: new insights into speciation and decomposition†

J. Kohl,a D. Wiedemann,*a S. I. Troyanov,b E. Palamidisa and M. Lercha

The nanoscaled ternary transition-metal fluorides Li₃MF₆ (M = V, Fe, Mn) and Li₂NiF₄ are promising candidates for cathode materials in high-voltage lithium-ion batteries. The fluoro lytic route to these compounds relies on thermal decomposition of a hitherto uncharacterised precursor mixture produced from acetylacetonates and hydrofluoric acid. By addition of pyridine, different cationic, electroneutral and anionic complexes containing the motifs [MF₆]n⁺ (n = 0–4) have been trapped and characterised by single-crystal X-ray diffraction and IR spectroscopy. Based on the results, a model of successive and incomplete fluorination is proposed for the speciation and formation of the precursor. The decomposition of the latter has been monitored via thermogravimetry (TG) and differential scanning calorimetry (DSC).

Introduction

In search of new cathode materials for lithium-ion batteries during the last decade, ternary fluorides have become candidates of interest, because theoretical calculations had indicated an increase in redox potential when substituting fluorine for oxygen.1 Because of their high lithium content and their variability in oxidation numbers, the ternary fluorides Li₃MF₆ (M: transition metal) are a focus of research. The preparation of nanosized particles is important with regard to fluorides exhibiting low electrical conductivity. Detailed descriptions of the syntheses and scrutinious electrochemical characterisations of Li₃FeF₆ and Li₃VF₆ are available.2 4 In 2012, we reported an approach for the synthesis of ternary Li₃MF₆ on the basis of the fluoro lytic sol–gel process developed by Kemnitz et al., who described the preparation of a high-surface aluminium fluoride.5 6 The starting materials of our route are lithium tert-butoxide and a transition-metal acetylacetonate [M(acac)₃], which are reacted with an excess of hydrogen fluoride in an organic solvent (cf. Scheme 1).

The precursor obtained in this first step is then calcined in a dinitrogen atmosphere to form the ternary fluoride. Using this protocol, either modification of Li₃VF₆ can be prepared in excellent yield: heating of the sample to 300 °C followed by slow cooling to room temperature results in the formation of monoclinic β-Li₃VF₆, whereas heating the precursor to 700 °C and quenching to room temperature results in the formation of orthorhombic α-Li₃VF₆. Moreover, β-Li₃VF₆ can be prepared with domain sizes smaller than 50 nm. While monoclinic β-Li₃CrF₆ can be synthesised in good yield, the yields of other ternary fluorides are considerably lower—and Li₃MnF₆ as well as Li₃CoF₆ cannot at all be synthesised following this route. Monoclinic Li₃FeF₆ and Li₃MnF₅ are obtained in moderate to low yields together with the difluorides MF₂. In contrast to this, the method can be successfully applied to the system Li–Ni–F: Li₃NiF₄ is prepared in high yields with domain sizes of 55 nm.7 The precursors contain highly amorphous fractions, making it impossible to get information about their composition by X-ray powder diffraction techniques. Only the existence of LiF and Li₂SiF₆ in the precursor materials has been confirmed so far. As shown by elemental analyses, the precursors contain high amounts of carbon, hydrogen and oxygen indicating the presence of organic residues. For example, the Li₃VF₆ precursor additionally contains acetylacetonato ligands bound to vanadium(III) as well as hexafluoridovanadate(III). This has been confirmed by IR spectroscopy and ³¹H-NMR
s spectroscopy in solution.6 The material obtained from precursor decomposition contains about 2% residual carbon. However, it was suggested that the precursor be a mixture of several species. Accurate information about its composition is essential for optimising precursor synthesis and decomposition. Bearing this in mind, we have chosen to try and stabilise single species by providing additional donor molecules and crystallise the compounds thus obtained.6 Using this technique, the first of a whole cascade of fluorination steps has been identified and its product, after addition of acetonitrile, \([\text{VIIIF} \text{(acac)}]_3\) crystalllographically characterised. In this work, we report on further experiments of the same kind. By addition of pyridine, we stabilised four new species in the system Li–V–F. These reflect the stepwise fluorination process of the starting material \([\text{VIII(acac)}]_3\), leading to \([\text{VF}_4]\). We have also successfully transferred this concept to Li$_2$MnF$_5$ and Li$_2$NiF$_5$ precursors.

**Experimental**

**Analysis and characterisation**

NMR spectroscopy. Liquid-phase NMR spectra were recorded on a “Bruker ARV 400” at room temperature. Chemical shifts refer to SiMe$_4$ and VOCl$_3$ for $^1$H and $^{51}$V, respectively. They were calibrated with respect to the solvent proton signal for $^1$H or an electronically stored frequency for $^{51}$V.

FT-IR spectroscopy. IR spectra of CsI pellets were measured with a “Nicolet Series II Magna 750” in transmission mode.

Elemental analysis. Carbon and hydrogen contents were determined by combustion analysis using a “Thermo Finnigan FlashEA 1112 NC” analyser. Deviations from calculated element contents result from solvent residues and difficulties in the mechanical separation of the crystalline compounds 1a, 1b and 1d.

Thermal analysis. Thermal analysis was performed on a simultaneous thermobalance (STA) prototype L811 (Linseis GmbH, Selb). Samples were heated in corundum crucibles to 600 °C with 3 °C min$^{-1}$. Absolute pyridine (5 mL) was added to the Li$_2$NiF$_4$ precursor and stirred overnight at 50 °C. After sedimentation of excess material, the overlaying solution was filled into small glass containers that were afterwards sealed with plastic caps. A small hole was drilled into each cap, through which the solvent evaporated slowly. After a few days, light blue crystals formed.

**Preparation of single crystals**

\([\text{VIII(acac)}]_3\) (1a), \([\text{VIIIF} \text{(py)}]_4\)BF$_4$ (1b) and \([\text{VIIIF} \text{(py)}]_3\) (1d). The Li$_2$VF$_5$ precursor was prepared according to a standard procedure.6 Absolute pyridine (5–8 mL) was added to the Li$_2$VF$_5$ precursor (500–600 mg). The mixture was stirred overnight at 50 °C. The resulting greenish-brown solution was filled into glass tubes that were positioned in a capped Schlenk tube containing n-pentane or diethyl ether (20 mL). After one to three days, blue-green columns (1b), red needles (1a), and purple prisms (1d) formed.

**Analytical data for 1a.** NMR: $\delta_1$ (400 MHz; CDCl$_3$) 7.1 (2 H, br s, \textit{meta}-H), 7.7 (1 H, br s, \textit{para}-H), 8.6 (2 H, br s, \textit{ortho}-H), 40.7 (1 H, s, CH), 45.6 (3 H, s, Me) and 55.5 (br s, acac). $\delta_2$ (105.2 MHz; CDCl$_3$) $-$850.86. IR: $\nu_{\max}/cm^{-1}$ 3100–2800w (s$\nu$C–H) and 1605m (s$\nu$C–Cl)$_{\text{py}}$, 1575m (s$\nu$C=O)$_{\text{acac}}$, 1448s (m$\nu$C–Cl)$_{\text{py}}$, 1448s (m$\nu$C–Cl)$_{\text{py}}$, 1375w (m$\nu$C–O)$_{\text{acac}}$, 1286w, 1213w, 1067w, 1043m, 766m (s$\gamma$C–H)$_{\text{py}}$, 702s (s$\gamma$C–H)$_{\text{py}}$, 638m (s$\gamma$C–H)$_{\text{py}}$, 578s, 561vs, 537m (s$\nu$V=O), 450m (s$\nu$N$_{\text{py}}$–V), 418w and 330s (s$\nu$F–F$^\prime$). Anal. found: C, 52.3; H, 5.2; N, 8.2.

**Analytical data for 1b.** NMR: $\delta_d$ (400 MHz; CDCl$_3$) 7.32 (2 H, br s, \textit{meta}-H), 7.70 (1 H, br s, \textit{para}-H) and 8.63 (2 H, br s, \textit{ortho}-H). $\delta_2$ (105.2 MHz; CDCl$_3$) $-$853.36. IR: $\nu_{\max}/cm^{-1}$ 3150–2800w (s$\nu$C–H)$_{\text{py}}$, 1605s (s$\nu$C–Cl)$_{\text{py}}$, 1483m (s$\nu$C–Cl)$_{\text{py}}$, 1448s (m$\nu$C–Cl)$_{\text{py}}$, 1217m, 1101s, 1058s, 1043s, 950m, 770m (s$\gamma$C–H)$_{\text{py}}$, 709m (s$\gamma$C–H)$_{\text{py}}$, 697s (s$\nu$V=O), 540m (s$\nu$C–H)$_{\text{py}}$, 520w, 499w, 440m (s$\nu$N$_{\text{py}}$–V), 390m (s$\nu$F–F$^\prime$) and 278m (s$\nu$N$^\prime$). Anal. found: C, 48.95; H, 4.2; N, 11.2.

**[pyH][VIIIF\text{(py)}]_2\text{SiF}_6 \text{(1c).}** A saturated solution of the Li$_2$VF$_5$ precursor in absolute pyridine was prepared and stirred overnight at 50 °C. After sedimentation of excess material, the overlaying solution was filled into small glass containers that were afterwards sealed with plastic caps. A small hole was drilled into each cap, through which the solvent evaporated slowly. After a few days, light blue crystals formed.

**[(pyH)VIIIF\text{(py)}]_2\text{SiF}_6 \text{•ETO} \text{H (1e).}** The standard procedure for the preparation of the Li$_2$VF$_5$ precursor was performed with pyridine as solvent. After addition of hydrogen–fluoride solution and stirring the reaction solution for two hours, the excess hydrogen fluoride and one third of the solvent were evaporated under reduced pressure. The residual solution was stored in the refrigerator at $-$30 °C. After 24 hours, black-green plates formed.

**[Mn\text{IIIF}\text{(py)}]_2\text{[SiF}_6\text{(py)] (2a) and [Mn\text{IIIF}\text{(py)}]_3 \text{(2b).}** A Li$_2$MnF$_5$ precursor was prepared from Mn(OAc)$_2$·2H$_2$O (Ac: acetyl) according to a standard procedure.6 It was stirred overnight in absolute pyridine (8 mL) at 50 °C. The resulting orange-brown solution was filled into glass tubes that were positioned in a capped Schlenk tube containing n-pentane or diethyl ether (10 mL). After four days, orange-brown crystals (2a) formed. From a few millilitres of the mother liquor stored for five weeks at r.t., orange-brown prisms (2b) were obtained.

**[Ni\text{IIIF}\text{(py)}]_3 \text{(3a).}** A Li$_2$NiF$_5$ precursor was prepared from [Ni(acac)$_3$]$_2$ in ethanol according to a standard procedure.7 Absolute pyridine (5 mL) was added to the Li$_2$NiF$_5$ precursor (500–600 mg). The mixture was stirred overnight at 50 °C. The resulting green solution was filled into glass tubes that were positioned in a capped Schlenk tube filled with n-pentane or diethyl ether (20 mL). After one to three days, light blue crystals (3a) formed. After a further few weeks, purple crystals of [Ni\text{IIIF}\text{(acac)}]$_2\text{[py]}$ (3b) began to grow. Anal. found: C, 58.1; H, 4.9; N, 13.2. Calc. for C$_{20}$H$_{28}$BF$_2$N$_2$V (413.09): C, 58.15; H, 4.9; N, 13.6%.

**Single-crystal X-ray diffraction**

Data were collected at 150.00(10) K using an “Oxford Diffraction Xcalibur S” diffractometer equipped with a goniometer in $\kappa$ geometry, a “Sapphire 3” CCD-detector, a graphite-monochromated “Enhance” Mo-$K$$_{\alpha}$ source ($\lambda = 0.71073$ Å) and a
“Cryojet XL” sample cooler. Diffraction images were integrated with CRYSALIS PRO. An analytical numeric absorption correction was performed using a multifaceted-crystal model. Structures were solved with SHELXT-2014 using a dual-space method and refined with SHELXL-2014 against $F^2$ data using the full-matrix least-squares algorithm. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically with standard riding-models. Molecular graphics were produced using ORTEP-3 for Windows.

The crystal of [VIIIF$_2$(py)$_2$] (1a) was a merohedral twin of type II by rotation of 180° around [100] in reciprocal space (fraction of second component: 0.291[1]) as discovered by the use of COSET.

The tetrafluoroborate ion in [VIIIF$_2$(py)$_3$]BF$_4$ (1b) is disordered over a position of higher symmetry and was treated using enhanced rigid-bond restraints.

The crystal of (pyH)[VIIIF$_2$(py)$_4$]SiF$_6$ (1c) was twinned by rotation of ~90.5869° around [001] in direct space (fraction of second component: 0.163[2]). Its pyridinium ion is rotationally disordered over a special position and constructed from two symmetry-independent atoms. It was modelled as an occupationally disordered species, with C$_{50}$/N$_{50}$ occupations of 0.375/0.625 to keep the stoichiometry. The position was chosen because of the possibility of hydrogen bonding. The structure of 1c contains a void of ca. 67 Å$^3$ that was checked for unmodelled electron density by using difference Fourier maps as well as PLATON/SQUEEZE. Neither procedure showed a significant residual.

Structure refinement for [VIIIF$_2$(py)$_3$] (1d) did not lead to satisfactory results. Probably because of unresolved twinning, partial substituional (solid solution) or rotational disorder of the complex molecules, R factors of the final model were very high, the weighting scheme did not converge to sensible values and large residual electron-density maxima were found at physically unreasonable positions. Therefore, the suggested structure is to be understood as merely modelling connectivity and cell content for the major component.$^4$

Because the crystal system of (pyH)[VIIIF$_2$(py)$_3$]$_{3/2}$EtOH (1e) initially seemed to be orthorhombic, an inappropriate data-collection strategy had been chosen resulting in a somewhat lower completeness. In spite of this shortcoming, the structure is of high quality. One pyridinium ion (N50–C52) is rotationally disordered over a special position and constructed from three symmetry-independent atoms. It was modelled as an occupationally disordered species with C50/N50 occupations of 0.5 each to keep the stoichiometry. The position was chosen because of the possibility of hydrogen bonding and the electron density found. The oxygen-borne hydrogen atom was refined with a restrained 1,2-distance (0.84 Å) and $U_{	ext{iso}}$(H(60)) = 1.2 $U_{	ext{cal}}$(060). The nitrogen-borne hydrogen atom in the disordered pyridinium ion was fully constrained to the nitrogen atom. The one in the ordered pyridinium ion (N40–C45) was refined with a restrained 1,2-distance (0.88 Å), a same-1,3-distance restraint and $U_{	ext{iso}}$(H(40)) = 1.2 $U_{	ext{cal}}$(N(40)).

The crystal of [MnVIIIF$_2$(py)$_3$] (2b) was twinned by rotation of ca. 180° around (001) in direct space (fraction of second component: 0.356[3]). Some reflections had to be excluded from the refinement because of problems properly separating them.

CCDC 1063076–1063078 and 1063080–1063083 contain the supplementary crystallographic data for this paper.

Results and discussion

Species from the Li$_3$VF$_6$ precursor

The following pyridine adducts of species contained in the Li$_3$VF$_6$ precursor were isolated (py: pyridine): [VIIIF$_2$(py)$_3$] (1a), [VIII(acac)F$_2$(py)$_3$]BF$_4$ (1b), (pyH)[VIIIF$_2$(py)$_4$]SiF$_6$ (1c), [VIIIF$_2$(py)$_3$]BF$_4$ (1d) and (pyH)[VIII(acac)F$_2$(py)$_3$]$_{3/2}$EtOH (1e). Because hydrogen fluoride reacts with the glassware used during the precursor synthesis,$^6$ tetrafluoroborate and hexafluorosilicate are present in the precursor solutions. The diffusion method, as described in the experimental part, yielded crystals of compounds 1a, 1b and 1d that always co-crystallise and are prone to twinning. Crystals of 1c are formed on slow evaporation of the solvent in air. Cooling crystallisation of 1e occurred when storing reaction mixtures in pyridine at ~30 °C. Crystal data and refinement details for 1a-e are summarised in Table 1.

In the crystal, [VIII(acac)F$_2$(py)$_3$] (1a) forms chains along [010] through dispersive C–H···F contacts between fluoro ligands and hydrogen atoms of the acetylacetonato ligand [d(H···F) ≈ 2.4 Å]. The chains are connected by further C–H···F contacts along [100] [d(H···F) ≈ 2.5 Å] and dispersive aromatic contacts along [010]. The complex is a slightly distorted coordination octahedron with the pyridine ligands in a trans arrangement (cf. Table 2). In 1b and 1c, the [VIIIF$_2$(py)$_4$]$^+$ units adopt a trans octahedral coordination geometry, which is only slightly distorted. The pyridine rings in 1b are not coplanar to the V–N–F coordination planes, but slightly twisted out of the latter, while pairs of diagnostically opposed pyridine rings are coplanar (Fig. 1).

The [VIIIF$_2$(py)$_3$]$^+$ and BF$_4^-$ ions in 1b form a three-dimensional network. 1c crystallises in a layered structure. In [001] direction, layers of [VIIIF$_2$(py)$_3$]$^+$ units alternate with layers of [SiF$_6^{2-}$] and pyridinium ions, which are associated by hydrogen bonds. Along [001], the [SiF$_6^{2-}$] ions are located in channels built by the cations. The V–F bonds in the cationic complexes 1b and 1c (ca. 1.76 Å) are shorter than in the electroneutral complex 1a (1.85–1.86 Å). The anionic complex 1c has the longest V–F bonds of the vanadium species described in this work with up to 1.9229(18) Å (cf. Table 2).

This trend is easily rationalised by assuming an increasingly effective shielding of the central ion’s positive charge by the growing number of negatively charged ligands and, thus, a decrease in the electrostatic attraction per fluoro ligand. For comparison, it should be noted that the V–F distance in VF$_3$ is 1.94 Å, whereas it varies from 1.89 to 1.97 Å in β-Li$_3$VF$_6$. In both cases, the octahedral (bridging) F$_6$ coordination environ-

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1 Crystal data: C$_{50}$H$_{51}$N$_5$F$_8$V$_3$, M = 345.24, orthorhombic, a = 8.2723(5) Å, b = 12.6821(13) Å, c = 30.6745(19) Å, $\beta$ = 150.00(10) K, space group Pbcn, Z = 8.
**Table 1** Details of the refinement for 1a–c and 1e

<table>
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<tr>
<th>Crystal data</th>
<th>[VIIIF3(py)3] (1a)</th>
<th>[VIIIF2(py)4]BF4 (1b)</th>
<th>(pyH)[VIIIF2(py)4]SiF6 (1c)</th>
<th>(pyH)[VIIIF2(py)4]2EtOH (1e)</th>
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<tr>
<td>CCDC no.</td>
<td>1063076</td>
<td>1063077</td>
<td>1063078</td>
<td>1063080</td>
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<tr>
<td>Chemical formula</td>
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<td>C20H20BF4N2V</td>
<td>C20H20BF4N2SiV</td>
<td>C20H20BF4N2SiV</td>
</tr>
<tr>
<td>Crystal system, space group</td>
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<td>Monoclinic, I2/a</td>
<td>Tetragonal, P4/mnm</td>
<td>Monoclinic, P2₁/n</td>
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<td>α (Å)</td>
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<td>14.0214(17)</td>
<td>10.8047(2)</td>
<td>8.4345(6)</td>
</tr>
<tr>
<td>β (Å)</td>
<td>8.0367(4)</td>
<td>12.8277(10)</td>
<td>10.8047(2)</td>
<td>31.4088(12)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>13.1548(12)</td>
<td>13.4718(17)</td>
<td>12.6865(4)</td>
<td>10.9799(6)</td>
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<tr>
<td>α (°)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
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<td>90</td>
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</tr>
<tr>
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<td>111.971(7)</td>
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<td>2</td>
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<tr>
<td>Crystal size (mm³)</td>
<td>0.54 x 0.12 x 0.06</td>
<td>0.70 x 0.19 x 0.16</td>
<td>0.32 x 0.30 x 0.24</td>
<td>0.39 x 0.18 x 0.18</td>
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**Table 2** Selected bond lengths (Å) for 1a–c and 1e

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<th></th>
<th>[VIII(acac)F2(py)2] (1a)</th>
<th>[VIIIF2(py)4]BF4 (1b)</th>
<th>(pyH)[VIIIF2(py)4]SiF6 (1c)</th>
<th>(pyH)[VIIIF2(py)4]2EtOH (1e)</th>
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<tr>
<td>V–F</td>
<td>1.8515(17)</td>
<td>1.7658(16)</td>
<td>1.762(3) (2×)</td>
<td>1.8832(19)</td>
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<td></td>
<td>1.8603(17)</td>
<td>1.7659(16)</td>
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<td>1.8876(17)</td>
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<tr>
<td>V–N</td>
<td>2.156(2)</td>
<td>2.145(2)</td>
<td>2.134(3) (2×)</td>
<td>1.8837(19)</td>
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<td></td>
<td>2.164(2)</td>
<td>2.150(2)</td>
<td></td>
<td>1.8876(18)</td>
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<tr>
<td>V–O</td>
<td>2.011(2)</td>
<td>2.015(2)</td>
<td></td>
<td>1.9170(18)</td>
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<td></td>
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</tr>
</tbody>
</table>

The crystals obtained from 1d were of insufficient quality to allow more than an assessment of connectivity and cell content for the major component, the [VIIIF3(py)3] molecule, that contains an octahedrally coordinated vanadium ion and assumes a mer configuration.†

(1) View Article Online


displacement effectively shields the charge of the central vanadium(III) ion. Examples with vanadium(III) in a pure F2(py)4 coordination have hitherto been unknown.

However, an example for a compound with a di-cis-1,4,7,11-tetraazacyclodecine complex [VIII(C22H23N4)F2]PF6 described by Schumann,† in which the configuration of the VP2 unit is not yet clarified. Another known compound is the complex [VIII(bipy)F2]BF4 (bipy: 2,2’-bipyridine), in which a vanadium ion is coordinated octahedrally by two cis-fluorido and the bidentate 2,2’-bipyridine ligands.18
symmetry in the complex containing N30–C35. The central ions are coordinated in a distorted octahedral fashion by four fluorido and two trans arranged pyridine ligands. As regards bond lengths and angles, the complex containing V2 is more symmetric than the one containing V1. The V2 unit interacts with two pyridinium ions (containing N40) via hydrogen bonds. Such are also formed between the V1 unit and the ethanol molecule as well as the disordered pyridinium ion containing N50. The packing of the molecules in 1e can be described as a layered structure parallel to (010). Every layer is built of three sublayers with the sequence V1–V2–V1. Within these sublayers, complexes interact via the hydrogen bonds mentioned above.

Species from the Li2MnF5 and Li2NiF4 precursors
As noted in the introduction, the species [MnIIIF2(py)4][SiF5(py)] (2a), [MnIIIF3(py)3] (2b) and [NiIIF2(py)4] (3a) were isolated from the systems Li–Mn–F and Li–Ni–F and crystallographically characterised (see Table 3). The fluorosilicate anion again is a result of the reaction of hydrogen fluoride with the glassware during precursor synthesis. 3a has long been known, but no crystal structure has been reported so far. The hydrates [NiIIF2(py)4]·xH2O (x = 2 and 7/3) have been known and characterised before. From the same mother liquor as 3a, purple crystals of [NiII(acac)2(py)2] (3b) formed after four weeks. This compound has already been reported and both, crystallographically and spectroscopically, characterised.

2a forms a structure with alternating layers of [MnIII F2(py)4] and [SiF5(py)] ions in (100). The trivalent manganese complex has a nearly undistorted octahedral coordination sphere with the fluorido ligands in a trans position (see Fig. 2). The pyridine ligands containing N20 are twisted by 33.6° relative to the N10–V1–F1 plane. At 1.7884(10) Å, the Mn–F bonds (see Table 4) are slightly shorter than those reported for MnF3 (1.7977–2.1057 Å) and MnF3·3H2O.
In the group of divalent manganese compounds [MnIIIF3(py)3]+, species with X = Cl, Br and I (but not F) are known, having a molecular structure similar to 2a. There are several compounds containing the structure motif [MnIIIF2(py)4]− (M: transition metal, e.g., the chromium compounds [CrF2(py)4]X (X = ClO4, Br, I), NO3, PF6)1,2,32 and the cobalt compound [CoF2(py)4]ClO4·½H2O.33 Together with 1b and 1c, 2a adds to the hitherto known set of [MnIIIF2(py)4]− species. A special feature of 2a is the [SiF5(py)]2− ion. Pyridine fluorosilicates or their polymeric forms have not previously been described in the literature.29,30

In the preparation of 2a, 2b and 2c, different space group (Pc instead of P21/c as emulated by twinning). The asymmetric unit contains two complexes differing in the orientation of the pyridine ligands with respect to each other and their tilting with respect to the metal–nitrogen bond. In 2b, both crystallographically independent moieties form layers in (100) connecting symmetry equivalent complexes only through dispersive C–H⋯F contacts. The layers interact via π stacks along [010] to form a three-dimensional network.

The molecular structure of [NiIIIF2(py)4] (3a) is comparable to the [MnIIIF2(py)4]− species discussed before (see Table 4). A distorted octahedral coordination with trans aligned fluorido ligands is the basic structural motif. At 2.0061(9) Å, the Ni–F bond length is in the same range as for NiF2 (given as 1.98(1)–2.04(2) Å or 1.997(1)–2.011(1) Å),40,41 and for the hydrates [NiIIIF2(py)4]·2H2O (2.0424(8) Å) and [NiIIIF2(py)4]·7/3H2O (2.0154(4) Å). The Ni–N bond lengths and coordination angles are also comparable to those in the latter compounds. The molecules of 3a form chains along a, in which the Ni10-containing pyridine ligands interact via π stacks.

### Successive flouinaring of the primary metal precursors

The existence of certain Li, MF6 precursor species can be inferred from the isolation of their solvent adducts. Incorporating [VIII(acac)2(CH3CN)2]BF4,6 the most complete sequence...
of fluorination products was found for the Li₃VF₆ precursor. A suitable model for the fluorination of metal acetylacetonates in the precursor-formation process using the example of Li₃VF₆ is shown in Scheme 2. Starting from [V³⁺(acac)₃], five fluorination steps can be distinguished: first, an acetylacetonato ligand has to be eliminated, leaving behind a cationic {VIII(acac)₂⁺} core as evidenced by the isolation of [VIII(acac)₂(CH₃CN)₂]BF₄ and [VIII(acac)₂F]₆.⁴² After elimination
of another acetylacetonato ligand and further fluorination, a \(\{\text{VI}^\text{II} (\text{acac})_2\}^+\) core is formed, which has been trapped in 1a. Neither \(\{\text{VI}^\text{II} (\text{acac})F_2\}\) nor \(\{\text{VI}^\text{II} (\text{acac})F_2(py)_2\}\) have been described in the literature so far. The \(\{\text{VI}^\text{II} (\text{acac})F_2\}\) core reacts with two more equivalents of HF, forming \(\{\text{VF}_3\}\) and finally \(\{\text{VF}_4\}\), which were trapped in 1d and 1e as shown in Scheme 2.

When the starting materials \(\{\text{VI}^\text{II} (\text{acac})_3\}\) and LiO\(\text{Bu}\) are reacted with hydrogen–fluoride solution, increasingly more fluorinated species (up to \(\{\text{VF}_4\}\) ) are formed within a chemical equilibrium. Although an excess of hydrogen fluoride is used, exhaustive fluorination is not accomplished.

The question remains how Li\(_3\)VF\(_6\) is formed during the decomposition of the inhomogeneous precursor material. For precursor synthesis, LiO\(\text{Bu}\) and \(\{\text{VI}^\text{II} (\text{acac})_3\}\) are reacted in the ratio 3 : 1 with an excess of HF to achieve a stoichiometry of \(\text{F}_3\text{Li}_3\text{V}\). However, the precursor can neither be Li\(_3\)VF\(_6\) nor a stoichiometric mixture of LiF and VF\(_3\), as elemental analysis shows carbon, hydrogen and oxygen to be present in considerable amounts. During precursor decomposition, the following steps occur: while heating, residual solvent evaporates and is carried away by the gas flow. In general, at about 200 °C, acetylacetonates start to decompose,\(^{43}\) pure \(\{\text{VI}^\text{II} (\text{acac})_3\}\) was reported to decompose at about 250 °C.\(^{44}\) To avoid oxidation, working under a dinitrogen atmosphere is necessary. Under these conditions, organic residues are carbonised, giving rise to the black colour of the Li\(_3\)VF\(_6\) material and its residual carbon content. Before reaching 300 °C, the decomposition of Li\(_2\)SiF\(_6\) to LiF and SiF\(_4\) starts. Gaseous SiF\(_4\) is also carried away by the gas flow. Normally, the decomposition of Li\(_2\)SiF\(_6\) should occur at higher temperature as reported in the literature: at 290 °C\(^{45}\) or 350–370 °C\(^{46}\) in dry air. We have not found any Li\(_2\)SiF\(_6\) in Li\(_3\)VF\(_6\) precursor samples prepared under dinitrogen at 300 °C. This indicates that the decomposition of Li\(_2\)SiF\(_6\) occurs at lower temperatures under precursor decomposition conditions as compared to pure samples. To substantiate this, a sample of pure Li\(_2\)SiF\(_6\) prepared from Li\(_2\)CO\(_3\) and aqueous H\(_2\)SiF\(_6\) was calcined for four hours at 240 °C under dinitrogen flow. X-ray powder diffraction showed that the product was a mixture of Li\(_2\)SiF\(_6\) and LiF. At 300 °C, the formation of monoclinic \(\beta\)-Li\(_3\)VF\(_6\) as the main component is observed, so that the decomposition of the fluorinated species and their reaction with LiF can be assumed.

To verify this concept, the precursor decomposition was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC, see Fig. 3). The sample loses 12.9% of its mass up to 180 °C. This is in the temperature range of a possible solvent loss. Between 180 and 350 °C, the sample loses another 12.5% of its mass, while acetylacetonate and Li\(_2\)SiF\(_6\) decompose. From 233 to 250 °C, a DSC signal for an exothermic process appears with its maximum at about 239 °C. As the precursor contains a plethora of species, which can react with each other during decomposition, we have unfortunately been unable to clarify the origin of this signal. However, we have ruled out the decomposition of Li\(_2\)SiF\(_6\) or acetylacetonate compounds (e.g., \(\{\text{VF}_3\}\)) , because these processes are known to be endothermic.\(^{44,47}\)

Upon reaching the final temperature of 600 °C, the sample had lost a total of 30.3% of its mass. This value is in the typical range of losses observed during decomposition (25–40% for Li\(_3\)VF\(_6\) precursors).

It is safe to assume that similar processes occur with Li\(_2\)MnF\(_5\) and Li\(_2\)NiF\(_4\) precursors. In the system Li–Mn–F, \(\{\text{MnF}_3\}_2^+\) and \(\{\text{MnF}_4\}_2^+\) were captured—in analogy to the system Li–V–F (see Scheme 3). Species with the core \(\{\text{Mn}^\text{III} (\text{F})_{x-y}\}\) have not been found so far for \(x = 4\) and 5. In the system Li–N–F, \(\{\text{Ni (acac)}_3\}\) partly reacts with hydrogen fluoride to form NiF\(_2\), as indicated by the presence of 3a (see Scheme 4). It is as yet
unknown if anionic fluoridometal species exist in these systems. Finally, Li₂MnF₅ and Li₃NiF₆ will be formed when the mixture of transition-metal species and LiF is heated under dinitrogen flow.

Conclusions

The results presented above give detailed insight into the processes of the fluoroalytic sol-gel synthesis of ternary lithium transition-metal fluorides. After stabilising precursor species with pyridine and growing single crystals from the pyridine solutions, it became apparent that the precursor is a mixture with pyridine and growing single crystals from the pyridine transition-metal fluorides. After stabilising precursor species better understood. In the case of the synthesis of Li₃VF₆ starting from [VII(acac)₃], four fluorination steps were identified by isolating and characterising the pyridine adducts 1a–e. Further experiments with Li₂MnF₅ and Li₂NiF₄ precursors led to the species 2a–b and 3a. In addition, first attempts to isolate species from the system Li–Fe–F already indicate the presence of [FeIII(F₂(py))₄]BF₄. This demonstrates that the conclusions made for Li₂VF₆ are transferable to the fluoroalytic sol-gel synthesis of other ternary fluorides in general. The elucidation of these processes is necessary for further research on the notoriously low yields of Li₂MnF₅ and Li₃FeF₆, as well as the reduction occurring in these systems. As mentioned in the introduction, Li₂MnF₅ and Li₃FeF₆ were invariably obtained together with the difluorides MF₂. The question, whether divalent species are already formed during precursor synthesis, is important for addressing this issue. Stabilisation with additional solvent ligands such as pyridine is a promising method to help clarify these open questions.

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Notes and references


