Electronic Supplementary Information

# $A_x(H_3O)_{2-x}Mn_5(HPO_3)_6$ (A= Li, Na, K and $NH_4$): Open-Framework Manganese(II) Phosphites Templated by Mixed Cationic Species

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## S1. Structure refinement

Three main residual electron densities were observed inside the hexagonal pores which were found to be non-interpretable. Several attempts without success were realized in order to crystallographically define the electron densities belonging to these highly disordered extraframework species.

| *Density* | *x* | *y* | *z* | *Wickoff letter* | *Occ. Factor* | $e^{-}Å^{-3}$ |
|---|---|---|---|---|---|---|
| Q1 | 0.0647 | 0.1358 | 0.6786 | 12g | 1.0 | 6.07 |
| Q2 | 0.0000 | 0.0000 | 0.8408 | 4c | 0.33333 | 3.75 |
| Q3 | 0.0000 | 0.0000 | 1.0000 | 2b | 0.16667 | 2.59 |

***Assumption 1:*** *Q3 = Li; Q1 and Q2 = $H_2O$. Disorder parts with complementary occupation factors (PART 1 = Q3/Q1 and PART 2 = Q2).*

*This way, an occupation factor of 0.53 was calculated for the Li atom, which is in perfect accordance with the chemical analysis. However, this structural model implies too much short O-O distances, 2.3-2.5 Å from the $H_2O$ molecule (Q1) to the framework, what makes this model invalid.*

***Assumption 2:*** *Q1 or Q2 sites occupied by Li atoms results in occupation factors too much high, what is incongruent with the chemical analysis, as well as it would suppose a positive charge excess.*

**Table S1.** Bond distances (Å) and angles (°) for **1-Li**.

***Mn(1)O$_6$ octahedron***

| ***Mn(1)*** | **O(2)** | **O(2)$^{iv}$** | **O(1)** | **O(1)$^{iv}$** | **O(3)$^{iv}$** | **O(3)** |
|---|---|---|---|---|---|---|
| **O(3)** | 90.5(2) | 91.6(2) | 78.5(2) | 99.1(2) | 176.8(3) | ***2.230(4)*** |
| **O(3)$^{iv}$** | 91.6(2) | 90.5(2) | 99.1(2) | 78.5(2) | ***2.230(4)*** | |
| **O(1)$^{iv}$** | 168.1(2) | 90.0(2) | 85.1(3) | ***2.168(5)*** | | |
| **O(1)** | 90.0(2) | 168.1(2) | ***2.168(5)*** | | | |
| **O(2)$^{iv}$** | 96.7(3) | ***2.149(6)*** | | | | |
| **O(2)** | ***2.149(6)*** | | | | | |

***Mn(2)O$_6$ octahedron***

| ***Mn(2)*** | **O(3)$^{i}$** | **O(3)$^{iii}$** | **O(3)** | **O(1)** | **O(1)$^{iii}$** | **O(1)$^{i}$** |
|---|---|---|---|---|---|---|
| **O(1)$^{i}$** | 79.0(2) | 162.7(2) | 92.6(2) | 83.8(2) | 83.8(2) | ***2.194(5)*** |
| **O(1)$^{iii}$** | 92.6(2) | 79.0(2) | 162.7(2) | 83.8(2) | ***2.194(5)*** | |
| **O(1)** | 162.7(2) | 92.6(2) | 79.0(2) | ***2.194(5)*** | | |
| **O(3)** | 103.4(1) | 103.4(1) | ***2.186(5)*** | | | |
| **O(3)$^{iii}$** | 103.4(1) | ***2.186(5)*** | | | | |
| **O(3)$^{i}$** | ***2.186(5)*** | | | | | |

***Piramid [HP(1)O$_3$]***

| ***P(1)*** | **O(1)** | **O(3)$^{v}$** | **O(2)$^{iii}$** | **H(1)** |
|---|---|---|---|---|
| **H(1)** | 105(3) | 107(3) | 107(3) | ***1.26(7)*** |
| **O(2)$^{iii}$** | 112.1(3) | 114.1(3) | ***1.540(6)*** | |
| **O(3)$^{v}$** | 111.2(3) | ***1.535(4)*** | | |
| **O(1)** | ***1.528(5)*** | | | |

***Symmetry codes**: i = -x+y, -x+1, z; ii = -y+1, -x+1, z-1/2; iii = -y+1, x-y+1, z; iv = y, x, -z+3/2; v = -y+1, -x+1, z+1/2.*

**Table S2.** Pattern Matching and Rietveld refinement parameters for **1-Li**, **2-Na**, **3-K** and **4-$NH_4$**.

| **Sample** | **1-Li** | | **2-Na** | | **3-K** | | **4-$NH_4$** | |
|---|---|---|---|---|---|---|---|---|
| Formula | $Li_{0.55}(H_3O)_{1.45}$-$Mn_5(HPO_3)_6$ | | $Na_{0.72}(H_3O)_{1.28}$-$Mn_5(HPO_3)_6$ | | $K_{0.3}(H_3O)_{1.7}$-$Mn_5(HPO_3)_6$ | | $(NH_4)_{0.59}(H_3O)_{1.41}$-$Mn_5(HPO_3)_6$] | |
| M. Weight (g/mol) | 785.97 | | 795.47 | | 798.64 | | 792.04 | |
| Z | 2 | | 2 | | 2 | | 2 | |
| *Analysis Method* | *Pattern Matching* | *Rietveld Analysis* | *Pattern Matching* | *Rietveld Analysis* | *Pattern Matching* | *Rietveld Analysis* | *Pattern Matching* | *Rietveld Analysis* |
| a, Å | 10.4618(5) | 10.4629(7) | 10.4881(7) | 10.4935(9) | 10.4380(7) | 10.4430(17) | 10.4699(9) | 10.4760(12) |
| c, Å | 9.4057(8) | 9.4073(11) | 9.3984(10) | 9.3970(12) | 9.4076(10) | 9.4082(16) | 9.4350(12) | 9.4382(15) |
| V, $Å^3$ | 891.5(1) | 891.9(1) | 895.3(1) | 896.1(2) | 887.7(1) | 888.6(3) | 895.7(2) | 897.0(2) |
| $N^{er}$ Reflections | 260 | 278 | 262 | 289 | 260 | 283 | 261 | 294 |
| Profile Parameters | 36 | 36 | 35 | 35 | 36 | 36 | 35 | 36 |
| Structure Parameters | ---------- | 16 | ---------- | 16 | ---------- | 16 | ---------- | 16 |
| $R_{Bragg}$ | 1.29 | 18.4 | 1.00 | 14.3 | 1.13 | 19.5 | 0.82 | 20.2 |
| $R_f$ | 1.97 | 8.58 | 1.05 | 6.42 | 1.28 | 8.75 | 0.78 | 18.2 |
| $R_p$ | 21.1 | 29.0 | 19.1 | 25.3 | 22.5 | 31.2 | 21 | 28.5 |
| $R_{wp}$ | 26.0 | 33.7 | 25.3 | 29.7 | 28.7 | 36.6 | 28 | 33.2 |
| $R_{exp}$ | 19.53 | 17.94 | 17.76 | 16.22 | 21.31 | 19.44 | 19.33 | 19.26 |
| $\chi^2$ | 1.77 | 3.53 | 2.02 | 3.35 | 1.82 | 3.54 | 2.10 | 2.97 |

**Table S3.** Coordination environment bond distances (Å) and bond valence calculations for **1-Li**, **2-Na**, **3-K** and **4-$NH_4$** from the Rietveld analysis (without taking into account the extraframework species).

**1-Li**

| *Bond distances (Å)* | | *Bond Valence* | *Bond distances (Å)* | | *Bond Valence* |
|---|---|---|---|---|---|
| (Mn1)-(O1) | 2.196(12) | 0.334(11) | (Mn2)-(O1) | 2.205(20) | 0.326(18) |
| (Mn1)-(O1) | 2.1961(20) | 0.334(18) | (Mn2)-(O1) | 2.205(15) | 0.326(13) |
| (Mn1)-(O2) | 2.168(18) | 0.360(18) | (Mn2)-(O1) | 2.205(17) | 0.326(15) |
| (Mn1)-(O2) | 2.168(18) | 0.360(17) | (Mn2)-(O3) | 2.203(19) | 0.328(16) |
| (Mn1)-(O3) | 2.235(21) | 0.300(17) | (Mn2)-(O3) | 2.203(19) | 0.328(17) |
| (Mn1)-(O3) | 2.235(21) | 0.300(17) | (Mn2)-(O3) | 2.202(30) | 0.328(27) |
| | **Mn(1) SUM** | ***1.99(4)*** | | **Mn(2) SUM** | ***1.96(4)*** |

**2-Na**

| | | | | | |
|---|---|---|---|---|---|
| (Mn1)-(O1) | 2.196(12) | 0.334(10) | (Mn2)-(O1) | 2.202(18) | 0.328(16) |
| (Mn1)-(O1) | 2.196(18) | 0.334(16) | (Mn2)-(O1) | 2.202(13) | 0.329(12) |
| (Mn1)-(O2) | 2.168(15) | 0.360(15) | (Mn2)-(O1) | 2.202(15) | 0.329(13) |
| (Mn1)-(O2) | 2.168(15) | 0.360(14) | (Mn2)-(O3) | 2.199(19) | 0.331(17) |
| (Mn1)-(O3) | 2.238(21) | 0.298(17) | (Mn2)-(O3) | 2.199(19) | 0.331(17) |
| (Mn1)-(O3) | 2.238(22) | 0.298(17) | (Mn2)-(O3) | 2.198(30) | 0.332(27) |
| | **Mn(1) SUM** | ***1.98(4)*** | | **Mn(2) SUM** | ***1.98(4)*** |

**3-K**

| | | | | | |
|---|---|---|---|---|---|
| (Mn1)-(O1) | 2.201(12) | 0.329(11) | (Mn2)-(O1) | 2.212(21) | 0.320(18) |
| (Mn1)-(O1) | 2.201(20) | 0.329(18) | (Mn2)-(O1) | 2.211(15) | 0.321(13) |
| (Mn1)-(O2) | 2.165(18) | 0.363(17) | (Mn2)-(O1) | 2.211(17) | 0.321(15) |
| (Mn1)-(O2) | 2.165(17) | 0.363(17) | (Mn2)-(O3) | 2.208(21) | 0.324(18) |
| (Mn1)-(O3) | 2.243(22) | 0.294(17) | (Mn2)-(O3) | 2.207(19) | 0.324(17) |
| (Mn1)-(O3) | 2.243(22) | 0.294(18) | (Mn2)-(O3) | 2.207(30) | 0.324(27) |
| | **Mn(1) SUM** | ***1.97(4)*** | | **Mn(2) SUM** | ***1.93(5)*** |

**4-$NH_4$**

| | | | | | |
|---|---|---|---|---|---|
| (Mn1)-(O1) | 2.192(12) | 0.338(11) | (Mn2)-(O1) | 2.205(19) | 0.326(17) |
| (Mn1)-(O1) | 2.192(19) | 0.338(17) | (Mn2)-(O1) | 2.204(14) | 0.326(13) |
| (Mn1)-(O2) | 2.158(16) | 0.371(16) | (Mn2)-(O1) | 2.205(16) | 0.326(14) |
| (Mn1)-(O2) | 2.157(15) | 0.371(15) | (Mn2)-(O3) | 2.197(20) | 0.333(18) |
| (Mn1)-(O3) | 2.240(21) | 0.297(17) | (Mn2)-(O3) | 2.196(18) | 0.334(17) |
| (Mn1)-(O3) | 2.240(22) | 0.297(17) | (Mn2)-(O3) | 2.196(30) | 0.334(27) |
| | **Mn(1) SUM** | ***2.01(4)*** | | **Mn(2) SUM** | ***1.98(4)*** |

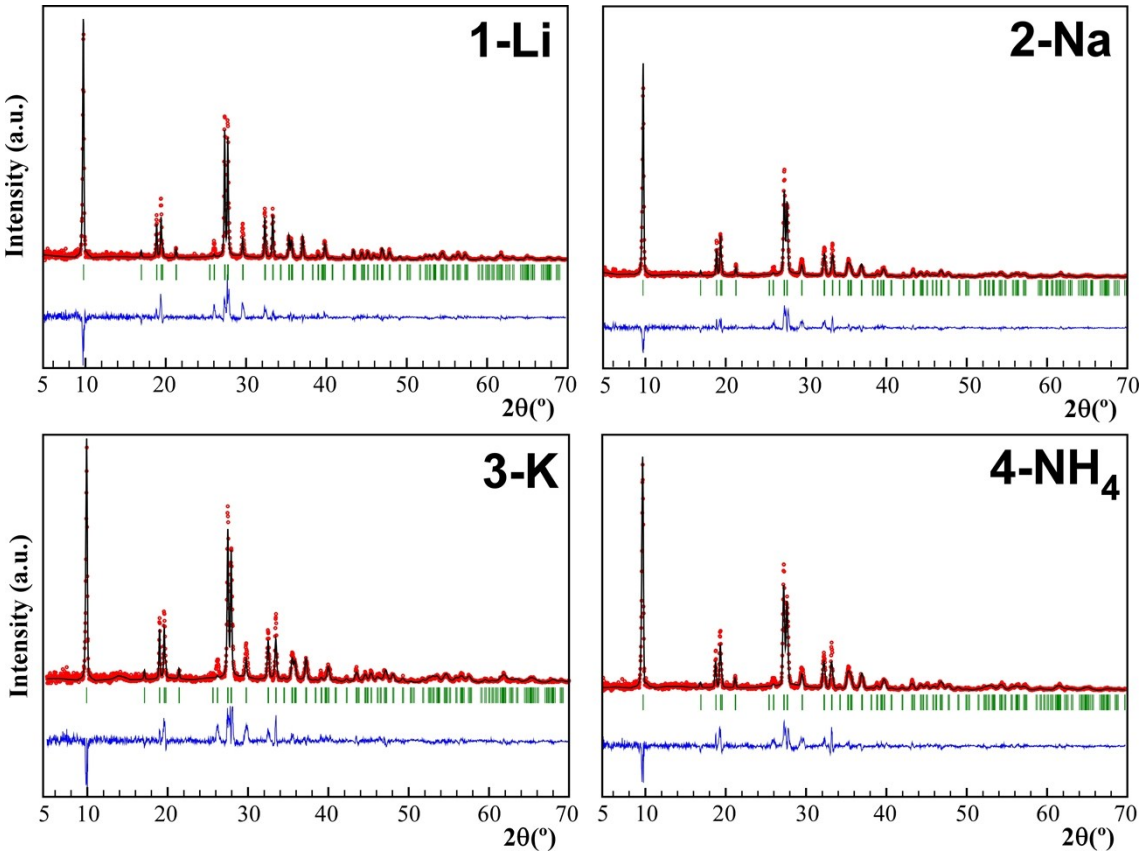


**Figure S1.** Observed (red dots), calculated (black line) and difference X-ray powder diffraction pattern (blue line) for the Rietveld analysis, without taking into account the extraframework sites, of **1-Li**, **2-Na**, **3-K** and **4-NH$_4$** compounds

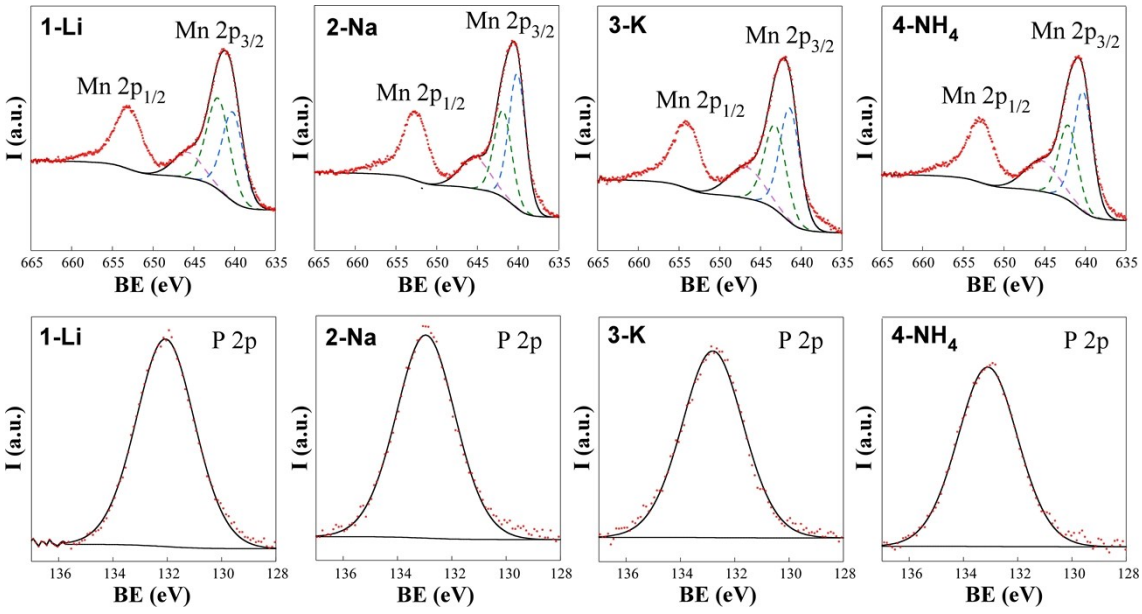


**Figure S2.** XPS spectra of compounds **1-Li**, **2-Na**, **3-K** and **4-NH$_4$**.

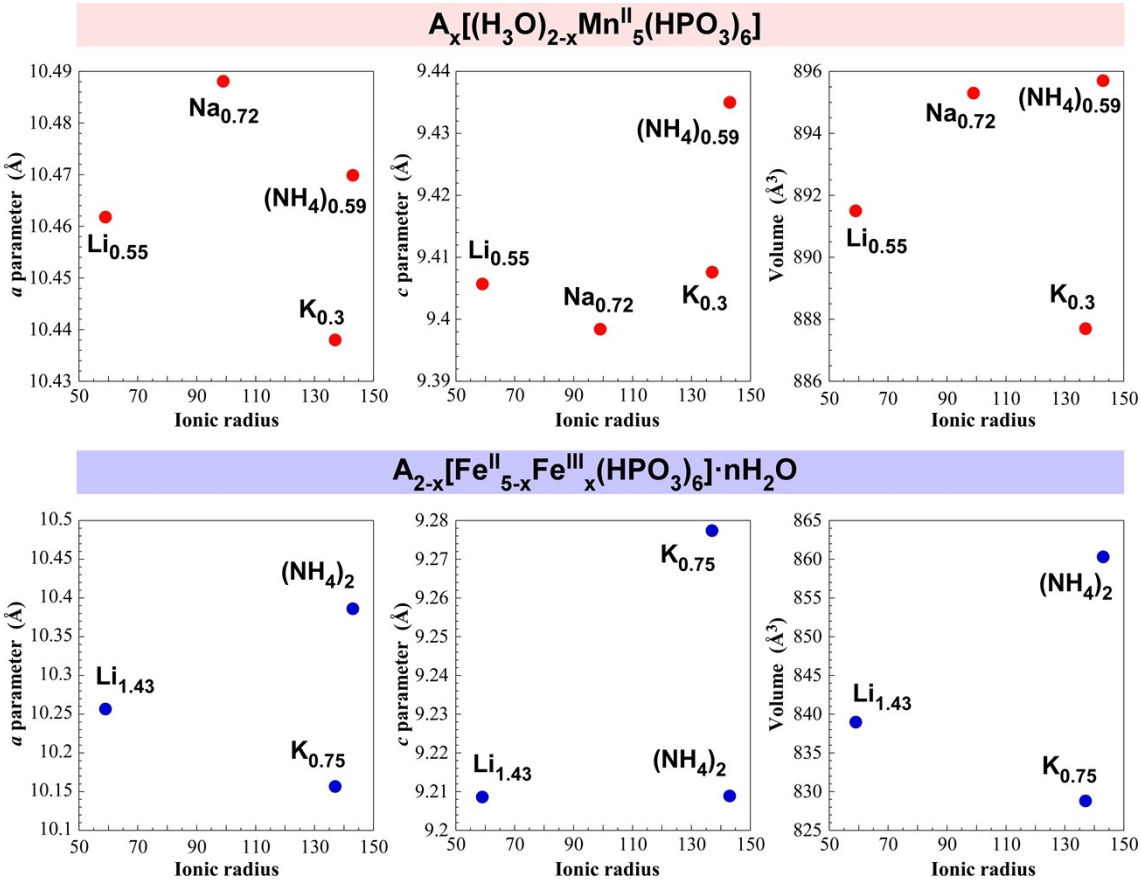


**Figure S3.** Comparison of unit cell parameters versus A ionic radius in $A_x(H_3O)_{2-x}Mn_5(HPO_3)_6$ system (**1-Li**, **2-Na**, **3-K** and **4-NH$_4$**) and iron compounds $A_{2-x}[Fe^{II}_{5-x}Fe^{III}_x(HPO_3)_6]\cdot nH_2O$ previously reported. The numbers in brackets indicate the atoms per unit formula of A species.

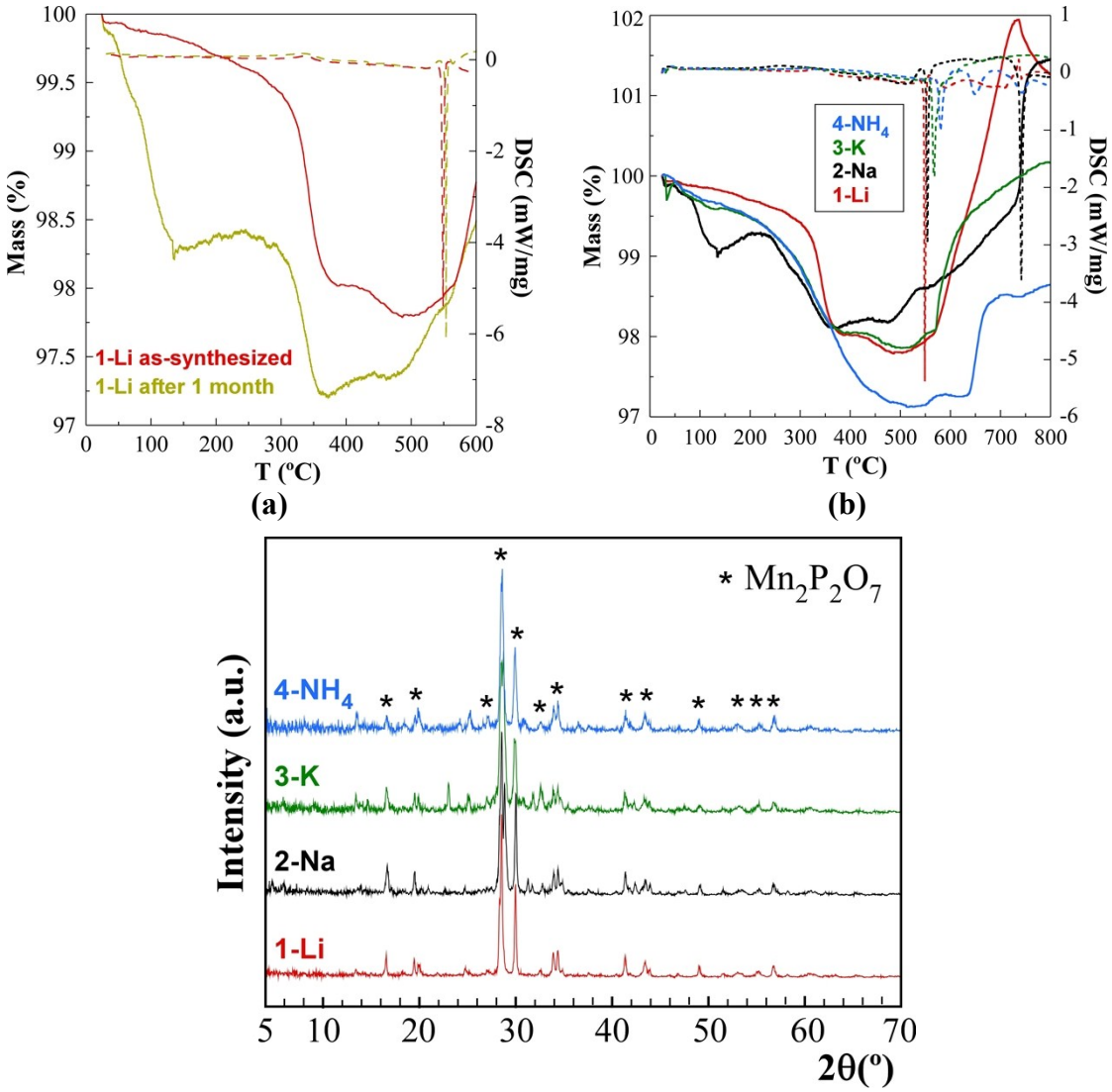


**Figure S4. (a)** Comparison of thermal analysis (TGA, DSC) of **1-Li** as-synthesized and exposed a month to ambient conditions. **(b)** Thermal analysis (TGA, DSC) of **1-Li**, **2-Na**, **3-K** and **4-NH$_4$**. **(c)** Diffraction patterns of calcination products after heat treatment.

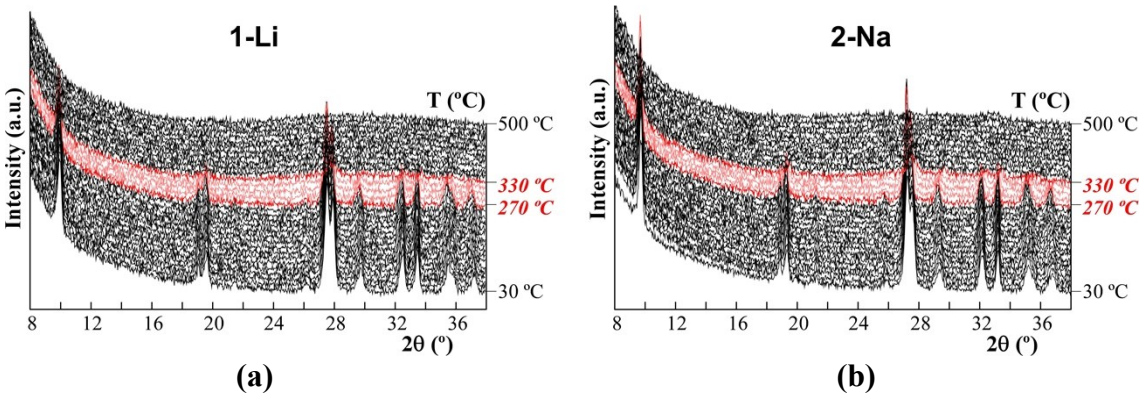


**Figure S5.** Thermodiffractograms of **(a) 1-Li** and **(b) 2-Na**.

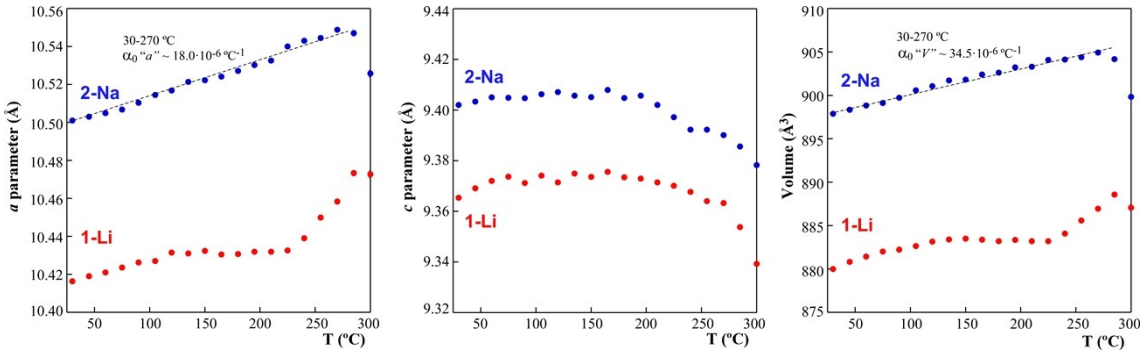


**Figure S6.** Thermal evolution of the parameters and volume of the unit cells for **1-Li** and **2-Na** in the 30 to 300 ºC temperature range.

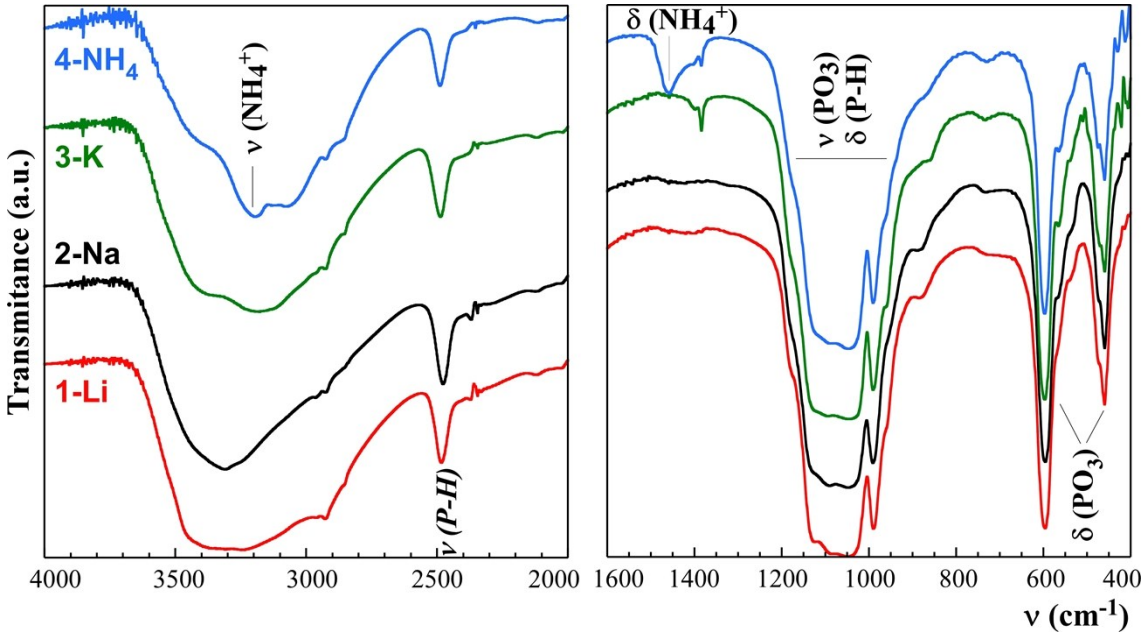


**Figure S7.** Infrared spectra of **1-Li**, **2-Na**, **3-K** and **4-NH$_4$**.

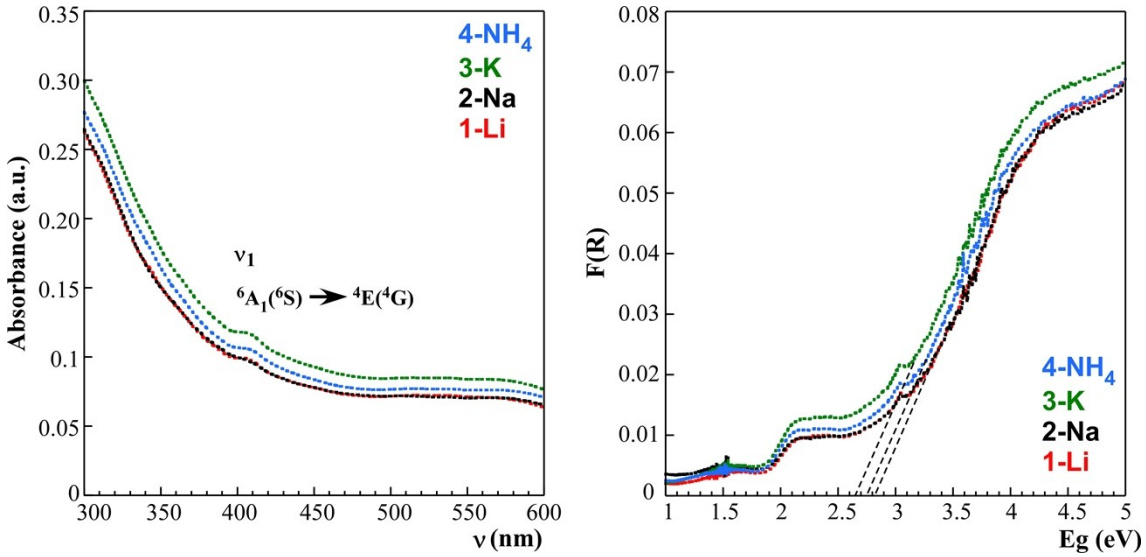


**Figure S8. (a)** UV-Vis diffuse absorbance spectra and **(b)** the corresponding F(R) *vs* E (eV) curves of **1-Li**, **2-Na**, **3-K** and **4-NH$_4$**.

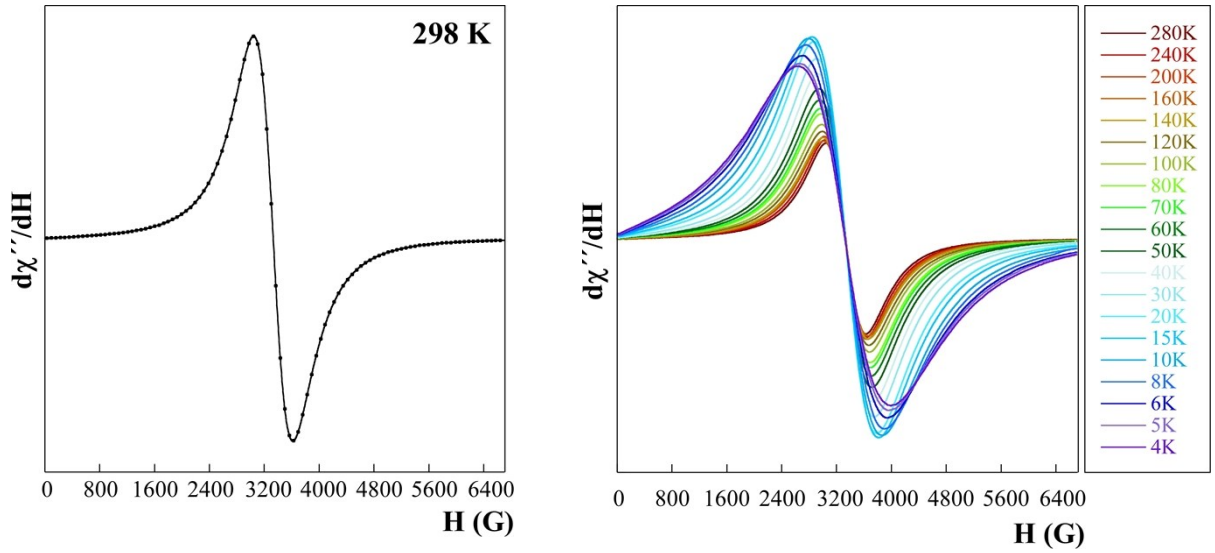


**Figure S9. (a)** X-band powdered EPR spectra at room temperature for **1-Li**. **(b)** Thermal evolution in the 280 to 4K temperature range of **1-Li**.

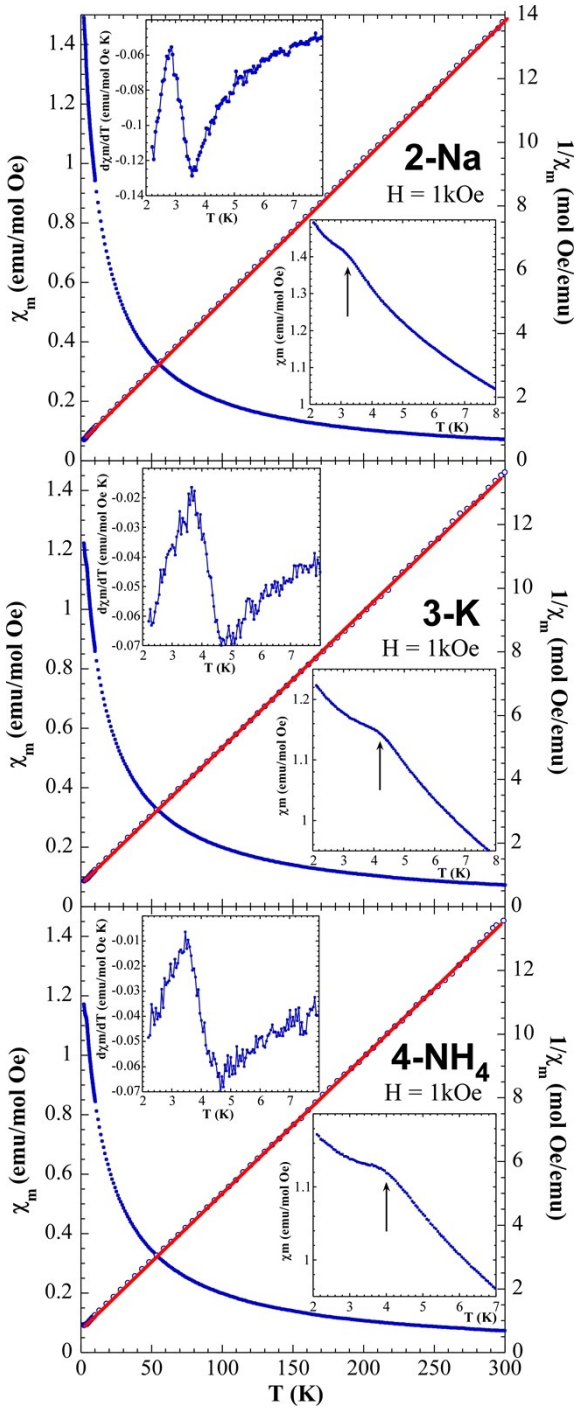


**Figure S10.** Temperature dependence of the molar susceptibility ($\chi_m$) and $1/\chi_m$ measured at 1 kOe for **2-Na**, **3-K** and **4-NH$_4$** compounds. The solid red lines are the fits according to Curie–Weiss law. The insets show an enlargement of the low temperature region, in the lower the susceptibility ($\chi_m$) and in the upper the derivative of the susceptibility ($d\chi_m/dT$).

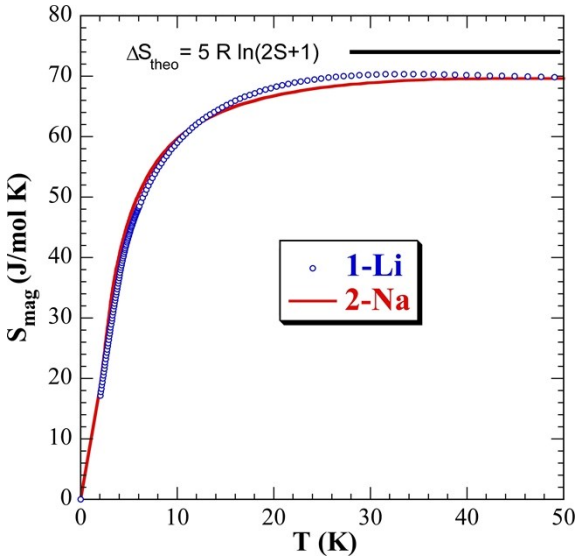


**Figure S11.** Thermal dependence of the magnetic entropy ($S_{mag}$) of **1-Li** and **2-Na** compounds. The horizontal solid line represents the theoretical value, $\Delta S_{theo}= 5R \ln (2S+1)= 74.2$ J/mol K, expected for 5 magnetic ions with a $S$=5/2 spin state.

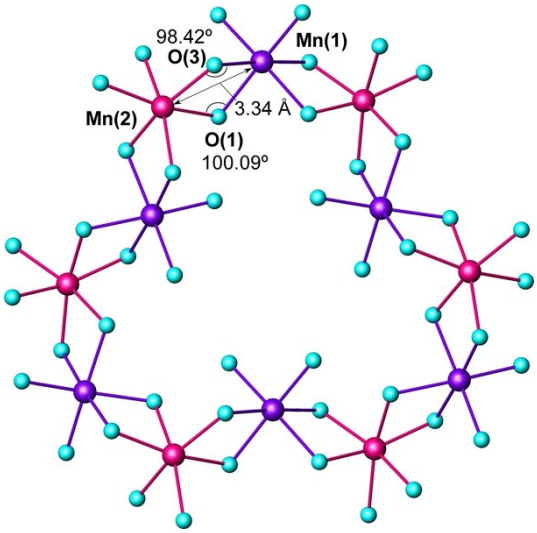


**Figure S12.** Schematic view of the most important magnetic exchange pathways for **1-Li**.