# **Electronic Supplementary Information**

## Three to Tango Requires a Site-Specific Substitution: Hetero*tri*metallic Molecular Precursor for High-Voltage Batteries

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#### **Experimental Section. General Procedures**

All manipulations were carried out in a dry, oxygen-free argon atmosphere by employing standard Schlenk and glove box techniques. Anhydrous manganese(II) chloride (MnCl<sub>2</sub>), anhydrous cobalt(II) chloride (CoCl<sub>2</sub>), lithium methoxide (LiOMe), and 2,2,6,6-tetramethyl-3,5heptanedione (Hthd) were purchased from Sigma-Aldrich and used as received. Li(thd) was prepared according to the previously published procedure.<sup>1</sup> The attenuated total reflection (ATR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained on a Bruker Avance 400 spectrometer at 400 MHz for <sup>1</sup>H and at 155.5 MHz for <sup>7</sup>Li. Chemical shifts ( $\delta$ ) are given in ppm relative to the residual solvent peaks for <sup>1</sup>H, and to the <sup>7</sup>Li peak of external standard (0.1 M solution of LiCl in D<sub>2</sub>O). Mass spectra were acquired using a DART-SVP ion source (IonSense, Saugus, MA, USA) coupled to a JEOL AccuTOF time-offlight mass spectrometer (JEOL USA, Peabody, MA, USA) in positive ion mode. Spectra were recorded over the mass range of m/z 50–2000 at one spectrum per second with a gas heater temperature of 350 °C. Thermogravimetric (TGA) measurements were carried out under air at a heating rate of 5 °C/min using a TGA 2050 Thermogravimetric Analyzer, SDT Q600 V20.9 Build 20 Instruments. Thermal decomposition of heterometallic precursors was studied in air at ambient pressure. The solid samples (ca. 40 mg) were placed into a 20 mL Coors high-alumina crucible (Aldrich) and heated at a rate of ca. 35 °C/min in a muffle furnace (Lindberg Blue M). The decomposition residues were analyzed by X-ray powder diffraction. X-ray powder diffraction data were collected on a Bruker D8 Advance diffractometer (Cu Ka radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, step of 0.02° 20, 20 °C). The crystalline samples under investigation were ground and placed in the dome-like airtight zerobackground holders inside a glove box. Le Bail fit for powder diffraction patterns has been performed using TOPAS, version 4 software package (Bruker AXS, 2006). Magnetic properties were measured on polycrystalline samples, using a superconducting quantum interference device (SQUID) magnetometer MPMS-XL (Quantum Design). The samples were contained in sealed NMR tubes to avoid oxidation. Magnetic susceptibility was measured in a direct-current (DC) applied magnetic field of 0.1 T in the 1.8-300 K temperature range. Field-dependent magnetization data were collected at 1.8 K with the DC applied magnetic field varying from 0 to 7 T. The data were corrected for the diamagnetic contribution from the sample holder and for the intrinsic diamagnetism using tabulated constants.<sup>2</sup> The LiMn<sub>2-x</sub>Co<sub>x</sub>O<sub>4</sub> oxide samples for electron diffraction investigation were prepared by crushing the microcrystalline powder in a mortar in ethanol and depositing drops of suspension onto holey carbon grids. Electron diffraction (ED) patterns, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray (EDX) spectra were obtained with an aberration-corrected Titan G3 electron microscope that is operated at 200 kV and equipped with Super-X EDX system.

#### **Synthesis of Heterometallic Precursors**

#### LiMnCo(thd)5 (1a)

*Solid State Synthesis.* Anhydrous MnCl<sub>2</sub> (10 mg, 0.079 mmol) and CoCl<sub>2</sub> (10 mg, 0.079 mmol) were finely ground in an agate mortar. The resultant powder was mixed with Li(thd) (76 mg, 0.40 mmol) and sealed in an evacuated glass ampule, which was placed in an electric furnace. The ampule was kept at 110 °C for 6 weeks to allow purple crystals to be deposited in the cold section of the container, where the temperature was set approximately 5 °C lower. Yield is *ca.* 54 mg (65%, crystals collected).

*Solution Synthesis*. A mixture of Li(thd) (378 mg, 1.98 mmol), MnCl<sub>2</sub> (50 mg, 0.40 mmol), and CoCl<sub>2</sub> (50 mg, 0.40 mmol) in 50 mL of anhydrous toluene was refluxed (at *ca.* 111 °C) for 3 weeks, resulting in a cloudy purple solution. After LiCl was filtered off, the solvent was evaporated under vacuum at room temperature. The final product was obtained by further drying the residue under vacuum at 80 °C overnight. Yield is *ca.* 370 mg (90%). The purity of crystalline product was confirmed by X-ray powder diffraction (Figure S1 and Table S1).

#### LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (1b)

*Solid State Synthesis.* Anhydrous MnCl<sub>2</sub> (29 mg, 0.23 mmol) and CoCl<sub>2</sub> (10 mg, 0.077 mmol) were finely ground in an agate mortar. The resultant powder was mixed with Li(thd) (146 mg, 0.77 mmol) and sealed in an evacuated glass ampule, which was placed in an electric furnace. The ampule was kept at 110 °C for 1 month to allow light-purple crystals to be deposited in the cold section of the container, where the temperature was set approximately 5 °C lower. Yield is *ca.* 112 mg. (70%, crystals collected).

*Solution Synthesis*. A mixture of Li(thd) (438 mg, 2.30 mmol), MnCl<sub>2</sub> (87 mg, 0.69 mmol), and CoCl<sub>2</sub> (30 mg, 0.24 mmol) in 50 mL of anhydrous toluene was refluxed (at *ca.* 111 °C) for 2 weeks, resulting in a cloudy purple solution. After LiCl was filtered off, the solvent was evaporated under vacuum at room temperature. The final product was obtained by further drying the residue under vacuum at 80 °C overnight. Yield is *ca.* 430 mg (90%). The purity of crystalline product was confirmed by X-ray powder diffraction (Figure S2 and Table S2).



### X-ray Powder Diffraction Analysis of Heterometallic Precursors

Figure S1. X-ray powder diffraction pattern of LiMnCo(thd)<sub>5</sub> (1a) and the Le Bail fit. The red and blue curves are experimental and calculated patterns, respectively. The grey line is the difference curve with the theoretical positions shown at the bottom as black lines.

 Table S1. Unit Cell Parameters for LiMnCo(thd)5 (1a) Obtained from the Le Bail Fit and from the Single Crystal Data

	Le Bail Fit (20 °C) Single Crystal (-173	
Sp. Gr.	P	-1
a (Å)	11.590(2)	11.5810(13)
<i>b</i> (Å)	20.246(4)	20.328(2)
<i>c</i> (Å)	27.885(6)	27.709(3)
α (°)	68.834(3)	68.6870(10)
$\beta$ (°)	88.406(4)	88.4340(10)
γ (°)	80.583(3)	80.5250(10)
$V(\text{\AA}^3)$	6014.3(6)	5990.2(12)



**Figure S2.** X-ray powder diffraction pattern of  $\text{LiMn}_{1.5}\text{Co}_{0.5}(\text{thd})_5$  (**1b**) and the Le Bail fit. The red and blue curves are experimental and calculated patterns, respectively. The grey line is the difference curve with the theoretical positions shown at the bottom as black lines.

	Le Bail Fit (20 °C)	Single Crystal (173 °C)
Sp. Gr.		<i>P</i> -1
a (Å)	11.580(2)	11.5679(4)
<i>b</i> (Å)	20.263(2)	20.2647(6)
<i>c</i> (Å)	27.782(2)	27.7420(7)
α (°)	68.684(2)	68.6974(7)
β (°)	88.512(2)	88.5520(8)
γ (°)	80.506(2)	80.5081(8)
$V(\text{\AA}^3)$	5985.6(8)	5971.7(3)

**Table S2.** Unit Cell Parameters for LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) Obtained from the Le Bail Fit and from the Single Crystal Data

#### **Crystal Growth**

*Single Crystal X-ray Diffraction.* Block-shaped crystals of LiMnCo(thd)<sup>5</sup> (1a) suitable for X-ray structural measurements were obtained directly from the solid state reaction described above: sublimation of the bulk material in an evacuated glass ampule placed in an electric furnace at 100 °C with a temperature gradient of approximately 5 °C along the length of the container.

*Single Crystal Resonant Diffraction.* Very small crystals of heterometallic precursor  $LiMn_{1.5}Co_{0.5}(thd)_5$  (**1b**) suitable for the resonant diffraction measurements were obtained directly from the solid state reaction described above: sublimation of the bulk material in an evacuated glass ampule placed in an electric furnace at 100 °C with a temperature gradient of approximately 5 °C along the length of the container.

Compound	LiMnCo(thd)5 (1a)	LiMn1.5C00.5(thd)5 (1b)	LiMn2(thd)5
Shape	block	block	block
Color	dark-purple	purple	bright-yellow
Crystal Growth Method	sublimation	sublimation	sublimation
Temperature (°C)	100	100	105
Volatility (°C)	90	90	90
Decomposition (°C)	115	115	110

	Table S3. Single	Crystal Growth	Conditions and	Properties of	of Heterometallic	Precursors.
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#### Single Crystal X-ray Crystallographic Procedures

The single crystal diffraction data for  $LiMnCo(thd)_5$  (1a) were measured at 100 K on a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite monochromated Mo  $K_{\alpha}$ radiation source ( $\lambda = 0.71073$  Å). Data reduction and integration were performed with the Bruker software package SAINT (version 8.34A).<sup>3</sup> Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).<sup>4</sup> The structure was solved by SHELXT (version 2014/5)<sup>5</sup> and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2016/6)<sup>6</sup> software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions for structure factor calculations with  $U_{iso}(H) = 1.2 U_{eq}(C)$  and  $U_{iso}(H) = 1.5 U_{eq}(C)$  for methyl groups. The highly disordered molecule in the asymmetric unit was modeled with anisotropic thermal parameters using similarity restraints (SAME command in SHELXL). One of the tert-butyl groups in the ordered molecule was also modeled with anisotropic thermal parameters using similarity restraints (SAME command in SHELXL). The displacement parameters of disordered parts were also restrained with the combination of RIGU/SIMU commands. All restraint commands were applied using their SHELXTL program default estimated standard deviations. Crystallographic data, details of the data collection and structure refinement for LiMnCo(thd)5 (1a) are listed in Table S4.

#### **Resonant Diffraction Crystallographic Procedures**

A single crystal of LiMn1.5C00.5(thd)5 (1b) heterometallic complex was mounted on a glass fiber and cooled to 100 K using an Oxford Instruments Cryojet cryostat. The Bruker D8 diffractometer, integrated with an APEX-II CCD detector, was modified for synchrotron use at the NSF's ChemMatCARS 15-ID-B beamline at the Advanced Photon Source (Argonne National Laboratory). Diffraction data were collected at seven different energies with 0.5 s frames using  $\phi$  scans, while manually attenuating the beam to minimize overages of individual pixels. Data reduction and integration were performed with the Bruker APEX3 software package (Bruker AXS, version 2015.5-2). Data were scaled and corrected for absorption effects using the multi-scan procedure as implemented in SADABS (Bruker AXS, version 2014/5, part of Bruker APEX3 software package). The structure was solved by SHELXT<sup>5</sup> and refined by a full-matrix least-squares procedure using OLEX2.<sup>5, 7, 8</sup> The scan at 30.0 keV, which is energetically well above the atomic absorption energies, provided a least-squares refinement of all model positional and displacement parameters. Crystallographic data, details of the data collection and structure refinement for LiMn1.5C00.5(thd)5 (1b) are listed in Table S4.

A total of seven datasets were collected for the LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) crystal, among those six anomalous diffraction data sets were collected near or at the absorption *K*-edges of Mn and Co. Three datasets spanning the absorption *K*-edges of each metal were collected. Mn *K*-edge: 6.489 keV (1.9107 Å), 6.539 keV ( $\lambda = 1.8961$  Å), and 6.589 keV (1.8817 Å); Co *K*-edge: 7.659 keV (1.6188 Å), 7.709 keV ( $\lambda = 1.6083$  Å), and 7.759 (1.5979 Å). Drop of electron density at the particular metal site followed by its increase assured covering of the *K*-edge of the metal (Figures S7, S8). For further refinement of Mn/Co site compositions, anomalous data sets collected at the lower-energy side of the absorption edge were used to minimize solid-state effects neglected for calculations of dispersion factors.<sup>9-12</sup> The corresponding occupancies were constrained such as the total site occupation did not exceed unity. GSAS-II refinement package<sup>13</sup> allows utilization of multiple diffraction data sets for refinement of the common crystallographic model. This method has the benefits of reporting refined values with standard uncertainties and provides a straightforward scaling of the different anomalous data sets. The converged positional and displacement parameters of the structural model derived from the 30 keV data were utilized and kept fixed while the Mn/Co occupancies of the two metal sites were refined. For refinement, each metal site was described as occupied by both Mn and Co with their coordinates fixed to be the same and their sum of occupancies constrained to 1. For the second fully disordered molecule, occupancies of Co and Mn were constrained to be the same and their sum of occupancies constrained to be 0.5 for each of two enantiomeric parts. Difference Fourier electron density maps at the Mn and Co *K*-edges were obtained by generating structure factor files without least-square refinements of the atomic model derived from the data set at 30 keV with the reflection data obtained at the respective metal absorption edges. The maps were visualized with the program OLEX2.<sup>7</sup>

Compound	LiMnCo(thd)5(1a)	LiMn1.5C00.5(thd)5 (1b)
Empirical formula	C55H95CoLiMnO10	C55H95C00.5LiMn1.5O10
Formula weight	1037.11	1035.12
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.41328
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	11.5810(13)	11.5679(4)
<i>b</i> (Å)	20.328(2)	20.2647(6)
<i>c</i> (Å)	27.709(3)	27.7420(7)
α (°)	68.6870(10)	68.6974(7)
$\beta(^{\circ})$	88.4340(10)	88.5520(8)
$\gamma(^{\circ})$	80.5250(10)	80.5081(8)
$V(Å^3)$	5990.2(12)	5971.7(3)
Ζ	4	4
$ ho_{ m calcd}  ( m g \cdot  m cm^{-3})$	1.150	1.151
$\mu$ (mm <sup>-1</sup> )	0.537	0.124
<i>F</i> (000)	2240	2236
Crystal size (mm)	0.350×0.320×0.180	0.024×0.023×0.011
$\theta$ range for data	1.558-28.281	0.636-15.996
Reflections collected	53088	170703
Independent reflections	27027, [ $R_{int} = 0.0333$ ]	28845, $[R_{int} = 0.0916]$
Transmission factors	0.8790/1	0.9357/1
Data/restraints/params.	27027/3733/1857	28845/2781/1868
$R1,^{a} wR2^{b} (I > 2\sigma(I))$	0.0554, 0.1326	0.0465, 0.1099
$R1$ , <sup>a</sup> $wR2^{b}$ (all data)	0.0918, 0.1553	0.0735, 0.1238
Quality-of-fit <sup>c</sup>	1.024	1.018
Largest diff. peak and hole	0.777 and -0.563	0.652 and -0.528

Table S4. Crystal Data and Structure Refinement Parameters for LiMnCo(thd)5 (1a) and LiMn1.5Co0.5(thd)5 (1b).

 ${}^{a}R1 = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR2 = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]].$   ${}^{c}Quality-of-fit = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / (N_{obs} - N_{params})]^{1/2}, \text{ based on all data.}$ 

#### Solid State Structures of Heterometallic Precursors



**Figure S3.** Molecular structure of the ordered unit in LiMnCo(thd)<sup>5</sup> (1a) drawn with thermal ellipsoids at 40% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only metal and oxygen atoms are labeled. The lithium–oxygen and transition metal–oxygen bonds to the thd ligands involved in bridging interactions are shown in blue.

Bond distances					
Mn(1)–O(1)*	2.1641(18)	Co(1)–O(3)*	2.0910(17)	Li(1)-O(1)**	2.003(5)
Mn(1)–O(4)*	2.1972(16)	Co(1)–O(4)*	2.1427(16)	Li(1)–O(2)	1.827(5)
Mn(1)-O(7)*	2.3229(17)	Co(1)–O(5)	2.0190(17)	Li(1)-O(3)*	2.094(5)
Mn(1)–O(8)*	2.3143(16)	Co(1)–O(6)	1.9907(17)	Li(1)-O(8)*	1.942(5)
Mn(1)–O(9)	2.0786(17)	Co(1)–O(7)*	2.1367(17)		
Mn(1)-O(10)	2.0561(17)	Co(1)–O(8)*	2.2555(16)		
		Angles		1	
O(1)-Mn(1)-O(4)	80.68(6)	O(3)–Co(1)–O(4)	77.98(6)	O(1)–Li(1)–O(3)	148.8(3)
O(1)-Mn(1)-O(7)	142.09(6)	O(3)–Co(1)–O(7)	149.24(7)	O(2)–Li(1)–O(1)	106.2(2)
O(1)-Mn(1)-O(8)	77.50(6)	O(3)–Co(1)–O(8)	81.05(6)	O(2)–Li(1)–O(3)	132.2(3)
O(4)-Mn(1)-O(7)	77.15(6)	O(4)-Co(1)-O(8)	80.11(6)	O(2)–Li(1)–O(8)	97.1(2)
O(4)-Mn(1)-O(8)	77.71(6)	O(5)-Co(1)-O(3)	101.09(7)	O(8)–Li(1)–O(1)	88.83(18)
O(8)-Mn(1)-O(7)	68.01(6)	O(5)-Co(1)-O(4)	91.96(6)	O(8)–Li(1)–O(3)	90.64(19)
O(9)–Mn(1)–O(1)	103.29(7)	O(5)–Co(1)–O(7)	103.09(7)		
O(9)-Mn(1)-O(4)	169.17(6)	O(5)-Co(1)-O(8)	171.23(6)		
O(9)-Mn(1)-O(7)	94.09(6)	O(6)-Co(1)-O(3)	97.25(7)		
O(9)–Mn(1)–O(8)	93.19(6)	O(6)-Co(1)-O(4)	174.92(7)		
O(10)–Mn(1)–O(1)	118.27(7)	O(6)-Co(1)-O(5)	90.66(7)		
O(10)-Mn(1)-O(4)	100.69(6)	O(6)-Co(1)-O(7)	101.19(7)		
O(10)-Mn(1)-O(7)	95.95(6)	O(6)-Co(1)-O(8)	97.54(7)		
O(10)–Mn(1)–O(8)	163.91(6)	O(7)–Co(1)–O(4)	82.45(6)		
O(10)-Mn(1)-O(9)	86.41(7)	O(7)–Co(1)–O(8)	72.33(6)		

**Table S5.** Selected Bond Distances (Å) and Angles (deg.) for the Ordered Unit in the Structureof LiMnCo(thd)5 (1a).

\* – bridging oxygen; \*\* – chelating-bridging oxygen



**Figure S4.** Two parts (enantiomers) of the disordered unit in the structure of [LiMnCo(thd)<sub>5</sub>] cocrystallized in a 1:1 ratio. All hydrogen atoms and 'Bu groups are omitted for clarity.



**Figure S5.** Different 3*d* transition metal position assignments in the ordered unit of the molecular structure of heterometallic precursor  $LiMnCo(thd)_5$  (1a). See Table S6 for the results of structure refinement.

	<i>R</i> 1	<i>S</i> *	Highest <i>Q</i> Peak	Uiso M(left)	Uiso M(right)
LiMnCo(thd)5 (Figure S5a)	0.0554	1.024	0.43 (0.90 Å from Co(1)) -0.56 (0.67 Å from Co(1)) 0.30 (1.04 Å from Mn(1))	0.02260(9)	0.02609(9)
LiMn2(thd)5 (Figure S5b)	0.0540	1.002	0.84 (0.55 Å from Mn(1)) 0.33 (0.95 Å from Mn(2)) -0.28 (0.68 Å from Mn(2))	0.02419(9)	0.01966(9)
LiCoMn(thd)5 (Figure S5c)	0.0563	1.118	0.43 (0.95 Å from Mn(1)) -0.41 (0.60 Å from Co(1))	0.03101(9)	0.01828(9)
LiCo2(thd)5 (Figure S5d)	0.0602	1.121	-0.69 (0.64 Å from Co(2)) -0.61 (0.60 Å from Co(1)) 0.54 (0.78 Å from Co(1))	0.02938(10)	0.02465(10)
LiMnCo(thd)5 (Figure S5e)	0.0558	1.031	0.68 (0.64 Å from Mn/Co(2)) -0.48 (0.67 Å from Mn/Co(1))	0.02682(10)	0.02220(9)

**Table S6.** Refinement Results for the Crystal Structure of LiMnCo(thd)5 (1a) Based on Different3d Transition Metal Position Assignments (Figure S5).

\* S value is obtained by refinement based on the weighting scheme: WGHT 0.0772 0.6569



**Figure S6.** Molecular structure of the ordered unit in LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) drawn with thermal ellipsoids at 40% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only metal and oxygen atoms are labeled. The lithium–oxygen and transition metal–oxygen bonds to the thd ligands involved in bridging interaction are shown in blue. The M(1) position was refined with a mixed-occupancy of Mn/Co = 0.5:0.5.

Bond distances					
Mn(2)–O(1)*	2.1645(12)	M(1)–O(3)*	2.1087(13)	Li(1)-O(1)**	1.997(4)
Mn(2)–O(4)*	2.1991(12)	M(1)–O(4)*	2.1552(12)	Li(1)–O(2)	1.825(3)
Mn(2)–O(7)*	2.3240(12)	M(1)–O(5)	2.0373(13)	Li(1)-O(3)*	2.091(4)
Mn(2)–O(8)*	2.3057(12)	M(1)–O(6)	2.0052(13)	Li(1)–O(8)*	1.941(3)
Mn(2)–O(9)	2.0761(12)	M(1)-O(7)*	2.1516(13)		
Mn(2)–O(10)	2.0563(13)	M(1)–O(8)*	2.2674(12)		
		Angles		1	
O(1)–Mn(2)–O(4)	80.57(5)	O(3)–M(1)–O(4)	77.29(5)	O(1)–Li(1)–O(3)	149.34(19)
O(1)-Mn(2)-O(7)	142.38(5)	O(3)–M(1)–O(7)	148.20(5)	O(2)–Li(1)–O(4)	96.88(15)
O(1)-Mn(2)-O(8)	77.56(4)	O(3)–M(1)–O(8)	80.59(5)	O(2)–Li(1)–O(1)	105.78(16)
O(4)-Mn(2)-O(7)	77.54(4)	O(4)–M(1)–O(8)	79.37(4)	O(2)–Li(1)–O(3)	132.12(19)
O(4)–Mn(2)–O(8)	77.65(4)	O(5)–M(1)–O(3)	101.35(5)	O(8)–Li(1)–O(4)	90.71(14)
O(8)–Mn(2)–O(7)	68.12(4)	O(5)–M(1)–O(4)	92.60(5)	O(8)–Li(1)–O(8)	89.19(13)
O(9)–Mn(2)–O(1)	103.40(5)	O(5)–M(1)–O(7)	103.71(5)		
O(9)–Mn(2)–O(4)	169.21(5)	O(5)–M(1)–O(8)	171.18(5)		
O(9)-Mn(2)-O(7)	93.75(5)	O(6)-M(1)-O(3)	97.52(5)		
O(9)–Mn(2)–O(8)	93.29(5)	O(6)-M(1)-O(4)	174.68(5)		
O(10)–Mn(2)–O(1)	118.23(5)	O(6)-M(1)-O(5)	89.53(5)		
O(10)–Mn(2)–O(4)	100.77(5)	O(6)-M(1)-O(7)	101.93(5)		
O(10)-Mn(2)-O(7)	95.80(5)	O(6)-M(1)-O(8)	98.79(5)		
O(10)–Mn(2)–O(8)	163.87(5)	O(7)–M(1)–O(4)	82.30(5)		
O(10)-Mn(2)-O(9)	86.29(5)	O(7)–M(1)–O(8)	71.80(4)		
				1	

**Table S7.** Selected Bond Distances (Å) and Angles (deg.) for the Ordered Unit in the Structure of LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**).

\* – bridging oxygen; \*\* – chelating-bridging oxygen



**Figure S7.** Difference Fourier electron density maps at the Co *K*-edge for ordered (top) and disordered (bottom) units in the structure of LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) (grid spacing is 0.05 Å).



**Figure S8.** Difference Fourier electron density maps at the Mn *K*-edge for ordered (top) and disordered (bottom) units in the structure of LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) (grid spacing is 0.05 Å).

### Crystal Structure of the Parent LiMn<sub>2</sub>(thd)<sub>5</sub> Molecule



**Figure S9.** Solid state structure of ordered unit in LiMn<sub>2</sub>(thd)<sub>5</sub>.<sup>1</sup> Hydrogen atoms and *tert*-butyl groups are omitted for clarity.

Table S8. Selected O-Mn-O Angles around Mn1 and Mn2 Positions in the Structure of LiMn2(thd)5.<sup>1</sup>

	Angles (°)		Angles (°)		
O-Mn1-O			O-Mn2-O		
O1–Mn1–O3	104.77(10)	O4–Mn2–O3	68.41(8)		
O1–Mn1–O5	102.29(10)	O6–Mn2–O3	78.32(9)		
O1-Mn1-O6	94.17(9)	O6–Mn2–O4	77.41(8)		
O2-Mn1-O1	87.46(10)	O7–Mn2–O3	92.98(9)		
O2-Mn1-O3	102.98(10)	O7–Mn2–O4	93.47(9)		
O2-Mn1-O4	100.81(9)	O7–Mn2–O10	103.81(10)		
O2-Mn1-O5	98.33(10)	O8–Mn2–O3	95.90(9)		
O3–Mn1–O4	70.93(8)	O8–Mn2–O6	100.81(9)		
O5–Mn1–O4	79.35(9)	O8–Mn2–O7	86.38(10)		
O5-Mn1-O6	75.84(9)	O8-Mn2-O10	117.47(10)		
O6–Mn1–O3	82.06(9)	O10–Mn2–O4	77.84(9)		
O6–Mn1–O4	77.87(9)	O10-Mn2-O6	80.19(9)		
σ	12.19	σ	13.95		
$\sigma = \{\Sigma[(x_n-90)^2]/$	$\sigma = \{ \Sigma[(x_n - 90)^2] / (n - 1) \}^{\frac{1}{2}}$				

	LiMnCo(thd)5 (1a)	LiMn <sub>1.5</sub> Co <sub>0.5</sub> (thd) <sub>5</sub> (1b)	LiMn <sub>2</sub> (thd) <sub>5</sub>
Sp. Gr.		<i>P</i> -1	
Ζ		4	
a (Å)	11.5810(13)	11.5679(4)	11.590(2)
<b>b</b> (Å)	20.328(2)	20.2647(6)	20.246(4)
c (Å)	27.709(3)	27.7420(7)	27.885(6)
α (Å)	68.6870(10)	68.6974(7)	68.834(3)
<b>β</b> (Å)	88.4340(10)	88.5520(8)	84.406(4)
γ (Å)	80.5250(10)	80.5081(8)	80.583(3)
$V(\text{\AA}^3)$	5990.2(12)	5971.7(3)	6014(2)

**Table S9.** Unit Cell Parameters of Heterometallic Compounds LiMnCo(thd)5 (1a),LiMn1.5C00.5(thd)5 (1b), and LiMn2(thd)5.1

## ATR-IR Spectrum of Heterometallic Precursors



Figure S10. The attenuated total reflection (ATR) spectrum of LiMnCo(thd)5 (1a).



Figure S11. The attenuated total reflection (ATR) spectrum of LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (1b).

### Multinuclear NMR Investigation of LiMnCo(thd)<sub>5</sub> (1a).

## <sup>1</sup>H in CDCl<sub>3</sub>



Figure S12. <sup>1</sup>H NMR spectrum of LiMnCo(thd)<sub>5</sub> (1a) in CDCl<sub>3</sub> recorded at room temperature.



Figure S13. <sup>7</sup>Li NMR spectrum of LiMnCo(thd)<sub>5</sub> (1a) in CDCl<sub>3</sub> recorded at room temperature.



Figure S14. <sup>1</sup>H NMR spectrum of LiMnCo(thd)<sub>5</sub> (1a) in  $d^6$ -acetone recorded at room temperature.

<sup>7</sup>Li in Acetone



Figure S15. <sup>7</sup>Li NMR spectrum of LiMnCo(thd)<sub>5</sub> (1a) in  $d^6$ -acetone recorded at room temperature.



Figure S16. <sup>1</sup>H NMR of LiMnCo(thd)<sub>5</sub> (1a) in D<sub>2</sub>O recorded at room temperature.

## <sup>7</sup>Li in D<sub>2</sub>O



Figure S17. <sup>7</sup>Li NMR of LiMnCo(thd)<sub>5</sub> (1a) in D<sub>2</sub>O recorded at room temperature.



Figure S18. <sup>1</sup>H NMR spectra of LiMnCo(thd)<sub>5</sub> (1a) and Li(thd) in  $d^6$ -DMSO recorded at room temperature.



**Figure S19.** <sup>7</sup>Li NMR spectra of LiMnCo(thd)<sub>5</sub> (1a) and Li(thd) in *d*<sup>6</sup>-DMSO recorded at room temperature.

#### **DART Mass Spectra of Heterometallic Precursors**



**Figure S20.** Positive-ion DART mass spectrum of solid LiMnCo(thd)<sub>5</sub> (1a). The isotope distribution patterns for the  $[LiMnCoL_4]^+$  (L = thd) ion is inset (black and purple lines are experimental and calculated patterns, respectively).

Ions	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Δ	% Base
$[LiMnCoL_5 + H]^+$	1037.5812	1037.5877	-0.0065	6.0
[LiMnCoL₄] <sup>+</sup>	853.4409	853.4414	-0.0005	10.0
$[MnCoL_4 + H]^+$	847.4302	847.4331	-0.0029	39.9
$[\mathrm{Li}_{2}\mathrm{CoL}_{4}+\mathrm{H}]^{+}$	806.5209	806.5272	-0.0063	5.0
$[\text{Li}_{2}\text{MnL}_{4} + \text{H}]^{+}$	802.5297	802.5321	-0.0024	33.9
[MnCoL <sub>3</sub> ] <sup>+</sup>	663.2883	663.2868	0.0015	2.7
[Li <sub>2</sub> CoL <sub>3</sub> ] <sup>+</sup>	622.3808	622.3809	-0.0001	11.6
$[\mathrm{Li}_{2}\mathrm{MnL}_{3}]^{+}$	618.3880	618.3857	0.0023	10.9
$[LiCoL_3 + H]^+$	616.3705	616.3726	-0.0021	1.8
$[\text{LiMnL}_3 + \text{H}]^+$	612.3791	612.3775	0.0016	13.1
$\left[\operatorname{CoL}_2 + \operatorname{H}\right]^+$	426.2218	426.2180	-0.0038	67.0
$[MnL_2 + H]^+$	422.2228	422.2229	-0.0001	57.9
$\left[\mathbf{L}+\mathbf{2H}\right]^{+}$	185.1570	185.1542	0.0028	100

**Table S10.** Assignment of Ions Detected in the Positive-Ion DART Mass Spectrum of LiMnCoL<sub>5</sub> (1a) (L = thd =  $C_{11}H_{19}O_2$ ).

**Table S11.** Assignment of  $[LiMnCoL_4]^+$  Ions Detected in Positive-Ion DART Mass Spectrum ofSolid LiMnCoL5 (1a) (L = thd = C11H19O2).

Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental Abundance (%)	Theoretical Abundance (%)	Δ
852.4398	852.4404	7.8	7.9	-0.0006
853.4409	853.4413	100	100	-0.0005
854.4438	854.4447	45.8	47.9	-0.0009
855.4467	855.4478	12.6	13.0	-0.0011
856.4491	856.4508	1.8	2.5	-0.0017

Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental Abundance (%)	Theoretical Abundance (%)	Δ
847.4302	847.4331	100	100	-0.0029
848.4361	848.4365	48.8	47.2	-0.0004
849.4380	849.4396	13.3	14.6	-0.0016
850.4372	850.4426	2.6	3.9	-0.0054

**Table S12.** Assignment of  $[MnCoL_4+H]^+$  Ions Detected in Positive-Ion DART Mass Spectrumof Solid LiMnCoL5 (1a) (L = thd = C11H19O2).



**Figure S21.** Positive-ion DART mass spectrum of solid LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**). Spectrum in the inset (a) represents isotope distribution patterns of  $[LiMn_2L_4]^+$  and  $[MnCoL_4 + H]^+$  ions that are partially overlapped (orange/blue and black are calculated and experimental patterns, respectively). The isotope distribution pattern for the  $[LiMnCoL_4]^+$  ion is shown in the inset (b) (purple and black lines are calculated and experimental patterns, respectively).

Peak, <i>m/z</i>	[LiMn <sub>2</sub> L <sub>4</sub> ] <sup>+</sup>	[MnCoL <sub>4</sub> +H] <sup>+</sup>
847		100%
848	7.9%	48.8%
849	100%	13.3%
850	47.9%	2.6%
851	13.0%	0.4%
852	2.5	
853	0.4%	

**Table S13.** Relative Intensities of the Simulated Isotope Distribution Peaks for the  $[LiMn_2L_4]^+$  and  $[MnCoL_4+H]^+$  (L = thd) Ions.

Ions	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Δ	% Base
[LiMnCoL4] <sup>+</sup>	853.4409	853.4413	-0.0004	7.00
[LiMn <sub>2</sub> L <sub>4</sub> ] <sup>+</sup>	849.4423	849.4461	-0.0038	8.18
$\left[\mathrm{MnCoL}_4 + \mathrm{H}\right]^+$	847.4290	847.4331	-0.0041	35.57
$\left[\mathbf{Mn_2L_4}+\mathbf{H}\right]^+$	843.4370	843.4379	-0.0009	4.11
[MnCoL <sub>3</sub> ] <sup>+</sup>	663.2963	663.2868	0.0095	1.49
[Li2CoL3] <sup>+</sup>	622.3864	622.3807	0.0057	31.10
[Li <sub>2</sub> MnL <sub>3</sub> ] <sup>+</sup>	618.3959	618.3856	0.0103	5.73
[LiCoL3+H] <sup>+</sup>	616.3825	616.3725	0.0100	7.53
[LiMnL <sub>3</sub> +H] <sup>+</sup>	612.3859	612.3774	0.0085	13.59
[CoL <sub>2</sub> +H] <sup>+</sup>	426.2176	426.2180	-0.0004	100
[MnL <sub>2</sub> +H] <sup>+</sup>	422.2261	422.2229	0.0032	14.73

**Table S14.** Assignment of Ions Detected in the Positive-Ion DART Mass Spectrum of LiMn<sub>1.5</sub>Co<sub>0.5</sub>L<sub>5</sub> (**1b**) (L = thd = C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>).

**Table S15.** Assignment of  $[LiMnCoL_4]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Solid LiMn<sub>1.5</sub>Co<sub>0.5</sub>L<sub>5</sub> (1) (L = thd = C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>).

Measured, <i>m/z</i>	Calculated m/z	Experimental	Theoretical	1
		Abundance (%)	Abundance (%)	2
852.4393	852.4404	8.1	7.9	-0.0011
853.4409	853.4413	100	100	-0.0004
854.4405	854.4447	45.2	47.9	-0.0042
855.4459	855.4478	13.3	13.0	-0.0019
856.4494	856.4508	1.2	2.5	-0.0014



**Figure S22.** Simulated isotope distribution pattern (red) that consists of 18.7% of  $[LiMn_2L_4]^+$  and 81.3% of  $[MnCoL_4 + H]^+$  ions and experimental pattern (black).

**Table S16.** Comparasion of the Simulated Isotope Distribution Pattern that Consists of 18.7% of $[LiMn_2L_4]^+$  and 81.3% of  $[MnCoL_4 + H]^+$  Ions with Experimental Pattern.

Measured, <i>m/z</i>	Experimental Abundance (%)	Theoretical Abundance (%)
847.4290	100	100
848.4335	47.5	48.8
849.4423	19.8	23.0
850.4465	9.6	11.0
851.4528	2.5	3.0



**Figure S23.** Comparison of positive-ion DART mass spectra of (a) LiMnCo(thd)<sup>5</sup> (1a), (b) LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sup>5</sup> (1b), (c) LiMn<sub>2</sub>(thd)<sup>5</sup> and (d) theoretical isotope distribution patterns of  $[LiMn_2L_4]^+$ ,  $[LiMnCoL_4]^+$  and  $[LiCo_2L_4]^+$  ions (L = thd = C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>).

#### **Theoretical Calculations**

All geometry optimizations were performed at the DFT level of theory with a help of hybrid exchange-correlation functional PBE0 with Grimme's<sup>14, 15</sup> empiric dispersion corrections (here D3 type<sup>16</sup>). All atoms were described by TZVP basis sets. Relativistic effects were accounted explicitly through the ZORA approximation. The nature of stationary points on the potential energy surface (PES) was determined by calculation of the full Hessian matrix followed by computing harmonic vibrational frequencies. In order to accelerate calculations, all structures were pre-optimized using recently proposed method PBEh-3c.<sup>17</sup> In order to obtain better evaluation of energetics, single-point calculations were performed with recently developed double-hybrid DFT functional with empiric dispersion corrections (here B2PLYP-D3<sup>18</sup>). In order to accelerate calculations, the "chain-of-spheres" algorithm<sup>19</sup> was applied (RIJCOSX keyword in ORCA terminology). All calculations at this level of theory were performed using ORCA (v. 4.0.0) program suite.<sup>20</sup>

I (MM/(thd)-	Energy, a.u.		
	B2PLYP-D/TZVP/ZORA		
LiMnCo(thd)5 (Fig. S5a)	-80.26 kcal/mol		
LiMn <sub>2</sub> (thd) <sub>5</sub> (Fig. S5b)	-82.76 kcal/mol		
LiCoMn(thd)5 (Fig. S5c)	-76.10 kcal/mol		
LiCo <sub>2</sub> (thd) <sub>5</sub> (Fig. S5d)	-72.84 kcal/mol		

Table S17. Absolute Energies for all Systems at the B2PLYP-D Level of Theory.



Thermogravimetric Analysis (TGA) of Heterometallic Precursors

Figure S24. TGA diagrams of LiMnCo(thd)5 (1a, blue) and LiMn1.5Co0.5 (1b, red) recorded under air.

#### **Thermal Decomposition of Heterometallic Precursors**

Thermal decomposition of LiMnCo(thd)<sub>5</sub> (1a)



Figure S25. X-ray powder diffraction patterns of LiMnCoO<sub>4</sub> obtained by thermal decomposition of heterometallic precursor LiMnCo(thd)<sub>5</sub> (1a) at 400  $^{\circ}$ C (a) and at 550  $^{\circ}$ C (b).



**Figure S26.** X-ray powder diffraction pattern of LiMnCoO<sub>4</sub> obtained by thermal decomposition of heterometallic precursor LiMnCo(thd)<sub>5</sub> (**1a**) at 400 °C and the Le Bail fit. Blue and red lines are experimental and calculated patterns, respectively. Grey line is the difference curve with theoretical peak positions shown as black bars at the bottom.



Figure S27. X-ray powder diffraction pattern of LiMnCoO<sub>4</sub> obtained by thermal decomposition of heterometallic precursor LiMnCo(thd)<sub>5</sub> (1a) at 550 °C and the Le Bail fit. Blue and red lines are experimental and calculated patterns, respectively. Grey line is the difference curve with theoretical peak positions shown as black bars at the bottom.

**Table S18.** Comparison of the Unit Cell Parameters of LiMnCoO<sub>4</sub> Oxide Obtained by Thermal Decomposition of Heterometallic Precursor LiMnCo(thd)<sub>5</sub> (**1a**) at Different Temperatures with the Literature Data.

	400 °C	550 °C	Literature Data <sup>21</sup>
Space Group	Fd-3m		
<i>a</i> (Å)	8.0571(2)	8.0566(2)	8.05679(3)

Thermal decomposition of LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (1b)



**Figure S28.** X-ray powder diffraction patterns of LiMn<sub>1.5</sub>Co<sub>0.5</sub>O<sub>4</sub> obtained by thermal decomposition of heterometallic precursor LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) at 400 °C (a) and at 550 °C (b).



**Figure S29.** X-ray powder diffraction pattern of  $LiMn_{1.5}Co_{0.5}O_4$  obtained by thermal decomposition of heterometallic precursor  $LiMn_{1.5}Co_{0.5}(thd)_5$  (**1b**) at 400 °C and the Le Bail fit. Blue and red lines are experimental and calculated patterns, respectively. Grey line is the difference curve with theoretical peak positions shown as black bars at the bottom.



**Figure S30.** X-ray powder diffraction pattern of LiMn<sub>1.5</sub>Co<sub>0.5</sub>O<sub>4</sub> obtained by thermal decomposition of heterometallic precursor LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) at 550 °C and the Le Bail fit. Blue and red lines are experimental and calculated patterns, respectively. Grey line is the difference curve with theoretical peak positions shown as black bars at the bottom.

**Table S19.** Comparison of the Unit Cell Parameters of LiMn<sub>1.5</sub>Co<sub>0.5</sub>O<sub>4</sub> Oxide Obtained by Thermal Decomposition of Heterometallic Precursor LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (**1b**) at Different Temperatures with the Literature Data.

	400 °C	550 °C	Literature Data <sup>22</sup>
Space Group	Fd-3m		
<i>a</i> (Å)	8.1325(3)	8.1310(6)	8.1379(2)

Electron Microscopy Investigation of the LiMn<sub>2-x</sub>Co<sub>x</sub>O<sub>2</sub> Oxides



Figure S31. Electron diffraction patterns of LiMn<sub>1.5</sub>Co<sub>0.5</sub>O<sub>4</sub> obtained from the thermal decomposition of heterometallic precursor LiMn<sub>1.5</sub>Co<sub>0.5</sub>(thd)<sub>5</sub> (1b) at 550 °C.



Figure S32. TEM (a) and HAADF-STEM (b) images of  $LiMn_{1.5}Co_{0.5}O_4$  obtained from the thermal decomposition of heterometallic precursor  $LiMn_{1.5}Co_{0.5}(thd)_5$  (1b) at 550 °C.



**Figure S33.** HAADF-STEM image of LiMnCoO<sub>4</sub> along with the maps of the Mn and Co  $K_{\alpha}$  EDX signals and the color-coded mixed compositional map.



**Figure S34.** HAADF-STEM image of LiMn<sub>1.5</sub>Co<sub>0.5</sub>O<sub>4</sub> along with the maps of the Mn and Co  $K_{\alpha}$  EDX signals and the color-coded mixed compositional map.

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