# **Electronic Supplementary Information**

# Three body problem: Genuine hetero*tri*metallic molecule *vs.* a mixture of two parent hetero*bi*metallic molecules

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

All of the manipulations were carried out in a dry, oxygen-free argon atmosphere by employing standard Schlenk and glove box techniques. Anhydrous cobalt (II) chloride (CoCl<sub>2</sub>), nickel (II) chloride (NiCl<sub>2</sub>), magnesium chloride (MgCl<sub>2</sub>), lithium methoxide (LiOMe), lithium bis(trimethylsilyl)amide and tert-butyl acetoacetate (Htbaoac) were purchased from Sigma-Aldrich and used upon received. Li(tbaoac), Co(tbaoac)<sub>2</sub>, Mg(tbaoac)<sub>2</sub>, Ni(tbaoac)<sub>2</sub>, Li<sub>2</sub>Co<sub>2</sub>(tbaoac)<sub>6</sub>, and Li<sub>2</sub>Mg<sub>2</sub>(tbaoac)<sub>6</sub> were prepared according to the procedures described in literature.<sup>1, 2</sup> The yields of heterotrimetallic compounds Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1), Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2), and  $Li_2NiMg(tbaoac)_6$  (3) were calculated based on mass of the bulk product isolated from the corresponding reactions. The attenuated total reflection (ATR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained on a Bruker Advance 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-of-flight mass spectrometer (JEOL USA, Peabody, MA, USA) in positive ion mode. Spectra were recorded over the mass range of m/z 100–2000 at one spectrum per second with a gas heater temperature of 350 °C. Thermal decomposition of heterometallic precursors was studied in air at ambient pressure. The solid sample (ca. 40 mg) was 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  $0.02^{\circ} 2\theta$ , 20 °C). The crystalline samples under investigation were ground and placed in the dome-like airtight zero-background holders. Le Bail fit for powder diffraction patterns has been performed using TOPAS, version 4 software package (Bruker AXS, 2006). The LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> oxide sample for electron diffraction investigation was 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 a FEI Osiris electron microscope operated at 200 kV and equipped with a Super-X EDX system.

#### Synthesis of Heterobimetallic Complex Li2Ni2(tbaoac)6

*Method I.* A flask was loaded with Li(tbaoac) (0.500 g, 3.05 mmol) and Ni(tbaoac)<sub>2</sub> (1.135 g, 3.05 mmol) under argon atmosphere, and 50 mL of dry, oxygen-free dichloromethane was added. The green solution was stirred at room temperature for 6 h. The solvent was evaporated under vacuum at room temperature. Yield was *ca.* 1.472 g (90%). Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> is getting decomposed at the temperatures higher than 165 °C and is soluble in all common solvents. The purity of the bulk crystalline product was confirmed by X-ray powder diffraction analysis (Figure S1 and Table S4).

*Method II.* A flask was loaded with Li(tbaoac) (379 mg, 2.31 mmol) and NiCl<sub>2</sub> (100 mg, 0.769 mmol) under argon atmosphere, and 50 mL of dry, oxygen-free ethanol was added. The suspension was refluxed for 7 days, until the solution turned clear. The solvent was evaporated under vacuum at room temperature and the green solid residue was further dried under vacuum at 100 °C overnight. The final green product was isolated by extraction with dichloromethane followed by evaporation of the solvent at room temperature. Yield was *ca*. 0.372 g (90 %).

*Method III.* A mixture of Li(tbaoac) (57 mg, 0.35 mmol) and anhydrous NiCl<sub>2</sub> (15 mg, 0.12 mmol) was sealed in an evacuated glass ampule and was kept at 150 °C for 7 days during which the mixture turned to green color. The final product was resublimed at 145 °C under dynamic vacuum condition (cold finger). Yield was *ca.* 53 mg (85 %).

*Method IV.* A mixture of Li(tbaoac) (20 mg, 0.12 mmol) and Ni(tbaoac)<sub>2</sub> (46 mg, 0.12 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace without temperature gradient. The ampule was kept at 150 °C for 7 days. The resulting green product was further purified by dynamic vacuum sublimation (cold finger) at 160 °C. Yield was *ca.* 54 mg (82 %).

#### Synthesis of Heterotrimetallic Precursors

#### Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1)

*Method I.* A flask was loaded with Li(tbaoac) (0.500 g, 3.05 mmol), Co(tbaoac)<sub>2</sub> (0.568 g, 1.53 mmol) and Ni(tbaoac)<sub>2</sub> (0.568 g, 1.53 mmol) under argon atmosphere, and 50 mL of dry, oxygen-free 1,2-dichloroethane (DCE) was added. The brown solution was stirred under

different conditions as described below (Table S1). In all experiments, the solvent was evaporated under vacuum at room temperature and the brown solid residue was further dried under vacuum at 100 °C overnight. The bulk crystalline product was analyzed by X-ray powder diffraction (Figure S2 and Table S5).

Table S1. Synthetic Conditions for the Preparation of Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1)

Temperature	room temperature	reflux (ca. 84°C)	reflux (ca. 84°C)
Time	24 hours	24 hours	14 days
Yield	<i>ca.</i> 1.538 g (94%)	<i>ca.</i> 1.521 g (93%)	<i>ca.</i> 1.554 g (95%)

*Method II.* A mixture of Li(tbaoac) (20 mg, 0.12 mmol), Co(tbaoac)<sub>2</sub> (23 mg, 0.06 mmol), and Ni(tbaoac)<sub>2</sub> (23 mg, 0.06 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace without temperature gradient. The ampule was kept at 150 °C for 7 days. The resulting brown product was further purified by dynamic vacuum sublimation (cold finger) at 160 °C. Yield was *ca.* 60 mg (90 %).

#### Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2)

*Method I.* A flask was loaded with Li(tbaoac) (97 mg, 0.59 mmol), Co(tbaoac)<sub>2</sub> (110 mg, 0.30 mmol) and Mg(tbaoac)<sub>2</sub> (100 mg, 0.30 mmol) under argon atmosphere, and 50 mL of dry, oxygen-free 1,2-dichloroethane (DCE) was added. The purple solution was stirred under different conditions as described below (Table S2). The solvent was evaporated under vacuum at room temperature and the purple solid residue was further dried under vacuum at 100 °C overnight. The bulk crystalline product was analyzed by X-ray powder diffraction (Figure 3 and Table 6).

Table S2. Synthetic Conditions for the Preparation of Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2)

Temperature	room temperature	reflux (ca. 84°C)	reflux (ca. 84°C)
Time	24 hours	24 hours	14 days
Yield	<i>ca.</i> 280 mg (91%)	<i>ca.</i> 292 mg (95%)	<i>ca.</i> 286 mg (93%)

*Method II.* A mixture of Li(tbaoac) (29 mg, 0.18 mmol), Co(tbaoac)<sub>2</sub> (33 mg, 0.09 mmol), and Mg(tbaoac)<sub>2</sub> (30 mg, 0.09 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace without temperature gradient. The ampule was kept at 150 °C for 7 days. The resulting purple product was further purified by dynamic vacuum sublimation (cold finger) at 160 °C. Yield was *ca.* 78 mg (85 %).

#### Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (3)

*Method I.* A flask was loaded with Li(tbaoac) (97 mg, 0.59 mmol), Ni(tbaoac)<sub>2</sub> (110 mg, 0.30 mmol) and Mg(tbaoac)<sub>2</sub> (100 mg, 0.30 mmol) under argon atmosphere, and 50 mL of dry, oxygen-free 1,2-dichloroethane (DCE) was added. The green solution was stirred under different conditions as indicated below (Table S3). The solvent was evaporated under vacuum at room temperature and the green solid residue was further dried under vacuum at 100 °C overnight. The bulk crystalline product was analyzed by X-ray powder diffraction (Figure 4 and Table 7).

Table S3. Synthetic Conditions for the Preparation of Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (3)

Temperature	room temperature	reflux (ca. 84°C)	reflux (ca. 84°C)
Time	24 hours	24 hours	14 days
Yield	<i>ca.</i> 286 mg (93%)	<i>ca.</i> 295 mg (96%)	<i>ca.</i> 279 mg (91%)

*Method II.* A mixture of Li(tbaoac) (29 mg, 0.18 mmol), Ni(tbaoac)<sub>2</sub> (33 mg, 0.09 mmol), and Mg(tbaoac)<sub>2</sub> (30 mg, 0.09 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace without temperature gradient. The ampule was kept at 150 °C for 7 days. The resulting green product was further purified by dynamic vacuum sublimation (cold finger) at 160 °C. Yield was *ca.* 80 mg (87 %).



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

**Figure S1.** X-ray powder pattern of Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> and the Le Bail fit. Red and green curves are experimental and calculated patterns overlaid. Blue and black profiles are calculated single peak patterns for two polymorph modifications with theoretical peak positions shown at the bottom as blue and black lines (triclinic and monoclinic modifications, respectively). Grey line is the difference curve.



Figure S2. X-ray powder pattern of  $Li_2CoNi(tbaoac)_6$  (1) and the Le Bail fit. Red and green curves are experimental and calculated patterns overlaid. Blue and black profiles are calculated single peak patterns for two polymorph modifications with theoretical peak positions shown at the bottom as blue and black lines (triclinic and monoclinic modifications, respectively). Grey line is the difference curve.



**Figure S3.** X-ray powder pattern of  $Li_2CoMg(tbaoac)_6$  (2) and the Le Bail fit. Red and green curves are experimental and calculated patterns overlaid. Blue and black profiles are calculated single peak patterns for two polymorph modifications with theoretical peak positions shown at the bottom as blue and black lines (triclinic and monoclinic modifications, respectively). Grey line is the difference curve.



**Figure S4.** X-ray powder pattern of Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (**3**) and the Le Bail fit. Red and green curves are experimental and calculated patterns overlaid. Blue and black profiles are calculated single peak patterns for two polymorph modifications with theoretical peak positions shown at the bottom as blue and black lines (triclinic and monoclinic modifications, respectively). Grey line is the difference curve.

	Li <sub>2</sub> Ni <sub>2</sub> (tbaoac) <sub>6</sub>					
	Le Bail	Fit (20 °C)	Single Crystal (-173 °C)			
Sp. Gr.	$P2_{1}/n$	<i>P</i> -1	<i>P</i> -1			
a (Å)	12.228(2)	11.412(1)	11.408(2)			
b (Å)	9.624(2)	12.256(1)	12.249(2)			
c (Å)	19.035(5)	12.552(1)	12.519(2)			
α (°)	90	103.642(1)	103.4770(18)			
β (°)	94.75(2)	107.181(1)	107.0880(17)			
γ (°)	90	110.863(1)	110.7970(17)			
$V(Å^3)$	2232.9(8)	1449.5(8)	1447.5(4)			

**Table S4.** Unit Cell Parameters for Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>3</sub> Obtained from the Le Bail Fit and from the Single Crystal Data

 Table S5. Unit Cell Parameters for Li2CoNi(tbaoac)6 (1) Obtained from the Le Bail Fit and from the Single Crystal Data

$Li_2CoNi(tbaoac)_6(1)$					
	Le Bail	Single Crystal (-173 °C)			
Sp. Gr.	$P2_1/n$	<i>P</i> -1	<i>P</i> -1		
a (Å)	12.231(2)	11.443(1)	11.4322(11)		
<i>b</i> (Å)	9.653(2)	12.281(1)	12.2773(11)		
c (Å)	19.113(2)	12.526(1)	12.5149(12)		
α (°)	90	103.257(1)	103.535(2)		
β (°)	94.82(2)	107.482(1)	107.265(2)		
γ (°)	90	110.814(1)	110.653(2)		
$V(\dot{A}^3)$	2248.9(9)	1454.1(9)	1452.5(2)		

	$Li_2CoMg(tbaoac)_6$ (2)					
	Le Bai	l Fit (20 °C)	Single Crystal (-173 °C)			
Sp. Gr.	$P2_1/n$	<i>P</i> -1	<i>P</i> -1			
a (Å)	12.258(2)	11.569(2)	11.5502(8)			
b (Å)	9.571(2)	12.301(2)	12.2971(9)			
<i>c</i> (Å)	19.250(5)	12.553(2)	12.5192(9)			
α (°)	90	103.475(1)	103.554(2)			
β (°)	94.99(2)	107.154(1)	107.079(2)			
γ (°)	90	110.802(1)	110.959(2)			
$V(Å^3)$	2249.9(7)	1477.3(6)	1468.06(18)			

**Table S6.** Unit Cell Parameters for  $Li_2CoMg(tbaoac)_6$  (2) Obtained from the Le Bail Fit and from the Single Crystal Data

 Table S7. Unit Cell Parameters for Li2NiMg(tbaoac)6 (3) Obtained from the Le Bail Fit and from the Single Crystal Data

Li <sub>2</sub> NiMg(tbaoac) <sub>6</sub> ( <b>3</b> )					
	Le Bail	Fit (20 °C)	Single Crystal (-173 °C)		
Sp. Gr.	$P2_{1}/n$	<i>P</i> -1	<i>P</i> -1		
a (Å)	12.314(2)	11.601 (2)	11.5228(8)		
<i>b</i> (Å)	9.569(2)	12.274(2)	12.2661(8)		
c (Å)	19.202(5)	12.641(2)	12.5357(8)		
α (°)	90	103.241(1)	103.595(2)		
β (°)	94.80(2)	106.994(1)	106.954(2)		
γ (°)	90	111.102(1)	111.073(2)		
$V(\dot{A}^3)$	2254.7(8)	1489.4(4)	1462.28(17)		

#### **Crystal Growth**

Block-shaped crystals of Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> suitable for structural measurements were obtained by keeping its saturated solution in dichloromethane at around -20 °C for 2 days. Single crystals of Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1), Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2) and Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (3) were obtained by keeping their saturated solutions in diethyl ether at around -20 °C for 1-3 days. The details of crystal growth experiments are summarized in the Table S8.

Compound	Li <sub>2</sub> Co <sub>2</sub> (tbaoac) <sub>6</sub>	Li2Ni2(tbaoac)6	Li <sub>2</sub> Mg <sub>2</sub> (tbaoac) <sub>6</sub>	1	2	3
Shape	block	block	block	block	block	block
Color	purple	green	colorless	brown	purple	green
Crystal Growth	Crystal Growth		CH <sub>2</sub> Cl <sub>2</sub> /C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	diethyl	diethyl	diethyl
Method	subminution	0112012		ether	ether	ether
Temperature (°C)	140	-20	-20	-20	-20	-20
Time (days)	5	2	7	1	3	3
Volatility (°C)	140	140*	145*	140*	140*	140*
Decomposition (°C)	160	165*	165*	170*	165*	165*

Table S8. Single Crystal Growth Conditions and Properties of Heterometallic Complexes

\* Dynamic vacuum conditions (cold finger)

#### **X-ray Crystallographic Procedures**

The single crystal diffraction data for Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> were collected on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073$  Å). The single crystal diffraction data for Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1) were measured at 100 K on a Bruker D8 fixed-*chi* with Pilatus1M CdTe pixel array detector (synchrotron radiation at  $\lambda = 0.41328$  Å) located at the Advanced Photon Source, Argonne National Laboratory (ChemMatCARS, Sector 15). Data were collected using  $\phi$  scans. The single crystal diffraction data for compounds 2 and 3 were measured on a Bruker D8 VENTURE with PHOTON 100 CMOS shutterless mode detector system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073$  Å). Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).<sup>3</sup> Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2014/5).<sup>4</sup> The structures were solved by SHELXT and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2017/1)<sup>5</sup> software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions for structure factor calculations with  $U_{iso}(H) = 1.2U_{eq}(C)$  and  $U_{iso}(H) = 1.5U_{eq}(C)$  for methyl groups. All disordered parts were modeled with anisotropic thermal parameters using similarity restraints (SAME command in SHELXL) and were also restrained with the combination of RIGU/SIMU commands. In the structure of Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1), the M<sup>II</sup> position was fixed as occupied by both Co and Ni with a ratio of 1:1. In the structure of Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2), the M<sup>II</sup> position was found to be occupied by both Mg and Co with Mg:Co ratio refined as 47%:53%. In the structure of Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (**3**), the M<sup>II</sup> position was found to be occupied by both Mg and Ni with Mg:Ni ratio refined as 53%:47%. Metal atomic coordinates and anisotropic displacement parameters in these structures were constrained by applying the EXYZ and EADP instructions. Crystallographic data and details of the data collection and structure refinement for all reported compounds are listed in Table S6.

Compound	Li2Ni2(tbaoac)6	1	2	3
Empirical formula	$C_{48}H_{78}Li_2Ni_2O_{18}$	C48H78CoLi2NiO18	$C_{48}H_{78}Co_{1.06}Li_2Mg_{0.94}O_{18}$	$C_{48}H_{78}Li_2Mg_{1.07}Ni_{0.93}O_{18}$
Formula weight	1074.40	1074.62	1042.46	1037.73
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.41328	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	11.408(2)	11.4322(11)	11.5502(8)	11.5228(8)
<i>b</i> (Å)	12.249(2)	12.2773(11)	12.2971(9)	12.2661(8)
<i>c</i> (Å)	12.519(2)	12.5149(12)	12.5192(9)	12.5357(8)
α (°)	103.4770(18)	103.535(2)	103.554(2)	103.595(2)
$\beta(^{\circ})$	107.0880(17)	107.265(2)	107.079(2)	106.954(2)
γ(°)	110.7970(17)	110.653(2)	110.959(2)	111.073(2)
$V(Å^3)$	1447.5(4)	1452.5(2)	1468.06(18)	1462.28(17)
Ζ	1	1	1	1
$ ho_{ m calcd}  ( m g \cdot  m cm^{-3})$	1.233	1.229	1.179	1.178
$\mu$ (mm <sup>-1</sup> )	0.714	0.162	0.381	0.384
<i>F</i> (000)	572	571	556	555
Crystal size (mm)	0.380×0.120×0.100	0.010×0.012×0.017	0.340×0.140×0.100	0.450×0.150×0.030
$\theta$ range (°)	1.838–27.612	1.218-20.366	2.866-33.185	3.126-27.878
Reflections collected	16490	62588	60514	55082
Independent	6513	13227	11144	6944
reflections	$[R_{\rm int} = 0.0234]$	$[R_{\rm int} = 0.0435]$	$[R_{\rm int} = 0.0395]$	$[R_{\rm int} = 0.0291]$
Transmission factors	0.9638/1	0.9242/1	0.9291/1	0.9305/1
(min/max)				
Data/restr./params.	6513/0/328	13227/0/329	11144/0/329	6944/0/329
$R1,^{a} wR2^{b} (I > 2\sigma(I))$	0.0280/0.0691	0.0337/0.0881	0.0383/0.0749	0.0318/0.0654
$R1$ , <sup>a</sup> $wR2^{b}$ (all data)	0.0303/0.0714	0.0391/0.0905	0.0516/0.0810	0.0406/0.0688
Quality-of-fit <sup>c</sup>	1.044	1.078	1.093	1.094
Largest diff. peak and	0.327 and -0.330	0.712 and -0.770	0.463 and -0.311	0.281 and -0.257
hole (ē·Å <sup>-3</sup> )				

**Table S9.** Crystal Data and Structure Refinement Parameters for  $Li_2Ni_2(tbaoac)_6$ , $Li_2CoNi(tbaoac)_6$  (1),  $Li_2CoMg(tbaoac)_6$  (2), and  $Li_2NiMg(tbaoac)_6$  (3)

 ${}^{a}R1 = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR2 = [\Sigma [w(F_{o}{}^{2} - F_{c}{}^{2})^{2}] / \Sigma [w(F_{o}{}^{2})^{2}]].$ 

°Quality-of-fit =  $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{\frac{1}{2}}$ , based on all data.

#### Solid State Structures of Heterometallic Compounds



**Figure S5.** Solid state structure of heterometallic complex Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> drawn with thermal ellipsoids at the 40% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only metal and oxygen atoms are labeled. The lithium–oxygen and nickel–oxygen bonds to the tbaoac ligands involved in bridging interactions are shown in blue.

Bond Di	stances	Angles		Angl	es
Ni(1)–O(1)	2.0142(9)	O(1)–Ni(1)–O(4)	169.85(4)	O(2)–Li(1)–O(4)	91.33(10)
Ni(1)-O(2)**	2.0071(9)	O(1)-Ni(1)-O(4A)	92.79(4)	O(2)–Li(1)–O(6)	118.57(12)
Ni(1)-O(4)*	2.1249(9)	O(1)-Ni(1)-O(5A)	93.33(4)	O(3)–Li(1)–O(2)	124.34(12)
Ni(1)-O(4A)*	2.1368(9)	O(2)–Ni(1)–O(1)	89.92(4)	O(3)–Li(1)–O(4)	100.45(11)
Ni(1)-O(5A)	2.0185(9)	O(2)–Ni(1)–O(4)	82.97(4)	O(3)–Li(1)–O(6)	115.35(12)
Ni(1)-O(6A)**	2.0026(9)	O(2)-Ni(1)-O(4A)	96.88(4)	O(6)–Li(1)–O(4)	91.23(10)
		O(2)-Ni(1)-O(5A)	90.32(4)		
Li(1)–O(2)*	1.871(2)	O(4)-Ni(1)-O(4A)	80.94(4)		
Li(1)–O(3)	1.840(2)	O(5A)-Ni(1)-O(4)	93.94(4)		
Li(1)-O(4)**	1.957(2)	O(5A)-Ni(1)-O(4A)	170.55(4)		
Li(1)-O(6)*	1.877(2)	O(6A)-Ni(1)-O(1)	90.66(4)		
		O(6A)-Ni(1)-O(2)	179.38(4)		
		O(6A)-Ni(1)-O(4)	96.43(4)		
		O(6A)-Ni(1)-O(4A)	82.86(4)		
		O(6A)-Ni(1)-O(5A)	89.88(4)		

Table S10. Selected Bond Distances (Å) and Angles (deg.) in the Structure of Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub>

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



**Figure S6.** Solid state structure of heterometallic complex  $Li_2M_2(tbaoac)_6$  (1) (M = Co/Ni at 1:1 ratio) drawn with thermal ellipsoids at the 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 tbaoac ligands involved in bridging interactions are shown in blue.

**Table S11.** Selected Bond Distances (Å) and Angles (deg.) in the Structure of Li2CoNi(tbaoac)6(1)

Bond Di	Bond Distances		Angles		28
M(1)–O(1)	2.0333(6)	O(1)-M(1)-O(4)	169.00(2)	O(2)–Li(1)–O(4)	91.23(7)
M(1)-O(2)**	2.0177(6)	O(1)–M(1)–O(4A)	92.81(3)	O(2)–Li(1)–O(6)	118.61(9)
M(1)-O(4)*	2.1370(6)	O(1)–M(1)–O(5A)	93.06(3)	O(3)–Li(1)–O(2)	124.74(9)
M(1)-O(4A)*	2.1571(6)	O(2)–M(1)–O(1)	89.04(3)	O(3)–Li(1)–O(4)	100.05(8)
M(1)-O(5A)	2.0420(6)	O(2)–M(1)–O(4A)	82.64(2)	O(3)–Li(1)–O(6)	115.01(9)
M(1)-O(6A)**	2.0128(6)	O(2)–M(1)–O(4A)	97.28(2)	O(6)–Li(1)–O(4)	91.34(7)
		O(2)–M(1)–O(5A)	91.22(3)		
Li(1)-O(2)*	1.8800(17)	O(4)–M(1)–O(4A)	81.17(2)		
Li(1)–O(3)	1.8497(17)	O(5A)–M(1)–O(4)	94.30(3)		
Li(1)-O(4)**	1.9598(17)	O(5A)–M(1)–O(4A)	169.75(2)		
Li(1)-O(6)*	1.8857(17)	O(5A)–M(1)–O(1)	91.72(3)		
		O(6A)–M(1)–O(2)	179.21(2)		
		O(6A)-M(1)-O(4)	96.58(2)		
		O(6A)-M(1)-O(4A)	82.49(2)		
		O(6A)-M(1)-O(5A)	88.94(3)		

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

		Li <sub>2</sub> CoNi(tbaoac) <sub>6</sub>	Li2Co2(tbaoac)6	Li2Ni2(tbaoac)6
	<b>R</b> 1	0.0337	0.0349	0.0337
	Sa	1.078	1.108	1.115
Highest <i>Q</i> peak and hole		0.71 (0.61 Å from M <sup>II</sup> ) -0.77 (0.66 Å from M <sup>II</sup> )	0.80 (0.53 Å from M <sup>II</sup> ) -0.69 (0.69 Å from M <sup>II</sup> )	0.68 (0.66 Å from M <sup>II</sup> ) -0.86 (0.62 Å from M <sup>II</sup> )
	O(1)	2.0333(6)	2.0333(7)	2.0331(7)
	O(2) <sup>c</sup>	2.0177(6)	2.0175(7)	2.0180(6)
	O(4) <sup>b</sup>	2.1370(6)	2.1371(6)	2.1370(6)
MII	O(4A) <sup>b</sup>	2.1571(6)	2.1347(9)	2.1574(6)
	O(5A)	2.0420(6)	2.1566(6)	2.0421(7)
	O(6A) <sup>c</sup>	2.0128(6)	2.0125(7)	2.0132(6)
	$U_{ m iso}$	0.01223	0.01204	0.01241
	O(2) <sup>b</sup>	1.8800(17)	1.8810(18)	1.8790(17)
	O(3)	1.8497(17)	1.8489(17)	1.8504(17)
Li	O(4) <sup>c</sup>	1.9598(17)	1.9592(18)	1.9604(18)
	O(6) <sup>b</sup>	1.8857(17)	1.8862(18)	1.8853(17)
	U <sub>iso</sub>	0.0177	0.0187	0.0168

Table	<b>S12.</b>	Refinement	Results	of the	Crystal	Structure	of Li <sub>2</sub> Co	Ni(tbaoac) <sub>6</sub>	(1)	Based	on
Differe	ent 3d	Transition M	letal Ass	ignmen	ts						

<sup>a</sup> *S* value is obtained by refinement based on weighting scheme: WGHT 0.044200 0.279300; <sup>b</sup> – bridging oxygen; <sup>c</sup> – chelating-bridging oxygen.



**Figure S7.** Solid state structure of heterometallic complex  $Li_2M_2(tbaoac)_6$  (2) (M = Co/Mg at 0.53:0.47 ratio) drawn with thermal ellipsoids at the 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 tbaoac ligands involved in bridging interactions are shown in blue.

**Table S13.** Selected Bond Distances (Å) and Angles (deg.) in the Structure of Li2CoMg(tbaoac)6(2)

Bond Distances		Angles		Angle	5
M(1)–O(1)	2.0478(7)	O(1)-M(1)-O(4)	167.33(3)	O(2)–Li(1)–O(4)	91.05(8)
M(1)–O(2)**	2.0331(7)	O(1)-M(1)-O(4A)	92.95(3)	O(2)–Li(1)–O(6)	118.94(9)
M(1)-O(4)*	2.1440(7)	O(1)-M(1)-O(5A)	92.95(3)	O(3)–Li(1)–O(2)	124.76(10)
M(1)-O(4A)*	2.1640(7)	O(2)–M(1)–O(1)	87.23(3)	O(3)–Li(1)–O(4)	100.02(8)
M(1)-O(5A)	2.0603(7)	O(2)–M(1)–O(4)	82.37(3)	O(3)–Li(1)–O(6)	114.82(9)
M(1)-O(6A)**	2.0259(7)	O(2)-M(1)-O(4A)	98.18(3)	O(6)-Li(1)-O(4)	90.92(8)
		O(2)-M(1)-O(5A)	92.60(3)		
Li(1)-O(2)*	1.8887(18)	O(4)-M(1)-O(4A)	81.44(3)		
Li(1)-O(3)	1.8531(18)	O(5A)-M(1)-O(4)	94.72(3)		
Li(1)-O(4)**	1.9670(18)	O(5A)-M(1)-O(4A)	167.94(3)		
Li(1)-O(6)*	1.8956(18)	O(6A)-M(1)-O(1)	93.32(3)		
		O(6A)-M(1)-O(2)	179.37(3)		
		O(6A)-M(1)-O(4)	97.11(3)		
		O(6A)-M(1)-O(4A)	82.09(3)		
		O(6A)-M(1)-O(5A)	87.08(3)		

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



**Figure S8.** Solid state structure of heterometallic complex  $Li_2M_2(tbaoac)_6$  (**3**) (M = Ni/Mg at 0.47:0.53 ratio) drawn with thermal ellipsoids at the 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 tbaoac ligands involved in bridging interactions are shown in blue.

**Table S14.** Selected Bond Distances (Å) and Angles (deg.) in the Structure of Li2NiMg(tbaoac)6(3)

Bond Distances		Angles		Angles		
M(1)–O(1)	2.0285(8)	O(1)-M(1)-O(4)	168.23(3)	O(2)–Li(1)–O(4)	91.13(9)	
M(1)–O(2)**	2.0278(8)	O(1)-M(1)-O(4A)	92.94(3)	O(2)–Li(1)–O(6)	119.09(11)	
M(1)-O(4)*	2.1302(8)	O(1)-M(1)-O(5A)	93.41(3)	O(3)–Li(1)–O(2)	124.50(11)	
M(1)-O(4A)*	2.1360(8)	O(2)–M(1)–O(1)	88.03(3)	O(3)–Li(1)–O(4)	100.33(10)	
M(1)-O(5A)	2.0342(8)	O(2)–M(1)–O(4)	82.77(3)	O(3)–Li(1)–O(6)	114.87(11)	
M(1)-O(6A)**	2.0199(8)	O(2)–M(1)–O(4A)	97.71(3)	O(6)–Li(1)–O(4)	90.80(8)	
		O(2)-M(1)-O(5A)	91.70(3)			
Li(1)-O(2)*	1.878(2)	O(4)-M(1)-O(4A)	81.10(3)			
Li(1)-O(3)	1.849(2)	O(5A)-M(1)-O(4)	94.18(3)			
Li(1)-O(4)**	1.973(2)	O(5A)-M(1)-O(4A)	168.82(3)			
Li(1)-O(6)*	1.887(2)	O(6A)-M(1)-O(1)	92.37(3)			
		O(6A)-M(1)-O(2)	179.37(3)			
		O(6A)-M(1)-O(4)	96.91(3)			
		O(6A)-M(1)-O(4A)	82.77(3)			
		O(6A)-M(1)-O(5A)	87.78(3)			

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

**Table S15.** Averaged Metal–Oxygen Bond Distances (Å) in the Structures of Heterobimetallic  $Li_2M_2(tbaoac)_6$  (M = Co, Ni, and Mg) and Heterotrimetallic  $Li_2MM'(tbaoac)_6$  (M/M' = Co/Ni (1), Co/Mg (2), and Ni/Mg (3)) Compounds

	M–O <sub>c</sub> <sup>a</sup>	M–O <sub>c-b</sub> <sup>b</sup>	M–O <sub>b</sub> <sup>c</sup>	Li–O
Li <sub>2</sub> Co <sub>2</sub> (tbaoac) <sub>6</sub> <sup>1</sup>	2.062(2)	2.028(2)	2.160(2)	1.897(4)
Li <sub>2</sub> Ni <sub>2</sub> (tbaoac) <sub>6</sub>	2.016(1)	2.005(1)	2.131(1)	1.886(2)
Li <sub>2</sub> Mg <sub>2</sub> (tbaoac) <sub>6</sub> <sup>2</sup>	2.027(2)	2.028(2)	2.131(2)	1.895(4)
Li <sub>2</sub> CoNi(tbaoac) <sub>6</sub> (1)	2.038(1)	2.015(1)	2.147(1)	1.899(2)
Li <sub>2</sub> CoMg(tbaoac) <sub>6</sub> (2)	2.054(1)	2.030(1)	2.154(1)	1.901(2)
Li2NiMg(tbaoac)6 (3)	2.031(1)	2.024(1)	2.133(1)	1.897(2)

<sup>a</sup>c – chelating; <sup>b</sup>c-b – chelating–bridging; <sup>c</sup>b – bridging.

## **ATR-IR** Spectra of Heterometallic Compounds



Figure S9. The attenuated total reflection (ATR) spectrum of Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub>.



Figure S10. The attenuated total reflection (ATR) spectrum of Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> (1).



Figure 11. The attenuated total reflection (ATR) spectrum of  $Li_2CoMg(tbaoac)_6$  (2).



Figure 12. The attenuated total reflection (ATR) spectrum of Li2NiMg(tbaoac)<sub>6</sub> (3).

#### **DART Mass Spectra of Heterometallic Compounds**



**Figure S13.** Positive-ion DART mass spectrum of solid Li<sub>2</sub>Co<sub>2</sub>(tbaoac)<sub>6</sub>. The isotope distribution pattern for the  $[M-L]^+$  (M = Li<sub>2</sub>Co<sub>2</sub>(tbaoac)<sub>6</sub> ion is shown in the inset (blue and red lines are experimental and calculated patterns, respectively)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Δ	Relative Intensity, %
[Li2C02L5] <sup>+</sup>	917.3237	917.3307	-0.0070	79.4
[Li <sub>2</sub> CoL <sub>4</sub> +H] <sup>+</sup>	702.3141	702.3189	-0.0045	13.0
$[LiCo_2L_4]^+$	753.2212	753.2283	-0.0071	1.5
$[Co_2L_4+H]^+$	747.2159	747.2201	-0.0042	3.4
$[Co_2L_3]^+$	589.1196	589.1258	-0.0062	25.1
[LiCoL3+H] <sup>+</sup>	538.2112	538.2164	-0.0052	5.2
[CoL2+H] <sup>+</sup>	374.1097	374.1140	-0.0043	100

**Table S16.** Assignment of Ions Detected in Positive-Ion DART Mass Spectrum of $Li_2Co_2(tbaoac)_6$  (M =  $Li_2Co_2(tbaoac)_6$ , L =  $tbaoac = C_8H_{13}O_3$ )

**Table S17.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Solid $Li_2Co_2(tbaoac)_6$  (M =  $Li_2Co_2(tbaoac)_6$ , L =  $tbaoac = C_8H_{13}O_3$ )

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental Abundance (%)	Theoretical Abundance (%)	Δ
	916.3242	916.3299	17.9	15.6	-0.0057
	917.3237	917.3307	100	100	-0.0070
[M–L] <sup>+</sup>	918.3297	918.3343	48.7	43.5	-0.0046
	919.3301	919.3370	17.9	12.3	-0.0069
	920.3354	920.3398	1.5	2.6	-0.0044



**Figure S14.** Positive-ion DART mass spectrum of solid Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub>. The isotope distribution pattern for the  $[M-L]^+$  (M = Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> ion is shown in the inset (blue and red lines are experimental and calculated patterns, respectively)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Δ	Relative Intensity, %
[Li3Ni2L6] <sup>+</sup>	1079.4446	1079.4375	0.0071	5.4
[Li2Ni2L5] <sup>+</sup>	915.3322	915.3350	-0.0028	100
[LiNi2L4] <sup>+</sup>	751.2417	751.2326	0.0091	3.6
[Li <sub>2</sub> NiL <sub>4</sub> +H] <sup>+</sup>	701.3283	701.3270	0.0013	6.3
$[Ni_2L_3]^+$	587.1360	587.1301	0.0059	15.3
[LiNiL3+H] <sup>+</sup>	537.2190	537.2186	0.0004	6.3
[NiL <sub>2</sub> +H] <sup>+</sup>	373.1184	373.1161	0.0023	88.2

**Table S18.** Assignment of Ions Detected in Positive-Ion DART Mass Spectrum of $Li_2Ni_2(tbaoac)_6$  (M =  $Li_2Ni_2(tbaoac)_6$ , L = tbaoac =  $C_8H_{13}O_3$ )

**Table S19.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Solid $Li_2Ni_2(tbaoac)_6$  (M =  $Li_2Ni_2(tbaoac)_6$ , L = tbaoac =  $C_8H_{13}O_3$ )

Ion	Massurad m/z	Calculated m/r	Experimental	Theoretical	4
1011	wieasureu m/2	Calculated <i>m/2</i>	Abundance (%)	Abundance (%)	2
	914.3320	914.3342	14.4	15.5	-0.0022
	915.3322	915.3352	100	100	-0.0030
	916.3353	916.3366	48.1	55.2	-0.0013
	917.3243	917.3321	85.0	89.6	-0.0078
[ <b>M</b> –L] <sup>+</sup>	918.3312	918.3336	38.6	43.3	-0.0024
	919.3244	919.3300	35.3	37.0	-0.0056
	920.3284	920.3310	14.2	15.9	-0.0026
	921.3216	921.3284	8.6	11.0	-0.0068
	922.3260	922.3294	3.9	4.3	-0.0034



**Figure S15.** Positive-ion DART mass spectrum of bulk product Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (**2**) obtained by reflux in dichloroethane for 14 days. The isotope distribution patterns for the  $[M-L]^+$  (M = Li<sub>2</sub>Co<sub>2</sub>(tbaoac)<sub>6</sub>, Li<sub>2</sub>Mg<sub>2</sub>(tbaoac)<sub>6</sub>, or Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub>) ions are shown in the inset (blue and red lines are experimental and calculated patterns, respectively).

Ion	Measured, <i>m/z</i>	Calculated, <i>m</i> / <i>z</i>	Δ	Relative Intensity, %
[Li2C02L5] <sup>+</sup>	917.3398	917.3307	0.0091	27.5
[Li2CoMgL5] <sup>+</sup>	882.3878	882.3826	0.0056	81.0
[Li2Mg2L5] <sup>+</sup>	847.4285	847.4344	-0.0059	49.2
[LiCo2L4] <sup>+</sup>	753.2208	753.2283	-0.0075	1.0
[LiCoMgL <sub>4</sub> ] <sup>+</sup>	718.2750	718.2801	-0.0051	4.8
[LiMg <sub>2</sub> L <sub>4</sub> ] <sup>+</sup>	683.3314	683.3320	-0.0006	1.6
$[Co_2L_4+H]^+$	747.2200	747.2201	-0.0001	2.1
[CoMgL <sub>4</sub> +H] <sup>+</sup>	712.2664	712.2719	-0.455	10.1
$[Mg_2L_4+H]^+$	677.3248	677.3238	0.0010	2.0
[Co <sub>2</sub> L <sub>3</sub> ] <sup>+</sup>	589.1201	589.1258	-0.0057	37.6
[CoMgL <sub>3</sub> ] <sup>+</sup>	554.1736	554.1776	-0.0040	2.7
[Li2CoL4+H] <sup>+</sup>	702.3147	702.3189	-0.0042	2.5
[Li <sub>2</sub> MgL <sub>4</sub> +H] <sup>+</sup>	667.3647	667.3708	-0.0061	5.4
$[Li_2CoL_3]^+$	544.2230	544.2246	-0.0016	2.6
[Li2MgL3] <sup>+</sup>	509.2718	509.2765	-0.0047	6.9
[CoL <sub>2</sub> +H] <sup>+</sup>	374.1150	374.1140	0.0010	100
$[MgL_2+H]^+$	339.1698	339.1658	0.0040	17.9

**Table S20.** Assignment of Ions Detected in Positive-Ion DART Mass Spectrum of $Li_2CoMg(tbaoac)_6$  (2) (L = tbaoac= C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

**Table S21.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum ofLi2CoMg(tbaoac)6 (2) (M = Li2CoMg(tbaoac)6, L = tbaoac = C8H13O3)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental	Theoretical	Δ
			Abundance (%)	Abundance (%)	
	881.3859	881.3818	15.4	16.0	0.0041
	882.3878	882.3826	100	100	0.0052
[ <b>M</b> –L]+	883.3921	883.3860	45.1	43.4	0.0061
	884.3882	884.3802	14.8	14.1	0.0080
	885.3914	885.3840	7.6	6.1	0.0074
	886.3913	886.3869	1.2	1.3	0.0044

**Table S22.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2) (M = Li<sub>2</sub>Co<sub>2</sub>(tbaoac)<sub>6</sub>, L = tbaoac = C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental	Theoretical	Δ
	, -	, -	Abundance (%)	Abundance (%)	
	916.3378	916.3300	16.8	16.0	0.0078
	917.3398	917.3307	100	100	0.0091
[ <b>M</b> –L] <sup>+</sup>	918.3403	918.3342	42.5	43.4	0.0061
	919.3457	919.3375	10.5	9.3	0.0082
	920.3489	920.3409	1.9	1.3	0.0080

**Table S23.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (2) (M = Li<sub>2</sub>Mg<sub>2</sub>(tbaoac)<sub>6</sub>, L = tbaoac = C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental Abundance (%)	Theoretical Abundance (%)	Δ
[ <b>M</b> –L] <sup>+</sup>	846.4298	846.4336	17.1	16.0	-0.0038
	847.4285	847.4344	100	100	-0.0059
	848.4302	848.4379	44.8	43.4	-0.0077
	849.4279	849.4321	30.0	28.1	-0.0058
	850.4301	850.4354	12.5	12.2	-0.0053
	851.4299	851.4369	7.5	7.9	-0.0070



**Figure S16.** Positive-ion DART mass spectrum of bulk product Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (**3**) obtained by reflux in dichloroethane for 14 days. The isotope distribution patterns for the  $[M-L]^+$  (M = Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub>, Li<sub>2</sub>Mg<sub>2</sub>(tbaoac)<sub>6</sub>, or Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub>) ions are shown in the inset (blue and red lines are experimental and calculated patterns, respectively).

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Δ	Relative Intensity, %
$[Li_2Ni_2L_5]^+$	915.3389	915.3350	0.0039	31.1
[Li2NiMgL5] <sup>+</sup>	881.3862	881.3847	0.0015	84.6
$[Li_2Mg_2L_5]^+$	847.4364	847.4344	0.0020	52.0
[LiNiMgL4] <sup>+</sup>	717.2786	717.2823	-0.0037	7.6
$[LiMg_2L_4]^+$	683.3246	683.3320	-0.0074	5.1
[NiMgL <sub>4</sub> +H] <sup>+</sup>	711.2741	711.2797	-0.0056	6.1
[NiMgL <sub>3</sub> ] <sup>+</sup>	553.1727	553.1798	-0.0071	6.6
[Li2MgL4+H] <sup>+</sup>	667.3650	667.3708	-0.0058	39.6
[Li2NiL3] <sup>+</sup>	543.6534	543.6628	-0.0094	5.1
[Li2MgL3] <sup>+</sup>	509.2701	509.2765	-0.0064	34.8
$[NiL_2+H]^+$	372.1072	373.1161	-0.0089	100
$[MgL_2+H]^+$	339.1577	339.1658	-0.0081	49.2

**Table S24.** Assignment of Ions Detected in Positive-Ion DART Mass Spectrum of $Li_2NiMg(tbaoac)_6$  (3) (L = tbaoac= C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

**Table S25.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (**3**) (M = Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub>, L = tbaoac = C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental	Theoretical	1
1011			Abundance (%)	Abundance (%)	_
	880.3856	880.3839	14.7	15.3	0.0017
	881.3862	881.3847	100	100	0.0015
[M–L] <sup>+</sup>	882.3895	882.3867	62.4	62.9	0.0028
	883.3879	883.3833	70.0	69.8	0.0056
	884.3882	884.3843	35.4	34.5	0.0039
	885.3869	885.3823	20.8	20.7	0.0046
	886.3877	886.3830	9.0	8.1	0.0047
	887.3861	887.3811	5.1	4.2	0.0050

Ion	Massured w/z Calculated w/z	Experimental	Theoretical	4		
1011	Vicasui cu, m/2 Carculateu, m/2		Abundance (%)	Abundance (%)	2	
	914.3389	914.3342	19.5	15.5	0.0046	
	915.3389	915.3352	100	100	0.0039	
[ <b>M</b> –L] <sup>+</sup>	916.3418	916.3366	53.5	55.2	0.0073	
	917.3369	917.3321	89.5	89.6	0.0063	
	918.3402	918.3336	37.7	43.3	0.0063	
	919.3356	919.3300	35.5	37.0	0.0096	
	920.3386	920.3310	12.6	15.9	0.0076	
	921.3335	921.3284	9.8	11.0	0.0051	
	922.3369	922.3297	3.0	4.3	0.0072	

**Table S26.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Li<sub>2</sub>NiMg(tbaoac)<sub>6</sub> (**3**) (M = Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub>, L = tbaoac = C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

**Table S27.** Assignment of  $[M-L]^+$  Ions Detected in Positive-Ion DART Mass Spectrum of Li<sub>2</sub>CoMg(tbaoac)<sub>6</sub> (**3**) (M = Li<sub>2</sub>Mg<sub>2</sub>(tbaoac)<sub>6</sub>, L = tbaoac = C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>)

Ion	Measured, <i>m/z</i>	Calculated, <i>m/z</i>	Experimental	Theoretical	1
1011			Abundance (%)	Abundance (%)	4
[ <b>M</b> –L] <sup>+</sup>	846.4361	846.4336	16.5	16.0	0.0025
	847.4364	847.4344	100	100	0.0020
	848.4367	848.4379	47.6	43.4	-0.0012
	849.4384	849.4321	32.5	28.1	0.0063
	850.4393	850.4354	14.2	12.2	0.0039
	851.4395	851.4369	8.2	7.9	0.0026

#### **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 empiric dispersion corrections (here D3 type). 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. 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). In order to accelerate calculations, the "chain-of-spheres" algorithm was applied (RIJCOSX keyword in ORCA terminology). All calculations at this level of theory were performed using ORCA (v. 4.0.0) program suite.

Li.MM'(theore)	Energy, a.u.		
LI2IVIIVI (tDabac)6	B2PLYP-D/TZVP/ZORA		
Li <sub>2</sub> Co <sub>2</sub> (tbaoac) <sub>6</sub>	-6045.296068921995		
Li <sub>2</sub> Ni <sub>2</sub> (tbaoac) <sub>6</sub>	-6301.908009166644		
Li2CoMg(tbaoac)6	-4846.781358094989		
Li2CoNi(tbaoac)6 (1)	-6173.602098624527		
Li <sub>2</sub> Mg <sub>2</sub> (tbaoac) <sub>6</sub>	-3648.265951823082		
Li2NiMg(tbaoac) <sub>6</sub> (3)	-4975.087048131715		
Li(tbaoac)	-546.176006468786		
Mg(tbaoac) <sub>2</sub>	-1277.839591952019		
Co(tbaoac) <sub>2</sub>	-2476.365167101902		
Ni(tbaoac) <sub>2</sub>	-2604.659025987001		

Table S28. Absolute Energies for all Systems at the B2PLYP-D Level of Theory

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



**Figure S17.** X-ray powder diffraction pattern of  $LiCo_{0.5}Ni_{0.5}O_2$  obtained by thermal decomposition of heterometallic precursor  $Li_2CoNi(tbaoac)_6$  (1) at 450 °C in air. The blue and red lines are experimental and calculated patterns from Le Bail fit, respectively. Grey line is the difference curve. Theoretical peak positions are shown in at the bottom as black lines.

**Table S29.** Comparison of the Unit Cell Parameters for LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> Oxide Obtained by Thermal Decomposition of Heterometallic Precursor Li<sub>2</sub>CoNi(tbaoac)<sub>6</sub> at 450°C with the Literature Data

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Figure S18. X-ray powder diffraction pattern of  $LiCo_{0.5}Ni_{0.5}O_2$  obtained by thermal decomposition of heterometallic precursor  $Li_2CoNi(tbaoac)_6$  (1) at 750 °C in air. The blue and red lines are experimental and calculated patterns from Lebail fit, respectively. Grey line is the difference curve. Theoretical peak positions are shown in at the bottom as black lines.

**Table S30.** Comparison of the Unit Cell Parameters for  $LiCo_{0.5}Ni_{0.5}O_2$  Oxide Obtained by Thermal Decomposition of Heterometallic Precursor  $Li_2CoNi(tbaoac)_6$  (1) at 750°C with the Literature Data

LiCo <sub>0.5</sub> Ni <sub>0.5</sub> O <sub>2</sub>		Literature Data <sup>6</sup>
	Space Group: <i>R</i> -3 <i>m</i>	
<i>a</i> = 2.8474(3) Å		<i>a</i> = 2.8422(2) Å
c = 14.0947(2) Å		c = 14.096(4) Å



**Figure S19.** X-ray powder diffraction pattern of the decomposition residue obtained by thermal decomposition of the 1:1 mixture of heterobimetallic precursors Li<sub>2</sub>Co<sub>2</sub>(tbaoac)<sub>6</sub> and Li<sub>2</sub>Ni<sub>2</sub>(tbaoac)<sub>6</sub> at 750 °C in air. The red and blue lines are assigned to Li<sub>0.4</sub>Ni<sub>1.5</sub>O<sub>2</sub> and LiCoO<sub>2</sub> phases, respectively. Unidentified peaks are marked with asterisk.

## Electron Microscopy Investigation of the LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> Oxide



**Figure S20.** HAADF-STEM image, the EDX elemental maps of Co, Ni, and the mixed compositional maps showing nanosized Ni-enriched areas (green).



**Figure S21.** HAADF-STEM image, the EDX elemental maps of Co, Ni, and the mixed compositional maps showing nanosized Ni-enriched areas (green).



**Figure S22.** HAADF-STEM image, the EDX elemental maps of Co, Ni, and the mixed compositional maps showing Co-rich and Ni-depleted crystals.

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