

Table S1. Selected hydrogen bonds parameters (Å, deg) for [CoL<sup>1</sup>Br][ZnL<sup>3</sup>(μ-uro)ZnBr<sub>5</sub>] (**1**), [CoL<sup>1</sup>Cl][ZnL<sup>3</sup>Br<sub>3</sub>] (**2**) and [CoL<sup>1</sup>Cl][ZnL<sup>3</sup>Cl<sub>3</sub>] (**3**).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> —H··· <i>A</i> (°)
<b>1</b>				
C18—H18B···Br1 <sup>i</sup>	0.97	2.89	3.610 (8)	132.1
C27—H27A···Br5 <sup>i</sup>	0.96	2.74	3.545 (11)	141.5
C51—H51A···Br6 <sup>i</sup>	0.97	2.71	3.611 (9)	154.6
C46—H46A···Br2 <sup>i</sup>	0.96	2.90	3.696 (12)	140.5
C17—H17C···Br4 <sup>ii</sup>	0.96	2.74	3.632 (9)	155.2
C26—H26C···Br5	0.96	2.93	3.750 (10)	143.7
<b>2</b>				
C16—H16A···Cl1	0.96	2.69	3.528 (14)	146.2
C26—H26A···Cl1	0.96	2.70	3.448 (18)	135.1
C36—H36A···Cl1	0.96	2.55	3.458 (17)	157.7
C14—H14···Cl1 <sup>iv</sup>	0.93	2.68	3.600 (11)	169.1
C18—H18A···Br2	0.97	2.89	3.657 (8)	136.5
C18—H18B···Br2 <sup>v</sup>	0.97	2.88	3.821 (9)	163.6
C27—H27B···Br3 <sup>v</sup>	0.96	3.01	3.831 (12)	143.8
C28—H28B···Br3 <sup>v</sup>	0.97	2.89	3.739 (8)	147.0
C38—H38A···Br3 <sup>v</sup>	0.97	2.94	3.385 (8)	109.0
N42—H42···Br4 <sup>vi</sup>	0.86	3.04	3.745 (6)	141.2
C46—H46C···Br3 <sup>vii</sup>	0.96	3.16	3.537 (10)	105.2
C47—H47A···Br4 <sup>vi</sup>	0.96	3.12	3.644 (11)	116.0
<b>3</b>				
C16—H16A···Cl1	0.96	2.73	3.488 (5)	136.3
C26—H26B···Cl1	0.96	2.52	3.437 (5)	159.5
C36—H36C···Cl1	0.96	2.61	3.452 (5)	146.7
C14—H14···Cl1 <sup>iv</sup>	0.93	2.73	3.610 (3)	159.1
C18—H18A···Cl2	0.97	2.80	3.571 (3)	136.9
C18—H18B···Cl2 <sup>v</sup>	0.97	2.77	3.708 (3)	163.4
C27—H27A···Cl3 <sup>v</sup>	0.96	2.90	3.747 (4)	148.0
C28—H28B···Cl3 <sup>v</sup>	0.97	2.77	3.624 (3)	146.7
C38—H38B···Cl3 <sup>v</sup>	0.97	2.87	3.309 (3)	108.7
N42—H42···Cl4 <sup>vi</sup>	0.86	2.68	3.426 (2)	145.4
C46—H46C···Cl3 <sup>vii</sup>	0.96	2.69	3.521 (4)	145.6
C47—H47A···Cl4 <sup>vi</sup>	0.96	2.79	3.542 (4)	135.5

Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $x+1, -y+1/2, z+1/2$ ; (iii)  $x, -y+1/2, z-1/2$ ; (iv)  $-x+1, y-1/2, -z+1/2$ ; (v)  $-x, -y, -z$ ; (vi)  $-x, y-1/2, -z+1/2$ ; (vii)  $-x, y+1/2, -z+1/2$ .

Table S2. Thermal decomposition of **1-3** complexes in air atmosphere

Decomposition	Stage	TG (°C)	$\Delta m_{\text{exp}}$ (%)	$\Delta m_{\text{calc}}$ (%)
[CoL <sup>1</sup> Br][ZnBr <sub>3</sub> (L <sup>2</sup> )ZnBr <sub>2</sub> (L <sup>3</sup> )] ( <b>1</b> )				
↓ {C <sub>6</sub> N <sub>2</sub> H <sub>12</sub> (L <sup>2</sup> )}	I	160-300	9,55	8,99
[CoL <sup>1</sup> Br] [ZnBr <sub>3</sub> N <sub>2</sub> ZnBr <sub>2</sub> (L <sup>3</sup> )]				
↓ - 6{Br}	II	300-480	35,50	38,70
[CoL <sup>1</sup> ] [ZnN <sub>2</sub> Zn(L <sup>3</sup> )]				
↓ -(C <sub>5</sub> NH <sub>8</sub> ) (L <sup>3</sup> )	III	480-680	27,88	29,30
↓ -0.75 L <sup>1</sup>				
↓ A	IV	680-900	19.42	20.77
Residue ZnCo <sub>2</sub> O <sub>4</sub> + ZnO				
[CoL <sup>1</sup> Cl][ZnL <sup>3</sup> Br <sub>3</sub> ] ( <b>2</b> )				
↓ - {Br}	I	160-390	9.95	9.53
{Co(L <sup>1</sup> )Br} { ZnL <sup>3</sup> Br <sub>2</sub> }				
↓ - {C <sub>18</sub> H <sub>27</sub> N <sub>7</sub> (L <sup>1</sup> )}	II	390-990	75.47	75.60
↓ - {C <sub>5</sub> NH <sub>8</sub> } (L <sup>3</sup> )}				
↓ - {Cl, 2Br}				
Residue {Co <sub>3</sub> O <sub>4</sub> + ZnO}				
[CoL <sup>1</sup> Cl][ZnL <sup>3</sup> Cl <sub>3</sub> ] ( <b>3</b> )				
↓ - . {C <sub>18</sub> H <sub>27</sub> N <sub>7</sub> (L <sup>1</sup> )}	I	190-480	52.96	53.61
↓ - {Cl}				
{Co} {ZnL <sup>3</sup> Cl <sub>3</sub> }				
↓ - . {C <sub>5</sub> H <sub>8</sub> N} (L <sup>3</sup> )}	II	480-970	25.91	26.71
Residue (Co <sub>2</sub> O <sub>3</sub> , ZnO)				