

Electronic Supplementary Information

Nano Spinel Cobaltites and Their Catalytic and Electrochemical Properties: Facile Synthesis of Metal (Co, Ni, and Zn) and Mixed Metal (Co-Ni and Co-Zn) Complexes of Schiff Bases Prepared from α -Ketoglutaric Acid and Ethyl Carbazate

Sheikdawood Parveen,^a Hung Huy Nguyen,^b Thathan Premkumar,^{*c} Horst Puschmann^d and
Subbiah Govindarajan^{*a}

Table S1. Analytical data

Compound	Color (% yield)	M.wt. (g/mol)	Mol. Formula	% Found (Calcd.)			
				C	H	N	M
H₂L.H₂O	White (94)	250.21	C ₈ H ₁₄ N ₂ O ₇	38.80 (38.40)	5.20 (5.63)	11.40 (11.19)	-
[Co(HL)₂]	Pink (85)	521.30	C ₁₆ H ₂₂ CoN ₄ O ₁₂	37.21 (36.86)	4.50 (4.25)	10.98 (10.74)	11.78 (11.30)
[Ni(HL)₂]	Green (89)	521.05	C ₁₆ H ₂₂ NiN ₄ O ₁₂	37.12 (36.88)	4.71 (4.25)	11.11 (10.75)	11.89 (11.26)
[Zn(HL)₂]	White (88)	527.74	C ₁₆ H ₂₂ ZnN ₄ O ₁₂	36.85 (36.41)	4.75 (4.20)	10.87 (10.61)	12.74 (12.38)
[Ni_{1/3}Co_{2/3}(HL)₂]	Grey (87)	521.23	C ₁₆ H ₂₂ Ni _{1/3} Co _{2/3} N ₄ O ₁₂	37.21 (36.87)	4.66 (4.22)	10.95 (10.75)	3.88 (3.75) Ni 7.00 (7.54) Co
[Zn_{1/3}Co_{2/3}(HL)₂]	Light pink (89)	523.46	C ₁₆ H ₂₂ Zn _{1/3} Co _{2/3} N ₄ O ₁₂	36.92 (36.70)	4.56 (4.20)	11.15 (10.70)	4.00 (4.16) Zn 7.82 (7.51) Co

Table S2. FT-IR and UV-visible data

Compound	IR spectroscopic data (cm ⁻¹)						Electronic spectroscopic data $\lambda_{\text{max}}(\text{nm}); (\epsilon[\text{M}^{-1}\text{cm}^{-1}])$
	$\nu_{\text{O-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$ asym.	$\nu_{\text{C=O}}$ sym.	$\nu_{\text{N-N}}$	
H₂L.H₂O	3456	3215	1663	-	-	1054	240 (25400); 293 (18900)
[Co(HL)₂]	3434	3209	1627	1542	1375	1048	241 (25900); 300(20200); 516 (350)
[Ni(HL)₂]	3434	3210	1625	1544	1375	1050	239 (25300); 293 (19300); 388 (6000); 645 (250)
[Zn(HL)₂]	3456	3112	1661	1536	1372	1054	242 (24200); 294 (18200)
[Ni_{1/3}Co_{2/3}(HL)₂]	3434	3095	1625	1542	1375	1050	240 (24300); 292 (19200); 384 (487); 521 (1800); 648 (160)
[Zn_{1/3}Co_{2/3} (HL)₂]	3431	3098	1674	1539	1376	1049	242 (24200); 293 (18500); 506 (240)

Table S3. Thermal data

Compounds	DTA peak temp (°C)	Thermogravimetry		Intermediates/End products
		Temp. range (°C)	Mass Loss% Obs. Calc'd	
H ₂ L.H ₂ O	(+)104,(+)168	80-180	7.00 7.20	Melting, dehydration
	(-)260	180-450	81.00 80.96	CH ₃ -CH=NH
	(-)481	400-650	100.0 100.0	Complete decomposition
[Co(HL) ₂]	(+)255	200-350	60.00 60.68	Cobalt propionate
	(-)390	350-600	85.00 84.64	Co ₃ O ₄
[Ni(HL) ₂]	(+)255	200-350	60.00 60.72	Nickel propionate
	(-)390	350-600	85.00 85.67	NiO
[Zn(HL) ₂]	(+)250	200-350	60.00 59.95	Zinc propionate
	(-)490	350-600	85.00 84.58	ZnO
[Ni _{1/3} Co _{2/3} (HL) ₂]	(+)260	200-350	60.00 6.83	Mixed-metal propionate
	(-)390	350-600	86.00 84.61	NiCo ₂ O ₄
[Zn _{1/3} Co _{2/3} (HL) ₂]	(+)250	200-350	60.00 60.43	Mixed-metal propionate
	(-)455	350-600	85.00 84.25	ZnCo ₂ O ₄

(+): endo; (-): exo

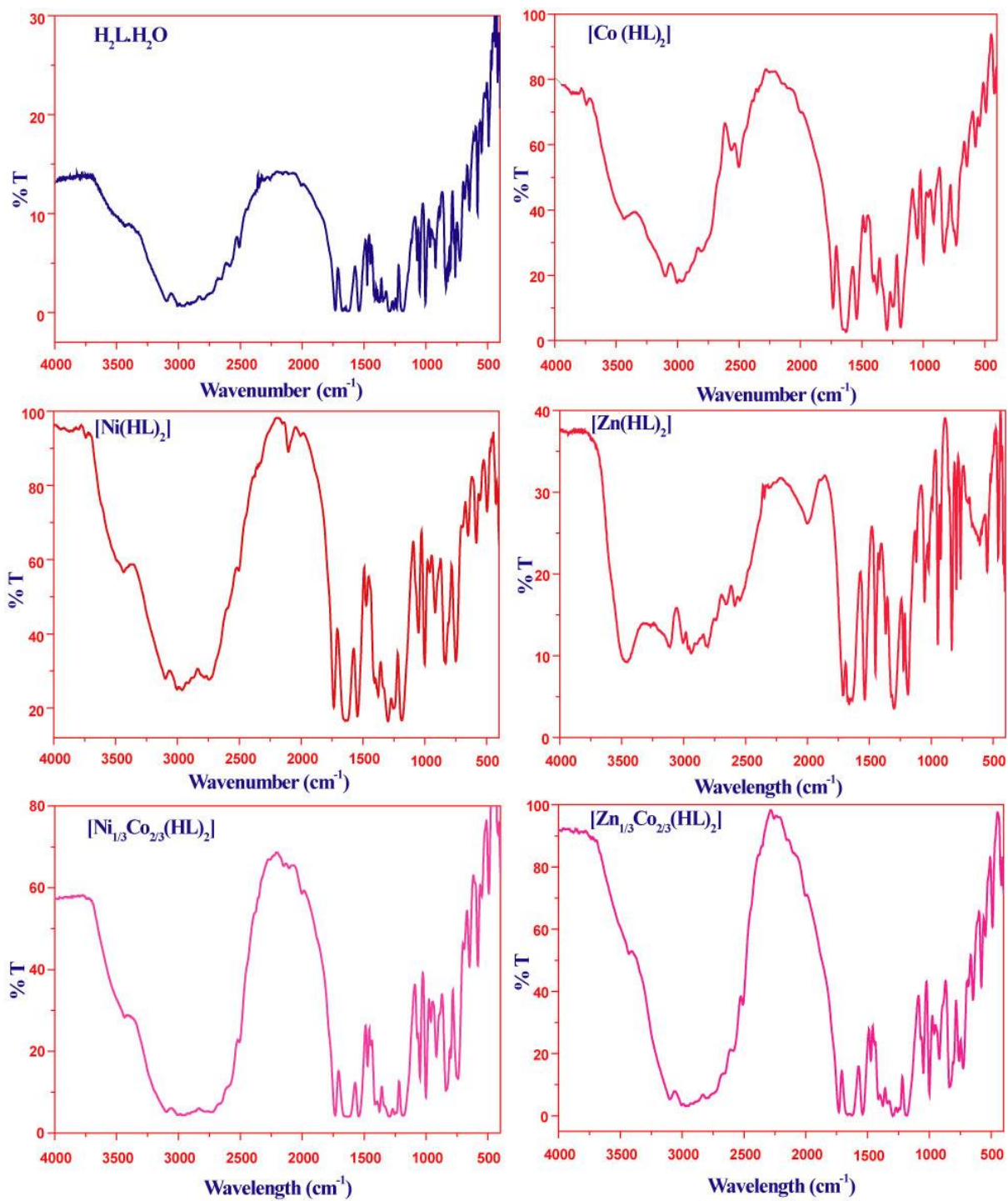


Fig. S1. FT-IR spectra of ligand and complexes.

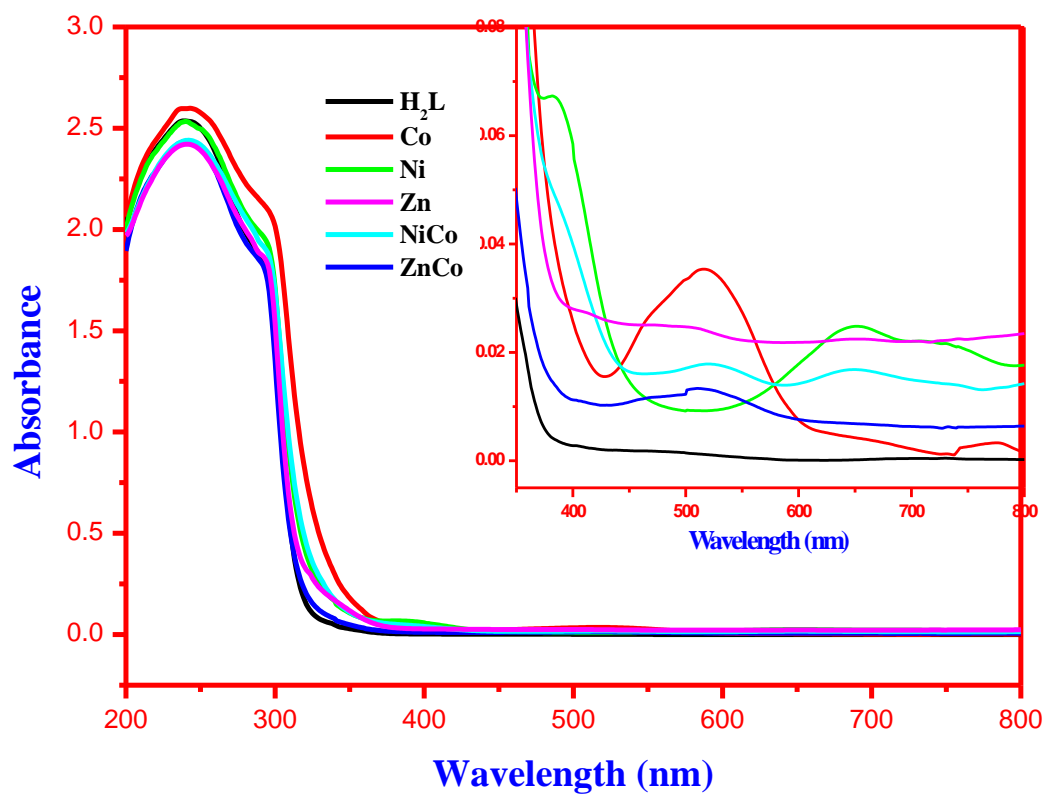


Fig. S2. UV-visible electronic absorption spectra for various ligands and complexes (10^{-3} M concentration).

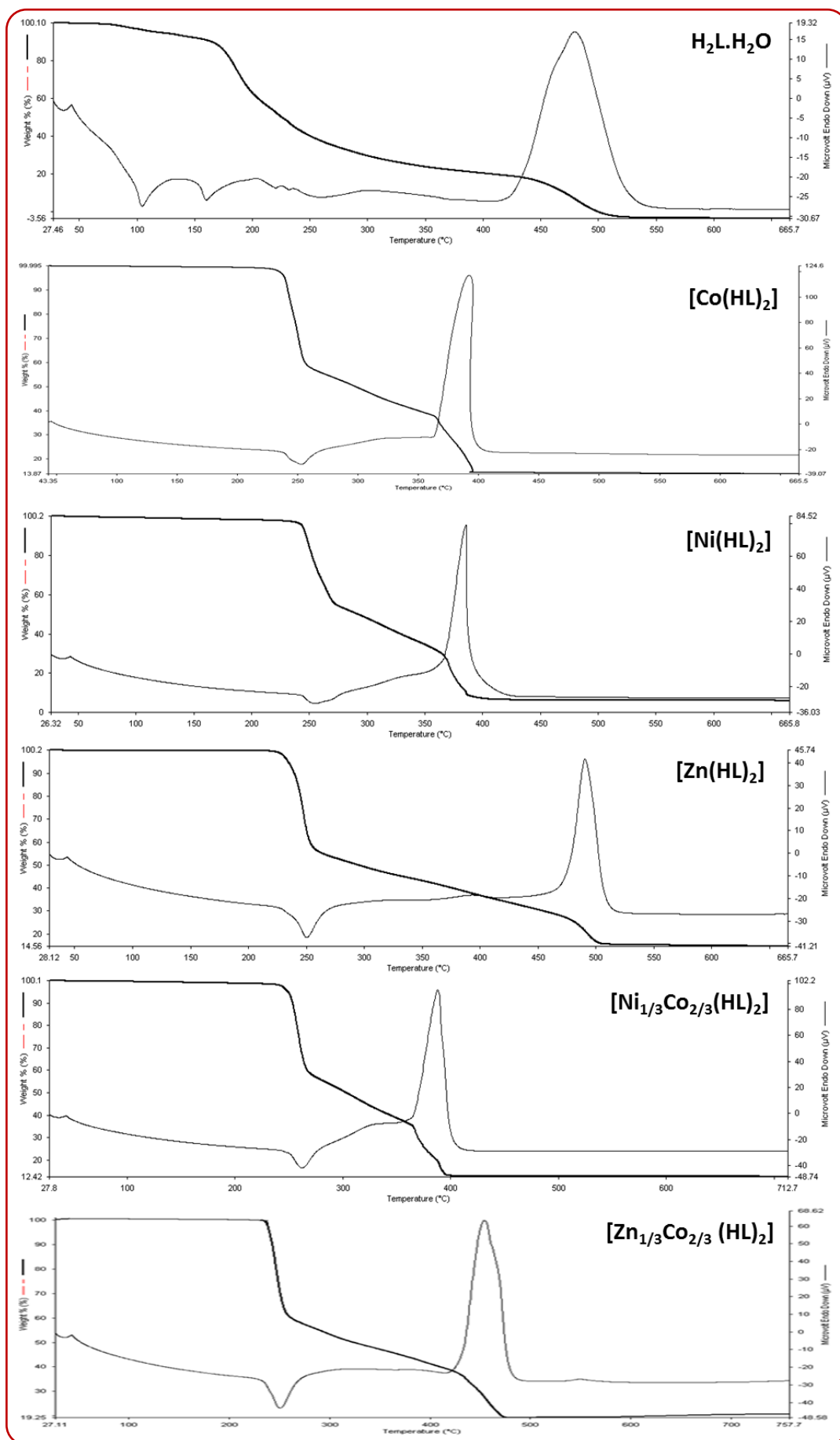


Fig. S3. Simultaneous TG-DTA of H_2L and complexes.

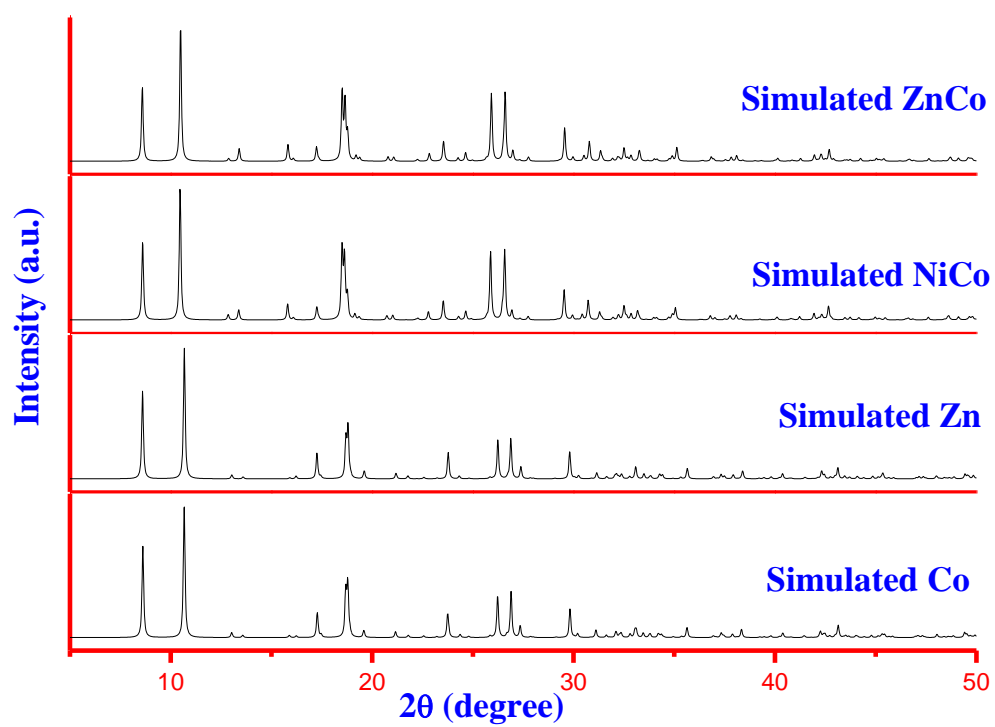


Fig. S4. PXRD patterns of the simulated single crystal crystallography data.

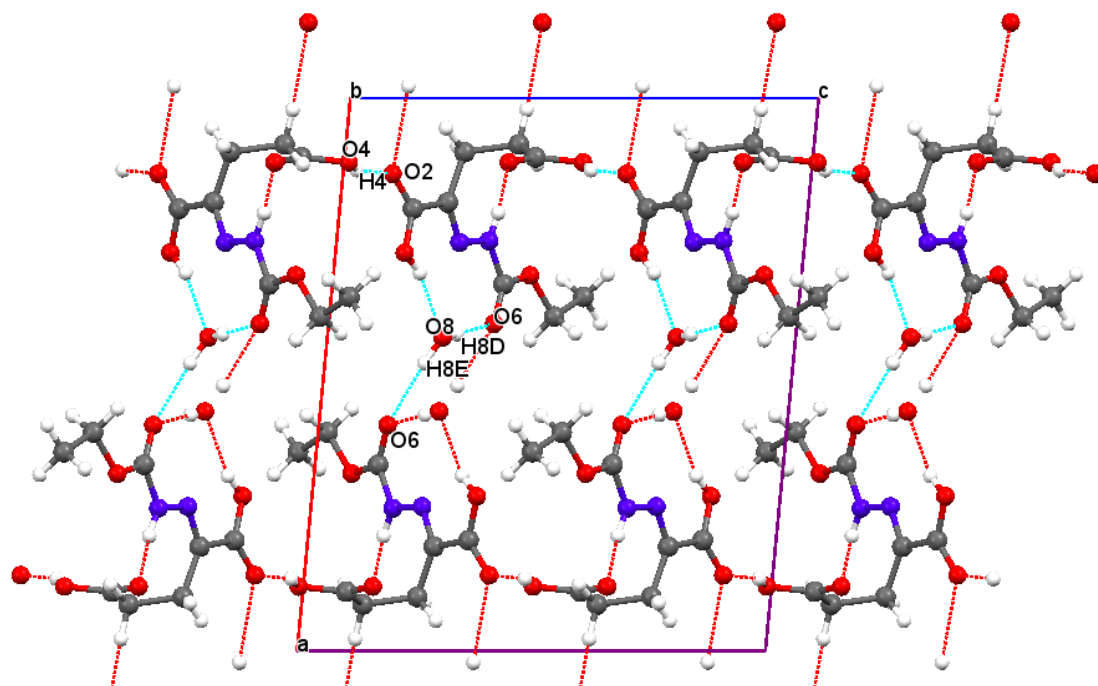


Fig. S5. Two dimensional structure of $\text{H}_2\text{L}\cdot\text{H}_2\text{O}$.

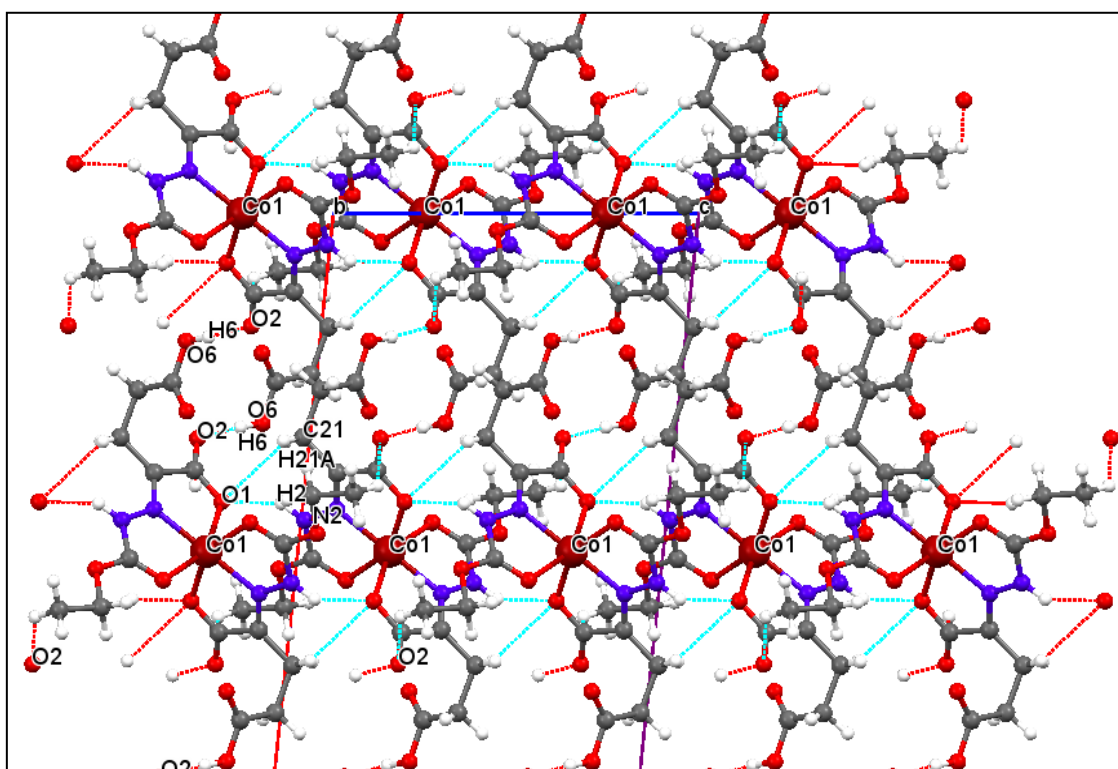


Fig. S6. 2D structure created by O-H...O, N-H...O and C-H...O hydrogen bonds in cobalt complex down the b-axis.

Table S4. Hydrogen bonding data

H₂L. H₂O					[Co(HL)₂]				
D-H...A	d(D-H)/ Å	d(A-H)/Å	d(D-A)/ Å	D-H-A^o	D-H...A	d(D-H) /Å	d(A-H)/ Å	d(D-A)/ Å	D-H-A /^o
N3-H3...O3 ⁱ	0.880	2.152	2.968	154.10	N2-H2...O1 ⁱ	0.808	1.907	2.666	135.06
O8-H8D...O6 ⁱⁱ	0.870	2.036	2.904	176.00	C2-H21B...O1 ⁱ	0.990	2.672	3.290	120.75
O8-H8E...O6 ⁱⁱⁱ	0.870	2.026	2.879	166.25	O6-H6...O2 ⁱⁱ	0.945	1.730	2.671	174.06
C4-H44B...O2 ^{iv}	0.990	2.638	3.612	167.6	C6-H6C...O2 ⁱⁱⁱ	0.980	2.644	3.371	131.11
O4-H4...O2 ^v	0.840	1.855	2.661	160.21					
i. x, -1+y, z		iv. -x, -1/2+y, 1/2-z			i. x, 1-y, -1/2+z		iii. -x, 1-y, -1/2+z		
ii. x, y, z		v. x, -1/2-y, -1/2+z			ii. 1/2+x, -1/2+y, z				
iii. 1-x, 1/2+y, 1/2-z									
[Zn(HL)₂]					[Ni_{0.33}Co_{0.67}(HL)₂]				
N2-H2...O2 ⁱ	0.870	1.906	2.674	158.59	N2-H2...O1 ⁱ	0.860	2.008	2.683	134.61
C6-H6B...O2 ⁱ	0.990	2.683	3.305	121.09	C8-H8A...O2 ⁱⁱ	0.960	2.669	3.407	133.98
O5-H5...O3 ⁱⁱ	0.840	1.838	2.673	172.61	O3-H3...O2 ⁱⁱⁱ	0.820	1.872	2.683	171.19
C3-H3C...O3 ⁱⁱⁱ	0.980	2.658	3.373	130.07					
i. x, 1-y, -1/2+z		iii. 2-x, 1-y, 1-z			i. x, 1-y, -1/2+z		iii. 1/2-x, -1/2+y, 1.5-z		
ii. 1.5-x, -1/2+y, 1.5-z					ii. 1-x, 1-y, 1-z				
[Zn_{0.33}Co_{0.67}(HL)₂]									
N2-H2...O1 ⁱ	0.860	2.016	2.694	135.07					
C3-H3B...O1 ⁱ	0.970	2.705	3.312	121.18					
O3-H3...O2 ⁱⁱ	0.820	1.864	2.679	172.06					
C8-H8C...O2 ⁱ	0.960	2.700	3.400	130.23					
i. x, 1-y, -1/2+z		ii. -1/2+x, -1/2+y, z							

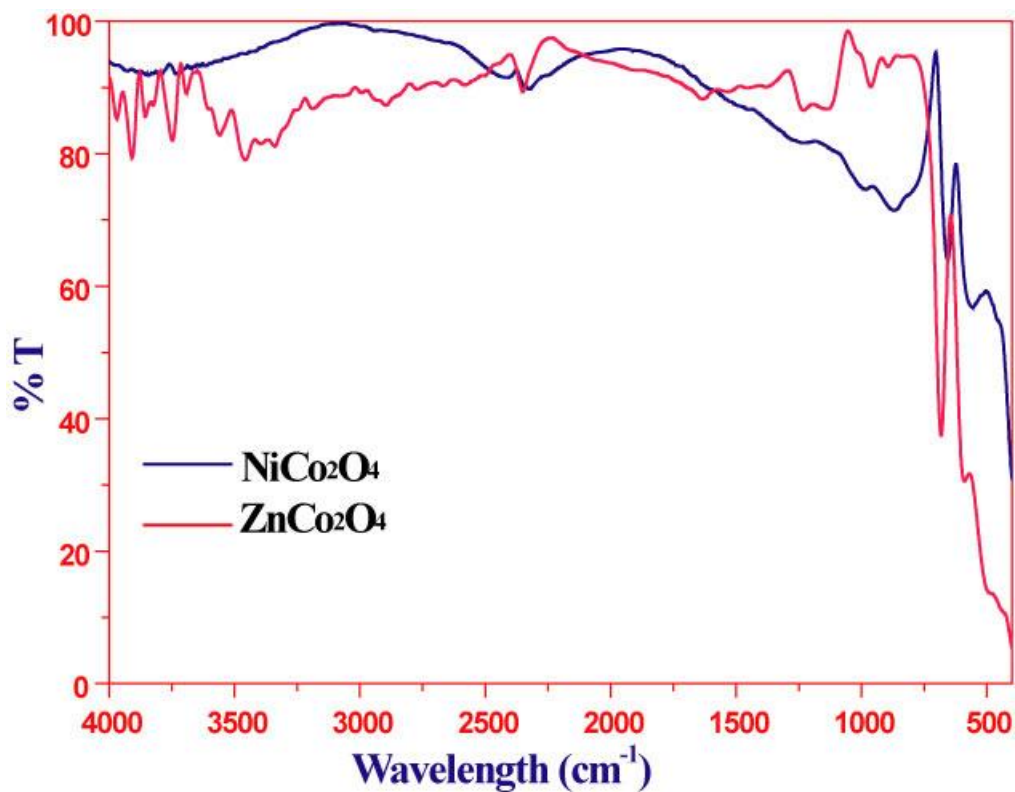


Fig. S7. FT-IR spectra of nanospinels.

Experimental

Synthesis of nanocrystalline NiCo₂O₄ and ZnCo₂O₄

The oxide nanomaterials were obtained by heating the mixed metal complexes to 500 °C in a muffle furnace and calcining for 4 h. The samples were slowly heated at a rate of 5 °C/min in a silica crucible, followed by calcination for about 4 h to attain homogeneity.

Materials and methods

All reagents and chemicals were of analytical reagent grade and were used without further purification. Double distilled water was used as a solvent for synthesis and analysis throughout the experiment. Elemental analysis for C, H, and N was performed using a Vario-ELIII elemental analyzer. Metal analyses were determined by complexometric titration using an EDTA (0.01 M) solution. The Fourier-Transform Infrared (FT-IR) spectra were recorded on a JASCO 4100 spectrophotometer on KBr pellets in the range of 4000-400 cm⁻¹. Electronic

absorption spectra were measured on a JASCO V-630 UV-vis spectrophotometer. The luminescence spectra were recorded with a Perkin-Elmer LS-55 spectrophotometer, with whole excitation and emission slit widths of 10 and 5 nm, respectively. Simultaneous TG-DTA studies were undertaken on a Perkin – Elmer SII thermal analyzer, and curves were obtained in air using platinum cups as holders with ~ 3 mg of each sample at a heating rate of 10 °C/min. Inductively coupled plasma atomic emission spectroscopy (ICPAES) was performed on a Perkin Elmer Optima 5300 DV spectrometer. The powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 PHASER powder diffraction instrument with K α radiation of the Cu target as the light source ($\lambda = 1.54056 \text{ \AA}$) and a silicon plate as the sample stage (holder). For the PXRD measurements, a continuous step-scan mode with a step width of 0.030°, an equilibrium time of 256 seconds per step, and operating conditions of 30 kV & 10 mA were used.

The intensities for the X-ray determination of compounds were collected with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a Bruker D8 Quest diffractometer equipped with a TRIUMPH monochromator and a CMOS detector. The crystal was kept at 300.0 K during data collection. Using Olex2,^[1] the structure was solved with the ShelXT^[2] structure solution program using intrinsic phasing and was refined with the ShelXL^[3] refinement package using least squares minimization.

The particle sizes and morphologies of the synthesized nanoparticles were determined by field emission scanning electron microscopy (FESEM) and energy dispersive spectrometry (EDS) on a JEOS JSM-6510. High-resolution transmission electron microscopy (HR-TEM) was carried out using a JEOL JEM 2100 instrument at an operating voltage 200 kV, using a carbon-coated copper grid. Meanwhile, selected area electron diffraction (SAED) was conducted to identify the crystallinity. XPS spectra were recorded by Kratos Axis-Ultra DLD, Kratos Analytical Ltd, Japan.

References

- [1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
- [2] G. M. Sheldrick, *ActaCryst. A* **2015**, *71*, 3.
- [3] G. M. Sheldrick, *ActaCryst. C* **2015**, *71*, 3.