

Supporting Information

Thiosemicarbazone appended calix[4]arene in 1, 3-distal configuration: synthesis, crystal structure, transition metal complexes with insights into antimicrobial and anticancer activity

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FT-IR Spectra of L and L-Co, L-Ni, L-Cu, L-Zn derivatives

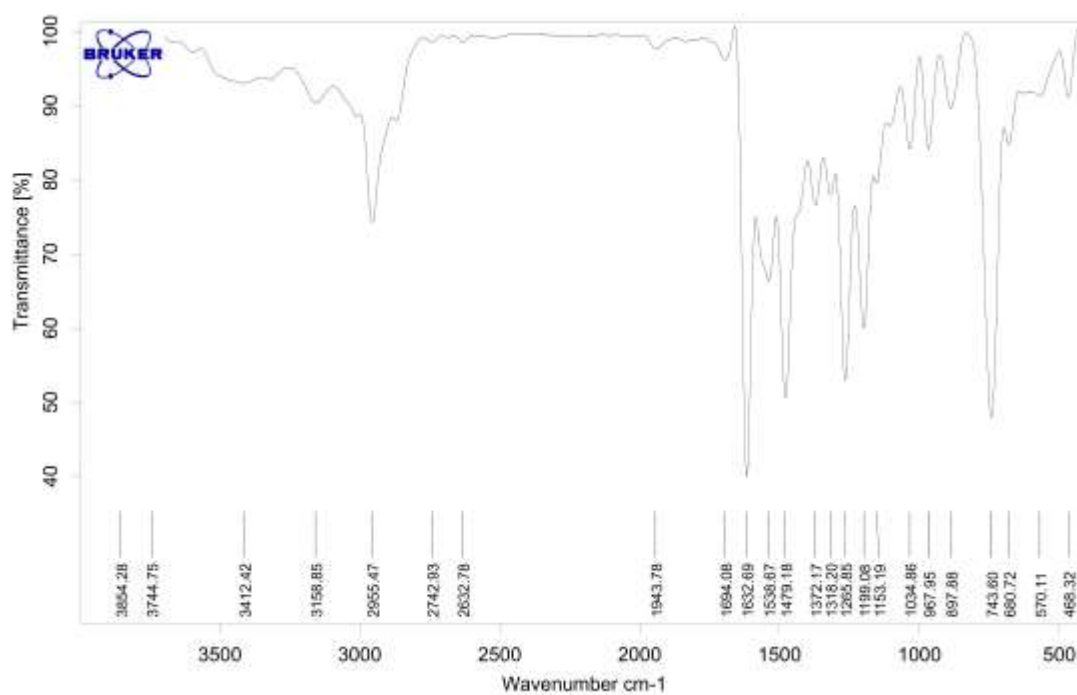


Figure S1: FT-IR spectrum of L (KBr pellet).

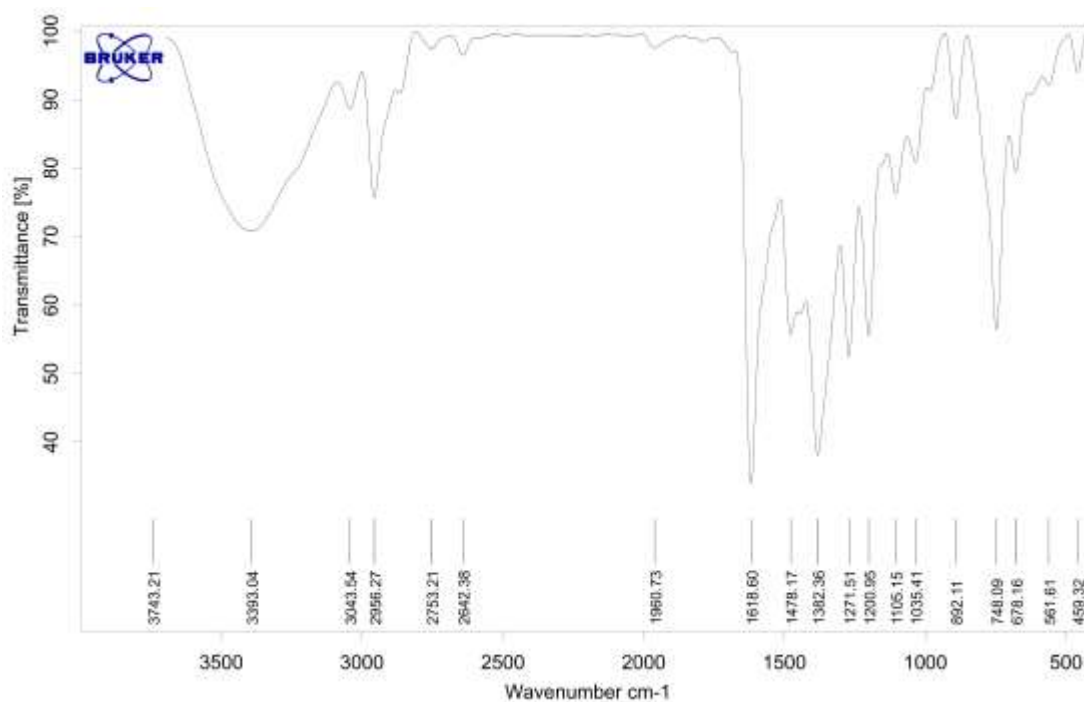


Figure S2: FT-IR spectrum of L-Co derivative (KBr pellet).

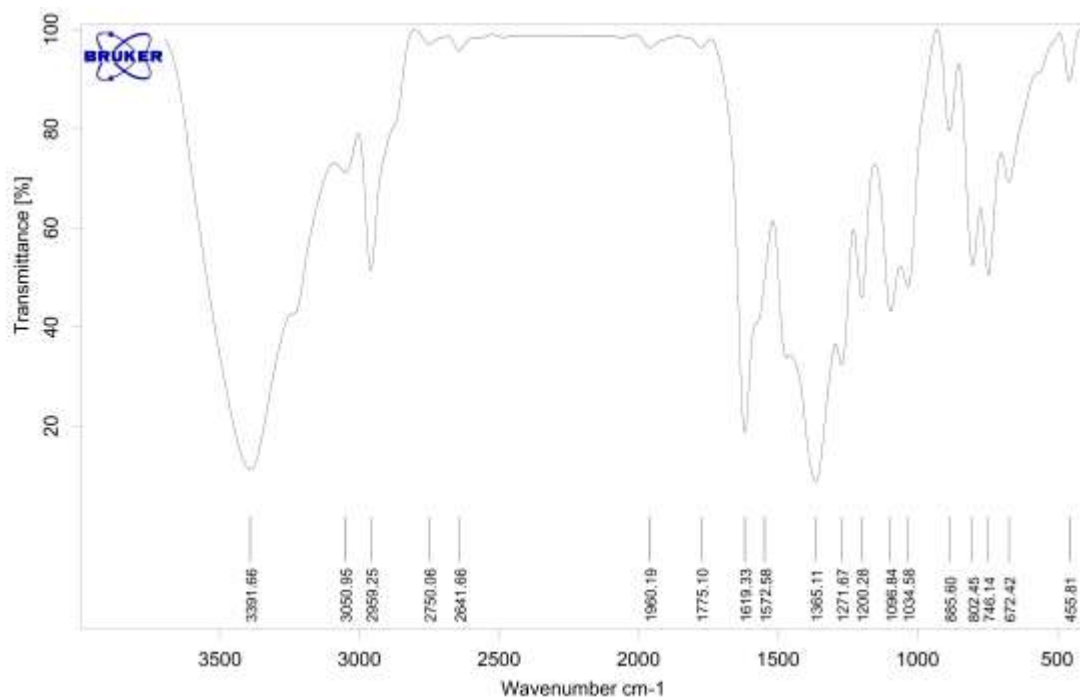


Figure S3: FT-IR spectrum of L-Ni derivative (KBr pellet).

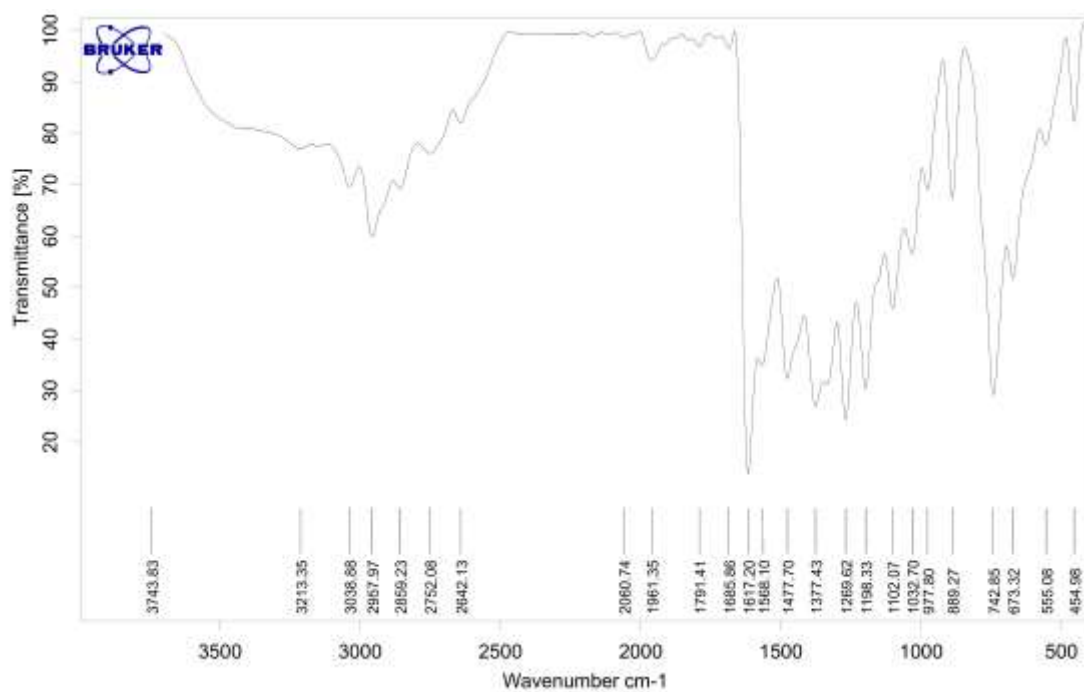


Figure S4: FT-IR spectrum of L-Cu derivative (KBr pellet).

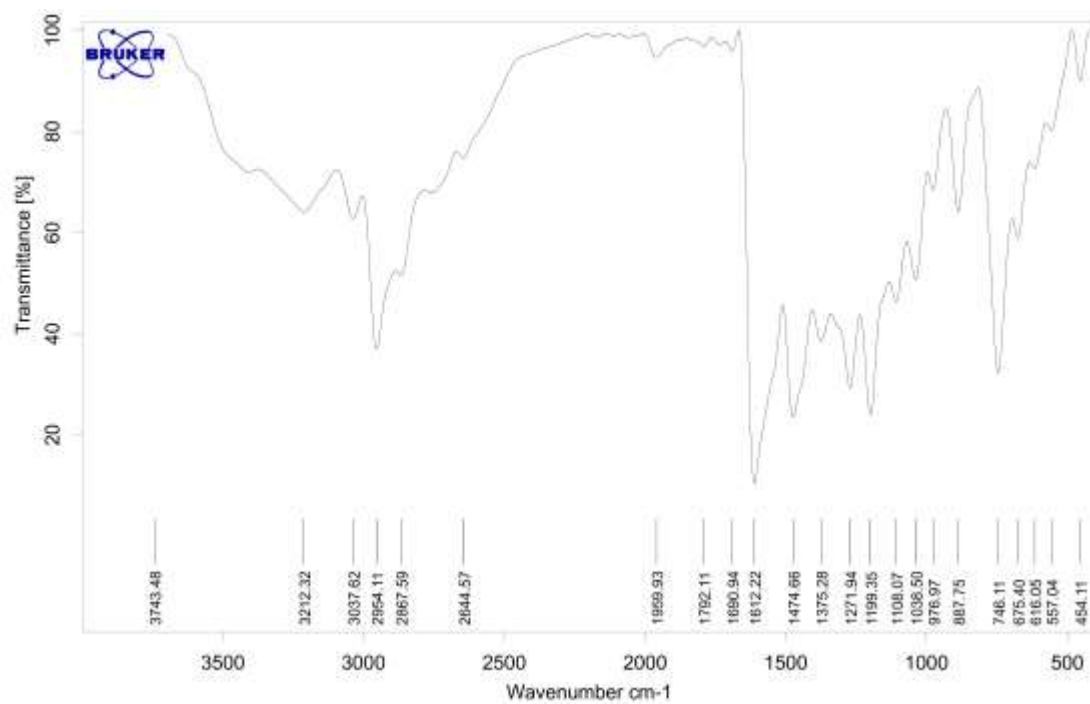


Figure S5: FT-IR spectrum of **L-Zn** derivative (KBr pellet).

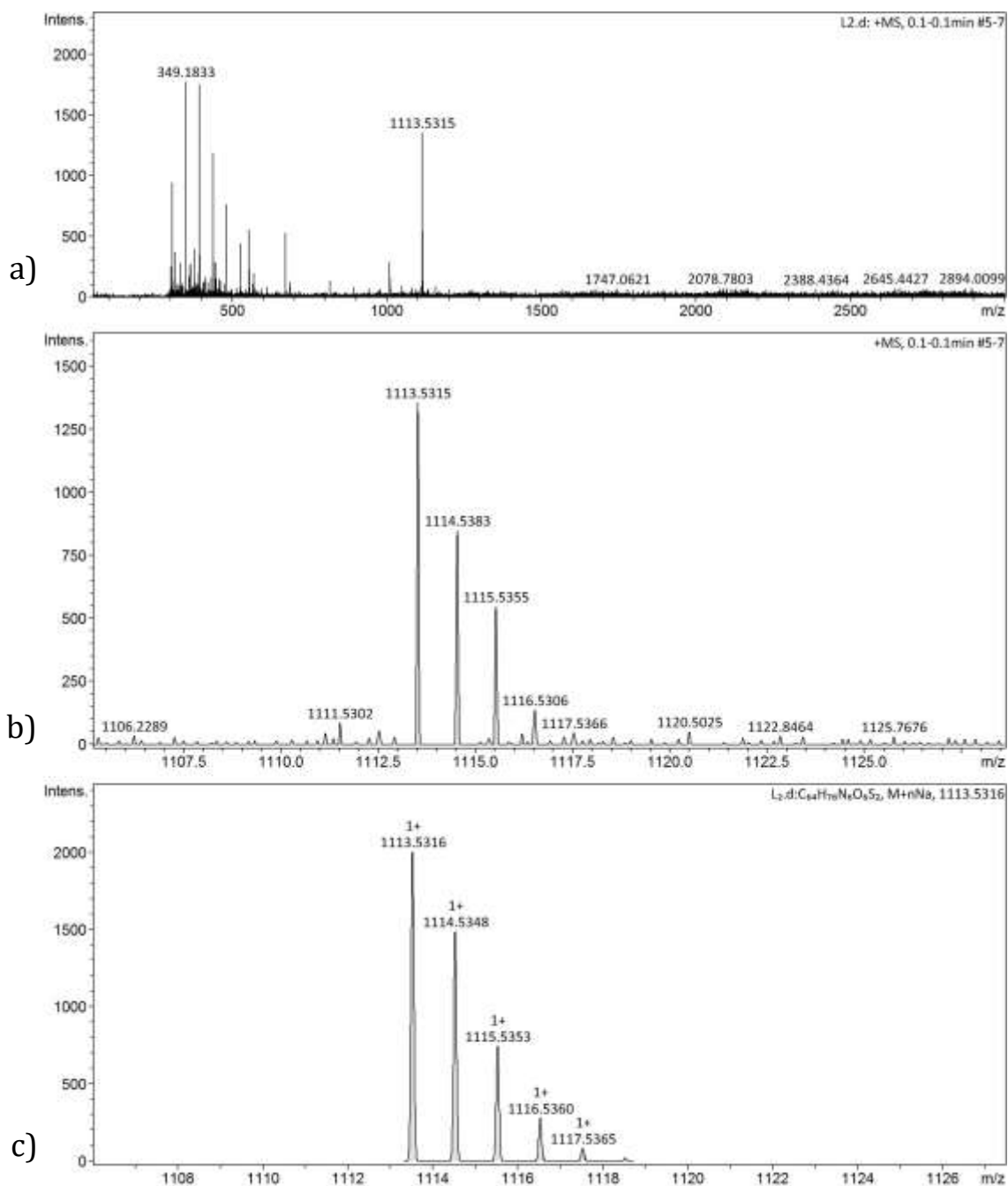


Figure S6: a) Positive-ion ESI High Resolution Mass Spectra (HRMS) of **L**. Observed (b) and calculated (c) isotopic distributions for LNa^+ , $[\text{C}_{64}\text{H}_{78}\text{N}_6\text{O}_6\text{S}_2\text{Na}]^+$.

Display Report

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Sample Name				
Comment				

Acquisition Parameter					
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Focus	Active	Set Capillary	-4500 V	Set Dry Heater	180 °C
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Scan End	3000 m/z	Set Collision Cell RF	800.0 Vpp	Set Divert Valve	Source

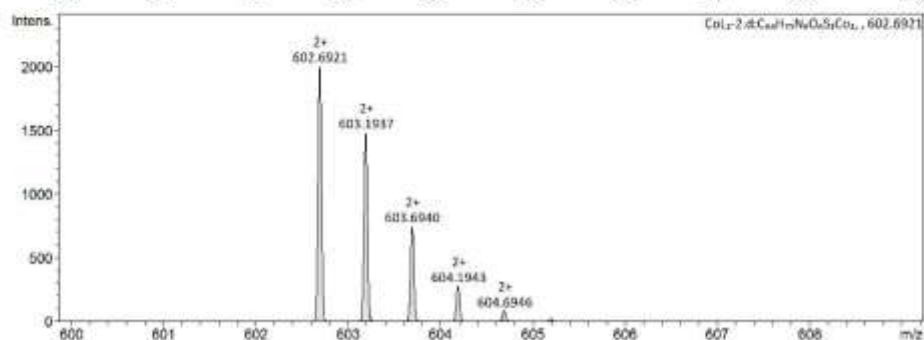
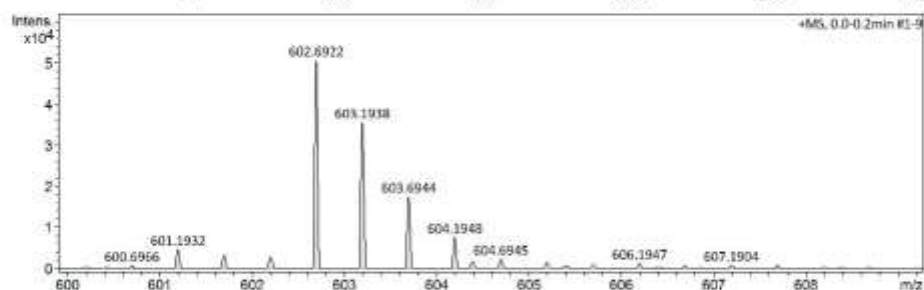
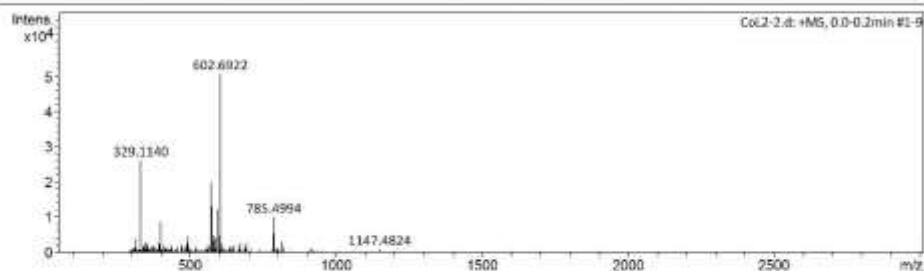


Figure S7: Positive-ion ESI High Resolution Mass Spectra (HRMS) of Co^{2+} derivative of L. Observed (middle) and calculated (bottom) isotopic distributions for $\text{LCo(II)Co(III)}^{2+}$, $[\text{C}_{64}\text{H}_{75}\text{N}_6\text{O}_6\text{S}_2\text{Co}_2]^{2+}$.

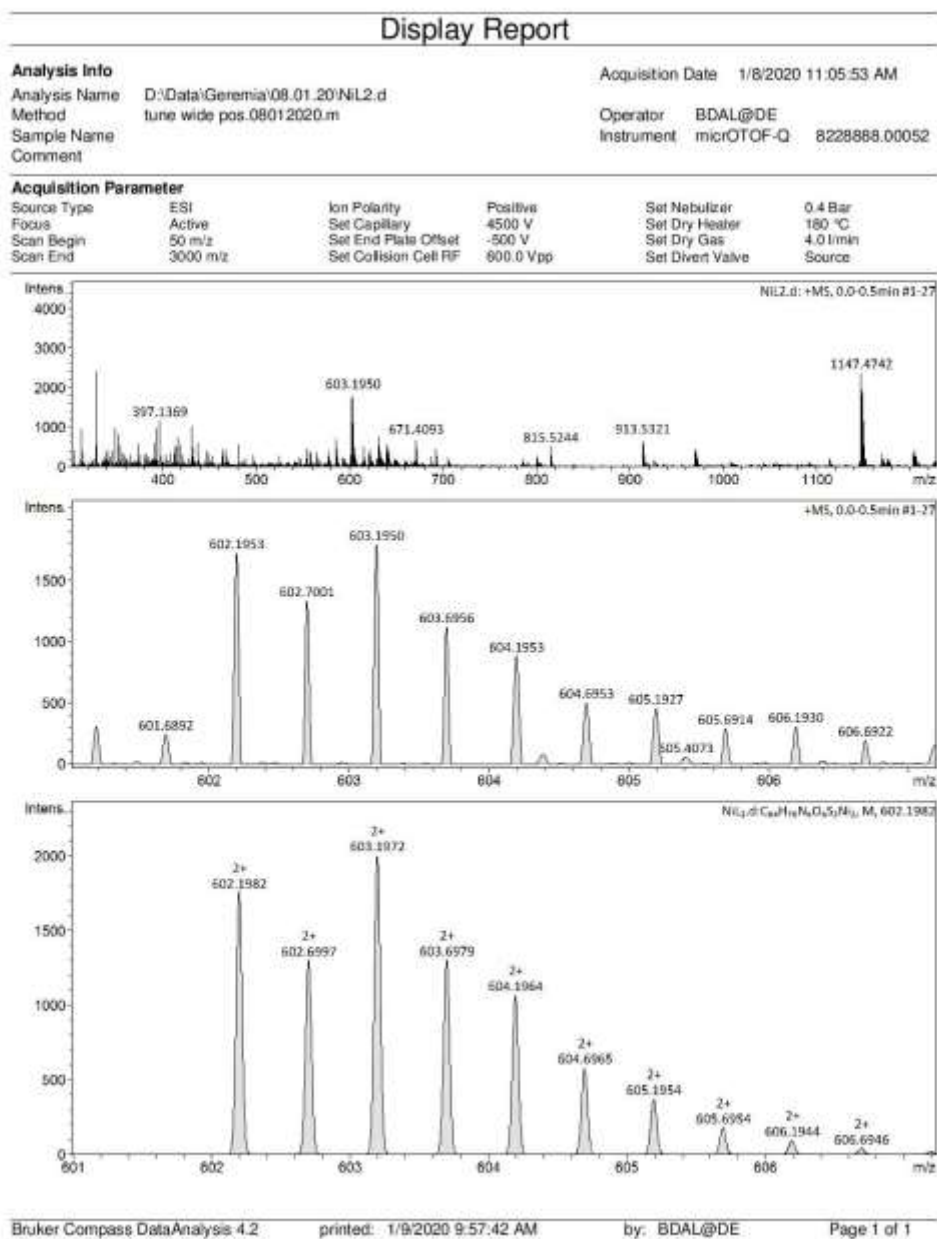


Figure S8: a) Positive-ion ESI High Resolution Mass Spectra (HRMS) of Ni²⁺ derivative of L. Observed (middle) and calculated (bottom) isotopic distributions for LNi(II)₂²⁺, [C₆₄H₇₆N₆O₆S₂Ni₂]²⁺.

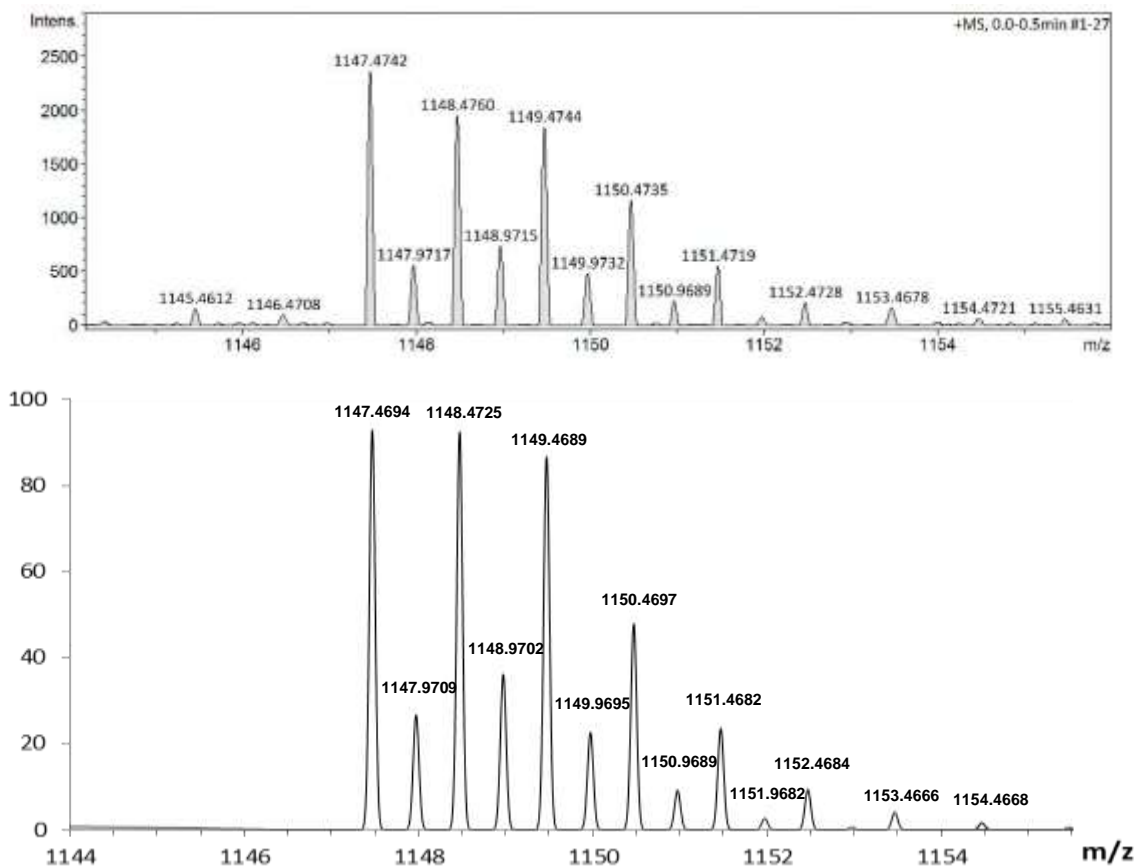
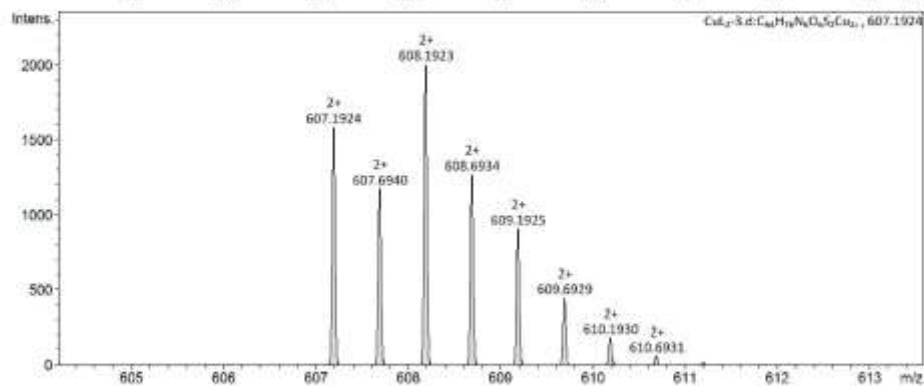
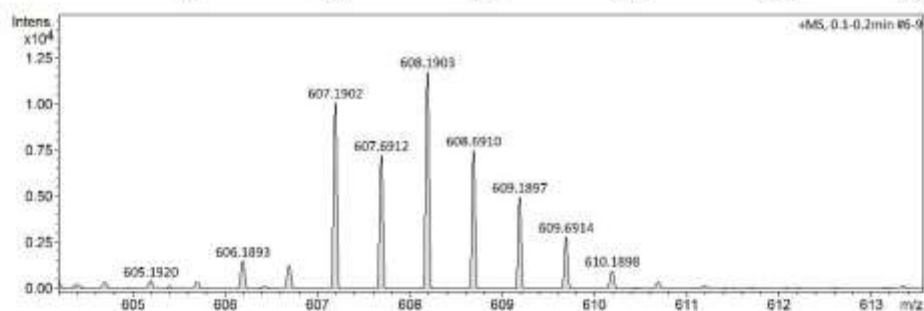
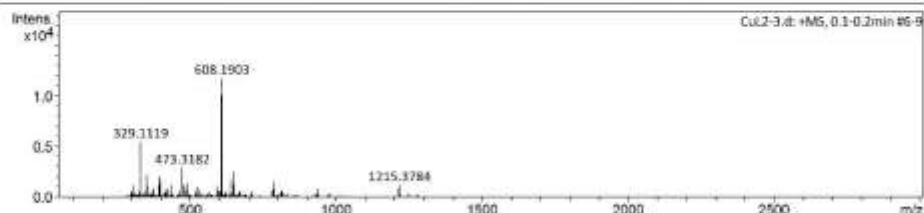


Figure S9: Observed (top) and calculated (bottom) isotopic distributions for a mixture containing 0.75 LNi(II)^+ , $[\text{C}_{64}\text{H}_{77}\text{N}_6\text{O}_6\text{S}_2\text{Ni}]^+$ and 0.25 $\text{L}_2\text{Ni(II)}_2^{2+}$, $[\text{C}_{128}\text{H}_{154}\text{N}_{12}\text{O}_{12}\text{S}_4\text{Ni}_2]^{2+}$. Masses were calculated by enviPat Web 2.2 (<http://www.envipat.eawag.ch/index.php>).

Display Report

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Sample Name				
Comment				

Acquisition Parameter					
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	900.0 Vpp	Set Divert Valve	Source



Bruker Compass DataAnalysis 4.2 printed: 1/8/2020 1:25:10 PM by: BDAL@DE Page 1 of 1

Figure S10: Positive-ion ESI High Resolution Mass Spectra (HRMS) of Cu^{2+} derivative of L. Observed (middle) and calculated (bottom) isotopic distributions for LCu(II)_2^{2+} , $[\text{C}_{64}\text{H}_{76}\text{N}_6\text{O}_6\text{S}_2\text{Cu}_2]^{2+}$.

Display Report

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Scan End	3000 m/z	Set Collision Cell RF	800.0 Vpp
		Set Nebulizer	0.4 Bar
		Set Dry Heater	180 °C
		Set Dry Gas	4.0 l/min
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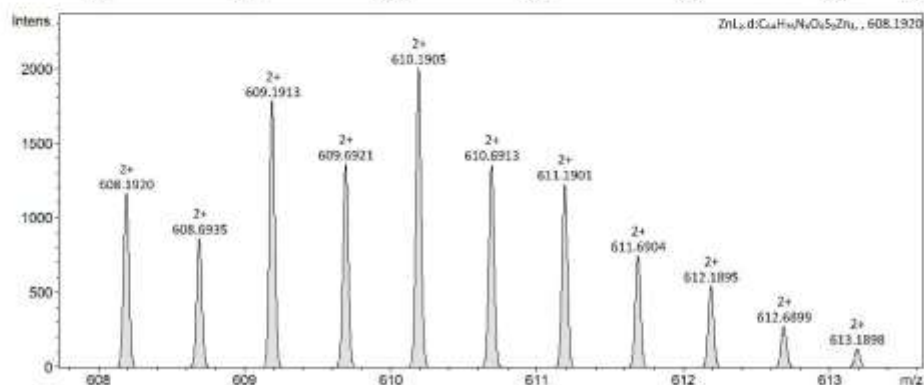
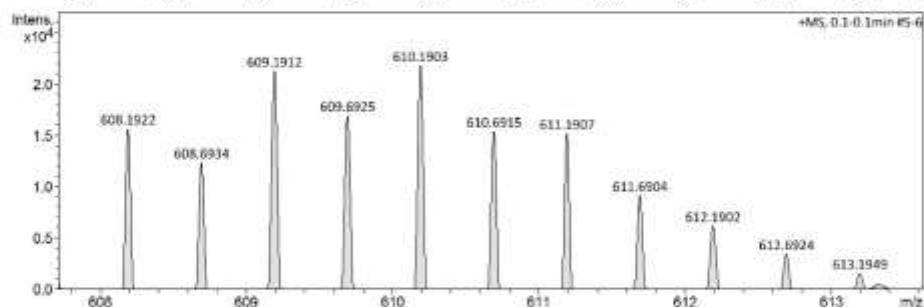
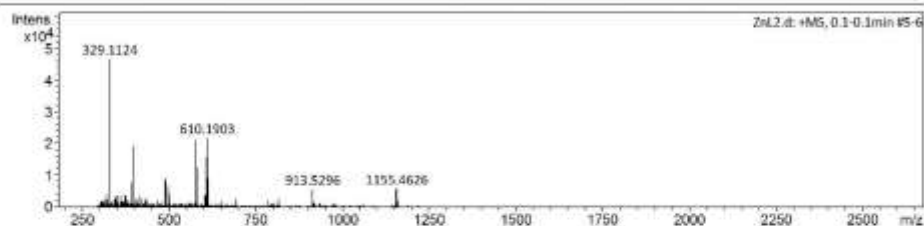


Figure S11: Positive-ion ESI High Resolution Mass Spectra (HRMS) of Zn^{2+} derivative of L. Observed (middle) and calculated (bottom) isotopic distributions for LZn(II)_2^{2+} , $[\text{C}_{64}\text{H}_{76}\text{N}_6\text{O}_6\text{S}_2\text{Zn}_2]^{2+}$.

Table S1. IR spectral data (cm⁻¹) of the ligand and its corresponding metal derivatives in KBr pellets.

Vibrational mode	Frequency in (cm ⁻¹)				
	L	LCo ²⁺	LNi ²⁺	LCu ²⁺	LZn ²⁺
C=N	1633	1618	1619	1617	1612
N-C=S	1539	shoulder	1572	1568	shoulder
C=S	898	892	885	889	887

Table S2. Crystal data and structure refinement for compound L.

Ligand L	
Empirical formula	(C ₆₄ H ₇₈ N ₆ O ₆ S ₂), H ₂ O
Formula weight	1109.46
Temperature (K)	100(2)
Wavelength (Å)	0.7
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions (Å, °)	<i>a</i> = 12.690(6), <i>α</i> = 104.44(4) <i>b</i> = 15.344(18), <i>β</i> = 98.01(4) <i>c</i> = 19.15(3), <i>γ</i> = 104.016(10)
Volume (Å ³)	3423(6)
<i>Z</i>	2
ρ_{calcd} (g/cm ³)	1.076
μ (mm ⁻¹)	0.122
F(000)	1188
Reflections collected	23853
Independent reflections	6918 [R(int) = 0.1328]
Data / restraints / parameters	6918 / 3 / 734
GooF	0.972
Final <i>R</i> indices [I>2σ(I)]	<i>R</i> ₁ = 0.0683, <i>wR</i> ₂ = 0.1677
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1359, <i>wR</i> ₂ = 0.2108
CCDC code	1944727

Table S3: Elemental analysis of the metal derivatives of **L**

L			
Metal salt	Proposed structure	Elemental analysis	
Co(NO ₃) ₂ ·6H ₂ O	[CoL](NO ₃) ₂ ·2H ₂ O	C, 58.66; H, 6.31; N, 8.55	Calculated
	C ₆₄ H ₈₂ N ₈ O ₁₄ S ₂ Co	C, 58.76; H, 5.97; N, 8.43	Found
Ni(NO ₃) ₂ ·6H ₂ O	[NiL](NO ₃) ₂	C, 60.33; H, 6.17; N, 8.79	Calculated
	C ₆₄ H ₇₈ N ₈ O ₁₂ S ₂ Ni	C, 60.32; H, 5.95; N, 8.99	Found
Cu(NO ₃) ₂ ·2H ₂ O	[CuL](NO ₃) ₂	C, 60.10; H, 6.15; N, 8.76	Calculated
	C ₆₄ H ₇₈ N ₈ O ₁₂ S ₂ Cu	C, 59.72; H, 5.98; N, 8.66	Found
Zn(NO ₃) ₂ ·4H ₂ O	[ZnL](NO ₃) ₂	C, 60.01; H, 6.14; N, 8.75	Calculated
	C ₆₄ H ₇₈ N ₈ O ₁₂ S ₂ Zn	C, 60.23; H, 6.01; N, 8.64	Found