Electronic Supplementary Information

Di- and tri-valent metal complexes with *tris*-amide-functionalised 1,4,7-triazacyclononane chelators

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Table S1 X-ray crystallographic parameters[a]

Compound	**[Ni(1)](NO$_3$)$_2$·1½CH$_3$OH**	**[Ni(2)](NO$_3$)$_2$·0.249H$_2$O**	**[Cu(1)]$_3$(NO$_3$)$_6$·1¼Et$_2$O·MeOH**
Formula	$C_{30}H_{36}N_8NiO_9$·1½CH_3OH	$C_{24}H_{48}N_8NiO_9$·0.249 H_2O	$[C_{30}H_{36}CuN_6O_3]_3(NO_3)_6$ ·1.25Et_2O·CH_3OH
M	759.426	655.892	2273.340
Crystal system	monoclinic	monoclinic	triclinic
Space group (no.)	P2$_1$/c (14)	P2$_1$/n (14)	P-1 (2)
a /Å	16.2195(5)	17.7391(7)	17.6146(3)
b /Å	19.5074(8)	11.5230(4)	17.6300(3)
c /Å	11.0872(3)	18.2239(7)	20.0301(3)
α /°	90	90	85.355(1)
β /°	95.999(3)	119.134(5)	80.554(1)
γ /°	90	90	60.327(2)
U /Å^3	3488.8(2)	3253.8(3)	5331.28(19)
Z	4	4	2
μ(Mo-K$_\alpha$) /mm^{-1}	0.625	0.656	0.681
F(000)	1598.644	1404.471	2382.868
Total no. reflns	45487	81694	124966
R_{int}	0.058	0.065	0.067
Unique reflns	8997	8412	27524
No. of params, restraints	755, 740	479, 350	1464, 384
GOF	1.0487	1.0326	1.0385
R_1, wR_2 [I > 2σ(I)][b]	0.057, 0.135	0.056, 0.124	0.058, 0.136
R_1, wR_2 (all data)	0.090, 0.149	0.083, 0.136	0.096, 0.154

Table S1 continued

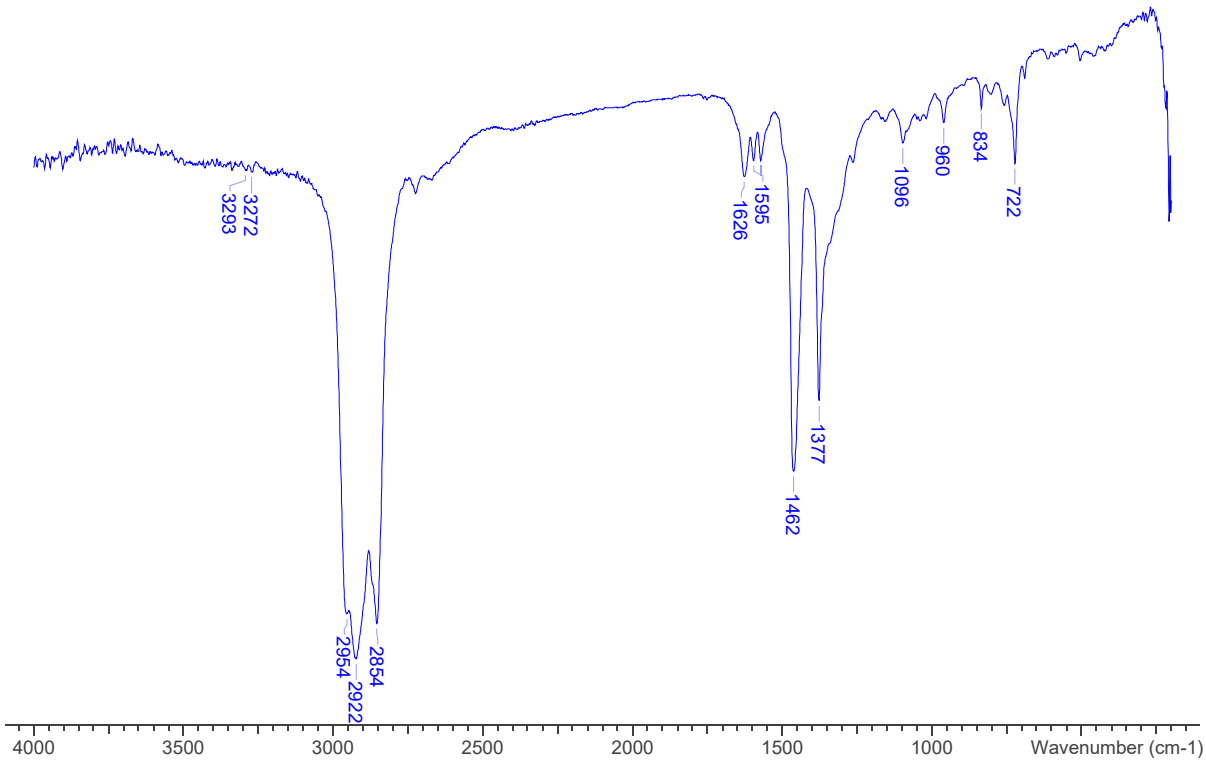
Compound	**[Cu(2))](NO$_3$)$_2$**	**[Co(1-H)](NO$_3$)$_2$·2MeOH**	**[Ga(3)](NO$_3$)·1½H$_2$O**
Formula	$C_{24}H_{48}CuN_8O_9$	$C_{30}H_{35}CoN_8O_9{\cdot}2CH_3OH$	$C_{18}H_{24}GaN_5O_8{\cdot}1½H_2O$
M	656.243	774.67	535.166
Crystal system	monoclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)
a /Å	16.4229(3)	10.8001(2)	8.7590(5)
b /Å	10.9307(2)	17.3514(3)	20.1534(14)
c /Å	17.9733(3)	19.5643(3)	12.8678(6)
α /°	90	90	90
β /°	103.813(2)	96.185(2)	108.467(6)
γ /°	90	90	90
U /Å^3	3133.15(10)	3644.95(11)	2154.5(2)
Z	4	4	4
μ(Mo-K$_\alpha$) /mm^{-1}	0.758	0.540	1.342
F(000)	1398.432	1624	1110
Total no. reflns	85801	74317	20958
R_{int}	0.038	0.043	0.053
Unique reflns	10252	9423	5491
No. of params, restraints	811, 0	494, 4	505, 566
GOF	1.0629	1.071	1.041
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.024, 0.051	0.057, 0.164	0.056, 0.146
R_1, wR_2 (all data)	0.036, 0.056	0.064, 0.169	0.085, 0.160

[a] common items: T = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$;

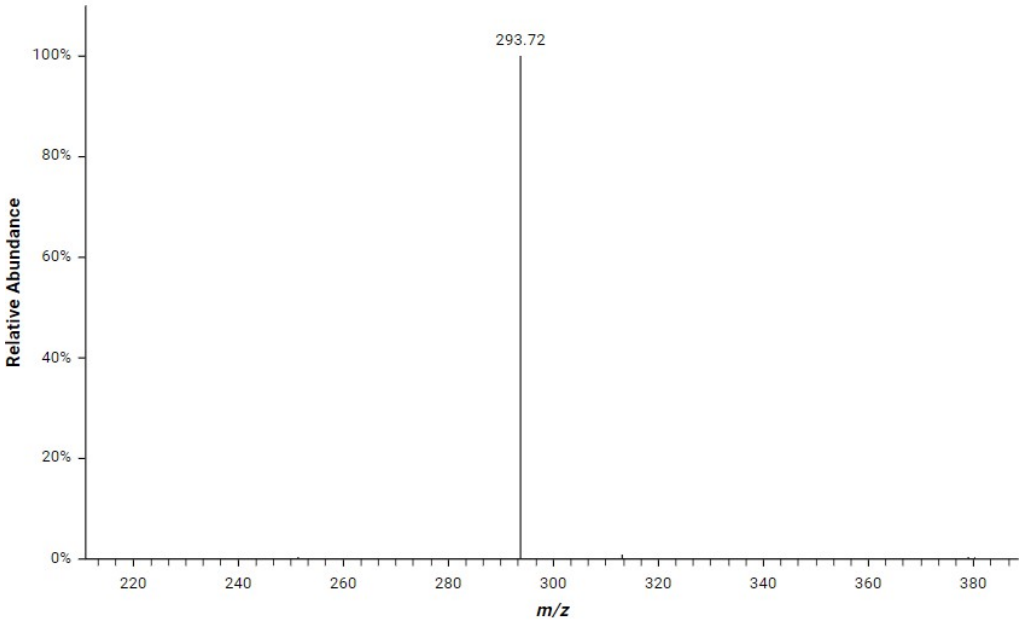
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$

Figure S1: Spectroscopic data for [Co(**1**-H)]$(NO_3)_2$

S1a: IR spectrum (Nujol)



S1b: ESI^+ MS (MeOH)



S1c: UV-vis spectrum (MeOH)

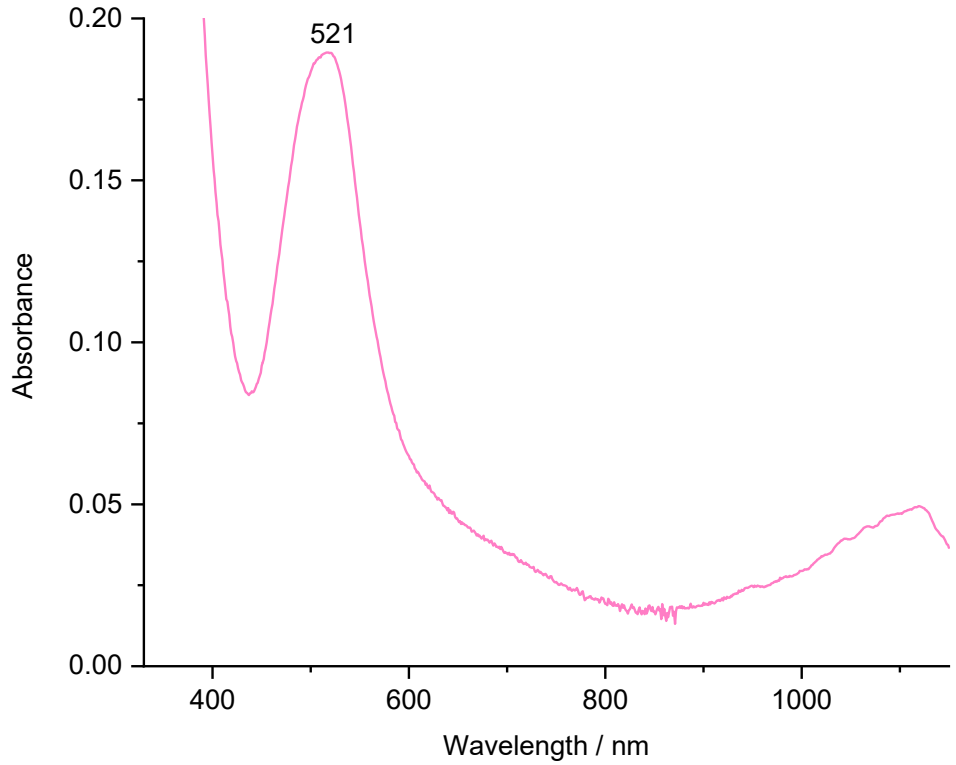
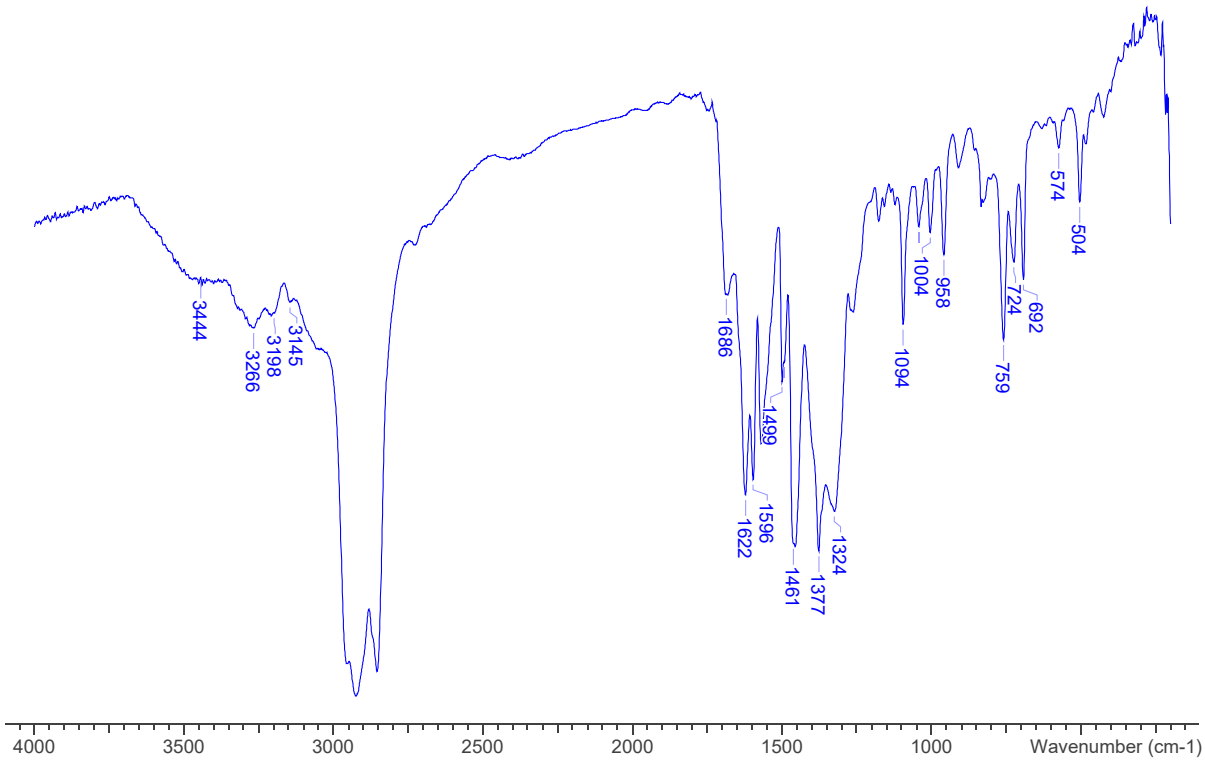
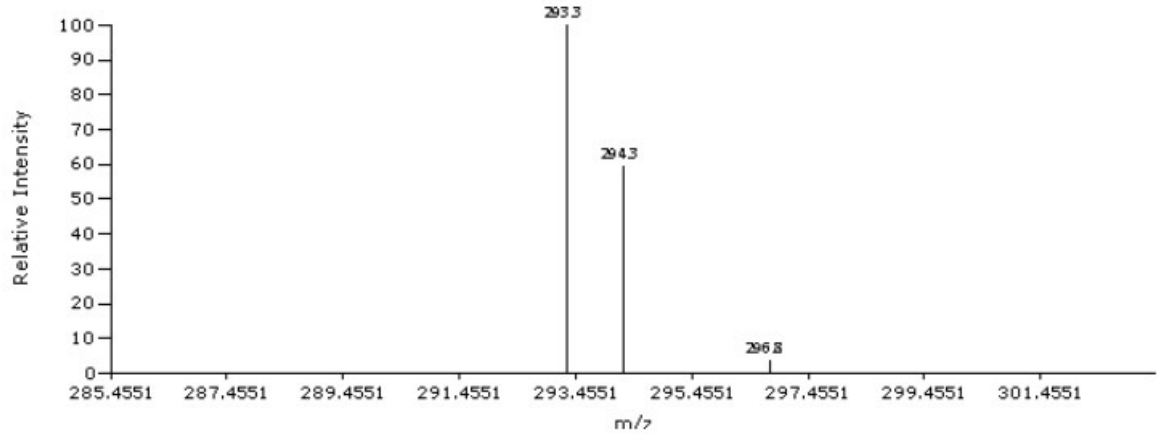


Figure S2: Spectroscopic data for [Ni(**1**)]$(NO_3)_2$

S2a: IR spectrum (Nujol).



S2b: ESI^+ MS (MeOH)



S2c: UV-Vis spectrum (MeOH)

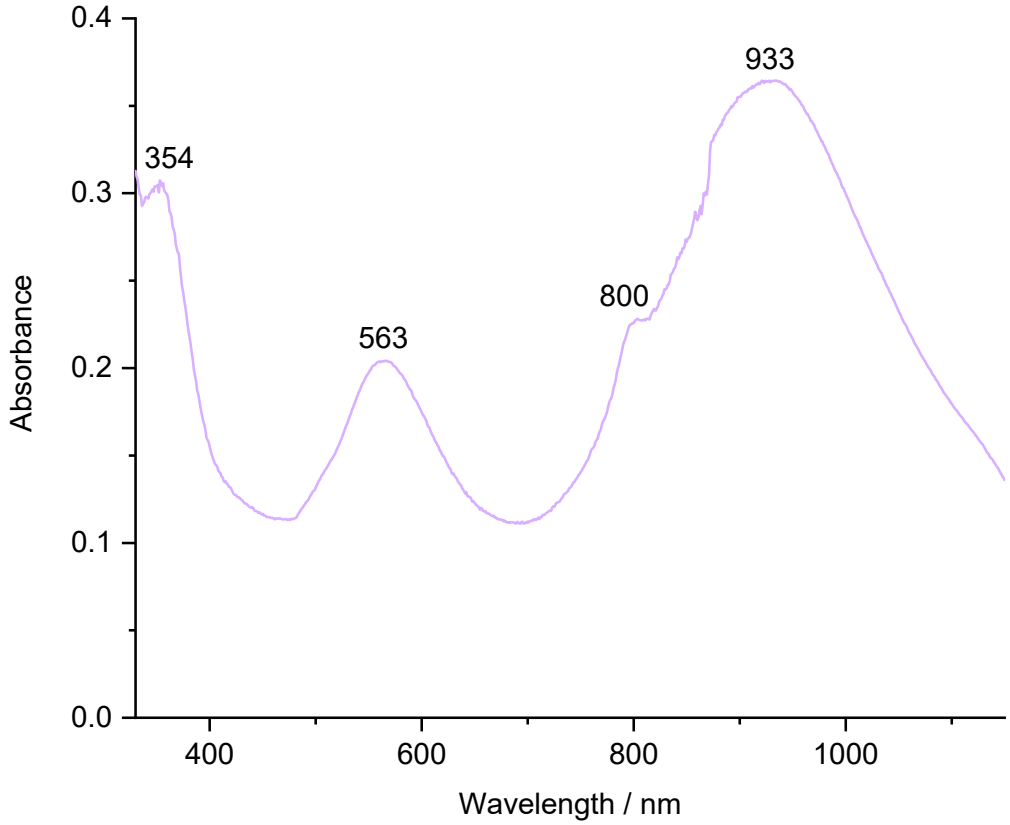
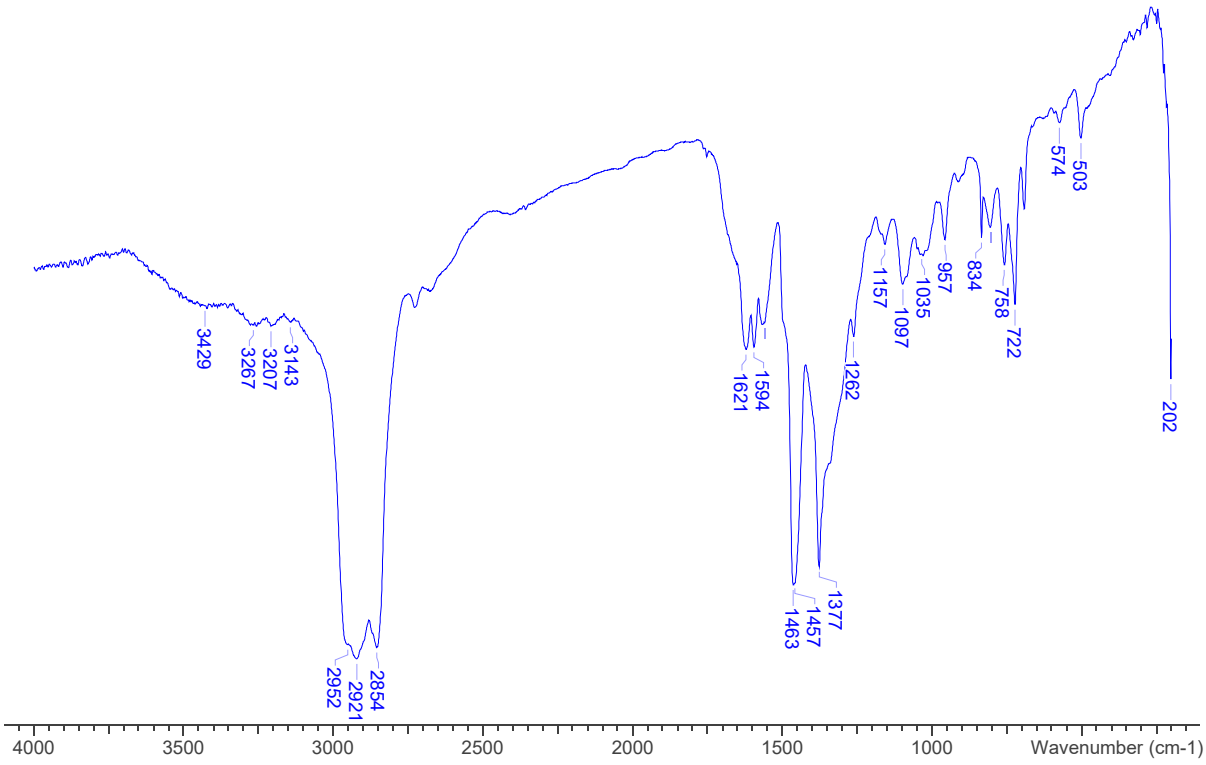
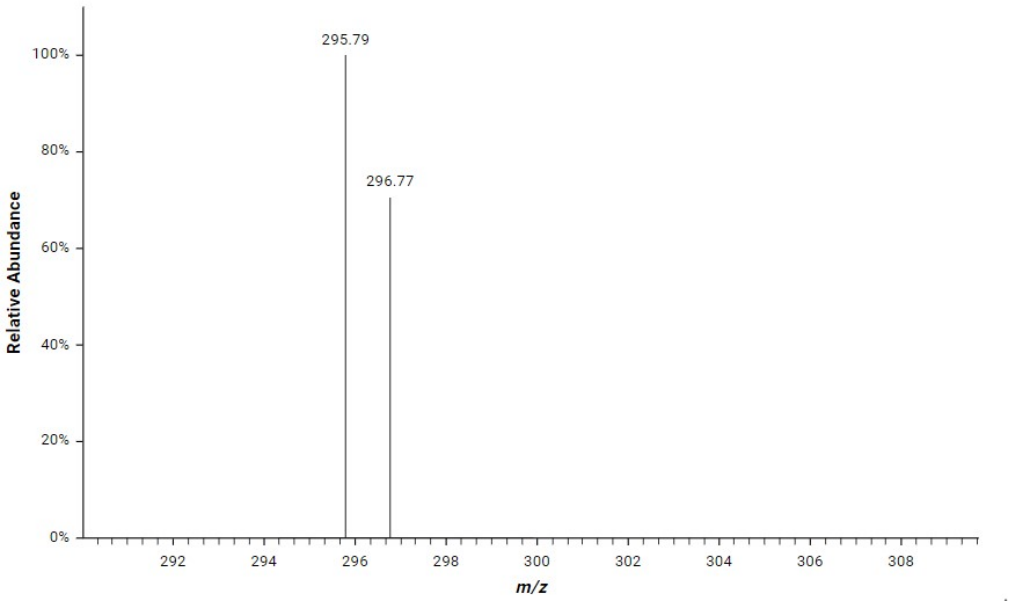


Figure S3: Spectroscopic data for [Cu(**1**)]$(NO_3)_2$

S3a: IR spectrum (Nujol):



S3b: ESI^+ MS (MeOH)



S3c: UV-Vis spectrum (MeOH)

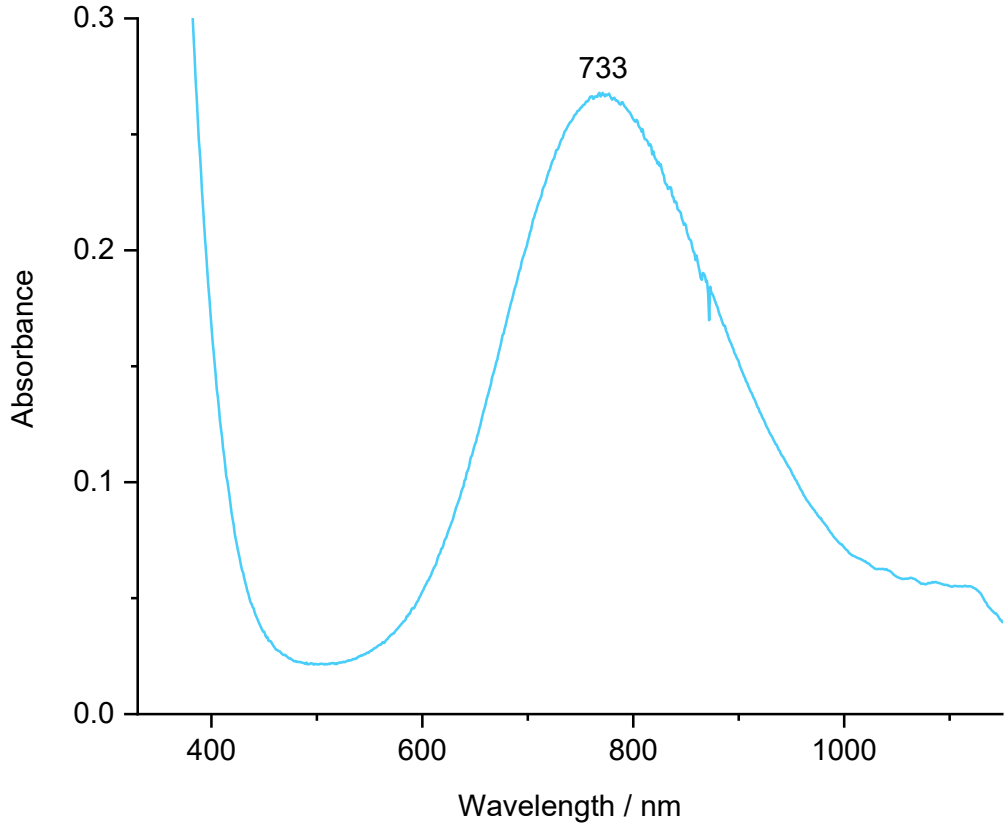
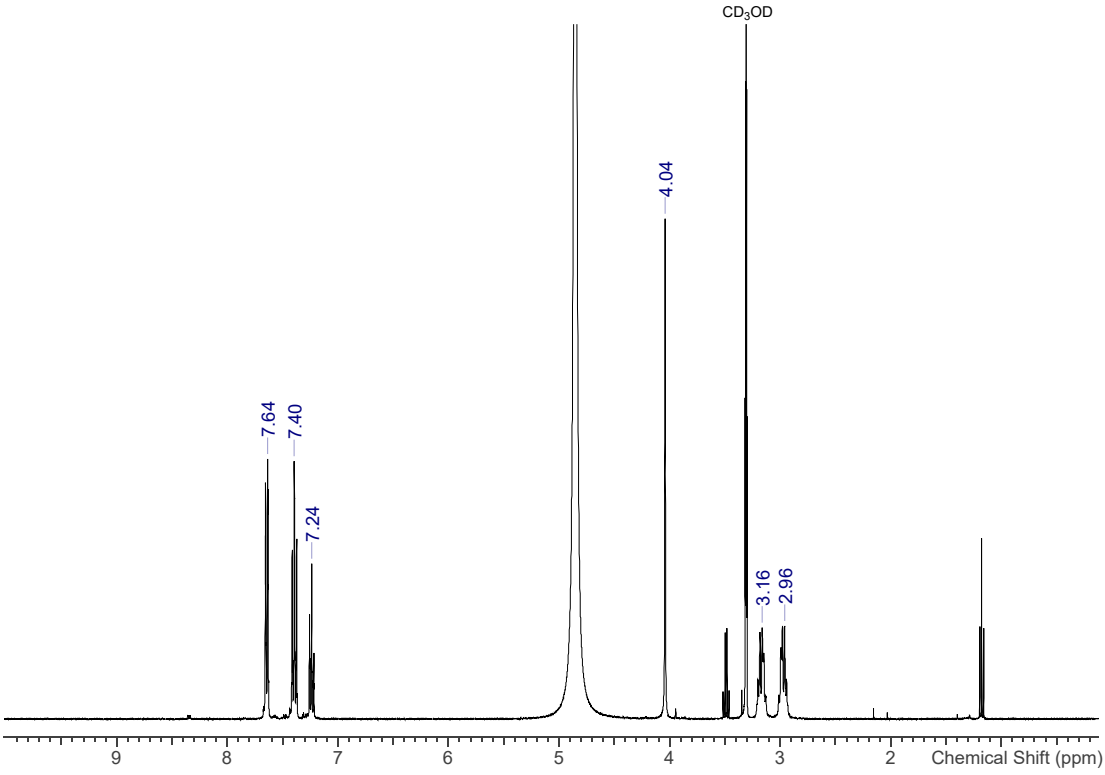
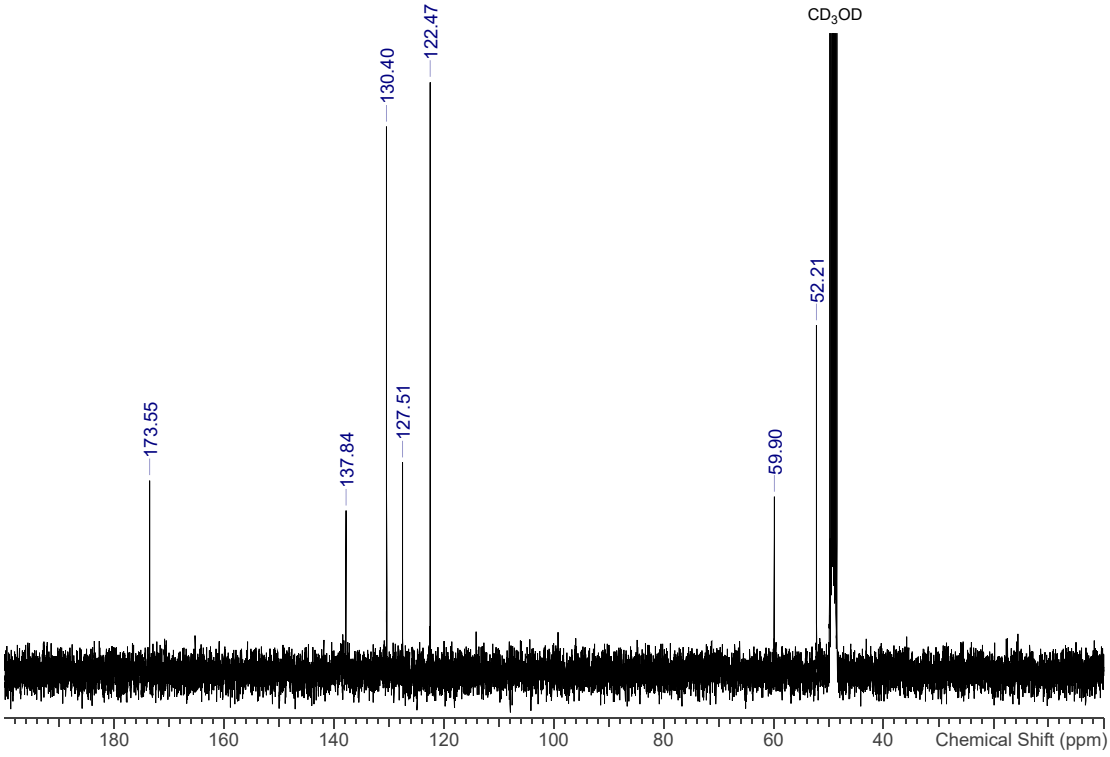


Figure S4: Spectroscopic data for [Zn(**1**)]$(NO_3)_2$

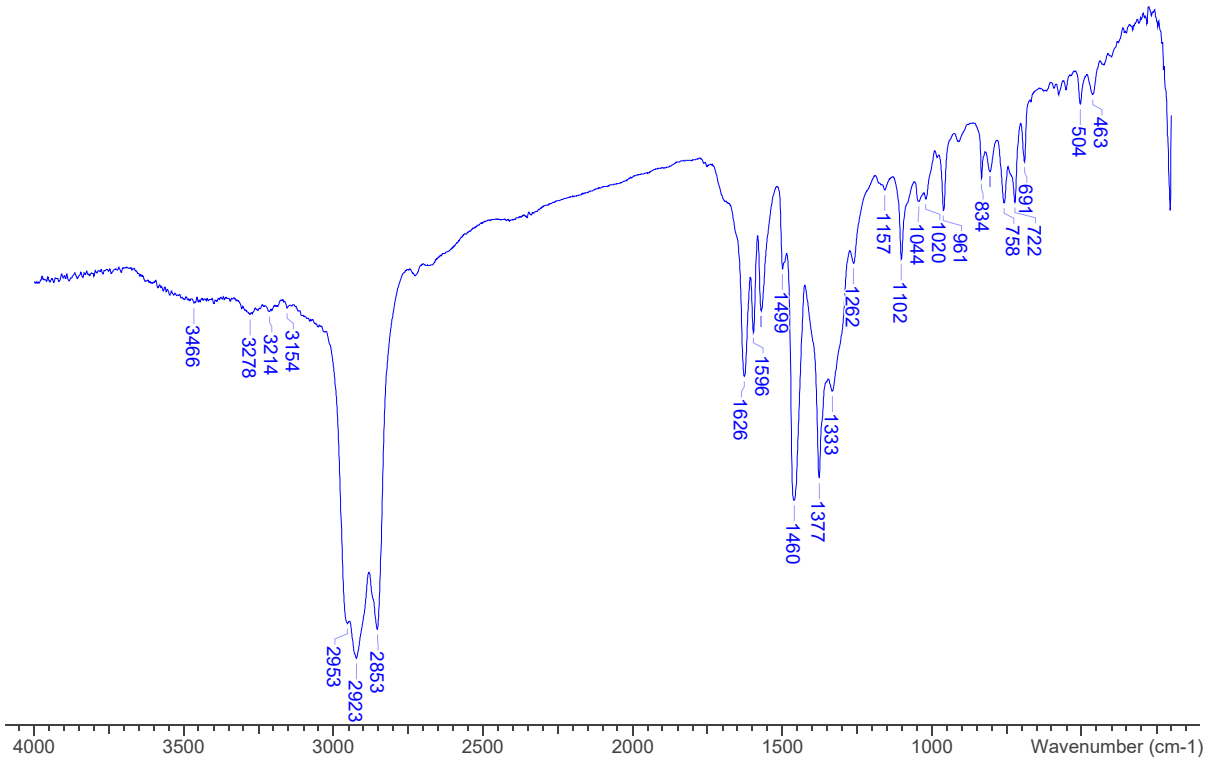
S4a: ^{1}H NMR spectrum (d_4-MeOH)



S4b: $^{13}C\{^1H\}$ NMR spectrum d_4-MeOH)



S4c: IR spectrum (Nujol)



S4d: ESI^{+} MS (MeOH)

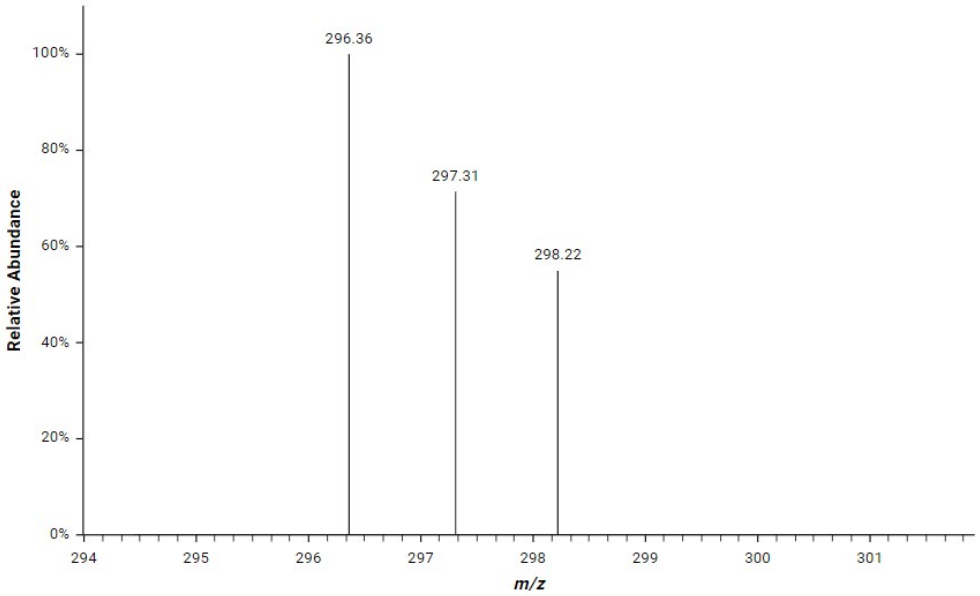
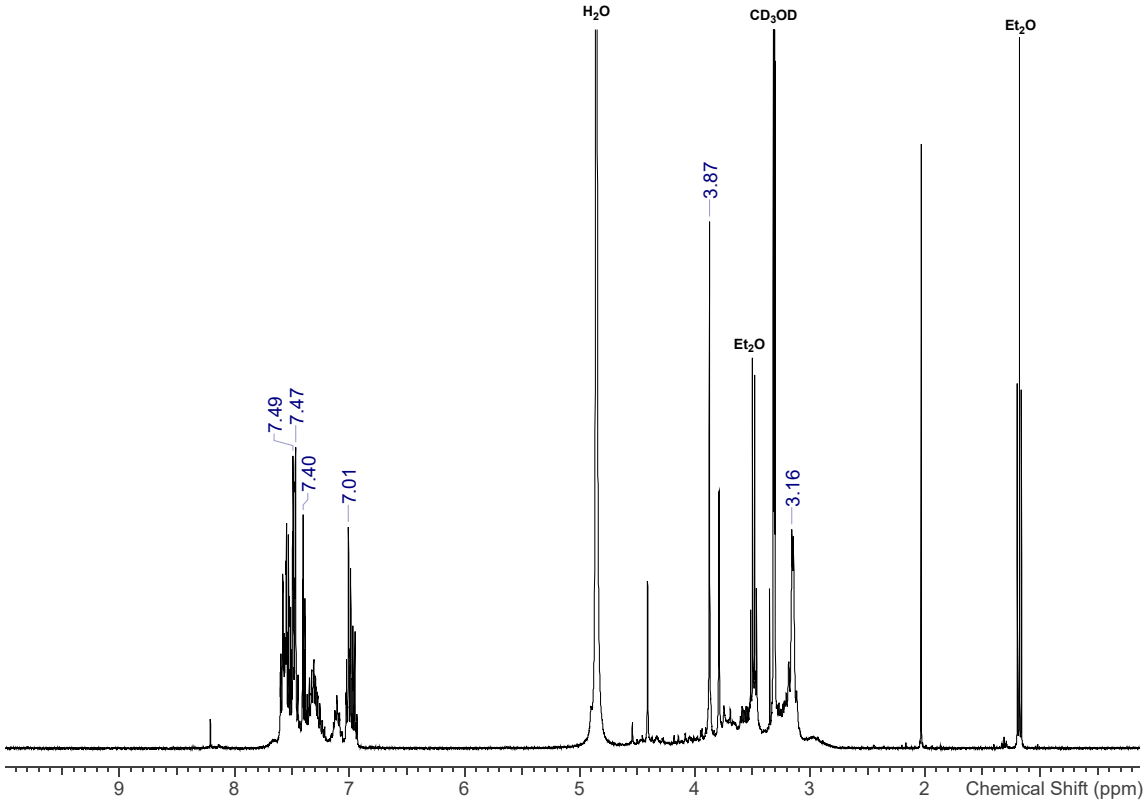
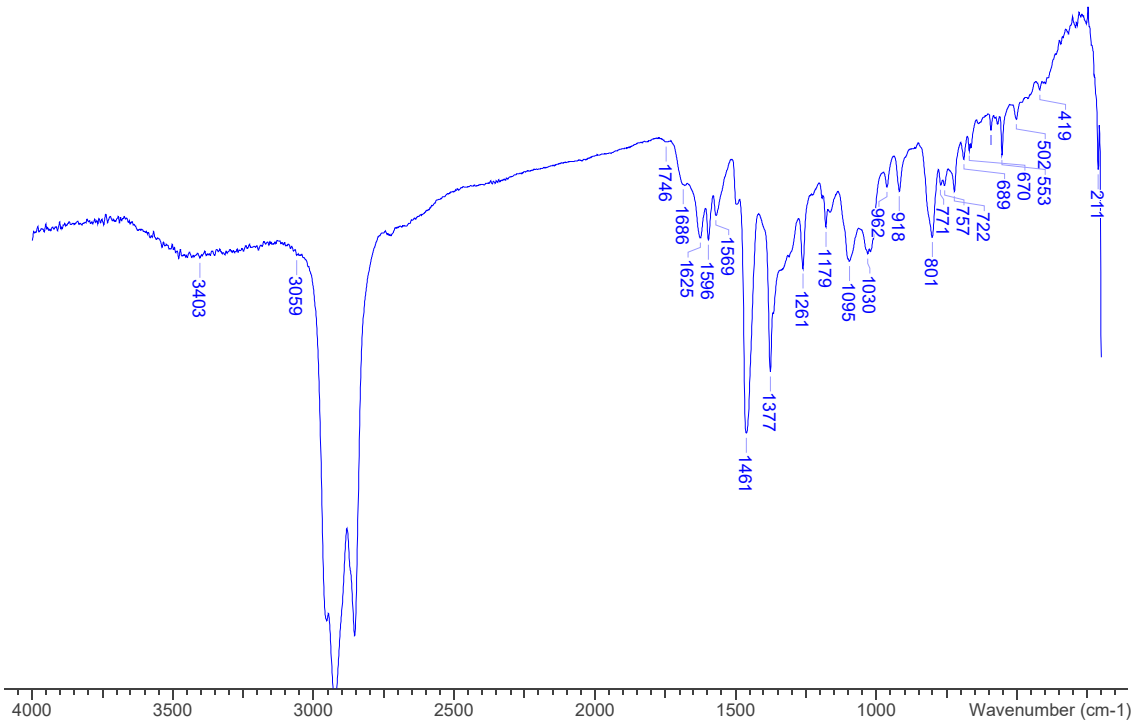


Figure S5: Spectroscopic data for [Ga(**1**)]$(NO_3)_3$

S5a: ^{1}H NMR spectrum (d_4-MeOH (isolated from RT, overnight)



S5b: IR spectrum (Nujol)



S5c: ^{1}H NMR spectroscopic data (d_4-MeOH) for preparation of [Ga(**1**)][NO_3]$_3$ over time at 80 °C (left) and RT (right) (note that some white precipitate also appeared after ~6 h)

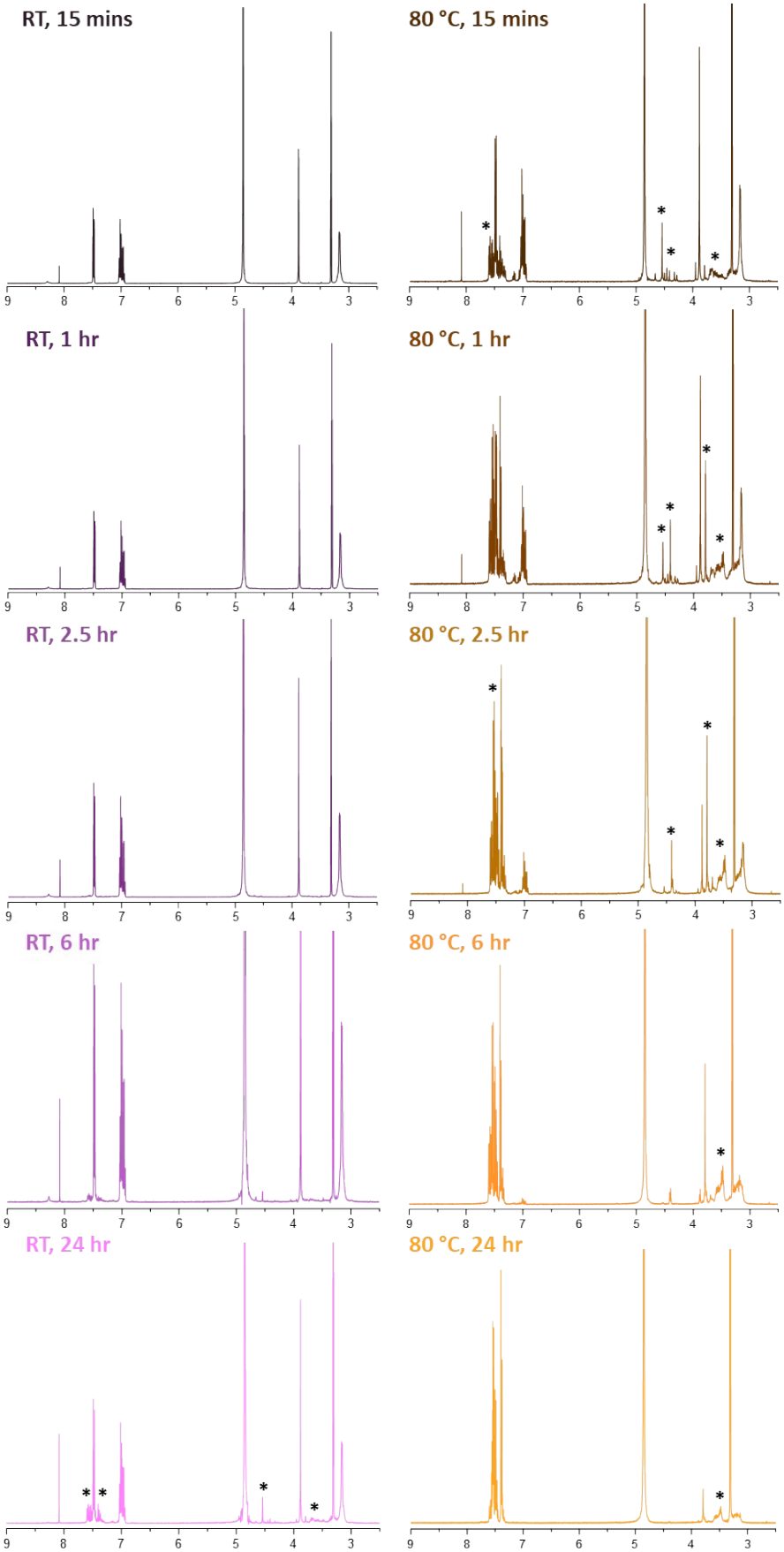
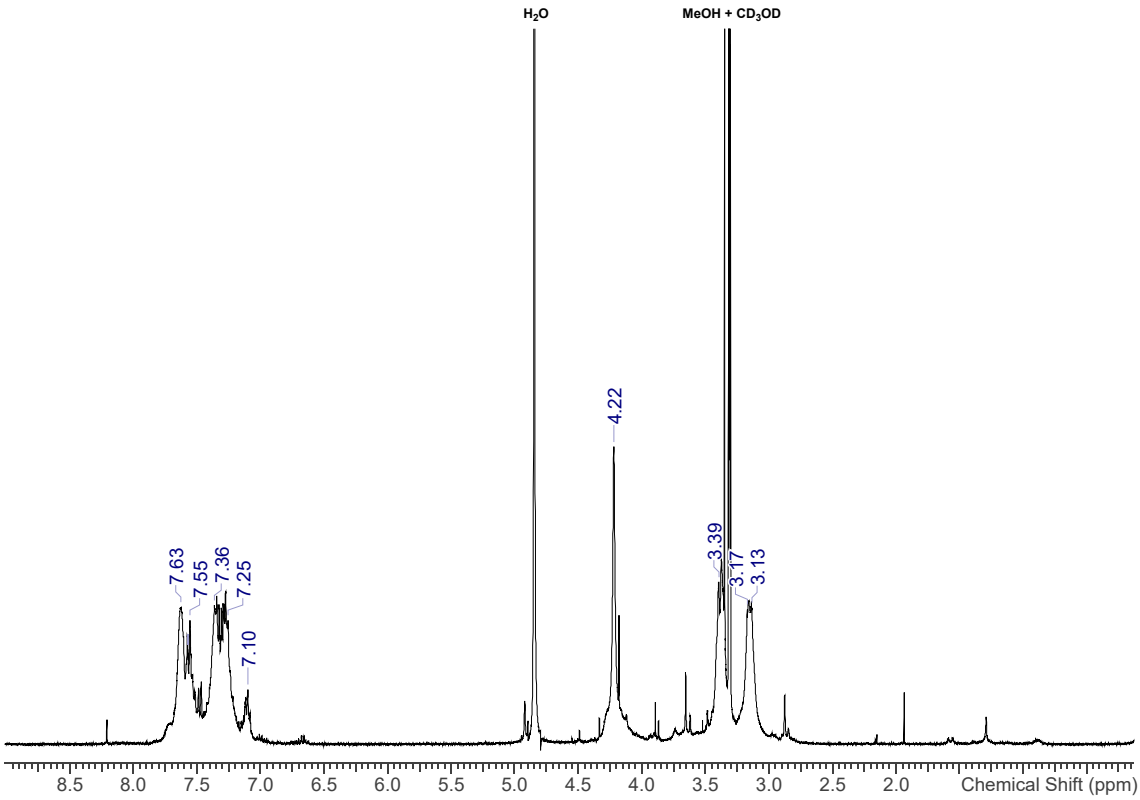


Figure S6: Spectroscopic data for [In(**1**)]$(NO_3)_3$

S6a: ^{1}H NMR spectrum (d_4-MeOH) - reaction conditions: RT, overnight



S6b: IR spectrum (Nujol)

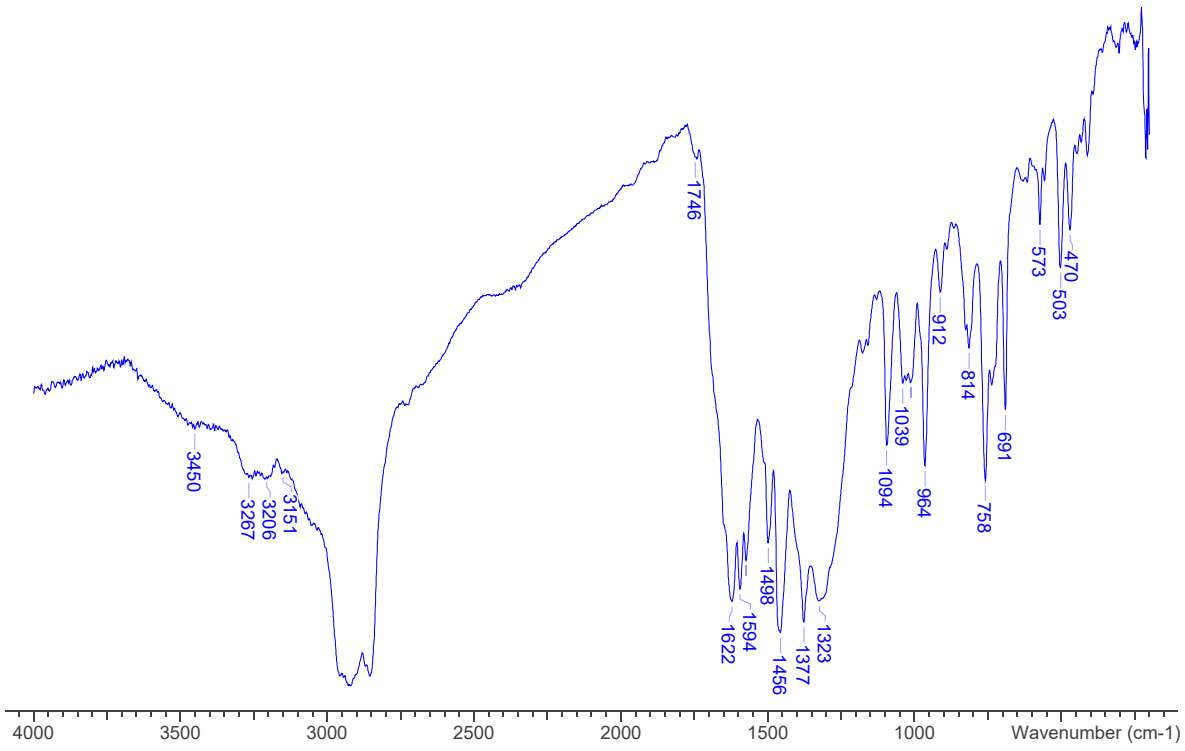
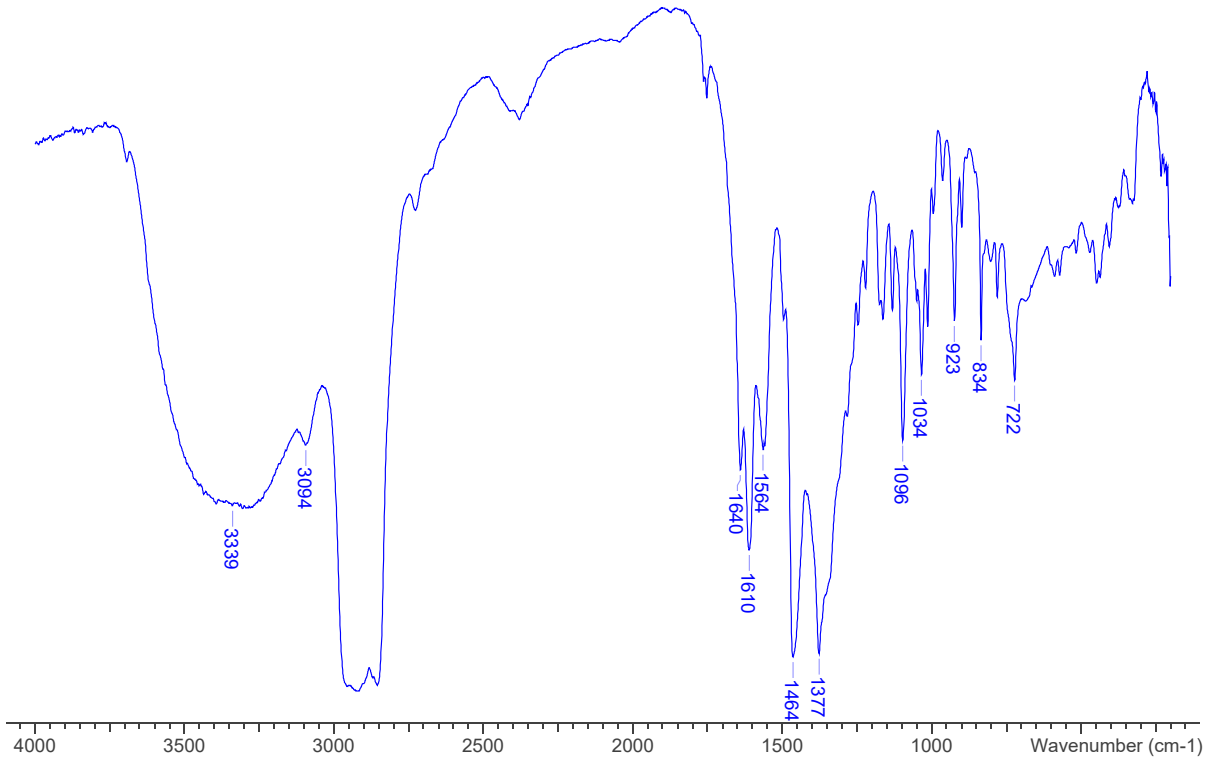
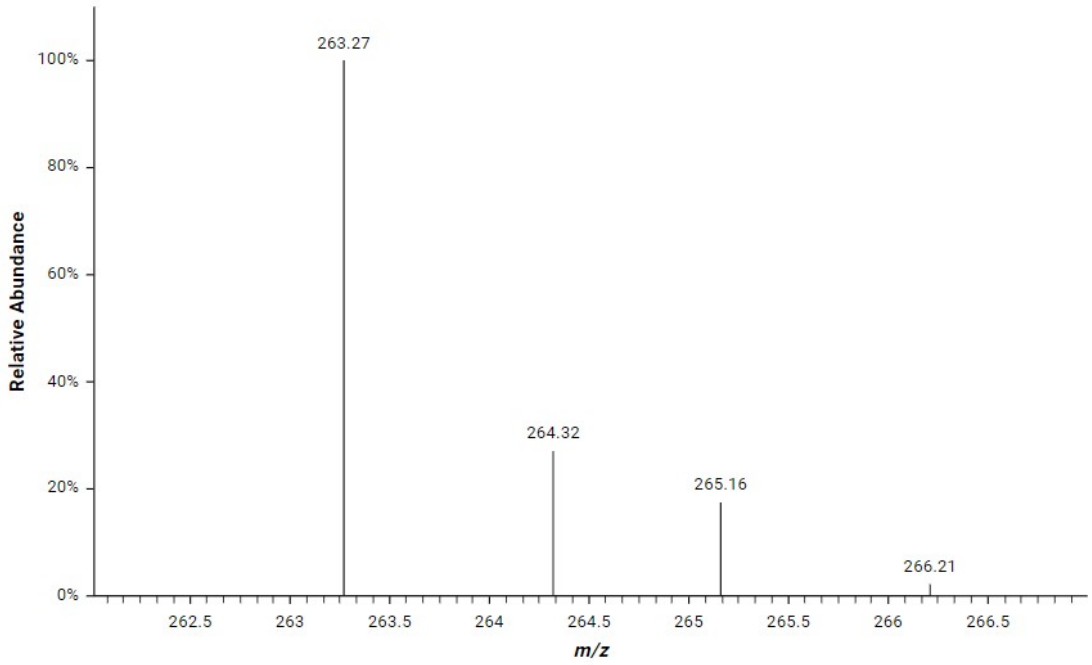


Figure S7: Spectroscopic data for [Ni(**2**)]$(NO_3)_2$

S7a: IR spectrum (Nujol)



S7b: ESI^+ MS (MeOH)



S7c: UV-Vis (MeOH)

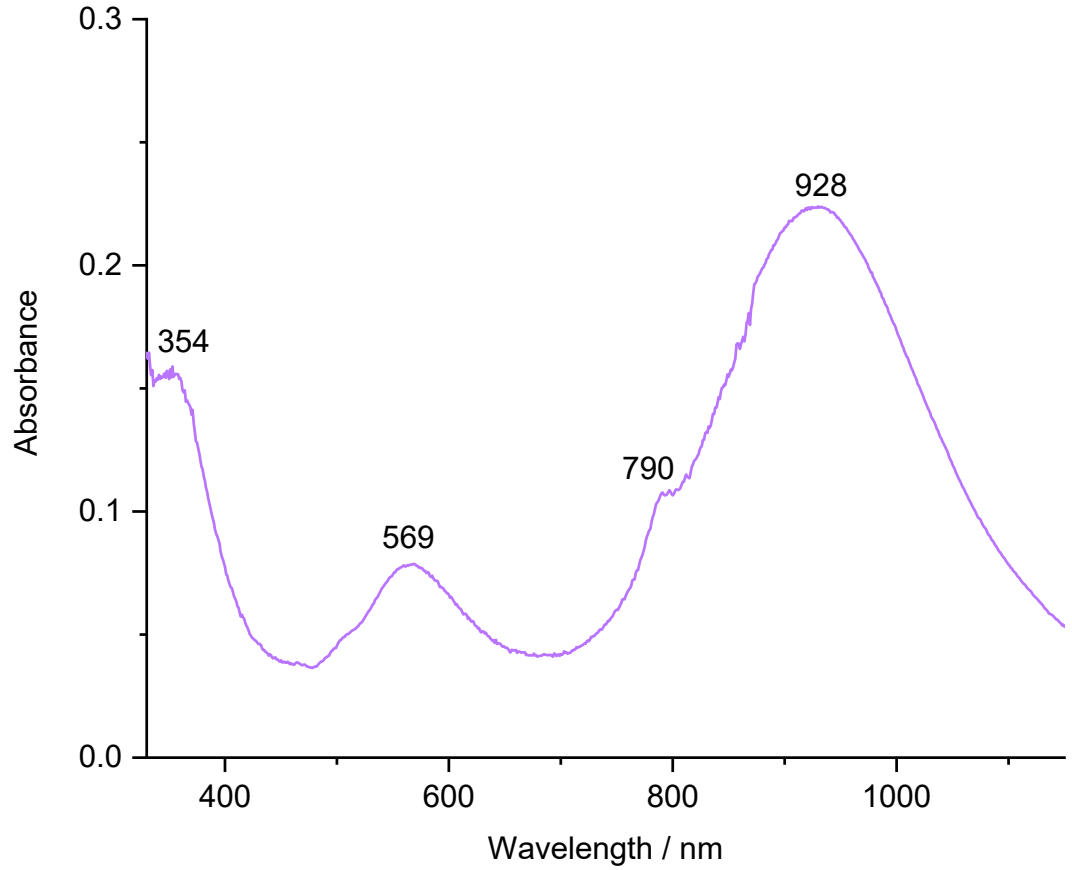
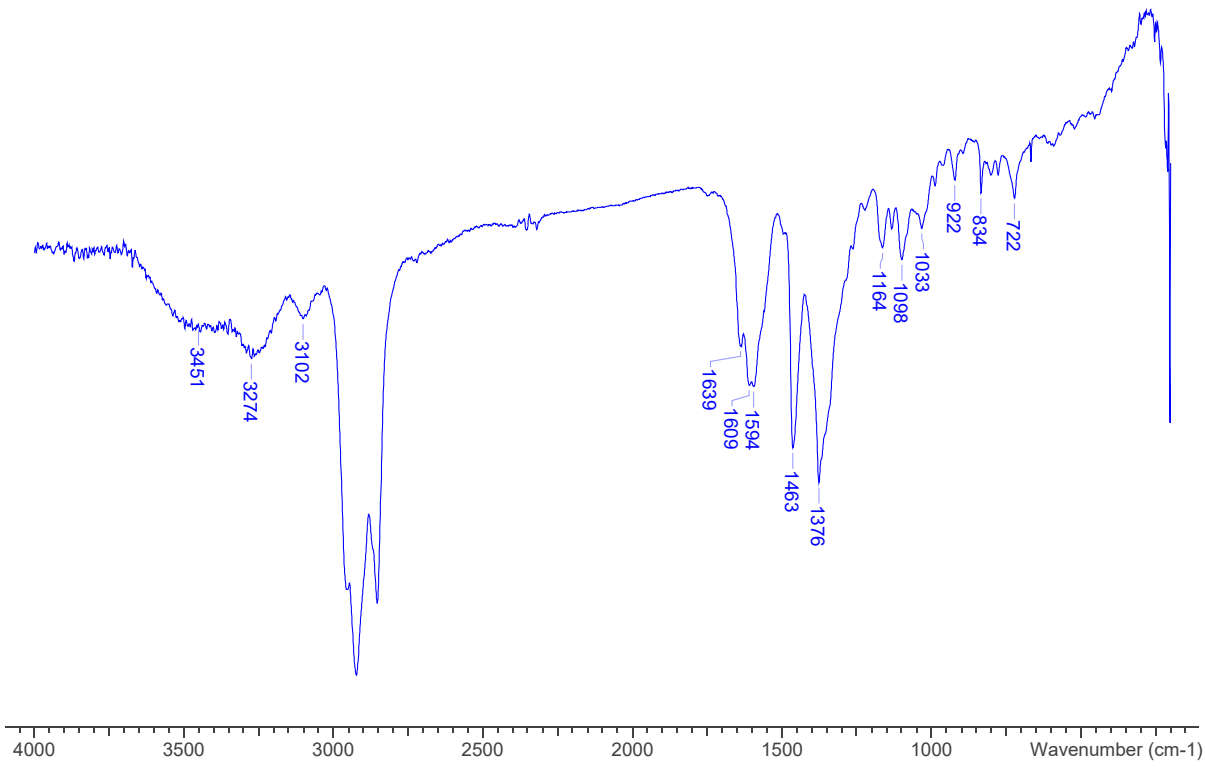
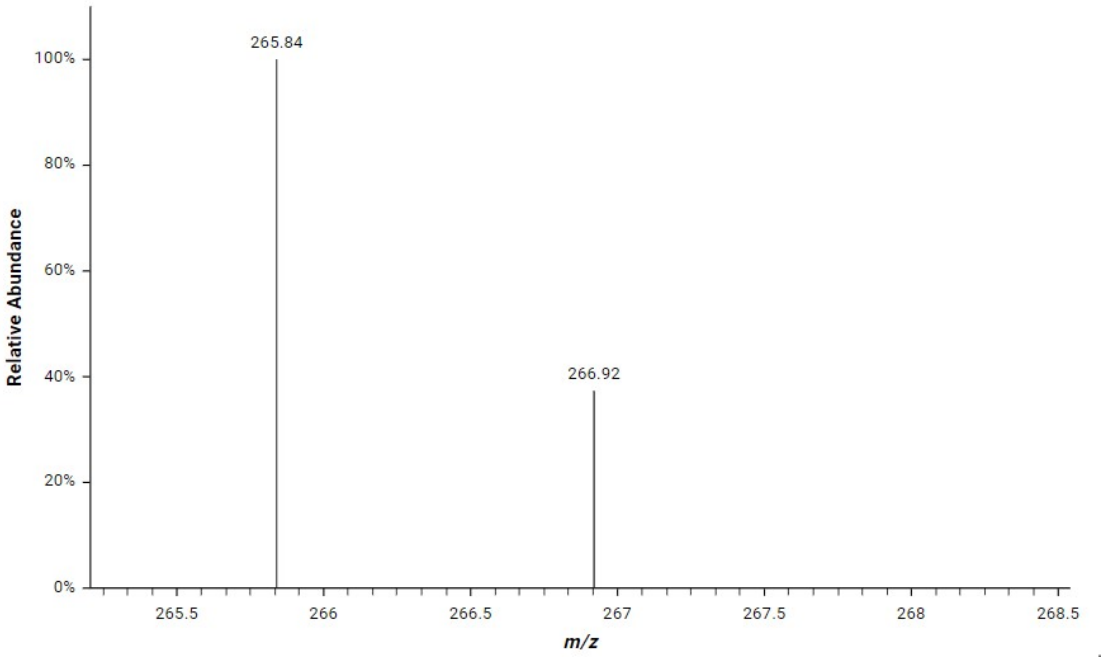


Figure S8: Spectroscopic data for [Cu(**2**)]$(NO_3)_2$

S8a: IR spectrum (Nujol)



S8b: ESI MS (MeOH)



S8c: UV-Vis spectrum (MeOH)

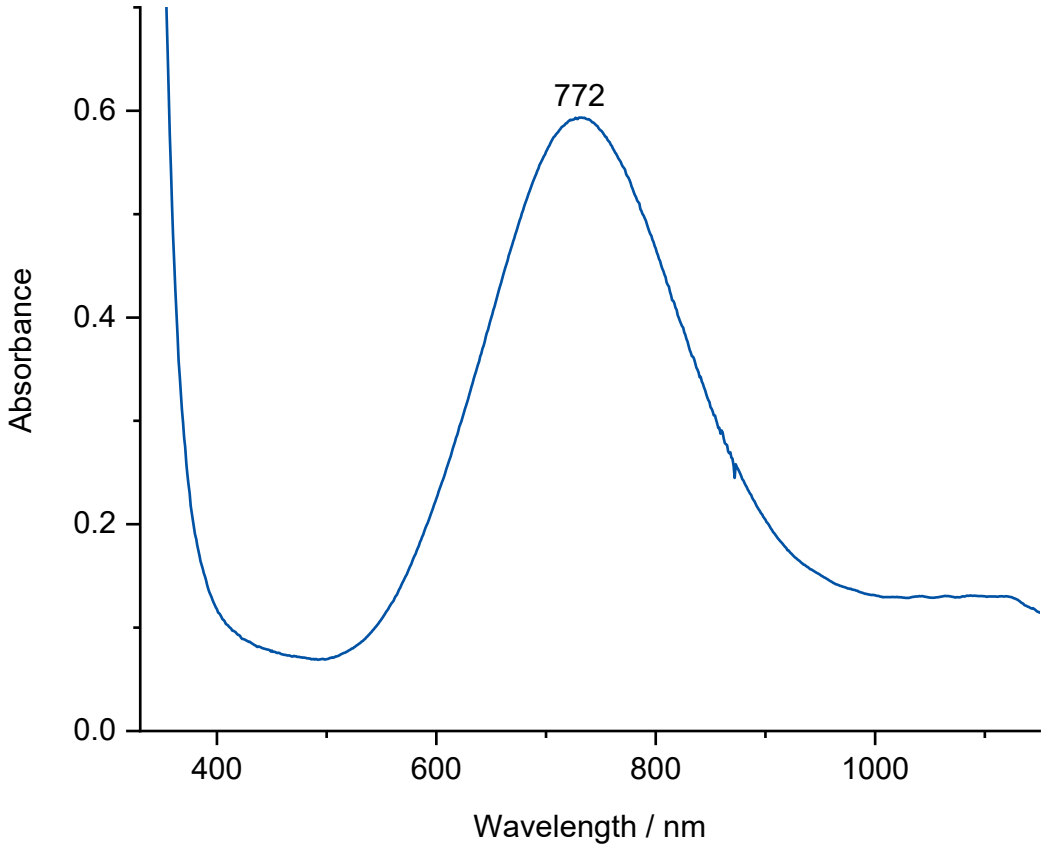
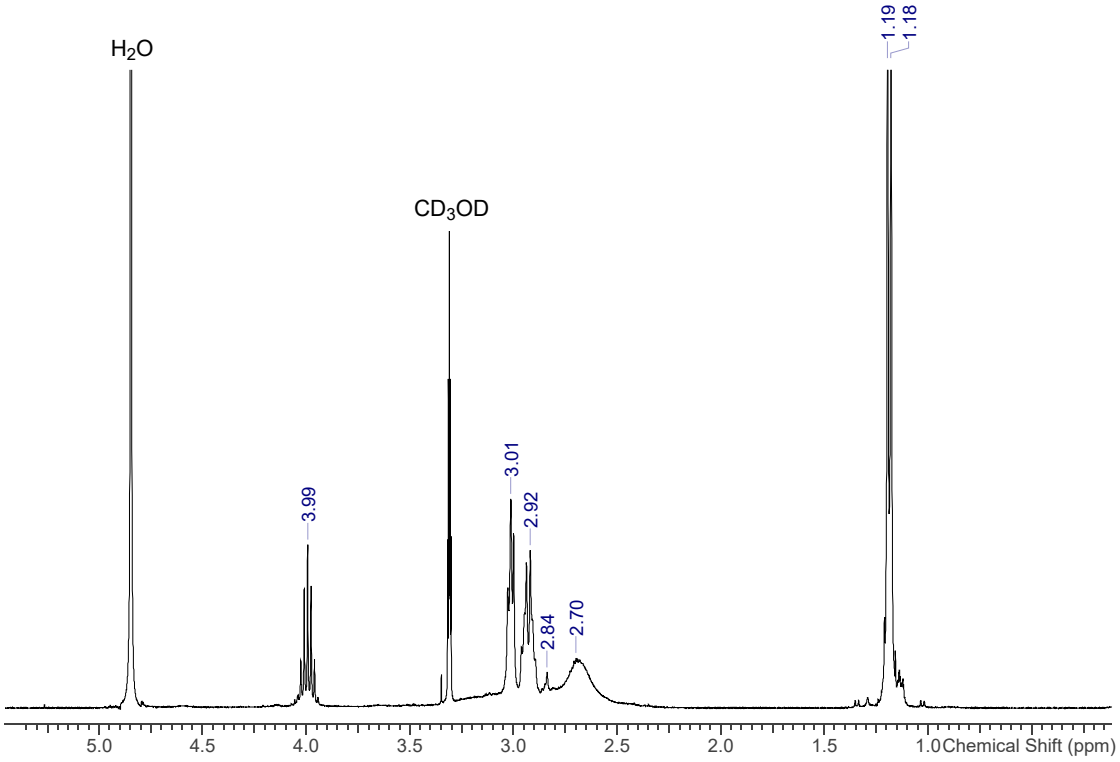
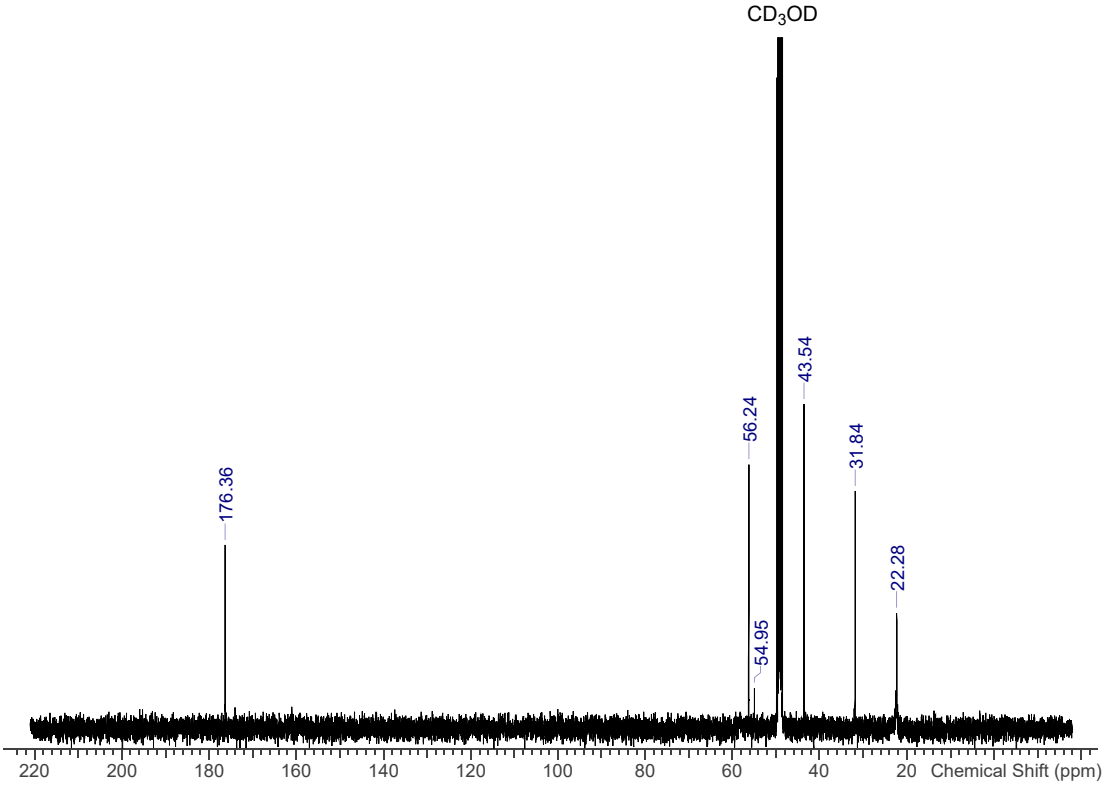


Figure S9: Spectroscopic data for [Zn(**2**)]$(NO_3)_2$

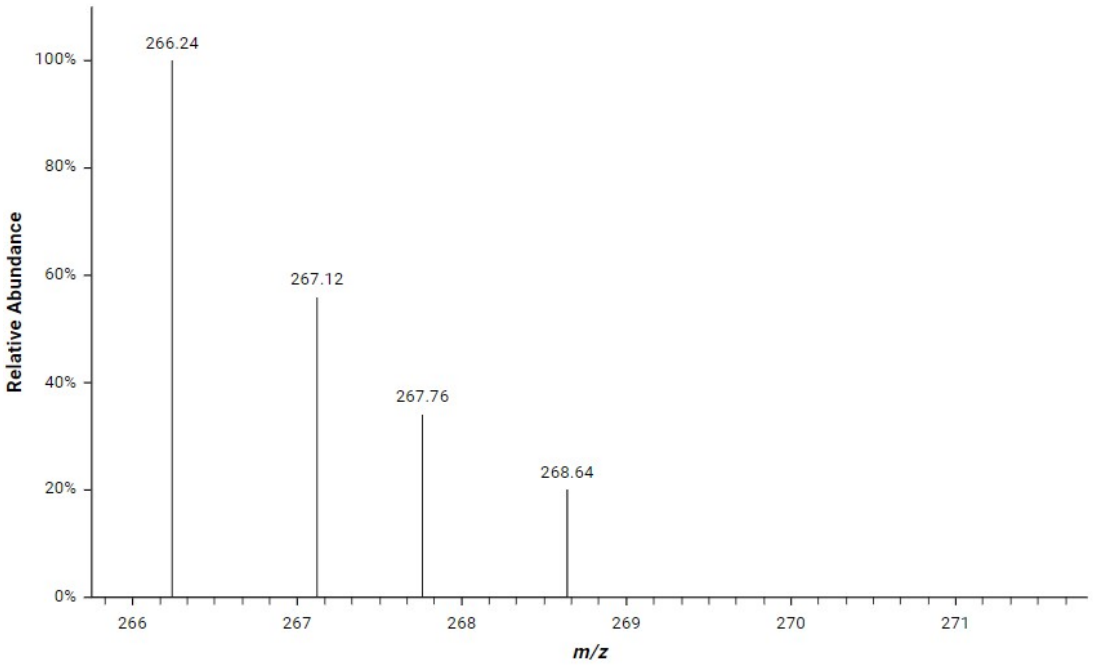
S9a: ^{1}H NMR spectrum (d4-MeOH)



S9b: ^{13}C{^{1}H} NMR spectrum (d_4-MeOH)



S9c: ESI^{+} MS (MeOH)



S9d: IR spectrum (Nujol)

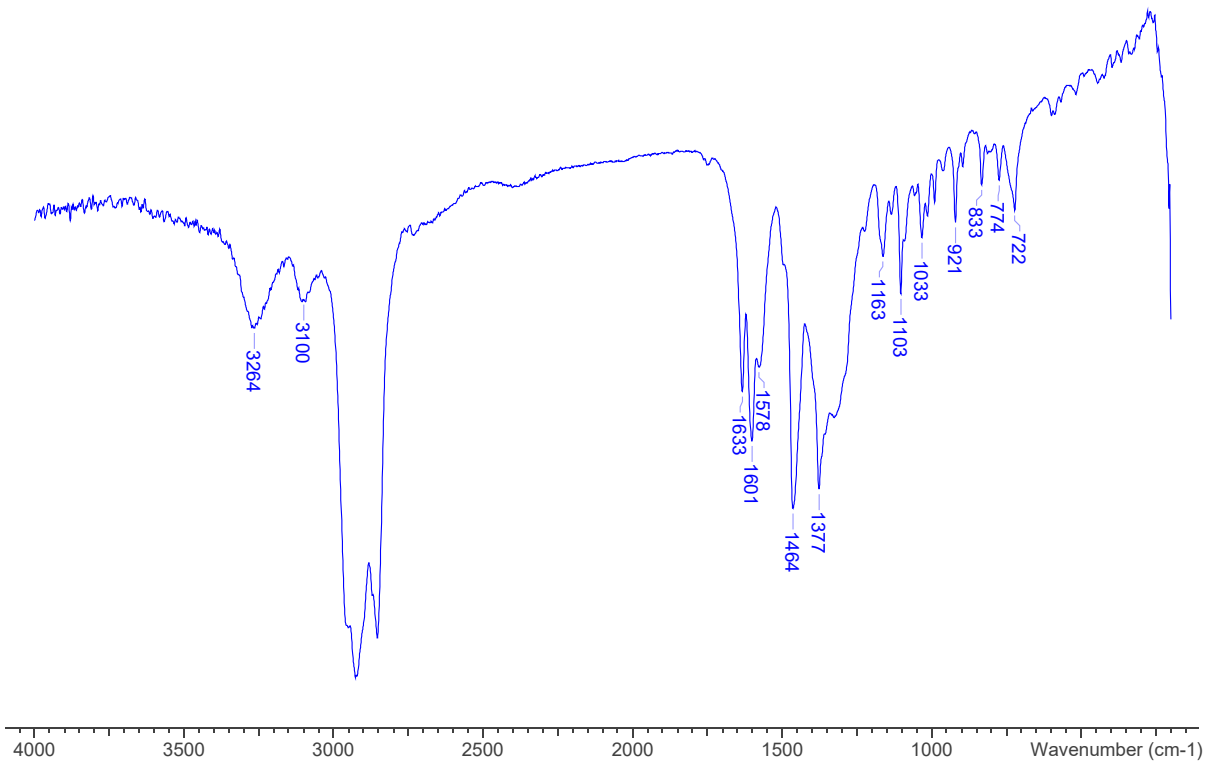
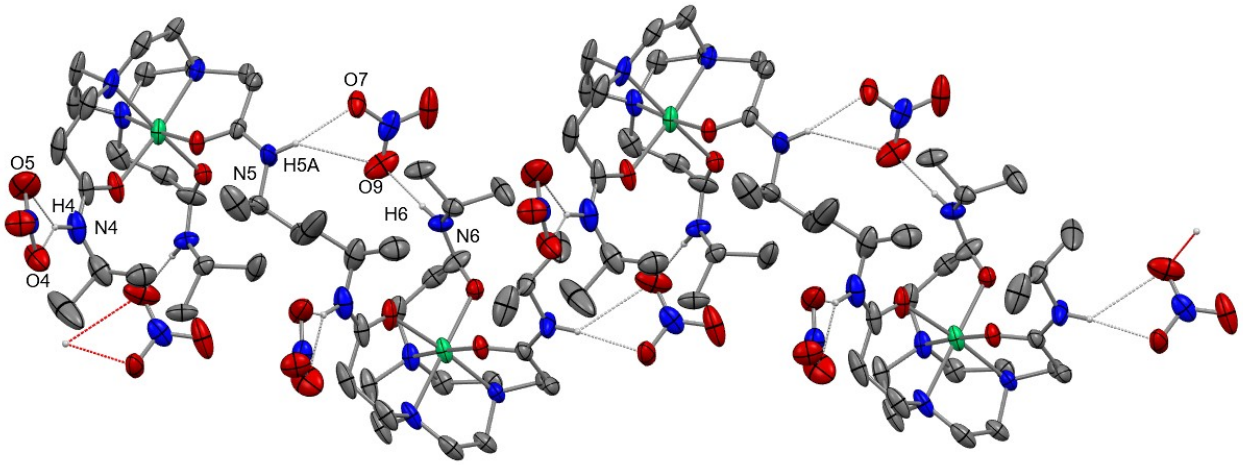


Figure S10: View of the 1D chain present in [Ni(**2**)]$(NO_3)_2$ formed via the H-bonds between the amide



NH groups and the nitrate anions.

Figure S11 Highlighting the variation in the twist angles at the three crystallographically independent copper centres in [Cu(**1**)]$(NO_3)_2$ (Cu2 is top right).

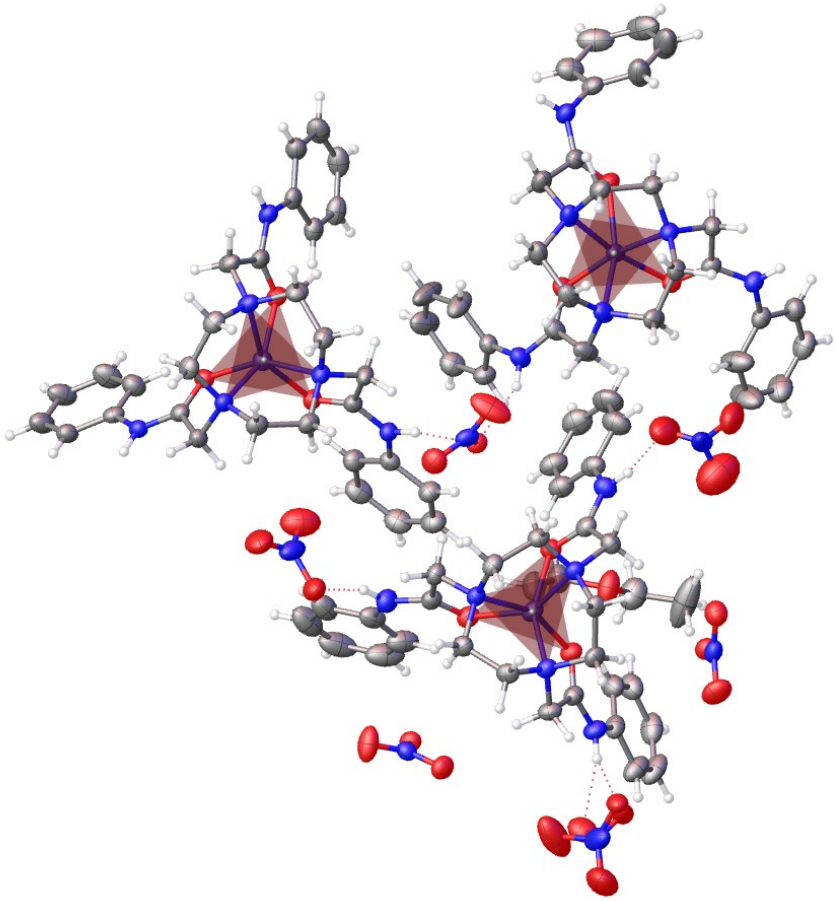


Figure S12 View of the 1D chain present in [Cu(**2**)]$(NO_3)_2$ formed via the H-bonds between the amide NH groups and the nitrate anions.