SUPPORTING INFORMATION

Cu(II), Mn(II) and Zn(II) complexes of hydrazones with quaternary ammonium moiety: synthesis, experimental and theoretical characterization and cytotoxic activity

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Table S1 Selected bond distances (Å) and angles (°) in $[Cu\mathbf{L^1}(N_3)(CH_3OH)]BF_4$

Cu1–N5	1.922(2)	N2–N3	1.377(3)
Cu1–N2	1.928(2)	N5–N6	1.209(3)
Cu1–O1	1.970(2)	N6–N7	1.131(3)
Cu1–N1	2.048(2)	B1–F1A	1.351(9)
Cu1–O2	2.533(2)	B1–F2A	1.430(1)
O1–C6	1.276(3)	B1–F3A	1.380(1)
N2–C4	1.298(3)	B1–F4A	1.320(1)
N3–C6	1.321(3)	B1–F1B	1.370(2)
		B1–F2B	1.240(2)
		B1–F3B	1.260(2)
		B1–F4B	1.390(2)
N5–Cu1–O1	98.51(9)	N6–N5–Cu1	122.1(2)
N2–Cu1–O1	79.33(8)	N7–N6–N5	176.2(3)
N5–Cu1–N1	100.8(1)	F1A–B1–F4A	117.0(8)
N2–Cu1–N1	80.73(9)	F1A–B1–F3A	106.2(7)

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O1–Cu1–O2	88.83(8)	F4A–B1–F3A	115.9(8)
N1–Cu1–O2	95.92(8)	F1A–B1–F2A	108.0(6)
N2–Cu1–O2	85.37(8)	F4A–B1–F2A	104.9(7)
N5–Cu1–O2	99.34(9)	F3A–B1–F2A	103.7(7)
N5–Cu1–N2	174.8(1)	F2B–B1–F1B	111.1(12)
O1–Cu1–N1	159.05(9)	F3B–B1–F1B	110.2(13)
		F1B–B1–F4B	102.9(10)
		F2B–B1–F3B	111.6(15)
		F2B–B1–F4B	120.9(12)
		F3B–B1–F4B	99.3(18)

Table S2 Selected bond distances (Å) and angles (°) in $[Mn_2\mathbf{L^1}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 2CH_3OH$

Mn1–N8	2.112(2)	N2–C4	1.288(3)
Mn1–O1	2.1879(16)	N2–N3	1.393(2)
Mn1–N5	2.229(2)	N3–C6	1.330(3)
Mn1–N5$^{\#}$	2.2425(19)	N5–N6	1.193(3)
Mn1–N2	2.2500(18)	N6–N7	1.142(3)
Mn1–N1	2.3668(19)	N8–N9	1.169(3)
O1–C6	1.264(3)	N9–N10	1.149(4)
N8–Mn1–O1	98.88(9)	O1–Mn1–N1	134.91(7)
N8–Mn1–N5	147.86(10)	N5–Mn1–N1	87.04(7)
O1–Mn1–N5	107.66(8)	N5$^{\#}$–Mn1–N1	138.40(8)
N8–Mn1–N5$^{\#}$	91.69(9)	N2–Mn1–N1	69.46(7)
O1–Mn1–N5$^{\#}$	86.40(8)	N6–N5–Mn1	126.85(16)
N5–Mn1–N5$^{\#}$	72.63(8)	N10–N9–N8	176.0(3)
N8–Mn1–N2	121.21(9)	N9–N8–Mn1	137.7(2)
O1–Mn1–N2	69.51(6)	N7–N6–N5	179.4(3)
N5–Mn1–N2	85.67(7)	Mn1–N5–Mn1$^{\#}$	107.37(8)
N5$^{\#}$–Mn1–N2	141.02(8)	N6–N5–Mn1$^{\#}$	123.06(15)
N8–Mn1–N1	86.84(9)		

Symmetry code # = 1−*x*, 1−*y*, 1−*z*.

Table S3 Selected bond distances (Å) and angles (°) in [Zn**L**^{1}(N_3)$_2$]

Zn1–N5	1.965(4)	N2–N3	1.377(4)
Zn1–N8	2.019(6)	N5–N6	1.161(6)
Zn1–N2	2.064(3)	N6–N7	1.158(6)
Zn1–N1	2.209(3)	N8–N9	0.899(5)
Zn1–O1	2.230(2)	N9–N10	1.212(6)
N2–C4	1.304(4)	O1–C6	1.244(4)
N3–C6	1.323(4)		
N5–Zn1–N8	115.1(2)	N8–Zn1–O1	97.18(16)
N5–Zn1–N2	121.42(17)	N2–Zn1–O1	73.08(10)
N8–Zn1–N2	123.30(18)	N1–Zn1–O1	149.06(12)
N5–Zn1–N1	102.84(15)	N6–N5–Zn1	122.5(3)
N8–Zn1–N1	96.46(17)	N7–N6–N5	178.5(6)
N2–Zn1–N1	76.21(13)	N9–N8–Zn1	122.7(5)
N5–Zn1–O1	96.26(14)	N8–N9–N10	169.2(7)

Table S4 Hydrogen bond parameters (Å,°) for [Cu**L**^{1}(N_3)(CH_3OH)]BF_4 complex

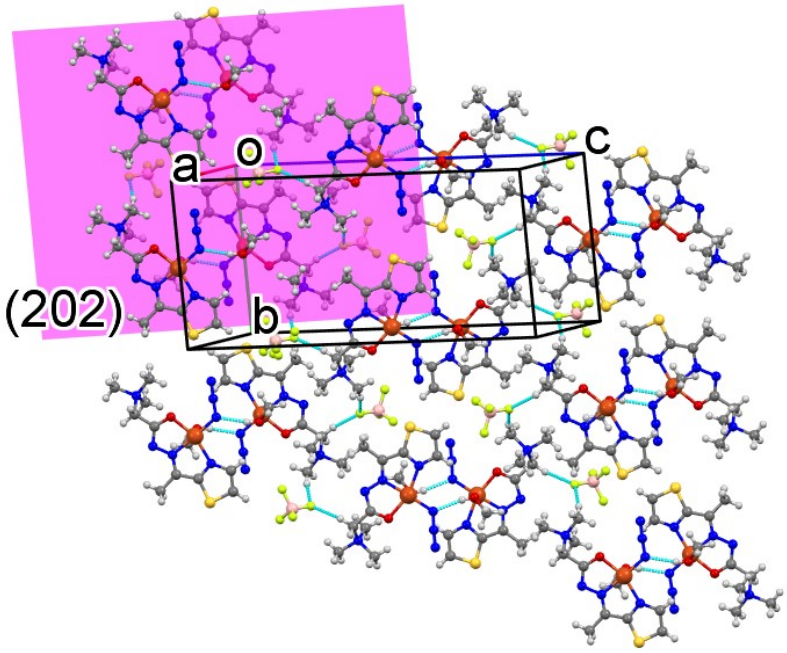
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Sym. code on A
O2–H2A···N5	0.82	2.00	2.809(3)	170	1−x,1−y, −z
C7−H7A···F1A	0.97	2.35	3.288(11)	162	½ −x,− ½ +y, ½ −z
C9–H9A···F1A	0.96	2.29	3.220(10)	164	
C10–H10C···F2A	0.96	2.52	3.397(11)	152	−1+x, y, z
C2–H2···F2B	0.93	2.52	3.262(18)	137	1−x, 1−y, −z
C5–H5B···F3B	0.96	2.53	3.40(3)	151	x, −1+y, z
C7–H7A···F1B	0.97	2.31	3.28(3)	177	½ −x,−½+y, ½ −z
C9–H9A···F1B	0.96	2.54	3.41(3)	150	
Intra C5–H5A···N3	0.96	2.52	2.919(4)	105	
Intra C9–H9C···O1	0.96	2.28	2.930(4)	124	

Table S5 Hydrogen bond parameters (Å,°) for $[Mn_2\mathbf{L^1}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 2CH_3OH$ complex

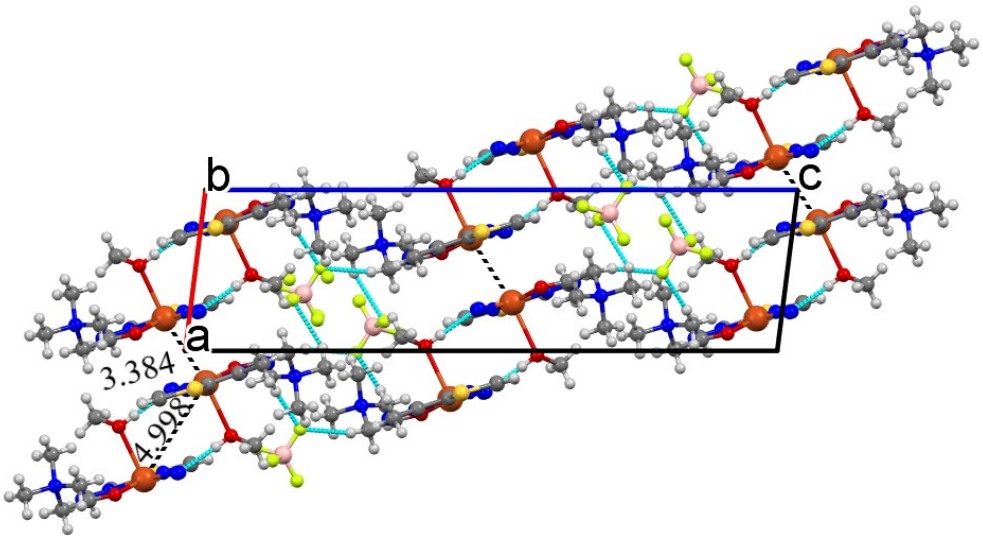
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Sym. code on A
O2–H2A···N3	0.82	2.03	2.835(3)	168	
C7–H7B···O2	0.97	2.40	3.298(4)	155	1−x, 2−y, 2−z
C9–H9B···N8	0.96	2.53	3.406(5)	151	−x, 1−y, 1−z
C9–H9C···O2	0.96	2.45	3.290(5)	147	1−x, 2−y, 2−z
C10–H10B···O1	0.96	2.55	3.491(4)	165	−x, 1−y, 1−z
Intra C5–H5A···N3	0.96	2.51	2.878(4)	103	
Intra C10–H10A···O1	0.96	2.37	2.978(4)	121	

Table S6 Hydrogen bond parameters (Å,°) for $[Zn\mathbf{L^1}(N_3)_2]$ complex

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Sym. code on A
C7–H7A···N10	0.97	2.38	3.334(6)	166	−x, 1/2+y, −1/2−z
Intra C9−H9A···N3	0.96	2.37	3.015(5)	124	
C10–H10C···O1	0.96	2.55	3.437(5)	154	−x, 2−y, −z



(a)



(b)

Fig. S1 (a) A view of the crystal packing of **1** showing hydrogen bonded dimers connected by means of intermolecular C–H···F hydrogen bonds (dashed blue lines) into (202) layers. (b) View of the neighboring (202) layers connected by means of intermolecular C–H···F hydrogen bonds. The intermolecular hydrogen bonds involving the major component of disordered BF_4^- anion are only considered.

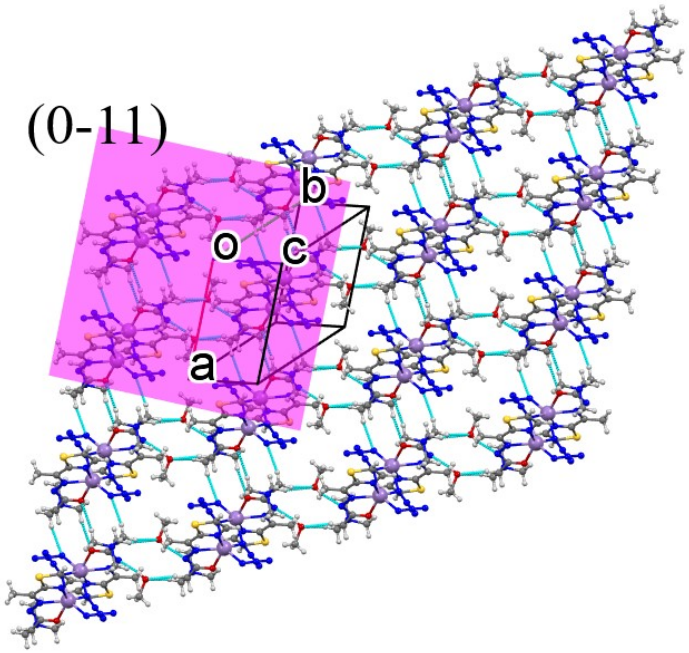


Fig. S2 A view of the crystal packing of **2** showing hydrogen bonded chains parallel with [100] connected by intermolecular O–H···N and C–H···O hydrogen bonds into (0−11) layers.

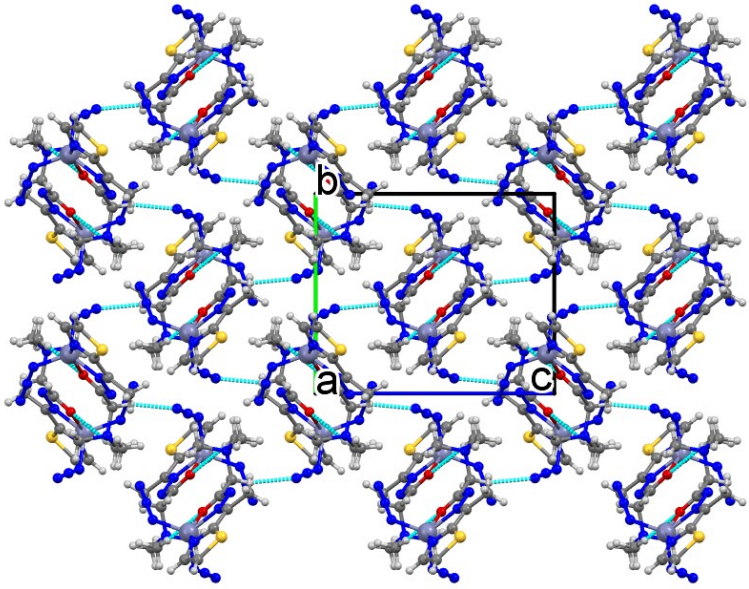


Fig. S3 A view of the crystal packing of **3** showing complex molecules connected by means of intermolecular hydrogen bonds C–H···N and C–H···O (dashed blue lines) into layer parallel with the (1 0 0) lattice plane. The molecules of **3** form dimers by means of C–H···O hydrogen bonds.

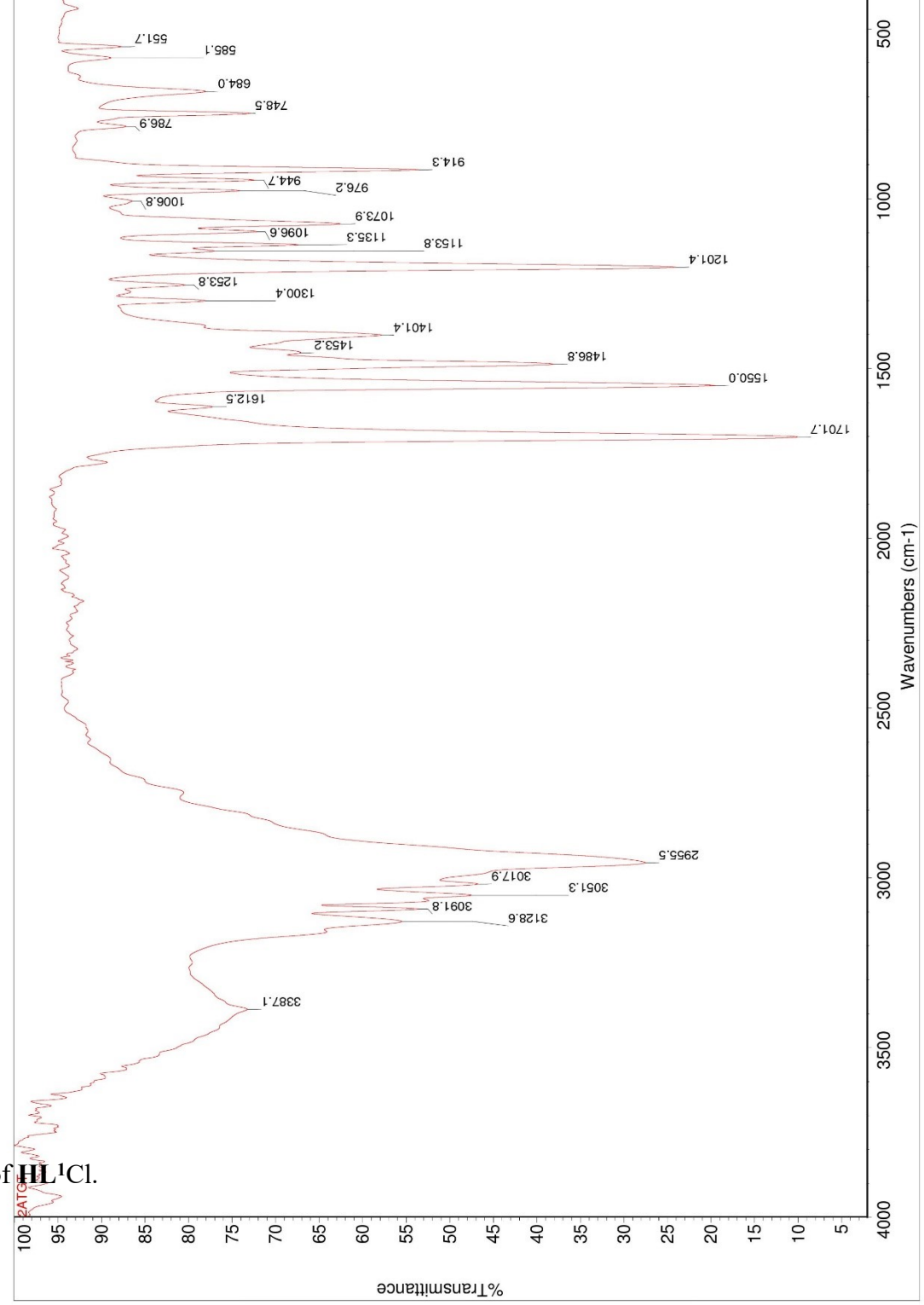


Fig. S4 IR spectra of **HL[1]**Cl.

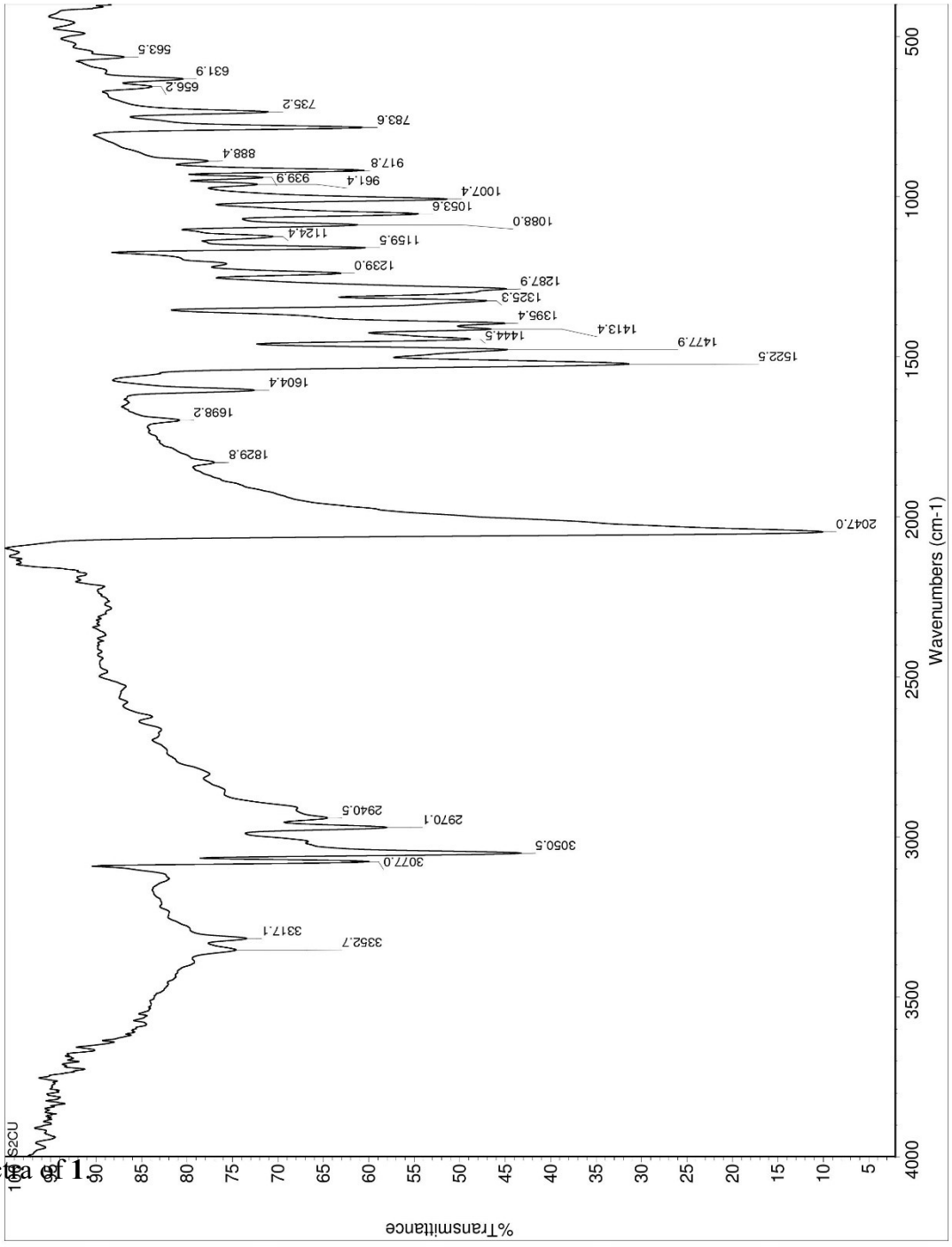


Fig. S5 IR spectra of **1**.

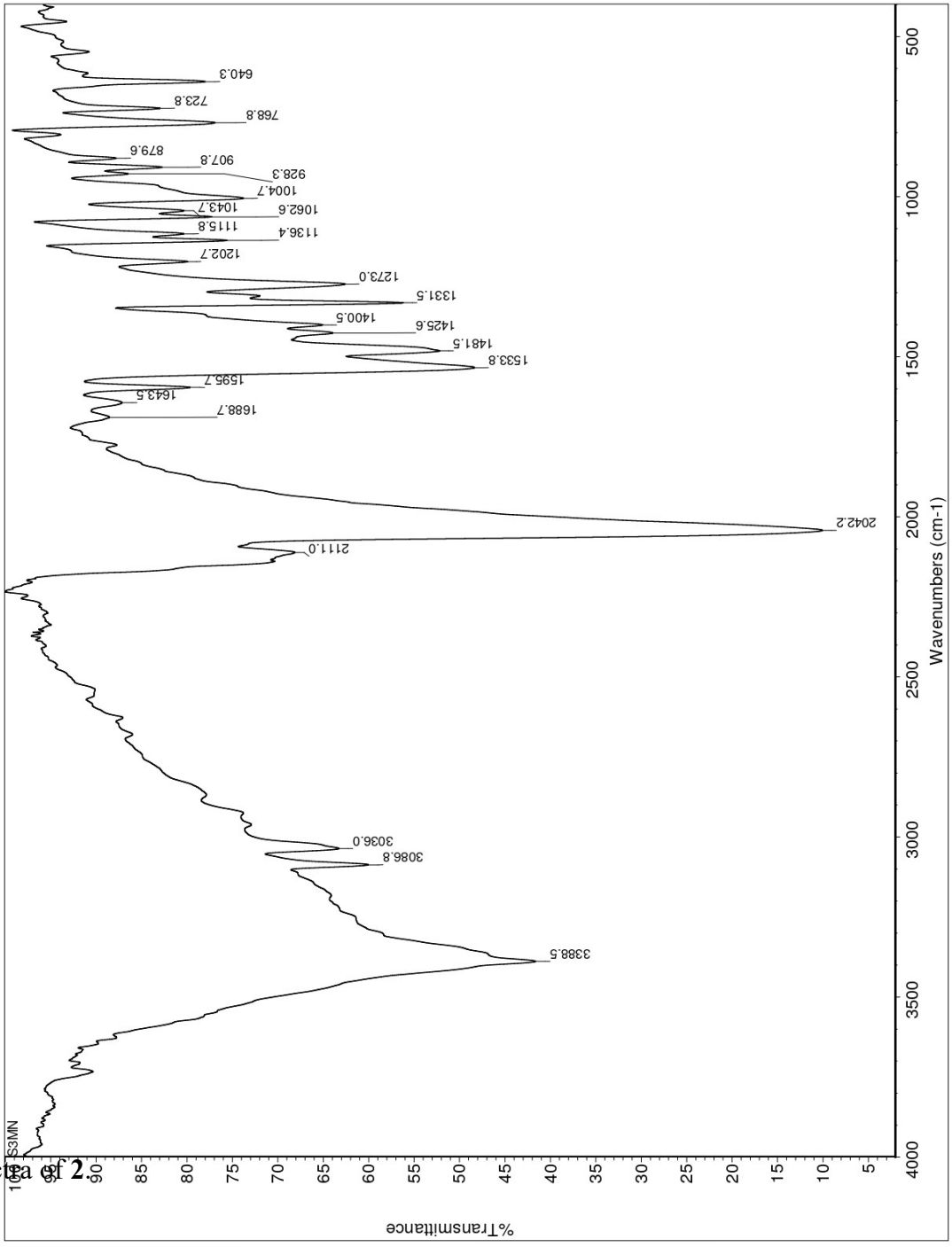


Fig. S6 IR spectra of **2**.

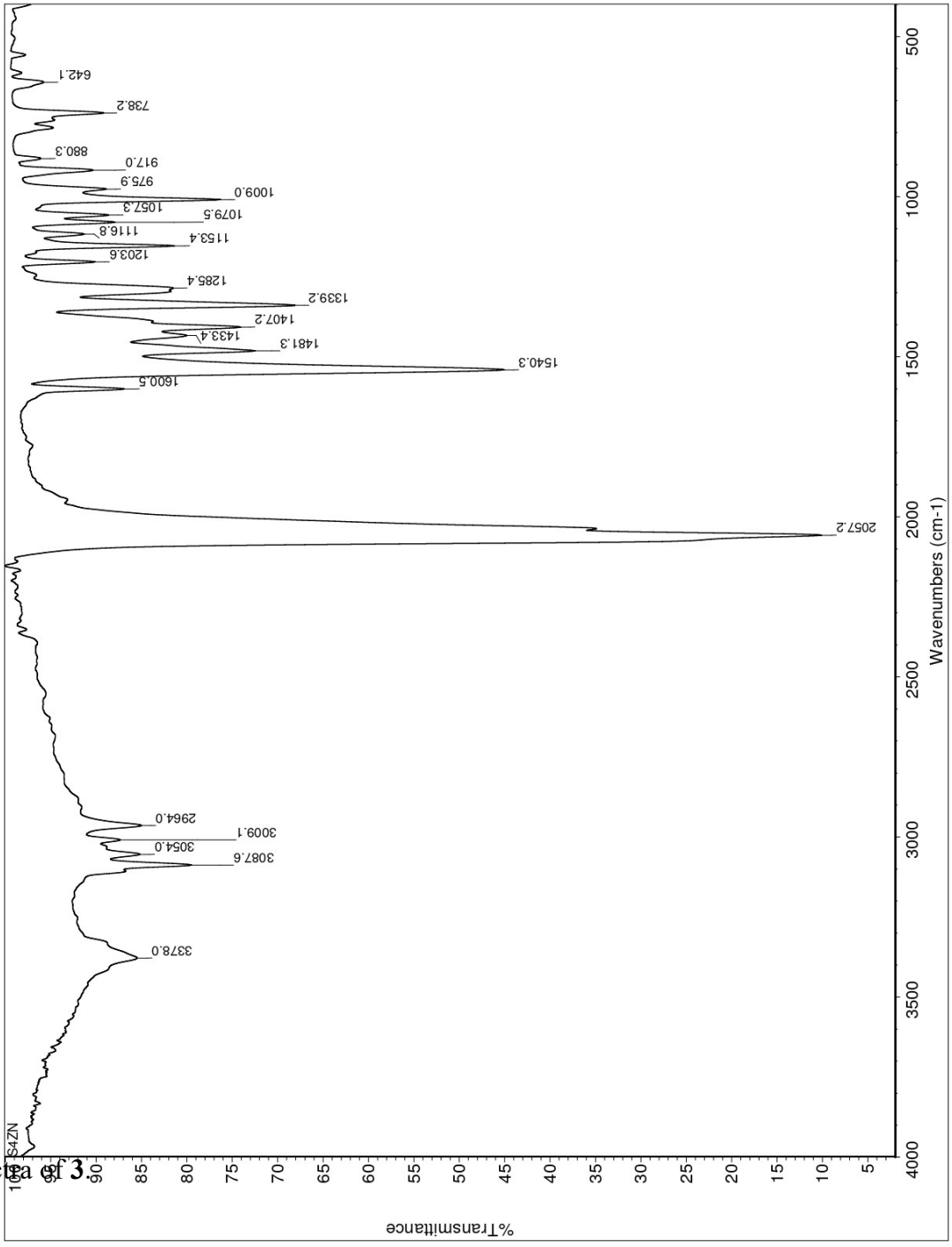


Fig. S7 IR spectra of **3**.

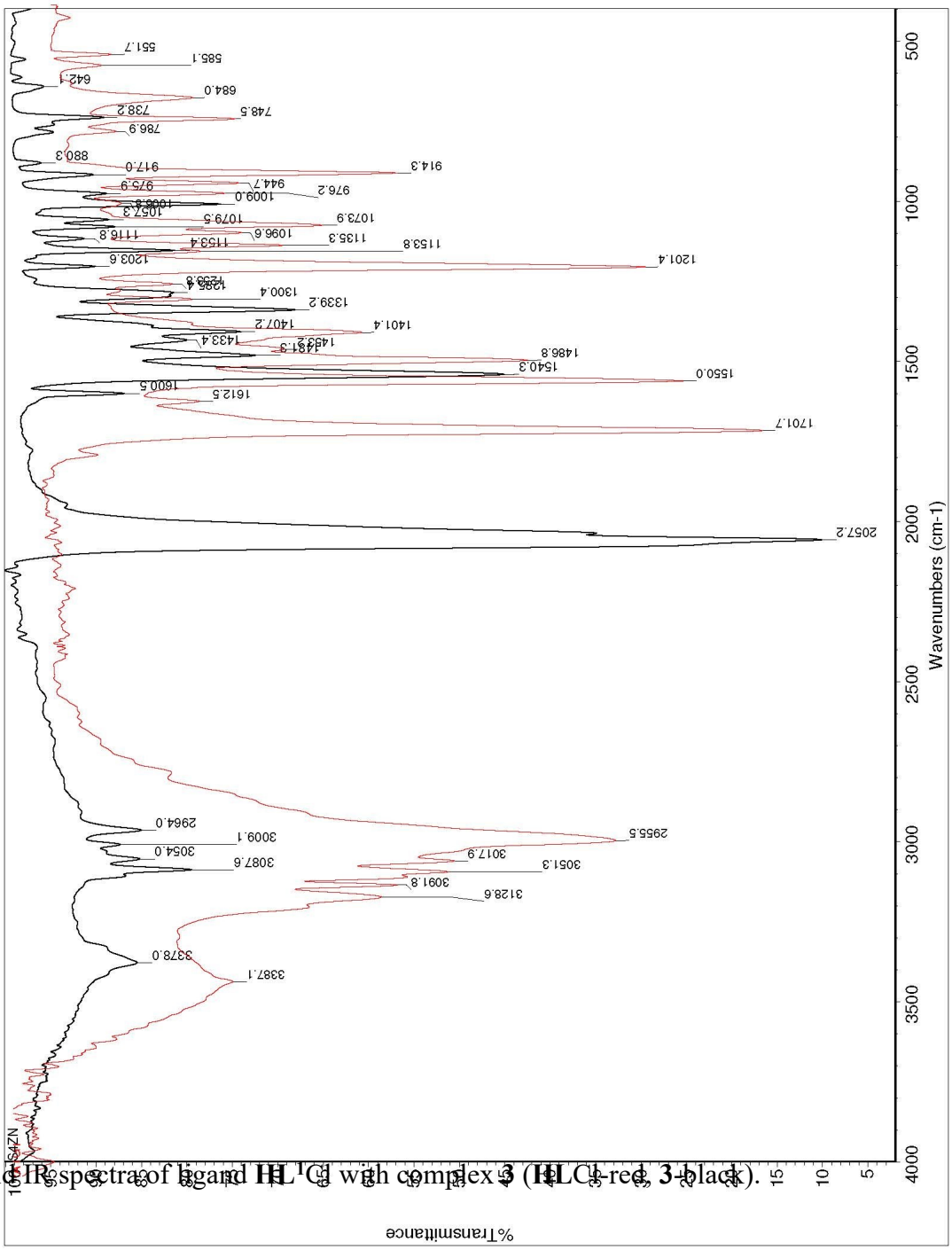


Fig. S8 Overlaid IR spectra of ligand HL^1Cl with complex **3** (HL^1Cl-red, **3**-black).

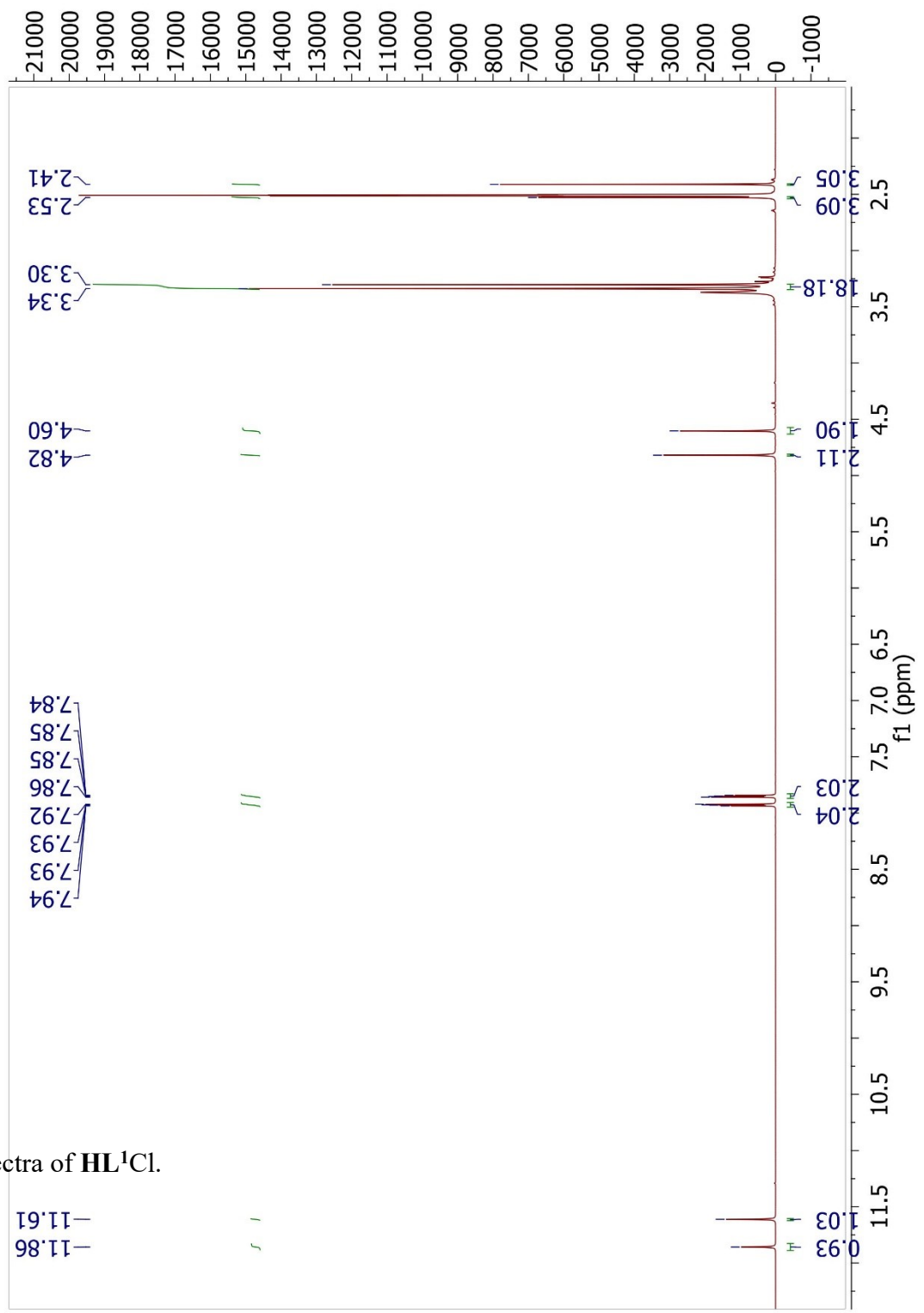


Fig. S8 ^{1}H NMR spectra of **HL^{1}**Cl.

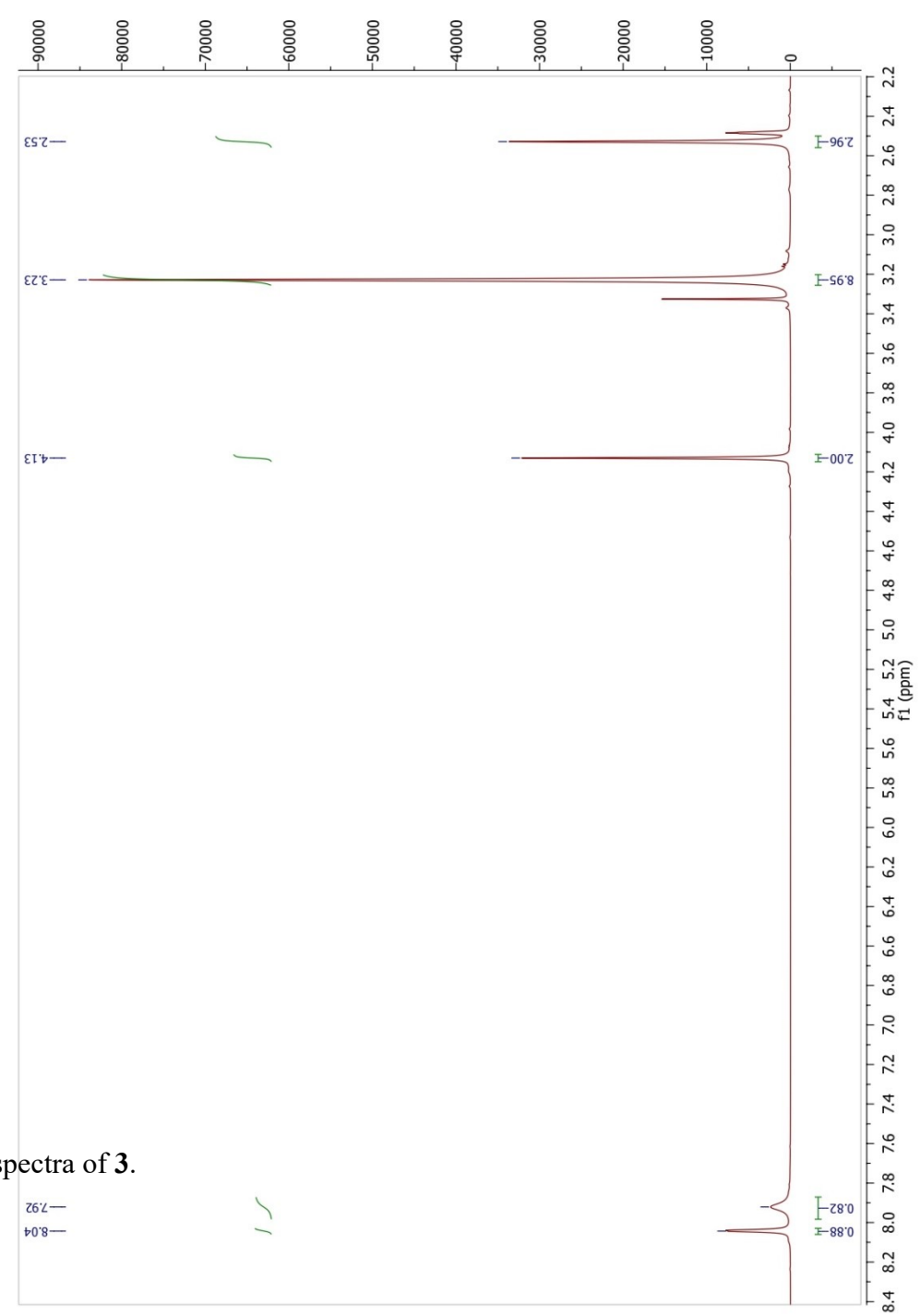


Fig. S9 ^{1}H NMR spectra of **3**.

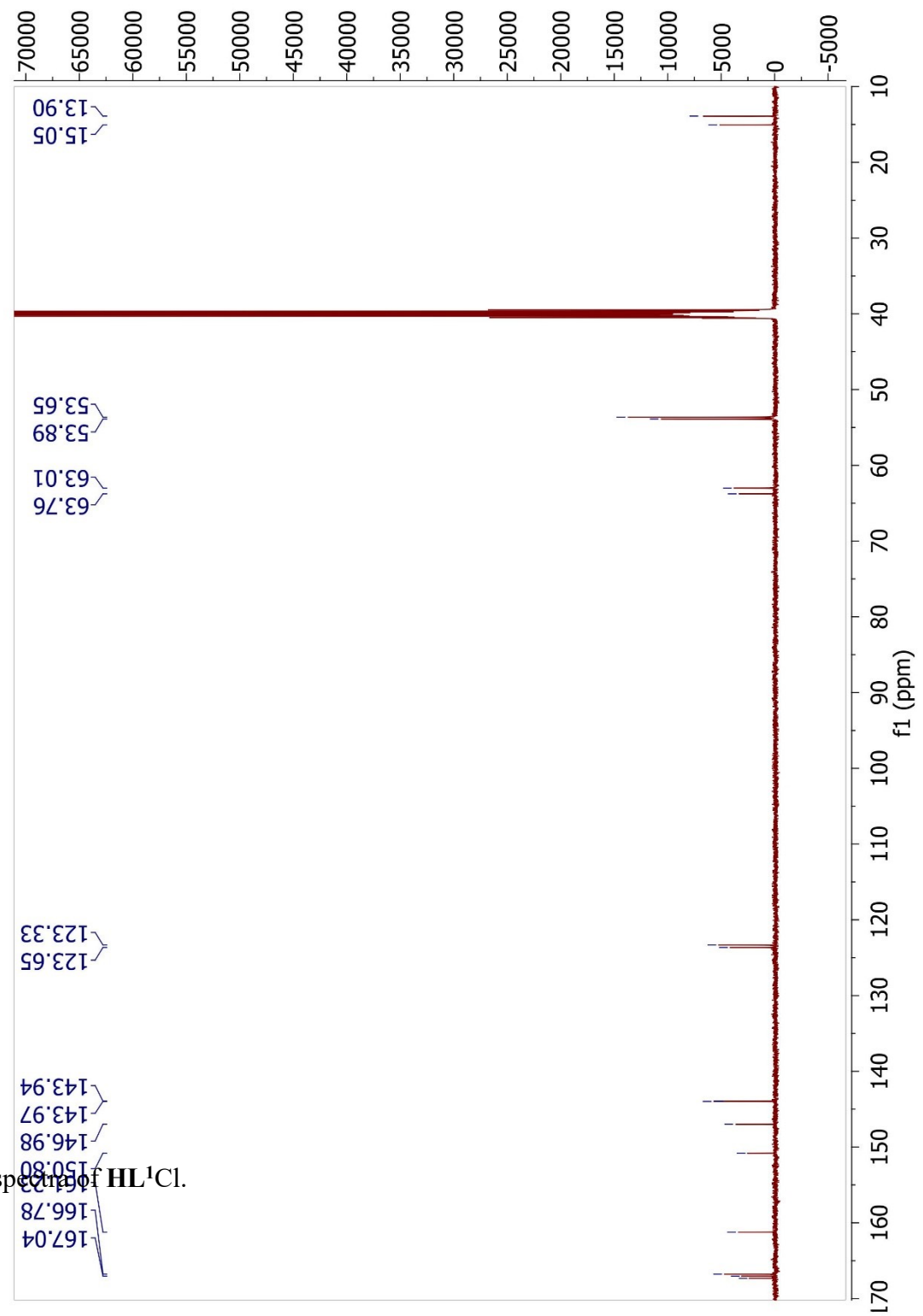


Fig. S10 ^{13}C NMR spectra of **HL^{1}Cl**.

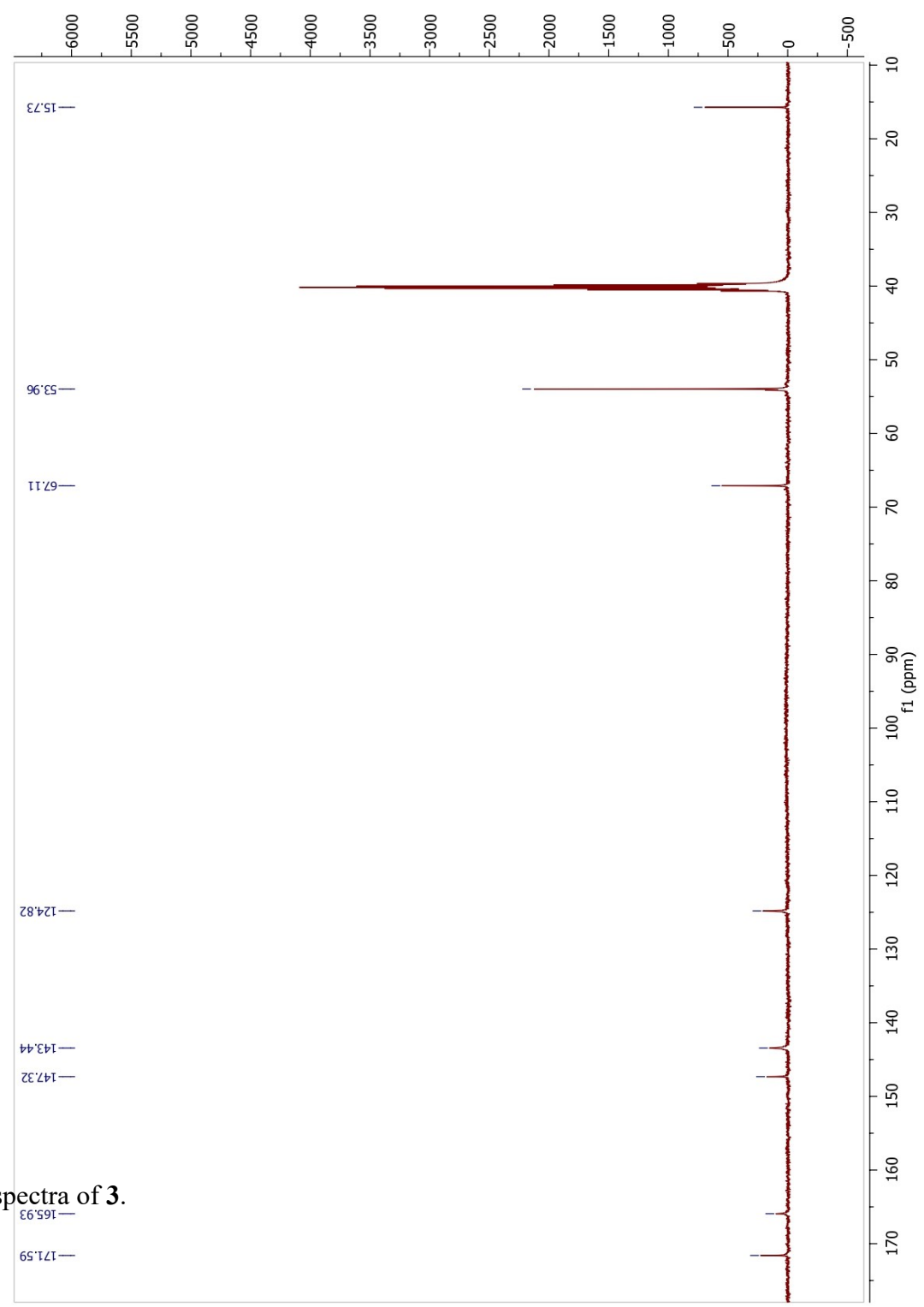
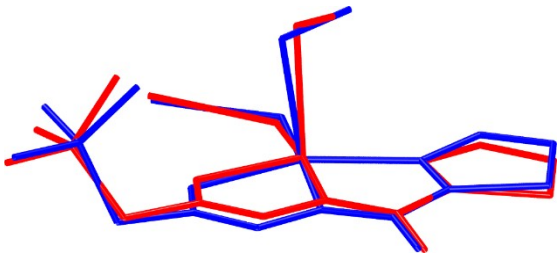
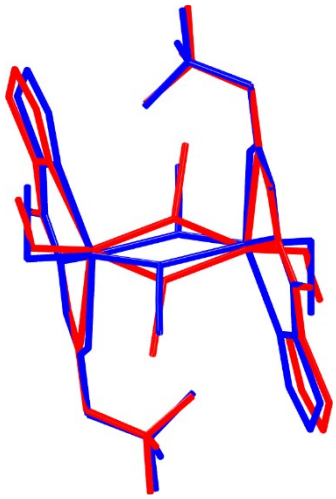


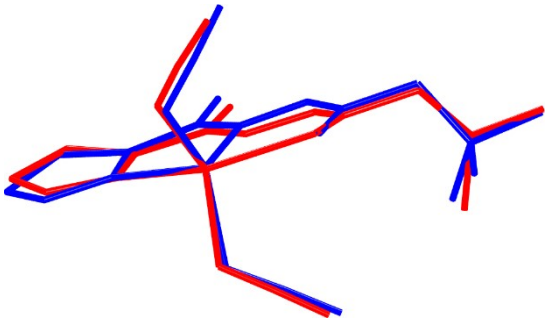
Fig. S11 ^{13}C NMR spectra of **3**.



$[Cu(\mathbf{L^1})(N_3)(CH_3OH)]^+$



$[Mn_2\mathbf{L^1}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$



$[Zn\mathbf{L^1}(N_3)_2]$

Fig. S12 Overlay between X-ray determined (red) and DFT optimized (blue) structures of $[Cu(\mathbf{L^1})(N_3)(CH_3OH)]^+$ (**1**), $[Mn_2\mathbf{L^1}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$ (**2**) and $[Zn\mathbf{L^1}(N_3)_2]$ (**3**)

Cartesian coordinates of all optimized structures

All structures from Table 1 in the main text are optimized at ZORA-BP86-D3/TZP-COSMO(DMSO) level of theory.

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[Cu2L12(N3)2(CH3OH)2]2+
Cu 1.340973 5.287717 0.744678
S 1.429499 0.908863 0.106665
O 0.456415 6.712519 1.861486
N 1.796774 3.447337 0.007823
N 0.381857 4.184492 2.031421
N -0.163673 4.825332 3.110273
N 0.464635 7.966988 4.564390
N 2.309108 6.384520 -0.505436
N 2.200227 7.587162 -0.409324
N 2.113996 8.752043 -0.372254
C 2.465791 2.936729 -1.067906
H 3.013616 3.604779 -1.727790
C 2.379927 1.569224 -1.178246
H 2.833172 0.918165 -1.918895
C 1.194296 2.499807 0.736031
C 0.452628 2.882606 1.930328
C -0.070001 1.909260 2.928930
H -0.948559 2.321295 3.435759
H 0.700231 1.706588 3.689148
H -0.333621 0.960592 2.448151
C -0.057958 6.138484 2.899174
C -0.587873 7.010990 4.012484
H -0.922765 6.383164 4.842394
H -1.418495 7.633211 3.660065
C 1.750184 7.227145 4.843116
H 2.166410 6.859418 3.899127
H 1.527140 6.394551 5.516566
H 2.441766 7.925964 5.320565
C 0.724927 9.101586 3.601417
H 1.485993 9.748400 4.045250
H -0.210122 9.653073 3.466300
H 1.059626 8.678450 2.652027
C -0.070363 8.536470 5.854626
H 0.656494 9.259312 6.234585
H -0.204891 7.718045 6.566518
H -1.025317 9.027602 5.648450
O 3.154454 5.424876 2.366515
H 3.874266 5.718618 1.775076

C	3.569803	4.178091	2.976607
H	4.514797	4.304324	3.520778
H	3.679971	3.384250	2.224217
H	2.781016	3.900777	3.683846
Cu	-1.342415	5.606484	-0.744940
S	-1.430583	9.985033	-0.104833
O	-0.458659	4.182210	-1.862936
N	-1.797900	7.446538	-0.007033
N	-0.384005	6.710309	-2.031730
N	0.160790	6.069883	-3.111216
N	-0.467113	2.928591	-4.567715
N	-2.309695	4.509282	0.505516
N	-2.200305	3.306678	0.409626
N	-2.113470	2.141811	0.372872
C	-2.466122	7.956595	1.069465
H	-3.013120	7.288183	1.729672
C	-2.380832	9.324139	1.179955
H	-2.833856	9.974799	1.921099
C	-1.195963	8.394398	-0.735215
C	-0.455179	8.012157	-1.930249
C	0.066055	8.986155	-2.928917
H	0.940508	8.572193	-3.441169
H	-0.707318	9.193877	-3.684607
H	0.335500	9.932551	-2.446858
C	0.054743	4.756645	-2.900898
C	0.584744	3.884723	-4.014699
H	0.919588	4.513225	-4.844102
H	1.415539	3.262560	-3.662610
C	-1.753226	3.667532	-4.846346
H	-2.170371	4.033789	-3.902205
H	-1.530633	4.501055	-5.518804
H	-2.443888	2.968557	-5.324900
C	-0.726830	1.792669	-3.606138
H	-1.486998	1.145578	-4.051098
H	0.208703	1.241978	-3.471113
H	-1.062461	2.214426	-2.656473
C	0.068707	2.360755	-5.858304
H	-0.657380	1.637583	-6.239105
H	0.202644	3.179950	-6.569425
H	1.024058	1.870314	-5.652326
O	-3.156779	5.469987	-2.365412
H	-3.876114	5.176024	-1.773496
C	-3.572624	6.717048	-2.974658
H	-4.517414	6.590700	-3.519166
H	-3.683447	7.510226	-2.221675
H	-2.783840	6.995400	-3.681492

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[CuL1(N3)(CH3OH)]+ – **complex 1**

Cu	1.214406	5.133193	1.028035
S	1.710534	0.730379	0.800364
O	0.305233	6.578359	2.111189
N	1.655629	3.258274	0.339310
N	0.427301	4.066209	2.461973
N	-0.130220	4.743798	3.510165
N	0.585482	7.735205	4.948699
N	1.867695	6.180475	-0.451394
N	1.751165	7.387466	-0.430135
N	1.671190	8.552516	-0.468033
C	2.323150	2.702662	-0.716033
H	2.696344	3.336946	-1.516003
C	2.448522	1.335520	-0.639515
H	2.925246	0.658998	-1.341354
C	1.264866	2.340852	1.234775
C	0.570914	2.766372	2.441689
C	0.122668	1.822119	3.502168
H	-0.184542	2.375218	4.394158
H	0.931540	1.124004	3.759307
H	-0.727109	1.224727	3.140112
C	-0.108559	6.045162	3.215655
C	-0.575535	6.959426	4.322817
H	-1.029505	6.368322	5.122640
H	-1.286095	7.704261	3.949911
C	1.728661	6.807549	5.278915
H	2.158183	6.424390	4.346389
H	1.345288	5.988137	5.893011
H	2.474991	7.383530	5.832463
C	1.070523	8.819200	4.016572
H	1.910907	9.324619	4.500101
H	0.247618	9.519682	3.849310
H	1.373008	8.355136	3.075442
C	0.077276	8.369449	6.218936
H	0.882362	8.976114	6.641823
H	-0.207846	7.574375	6.912987
H	-0.785219	8.995053	5.974172
O	3.115973	5.452703	2.473521
H	3.707511	6.017119	1.938854
C	3.855499	4.249042	2.806238
H	4.752744	4.494928	3.388455
H	4.138207	3.695033	1.900844
H	3.187766	3.632293	3.416633

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[CuL1(N3)]+

Cu	1.255229	5.066015	1.044533
S	1.552745	0.666138	0.668523
O	0.559268	6.516629	2.234664
N	1.653852	3.206207	0.318879
N	0.573386	4.002994	2.522821
N	0.034468	4.674228	3.589034
N	0.434758	7.924295	4.898232
N	1.943549	6.123080	-0.392625
N	1.859164	7.333920	-0.349904
N	1.811148	8.499015	-0.372721
C	2.198629	2.658026	-0.807079
H	2.558392	3.302191	-1.605368
C	2.227364	1.283012	-0.796045
H	2.602013	0.608220	-1.558959
C	1.261082	2.278752	1.201977
C	0.647996	2.699839	2.455418
C	0.169311	1.743925	3.489348
H	-0.121257	2.280442	4.396507
H	0.956883	1.014739	3.724798
H	-0.697939	1.184595	3.107790
C	0.074484	5.974584	3.312366
C	-0.530722	6.869023	4.368737
H	-0.839451	6.257777	5.221001
H	-1.396998	7.407749	3.967723
C	1.773640	7.304765	5.209152
H	2.231815	6.972450	4.274252
H	1.618051	6.460619	5.886449
H	2.395998	8.067082	5.684202
C	0.609017	9.045179	3.900715
H	1.320101	9.760586	4.322158
H	-0.364999	9.518456	3.748392
H	0.979370	8.618725	2.966075
C	-0.157825	8.486710	6.166366
H	0.495815	9.288016	6.521186
H	-0.219100	7.685271	6.907327
H	-1.153078	8.878804	5.940337

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[CuL1(N3)(CH3OH)(DMSO)]+

N	1.497662	3.276923	0.413907
C	1.105320	2.367671	1.313583
S	1.205515	0.740129	0.733064
C	1.788708	1.332191	-0.782615
C	1.876567	2.704360	-0.768483
C	0.610865	2.799745	2.612405

N	0.521797	4.103261	2.673898
N	0.128832	4.767445	3.801670
C	0.128375	6.077614	3.536697
C	-0.198910	6.956602	4.723792
N	1.021069	7.735113	5.216694
C	1.372526	8.840268	4.251449
Cu	1.002173	5.168116	1.113704
O	-1.143122	4.822572	0.153976
O	3.218238	5.626705	2.458392
C	3.977168	6.678251	1.816983
O	0.399305	6.638039	2.407315
N	1.600424	6.239369	-0.390006
N	1.354102	7.422428	-0.400032
N	1.136233	8.571816	-0.465566
C	0.265261	1.848071	3.705813
C	0.672230	8.342473	6.551632
C	2.202548	6.811761	5.385427
H	2.213500	3.332062	-1.589348
H	2.037199	0.644587	-1.584738
H	-0.039205	2.397814	4.600513
H	1.127613	1.208354	3.942090
H	-0.557488	1.189862	3.388866
H	-0.537158	6.337895	5.559229
H	-0.962455	7.699294	4.468848
H	2.497502	6.418413	4.405486
H	1.909023	5.995147	6.051057
H	3.016608	7.391488	5.828928
H	2.271351	9.339342	4.622926
H	0.533639	9.540895	4.214445
H	1.536934	8.396005	3.267260
H	1.522665	8.943651	6.884146
H	0.475936	7.533456	7.260190
H	-0.214555	8.970308	6.428758
H	4.922466	6.865099	2.346218
H	3.356845	7.580264	1.857256
H	4.175758	6.438804	0.763579
S	-0.980388	4.718122	-1.377966
C	-2.317784	3.613187	-1.918215
C	-1.657997	6.263014	-2.055653
H	-1.668290	6.186819	-3.149723
H	-2.667875	6.414534	-1.656056
H	-0.987746	7.069355	-1.738500
H	-2.330147	3.595879	-3.014967
H	-2.080331	2.617645	-1.527566
H	-3.271077	3.974694	-1.514023
H	3.758796	4.815362	2.419643

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[CuL1(N3)(DMSO)]+

S	2.274925	1.209008	-0.443017
C	2.125144	2.925532	-0.586287
C	1.386052	3.439435	0.451829
N	0.948347	2.497225	1.342529
C	1.339901	1.259375	1.007821
Cu	0.027932	2.456325	3.167643
C	0.988153	0.137368	1.866601
C	1.435272	-1.257855	1.604309
N	0.274578	0.537084	2.886936
N	-0.134376	-0.295791	3.890421
C	-0.807939	0.435056	4.782807
O	-1.071025	1.697661	4.702491
N	-0.413582	4.325773	3.366770
N	-0.583455	4.737261	4.493001
N	-0.752533	5.186254	5.559947
C	-1.254809	-0.313558	6.016323
N	-0.513008	0.155600	7.268757
C	-0.996333	1.518008	7.705945
C	-0.796760	-0.839413	8.365933
C	0.971804	0.208318	7.010246
O	1.873320	2.407730	4.581712
S	3.144928	1.942470	3.833320
C	4.327243	1.504495	5.135591
C	3.952150	3.462078	3.256583
H	1.136992	4.486333	0.606410
H	2.579248	3.451101	-1.420241
H	1.112834	-1.915027	2.416564
H	2.531021	-1.293042	1.517857
H	1.016673	-1.619550	0.653910
H	-1.039366	-1.379257	5.900463
H	-2.322326	-0.161370	6.208460
H	1.175710	0.980831	6.259030
H	1.294084	-0.772871	6.649763
H	1.466935	0.450397	7.954478
H	-0.432864	1.800748	8.599154
H	-2.063115	1.444145	7.934567
H	-0.828061	2.222961	6.888859
H	-0.314895	-0.484709	9.280731
H	-0.389271	-1.809400	8.069473
H	-1.879333	-0.903109	8.504905
H	4.918063	3.194793	2.811656
H	3.292522	3.897001	2.498439
H	4.074348	4.144606	4.105543

H 5.299543 1.314087 4.665773
H 4.384553 2.331125 5.853460
H 3.956976 0.590461 5.611459

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[CuL1(N3)(DMSO)2]+
C 2.134754 1.346149 -0.664803
C 2.044587 2.718270 -0.675172
N 1.554202 3.252862 0.481286
C 1.258283 2.318464 1.390674
S 1.581606 0.708318 0.844327
Cu 1.048041 5.097445 1.209914
O 3.197226 5.307707 2.435255
S 4.256096 5.577108 1.350611
C 4.515947 7.379632 1.343315
C 0.722515 2.714819 2.686252
N 0.544822 4.007710 2.743604
N 0.130294 4.659936 3.871138
C 0.104453 5.969596 3.606961
C -0.214789 6.850024 4.792206
N 0.990171 7.701229 5.198952
C 0.705992 8.274041 6.564248
N 1.610338 6.229841 -0.273032
N 1.424447 7.422684 -0.210248
N 1.274305 8.584840 -0.195215
O 0.372182 6.538352 2.480770
O -1.223442 4.705975 0.263394
S -1.579800 5.882034 -0.663719
C -3.199959 5.472298 -1.381678
C 0.455824 1.745353 3.786027
C 2.237269 6.852328 5.261630
C 1.200806 8.835451 4.224972
C -2.150568 7.223157 0.429594
C 5.848646 5.132722 2.108628
H 2.325413 3.372986 -1.496361
H 2.493783 0.684354 -1.446652
H 0.121266 2.276050 4.681562
H 1.365830 1.173051 4.017799
H -0.318314 1.026182 3.479990
H -0.474430 6.232261 5.655964
H -1.029970 7.546453 4.567584
H 2.488141 6.496477 4.254356
H 2.044663 6.007039 5.928254
H 3.042549 7.474819 5.661310
H 2.076974 9.400300 4.553825
H 0.310922 9.470556 4.242670

H 1.345807 8.409359 3.229752
H 1.538190 8.926887 6.840856
H 0.614981 7.448375 7.275038
H -0.226246 8.843613 6.515548
H -2.487996 8.060305 -0.193430
H -2.961339 6.844389 1.064125
H -1.286645 7.513639 1.037519
H -3.553134 6.340909 -1.951153
H -3.045277 4.619734 -2.051819
H -3.895953 5.217022 -0.573070
H 5.337305 7.611150 0.654305
H 3.587276 7.838773 0.989752
H 4.750122 7.708606 2.363091
H 6.652249 5.428030 1.422462
H 5.941625 5.643893 3.074604
H 5.845323 4.045237 2.239454

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[Mn2L12(μ-1,1-N3)2(N3)2]x2CH3OH – **complex 2**
Mn -1.025936 1.286561 -0.663518
S 1.236422 5.430007 -0.567085
N 0.345684 3.075121 -1.148209
N -1.506735 2.915333 0.753535
N -2.459704 2.671364 1.712639
N -3.918285 -0.158506 3.109340
N 0.421833 0.736672 1.063568
N 1.127202 1.570798 1.587587
N 1.780346 2.405575 2.079258
N -1.878940 1.477851 -2.577184
N -1.163749 1.355199 -3.540335
N -0.469437 1.235624 -4.482559
O -2.891474 0.769807 0.409580
C 1.267135 3.395989 -2.110964
H 1.448308 2.701981 -2.926725
C 1.861283 4.625357 -1.961972
H 2.612448 5.099120 -2.586103
C 0.200554 4.064515 -0.265197
C -0.781090 4.000141 0.809120
C -0.896338 5.108663 1.804870
H -1.727799 4.933512 2.492473
H -1.059479 6.064960 1.286460
H 0.035217 5.201965 2.381115
C -3.106810 1.532640 1.411896
C -4.191976 1.167309 2.404478
H -5.158912 1.061258 1.899617
H -4.264233 1.930180 3.184638

C	-2.498958	-0.189083	3.618774
H	-2.344796	0.701732	4.236637
H	-1.812875	-0.181794	2.765339
H	-2.367285	-1.095486	4.214386
C	-4.862515	-0.259626	4.280047
H	-4.709784	-1.230460	4.759378
H	-5.887005	-0.173529	3.908095
H	-4.637308	0.551463	4.977695
C	-4.159605	-1.320745	2.179667
H	-3.492348	-1.215930	1.321193
H	-5.204423	-1.291602	1.858057
H	-3.961309	-2.241773	2.734184
Mn	1.027912	-1.284246	0.662197
S	-1.232998	-5.428954	0.582672
N	-0.342128	-3.071915	1.154517
N	1.503728	-2.915659	-0.753478
N	2.454688	-2.674180	-1.715172
N	3.917131	0.150290	-3.119645
N	-0.421185	-0.734888	-1.064293
N	-1.128387	-1.569022	-1.585800
N	-1.783052	-2.403969	-2.075193
N	1.883528	-1.471979	2.575108
N	1.168188	-1.345216	3.537652
N	0.473296	-1.221607	4.478928
O	2.890971	-0.770286	-0.416921
C	-1.257096	-3.392515	2.123524
H	-1.434045	-2.697457	2.939373
C	-1.850450	-4.622919	1.980078
H	-2.597293	-5.096622	2.609411
C	-0.200767	-4.062584	0.272344
C	0.776466	-3.999539	-0.806115
C	0.886862	-5.108590	-1.801825
H	1.716186	-4.934756	-2.492334
H	1.050563	-6.064932	-1.283677
H	-0.046801	-5.200806	-2.374808
C	3.103741	-1.535753	-1.417822
C	4.188184	-1.174960	-2.412894
H	5.156309	-1.071032	-1.909867
H	4.256810	-1.939340	-3.191915
C	2.496592	0.184402	-3.625502
H	2.338101	-0.706871	-4.241629
H	1.812765	0.180374	-2.770267
H	2.366064	1.090278	-4.222148
C	4.858674	0.245996	-4.292985
H	4.708032	1.216455	-4.773743
H	5.883815	0.157065	-3.923526

H	4.628845	-0.565618	-4.988519
C	4.164807	1.313462	-2.192850
H	3.499287	1.212627	-1.332553
H	5.210296	1.281221	-1.873749
H	3.968516	2.234130	-2.748713
O	-2.021970	2.973456	4.454408
H	-2.187402	2.958990	3.464482
C	-0.618759	2.703569	4.638300
H	0.010371	3.439565	4.115502
H	-0.342507	1.698193	4.277373
H	-0.408539	2.757435	5.713357
O	2.014310	-2.978042	-4.456105
H	2.179576	-2.963310	-3.466159
C	0.611666	-2.705538	-4.640321
H	-0.018875	-3.439750	-4.116715
H	0.337528	-1.699198	-4.280416
H	0.401291	-2.760130	-5.715311

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[Mn2L12(μ-1,1-N3)2(N3)2]

Mn	-1.074979	1.242792	-0.686482
S	1.251578	5.351129	-0.542007
N	0.340218	3.009756	-1.148714
N	-1.613850	2.905556	0.645660
N	-2.610440	2.711512	1.567077
N	-3.896271	-0.047049	3.152309
N	0.214090	0.655488	1.184018
N	0.725502	1.495155	1.891060
N	1.188556	2.335760	2.558840
N	-1.944479	1.451190	-2.596355
N	-1.222496	1.449709	-3.561646
N	-0.522386	1.448056	-4.507647
O	-2.930847	0.702474	0.381053
C	1.305831	3.307800	-2.073717
H	1.505508	2.603663	-2.876258
C	1.916895	4.526829	-1.908042
H	2.702752	4.982077	-2.502513
C	0.176689	4.007057	-0.276517
C	-0.857273	3.968167	0.743803
C	-1.013697	5.054825	1.757121
H	-1.436302	4.640273	2.678566
H	-1.703086	5.828342	1.384756
H	-0.050707	5.532481	1.976011
C	-3.203053	1.535243	1.319971
C	-4.273345	1.189394	2.333494
H	-5.232595	0.964453	1.854506

H	-4.387436	2.016217	3.039902
C	-2.450145	0.027168	3.577512
H	-2.292586	0.973326	4.102740
H	-1.810518	-0.019441	2.689311
H	-2.243671	-0.812611	4.246342
C	-4.773676	-0.084006	4.376958
H	-4.547391	-0.998302	4.932361
H	-5.818810	-0.081272	4.055436
H	-4.557108	0.797466	4.986105
C	-4.130399	-1.297013	2.342754
H	-3.510235	-1.241841	1.445078
H	-5.189826	-1.336938	2.074803
H	-3.868712	-2.156851	2.964380
Mn	1.074979	-1.242792	0.686482
S	-1.251578	-5.351129	0.542007
N	-0.340218	-3.009756	1.148714
N	1.613850	-2.905556	-0.645660
N	2.610440	-2.711512	-1.567077
N	3.896271	0.047049	-3.152309
N	-0.214090	-0.655488	-1.184018
N	-0.725502	-1.495155	-1.891060
N	-1.188556	-2.335760	-2.558840
N	1.944479	-1.451190	2.596355
N	1.222496	-1.449709	3.561646
N	0.522386	-1.448056	4.507647
O	2.930847	-0.702474	-0.381053
C	-1.305831	-3.307800	2.073717
H	-1.505508	-2.603663	2.876258
C	-1.916895	-4.526829	1.908042
H	-2.702752	-4.982077	2.502513
C	-0.176689	-4.007057	0.276517
C	0.857273	-3.968167	-0.743803
C	1.013697	-5.054825	-1.757121
H	1.436302	-4.640273	-2.678566
H	1.703086	-5.828342	-1.384756
H	0.050707	-5.532481	-1.976011
C	3.203053	-1.535243	-1.319971
C	4.273345	-1.189394	-2.333494
H	5.232595	-0.964453	-1.854506
H	4.387436	-2.016217	-3.039902
C	2.450145	-0.027168	-3.577512
H	2.292586	-0.973326	-4.102740
H	1.810518	0.019441	-2.689311
H	2.243671	0.812611	-4.246342
C	4.773676	0.084006	-4.376958
H	4.547391	0.998302	-4.932361

H	5.818810	0.081272	-4.055436
H	4.557108	-0.797466	-4.986105
C	4.130399	1.297013	-2.342754
H	3.510235	1.241841	-1.445078
H	5.189826	1.336938	-2.074803
H	3.868712	2.156851	-2.964380

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[MnL1(N3)2]

Mn	-1.258778	1.403430	-1.104717
S	1.476073	5.157783	-0.549115
N	0.337854	2.994378	-1.381905
N	-1.408093	2.700598	0.594185
N	-2.326639	2.438956	1.582139
N	-3.941314	-0.354599	2.827409
N	-0.183773	-0.301065	-0.848391
N	-0.474255	-1.192349	-0.088086
N	-0.730209	-2.070629	0.645699
N	-2.163669	1.566830	-2.906785
N	-1.771819	2.100354	-3.914902
N	-1.424997	2.610436	-4.912136
O	-2.983148	0.727832	0.111964
C	1.249668	3.348580	-2.342054
H	1.362886	2.734491	-3.232763
C	1.962339	4.491085	-2.067049
H	2.734912	4.968172	-2.661865
C	0.334647	3.858866	-0.361626
C	-0.576195	3.702767	0.756885
C	-0.560858	4.606073	1.945570
H	-0.600112	4.009667	2.865736
H	-1.448879	5.254731	1.940655
H	0.334894	5.237042	1.959227
C	-3.080161	1.397164	1.203225
C	-4.150022	1.026668	2.209244
H	-5.138832	1.008449	1.736722
H	-4.140945	1.743892	3.035092
C	-2.525232	-0.499448	3.323503
H	-2.290914	0.354467	3.964649
H	-1.853419	-0.538403	2.461449
H	-2.460198	-1.433716	3.887492
C	-4.891922	-0.481256	3.990083
H	-4.787143	-1.485403	4.409533
H	-5.910176	-0.324159	3.624028
H	-4.632566	0.274440	4.736577
C	-4.238304	-1.445327	1.827921
H	-3.565495	-1.321504	0.976738

H -5.281102 -1.345579 1.514105
H -4.077727 -2.406769 2.323752

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cis-[MnL1(N3)2(DMSO)]
N 1.287430 6.402908 4.624859
C 2.032684 7.406786 4.151146
S 3.068966 6.935455 2.828580
C 2.457816 5.319203 2.947944
C 1.527839 5.229913 3.954382
C 1.973230 8.741404 4.720307
N 1.006215 8.877390 5.595607
N 0.914707 10.060847 6.287277
C -0.005154 9.931231 7.254296
O -0.719286 8.898161 7.526659
Mn 0.006116 7.128058 6.426476
O -1.655593 7.550589 4.903663
S -1.834534 6.385205 3.895730
C -3.600847 6.387575 3.486293
N -1.023697 5.401840 6.959938
N -0.823324 4.309183 6.497150
N -0.642975 3.233547 6.055086
N 1.653170 6.898245 7.748063
N 2.764740 7.115590 7.334136
N 3.843133 7.335476 6.921220
C 2.944640 9.816835 4.351640
C -0.107699 11.149689 8.147278
N 0.429837 10.864226 9.554339
C 0.641686 12.185465 10.246538
C -0.564435 10.047919 10.343009
C 1.740766 10.121709 9.479862
C -1.216286 7.024463 2.311821
H 0.992906 4.327908 4.247173
H 2.818095 4.539261 2.284327
H 3.323605 10.295015 5.263378
H 2.448281 10.596204 3.754787
H 3.787850 9.418486 3.775813
H -1.144966 11.477764 8.275081
H 0.500417 11.960573 7.736979
H 2.428394 10.692771 8.850077
H 1.562065 9.130085 9.049129
H 2.132606 10.032501 10.496551
H 0.966432 11.988069 11.271933
H -0.304661 12.733394 10.245706
H 1.408175 12.744748 9.703124
H -0.755732 9.124248 9.792169

H -1.483471 10.632615 10.441324
H -0.131845 9.846816 11.326883
H -4.133997 6.068664 4.388051
H -3.896856 7.401246 3.190747
H -3.765938 5.670021 2.673505
H -1.432016 6.283469 1.532847
H -1.702591 7.983497 2.099019
H -0.134974 7.151502 2.425372

49
trans-[MnL1(N3)2(DMSO)]
Mn 0.400532 3.976741 4.149176
S 2.801187 8.033488 4.057287
N 1.888639 5.658337 3.607371
N -0.219526 5.776754 5.259232
N -1.218940 5.648951 6.193310
N -2.320352 3.056021 8.097278
N 1.620964 3.446419 5.815243
N 2.153385 4.300937 6.477150
N 2.662425 5.141444 7.123659
N -0.655257 4.412620 2.309031
N -0.103788 4.776664 1.303803
N 0.427977 5.129022 0.313252
O -1.491879 3.519212 5.216630
C 2.986124 5.814003 2.801850
H 3.295630 4.999778 2.150261
C 3.614692 7.031262 2.905137
H 4.493261 7.388782 2.377310
C 1.654093 6.750006 4.337449
C 0.560297 6.827176 5.294591
C 0.426330 7.993934 6.220476
H -0.482514 7.890447 6.819938
H 0.385310 8.934091 5.650930
H 1.295492 8.048049 6.891540
C -1.780173 4.436895 6.064753
C -2.813095 4.140364 7.132411
H -3.749722 3.768036 6.702555
H -2.997544 5.035057 7.733899
C -0.901221 3.337566 8.524532
H -0.852953 4.356093 8.919291
H -0.243942 3.233723 7.654086
H -0.634027 2.610952 9.296499
C -3.218133 3.066976 9.306530
H -2.910789 2.253439 9.969544
H -4.249137 2.918643 8.973981
H -3.112843 4.031954 9.809924

C	-2.386264	1.696457	7.445844
H	-1.798107	1.736790	6.526165
H	-3.434238	1.476814	7.221803
H	-1.984772	0.964492	8.152307
O	0.834971	2.012499	3.341240
S	0.031333	1.540823	2.085042
C	0.536571	-0.189929	1.894138
H	0.402767	-0.712145	2.848745
H	-0.081934	-0.635428	1.105441
H	1.588510	-0.183430	1.590466
C	-1.652434	1.236974	2.689956
H	-2.232418	0.792844	1.872041
H	-1.601616	0.566560	3.555497
H	-2.058006	2.213950	2.970378

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[ZnL1(N3)2] – **complex 3**

Zn	3.741506	8.256832	0.356708
S	8.048698	7.941011	-1.188711
N	5.866460	7.692764	0.159386
N	4.334898	9.319522	-1.309893
N	3.479792	10.149897	-1.972780
N	0.861481	12.218160	-1.243570
N	3.761322	9.180766	2.124257
N	3.259279	10.275973	2.216096
N	2.787501	11.339072	2.349276
N	2.886144	6.467416	0.280889
N	1.986713	6.256700	-0.499205
N	1.113240	5.996837	-1.232106
O	1.901115	9.418501	-0.383668
C	6.786090	6.878967	0.763711
H	6.503749	6.299633	1.639790
C	8.027987	6.880754	0.174670
H	8.917418	6.330174	0.464185
C	6.379898	8.328054	-0.895298
C	5.581860	9.239070	-1.700418
C	6.145341	10.010297	-2.847615
H	6.035784	11.087663	-2.659852
H	5.585668	9.784253	-3.765517
H	7.204863	9.782401	-3.007679
C	2.260080	10.103689	-1.392588
C	1.253619	11.005104	-2.085125
H	1.683120	11.395283	-3.012555
H	0.325651	10.461932	-2.295631
C	0.008217	11.805872	-0.070299

H -0.897956 11.330322 -0.456323
H -0.244331 12.708072 0.493873
H 0.581621 11.104494 0.540230
C 2.091800 12.930933 -0.742695
H 2.586431 12.297196 -0.000710
H 1.771685 13.868164 -0.279353
H 2.751856 13.126123 -1.592093
C 0.071363 13.150290 -2.126282
H 0.716881 13.488974 -2.941295
H -0.257439 13.999276 -1.520732
H -0.791063 12.606580 -2.521490

78
[Zn2L12(μ-1,1-N3)2(N3)2]
Zn -1.088865 1.236139 -0.752088
S 1.285661 5.230126 -0.352080
N 0.463508 2.885638 -1.057284
N -1.632365 2.734108 0.578703
N -2.698503 2.524007 1.404214
N -4.082792 -0.150221 2.965999
N 0.161787 0.482987 1.297253
N 0.701085 1.343376 1.953255
N 1.163539 2.216155 2.577094
N -1.981840 1.697928 -2.581609
N -1.228657 1.713587 -3.522582
N -0.506325 1.732327 -4.449589
O -2.900690 0.492514 0.221939
C 1.487706 3.211642 -1.903371
H 1.759535 2.524077 -2.696982
C 2.064624 4.437989 -1.676388
H 2.885518 4.913528 -2.204028
C 0.219804 3.863785 -0.186758
C -0.886919 3.792538 0.752343
C -1.139968 4.845810 1.780611
H -1.378315 4.374729 2.741655
H -2.005852 5.458695 1.490002
H -0.271979 5.503673 1.903303
C -3.261215 1.337814 1.111931
C -4.421236 1.008602 2.027032
H -5.310318 0.705051 1.464247
H -4.646457 1.872279 2.658946
C -2.715548 0.051519 3.571546
H -2.690852 1.035628 4.047543
H -1.959139 -0.002347 2.779415
H -2.558922 -0.731814 4.318033
C -5.114414 -0.179460 4.064202

H	-4.906829	-1.039105	4.707291
H	-6.103269	-0.274465	3.607330
H	-5.042972	0.751085	4.633583
C	-4.126526	-1.454711	2.213216
H	-3.398620	-1.402612	1.400030
H	-5.136555	-1.585061	1.815363
H	-3.891163	-2.259028	2.914231
Zn	1.146699	-1.203680	0.708800
S	-1.256973	-5.190246	0.886759
N	-0.337443	-2.818986	1.330040
N	1.487901	-2.774388	-0.606198
N	2.431251	-2.628892	-1.580597
N	3.897627	-0.015272	-3.309705
N	-0.153499	-0.472524	-1.326760
N	-0.745363	-1.315846	-1.959076
N	-1.262851	-2.172065	-2.562350
N	2.278962	-1.488737	2.429217
N	1.646791	-1.473824	3.456141
N	1.043376	-1.461851	4.463963
O	2.883349	-0.577529	-0.507600
C	-1.181005	-3.110005	2.367079
H	-1.306250	-2.388017	3.168400
C	-1.780551	-4.345155	2.299588
H	-2.485376	-4.800467	2.988238
C	-0.247364	-3.833528	0.471765
C	0.698768	-3.815570	-0.632043
C	0.774376	-4.910716	-1.645542
H	0.934732	-4.480449	-2.640684
H	1.626384	-5.572007	-1.427742
H	-0.141225	-5.512880	-1.651717
C	3.083876	-1.465522	-1.404502
C	4.156069	-1.253700	-2.455836
H	5.144972	-1.119945	-2.002344
H	4.167522	-2.111901	-3.133473
C	2.446783	0.037538	-3.722760
H	2.206390	-0.890099	-4.249881
H	1.818641	0.130710	-2.829451
H	2.309362	0.893761	-4.388644
C	4.763347	-0.106175	-4.540075
H	4.628142	0.809200	-5.123001
H	5.805164	-0.206810	-4.223940
H	4.452724	-0.979266	-5.119643
C	4.266739	1.228079	-2.541317
H	3.667215	1.253101	-1.628644
H	5.331396	1.172885	-2.298055
H	4.073288	2.092335	-3.182391

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cis-[ZnL1(N3)2(DMSO)]

N	1.277058	6.387383	4.621534
C	2.002522	7.396377	4.140500
S	3.027825	6.938518	2.807119
C	2.440986	5.316342	2.934242
C	1.524656	5.216241	3.953265
C	1.939085	8.738617	4.703443
N	1.032234	8.861152	5.633811
N	0.923743	10.030394	6.330647
C	-0.023018	9.892480	7.279306
O	-0.774941	8.880530	7.500118
Zn	-0.001128	7.206892	6.347350
O	-1.531027	7.660189	4.693729
S	-1.771439	6.385786	3.849661
C	-3.560192	6.352006	3.547552
N	-1.163347	5.652144	6.898274
N	-0.746581	4.539143	6.694767
N	-0.376883	3.441589	6.506560
N	1.588926	6.852145	7.776350
N	2.701296	7.045927	7.358873
N	3.786889	7.244058	6.949877
C	2.847362	9.839973	4.260429
C	-0.103814	11.086890	8.207068
N	0.438464	10.751322	9.600380
C	0.658521	12.047816	10.335832
C	-0.555065	9.911825	10.365257
C	1.746581	10.006357	9.495997
C	-1.245135	6.823039	2.167175
H	1.003733	4.309396	4.252674
H	2.799921	4.541343	2.264203
H	3.228329	10.373511	5.139843
H	2.296363	10.568511	3.647443
H	3.690100	9.457527	3.673454
H	-1.135456	11.425467	8.350005
H	0.514132	11.900193	7.816336
H	2.432219	10.593206	8.878631
H	1.561565	9.027064	9.038772
H	2.144166	9.887366	10.507456
H	0.988388	11.814354	11.352005
H	-0.285702	12.598810	10.358781
H	1.424280	12.622327	9.807522
H	-0.748724	9.005228	9.787529
H	-1.473388	10.493906	10.483842
H	-0.120055	9.680166	11.341281
H	-4.035245	6.152559	4.514108

H -3.874921 7.323272 3.147440
H -3.777795 5.540449 2.842788
H -1.512115 5.997299 1.496583
H -1.734938 7.756523 1.867020
H -0.157158 6.945302 2.200177

49
trans-[ZnL1(N3)2(DMSO)]
Zn 0.379225 3.972412 4.196413
S 2.793078 7.914260 3.918201
N 1.916165 5.507149 3.619981
N -0.202771 5.702512 5.250570
N -1.230820 5.602550 6.142222
N -2.323585 3.110279 8.150473
N 1.556540 3.347278 5.883794
N 2.074098 4.222530 6.527402
N 2.573548 5.076361 7.164639
N -0.759613 4.444314 2.430860
N -0.209986 4.901077 1.463580
N 0.308930 5.339936 0.502717
O -1.477659 3.428116 5.246004
C 3.014621 5.620794 2.811793
H 3.335768 4.769562 2.216070
C 3.627520 6.850174 2.839505
H 4.503858 7.185771 2.294007
C 1.660686 6.639149 4.274716
C 0.546679 6.769408 5.207670
C 0.350815 8.011198 6.017290
H -0.470051 7.864448 6.725031
H 0.115107 8.864098 5.362985
H 1.268409 8.259701 6.568883
C -1.781385 4.374572 6.047242
C -2.827609 4.120675 7.114183
H -3.748337 3.700515 6.694634
H -3.041892 5.046745 7.655451
C -0.911613 3.441589 8.567273
H -0.878942 4.488422 8.881072
H -0.245337 3.277540 7.712730
H -0.643707 2.780484 9.395782
C -3.229463 3.184650 9.351370
H -2.920838 2.413698 10.063177
H -4.257416 3.009862 9.022209
H -3.133783 4.178059 9.798180
C -2.361922 1.711500 7.585036
H -1.772025 1.705481 6.665449
H -3.404937 1.457807 7.374319

H -1.947588 1.033031 8.335970
O 0.886908 2.115367 3.364115
S 0.140123 1.715629 2.046775
C 0.774361 0.049540 1.723954
H 0.661733 -0.562899 2.626067
H 0.202742 -0.366383 0.885285
H 1.827863 0.156415 1.446070
C -1.531435 1.245367 2.574246
H -2.067476 0.859727 1.698631
H -1.455292 0.489570 3.364200
H -1.999181 2.162067 2.946046

6
CH3OH
O 3.391228 5.271447 2.440298
H 4.227527 5.421267 1.959440
C 3.672723 4.299696 3.476390
H 4.424554 4.675240 4.187262
H 4.020474 3.346270 3.050010
H 2.731354 4.128422 4.010642

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DMSO
S 8.713472 23.444519 3.049680
O 8.630861 22.176474 3.914482
C 10.018348 23.133506 1.814023
H 10.933676 22.822662 2.332664
H 10.179212 24.056192 1.242357
H 9.650337 22.339401 1.155542
C 9.649441 24.667802 4.027449
H 9.031401 24.922865 4.894955
H 9.811032 25.555370 3.402995
H 10.602354 24.222773 4.339744