Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A Hemilabile 2-(2'-pyridyl)-imidazole Based Nickel(II) Complex: Proton-coupled-electron-transfer, Bactericidal and Cytotoxicity Studies†

Krishnendu Paramanik,[a] Nilaj Bandopadhyay,[a] Rakesh Debnath,[a] Suvojit Roy,[a] Muddukrishnaiah Kotakonda,[b] Mrinal Kanti Adak,[c] Bhaskar Biswas,*[a] and Hari Sankar Das*[a]

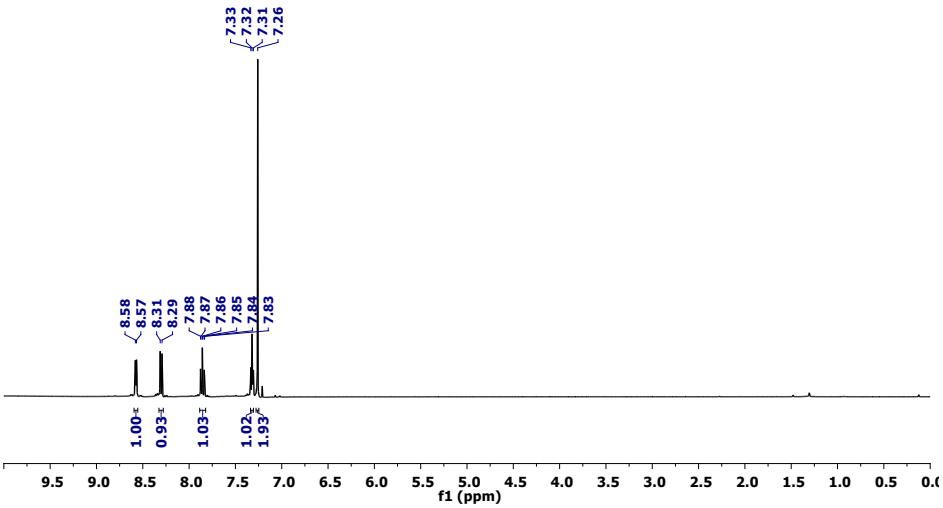


Fig. S1. ^{1}H NMR spectra of ligand **L**.

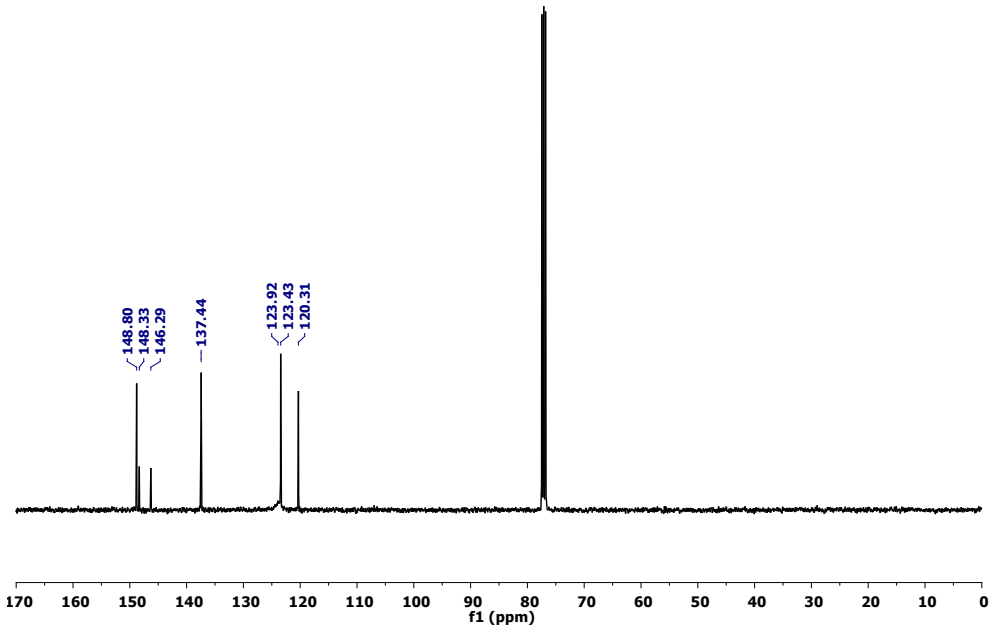


Fig. S2. $^{13}C\{^{1}H\}$ NMR spectra of ligand **L.**

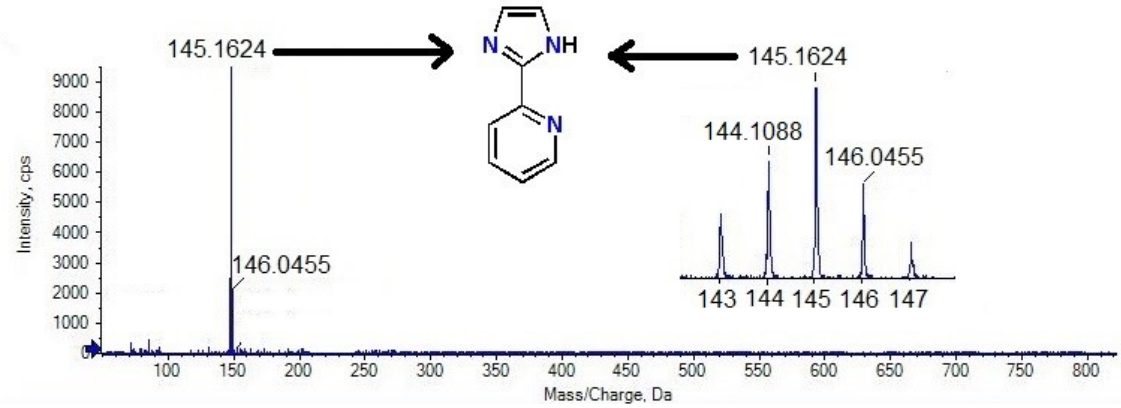


Fig. S3. ESI-MS spectrum of Ligand **L** in methanol.

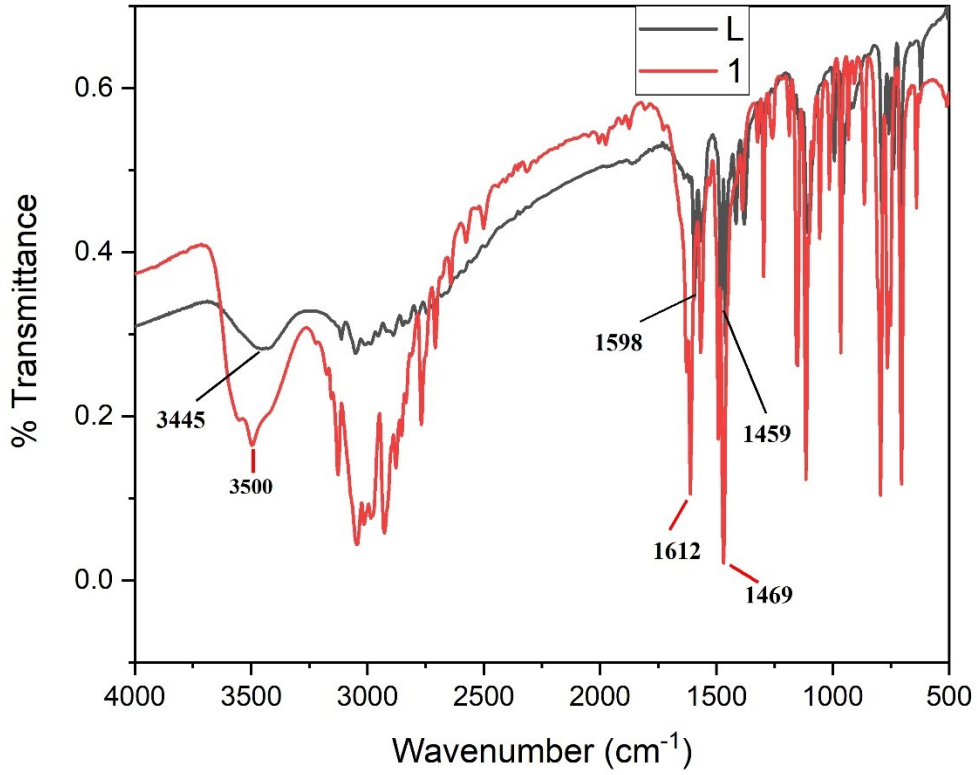


Fig. S4. FT-IR spectra of ligand L, complex **1.**

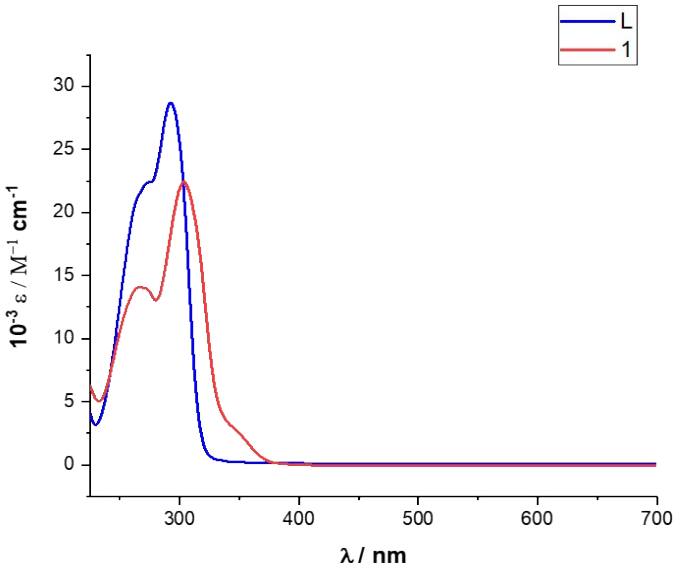


Fig. S5. UV-Vis spectra of the ligand, **L** and complex **1** in water.

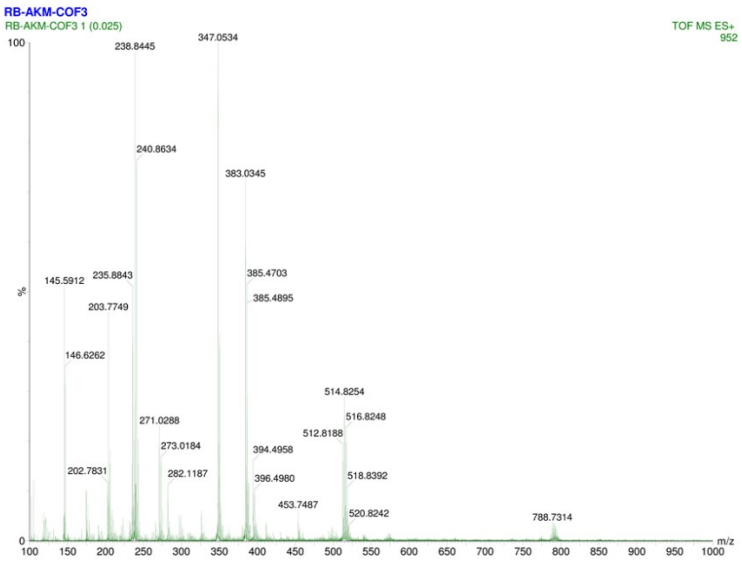


Fig. S6. ESI-MS spectrum of Complex **1** in methanol.

Synthesis of complex 1´:

The complex was synthesised according to the reported procedure.[1]

Yield: 0.265 g (~84%). Anal. calc. for $C_{16}H_{16}N_6NiO_2$(**1**): C, 50.17; H, 4.21; N, 21.94; Found: C, 50.43; H, 4.02; N, 21.67. IR (KBr, cm^{-1}; Fig. S6): 3425 ($\nu_{N\text{-}H}$), 1605 ($\nu_{C=N}$), 1496 ($\nu_{C\text{-}N,Py}$); ESI-MS (m/z; Fig. S7) calc. for $C_{16}H_{14}ClN_6Ni$ $[M + H]^+$ 383.08, found 383.0349.

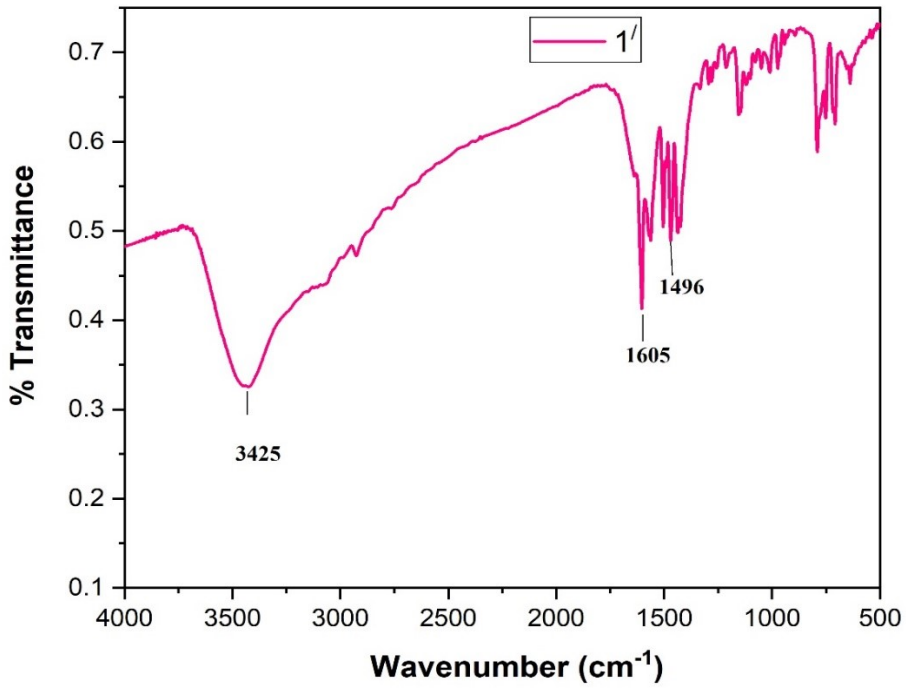


Fig. S7. FT-IR spectra of complex **1′**.

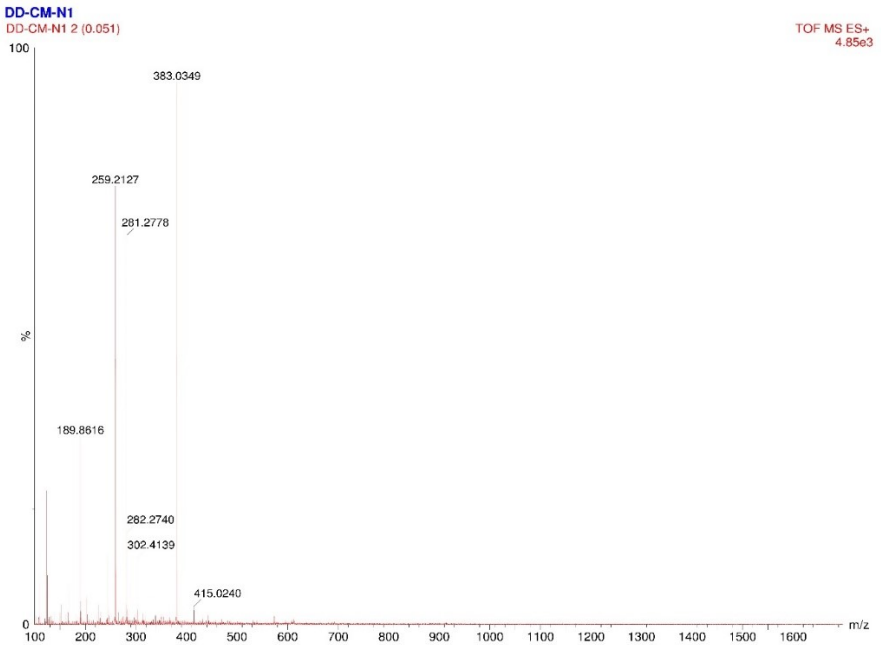


Fig. S8. ESI-MS spectrum of Complex **1′** in methanol.

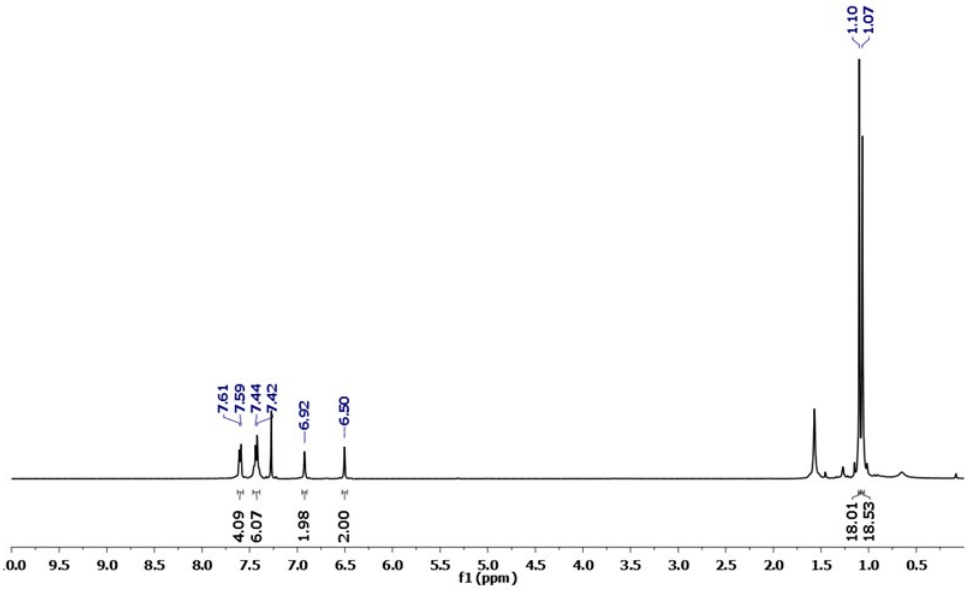


Fig. S9. ^{1}H NMR spectra of complex **2**.

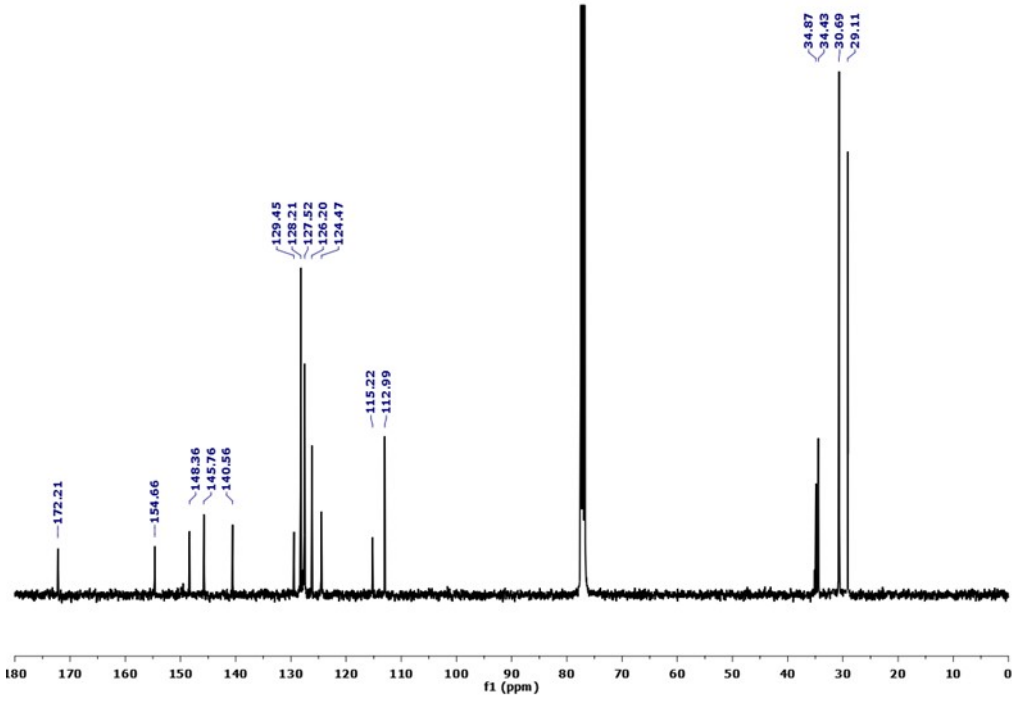


Fig. S10. $^{13}C\{^{1}H\}$ NMR spectra of complex **2.**

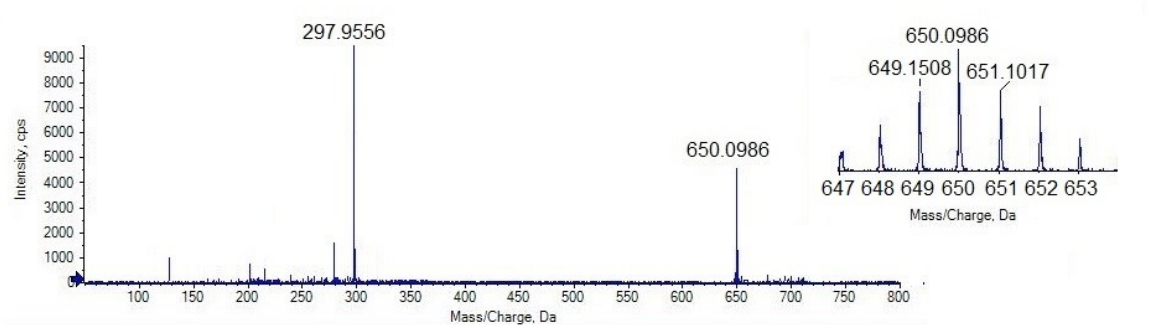


Fig. S11. ESI-MS spectrum of Complex **2** in methanol.

Table S1. Selected bond lengths (Å) and bond angles (°) for **1**

Bonds	Bond lengths		Bonds	Bond lengths	
	Experimental	Calculated		Experimental	Calculated
Ni1-Cl1	2.430(18)	2.514	Ni1-N1	2.122(17)	2.178
Ni1-N2	2.031(16)	2.041	C3-C2	1.305(17)	1.395
N1-C5	1.346(14)	1.365	N1-C1	1.317(14)	1.343
N2-C6	1.313(14)	1.338	N2-C8	1.373(14)	1.381
N3-C6	1.346(14)	1.371	N3-C7	1.363(15)	1.392
C6-C5	1.416(15)	1.451	C5-C4	1.365(15)	1.397
C8-C7	1.352(15)	1.375	C1-C2	1.400(16)	1.395
C4-C3	1.400(16)	1.394			

Bond angles	Experimental	Calculated	Bond angles	Experimental	Calculated
Cl1-Ni1-N1	88.79(18)	82.1920	Cl1-Ni1-N2	94.32(19)	90.7353
Cl1-Ni1-Cl1a	94.46(7)	96.7544	Cl1-Ni1-N1	171.14(17)	166.9277
Cl1-Ni1-N2	92.67(19)	90.7353	N1-Ni1-N2	78.9(2)	77.9765
Ni1-N2-C8	139.0(5)	135.3700	N1-Ni1-N1a	89.2(2)	93.2830
N1-Ni1-N2a	93.8(2)	100.3512	Ni1-N1-C1	128.0(5)	126.9364
Ni1-N2-C6	113.0(5)	114.3832	N2-Ni1-N2a	169.7(3)	177.6106
Ni1-N1-C5	113.2(5)	113.2178			

Table S2. Hydrogen bond parameters donor/acceptor scheme (Å,°) of Ni complex

D–H….A	D–H	H…..A	D…..A	D–H…A	Symmetry code
N3–H5 ... Cl1	0.8600	2.250	3.11(2)	174.00	1/2+x,y,1-z
C4–H4 ... Cl1	0.8600	2.864	3.724(2)	161.00	

π…π Interactions (Å,°) for Ni complex

Cg...Cg	Cg-Cg distance (Å)	Symmetry code
Cg(4)- Cg(4)	3.83	3/2-X,1-Y,Z

C-H…π Interactions (Å, º) for Ni complex

X-H...Cg	H...Cg (Å)	Symmetry code
C(1)-H(1)....Cg(1)	3.0	X,3/2-Y,1/2-Z
C(1)–H(1)…Cg(2)	3.23	X,Y,Z

Reproducibility of the single crystals of nickel complex 1

Despite several attempts to reproduce the single crystals of complex 1 for improving the measured data, we are failed to get the suitable crystals for XRD measurement. The current wet weather in the North-East region is hampering the slow evaporation method which was employed to obtain the single crystals earlier. Presently, crystallization of the complex 1 and similar substituted 2-pyridine-imidazole based nickel complexes are going on in our laboratory. We ensure you that we will keep trying to grow the suitable single crystals of the compound and record XRD data in keeping with the settings of the diffractometer as suggested by the learned reviewer. On further refinement of the present cif, we have found a disordered lattice water molecule in the crystal structure of 1. The revised cif with CCDC number 2131730 is now updated to CCDC link.

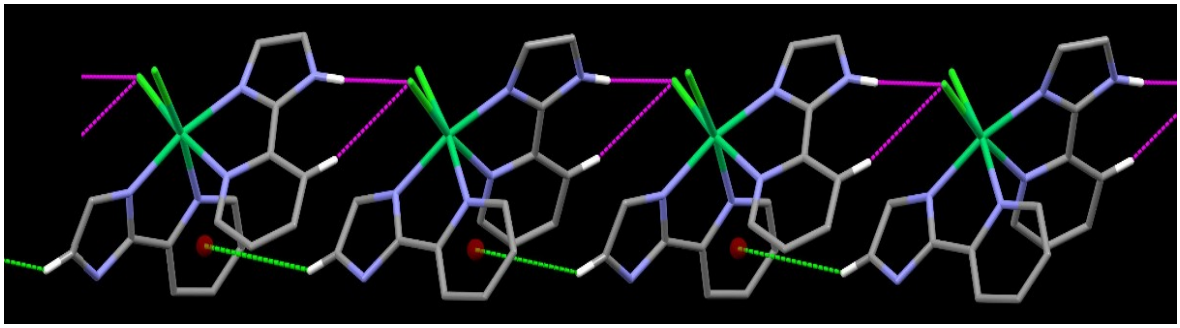


Fig. S12. N–H···Cl, C–H···Cl and C–H···π interactions mediated 1D supramolecular architecture of **1** in solid state

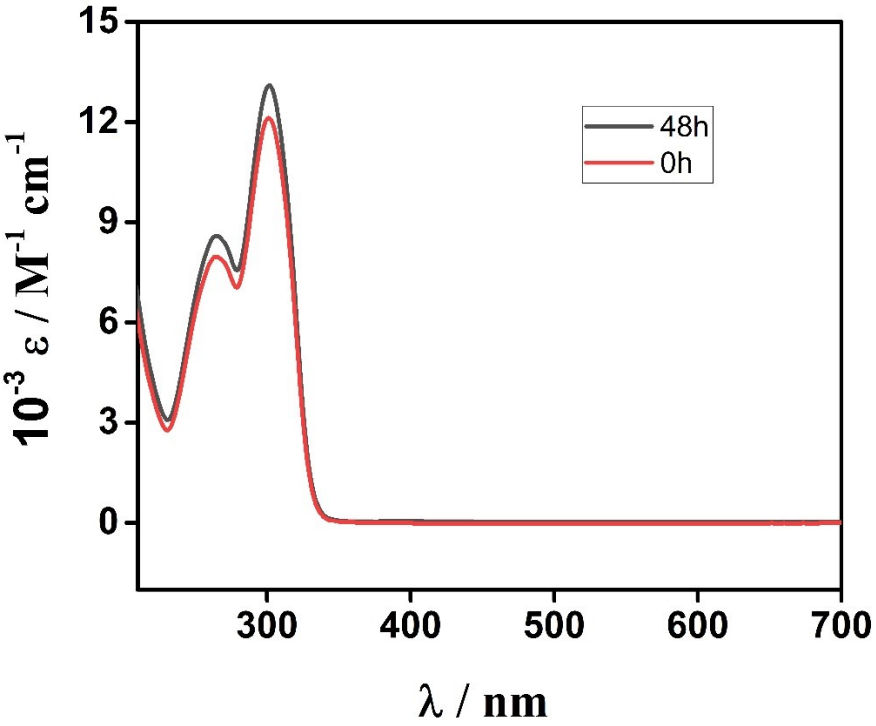


Fig. S13. Time-dependent UV-Vis spectra of **1** in water; (red for 0 min) and (black for 48 h).

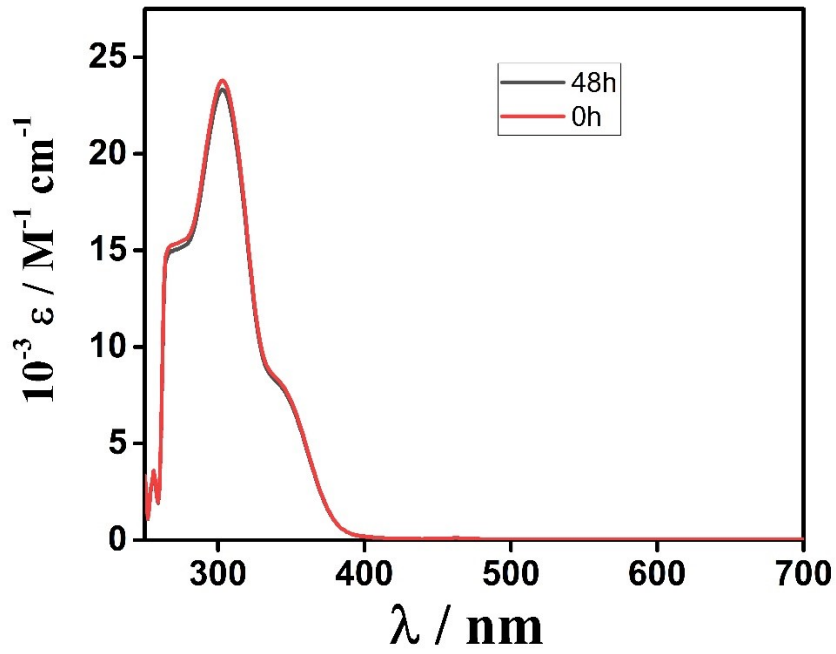


Fig. S14. Time-dependent UV-Vis spectra of **1** in DMF; (red for 0 min) and (black for 48 h).

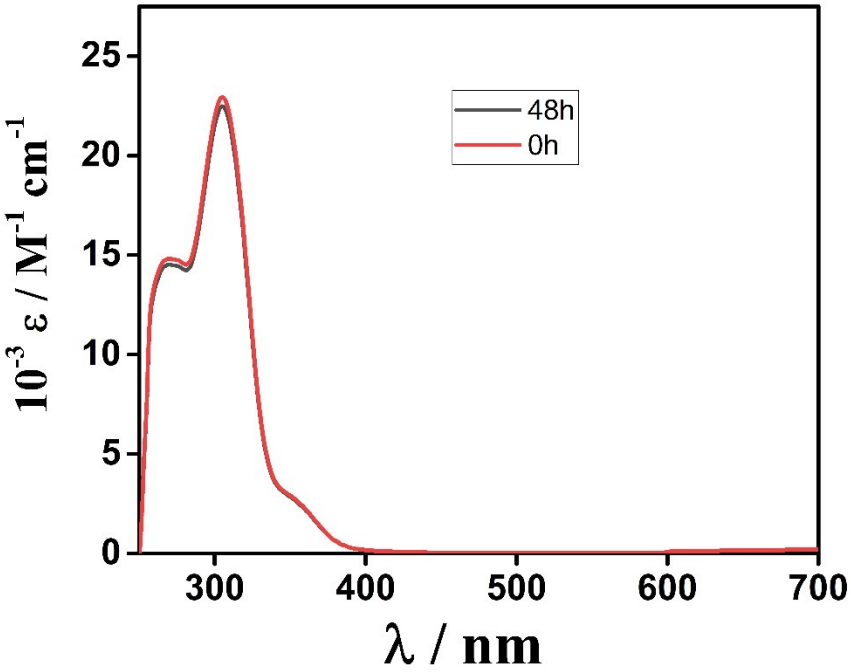


Fig. S15. Time-dependent UV-Vis spectra of **1** in DMSO; (red for 0 min) and (black for 48 h).

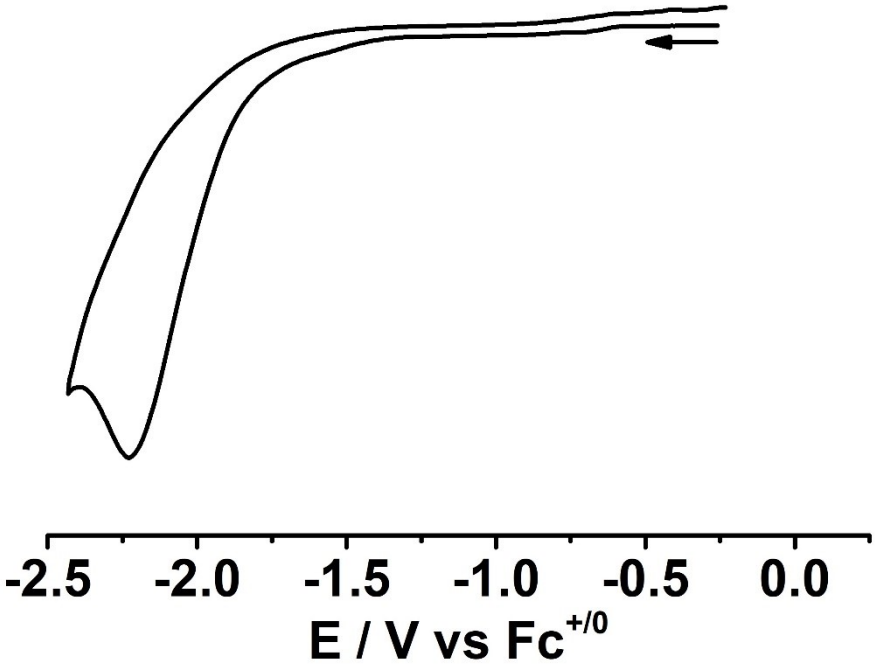


Fig. S16. Cyclic voltammogram of **L** in MeCN / 0.1 M NaCl at 298 K *vs* $Fc^{+/0}$.

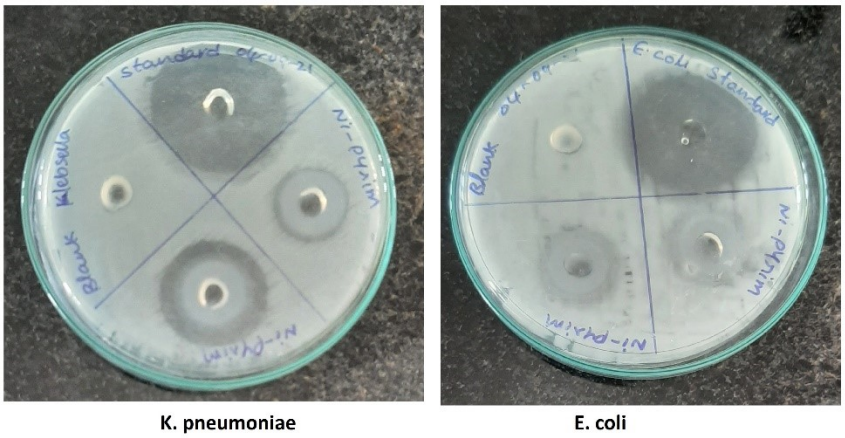


Fig. S17 Ni complex and ciprofloxacin induced bacterial screening studies

Table S3. Antibacterial activity of Ni complex (**1**) against *E. coli*, *K. pneumoniae*

S.NO	Test organism	Zone of Inhibition (mm) n=2			
		Ni complex (**1**)	Ni complex (**2**)	Ciprofloxacin (50µg)	DMSO (50µL)
1	*Escherichia coli*	8	6	23	-
3	*K. pneumoniae*	19	16	24	-

(-) no zone of inhibition observed

Table S4. Bactericidal activity of Ni complex (**1**) against clinical *K. pneumoniae*

S.NO	Test organism	MIC (mm) (µg/ml) n=3	MIC (mm) (µg/ml) n=3	MIC (mm) (µg/ml) n=3
		Ni complex (**1**)	Ni complex (**2**)	Ciprofloxacin
1	*K. pneumonia*	50	75	19

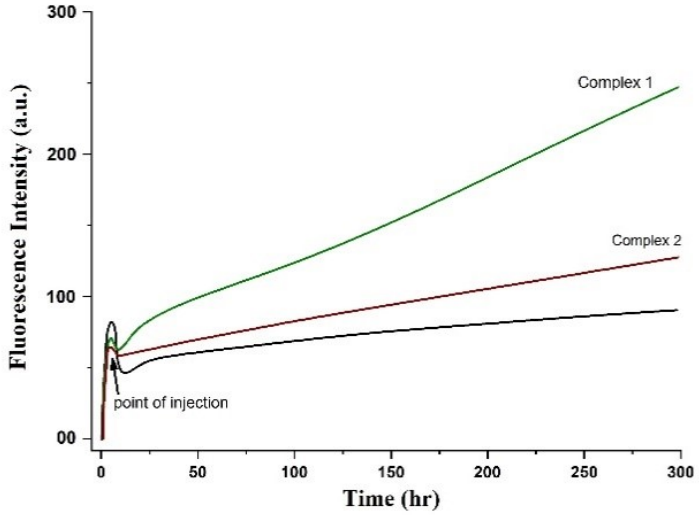


Fig. S18 Nickel complexes induced production of ROS as revealed from the change in fluorescence intensity with DCFH-DA oxidation in presence of **1** and **2** for *pseunamone.*

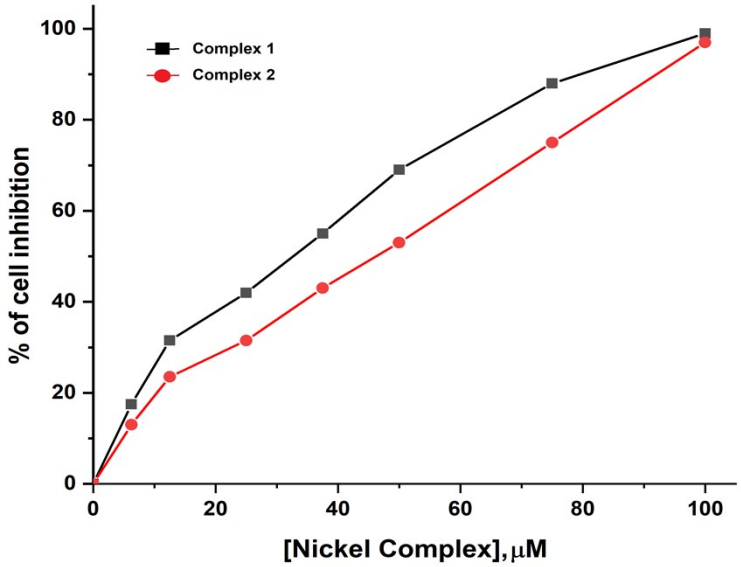


Fig. S19 Cell viability plot of the nickel complexes against HT-29 for 24 h

Computational details

Theoretical calculation :

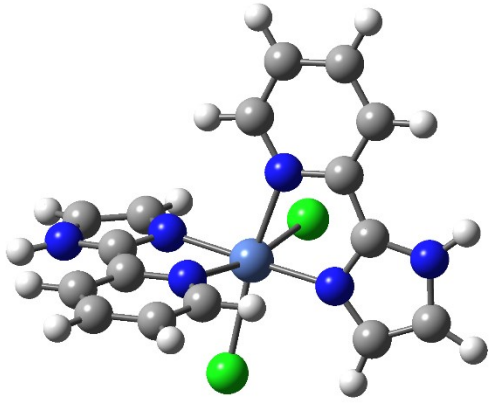
Table S5. Energies, enthalpies, and free energies (in Hartree) of the optimized geometries. calculated at ub3lyp level with basis set LanL2DZ for Ni complexes and 6-311g for other elements.

COMPOUND	ZPE	ΔE	ΔH	ΔG	E	H	G
Complex **1**	0.289418	0.311183	0.312127	0.235542	-1145.501132	-1145.500188	-1145.576773
Complex **2**	0.812179	0.857991	0.858935	0.730804	-3321.795141	-3321.794197	-3321.922328

Ligand **L**	0.140652	0.148610	0.149555	0.106804	-473.124466	-473.123522	-473.166273
Ligand **L'**	0.428369	0.450568	0.451512	0.375756	-907.901035	-907.900091	-907.975847
O_2	0.003314	0.005681	0.006625	-0.016728	-150.315800	-150.314856	-150.338209
H_2O_2	0.024514	0.027433	0.028378	0.002275	-151.527906	-151.526962	-151.553064
HCl	0.006096	0.008456	0.009401	-0.011854	-460.803150	-460.802206	-460.823460

Coordinates of all the optimised geometries:

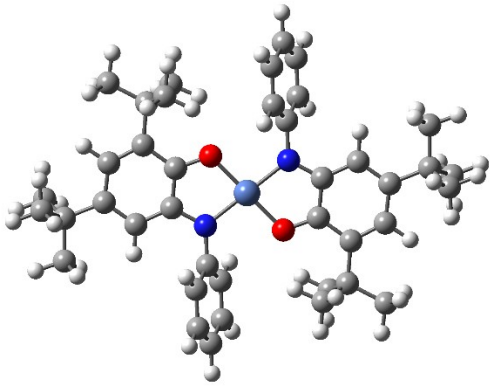
Complex 1



Ni	5.095000	11.985000	3.083000
Cl	3.445000	10.212000	3.274000
N	6.606000	10.568000	3.542000
N	5.277000	12.242000	5.089000
N	6.276000	11.721000	6.942000
H	6.800000	11.331000	7.500000
C	7.253000	9.775000	2.714000
H	7.037000	9.789000	1.810000
C	8.258000	8.909000	3.160000
H	8.694000	8.348000	2.560000
C	8.583000	8.896000	4.424000
H	9.266000	8.340000	4.722000
C	7.905000	9.717000	5.333000

H	8.103000	9.693000	6.241000
C	6.943000	10.555000	4.846000
C	6.176000	11.451000	5.627000
C	5.400000	12.725000	7.233000
H	5.262000	13.113000	8.066000
C	4.772000	13.046000	6.080000
H	4.115000	13.696000	5.976000
Cl	3.445000	13.758000	2.891000
N	6.606000	13.402000	2.623000
N	5.277000	11.728000	1.076000
N	6.276000	12.249000	-0.777000
H	6.800000	12.639000	-1.335000
C	7.253000	14.195000	3.451000
H	7.037000	14.181000	4.355000
C	8.258000	15.061000	3.005000
H	8.694000	15.622000	3.605000
C	8.583000	15.074000	1.741000
H	9.266000	15.630000	1.443000
C	7.905000	14.253000	0.832000
H	8.103000	14.277000	-0.076000
C	6.943000	13.415000	1.319000
C	6.176000	12.519000	0.538000
C	5.400000	11.245000	-1.068000
H	5.262000	10.857000	-1.901000
C	4.772000	10.924000	0.085000
H	4.115000	10.274000	0.189000

Complex 2



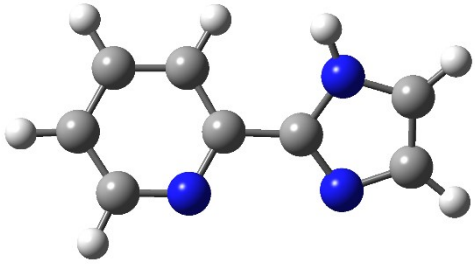
Ni	-0.000018	0.000052	-0.000073
O	1.272083	-1.328690	-0.034371
N	1.422583	1.205379	-0.112503
C	3.648277	-1.698417	-0.058552
C	3.522480	-3.223792	-0.170542
C	4.863521	-1.004248	-0.030651
H	5.636215	-1.522307	-0.050986
C	5.039256	0.375443	0.023136
C	6.440708	1.004743	0.157393
C	2.487654	-0.854745	-0.039074
C	1.358923	2.735779	-0.195938
C	4.904972	-3.918678	-0.196629
H	5.388770	-3.642669	-0.978242
H	4.786143	-4.871538	-0.215026
H	5.401319	-3.673506	0.588108
C	2.649885	0.563591	-0.096402
C	0.993519	4.769472	0.972086
H	0.812051	5.252146	1.746565
C	3.926039	1.197305	-0.018091

H	4.007468	2.121797	0.006595
C	1.107601	5.354230	-0.172813
H	1.078730	6.284627	-0.194182
C	2.808243	-3.575673	-1.480977
H	2.038414	-3.013178	-1.587741
H	2.532028	-4.494592	-1.458245
H	3.408245	-3.439127	-2.218597
C	1.156841	3.360930	0.997349
C	1.530527	3.078998	-1.513461
H	1.733819	2.561417	-2.258850
C	2.734614	-3.759546	1.045747
H	3.212522	-3.553103	1.851744
H	2.630306	-4.710567	0.967754
H	1.866934	-3.344298	1.072136
C	1.266512	4.688339	-1.358193
H	1.222822	5.191043	-2.138990
C	7.507012	0.122753	-0.405502
H	7.644720	-0.626042	0.178149
H	8.324445	0.620873	-0.484196
H	7.238887	-0.191752	-1.271562
C	6.676524	1.236495	1.655395
H	6.685083	2.179943	1.833911
H	7.517817	0.852604	1.910557
H	5.969845	0.822191	2.156867
C	6.513939	2.335103	-0.535220
H	6.272937	2.226432	-1.459886
H	7.407933	2.676993	-0.476148

H	5.906264	2.947651	-0.115437
O	-1.271629	1.327944	0.034418
N	-1.422619	-1.205274	0.112356
C	-3.648313	1.698521	0.058405
C	-3.522516	3.223896	0.170395
C	-4.863556	1.004352	0.030504
H	-5.635760	1.521561	0.051033
C	-5.039292	-0.375339	-0.023282
C	-6.440743	-1.004639	-0.157540
C	-2.487689	0.854850	0.038928
C	-1.358959	-2.735675	0.195791
C	-4.905007	3.918783	0.196482
H	-5.388315	3.641923	0.978289
H	-4.786179	4.871643	0.214879
H	-5.401354	3.673610	-0.588254
C	-2.650166	-0.563408	0.097222
C	-0.993555	-4.769368	-0.972233
H	-0.812086	-5.252042	-1.746712
C	-3.926074	-1.197200	0.017944
H	-4.007259	-2.122463	-0.005582
C	-1.107636	-5.354126	0.172666
H	-1.078765	-6.284523	0.194035
C	-2.808279	3.575777	1.480830
H	-2.038449	3.013282	1.587594
H	-2.532309	4.494775	1.459065
H	-3.408281	3.439232	2.218450
C	-1.156877	-3.360826	-0.997496

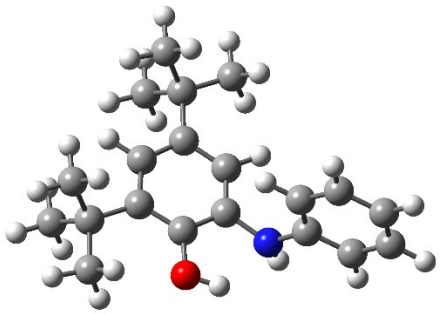
C	-1.530808	-3.078815	1.514281
H	-1.734100	-2.561234	2.259669
C	-2.734895	3.759729	-1.044928
H	-3.212557	3.553207	-1.851891
H	-2.630096	4.709901	-0.966740
H	-1.866970	3.344402	-1.072282
C	-1.266547	-4.688235	1.358046
H	-1.222368	-5.191789	2.139038
C	-7.507048	-0.122649	0.405355
H	-7.644265	0.625297	-0.178102
H	-8.324480	-0.620769	0.484049
H	-7.238923	0.191856	1.271416
C	-6.676070	-1.237241	-1.655348
H	-6.685119	-2.179839	-1.834057
H	-7.517852	-0.852500	-1.910704
H	-5.969390	-0.822937	-2.156820
C	-6.513975	-2.334999	0.535074
H	-6.272483	-2.227178	1.459934
H	-7.407968	-2.676889	0.476001
H	-5.905810	-2.948397	0.115485
H	1.137611	2.772271	1.890664
H	-1.137341	-2.772477	-1.891008

Ligand L



N	-1.068435	-0.853584	0.665822
N	-1.511807	1.113854	-0.636002
N	-3.493666	1.644504	-0.048449
H	-4.386011	1.598821	0.402346
C	-0.650027	-1.862257	1.367784
H	0.344669	-2.235970	1.252194
C	-1.514166	-2.471664	2.283731
H	-1.170090	-3.300468	2.856531
C	-2.781164	-2.010713	2.438897
H	-3.447946	-2.497025	3.117871
C	-3.191480	-0.889655	1.698875
H	-4.176305	-0.476208	1.806391
C	-2.296180	-0.344478	0.850059
C	-2.485306	0.784735	0.088865
C	-3.067787	2.588153	-0.909588
H	-3.629251	3.435509	-1.247485
C	-1.787374	2.256357	-1.266216
H	-1.133096	2.796664	-1.921509

Ligand L´



C	1.790219	-0.012929	0.597565
C	3.150887	-0.151533	0.903183
C	3.942220	0.986588	1.109523
C	3.372929	2.263235	1.010081
C	2.012039	2.401812	0.704987
C	1.220719	1.263724	0.498982
H	3.585522	-1.126390	0.978969
H	0.181724	1.369457	0.266236
O	4.180708	3.424427	1.220058
N	5.369405	0.841413	1.430295
C	1.386073	3.804654	0.595998
C	0.920868	-1.263535	0.369870
C	6.417090	-0.390801	-0.459004
C	7.164759	-0.406863	-1.644132
C	7.648222	0.792575	-2.183782
C	7.383911	2.008065	-1.538466
C	6.636338	2.024121	-0.353236
C	6.153064	0.824676	0.186665
H	6.047895	-1.306547	-0.047020
H	7.366514	-1.334932	-2.136888
H	8.219260	0.780319	-3.088607

H	7.752960	2.923835	-1.950673
H	6.434555	2.952261	0.139567
C	2.008295	3.937835	-0.806425
H	3.075100	3.945132	-0.724087
H	1.702953	3.110280	-1.412194
H	1.679167	4.850630	-1.257423
C	0.230078	4.629536	0.000140
H	0.574926	5.617521	-0.222722
H	-0.116273	4.161668	-0.897679
H	-0.571583	4.682533	0.706789
C	0.153084	3.104637	1.197176
H	0.254975	2.045270	1.086365
H	0.075675	3.348703	2.236042
H	-0.728061	3.433522	0.686921
H	5.513965	-0.014644	1.926513
H	4.884759	3.216831	1.838877
C	-0.208582	-0.929764	-0.622485
H	-0.813455	-0.142794	-0.222823
H	0.215523	-0.615994	-1.553302
H	-0.812594	-1.798553	-0.780668
C	1.791744	-2.395975	-0.205513
H	1.187872	-3.265014	-0.363957
H	2.576510	-2.627757	0.483877
H	2.215911	-2.081954	-1.136194
C	0.310309	-1.715061	1.709766
H	-0.293550	-2.584093	1.551713
H	1.095007	-1.946492	2.399370

H	-0.294800	-0.927904	2.109070

Reference:

1. B. Chiswell, F. Lions, and B. Morris, *Inorg. Chem.*, 1964, **3**, 110.