Electronic Supplementary Material (ESI) for ChemComm.

1,4-Diazacubane Crystal Structure Rectified as Piperazinium

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Supporting Information

Contents

S1. General

All chemicals and solvents employed in the syntheses were of reagent grade and used without further purification. The FT-IR spectra were measured with a PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer. The following abbreviations were used to report IR bands: s = strong, m = medium, w = weak. NMR spectra were recorded using a Bruker AS500 (500 MHz, 125 MHz) instrument. Chemical shifts (δ) are reported in parts per million (ppm) and referenced internally according to solvent: D_2O (^1H δ: 3.79 ppm, ^{13}C δ (1,4-dioxane reference): 67.2 ppm). The following abbreviation is used to report multiplicities: s = singlet. Low resolution electrospray mass spectroscopy was performed on a Thermo Scientific LCQ fleet mass spectrometer instrument. All acid digestions were carried out in a 4748A Parr Acid Digestion Vessel.

S2. Experimental Section

2a. Synthesis of $(C_4H_{12}N_2)$ $(NH_4)_2$ $[Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$ (H_2**5·A**)

In a 120 mL PTFE-lined vessel, nickel(II) nitrate hexahydrate (1.12 g, 4.00 mmol) was dissolved in ethylene glycol (9.2 mL, 160 mmol) under constant stirring after which sulfuric acid 98 % (0.44 mL, 8.0 mmol) was added followed by piperazine (0.688 g, 8.00 mmol) and hydrofluoric acid 40% (0.70 mL, 16 mmol). The PTFE-lined vessel was then placed in a sealed stainless steel acid digestion bomb and heated at 180°C for three days. The bomb was then cooled to room temperature over 12 hours, before opening it to collect H_2**5·A** as green rhombohedral crystals suitable for single crystal X-ray diffraction. The crystals were collected by filtration and washed several times with methanol until the supernatant became clear and then washed vigorously with water before being further characterised. FTIR (ATR, 4000-550 cm^{-1}): 3245 (s), 3162 (s), 2925 (s), 2838 (s), 2163 (w), 1892 (w), 1564 (m), 1490 (s), 1461 (s), 1430 (s), 1068 (s), 991 (s), 926 (s), 889 (s), 628 (s), 578 (s). ^1H-NMR (500 MHz, D_2O): δ (ppm) 3.52 (s, 8H); ^{13}C-NMR (125 MHz, D_2O (1,4-dioxane reference)): δ (ppm) 41.3.

The free amine was isolated via the addition of aqueous sodium hydroxide (6 M) to the washed crystals and collecting the supernatant. The supernatant was directly analysed. ^1H-NMR (500 MHz, D_2O): δ (ppm) 2.75 (s, 8H); ^{13}C-NMR (125 MHz, D_2O (1,4-dioxane reference): δ (ppm) 45.4. NMR spectrum matched D_2O piperazine standard.

2b. **Synthesis of $(C_4H_{12}N_2)[Ni_3(SO_4)_3(\mu_3\text{-}F)_2(H_2O)_2]$ (H_25·B)**

The procedure was identical to the synthesis of H_2**5**·**A** except the quantity of nickel(II) nitrate hexahydrate was halved (0.562 g, 2.00 mmol). Upon opening the acid digestion bomb yellow plate like crystals suitable for single crystal X-ray diffraction were collected from the brown monophasic mother liquor.

S3. Single Crystal X-ray Diffraction

Single crystal X-ray data of H_2**5·A** and H_2**5·B** were collected at 100(2) K using an XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer operating with graphite monochromated Mo-Kα radiation (0.71073 Å) with ω and ψ scans generated from micro-focus tubes. All data collected were integrated and reduced using the software package CrysAlisPro.[1] Subsequent solution, refinement and manipulations were performed on the Olex2 software package[2] and structures were solved by intrinsic phasing using SHELXT[3] followed by refinement with SHELXL.[4] Crystallographic data is summarised in Table S1. The piperazinium cation in $\mathbf{A}^-$ is twelve-fold disordered across a special position and was modelled using a rigid-body and suitable thermal parameter constraints. The original data for H_2**4·A** (CSD code: VEPHUU) was also reinvestigated. Refinement of this data with the new model (H_2**5·A-new** with piperazinium cations rather than 1,4-diazacubanium cations to yield H_2**5·A**) resulted in a significant enhancement of crystallographic statistics. Structures H_2**5·A**, H_2**5·A-new** and H_2**5·B** have been deposited in the Cambridge Structural Database (CCDC: 1913403-1913405) .

Table S1. Crystallographic data

Crystal Data	H_2**5·A** (also see VEPHUU01)	**Original** $[C_6N_2H_8][NH_4][Ni_3F_6(SO_4)_2]$ (VEPHUU, see also VEPHUU01) modelled with 1,4-diazacubane	H_2**5·A-new** Original data modelled with piperazinium	**$H_2$5·B** (also see AYUPAL)
Chemical Formula	$(NH_4)_2(C_4H_{12}N_2)[Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$	$[NH_4][C_6N_2H_8][Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$	$(NH_4)_2(C_4H_{12}N_2)[Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$	$(C_4H_{12}N_2)[Ni_3(SO_4)_3(\mu_3\text{-}F)_2(H_2O)_2]$
M_r	1819.32	626.48	1819.32	626.50
Crystal colour, habit	green, rhombohedral	green, rhombohedral	green, rhombohedral	yellow, platelets
Crystal size (mm)	0.24×0.20×0.12	0.26×0.22×0.18	0.26×0.22×0.18	0.09×0.09×0.03
Crystal system	trigonal	trigonal	trigonal	orthorhombic
Space group	*R-3m*	*R-3*	*R-3m*	*Pnma*

a/Å	7.304(6)	7.3166(3)	7.3166(3)	9.9382(2)
b/Å	7.304(6)	7.3166(3)	7.3166(3)	22.0085(6)
c/Å	25.900(5)	26.1924(5)	26.1924(5)	7.1872(2)
Volume/Å^3	1197(24)	1214.30(92)	1214.30(92)	1572.02(7)
Temperature	100(2)	130(2)	130(2)	100(2)
ρ_{calc}g/cm^3	2.525	2.608	2.525	2.647
μ/mm^{-1}	3.881	3.886	3.881	4.061
2Θ range for data collection/°	4.718 to 56.542	4.718 to 46.954	4.718 to 46.954	5.964 to 56.562
Reflections collected	5492	1673	1673	20071
Independent reflections	412	394	252	2006
Data/restraints/parameters	412/72/44	394/0/53	252/72/44	2006/0/137
Goodness-of-fit on F^2	1.120	1.16	1.104	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR2 = 0.0694	R_1 =0.0328, wR_2 = 0.0933	R_1 = 0.0204, wR_2 = 0.0531	R_1 = 0.0220, wR_2 = 0.0602
Final R indexes [all data]	R_1 = 0.0268, wR_2 = 0.0694	R_1 =0.0344, wR_2 = 0.0936	R_1 = 0.0212, wR_2 = 0.0534	R_1 = 0.0230, wR_2 = 0.0609
Largest diff. peak/hole / e Å^{-3}	0.71/-0.63	0.46/-0.69	0.31/-0.28	0.43/-0.60

Structural description of H_2**5**·**A**

The description of the Kagome structure ($(NH_4)_2(C_6N_2H_8)$ $[Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$) in the original article is largely correct, with the only significant change being the substitution of piperazinium (H_2**5**) cations for 1,4-diazacubanium (H_2**4**) cations. The asymmetric unit is shown in Figure S1. The structure consists of two-dimensional anionic sheets of NiF_4O_2 octahedra and SO_4 tetrahedra linked by Ni-F-Ni and Ni-O-S bonds. The ammonium cations are located in hexagonal channels within the layers, while the piperazinium cations are located between the layers.

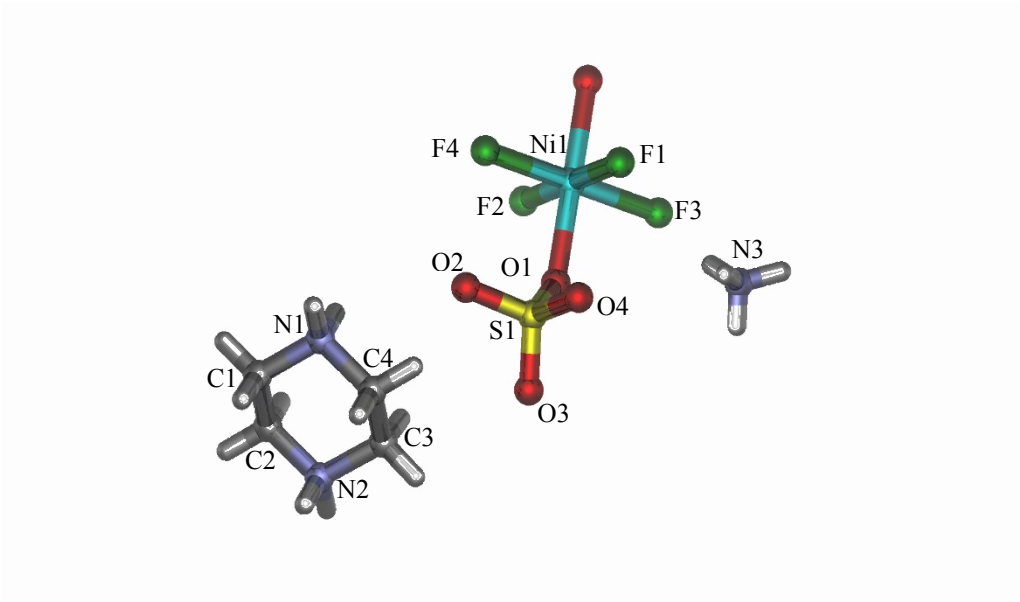


*Figure S1: Representation of part of the crystal structure of H_2**5** ·**A**. Disordered components have been omitted for clarity.*

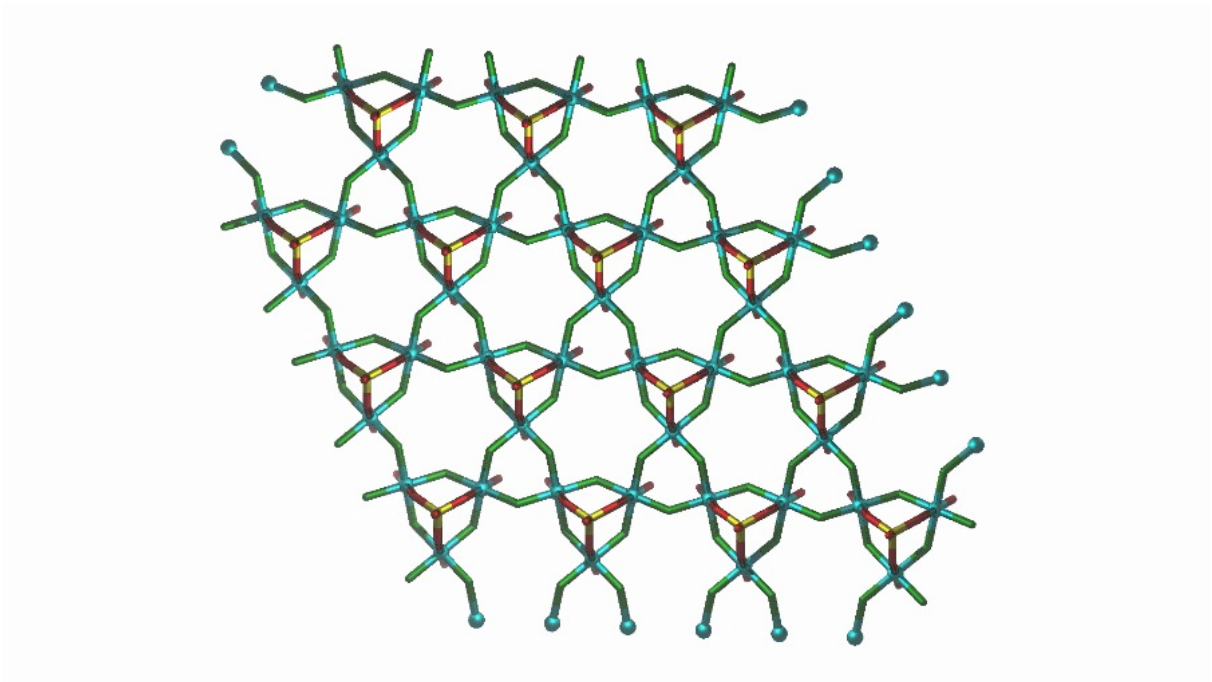


*Figure S2: Representation of the anionic two-dimensional sheets in the crystal structure of H_2**5** ·**A**.*

Structural description of $H_2$5·B

The structure of H_2**5·B** ($(H_2$**5**$)[Ni_3(SO_4)_3(\mu_3\text{-}F)_2(H_2O)_2]$) is very different to H_2**5·A** despite also consisting of two-dimensional anionic layers. The layers consist of NiF_2O_4 octahedra. There are three different nickel(II) sites in the asymmetric unit (Figure S2). The first octahedral nickel(II) (Ni1) is coordinated to two μ_3 bridging fluoride ligands and four bridging sulfate anions. While each of the other two nickel(II) (Ni2 and Ni3) centres are coordinated to two μ_3 bridging fluoride ligands, three bridging sulfate groups and one aqua ligand. Piperazinium counter ions are present between the two-dimensional layers.

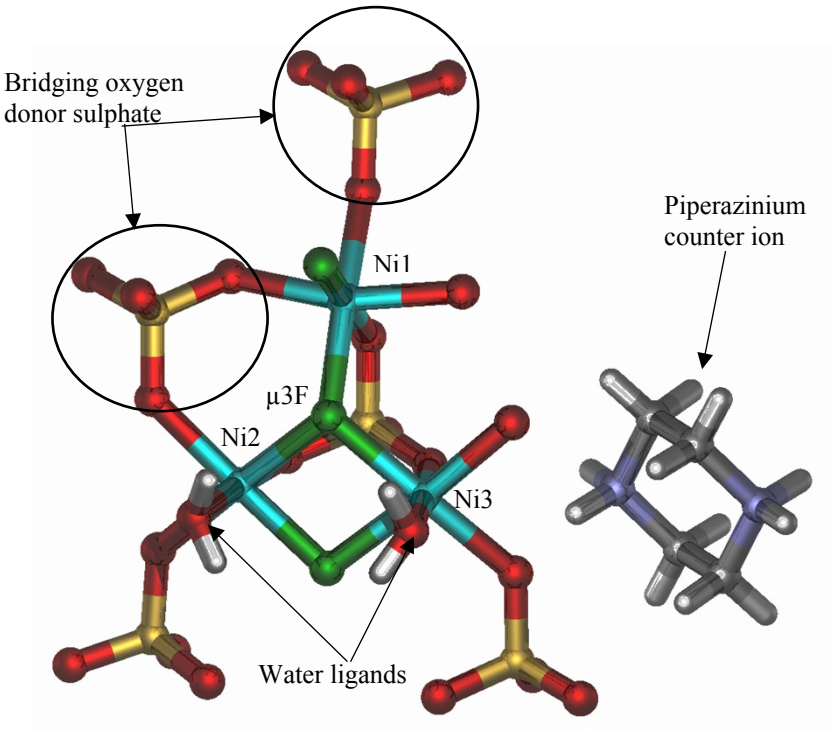


*Figure S3: Representation of part of the crystal structure of H_2**5·B**.*

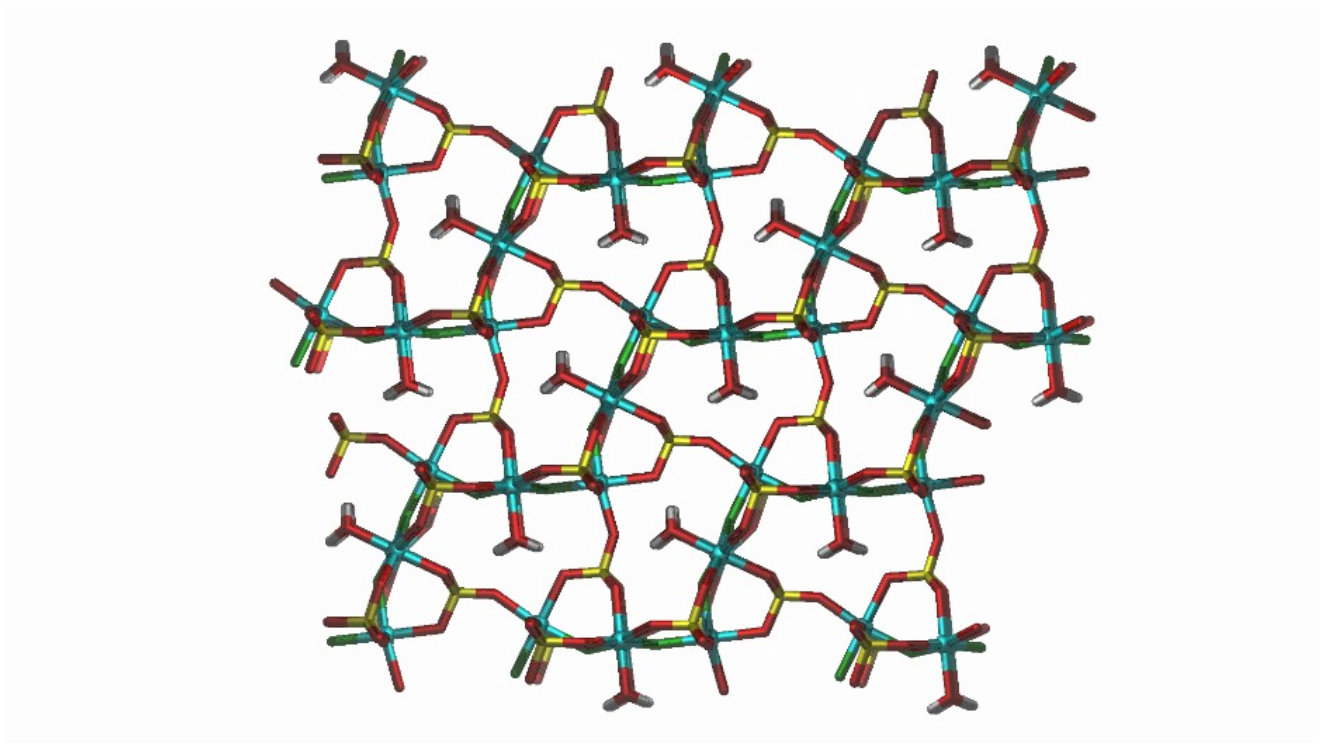


Figure S4. Representation of the anionic two-dimensional sheets in the crystal structure of H_2**5**·**B**.

S4. Computational methods

Enthalpies of reaction (ΔH) for the hypothetical formation of diazacubane were initially calculated at the M06-2X level of density functional theory,[5] with Grimme's D3 empirical dispersion correction,[6] and the Def2TZVPP basis set.[7,8] Geometries were optimised in the gas phase, with frequency calculations conducted in order to determine that the structures were minima (0 imaginary frequencies in all instances). To ensure the validity of the results, coordinates where then reoptimized using the high-accuracy CBS-QB3 composite method.[9] All calculations were conducted with Gaussian16, Rev A03.[10]

Data is reported as follows, all energies are in Hartrees:

CBS-QB3 geometry

CBS-QB3 energies

M06-2X geometry

M06-2X electronic energy (*E*), enthalpy (*H*) and Gibbs free energy (*G*)

acetylene

C	0.00000	0.00000	0.59917
C	0.00000	0.00000	-0.59917
H	0.00000	0.00000	-1.66190
H	0.00000	0.00000	1.66190

CBS-QB3 (0 K)= -77.187431
CBS-QB3 Energy= -77.184608
CBS-QB3 Enthalpy= -77.183663
CBS-QB3 Free Energy= -77.207046

C	0.00000	0.00000	-0.59716
C	0.00000	0.00000	0.59715
H	0.00000	0.00000	1.66055
H	0.00000	0.00000	-1.66053

E = -77.3259604
H = -77.294719
G = -77.31797

COT_diaza

C	-0.63447	1.37938	0.36727
C	0.63448	1.37938	-0.36727
H	0.88085	2.28776	-0.91073
C	1.56906	0.41407	-0.34548
H	2.50973	0.56177	-0.86739
N	1.56550	-0.72380	0.47838
C	0.59124	-1.53560	0.46604
H	0.63503	-2.38359	1.15602
C	-0.59124	-1.53560	-0.46604
H	-0.63504	-2.38359	-1.15601
N	-1.56550	-0.72380	-0.47838
H	-0.88084	2.28776	0.91073
C	-1.56906	0.41408	0.34548
H	-2.50973	0.56177	0.86739

CBS-QB3 (0 K)= -341.066730
CBS-QB3 Energy= -341.060282
CBS-QB3 Enthalpy= -341.059338
CBS-QB3 Free Energy= -341.096948

C	0.62504	1.47099	-0.38242
C	-0.62510	1.47096	0.38242
H	-0.85149	2.36276	0.95520
C	-1.55601	0.51437	0.35243
H	-2.48635	0.64182	0.89199
N	-1.54501	-0.60193	-0.49750
C	-0.57749	-1.40985	-0.48045
H	-0.60055	-2.24456	-1.18247
C	0.57754	-1.40982	0.48046
H	0.60070	-2.24459	1.18241
N	1.54503	-0.60187	0.49751
H	0.85141	2.36280	-0.95518
C	1.55599	0.51443	-0.35243
H	2.48633	0.64192	-0.89199

E = -341.646182
H = -341.528612
G = -341.565896

Diazacubane

C	1.03668	0.69107	0.45891
C	1.11676	-0.55228	-0.45898
C	-0.08024	1.24325	-0.45899
N	0.00008	0.00004	-1.36106
C	-1.03656	-0.69100	-0.45906
H	-0.14383	2.22813	-0.92043
C	-1.11676	0.55213	0.45905
C	0.08010	-1.24319	0.45906
H	2.00143	-0.98983	-0.92037
N	0.00012	0.00010	1.36105
H	1.85790	1.23855	0.92022
H	-2.00147	0.98949	0.92055
H	-1.85772	-1.23843	-0.92058
H	0.14351	-2.22803	0.92062

CBS-QB3 (0 K)= -340.932119
CBS-QB3 Energy= -340.927754
CBS-QB3 Enthalpy= -340.926810
CBS-QB3 Free Energy= -340.960223

C	0.48677	-1.13622	-0.45852
C	1.22720	-0.14659	0.45920
C	-0.74044	-0.98956	0.45922
N	-0.00017	0.00044	1.34702
C	-0.48692	1.13656	0.45875
H	-1.32969	-1.77721	0.91914
C	-1.22751	0.14631	-0.45929
C	0.74085	0.98960	-0.45931
H	2.20392	-0.26334	0.91910
N	0.00016	-0.00042	-1.34715
H	0.87416	-2.04046	-0.91835
H	-2.20452	0.26239	-0.91862
H	-0.87436	2.04093	0.91808
H	1.33079	1.77698	-0.91866

E = -341.5090884
H = -341.391421
G = -341.424622

Ethylene diamine

N	-1.86338	0.20534	-0.13235
C	-0.57707	-0.49983	-0.10655
H	-0.45890	-1.18292	0.75333
C	0.57707	0.49983	-0.10655
H	-0.49582	-1.11312	-1.00763
H	0.45890	1.18292	0.75332
H	0.49582	1.11311	-1.00763
N	1.86338	-0.20534	-0.13235
H	-2.03292	0.65794	0.76126
H	-2.62247	-0.45397	-0.26806
H	2.03292	-0.65794	0.76126
H	2.62247	0.45396	-0.26806

CBS-QB3 (0 K)= -190.162488
CBS-QB3 Energy= -190.156851
CBS-QB3 Enthalpy= -190.155907
CBS-QB3 Free Energy= -190.190300

N	1.84939	-0.20086	-0.03915
C	0.57050	0.50070	-0.04559
H	0.43789	1.18791	0.80242
C	-0.57050	-0.50070	-0.04559
H	0.50374	1.10080	-0.95318
H	-0.43789	-1.18791	0.80242
H	-0.50374	-1.10080	-0.95318
N	-1.84939	0.20086	-0.03915
H	1.98652	-0.68404	0.83997
H	2.61876	0.44698	-0.14161
H	-1.98652	0.68403	0.83997
H	-2.61876	-0.44698	-0.14161

E = -190.5050477
H = -190.387119
G = -190.421329

Dihydrogen

H	0.00000	0.00000	0.37199
H	0.00000	0.00000	-0.37199

CBS-QB3 (0 K)= -1.166078
CBS-QB3 Energy= -1.163718
CBS-QB3 Enthalpy= -1.162773
CBS-QB3 Free Energy= -1.177568

H	-0.00000	-0.00000	0.36951
H	0.00000	-0.00000	-0.36951

E = -1.1688691
H = -1.155385
G = -1.170168

Piperazine

C	0.73572	1.21152	-0.20436
N	1.37268	0.00014	0.31885
C	-0.73596	1.21137	0.20436
H	0.78956	1.28053	-1.30514
H	1.23854	2.08608	0.21828
C	0.73596	-1.21137	-0.20436
C	-0.73572	-1.21152	0.20436
H	1.23895	-2.08584	0.21828
H	0.78981	-1.28037	-1.30514
N	-1.37268	-0.00014	-0.31885
H	-0.78956	-1.28053	1.30514
H	-1.23854	-2.08608	-0.21828
H	-1.23895	2.08584	-0.21828
H	-0.78981	1.28037	1.30514
H	-2.36112	-0.00023	-0.09330
H	2.36112	0.00023	0.09330

CBS-QB3 (0 K)= -267.419620
CBS-QB3 Energy= -267.414157
CBS-QB3 Enthalpy= -267.413212
CBS-QB3 Free Energy= -267.448133

C	0.73147	1.20335	-0.20465
N	1.36601	0.00014	0.32076
C	-0.73171	1.20320	0.20465
H	0.78227	1.25702	-1.30210
H	1.23359	2.07801	0.20913
C	0.73171	-1.20320	-0.20465
C	-0.73147	-1.20335	0.20465
H	1.23400	-2.07777	0.20913
H	0.78252	-1.25687	-1.30210
N	-1.36601	-0.00014	-0.32076
H	-0.78227	-1.25702	1.30210
H	-1.23359	-2.07801	-0.20913
H	-1.23400	2.07777	-0.20913
H	-0.78252	1.25687	1.30210
H	-2.35391	-0.00023	-0.10663
H	2.35391	0.00023	0.10663

E = -267.9132417
H = -267.757574
G = -267.792267

Pyrazine

C	0.00000	1.13161	0.69741
C	0.00000	1.13161	-0.69741
N	-0.00000	-0.00000	-1.40537
C	-0.00000	-1.13161	-0.69741
C	-0.00000	-1.13161	0.69741
N	-0.00000	-0.00000	1.40537
H	0.00000	2.06340	1.25566
H	0.00000	2.06340	-1.25566
H	-0.00000	-2.06340	-1.25566
H	-0.00000	-2.06340	1.25566

CBS-QB3 (0 K)= -263.869824
CBS-QB3 Energy= -263.865616
CBS-QB3 Enthalpy= -263.864672
CBS-QB3 Free Energy= -263.895878

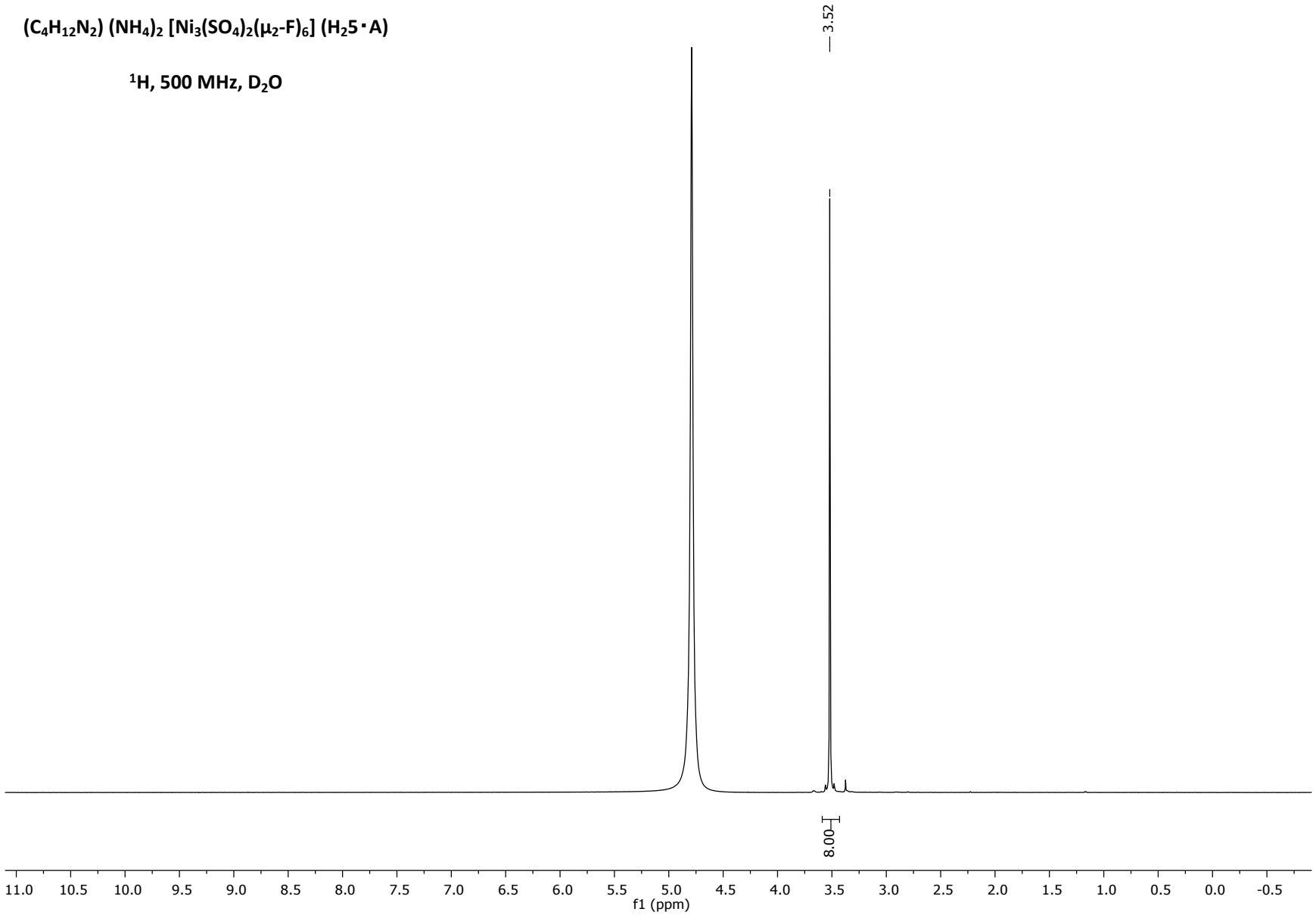
C	1.12698	-0.69481	0.00000
C	1.12698	0.69481	0.00000
N	0.00000	1.39647	-0.00000
C	-1.12698	0.69481	0.00000
C	-1.12698	-0.69481	-0.00000
N	0.00000	-1.39647	0.00000
H	2.05712	-1.25019	-0.00000
H	2.05712	1.25019	-0.00000
H	-2.05712	1.25019	0.00000
H	-2.05712	-1.25019	0.00000

E = -264.3046588
H = -264.222024
G = -264.254427

S5. ^{1}H and ^{13}C NMR Spectra

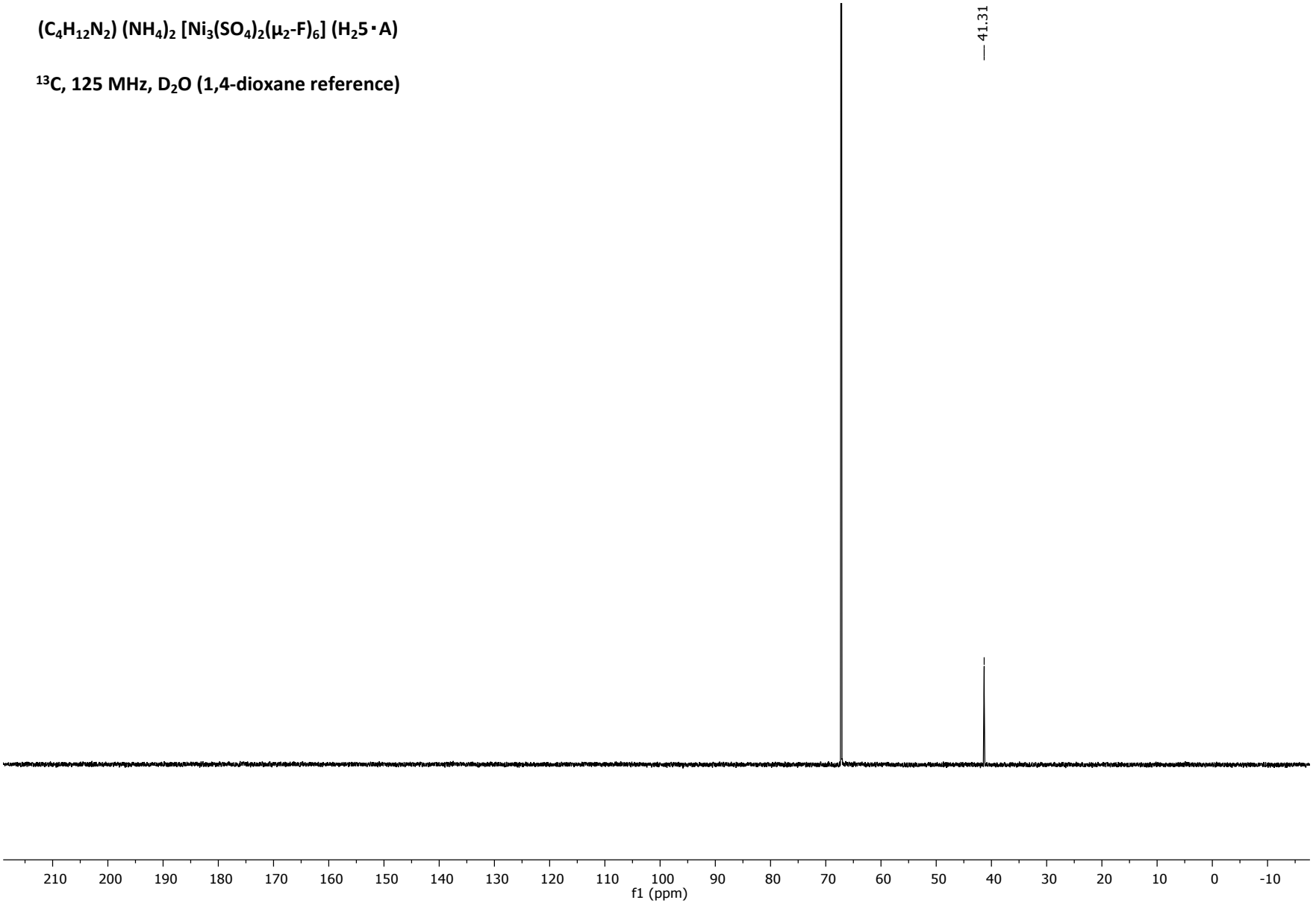
$(C_4H_{12}N_2)$ $(NH_4)_2$ $[Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$ (H_25·A)

^1H, 500 MHz, D_2O



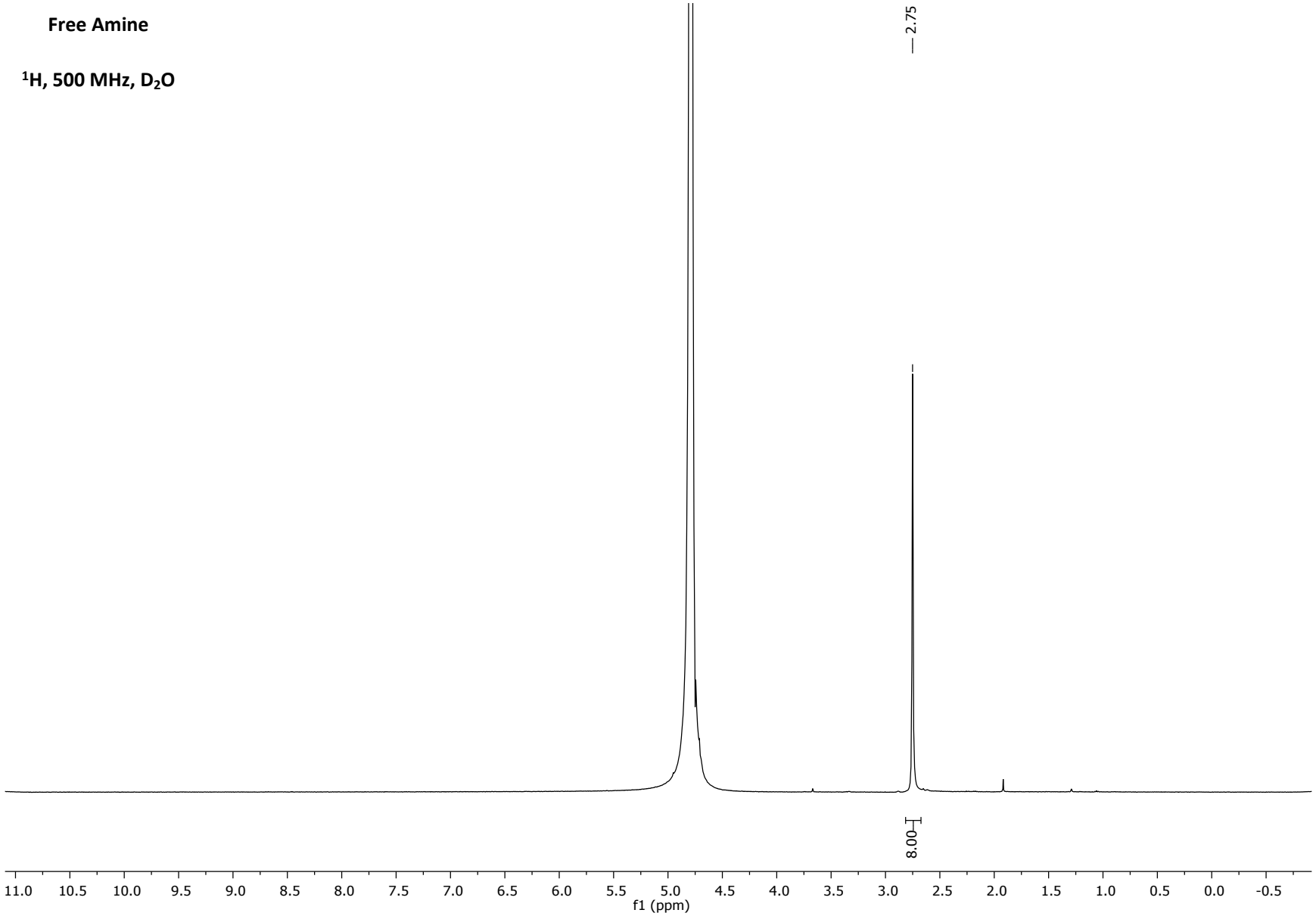
$(C_4H_{12}N_2)$ $(NH_4)_2$ $[Ni_3(SO_4)_2(\mu_2\text{-}F)_6]$ ($H_25 \cdot A$)

^{13}C, 125 MHz, D_2O (1,4-dioxane reference)



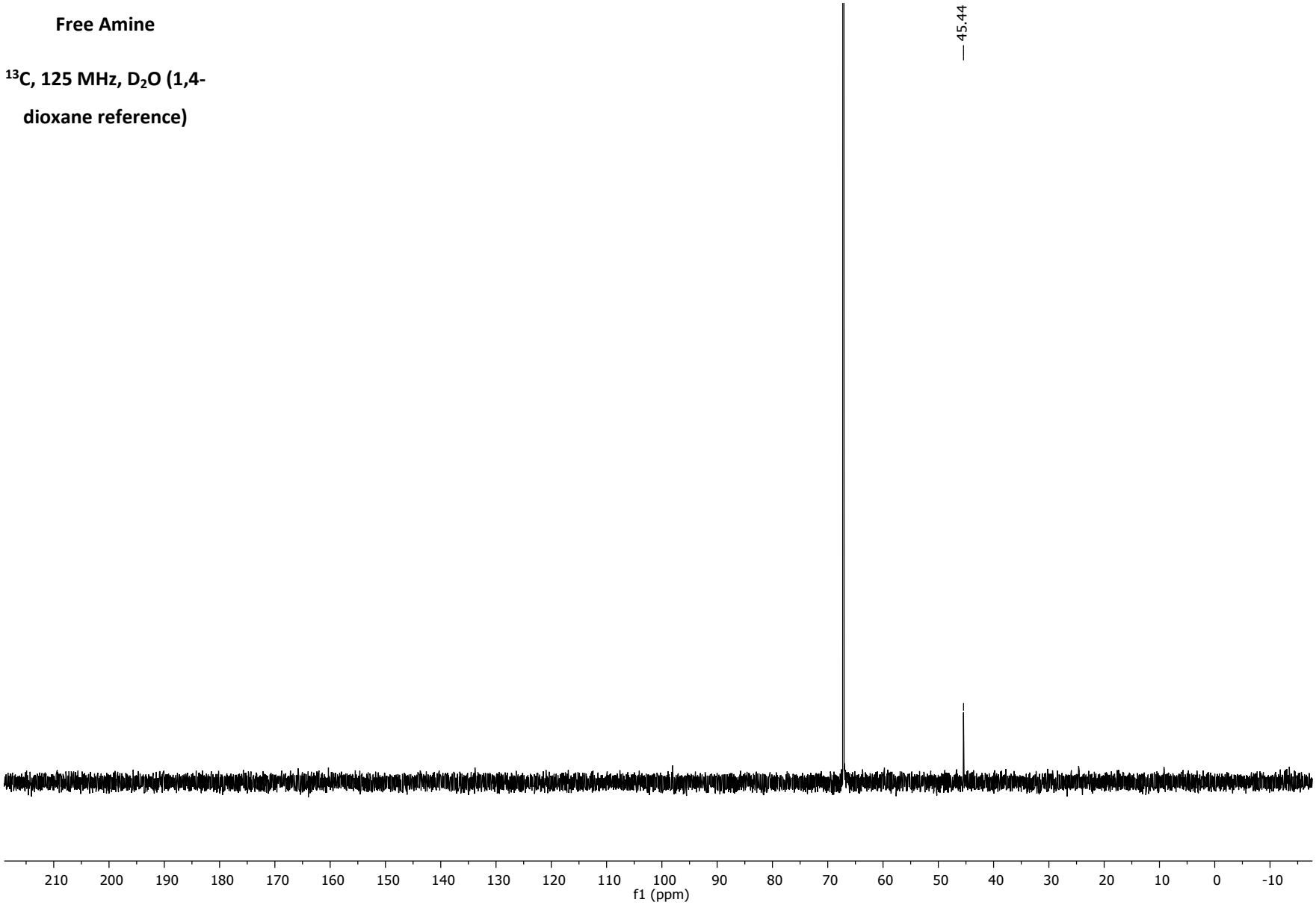
Free Amine

^{1}H, 500 MHz, D_2O



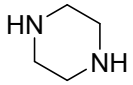
Free Amine

^{13}C, 125 MHz, D_2O (1,4-dioxane reference)



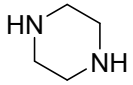
Piperazine

^{1}H, 500 MHz, D_2O



Piperazine

^{13}C, 125 MHz, D_2O (1,4-dioxane reference)



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