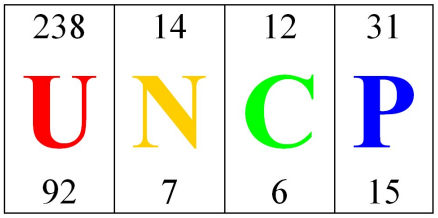

Synthesis and Isolation of β-cis-Dinitrobis(2-ampy)-cobalt(III)nitrate

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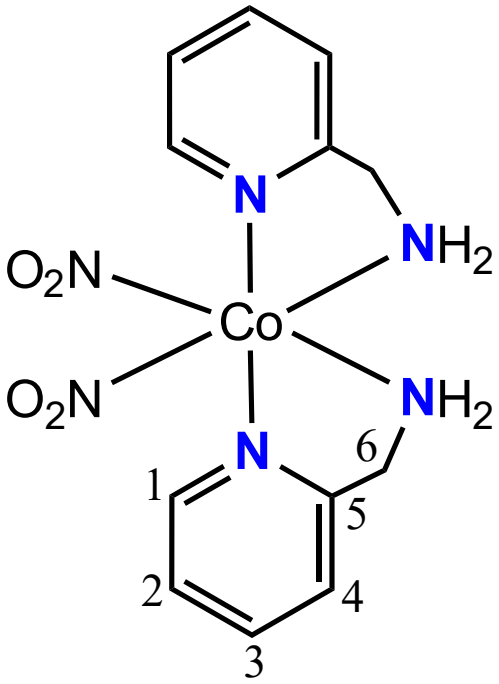
Abstract

The purpose of this experiment was to synthesize, isolate, and identify a sample of β-cis-Dinitrobis(2-ampy)-cobalt(III)nitrate. The compound was synthesized and isolated by successive extraction and then identified by utilizing C-13 NMR. A pure sample of β-cis-Dinitrobis(2-ampy)-cobalt(III)nitrate was produced, with an NMR showing a total of eight peaks within the aromatic region. Two-dimensional NMR was used to partially assign signals.

Background

For this compound, three different compounds are possible, α-cis, ϒ-cis, and β-cis. In a previous experiment, the α-cis isomer was synthesized and compared to the ϒ-cis. In this experiment, β-cis was synthesized.

The reason for synthesizing the β-cis isomer, is to observe the complexity in structure by analyzing the C-13 NMR. The C-13 NMRs for α and ϒ isomers will have 4 peaks from the two chemically equivalent pyridine rings. Due to the two rings of the β isomer being chemically nonequivalent, the spectrum would show 8 distinct peaks.

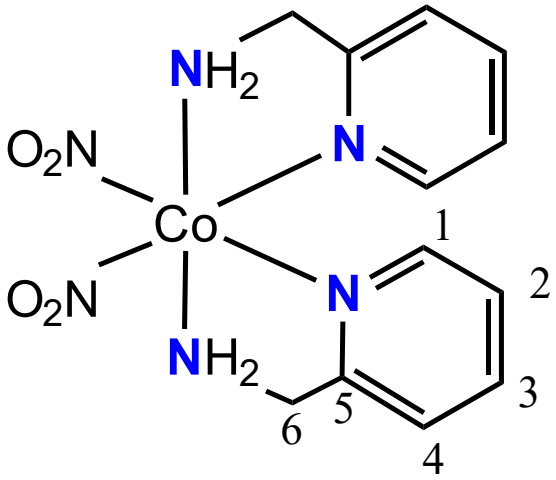


α-Cis

NO_2 groups cis

NH_2 groups cis

Pyridine-N groups trans

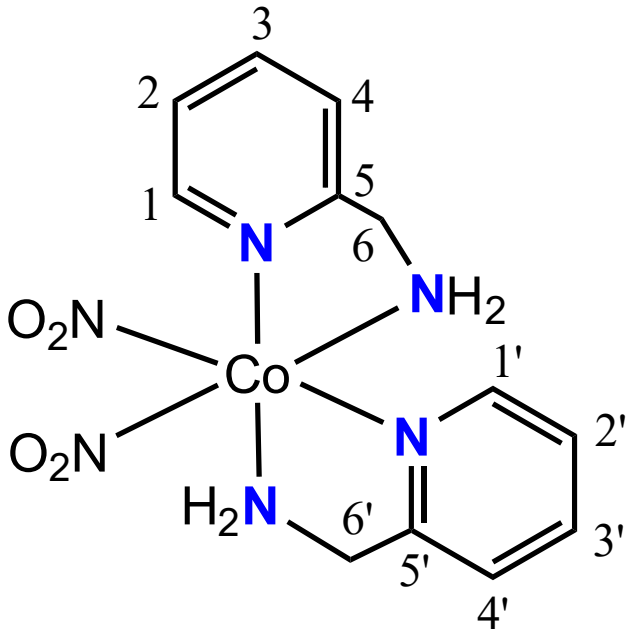


γ-Cis

NO_2 groups cis

NH_2 groups trans

Pyridine-N groups trans



β-Cis

NO_2 groups cis

NH_2 groups cis

Pyridine-N groups cis

Experimental

Initial synthesis

- 5.800g cobalt (II) nitrate and 3.005g sodium nitrite were dissolved in approximately 10 mL of distilled water.
- A solution of 4.3 mL of 2-picolylamine and 1.6 mL of concentrated acid was prepared and cooled in an ice bath.
- The cooled solution is then added to the cobalt (III) nitrate and sodium nitrite mixture and mixed thoroughly
- The mixture was oxidized for 1 hour
- After oxidation, the mixture was cooled in an ice bath, suction filtered, and washed with acetone
- The product was left to air-dry for 1 week
- The final yield of the product was 6.419g

Experimental (cont.)

- Extractions (3 Total)
  - The product was redissolved in the bare minimum amount of boiling water that would entirely dissolve the product. This was approximately 150 to 160 mL, 140 mL, and 80 mL of distilled water at a low boil for extractions 1 through 3 respectively.
  - After being fully dissolved, the solution is cooled in an ice bath
  - After cooling, suction filtration was performed in conjunction with grinding the product in acetone with a mortar and pestle
- After each extraction, a C-13 NMR was performed to evaluate the effectiveness and necessity of each extraction.

Experimental (cont.)

- Instrument used: Anasazi Eft 90 NMR Spectrometer
- When performing the C-13, the solvent used was D_6-DMSO
- To calibrate the NMR, the solvent peak was assigned to a multiplet value 39.5
- When performing a proton NMR, the solvent used was DSS

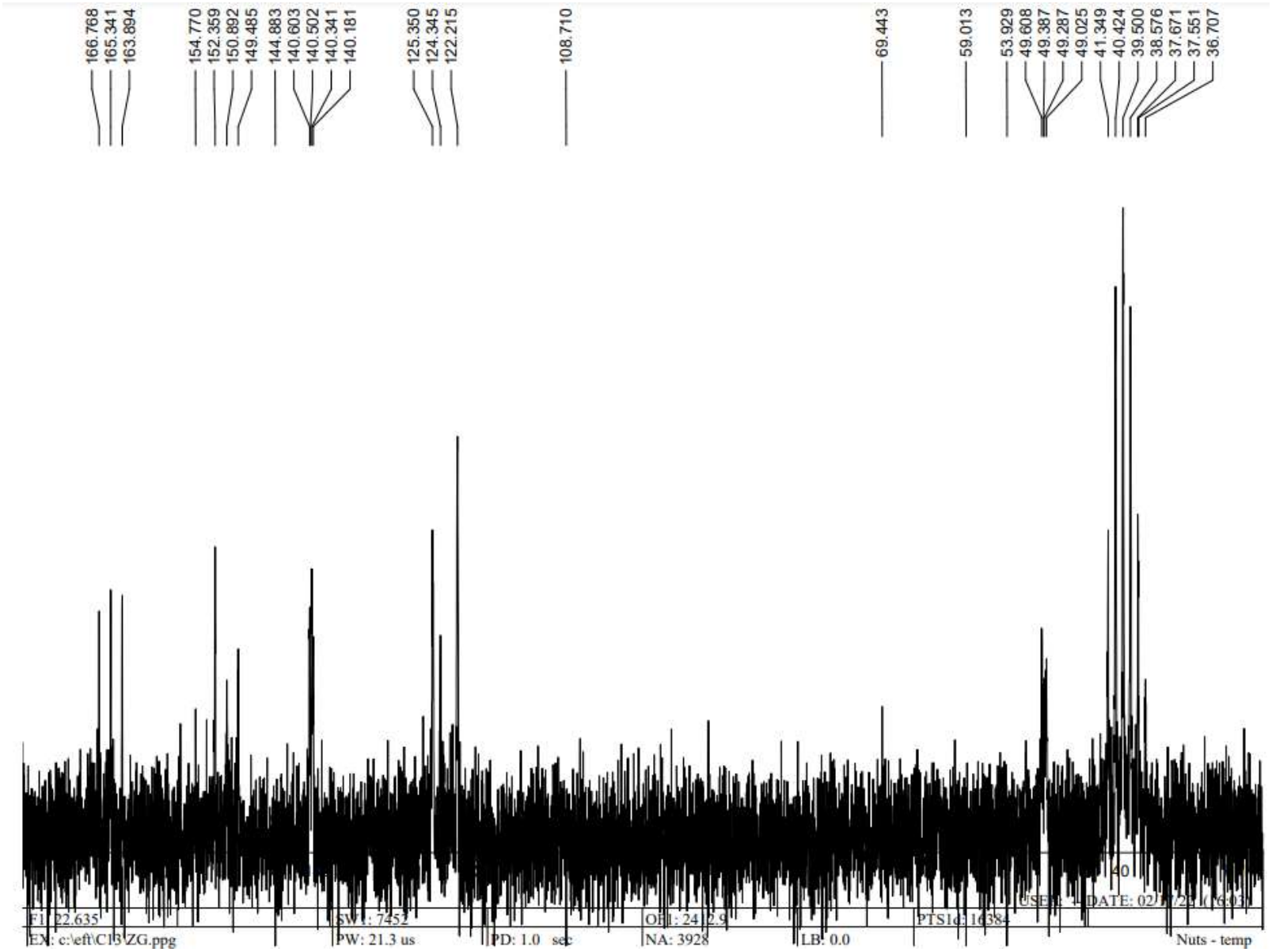
C-13 Analysis

The C-13 spectra is divided into four sets of three signals. Each set corresponding to C_1-C_4.

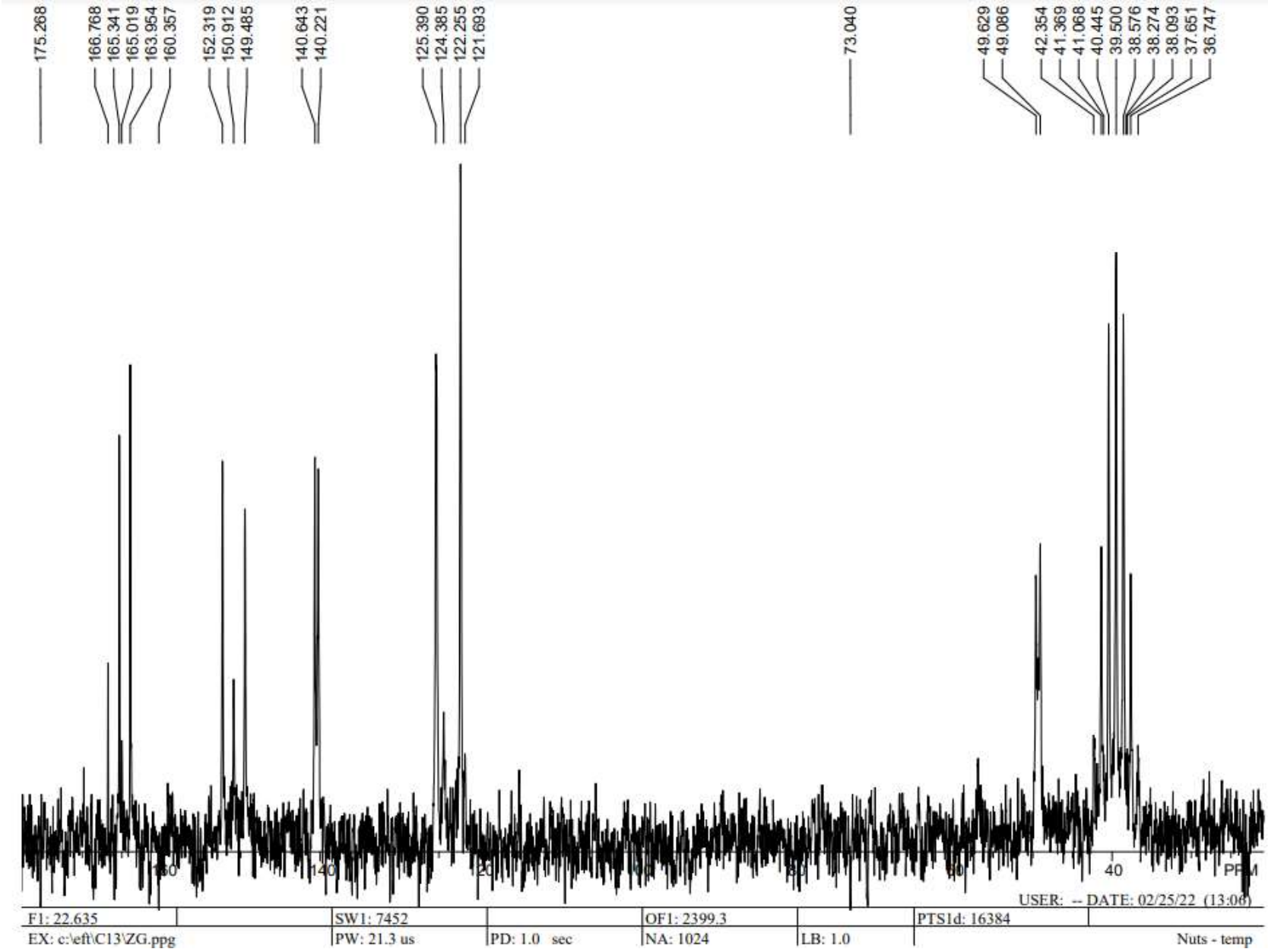
There was one signal in each set from the α-cis isomer, whose rings are chemically equivalent. There were two signals in each set from the β-cis isomer, whose rings are not chemically equivalent.

After the third extraction, any signals remaining from the α-cis isomer had disappeared.

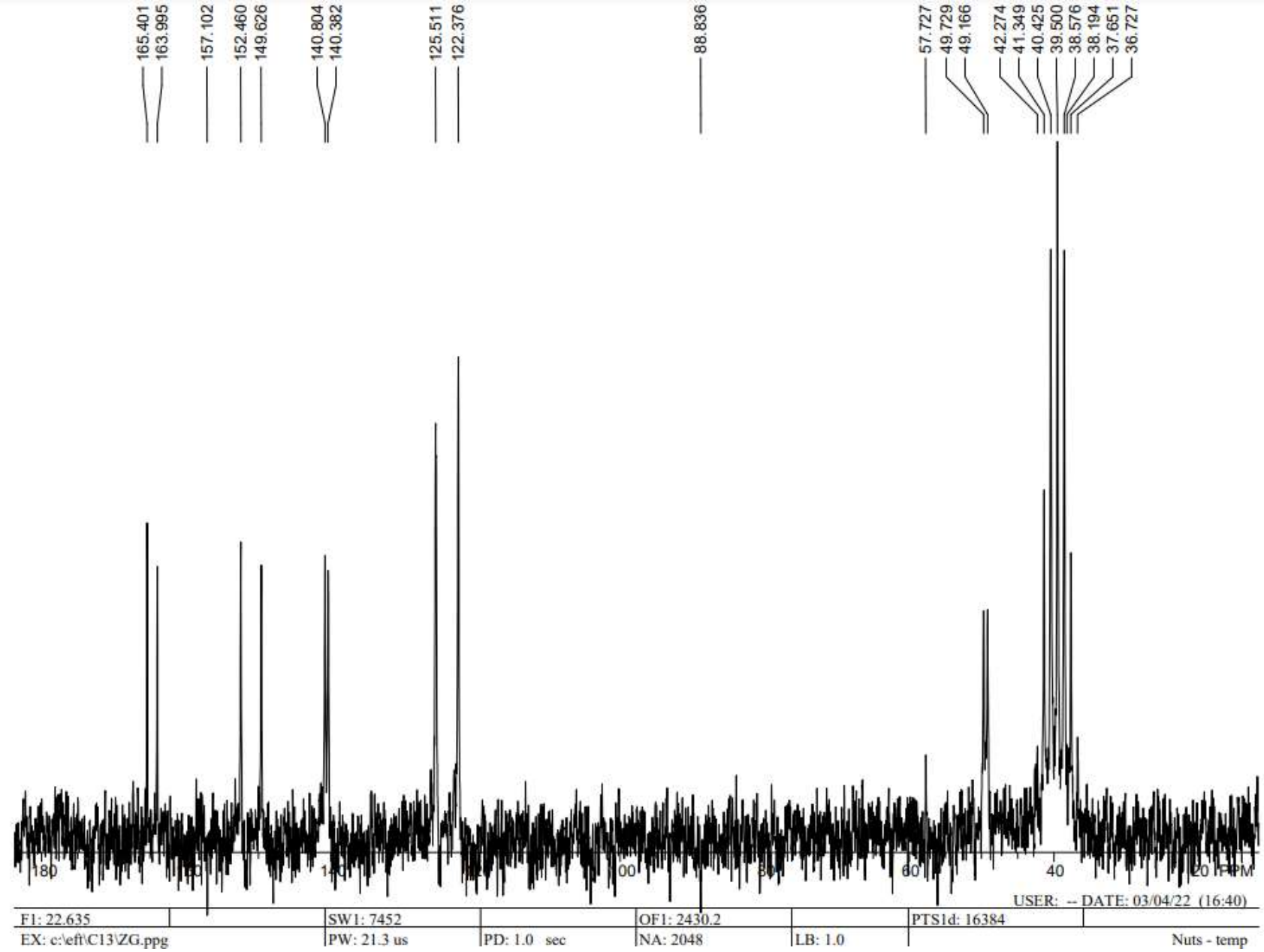
Sample After 1st Extraction



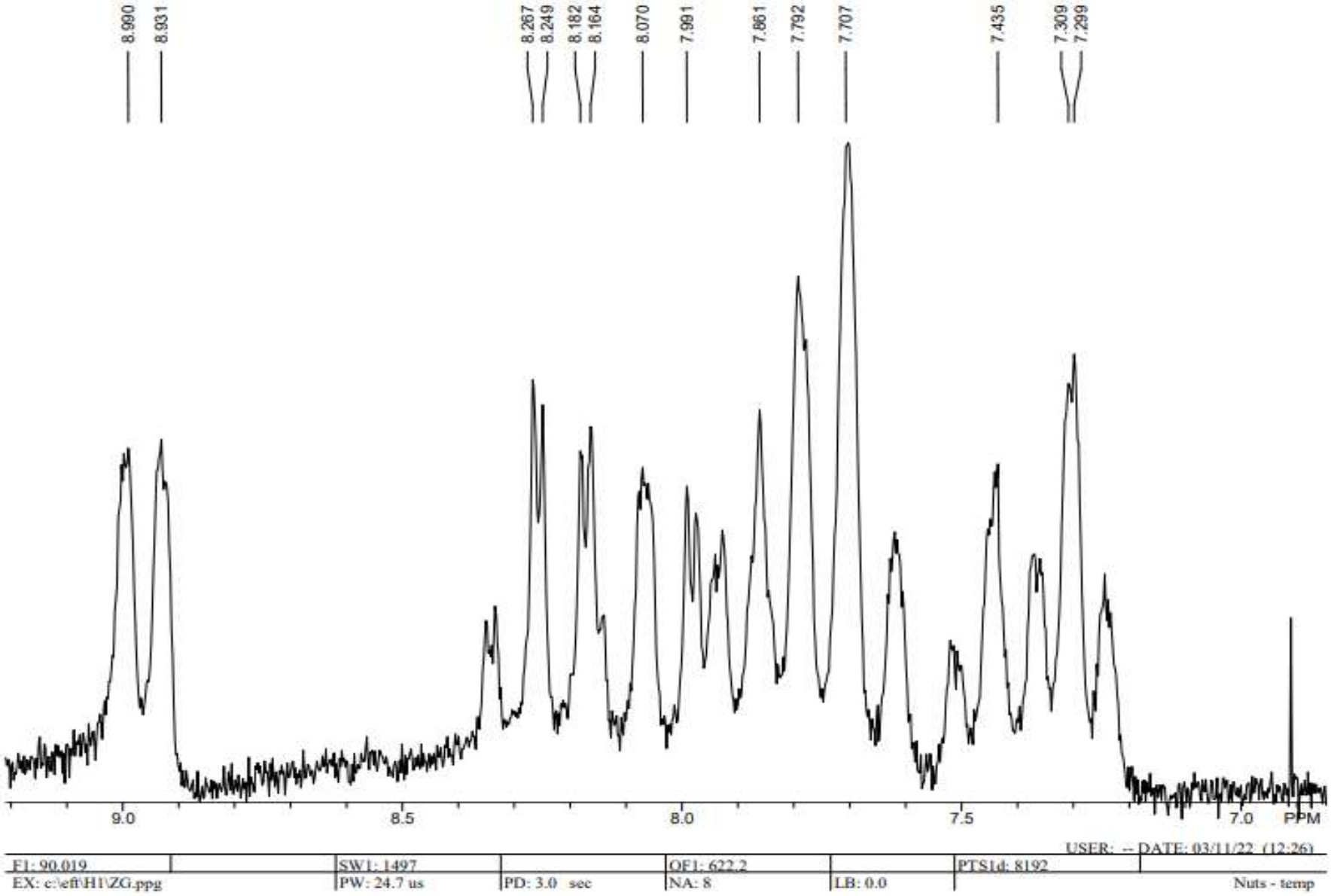
Sample After 2nd Extraction



Sample After 3rd Extraction



Proton NMR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8.249
8.182
8.164
8.070
7.991
7.861
7.792
7.707
7.435
7.309
7.299
9.0
8.5
8.0
7.5
7.0
PPM
USER: -- DATE: 03/11/22 (12:26)
F1: 90.019
SW1: 1497
OF1: 622.2
PTS1d: 8192
EX: c:\eft\H1\ZG.ppg
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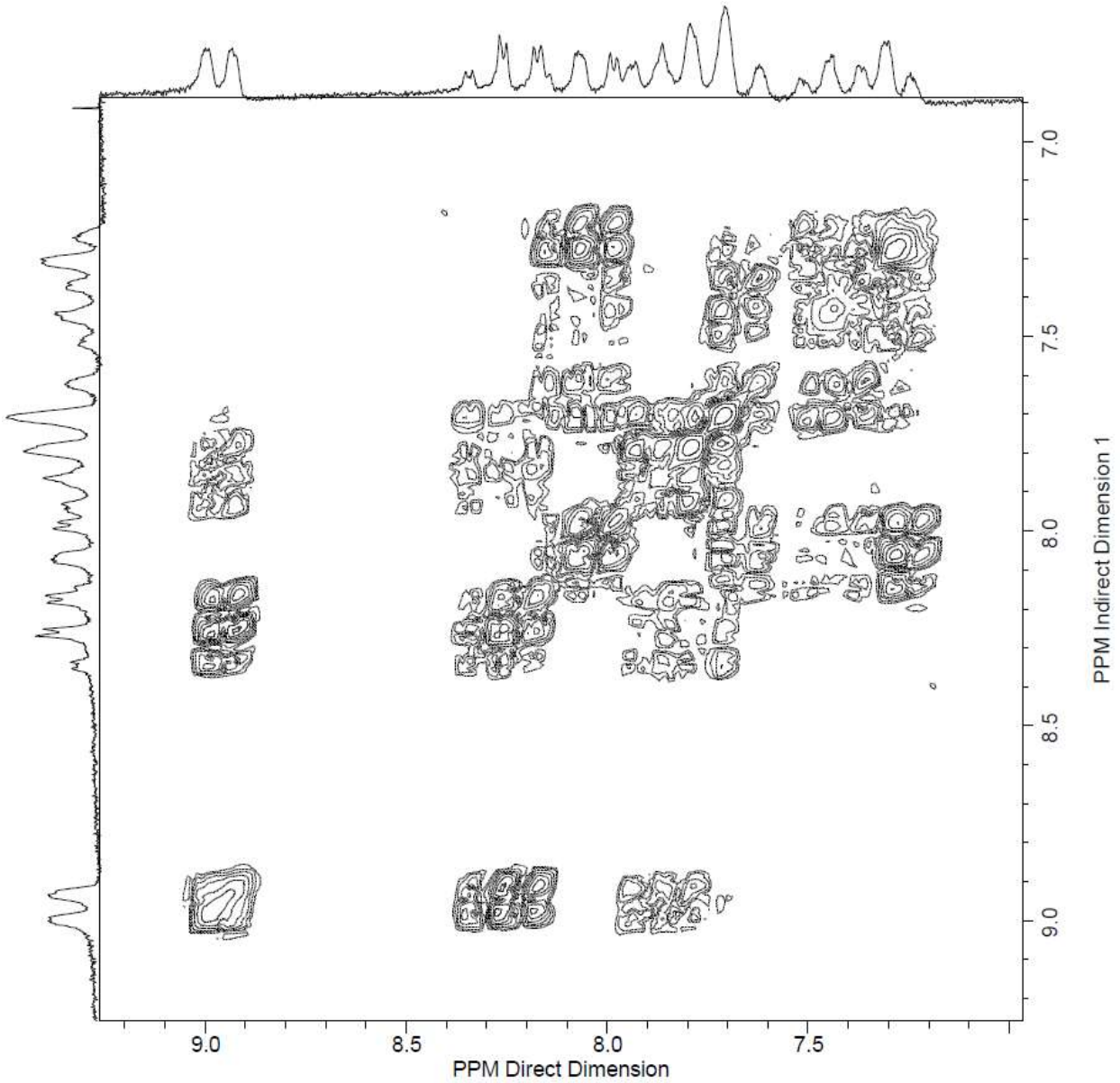
PD: 3.0 sec
NA: 8
LB: 0.0
Nuts - temp

COSY Spectrum



COSY Analysis

COSY, or correlated spectroscopy is used to establish connectivities between sets of protons.

The doublet at approximately 8.7 ppm is likely due to C_1 or C_1'. It is not possible to discern between the C_1 or C_1' without further experimentation.

The signal for the doublet was coupled to signals corresponding to 8.2ppm and 7.85ppm.

Special Thanks

Special Thanks to the UNCP Department of Chemistry and Physics for their funding of this research