

238	14	12	31
U	N	C	P
92	7	6	15



Synthesis and Spectral Analysis of [Co(trien)(ampy)]Cl₃

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ABSTRACT

The compound $[\text{Co}(\text{trien})(\text{ampy})]\text{Cl}_3$ was synthesized by a reaction between $[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ and 2-(aminomethyl)pyridine (ampy) using a mixture of ethanol and water as a solvent. The mixture was refluxed for ~4 hours then let rest at room temperature for one week. The crystals formed were removed by hand and dried. The product was dissolved in deuterium oxide and characterized by ^1H and ^{13}C NMR using an Anasazi Eft-90 NMR spectrometer. Analysis of the spectra ran using the NUTS program confirmed the successful formation of the desired compound with characteristic peaks corresponding to the asymmetric nature of the compound. The integrated proton spectrum confirms the chemical shift of the triethylenetetramine (trien) ligand.

OBJECTIVES

This compound $[\text{Co}(\text{trien})(\text{ampy})]\text{Cl}_3$ is similar to previously studied compounds but will produce a more complicated NMR spectrum due to its asymmetrical ligand. By creating this compound, it should be possible to compare the spectra to the symmetric compounds $[\text{Co}(\text{trien})(\text{bipy})]\text{Cl}_3$ and $[\text{Co}(\text{trien})(\text{phen})]\text{Cl}_3$ to see the extent to which the spectra can be assigned.

EXPERIMENTAL: SYNTHESIS

- [1] 5.003g [Co(trien)Cl₂]Cl was first combined with methanol in a mortar and pestle to remove HCl and suction filtered then repeated with acetone.
- [2] 4.113g of the product was recovered and stored.
- [3] 1.004g [Co(trien)Cl₂]Cl product was added to an Erlenmeyer flask with 45ml 200 proof ethanol and 5ml H₂O and stirred.
- [4] 0.346g 2-(aminomethyl)pyridine (ampy) and 1ml ethanol rinse was added to mixture and refluxed on a hot plate at 225°C for the remainder of the day then left alone to crystalize for one week.
- [5] Crystals were removed by hand and dried (0.239g)

EXPERIMENTAL: SPECTRAL ANALYSIS

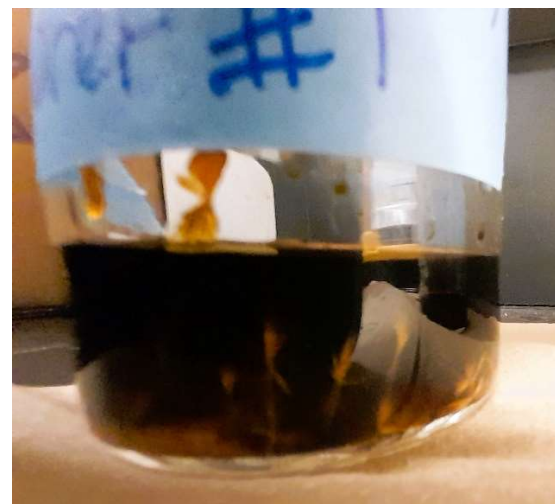
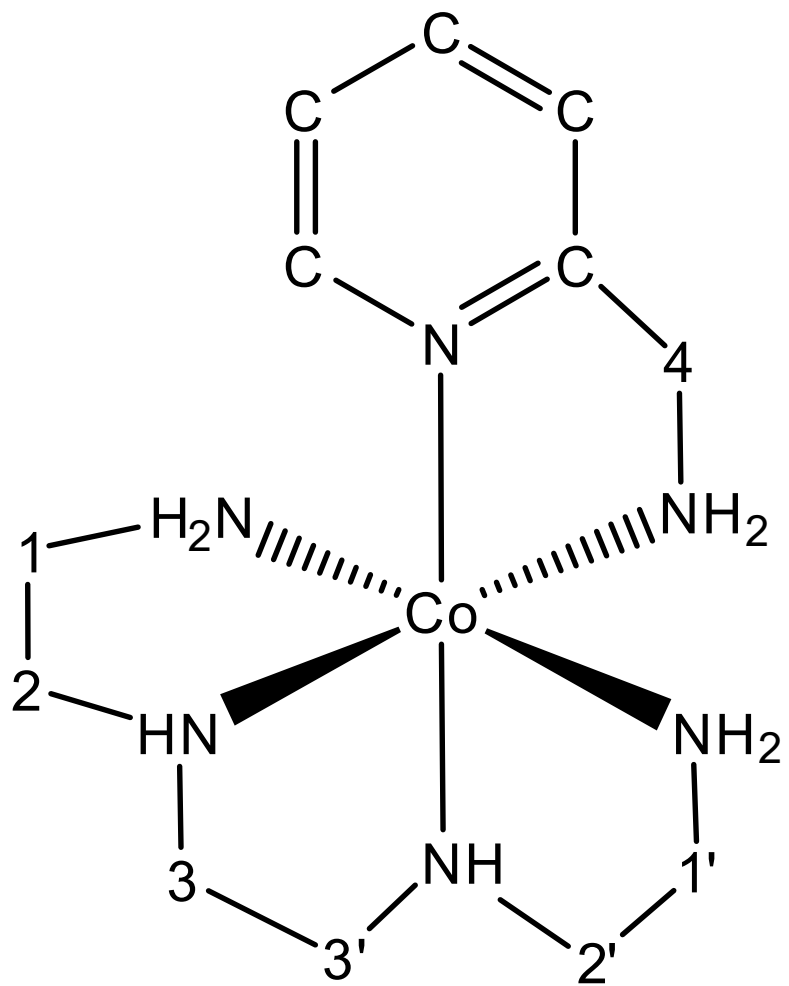
[1] NMR experiments performed on Anasazi Eft-90 NMR using D₂O as a solvent

[2] For the ¹³C spectra 1,4-dioxane was added and assigned a chemical shift of 67.400 ppm.

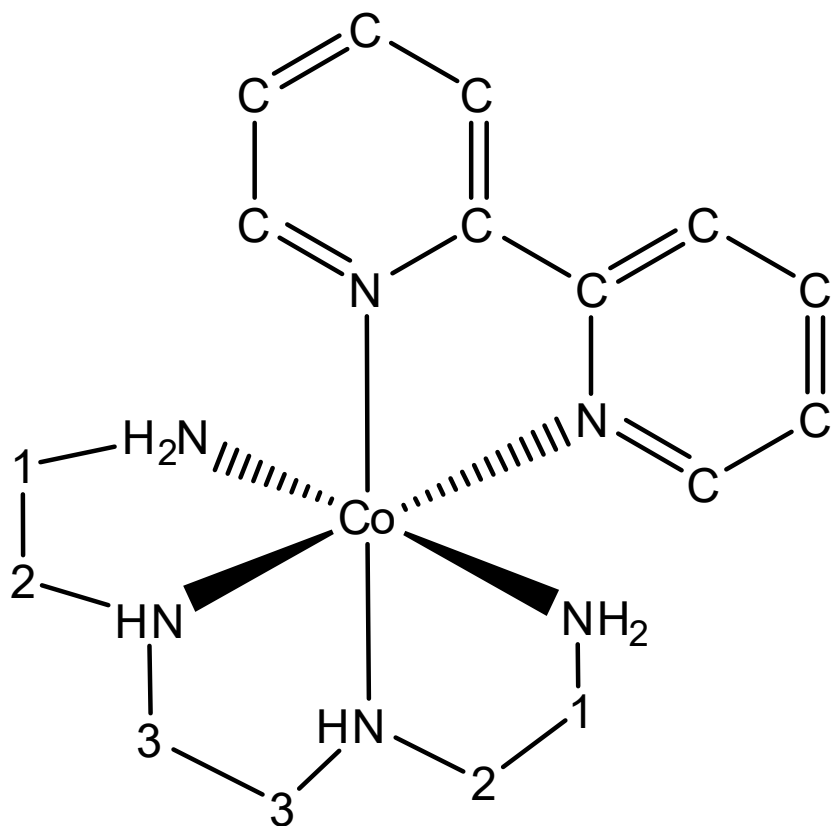
[3] The ¹H spectra used sodium trimethylsilylpropanesulfonate (DSS) as a reference assigned a chemical shift of 0.000 ppm, and the spectra was integrated.

[4] The [Co(ampy)(trien)]Cl₃ spectra were compared to previous spectra of [Co(trien)(bipy)]Cl₃ and [Co(trien)(phen)]Cl₃ to assign carbons to an extent.

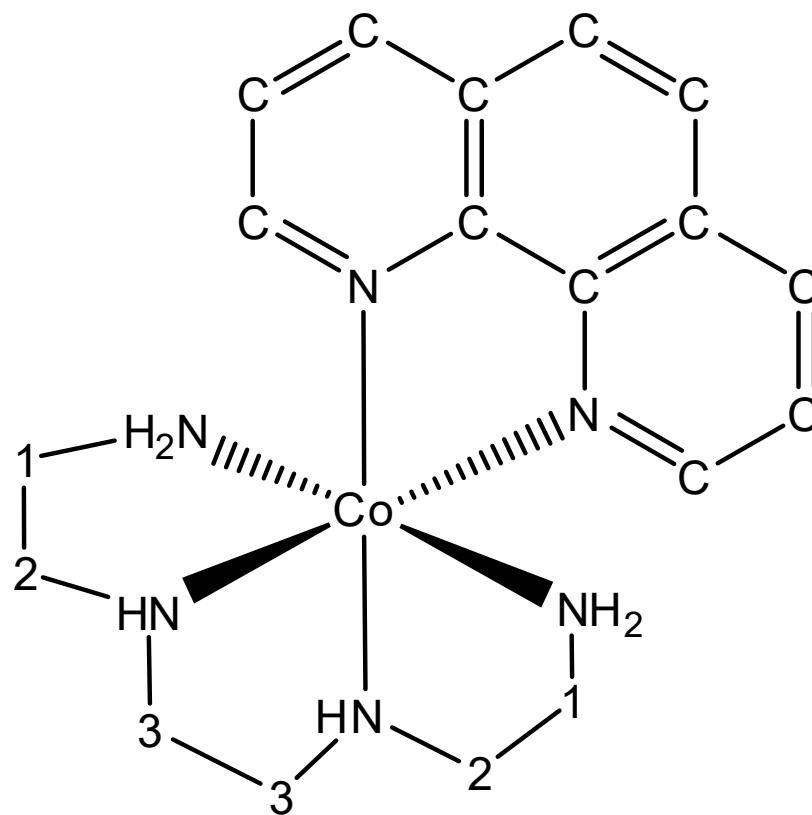
[5] A hetcor was produced to confirm predictions.



Previously Studied Compounds



[Co(trien)(bipy)]Cl₃



[Co(trien)(phen)]Cl₃

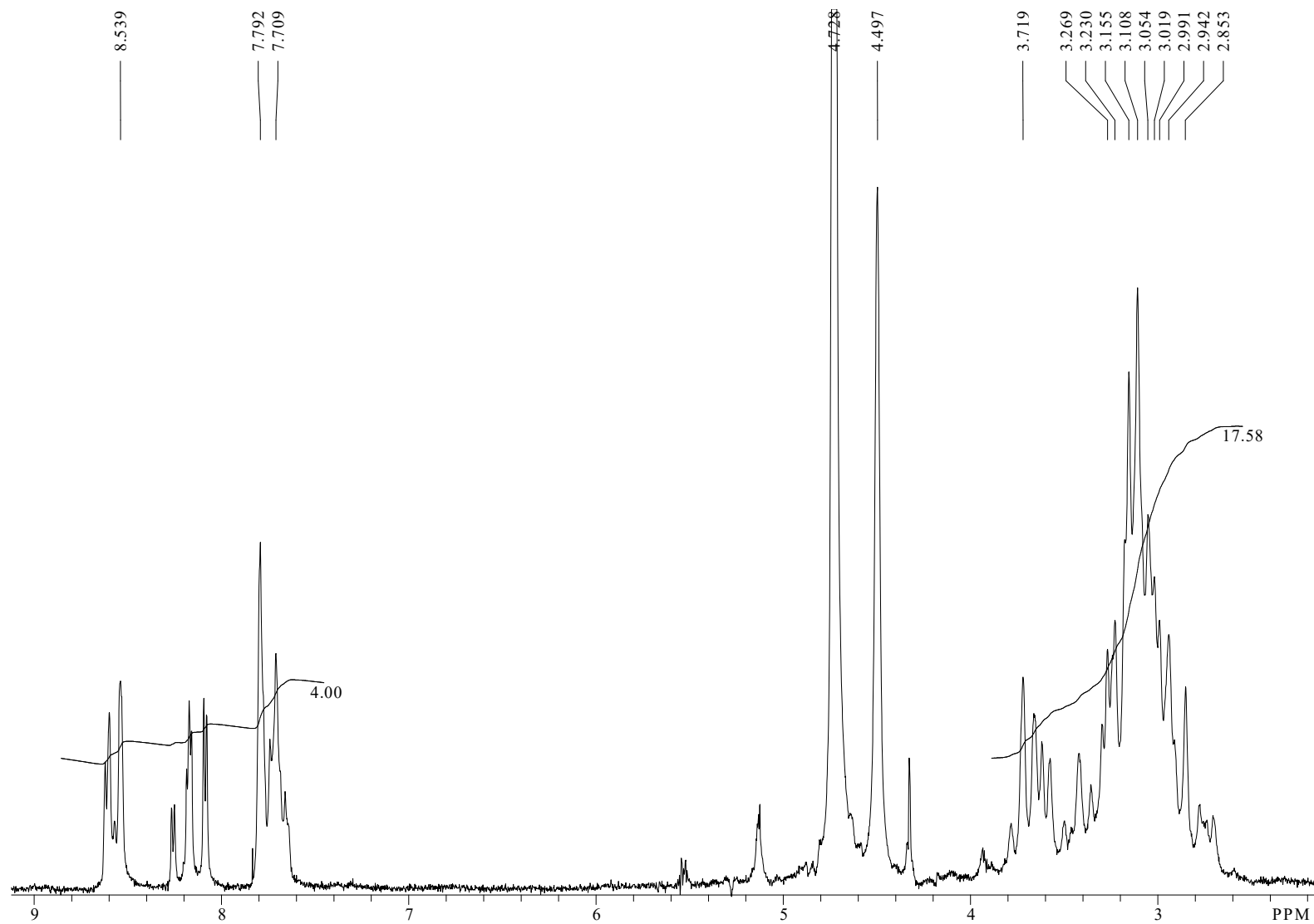
RESULTS AND DISCUSSION

The crystals extracted from the reaction were orange in color and began turning slightly green over time. To produce an NMR, the most orange crystals we collected and dissolved in D₂O to provide a reference.

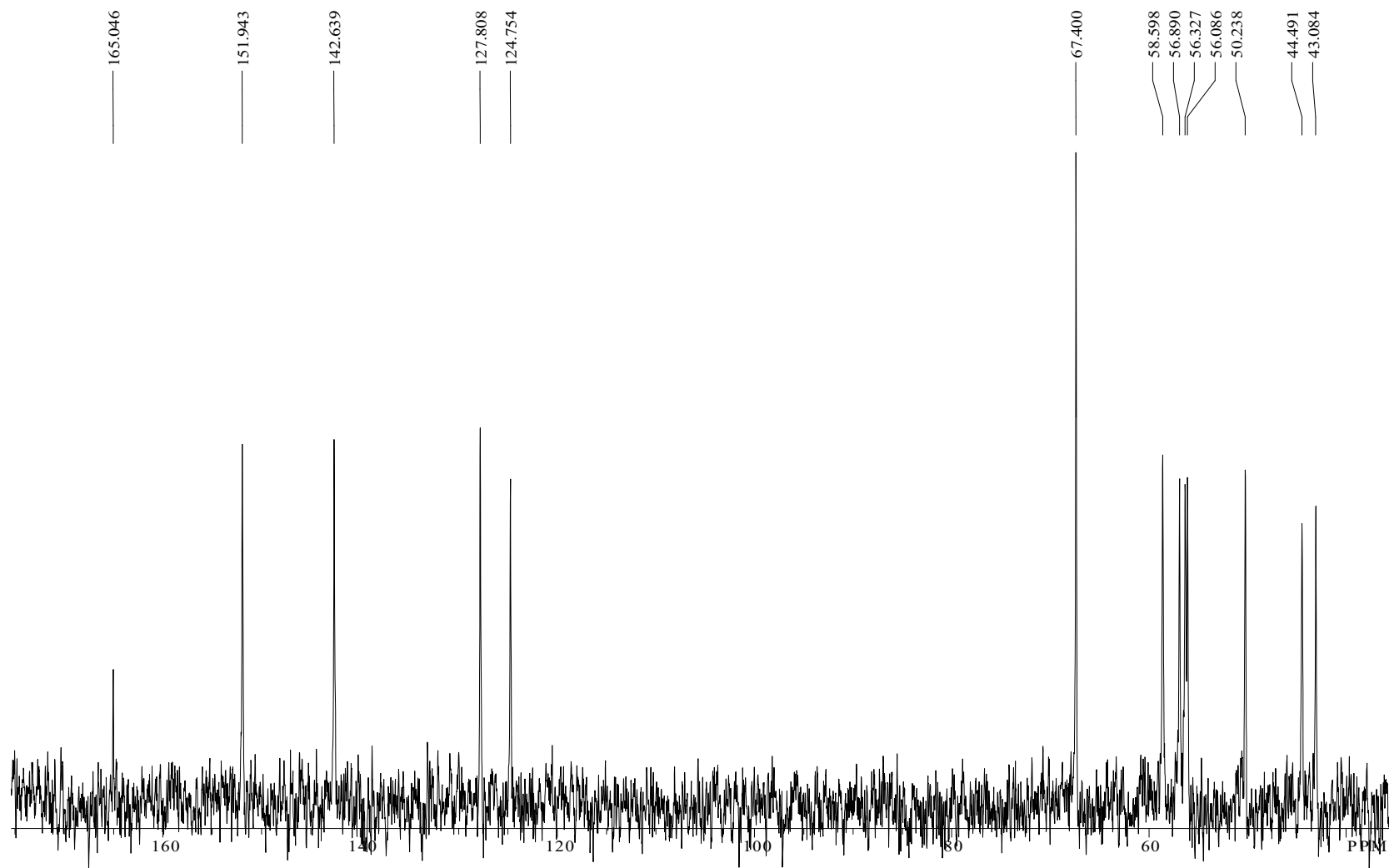
From the NMR spectra we can confirm the production of [Co(trien)(ampy)]Cl₃ due to the number of peaks on the ¹³C spectrum. A total of seven peaks were observed in the aliphatic region – six from trien and one from 2-(aminomethyl)pyridine.

When integrating the ¹H spectrum, the aromatic protons were assigned a value of 4; the aliphatic region integrated to 17.58, confirming the shift of the trien with the hydrogen atoms represented in the region under the curve.

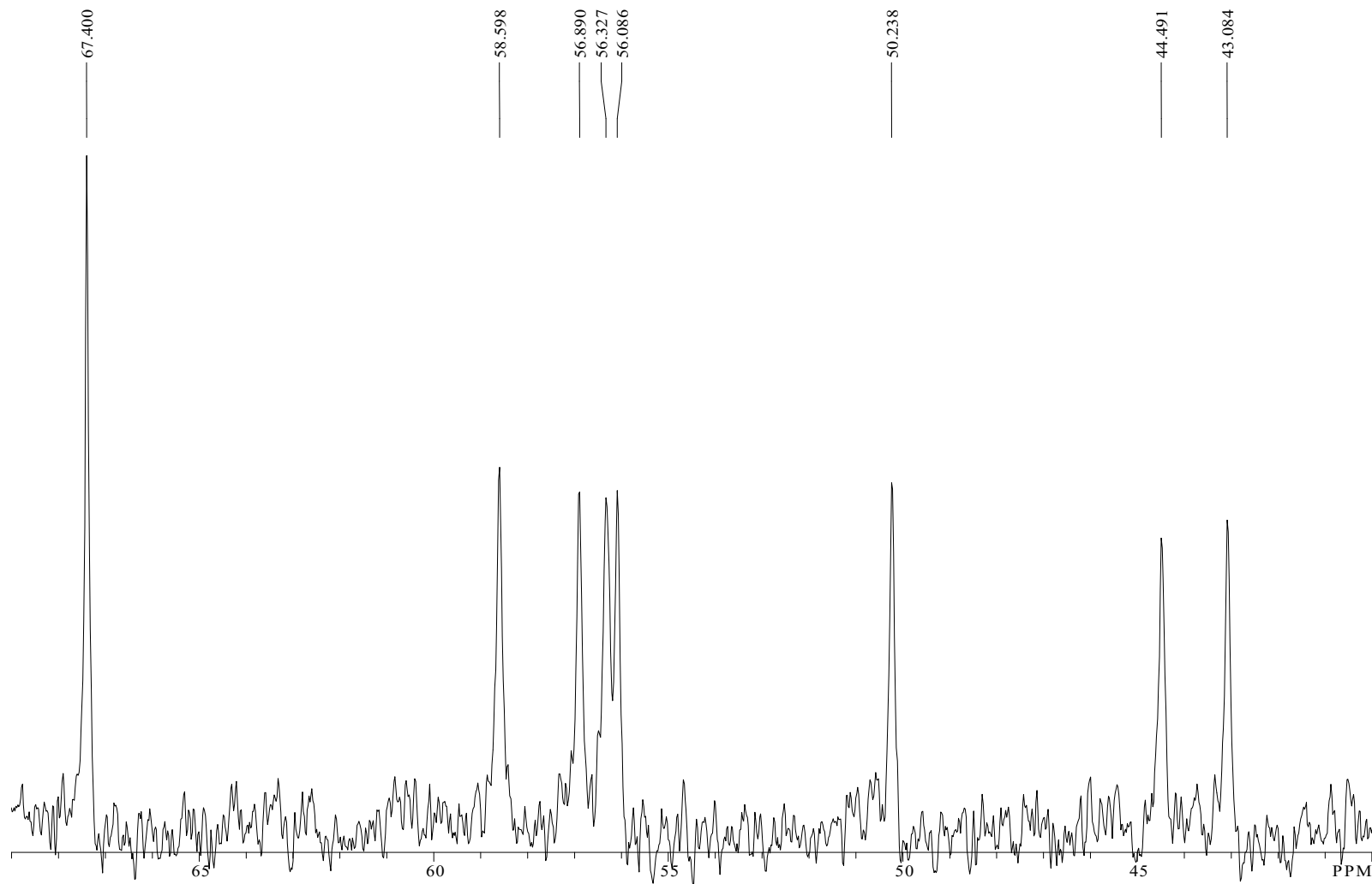
^1H Spectrum of $[\text{Co}(\text{trien})(\text{ampy})]\text{Cl}_3$



^{13}C Spectrum of $[\text{Co}(\text{trien})(\text{ampy})]\text{Cl}_3$

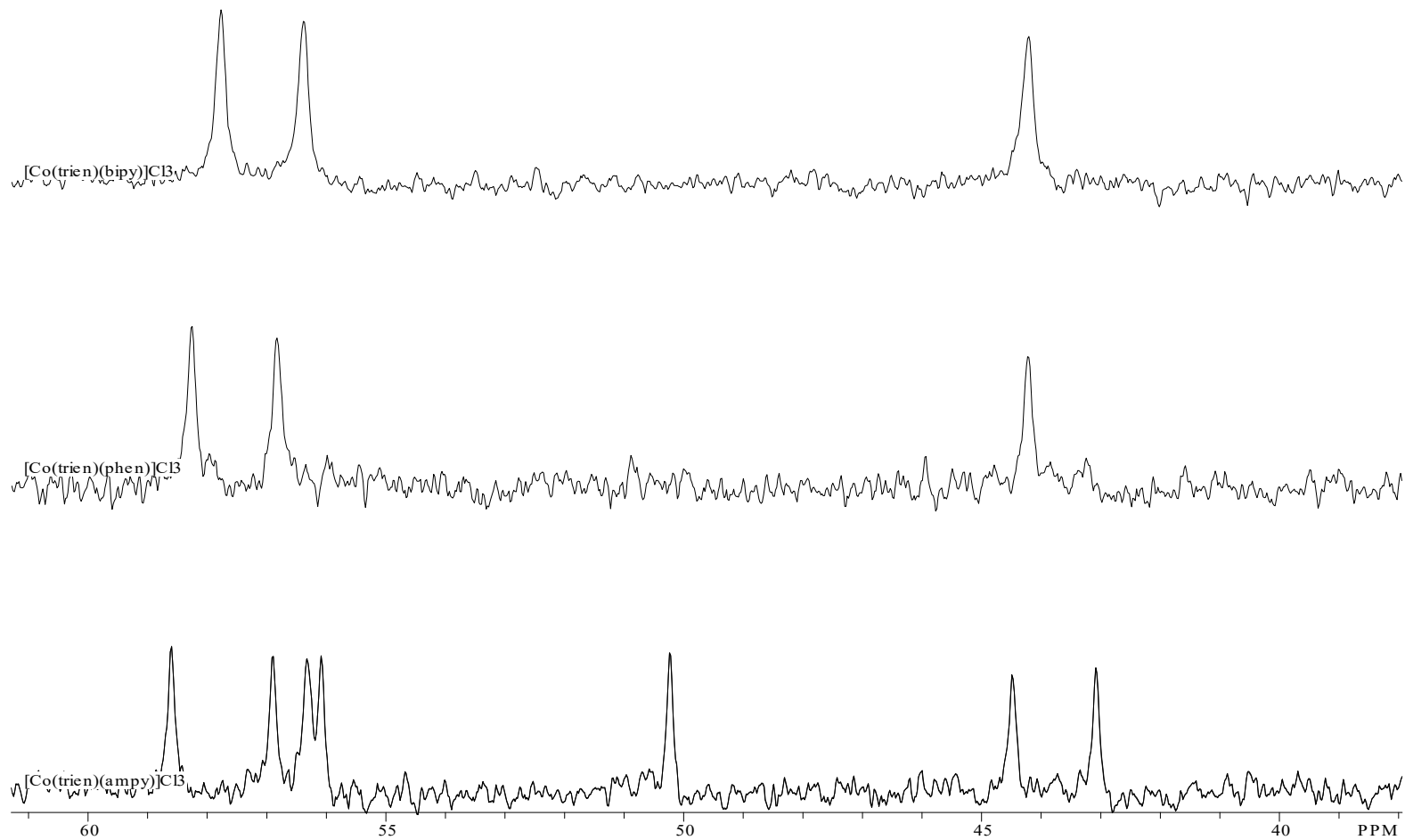


Zoomed ^{13}C Spectrum of $[\text{Co}(\text{trien})(\text{ampy})]\text{Cl}_3$

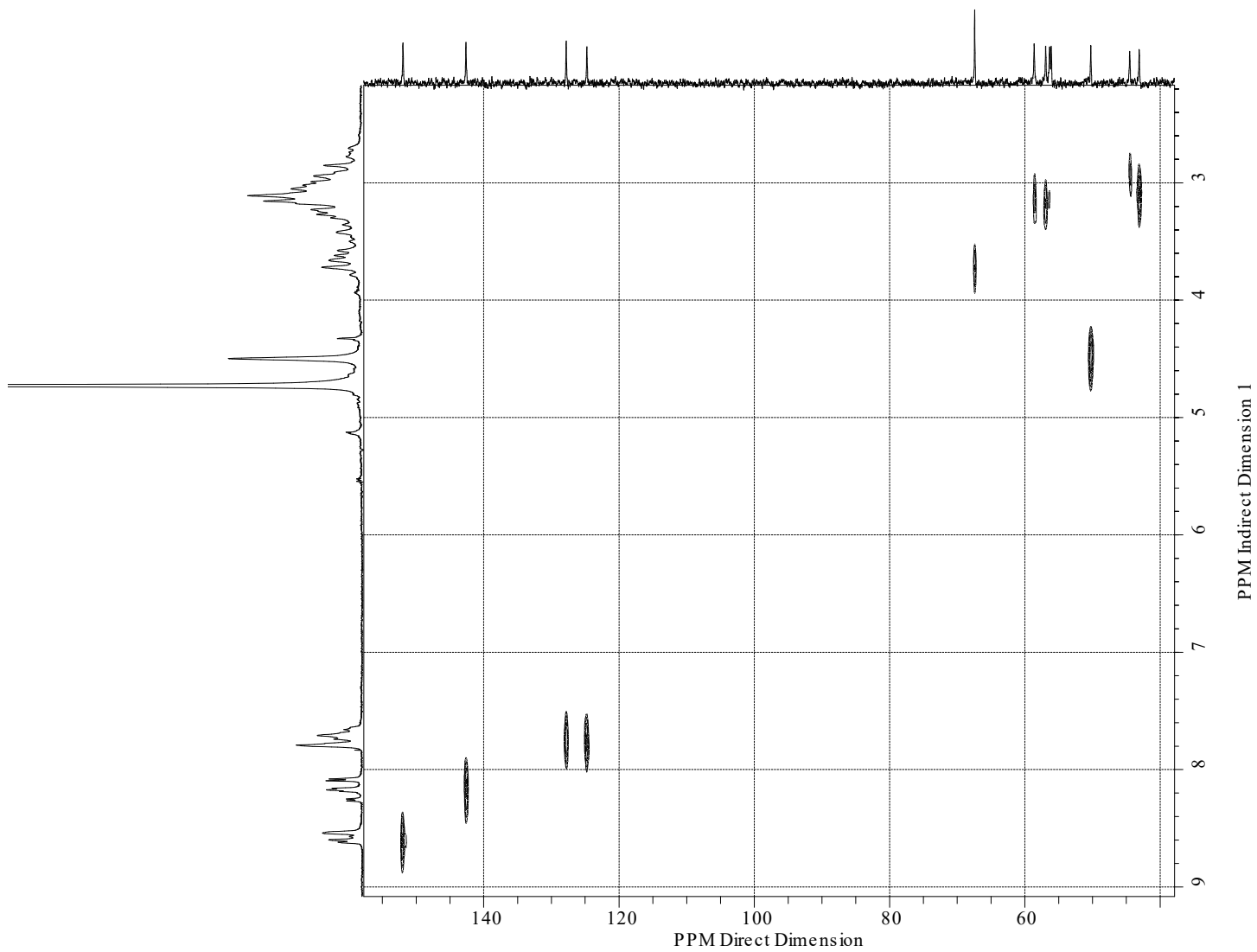


STACKED VIEW

[Co(trien)(bipy)]Cl₃ (top), [Co(trien)(phen)]Cl₃ (middle), [Co(trien)(ampy)]Cl₃ (bottom)



HETCOR



SPECTRAL ANALYSIS

The stacked view provides confirmation that each peak on the symmetrical molecules corresponds to two peaks on the asymmetrical molecule. For example, [Co(trien)(bipy)]Cl₃ shows a peak at 44.204 ppm and [Co(trien)(phen)]Cl₃ shows a peak at 44.224 ppm, assignable to C1. In the case of [Co(trien)(ampy)]Cl₃, this was replaced with two peaks at 43.084 and 44.491 ppm, allowing these to be assigned to C1 and C1' (but specific assignments were not possible.)

Furthermore, a ¹³C resonance at 50.238 ppm was present in the spectrum of [Co(trien)(ampy)]Cl₃ but not [Co(trien)(bipy)]Cl₃ or [Co(trien)(phen)]Cl₃, allowing it to be assigned to C4.

The heteronuclear correlation (hetcor) spectrum was used to relate carbon peaks with the protons attached to them. The above-mentioned ¹³C peak at 50.238 ppm showed a correlation to the 1H peak at 4.497 ppm (a singlet), allowing that to be assigned to the H4 protons.

Summary of ^{13}C Chemical Shifts

	C1	C2	C3	C4
[Co(trien)(bipy)]Cl ₃	44.204	57.768	56.384	N/A
[Co(trien)(phen)]Cl ₃	44.224	58.250	56.825	N/A
[Co(trien)(ampy)]Cl ₃	43.084 44.491	58.598 56.890	56.327 56.068	50.238

Conclusions

This experiment was reproducible and in each case the final product needed to sit untouched for a few days independent of how long it was collected to allow for crystallization. The first prep made by heating $[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$, ampy, and ethanol produced more crystals after rest, however the second prep did not. During each production, between 0.200 and 0.475g of product was collected. Another attempt involving the direct oxidation of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, trien, and ampy completely evaporated and did not yield crystals.

The peaks were able to be compared with previous compounds $[\text{Co}(\text{trien})(\text{bipy})]\text{Cl}_3$ and $[\text{Co}(\text{trien})(\text{phen})]\text{Cl}_3$ to determine the shift of C1, C2, and C3. Separate ^{13}C signals were observed for each compound, however, the individual carbons on the trien ligand (C1', C2', and C3') could not be distinguished from one another. The spectra obtained contained very little noise and did indicate that the desired product was obtained.