Preparation and NMR Analysis of $[Co(tren)(acac)]Cl_2$

Mark McClure and KC Tennant
Department of Chemistry and Physics
The University of North Carolina and Physics
Pembroke, NC

Abstract

The synthesis of $[Co(tren)(acac)]Cl_2$ was carried out and followed by 1-D and 2-D NMR analysis. The purpose of this study was to determine the effects of incorporating oxygen donor ligands into the open coordination sites of cobalt complexes containing tris(2-aminomethyl)amine (tren). Both the ^{1}H and ^{13}C spectra of the crystals were obtained in order to ensure the compound contained the methyl groups. Furthermore, the HETCOR program was used to confirm the coordination between the methyl group peaks displayed in the ^{1}H and ^{13}C spectra.

Reasons for Study

Previously studied compounds include $[Co(tren)(phen)]Cl_3$
(phen= 1,10-phenanthroline, a nitrogen donor ligand).

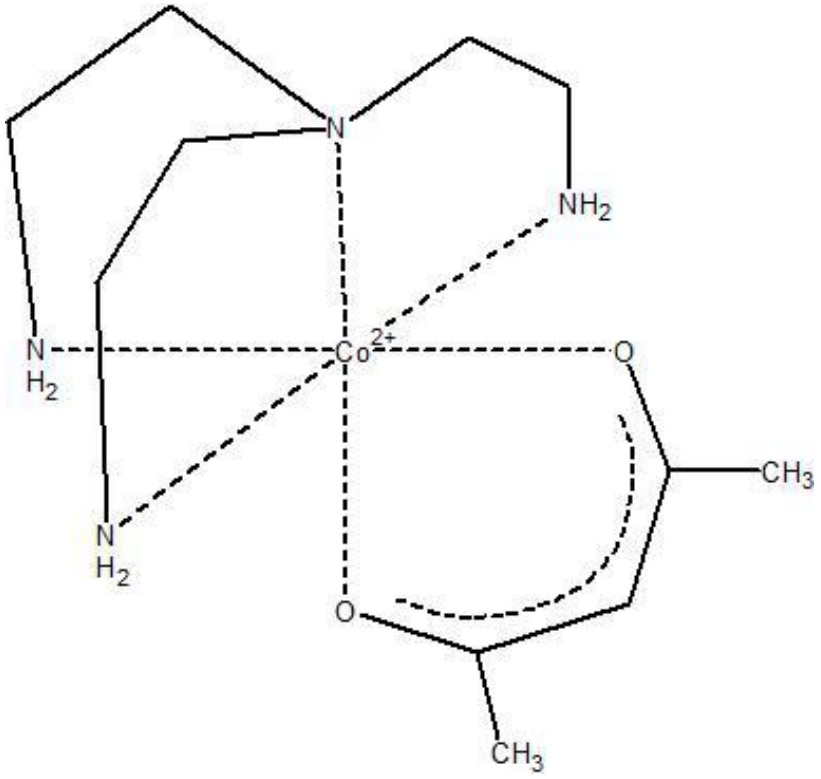
Current study focused on similar compounds $[Co(tren)(acac)]Cl_2$ and $[Co(tren)(C_2O_4)]Cl$.
(acac= acetylacetonate, $C_2O_4^{2-}$ = oxalate, both oxygen donor ligands).

The first compound has not yet been synthesized to our knowledge nor analyzed by NMR.

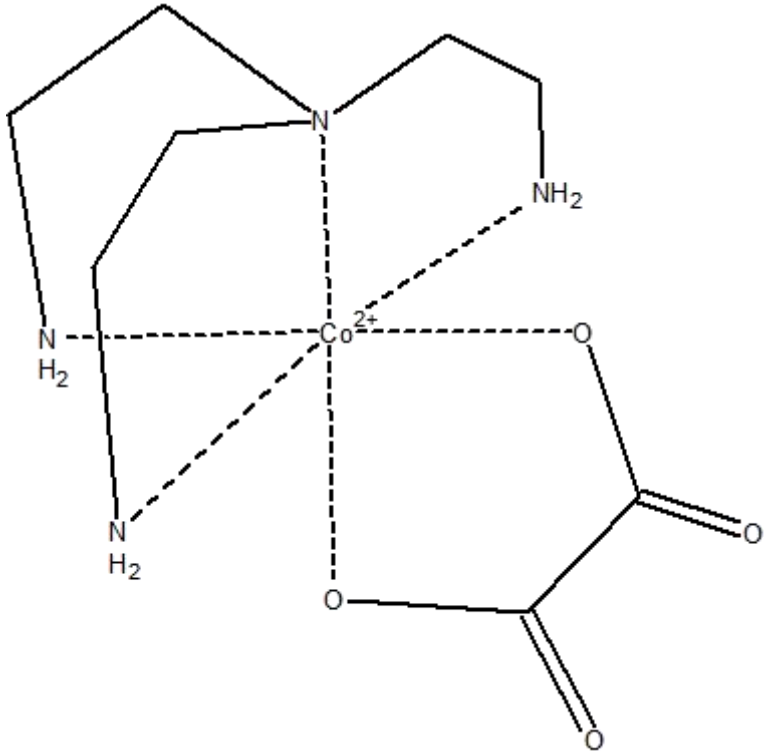
Comparison to spectrum of $[Co(tren)(C_2O_4)]Cl$ - Questionable whether or not acac and C_2O_4 will spread out the tren portion of the proton spectrum the same way phen does.

The asymmetrical coordination within the oxygen ligands means that the methyl groups in acac should appear as two separate peaks.

Structures of Compounds Studied



[Co(tren)(acac)]Cl_2



[Co(tren)(C_2O_4)]Cl

Experimental

Compound Synthesis - $[Co(tren)(acac)]Cl_2$

1.000 g $[Co(tren)(Cl_2)]Cl$ was combined in a beaker with 0.392g sodium acetylacetonate and 25 mL of distilled water.

The solution was heated to concentrate down and it was then refluxed for 4 days.

After refluxing, the solution was left covered by a watch glass to crystallize.

The solution was suction filtered to obtain maroon colored crystals.

Final mass obtained of the compound was 0.0213g

Experimental

Compound Synthesis - $[Co(tren)(C_2O_4)]Cl$

1.000 g $[Co(tren)(Cl_2)]Cl$ was combined in a beaker with 0.488g sodium oxalate monohydrate and 25 mL of distilled water.

The solution was heated to concentrate out, and a red solid appeared.

The crystals was separated out using suction filtration.

Experimental

Instrumentation

NMR analysis was performed on an Anasazi EFT-90 spectrophotometer.

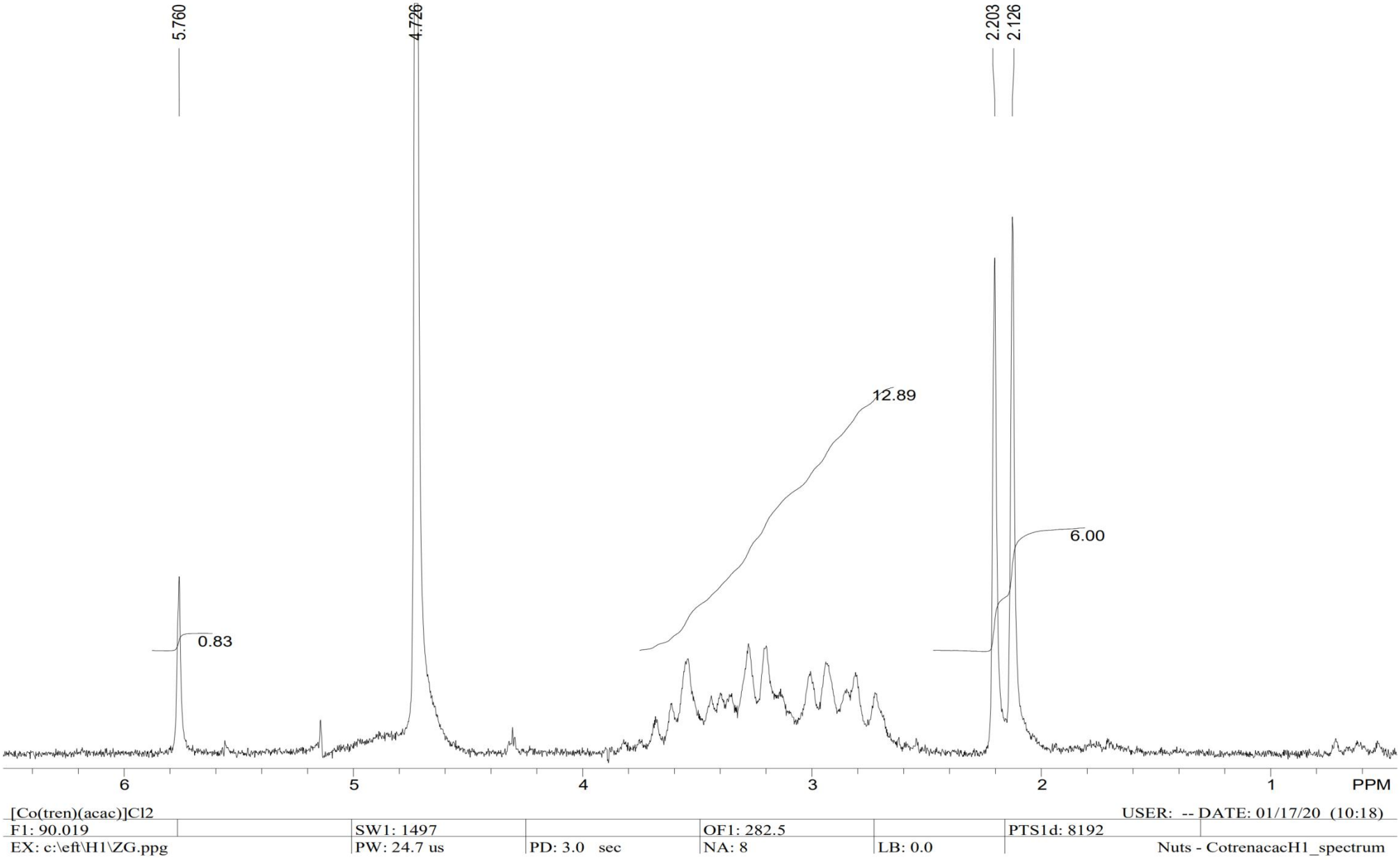
The NUTS processing software was used to prepare the spectra.

Each analysis used D_2O as a solvent.

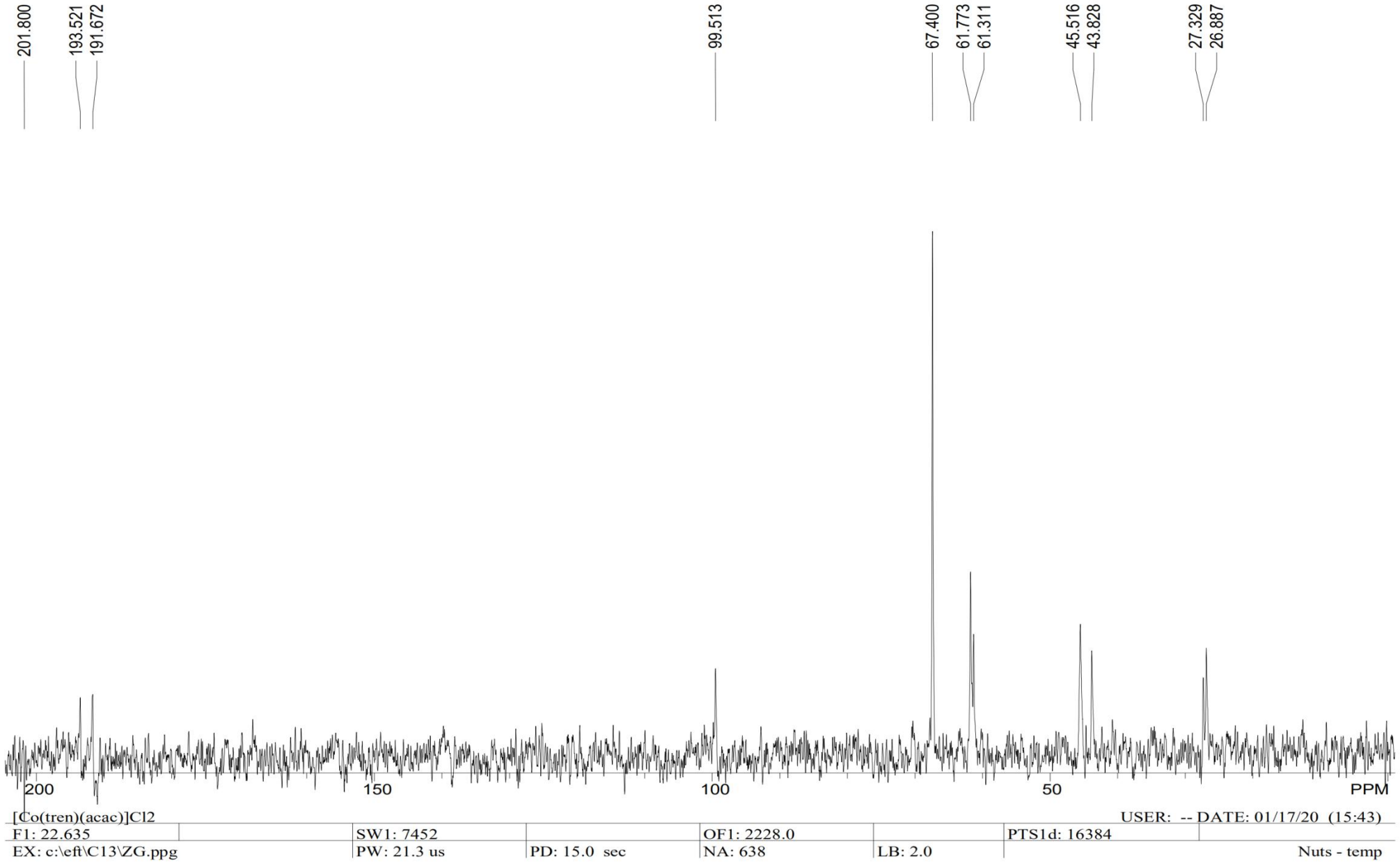
Calibration of the ^{1}H spectrum was to 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) assigned a value of 0.0 ppm.

Calibration of the ^{13}C spectrum was to 1,4-dioxane assigned a value of 67.4 ppm.

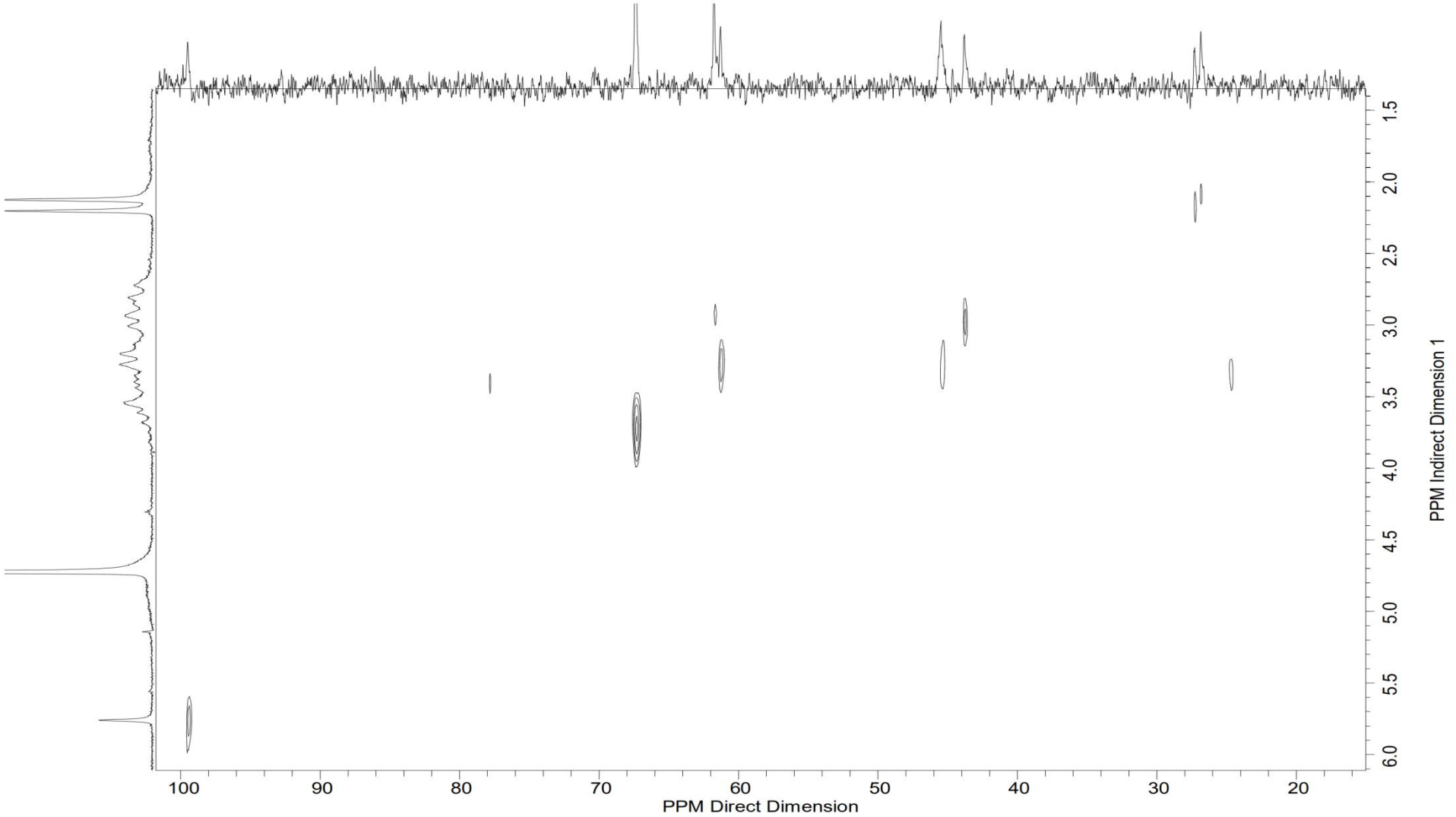
$[Co(tren)(acac)]Cl_2$ ^1H Spectrum



$[Co(tren)(acac)]Cl_2$ ^{13}C Spectrum



$[Co(tren)(acac)]Cl_2$ HETCOR



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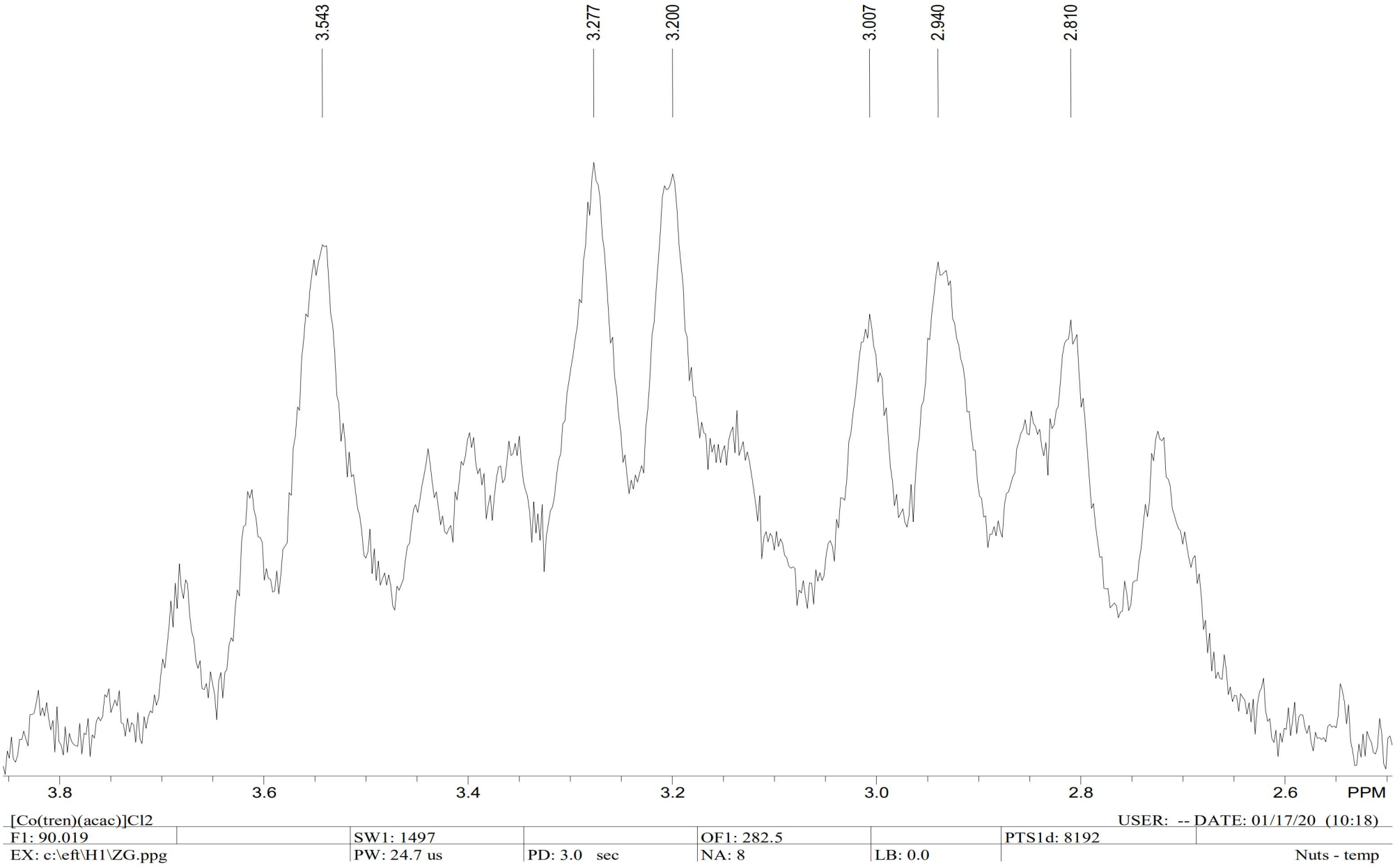
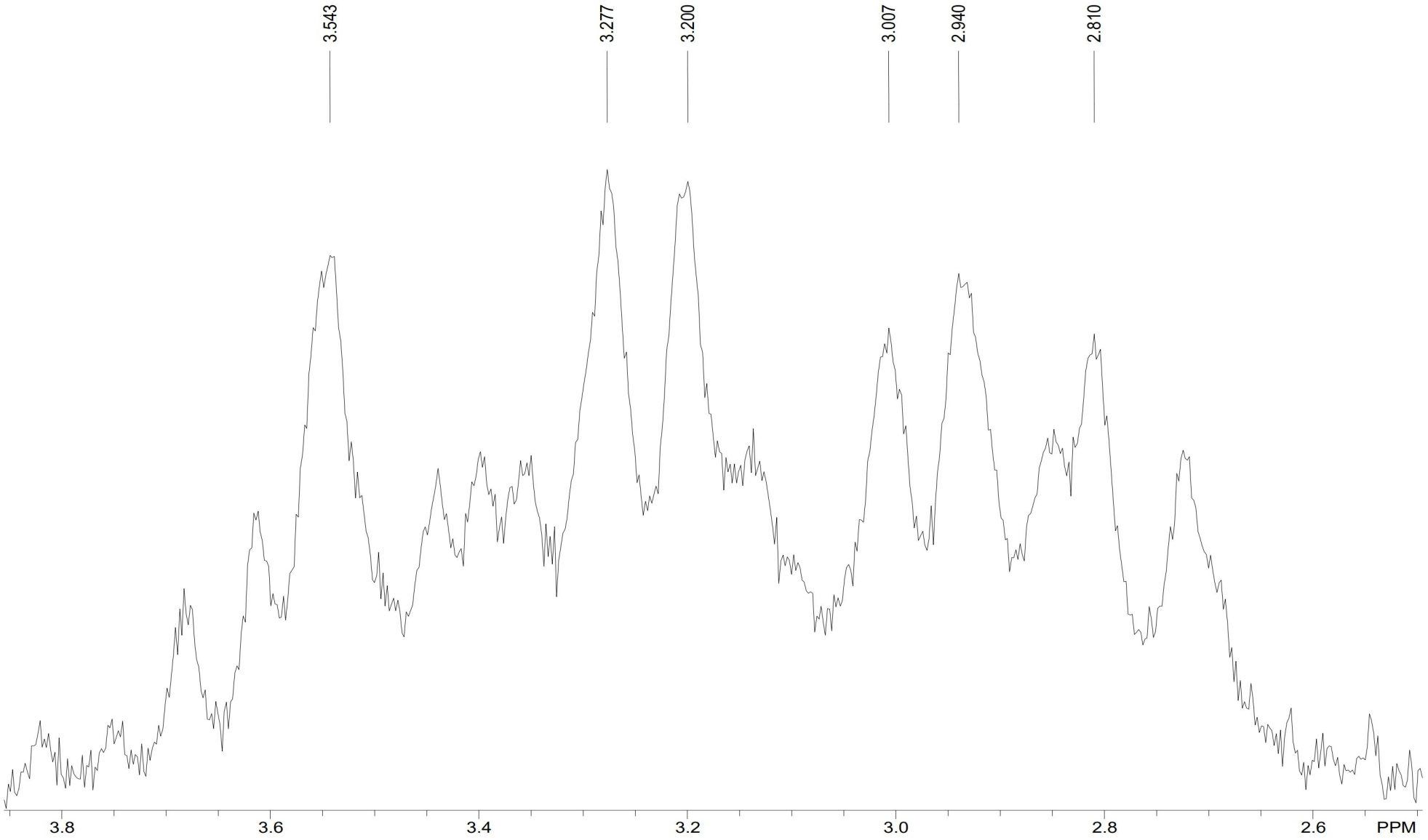
EX: c:\eft\C13\HETCOR.ppg		PW: 21.3 us	PD: 1.0 sec	NA: 128	LB: 4.0		Nuts - temp

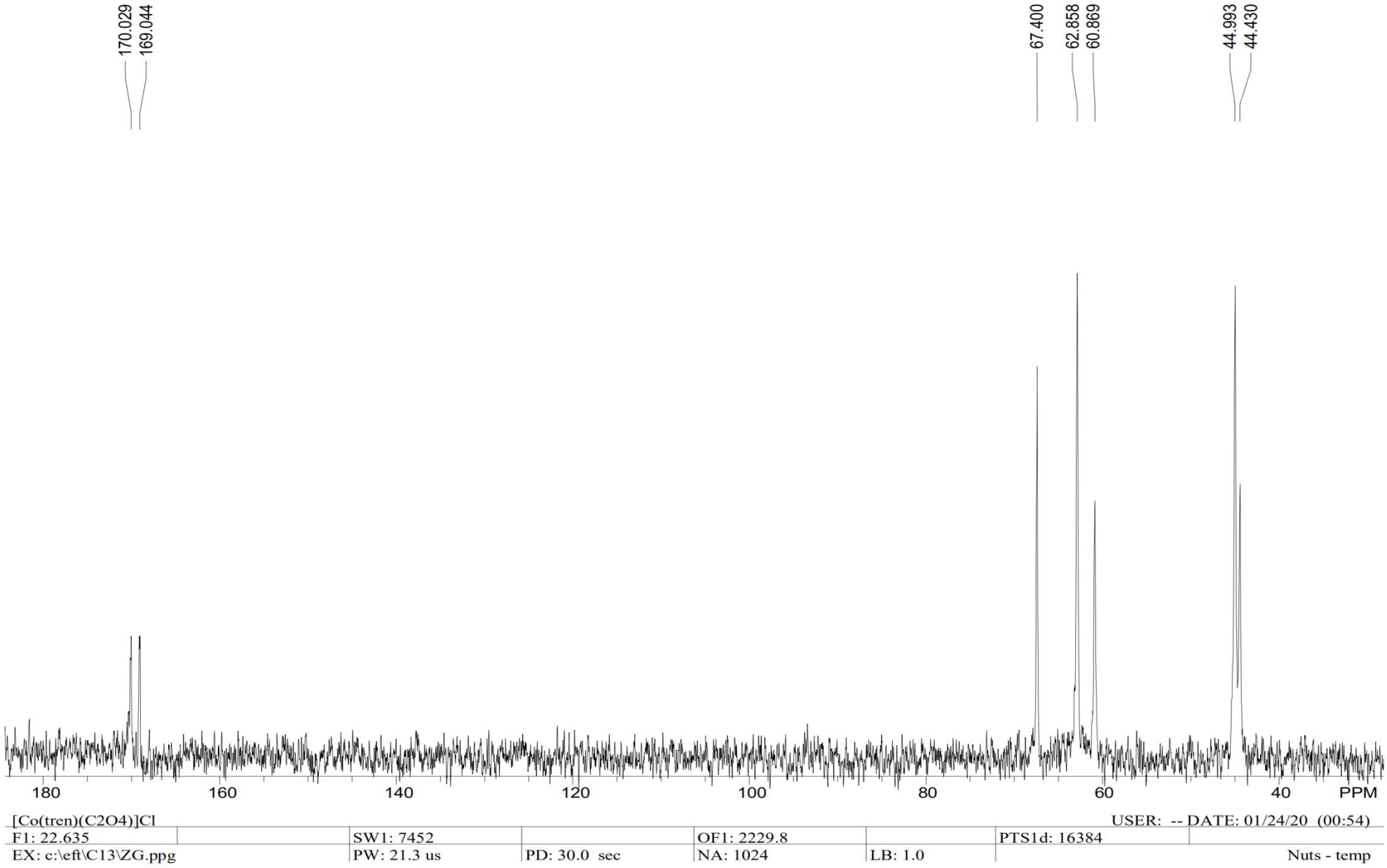
[Co(tren)(acac)]Cl_2 Tren Portion of ^1H Spectrum



[Co(tren)(C_2O_4)]Cl Tren Portion of ^{1}H Spectrum



[Co(tren)(C_2O_4)]Cl ^{13}C Spectrum



$[Co(tren)(acac)]Cl_2$ ^{1}H Analysis

Chemical Shift	Integration	Multiplicity	Assignment
2.0-2.4	6.00	Doublet	Methyl Groups
2.5-4.0	12.89	Multiplet	Tren
5.8-6.0	0.83	Singlet	CH

$[Co(tren)(acac)]Cl_2$ ^{13}C Analysis

Chemical Shift	Assignment
67.4	Dioxane
43.828, 45.516, 61.311, 61.773	Tren
26.887, 27.329	Methyl Groups
191.521, 191.672	Quaternary Carbons

Results and Discussion

Integration of the ^{1}H spectrum revealed the correct amount of protons were present in the compound $[Co(tren)(acac)]Cl_2$.

Due to the asymmetric coordination of the oxygen ligands, the methyl groups would appear as two separate peaks in the NMR spectra. This was confirmed in the ^{1}H and ^{13}C spectra.

The HETCOR program affirmed the correlation between the protons and carbons of the two methyl groups in the acac. However, the assignments of the peaks to the methyl groups could not be distinguished.

Comparison between the effects of oxalate and acac on the tren region of the proton spectra revealed that coordination with acac spreads the tren spectrum out while the oxalate seems to condense it.

Conclusions

A cobalt compound was synthesized which has not been previously studied to our knowledge.

Studies of 1-D and 2-D NMR analysis of the compound revealed that it contained the correct protons and carbons as expected.

The correspondence of the methyl group protons and carbons was further confirmed by the HETCOR analysis.

An attempt at synthesizing the compound [Co(tren)(mal)]Cl was not successful. This was done in efforts to further analyze the effects of oxygen ligands in the proton spectrum.
(mal= $C_3H_2O_4^{2-}$, an oxygen donor ligand)