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

A Two-Dimensional NMR Study of $[Co(phen)_2(NO_2)_2]Cl$

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Abstract

The compound [Co $(phen)_2(NO_2)_2$]Cl was synthesized and studied by one and two-dimensional NMR methods. The symmetry of this compound is different than those previously studied; while the two phenanthroline molecules are equivalent, within a given phenanthroline molecule each carbon and hydrogen gives a unique chemical shift. This had the effect of dividing the C-13 spectrum into sets of closely spaced signals. Assignments of these signals were possible after making a few assumptions and using a combination of COSY and HETCOR techniques.

Reasons for Study

Symmetry of this compound is different from those previously studied!

Previously studied compounds exhibited a symmetry axis allowing C-13 signals to be assigned in sets

$[Co(phen)_2(NO_2)_2]Cl$ contains non-equivalent phenanthroline rings, destroying the symmetry axis previously studied

C-13 signals can no longer be assigned in sets, and must be assigned individually

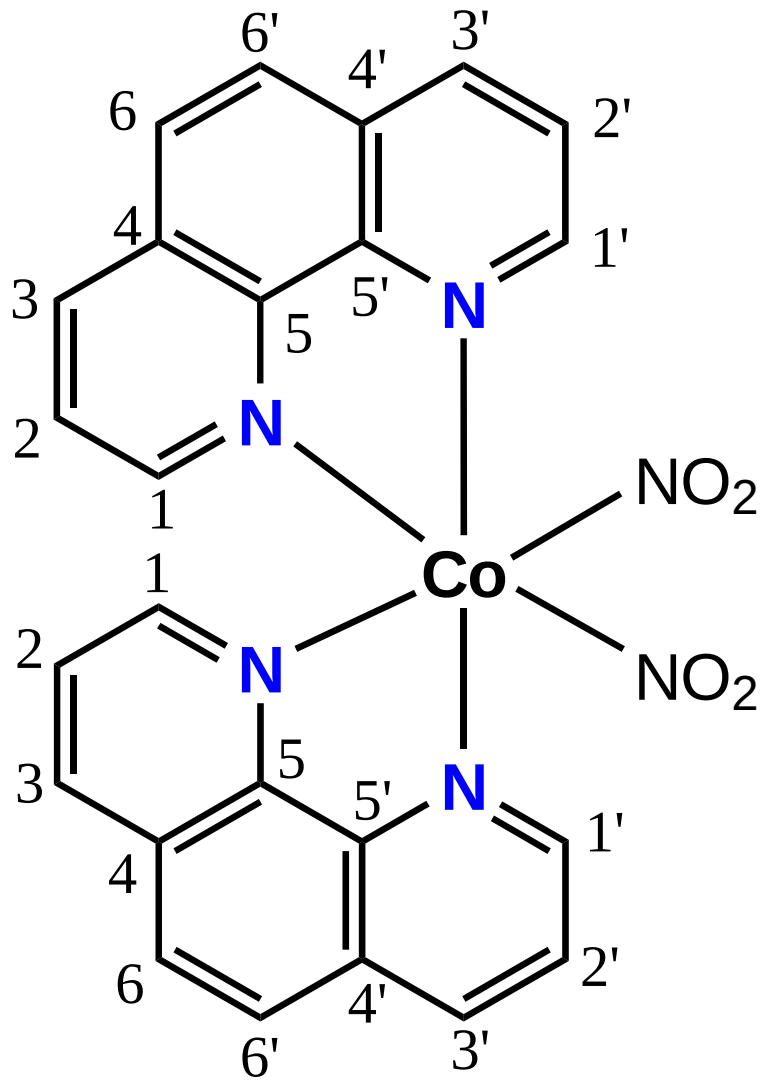


Figure 1. Structural Model of $[Co(phen)_2(NO_2)_2]+$

EXPERIMENTAL

Instrumentation

All experiments were performed on an Anasazi EFT-90 spectrometer

D_6-DMSO was used as the solvent in all cases

The C-13 spectra were calibrated on the DMSO peak, assigned a value of 39.51ppm

EXPERIMENTAL

Compound Synthesis

Dissolve 2.006 grams 1,10-Phenanthroline in 25mL Ethanol

Combine 0.696 grams Sodium Nitrite and 1.205 grams Cobalt Chloride Hexahydrate with 25mL water

Combine both solutions in a 250mL Erlenmeyer flask

Prepare diluted HCl by combining 2mL HCl with 8mL H_2O.

Add 2mL diluted HCl to flask

Place in ice. Connect vacuum hose with water trap to flask and allow oxidizing approximately 90 minutes

Filter product using vacuum filtration. Dry with Acetone. Obtain product mass

Figure 2. H-1 Spectrum of $[Co(phen)_2(NO_2)_2]^+$

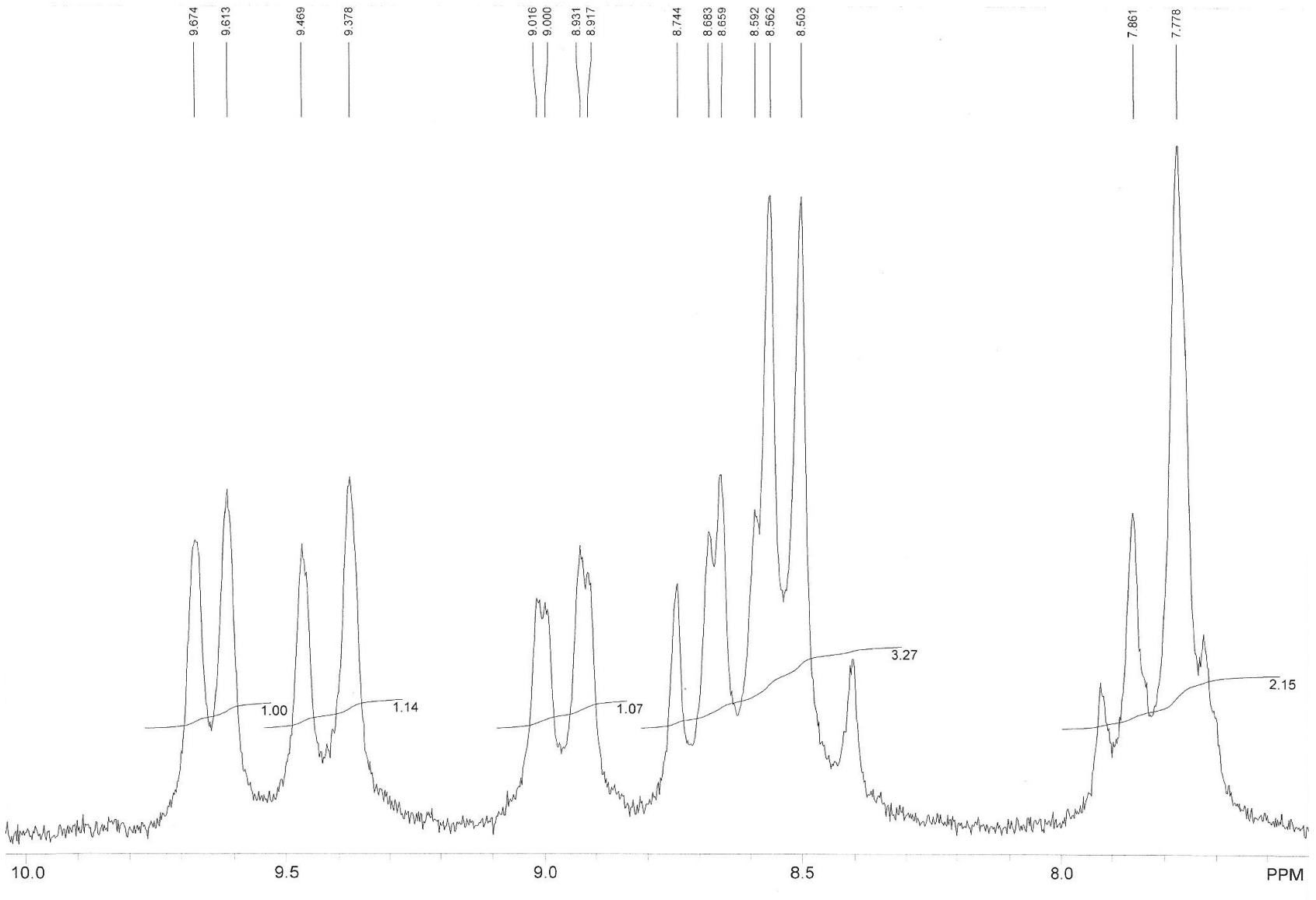


Figure 3. C-13 Spectrum of $[Co(phen)_2(NO_2)_2]^+$

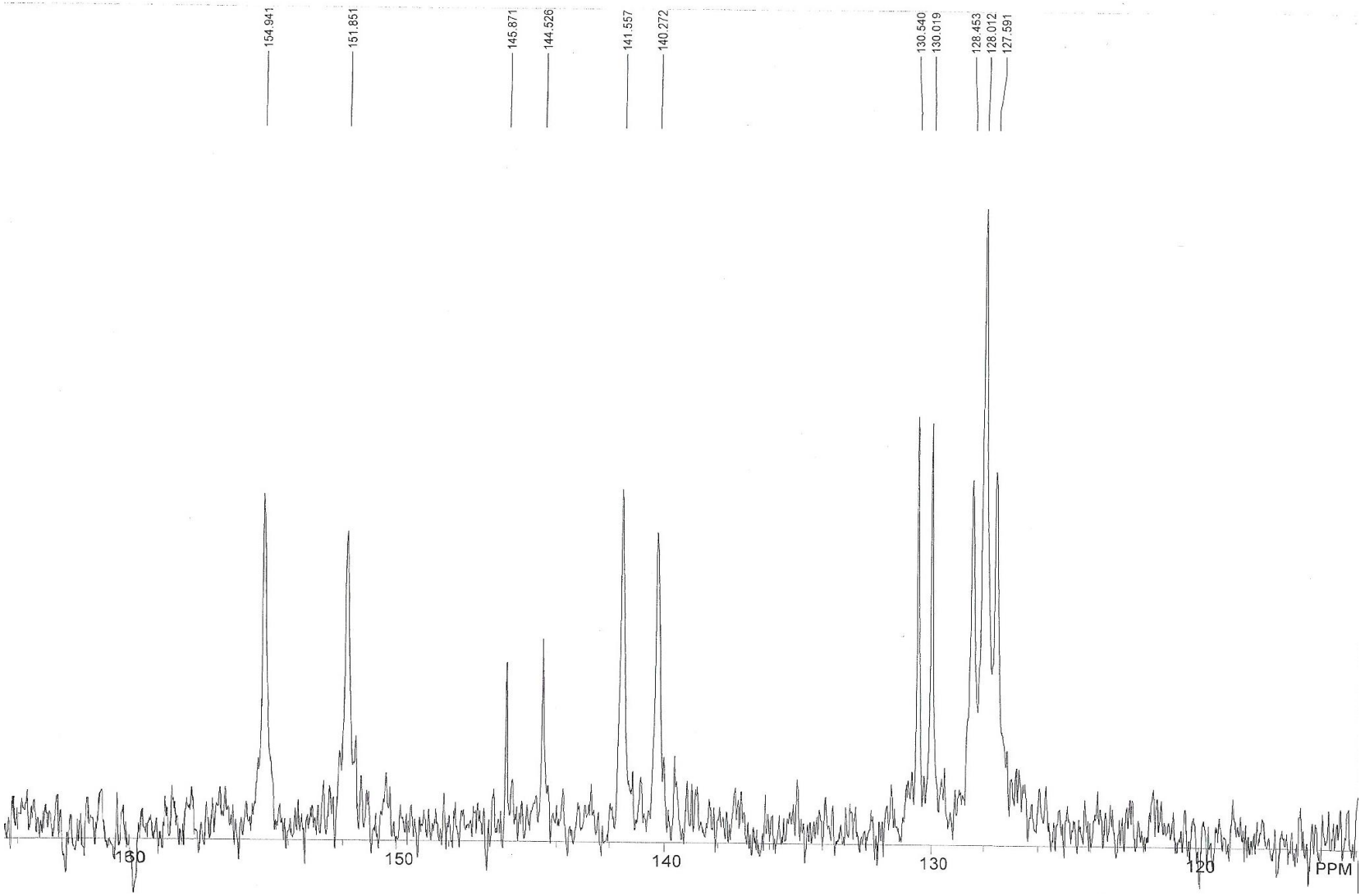


Figure 4. COSY Spectrum of $[Co(phen)_2(NO_2)_2]^+$

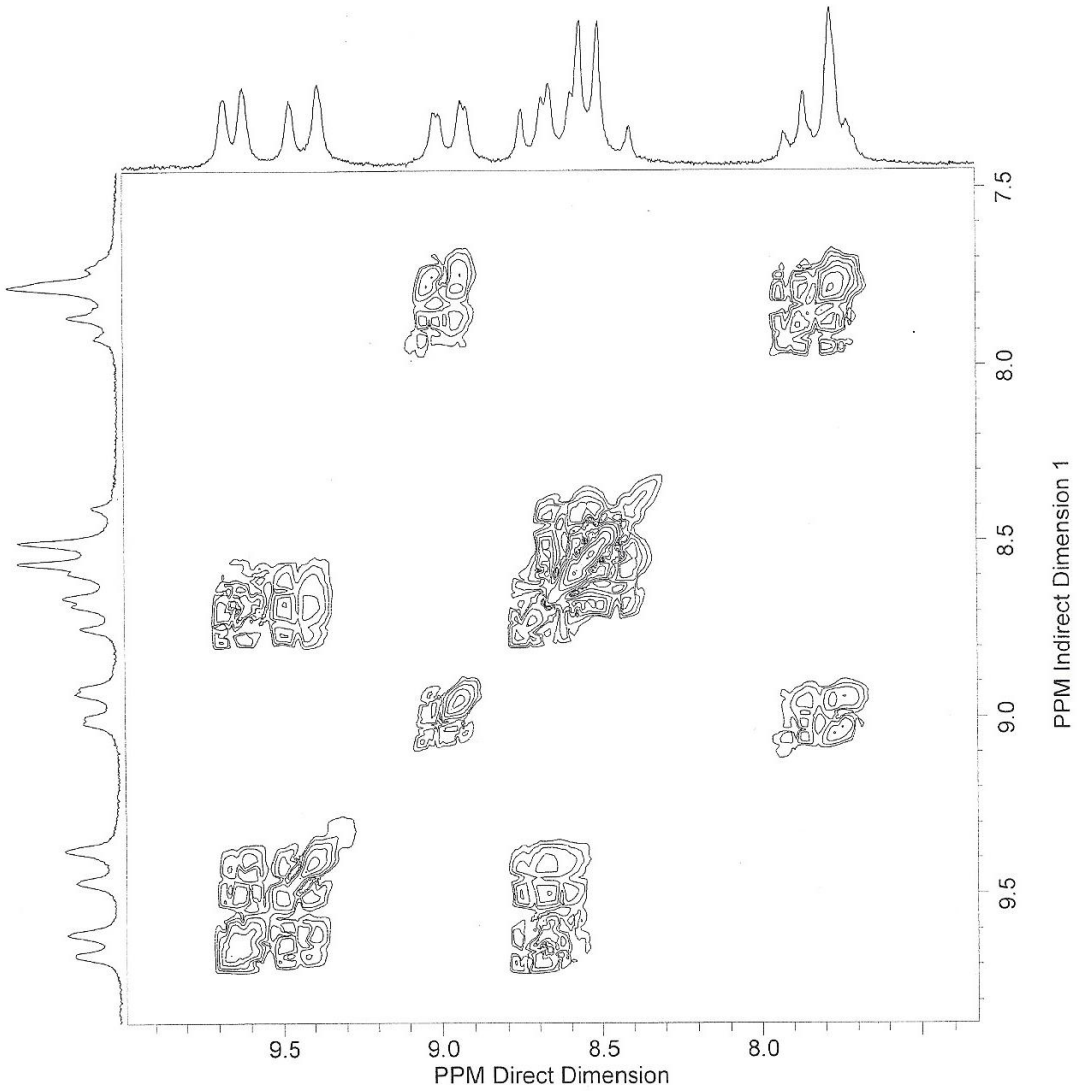
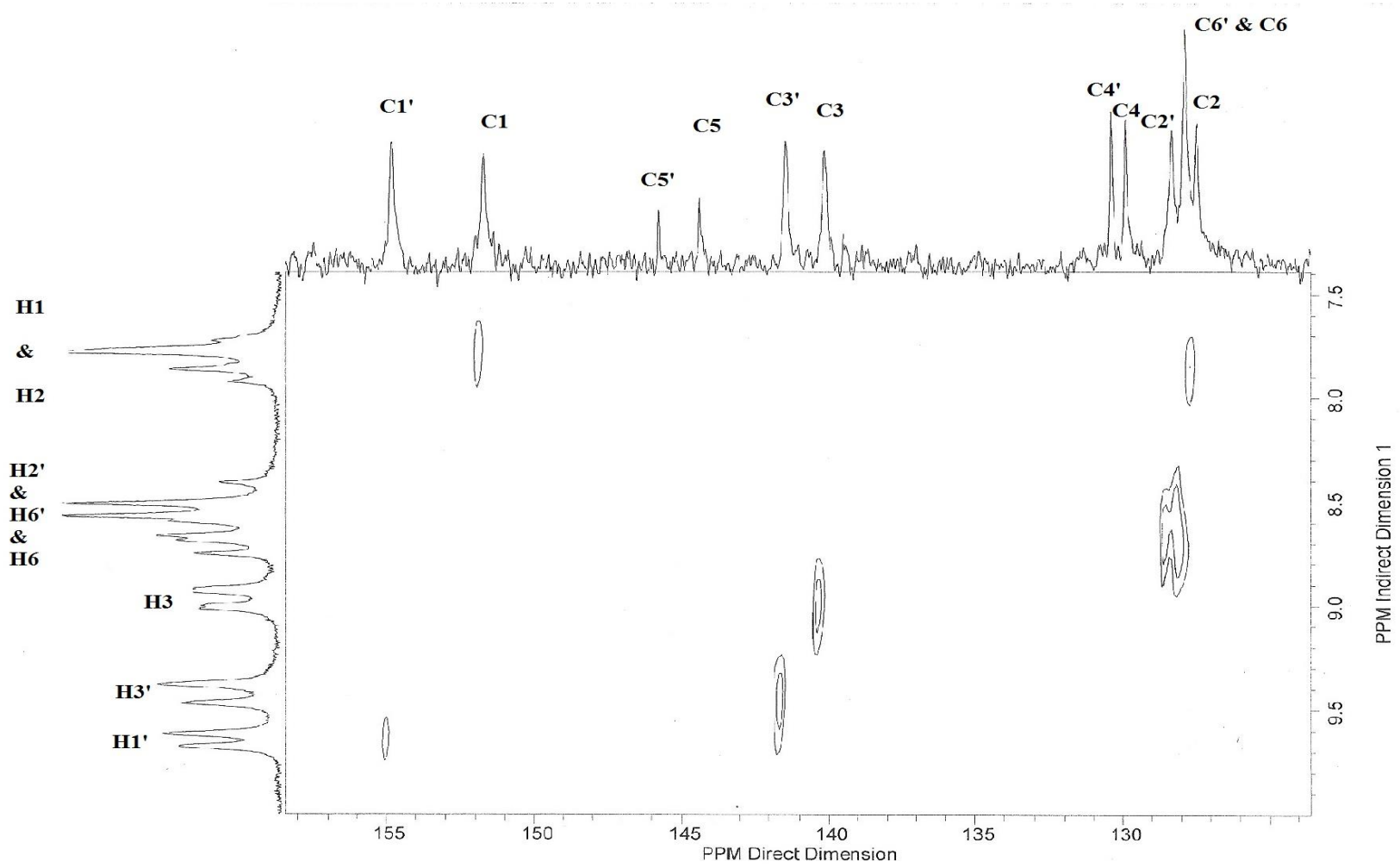


Figure 5. HETCOR Spectrum of $[Co(phen)_2(NO_2)_2]^+$



Assignments

Using H-1 spectrum, the signal shifted furthest downfield was assumed to be H1’

Using the HETCOR spectrum, assignment of H1’ allowed the assignment of C1’ (154.941 ppm)

H1’ is coupled to H2’ and H3’; COSY allowed assignment of these signals; Doublet at 9.424 ppm was assigned to H3’

Using the HETCOR spectrum, assignment of H3’ allowed the assignment of C3’ (141.557 ppm)

C-13 spectrum was divided into sets of closely spaced signals; assumed to be corresponding atoms on opposite sides of the molecule

Assignment of C1’ allowed assignment of C1 (151.851 ppm)

Assignment of C3’ allowed assignment of C3 (140.272 ppm)

Four signals did not show any correlations in HETCOR Spectrum indicating quaternary carbon atoms

Signals at 145.871 ppm and 144.526 ppm were shifted furthest downfield and assigned to C5’ and C5

Signals at 130.540 ppm and 130.019 ppm were assigned to C4’ and C4

Largest C-13 signal (only one) was assigned to C6’ and C6 because they are furthest away from the source of asymmetry

Tabulations of Chemical Shifts

	^{1}H Shift (ppm)	^{13}C Shift (ppm)	Δ ^{13}C Shift
1	7.778 – 7.861	151.851	
1’	9.644	154.941	3.090
2	7.778 – 7.861	127.591	
2’	8.503 – 8.744	128.453	0.862
3	8.966	140.272	
3’	9.424	141.557	1.285
4	N/A	130.019	
4’	N/A	130.540	0.521
5	N/A	144.526	
5’	N/A	145.871	1.345
6	8.503 – 8.744	128.012	
6’	8.503 – 8.744	128.012	0.000

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Acknowledgements

We would like to thank the UNCP PURC program for their funding of this research

We would also like to thank the UNCP department of Chemistry and Physics for their support of this research