

238	14	12	31
<b>U</b>	<b>N</b>	<b>C</b>	<b>P</b>
92	7	6	15

## **An NMR Study of $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]\text{Cl}$**

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## Abstract

The compound  $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]\text{Cl}$  was synthesized and analyzed using COSY, HETCOR, and J-resolved NMR programs. Due to the coordination of the bipyridine rings to the cobalt center and the symmetry of the two rings, the normal symmetry of the bipyridine is lost. Therefore, the proton and carbon signals received from each carbon in one ring of the bipyridine molecule are nearly equivalent to the signals given by the corresponding carbon in the second ring within the same molecule. The centers and multiplicities of the proton resonances were identified using the J-resolved program, while assignment of the carbon signals was achieved using the HETCOR program. The COSY program was used to establish connectivity between sets of coupled protons.

## Reasons for Study

The spectrum of  $[\text{Co}(\text{bipy})(\text{NO}_2)_2]\text{Cl}$  is expected to be more complex than that for the previously studied  $[\text{Co}(\text{phen})(\text{NO}_2)_2]\text{Cl}$

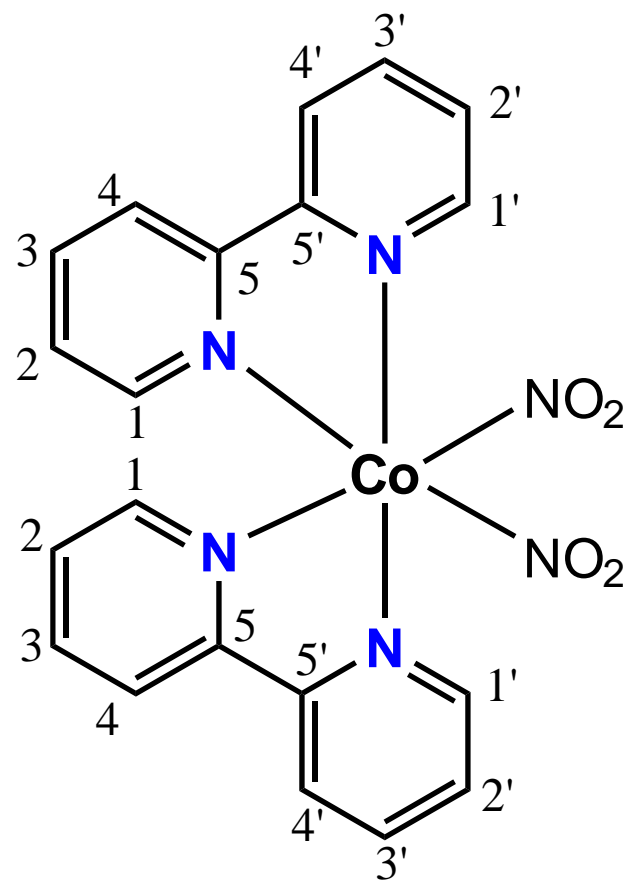
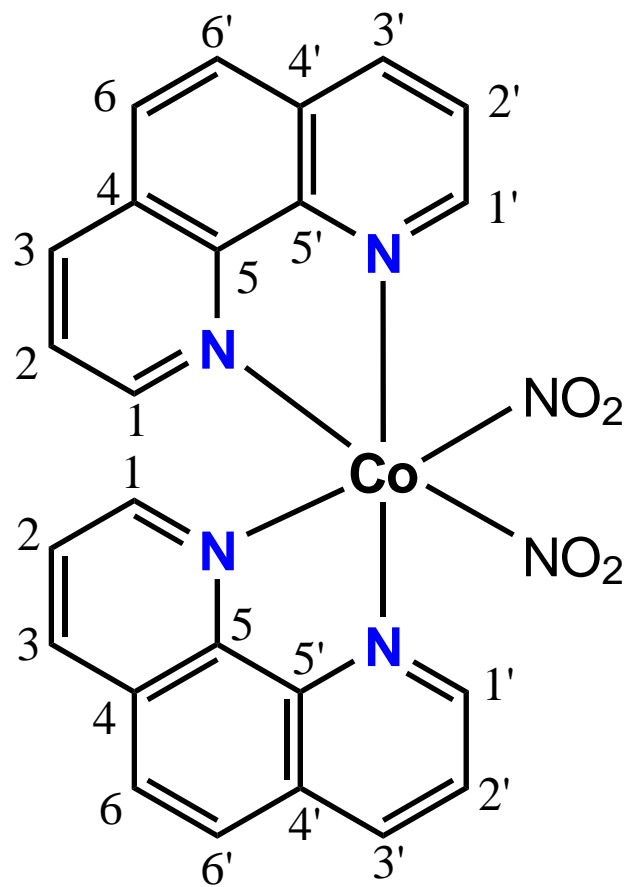
Compound not previously studied by two-dimensional NMR

Complete assignment of resonances has not been achieved

Each carbon atom has a single proton; splitting patterns simpler than compounds with ligands containing ethylene linkages (ethylenediamine, triethylenetetramine)

The symmetry of the two bipyridine rings of  $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]$  allows for assignment of the C-13 signals to be assigned in pairs.

## Structures of Studied Compounds



## **Experimental**

### **Instrumentation**

An Anasazi EFT-90 spectrophotometer was used to obtain all spectra.

Spectra were processed using NUTS software.

DMSO was used as a solvent in all experiments.

The C-13 spectrum was calibrated to the DMSO peak.

The H-1 spectrum was calibrated to DSS.

## Experimental

### Compound Synthesis

2.007 g of cobalt (II) chloride was dissolved in ~25.00 mL of diH<sub>2</sub>O. To this solution was added 1.16 of sodium nitrite.

2.62 g of dipyridyl was dissolved in ~25.00 mL of ethanol and stirred on a magnetic plate until a homogeneous solution was obtained.

The cobalt (II) chloride and sodium nitrite solution was combined with the dipyridyl solution. 8.40 mL of 1.0 M HCl was added.

Air was then pulled through the solution using a vacuum hose for approximately 90 minutes.

[Co(bipy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl was isolated through vacuum filtration and washed with acetone. 2.06 g were recovered.

## Splitting Patterns

H1 is split by H2 (large) and H3 (small)

H2 is split by H1 (large) and H4 (small)

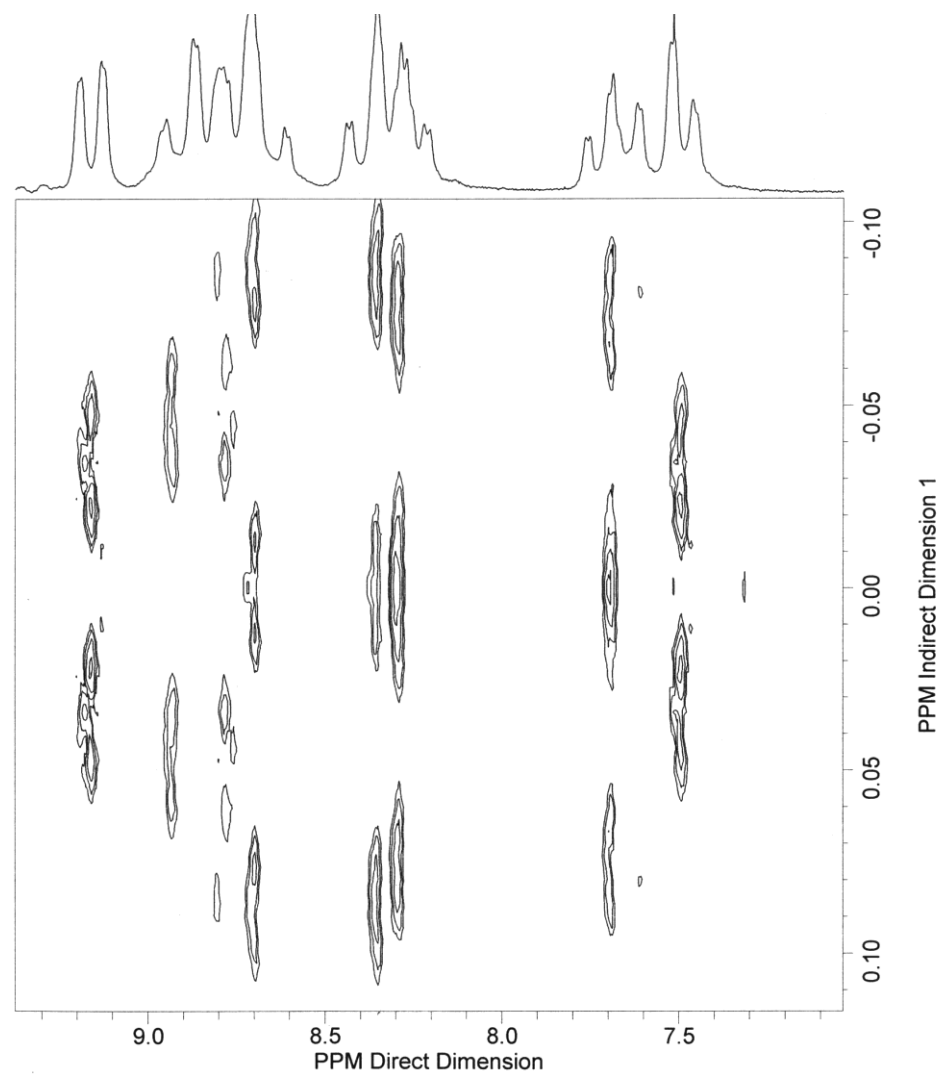
H3 is split by H2 (large), H4 (large), and H1 (small)

H4 is split by H3 (large) and H2 (small)

H1 and H4 have similar splitting patterns due to similar locations in the bipyridine ring

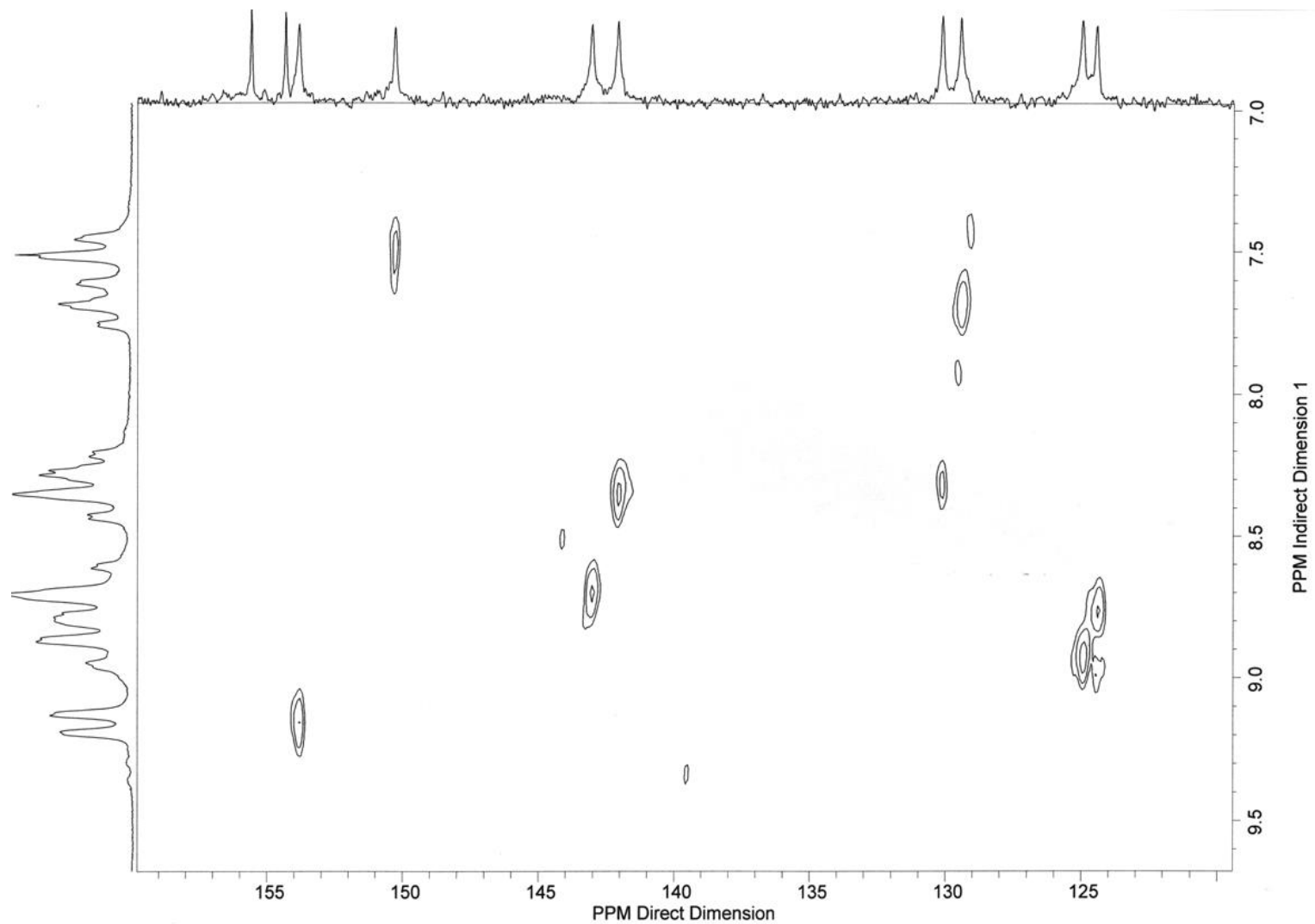
The splitting patterns of  $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]\text{Cl}$  are more complex than for  $[\text{Co}(\text{phen})_2(\text{NO}_2)_2]\text{Cl}$  due to the fact that in the latter C6 and C6' and only split each other

# J-Resolved Spectrum of $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]\text{Cl}$

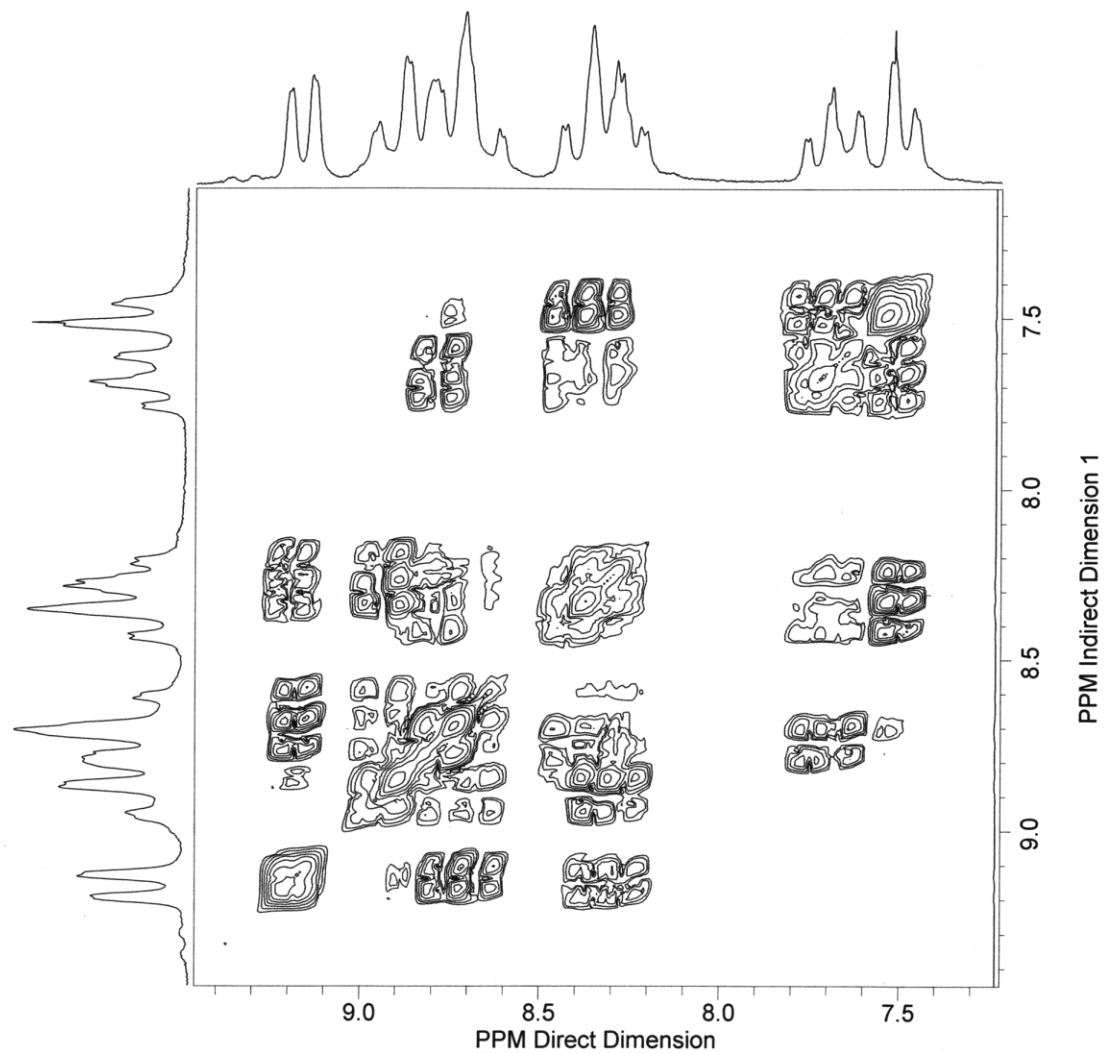




# HETCOR Spectrum of $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]\text{Cl}$



# COSY Spectrum of $[\text{Co}(\text{bipy})_2(\text{NO}_2)_2]\text{Cl}$



## Assignments - 1

The C-13 chemical shifts were observed to occur in pairs. It was assumed that each pair was due to the nearly-equivalent protons in the bipyridine rings (C1 and C1', C2 and C2', and so forth). It was further assumed that those closest to the center of asymmetry (the site of coordination) would have the smallest difference.

C1 and C1' were determined to have chemical shifts of 153.837 and 150.306 ppm (3.531 ppm)

C2 and C2' were determined to have chemical shifts of 130.139 and 129.457 ppm (0.682 ppm)

C3 and C3' were determined to have chemical shifts of 143.042 and 142.078 ppm ( $\Delta$  0.964 ppm)

C4 and C4' were determined to have chemical shifts of 125.002 and 124.460 ppm ( $\Delta$  0.542 ppm)

C5 and C5' were determined to have chemical shifts of 155.603 and 154.339 ppm ( $\Delta$  1.264 ppm)

## Assignments - 2

By using the J-resolved spectrum, the overlapping multiplets of the  $^1\text{H}$  spectrum were resolved. This allowed for assignment of the  $^1\text{H}$  signals

The multiplets appeared in sets with similar multiplicity. It was assumed that these represented similar protons in the dipyridyl rings ( $\text{H1}$  and  $\text{H1}'$ ,  $\text{H2}$  and  $\text{H2}'$ , and so on)

It was further assumed that those sets with the biggest difference in chemical shift would be observed for those protons closest to the donor atoms

## Assignments – 3

The signals at 9.15 ppm and 7.45 ppm ( $\Delta$  1.70 ppm) were assigned H1 and H1'. Being on the “ends” of the ring, these also had a simpler splitting pattern.

The signals at 8.30 and 7.69 ppm ( $\Delta$  0.61 ppm) were assigned to H2 and H2'.

The signals at 8.70 and 8.35 ppm ( $\Delta$  0.35 ppm) were assigned to H3 and H3'.

The signals at 8.82 and 8.75 ppm ( $\Delta$  0.07 ppm) were assigned to H4 and H4'. Also on the “ends” of the ring and had simpler splitting pattern.

In the heteronuclear correlation spectrum, the “sets” of  $^{13}\text{C}$  resonances correlated to these “sets” of  $^1\text{H}$  resonances

## Tabulation of Chemical Shifts

<b>Assignment</b>	<b><math>^1\text{H}</math> shift (ppm)</b>	<b><math>^{13}\text{C}</math> shift (ppm)</b>	<b><math>\Delta^1\text{H}</math> shift (ppm)</b>	<b><math>\Delta^{13}\text{C}</math> shift (ppm)</b>
1	9.15	153.837	1.70	3.531
1'	7.45	150.306		
2	8.30	130.139	0.61	0.682
2'	7.69	129.457		
3	8.70	143.042	0.35	0.964
3'	8.35	142.078		
4	8.82	125.002	0.07	0.542
4'	8.75	124.460		
5	n/a	155.603	n/a	1.264
5'	n/s	154.339		