TWO-DIMENSIONAL NMR ANALYSIS OF β-[Co(ampy)$_2$(NO$_2$)$_2$]NO$_3$

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Abstract

The compound β-cis [Co(ampy)$_2$(NO$_2$)$_2$]NO$_3$ was synthesized, isolated, and analyzed by NMR spectroscopy. The NMR experiments performed include ^{1}H, ^{13}C, COSY, and HETCOR. Based upon ^{13}C NMR it was believed that a pure sample of the β-cis isomer was obtained. Using two-dimensional NMR experiments it was possible to make partial assignments in the ^{1}H and ^{13}C spectra.

Introduction

The current line of study began with cobalt complexes containing a combination of tetradentate and aromatic bidentate ligands; examples include [Co(trien)(bipy)]Cl$_3$[1], [Co(trien)(phen)] Cl$_3$[1], and [Co(tren)(phen)]Cl$_3$[2-4]. These were of particular interest because the introduction of the aromatic ligand to the open coordination sites changed the ^{1}H spectrum of the tetradentate ligand, spreading it into a wider spectral width. A list of common ligand abbreviation, names, and formulas is shown in Table 1.

Complexes containing (2-aminomethyl)pyridine, or 2-picolylamine, are a logical extension of this research. This ligand differs from 2,2-bipyridine and 1,10-phenanthroline in that it contains one aromatic nitrogen donor atom and one aliphatic nitrogen donor atom. In *bis* complexes such as [Co(ampy)$_2$(NO$_2$)$_2$]$^+$ three different isomers are possible, as shown in Figure 1. The α-cis and γ-cis isomers are both symmetrical, making the two pyridine rings equivalent. The β-cis isomer lacks this symmetry, and the two pyridine rings are not equivalent.

These complexes have been studied by several researchers[5-6]. However, only ^{1}H NMR was reported. In a previous publication[7] COSY, HETCOR, and ^{13}C NMR spectra were reported for α-cis [Co(ampy)$_2$(NO$_2$)$_2$]NO$_3$. In the current research the same NMR experiments were performed on the β-cis isomer. Since the β-cis isomer is not symmetrical, this represents an increase in complexity from the previous study.

Table 1. Common Ligand Abbreviations, Names, and Formulas

Name	Abbreviation	Formula
Triethylenetetramine	trien	NH$_2$CH$_2$CH$_2$NHCH$_2$NHCH$_2$CH$_2$NH$_2$
Tris(2-aminoethyl)amine	tren	N(CH$_2$CH$_2$NH$_2$)$_3$
2,2-bipyridyl	bipy	C$_{10}$H$_8$N$_2$
1,10-phenanthroline	phen	C$_{12}$H$_8$N$_2$
(2-aminomethyl)pyridine	ampy	(C$_6$H$_4$N)CH$_2$NH$_2$
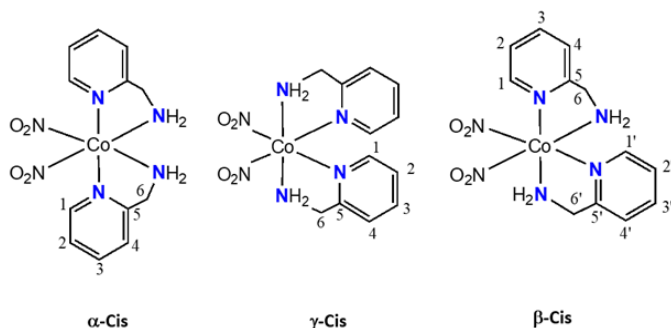
Figure 1. Three Isomers are Possible for [Co(ampy)$_2$(NO$_2$)$_2$]$^+$ ions

Experimental

The synthesis of β-[Co(ampy)$_2$(NO$_2$)$_2$]NO$_3$ was performed as reported by Michelsen [5]. Cobalt nitrate hexahydrate (5.800 g, 0.0200 mol) and sodium nitrite (3.005 g, 0.04355 mol) were dissolved in 10.0 ml of distilled water. Separately, a solution of 2-picolylamine (4.3 mL, 0.042 mol) and concentrated nitric acid (1.6 mL, 0.024 mol) was prepared and cooled in an ice bath. The two solutions were combined in a 125-mL sidearm flask and air was drawn through the resulting solution for one hour. The mixture was then cooled in an ice bath, suction filtered, and the product was washed with acetone. The product was left to air-dry for 1 week, and a yield of 6.419 g was obtained.

A total of three extractions were performed with boiling water to obtain a pure sample of the β-cis isomer, as determined by ^{13}C NMR. In each case the sample was dissolved in the minimal amount of boiling water, cooled on ice, and suction-filtered. The volumes of water used were 160 mL, 140 mL, and 80 mL. The final mass obtained as 1.940 grams.

D$_6$-DMSO (99.9% D) was obtained from Sigma-Aldrich and used as the solvent for all experiments. All NMR experiments were performed on an Anasazi Eft-90 NMR. For ^{1}H spectra 3-(trimethylsilyl)-1-propanesulfonic acid (DSS) was added as a chemical shift reference; for ^{13}C the solvent peak was used and assigned a value of 39.5 ppm[8].

Results and Discussion

The ^{13}C spectrum is shown in Figure 2, the HETCOR in Figure 3, and the COSY in Figure 4. The ^{13}C resonances are tabulated in Table 2, along with their proton correlations (from the heteronuclear correlation spectrum).

Before delving into a detailed analysis, some general features of the ^{13}C spectrum should be noted. First, the spectrum is divided into sets of two peaks, presumably from the same carbon atoms in the two different rings. This would seem to be corroborated by the fact that the chemical shift of the observed sets of peaks corresponds closely with previously reported spectrum of the α-cis isomer[7]. A comparison of ^{13}C chemical shifts of the two isomers is shown in Table 3.

Second, it is reasonable to expect that the chemical shift dif-

ference between the sets of peaks would be greatest closest to the coordination sites. In other words, the distance between the resonances arising from C1 and C1´ and between C5 and C5´ should be greatest because they are closest to the coordination sites. Furthermore, since proximity to the donor atoms should result in a downfield chemical shift, the spacing between the pairs of signals should be furthest apart downfield and become closer together moving upfield. This was, in fact, what was observed.

Finally, it should be noted that spectrum might initially appear to contain the incorrect number of signals. A total of ten signals should be present in the aromatic region, and only eight are observed. At first it was believed that C5 and C5´ might not be present. However, a second spectrum acquired with long delay time failed to show any additional peaks. As explained below it is believed that the low-field spectrometer used failed to resolve all of the resonances.

Beginning the assignments, the signals at 163.995 and 165.401 ppm (difference of 1.406 ppm) were assigned to C5 and C5´. These did not show a correlation to any ^{1}H resonances, and are shifted furthest downfield, which suggests that they are adja-
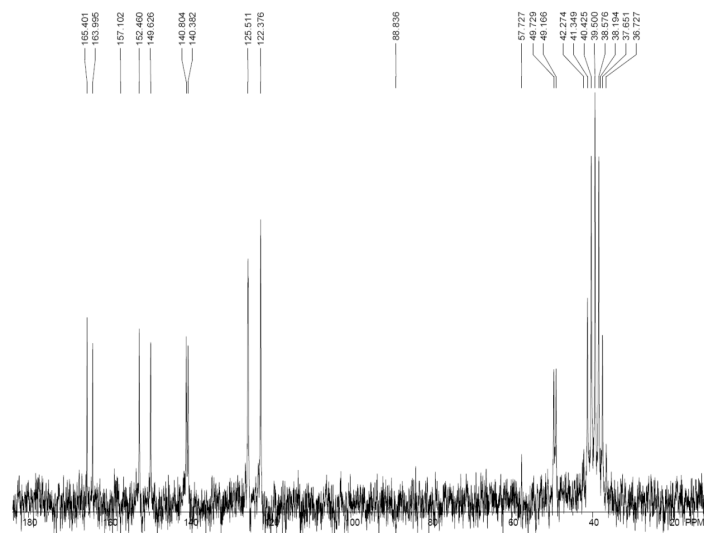
cent to the nitrogen donor atoms.

Next, the signals at 152.460 and 149.626 and ppm (difference of 2.834 ppm) were assigned to C1 and C1´. This assignment was made based on the spacing of the signals as well as the downfield chemical shift. Additionally, a proton doublet was located at approximately 9.0 ppm, which was assigned to H1 or H1´ on the basis of multiplicity, showed a correlation to the ^{13}C signal at 152.460.

The signals at 140.804 and 140.382 ppm (difference of 0.443 ppm) were assigned to C2 and C2´. The above-mentioned pro-

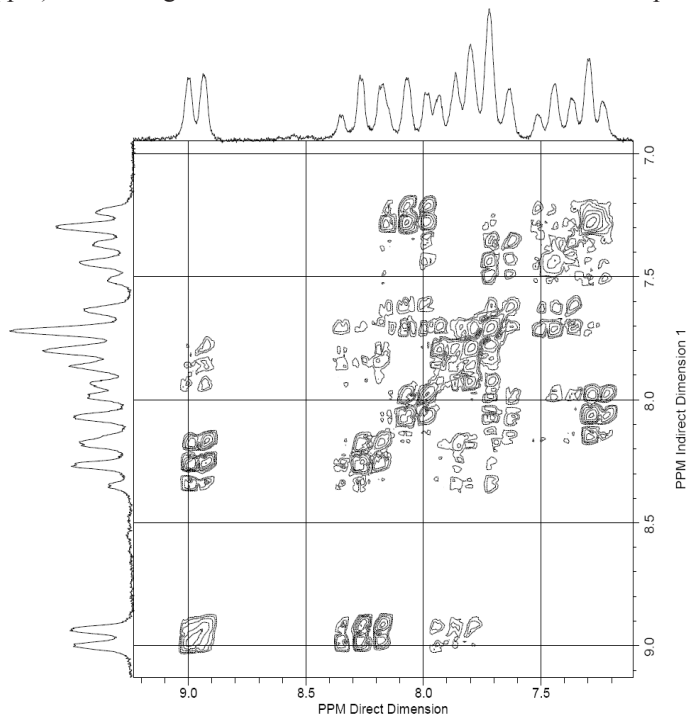**Figure 2**. ^{13}C Spectrum of $[Co(ampy)_2(NO_2)_2]NO_3$
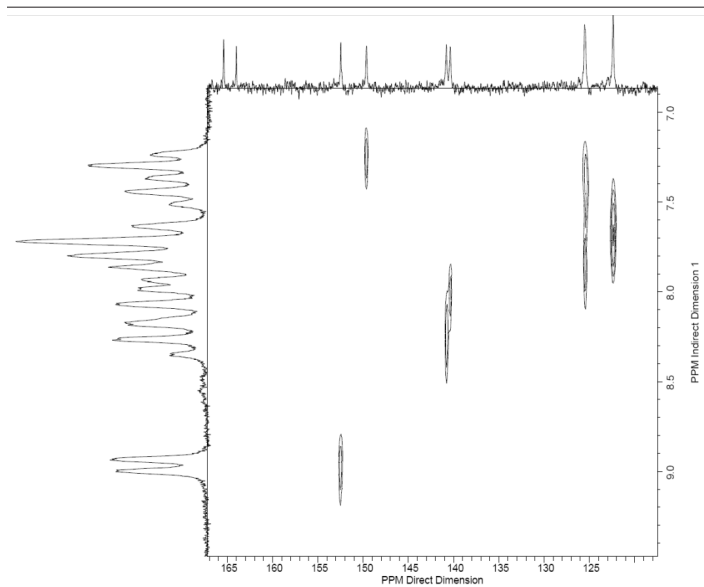
Figure 3. Heteronuclear Correlation Spectrum of $[Co(ampy)_2(NO_2)_2]NO_3$

Figure 4. COSY Spectrum of $[Co(ampy)_2(NO_2)_2]NO_3$

Table 2. Summary of ^{13}C chemical shifts and ^{13}C-^{1}H correlations

^{13}C Chemical Shift (ppm)	^{1}H Correlation (approximate, ppm)	Assignment
49.166	4.3	C6 or C6´
49.729	4.3	C6 or C6´
122.376	7.7	C3/C3´ or C4/C4´
125.511	7.4, 7.9	C3/C3´ or C4/C4´
140.382	8.1	C2 or C2´
140.804	8.3	C2 or C2´
149.626	7.3	C1 or C1´
152.460	9.0	C1 or C1´
163.995	None	C5 or C5´
165.401	None	C5 or C5´

Table 3. Comparison of ^{13}C Chemical Shift in α-cis and β-cis isomers (ppm)

β-cis isomer	α-cis isomer
49.166	49.253
49.729	
122.376	122.258
125.511	124.385
140.382	140.319
140.804	
149.626	150.914
152.460	
163.995	166.727
165.401	

ton doublet at approximately 9.0 ppm showed a cross peak in the COSY spectrum to another resonance at 8.2-8.3 ppm. These are the only two carbon signals to show any correlation to this region of the proton spectrum.

This leaves only the signals at 125.511 and 122.376 ppm. These are larger than the others, and it is believed that these are actually pairs of resonances that failed to be resolved. This is supported by the decreasing distance between pairs of signals moving downfield. Additionally, the carbon resonance at 125.511 ppm shows two different proton correlations in the heteronuclear correlation spectrum. Clearly, then, the signals at 125.511 and 122.376 ppm do arise from multiple carbon atoms. However, it was not possible to determine which arises from C3/C3′ and which arises from C4/C4′.

Some connectivities between the ^{13}C signals can be established by using the COSY and HETCOR spectra together. For example, it was already noted that in the COSY spectrum, cross peaks were observed between the regions at approximately 9.0 and 8.2-8.3 ppm. These two regions of the ^{1}H spectra correlate to ^{13}C signals at 152.460 and 140.804 ppm, establishing that these arise from adjacent carbon atoms. In a similar fashion, the COSY spectrum shows cross peaks between the regions at 7.3 ppm and 8.0 ppm. These two regions of the ^{1}H spectrum correlate to ^{13}C signals at 149.626 and 140.382 ppm, establishing that these rise from adjacent carbon atoms. However, it is *not possible to assign signals to a specific ring.*

Conclusions

The compound β-$[Co(ampy)_2(NO_2)_2]NO_3$ was isolated; the ^{1}H, ^{13}C, HETCOR, and COSY experiments were performed. Partial assignments were made in the ^{1}H and ^{13}C spectra of β-$[Co(ampy)_2(NO_2)_2]NO_3$. The ^{13}C resonances could be assigned in sets, and some connectivities could be established, but it was not possible to assign individual resonances. Furthermore, not all of the ^{13}C resonances could be resolved.

There are several directions in which this research might continue. What is needed is a way to assign one resonance (either ^{1}H or ^{13}C) to one specific ring; from there many specific assignments could be made. This might be accomplished by comparing the spectra obtained here to that of the other isomers. For example, while the ^{13}C spectra of the α-cis and β-cis isomers are similar, the ^{1}H spectra are different. The ^{1}H doublet observed here for the β-cis occurs at 9.0 ppm but in the α-cis isomer it occurs at only 8.5 ppm[7]. This *might* be used to differentiate the rings in different chemical environments, but more data is needed. The complete picture might be obtained from the γ-cis isomer, as the rings are in the same chemical environment (*trans* to the NH_2 groups) as *one* of the rings in the β-cis isomer.

Last, the study could greatly be enhanced with high-field spectra. This would greatly reduce the amount of overlap in both the ^{13}C and ^{1}H spectra.

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