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# Synthesis and Characterization of a New Functionalized Metal-Ligand Complex, $[Co(4\text{-}brbpy)_3]^{3+}$

Ronnie Keller
Chemistry
The University of North Carolina Asheville
One University Heights
Asheville, North Carolina 28804 USA

Faculty Advisor: Dr. Jason Schmeltzer

### Abstract

Cobalt complexes formed from 2,2’-bipyridine (bpy) have been used to study electron transfer mechanisms, facilitate redox reactions in solar cells, and catalyze the reduction of alkynes. However, there is comparatively less research into the preparation and use of functionalized cobalt-bpy complexes, notably those that could serve as reactants for additional chemical synthesis. In this research, a scheme for the synthesis and characterization of the as-yet unreported functionalized complex $[Co(4\text{-}brbpy)_3]^{3+}$ (4-brbpy = 4-bromo-2,2’-bipyridine) is proposed. The synthesis of this complex resembles that previously published for the related complex $[Co(4\text{-}fbpy)_3]^{3+}$ (4-fbpy = 4-fluoro-2,2’-bipyridine) with modifications to the scheme developed over time. Characterization of the synthesized product is carried out by ultraviolet/visible (UV/vis) absorption spectrophotometry and primarily by proton nuclear magnetic resonance ($^1H$ NMR) spectroscopy. Analysis of $^1H$ NMR spectra and accompanying COSY spectra suggest the precipitated solid product is the target $[Co(4\text{-}brbpy)_3]^{3+}$ complex. Spectroscopic measurements of $[Co(4\text{-}brbpy)_3]^{3+}$ are compared to those of the unfunctionalized complex $[Co(bpy)_3]^{3+}$ to understand how functionalization of the bpy ligand changes the $\delta^1H$ properties of these complexes.

## 1. Introduction

Metal-ligand complexes are coordination compounds in which a metal is centrally positioned and bound between multiple molecules referred to as ligands. The selective properties of the complex depend upon the identity of the metal and its oxidation state, the specific ligands used in coordination, and the geometry of the ligands around the metal. A large amount of research literature exists for transition metal-ligand complexes, though specific research of cobalt and functionalized 2,2'-bipyridine (bpy) containing complexes is underrepresented. Cobalt was chosen for study due to its immediate availability in the research laboratory and commercial affordability.

Metal-ligand complexes synthesized with the ligand bpy have been studied for the electron transfer between complexes,[1] as redox mediators for dye-sensitized solar cells,[2] and as catalysts for reduction of terminal alkynes to alkenes[3]. The bpy molecule itself is relatively simple and small compared to other ligands used in complex synthesis; e.g. 1,3-bis(2,4,6-trimethylphenyl)imidazolium is a bulky ligand with several substituents and a molar mass twice that of bpy. The bpy ligand is an L-type ligand, meaning that it coordinates to the metal cation via a Lewis acid-base reaction where both sigma bond electrons come from the ligand. More specifically, bpy is a bidentate ligand meaning it forms two bonds with the metal atom; all four bonding electrons come from the lone pair on the nitrogen atom of each pyridine ring at positions 1 and 1' (Figure 1). Without altering the ligand coordinations, the unmodified bpy complexes are generally unreactive in further chemical synthesis owing to bpy's most reactive sites, the nitrogens, being occupied by coordination to the metal. The lack of reactivity may be remedied through functionalization of the bpy that will primarily occur at the 4-position due to its steric accessibility. Complexes made with 4-bromo-2,2’-bipyridine (4-brbpy) may act as a substrate and transform functional groups to new moieties,[4] specifically in Grignard reactions.[5] They may also crosslink with similar or different complexes to form polymers.[6]

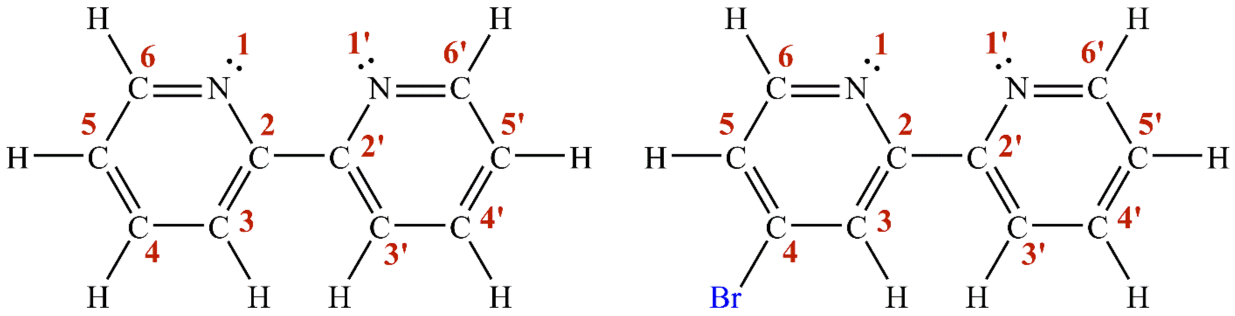

Figure 1. bpy (left) and 4-brbpy (right), molecular positions are numbered

It was decided to synthesize tris(4-bromo-2,2'-bipyridine)cobalt(III), abbreviated [Co(4-brbpy)$_3$]$^{3+}$, with a bromine functionalization at position 4 of the bpy. Given its simplicity in terms of having a single ligand in *tris* around the metal, it is curious to discover it has never been made. Such a complex could be reactive due to its functionalized ligands and serve as a substrate in additional chemistry. Another boon to the simplicity of [Co(4-brbpy)$_3$]$^{3+}$ is that due to its homoleptic nature, referring to all ligands having the same identity, any observed change in characterization between the functionalized bpy complex vs its unfunctionalized counterpart can be rationally attributed to the monosubstituted bromine; all three ligands will contribute equally and exclusively to any observed changes due to there being no other chemical species present as opposed to heteroleptic complexes with multiple ligands of different identities.

Given the similarities to existing complexes, the [Co(4-brbpy)$_3$]$^{3+}$ complex is anticipated to have octahedral molecular geometry with three 4-brbpy molecules occupying all six coordination sites on the cobalt. As is characteristic of metals with this geometry, the cobalt's outermost electron shell possesses 18 electrons, calculable via the neutral ligand and closed shell electron counting methods.[7]

Facial (*fac*) and meridional (*mer*) are geometric isomers that arise from having three monodentate ligands of the same identity in an octahedral species. Though 4-brbpy is a bidentate ligand, there are two different pyridine rings, but one is functionalized at the 4-position with a bromine and the other has a hydrogen in the 4-position. Thus it acts as two different monodentate ligands for the sake of isomerization. When a triangle is theoretically drawn linking the similar pyridines it will be either along the face of the octahedral geometry, in which case it is *fac*, or it will run through the center of the geometry, in this case *mer* (Figure 2). See Figure 3 for three-dimensional software generated *fac* and *mer* isomers of [Co(4-brbpy)$_3$]$^{3+}$.

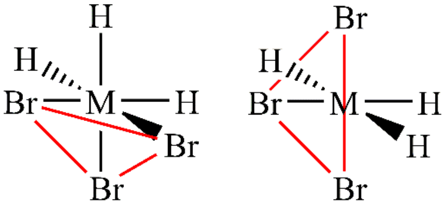

Figure 2. Isomers *fac* (left) and *mer* (right), metal (M), ligands (Br, H)

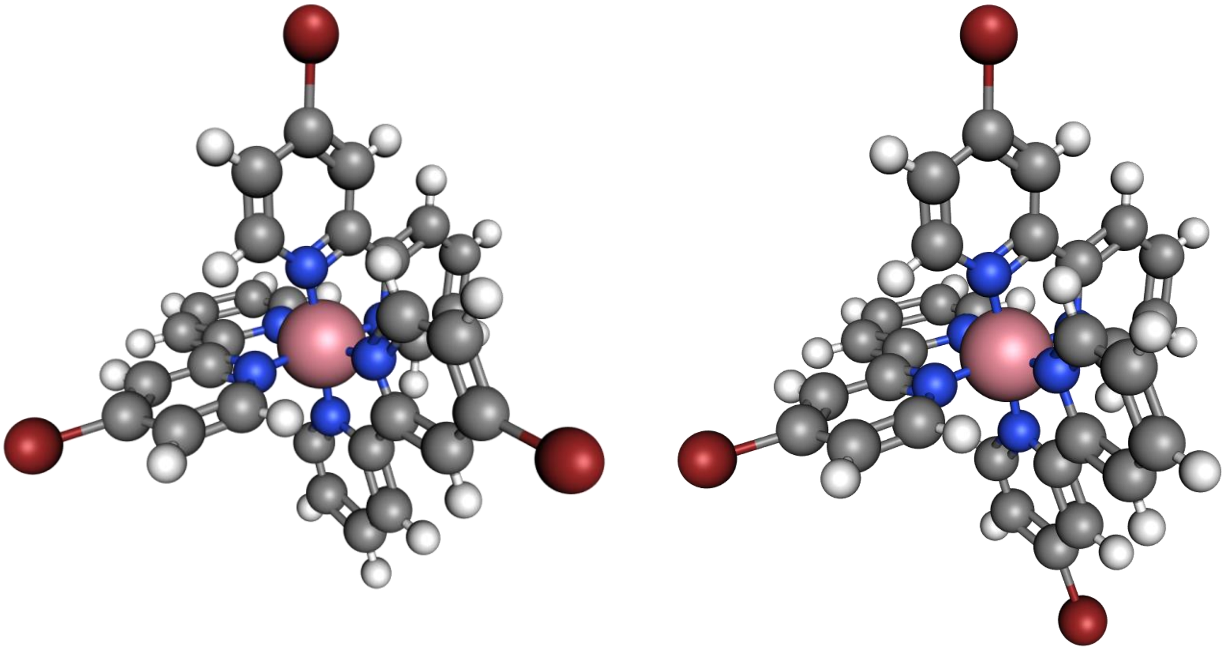

Figure 3. Isomers *fac* (left) and *mer* (right) for [Co(4-brbpy)$_3$]$^{3+}$, Co (pink), C (gray), N (blue), H (white), Br (red)

## 2. Background

Surprise at the lack of report for [Co(4-brbpy)$_3$]$^{3+}$ exists in that a nearly identical complex, [Co(4-fbpy)$_3$]$^{3+}$ (4-fbpy = 4-fluoro-2,2'-bipyridine) where the ligand is monosubstituted by a fluorine, has been reported and characterized by multiple NMR spectroscopic methods. This research, carried out by Fanqi Qu and colleagues, proposed a simple synthetic scheme for the complex in which a cobalt chloride precursor was aqueously dissolved with 4-fbpy reagent; the solution is oxidized with $H_2O_2$ and then precipitated. Qu's research studied the electron transfer mechanism of the cobalt(III) complex where it receives an electron from a similar cobalt(I) complex along a hydroxo-bridge resulting in two cobalt(II) complexes.[1] It is from Qu's paper that this research is largely inspired.

Cobalt-bpy complexes' use in solar power is a growing field of research. The [Co(bpy)$_3$]$^{3+}$ complex has been effectively applied as a redox mediator within dye-sensitized solar cells.[2] Photons from sunlight excite the dye electrons causing them to flow through titanium dioxide nanoparticles thus forming a gradient and producing a current. The current is collected and the electrons are reintroduced to the cell where [Co(bpy)$_3$]$^{3+}$ picks them up, becoming [Co(bpy)$_3$]$^{2+}$, and delivers the electrons back to the dye for a repeat of the cycle. This research of [Co(4-brbpy)$_3$]$^{3+}$ may provide another effective redox mediator for the study of dye-sensitized solar cells.

When [Co(bpy)$_3$]$^{2+}$ is photochemically reduced to [Co(bpy)$_3$]$^{1+}$, it becomes more reactive and will swap one of its ligands for a more electronically dense source. In the presence of an alkyne, such as phenylacetylene, a bpy will leave [Co(bpy)$_3$]$^{1+}$ and the cobalt will coordinate to the alkyne's triple bond.[3] In acidic conditions, the alkyne will be reduced to an alkene then uncoordinate from the cobalt, allowing the bpy ligand to recoordinate. Functionalization of the bpy ligand, such as in [Co(4-brbpy)$_3$]$^{2+}$, may affect the kinetic properties of reductions such as these.

Synthesis of [Co(4-brbpy)$_3$]$^{3+}$ was modeled after the general scheme of the similar reported complex, [Co(4-fbpy)$_3$]$^{3+}$. The scheme for the reported complex was adapted to synthesize the target complex and modified over time to be more efficient (Figure 4).

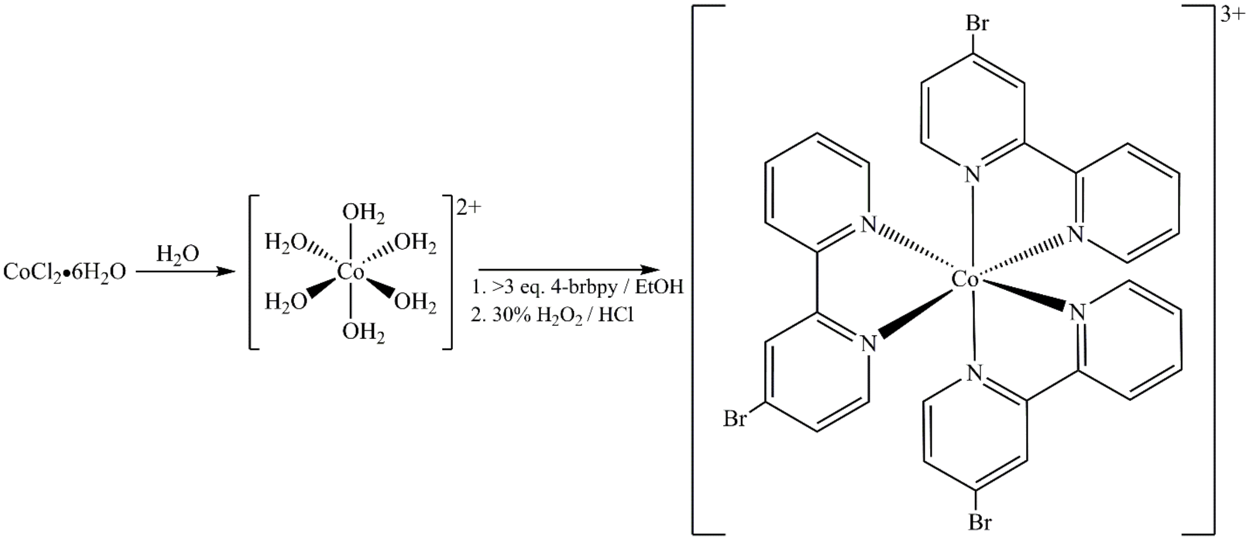

Figure 4. Synthetic scheme of $[Co(4\text{-brbpy})_3]^{3+}$ from a hexaaquacobalt(II) precursor

## 3. Experimental

IR analyses were acquired on a Thermo Scientific Nicolet iS10 FT-IR. UV/vis absorption analyses were acquired on a Shimadzu UV-1800. NMR analyses were acquired on a Varian Inova 400MHz. $CoCl_2 \cdot 6H_2O$, bpy, 4-brbpy, 30% $H_2O_2$, conc. HCl, $NaPF_6(s)$, $NaBF_4(s)$ and all solvents and rinses were obtained commercially. All mention of $H_2O$ pertains to deionized water.

### 3.1. Preparation of Saturated $NaPF_6(aq)$ Precipitating Agent

In a 2:1 ratio 4g $NaPF_6(s)$ was dissolved in 2g $H_2O$. This was done in excess of an hour before the precipitation step to ensure $NaPF_6(s)$ was adequately dissolved with some solid remaining insoluble.

### 3.2. Synthesis of $[Co(bpy)_3](PF_6)_3$

An aqueous hexaaquacobalt, $[Co(H_2O)_6]^{2+}(aq)$, solution was made by dissolving 0.12g (0.5mmol) $CoCl_2 \cdot 6H_2O$ in 10mL water in a 50mL beaker. This hexaaquacobalt solution is pink in color. To the hexaaquacobalt solution 0.26g (1.7mmol) bpy was added and dissolved over heat. Solution turned brownish-yellow. Some undissolved particles were present. Next, 0.5mL 30% $H_2O_2$ immediately followed by 0.5mL HCl were added to the solution dropwise by pipet. Upon addition of $H_2O_2$ and HCl, the previously mentioned foreign material dissolved. The temperature was raised higher from the previous setting, though kept below simmering. By recount of the reference synthesis by Qu, the solution is left over heat until it becomes viscous and “syrupy”, a marker of the oxidation.[1] This step took approximately 90min and the solution became orange-yellow. 10mL $H_2O$ was added as a precipitating medium. The saturated $NaPF_6$ was then delivered dropwise by pipet evenly over the solution until it no longer precipitated. The precipitated solid was vacuum filtered on a coarse fritted funnel. Water was used to rinse all solid from the beaker and onto the funnel. While still on vacuum the solid was washed dropwise with $H_2O$, then ethanol, and lastly diethyl ether. Product solid is bright yellow and was collected in a vial. The open vial was placed within a Büchner flask that was plugged and left on vacuum for minimum 12hrs for drying.

### 3.3. Preparation of Saturated $NaBF_4(aq)$ Precipitating Agent

3.265g $NaBF_4$ was dissolved in 5mL $H_2O$. See section in “Results and Discussion” regarding saturated $NaBF_4(aq)$. The precipitating agent was incorrectly prepared. Though effective in its application, it proved inefficient which is reflected by the poor synthesis yield.

### 3.4. Synthesis of $[Co(4\text{-brbpy})_3](BF_4)_3$

An aqueous $[Co(H_2O)_6]^{2+}$ solution was made by dissolving 0.1487g (0.625mmol) $CoCl_2{\cdot}6H_2O$ in 5mL $H_2O$ in a 50mL round bottom flask. Separately, 0.5g (2.125mmol) 4-brbpy was dissolved in absolute EtOH. The two solutions were mixed and then refluxed without stirring for 30 minutes. The now brown solution was allowed to cool to room temperature. Via pipet, 0.625mL 30% $H_2O_2$ followed by 0.625mL conc. HCl were added dropwise. The solution was left to react on light heat for 4 hours and experienced an obvious decrease in volume but, unlike the synthesis of $[Co(bpy)_3]^{3+}$, did not appear viscous or "syrupy". The solution ended up yellow in color. 10mL $H_2O$ was added to provide a medium for precipitation. Upon this addition of $H_2O$, a floating brown/gray solid formed at the top of the solution and another sedimentary solid formed at the bottom of the flask. These solids were filtered out on a coarse fritted funnel; the filtrate was collected to continue the synthesis. The solution was precipitated with the prepared $NaBF_4$(*aq*). All prepared precipitating agent was consumed, and the solution seemed to still precipitate. Precipitated solid was filtered on a coarse fritted funnel then washed with $H_2O$ and EtOH. The beige solid was collected in a vial and dried in the same vacuum apparatus as that of the $[Co(bpy)_3](PF_6)_3$ synthesis. This synthesis netted a 34.21% yield.

## 4. Results and Discussion

The functionalized ligand, 4-bromo-2,2'-bipyridine, is commercially available but is very expensive ($360/g). Therefore, it is important that the general practice of no ligand wasted is in place. The synthetic scheme this research has adapted is undetailed. Multiple trials were performed to first troubleshoot and then refine the synthetic techniques before actual synthesis of the target complex was performed. These trials were the synthesis of the unfunctionalized $[Co(bpy)_3]^{3+}$ complex. In solid phase, this complex's form is $[Co(bpy)_3](PF_6)_3$ in which three $PF_6^-$ ions balance the charge on the complex. Three separate syntheses were performed for $[Co(4\text{-brbpy})_3]^{3+}$, the last of which was altered from the first two and reported in "Experimental".

Literature search did not find the saturation point for $NaPF_6$ in water. A small-scale preliminary experiment was performed in which the saturation point of aqueous $NaPF_6$ was tested. Adequate saturation of $NaPF_6$ in water was found to occur in an approximate 2:1 ratio by mass at standard conditions, but it must be prepared fresh. It was discovered that storing saturated $NaPF_6$ for only a few days will result in a black gooey solid forming at the bottom of the saturated solution. Saturated $NaPF_6$ was used for precipitation in the syntheses of $[Co(bpy)_3]^{3+}$ and the first two syntheses of $[Co(4\text{-brbpy})_3]^{3+}$.

There was concern that small molecules might become trapped within the lattice of $[Co(4\text{-brbpy})_3](PF_6)_3$ due to the large size of the $PF_6^-$ anions and result in impurities. Molecules suspected to be susceptible to trapping are $H_2O$, $H_2O_2$, EtOH, and $Cl^-$ ions. For the latest synthesis of $[Co(4\text{-brbpy})_3]^{3+}$, saturated $NaBF_4$ was used to alleviate the molecule trapping concern; the $BF_4^-$ ions are smaller in size. In the preparation of saturated $NaBF_4$, a reference solubility of 97.3g / 100mL $H_2O$ was used. Multiple other references have proven this incorrect and the wrong reference can no longer be located. The correct solubility is 108g $NaBF_4$ / 100mL $H_2O$.[8]

Regarding the synthesis of $[Co(4\text{-brbpy})_3](BF_4)_3$, the yield was low (34.21%). It is expected that some potential product was lost during the unplanned filtration of the solid that formed during the addition of water before precipitation. Also, the solution was still precipitating when the prepared amount of $NaBF_4$(*aq*) was fully consumed. It is likely not all product was precipitated. Also supporting this was the filtrate color matching that of the precipitating solution (yellow). There were small impurities in the $^1H$ NMR that are attributed to the unplanned solid that was filtered out, however their integrations were not appreciable.

There was concern that $H_2O_2$ might oxidize the bromo functional group on 4-brbpy. No literature was found where $H_2O_2$ was used to oxidize aromatic bromo substituents. On the contrary, it is used in the bromination of aromatic rings[9] and other organic substrates.[10] To be absolutely certain, a side experiment was performed where 4-brbpy reagent was dissolved in EtOH. To this solution $H_2O_2$ and HCl were added and heat was applied to simulate the synthesis oxidation step. The 4-brbpy solid was recovered by rotary evaporation. This solid was analyzed with $^1H$ NMR and the spectrum matched that of the original 4-brbpy proving that no change had occurred.

## 4.1. IR Analyses

An infrared analysis was done for bpy and resembled that of a reference spectrum.[11] Infrared spectrums were also acquired for the 4-brbpy reagent and the $[Co(bpy)_3](PF_6)_3$ and $[Co(4\text{-}brbpy)_3](BF_4)_3$ products, but did not prove to be useful; the only easily identifiable peaks were generic aromatic carbon-carbon and carbon-hydrogen stretching and bending.

## 4.2. UV/vis Absorption Analyses

UV/vis absorption spectra were acquired for 0.001M samples of $CoCl_2$, $[Co(bpy)_3](PF_6)_3$, and $[Co(4\text{-}brbpy)_3](BF_4)_3$. Because the products were not soluble in water, the absorption analyses were done in $CH_3CN$. Additionally, $[Co(bpy)_3](PF_6)_3$ is poorly soluble in $CH_3CN$ and its sample was notably less than 0.001M. The complexes proved to absorb very strongly in the ultraviolet region. They both have a visible peak in the violet region which explains the yellowish coloration of the products. Large tailing from the strong ultraviolet absorption makes the visible peak for $[Co(bpy)_3](PF_6)_3$ impossible to pin-point, though it can be narrowed down to 400-450nm. The visible peak for $[Co(4\text{-}brbpy)_3](BF_4)_3$ is located at 451nm. Despite the $[Co(bpy)_3](PF_6)_3$ sample being less than 0.001M, it has over double the absorption at 451nm (0.2163) than $[Co(4\text{-}brbpy)_3](BF_4)_3$ at 451nm (0.0992) which suggests the bromo functionalization on bpy decreases the absorptive capacity of the cobalt complex.

## 4.3. $^1$H NMR Analyses

$^1$H NMR analyses were originally performed in deuterated DMSO but, due to DMSO's high freezing point, were redone with deuterated acetonitrile ($CD_3CN$). A lower freezing point allowed longer NMR analyses to be performed without samples freezing, COSY in particular. All $^1$H NMRs were updated with $CD_3CN$ using the most recently synthesized samples. $^1$H NMR signal location data is presented in Table 1.

Table 1. $\delta^1$H (ppm) of bpy and 4-brbpy ligands and their respective complexes

| **Compound** | **$^1$H 3** | **$^1$H 3'** | **$^1$H 4'** | **$^1$H 5** | **$^1$H 5'** | **$^1$H 6** | **$^1$H 6'** |
|---|---|---|---|---|---|---|---|
| **bpy** | -- | 8.41 | 7.86 | -- | 7.36 | -- | 8.64 |
| **4-brbpy** | 8.55 | 8.36 | 7.87 | 7.55 | 7.39 | 8.47 | 8.64 |
| **$[Co(bpy)_3](PF_6)_3$** | -- | 8.68 | 8.47 | -- | 7.72 | -- | 7.27 |
| **$[Co(4\text{-}brbpy)_3](BF_4)_3$** | 8.94 | 8.68 | 8.49 | 7.92 | 7.76 | 7.10[a] | 7.32[a] |

Each $\delta^1$H is reported as the average of each signal's outermost peaks

[a] $\delta^1$H is averaged from two separate, congruent signals

### *4.3.1. bpy*

An experimental $^1$H NMR spectrum was obtained for bpy reagent that closely resembles a reference spectrum.[12] On bpy there are eight total protons, but due to bpy's symmetry there are only four unique protons which suggest four total signals (labeled 3'-6', Figure 1). Proton (3') appears as a doublet, (4') as a triplet, (5') as a triplet, and (6') as a doublet. See Table 1 for signal locations.

### *4.3.2. $[Co(bpy)_3](PF_6)_3$*

The $^1$H NMR for $[Co(bpy)_3](PF_6)_3$ resembles the bpy spectrum in that there are only four signals of similar shape. On the complex there are a total of 24 protons, but due to homolepticity there are only four unique protons (labeled 3'-6', Figure 1). Combined with data from the COSY for $[Co(bpy)_3](PF_6)_3$, it is concluded that proton (3') experienced a downfield shift of 0.27 ppm, (4') experienced a downfield shift of 0.61 ppm, (5') experienced a downfield shift of 0.36 ppm, and (6') experienced an upfield shift of 1.37 ppm. See Table 1 for signal locations. All signals in $[Co(bpy)_3](PF_6)_3$ retained the shape of their counterpart signal in bpy. Shifts in $\delta^1$H and changes in the order of proton signals are likely due to coordination to the cobalt cation in which electron density was pulled away from the ligand via the nitrogen lone pairs. Another factor may be weak interactions between individual bpy ligands due to their close proximity to each other around the cobalt.

### *4.3.3. 4-brbpy*

A $^{1}$H NMR spectrum of the 4-brbpy reagent was taken to compare to the $[Co(4\text{-}brbpy)_3]^{3+}$ product. With the addition of the bromo substituent in 4-brbpy there are seven hydrogens, all of which are unique suggesting seven discrete signals in the spectrum. This is supported by the acquired spectrum for 4-brbpy which shows seven signals of equal integration. A coinciding COSY and a reference spectrum aided in labeling protons.[13] See protons labeled on 4-brbpy molecule (Figure 1). Protons (3'-6') on 4-brbpy (those on the unfunctionalized pyridine ring) appear at the same position with similar shapes to protons (3'-6') on bpy. This is consistent with Qu's NMR comparisons of bpy and 4-fbpy.[1] This suggests the bromine substitution only affects the protons on its corresponding pyridine ring. Proton (3) appears as a singlet, (5) as a doublet, and (6) as a doublet. See Table 1 for signal locations.

### *4.3.4. $[Co(4\text{-}brbpy)_3](BF_4)_3$*

A $^{1}$H NMR spectrum of synthesized $[Co(4\text{-}brbpy)_3](BF_4)_3$ was acquired (Figure 5). There are 21 protons on the complex, seven of which are unique (see 4-brbpy, Figure 1). Signals for protons (3-5, 3'-5') of $[Co(4\text{-}brbpy)_3](BF_4)_3$ resemble those of 4-brbpy in shape and integration. Signals for protons (6) and (6') of are split into widely spaced doublets that are identical in shape and integration. The compounded integration for the two complementary signals attributed to proton (6) matches that of protons (3-5, 3'-5'), likewise for proton (6'). The COSY (Figure 6) shows that both signals for proton (6) share the same neighbor, proton (5); the signals for proton (6') share a neighbor in (5'). After appropriate assignment of signals, it was concluded that proton (3) experienced a downfield shift of 0.39 ppm, (3') experienced an upfield shift of 0.32 ppm, (4') experienced a downfield shift of 0.62 ppm, (5) experienced a downfield shift of 0.37 ppm, (5') experienced an upfield shift of 0.37 ppm, (6) experienced an upfield shift of 1.37 ppm and split into two wide spaced doublet-doublets, and (6') experienced an upfield shift of 1.32 ppm and split into two widely spaced doublets. See Table 1 for signal locations.

Shifts are attributed to the delocalization of the nitrogen lone pairs from the 4-brbpy during coordination to cobalt and the expected loose interactions between ligands around the complex. As with bpy and $[Co(bpy)_3](PF_6)_3$, protons (3'-6') for 4-brbpy and $[Co(4\text{-}brbpy)_3](BF_4)_3$ appear at nearly the same location. Also, the proton shifts from 4-brbpy to $[Co(4\text{-}brbpy)_3](BF_4)_3$ for the bromo-functionalized ring are approximately equal to their mirrored counterparts on the unfunctionalized ring: protons (3) and (3') shifted 0.36 and 0.32 ppm downfield respectively, (5) and (5') both shifted 0.37 ppm downfield, (6) and (6') shifted 1.37 and 1.32 ppm upfield. The similar shifting pattern is evidence that coordination to the cobalt affects both rings in 4-brbpy equally.

The behavior of the wide splitting of protons (6) and (6') in this spectrum may be attributed to the geometric isomers *fac* and *mer* that were predicted in the complex. In the case of *fac*, all bromine atoms are on one side of the complex resulting in a more unequal distribution than for *mer*, in which there are two bromines in-line with the complex center and a third bromine off to the side. The different distributions of bromine around the complex create two separate environments which uniquely affect the protons. The signals for protons (5) and (5') do not behave as extremely, but they both seem to exhibit very minor splitting resulting in peak overlap. This overlap makes the signal shape rougher and more difficult to discern. The overlap is not apparent for protons (3, 3', 4') which suggests isomerism affects protons in a depreciative manner the farther from the complex center that they are positioned. Equal integrations of the doublets of (6) and (6') may suggest a geometric isomerism ratio of 1:1.

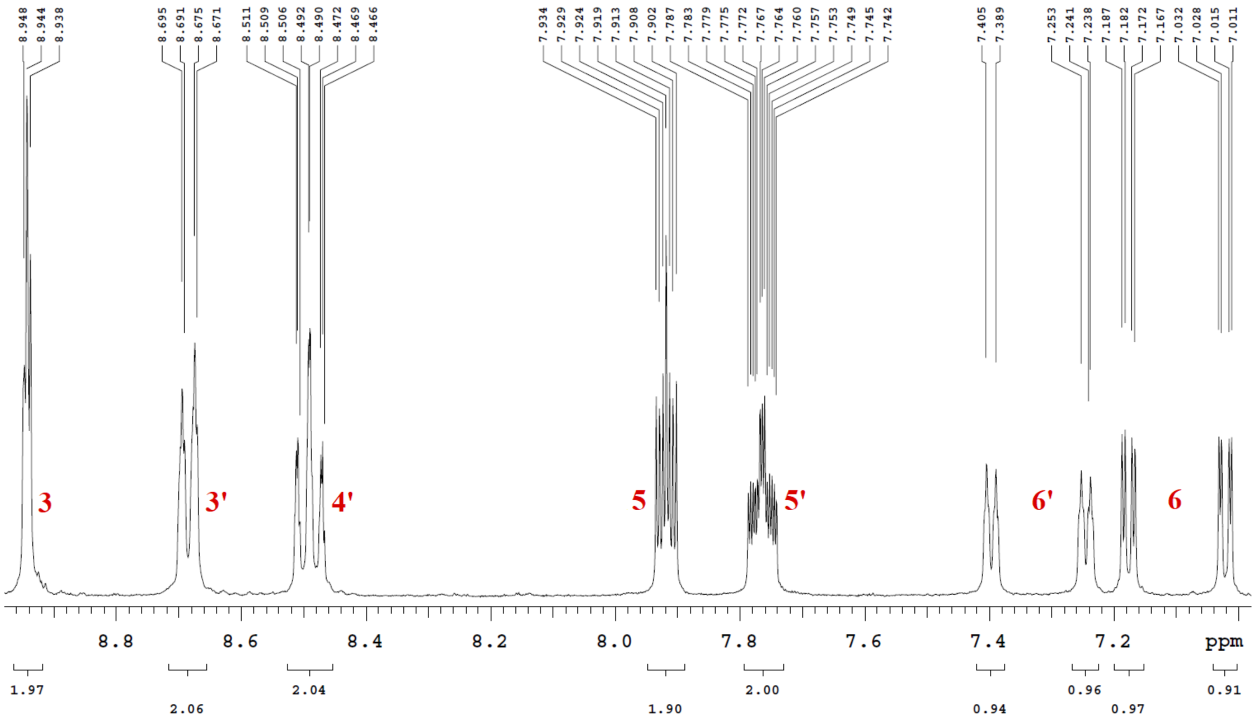

Figure 5. $^1$H NMR spectrum of [Co(4-brbpy)$_3$](BF$_4$)$_3$ in CD$_3$CN with proton labeled signals

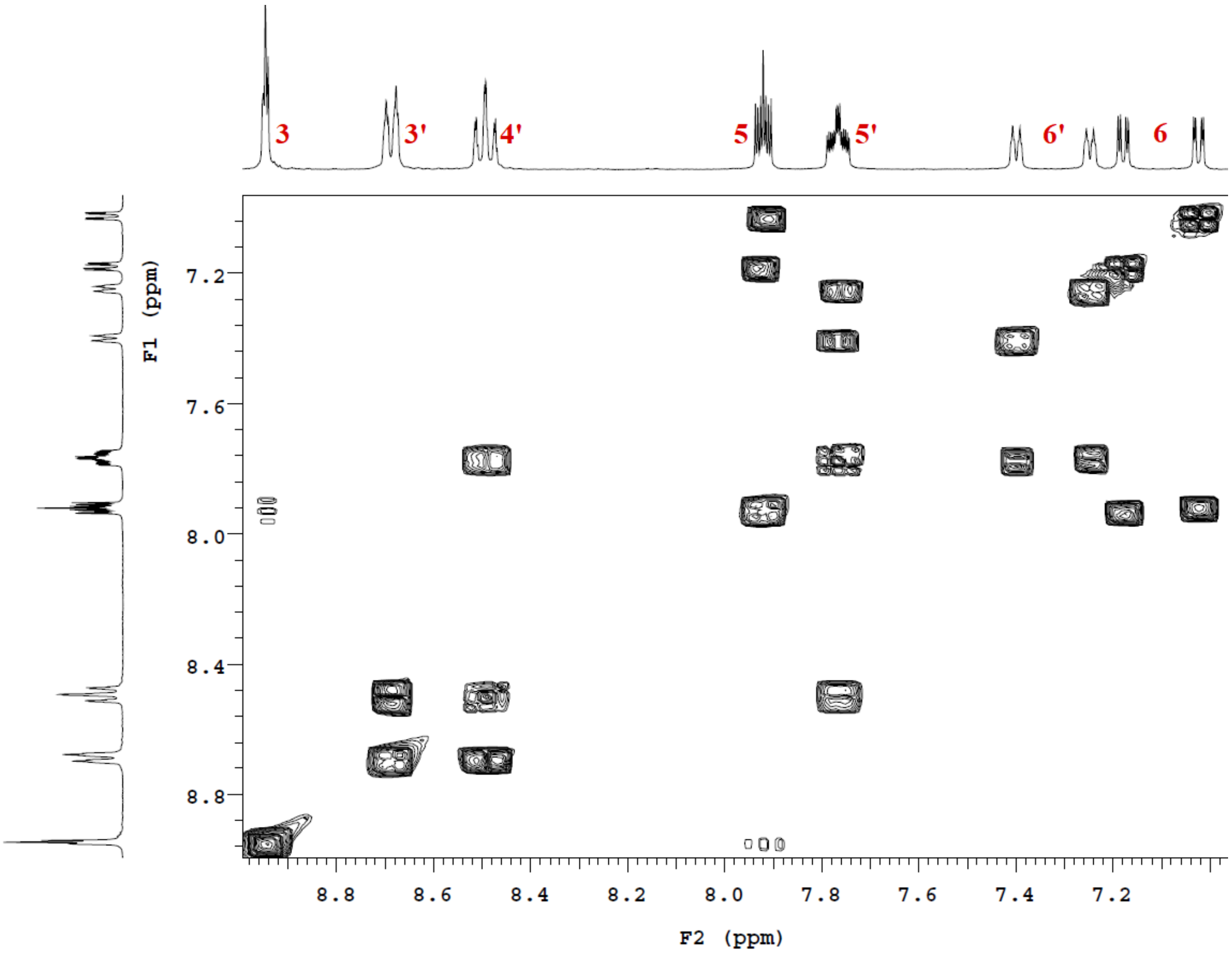

Figure 6. 2D COSY $^1$H NMR spectrum of $[Co(4\text{-}brbpy)_3](BF_4)_3$ in $CD_3CN$ with proton labeled signals

## 5. Conclusion

It cannot be determined with absolute certainty that 4-brbpy coordinates around cobalt in octahedral fashion without performing an advance structural analysis such as single crystal x-ray diffraction, which is not available at this facility. However, several other octahedral complexes of cobalt and different bpy derivatives are reported which strongly suggest a similar geometry for cobalt and 4-brbpy. There is no reason to suspect a tetrahedral or linear geometry.

$^1$H NMR spectra provide sufficient evidence that 4-brbpy successfully and exclusively coordinates to cobalt in the given synthetic conditions. The affect of the monosubstitution of bromine at the 4-position of cobalt-coordinated bpy is localized to the individual pyridine ring that it functionalizes; the unfunctionalized pyridine ring does not experience any appreciable change.

Research into the affects of *fac*/*mer* isomerism on $^1$H NMR is prudent, though it is not unfounded to state *fac*/*mer* isomers have a greater influence on protons that are closer to the complex center. A future experiment may attempt a separation of the isomers.

## 6. Acknowledgments

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