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NMR Study of the Coordinating Behavior of 2,6-bis(Benzimidazol-2′-yl)pyridine

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ABSTRACT: *The coordination sites of 2,6-bis(benzimidazol-2′-yl)pyridine (***1***) toward protons and the diamagnetic metal ions Li^+, Na^+, and Co^{3+} were investigated by NMR spectroscopy. Variable temperature ^1H and ^{13}C NMR experiments were performed on* **1** *in order to evaluate the tautomeric equilibrium and hydrogen bonding. Imidazole dicoordinated aromatic nitrogen atoms were protonated by trichloroacetic acid and the three N-dicoordinated atoms by fuming H_2SO_4. Reactions of the ligand* **1** *and benzimidazole* **2** *with metallic sodium or LiH afforded anionic species; the alkali metal ions appeared solvated by THF, but not by the ligands* **1** *or* **2***. In contrast, reaction of* **1** *with Co(III) produces the stable cation $[Co(\mathbf{1}\text{-}H)_2]^+$ with cobalt ion coordinated by two molecules of the monodeprotonated ligand.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:392–398, 2000

INTRODUCTION

Herein, we present some of our results in the study of the coordinating behavior of 2,6-bis(benzimidazol-2′-yl)pyridine (**1**), which is a useful and frequently used ligand for metal complexation [1–9].

This study is part of our continuing interest in the coordinating ability of aromatic nitrogenated molecules bearing sp^2 nitrogen atoms as present in pyrrole, pyridine, imines, anilines, or imidazole, especially because they can be part of strongly basic polydentate ligands [10–22]. Aromatic polydentate compounds show different behavior compared to their aliphatic analogs as a consequence of their planar conformation, which allows in some cases increased stability and better crystallizing ability. The polyfunctionality in benzimidazole containing ligands induces tautomeric and conformational equilibria in solution, which makes the assessment of the actual coordinating structures difficult; even more, these equilibria change upon coordination [15–18]. Therefore it is important to establish the actual tautomers or conformers in the free ligands as well as in their coordinated forms, which can be distinguished by a careful NMR study.

RESULTS AND DISCUSSION

2,6-bis(Benzimidazol-2′-yl)pyridine (**1**) has three dicoordinate and two pyrrole type nitrogen atoms. Three planar conformers or tautomers (**I–III**) can be proposed as shown in Figure 1. The transformation between them can be achieved by rotation of the

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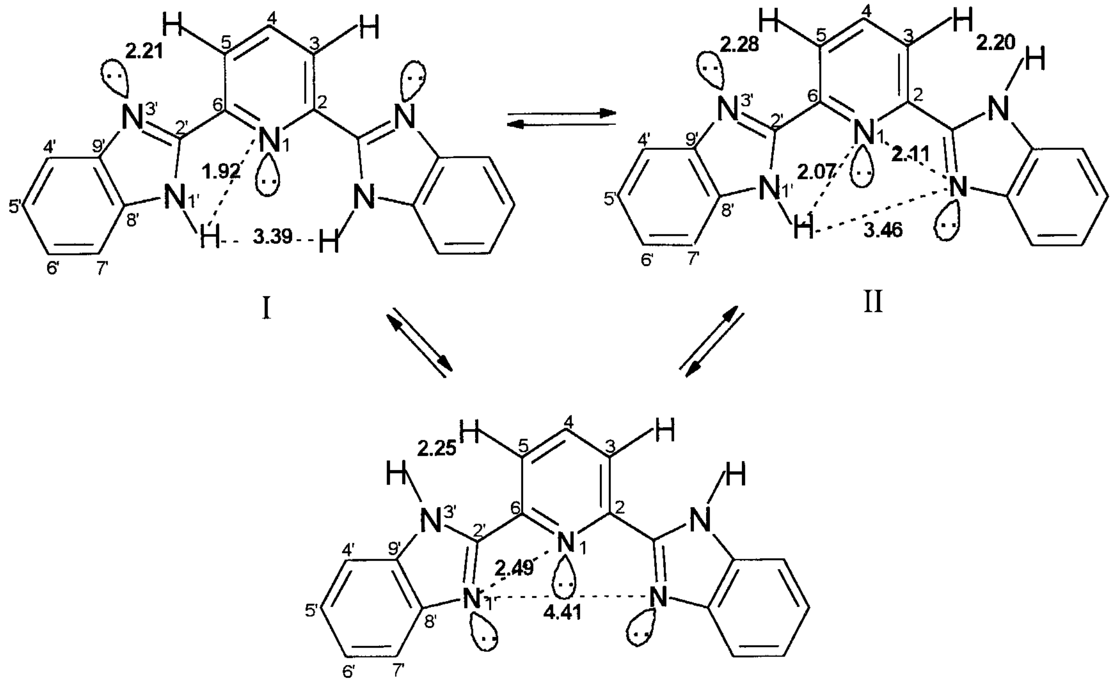


FIGURE 1 Tautomers or conformers of **1.** The calculated distances in Å (semiempirical method SCF PM3) between hydrogen atoms or between hydrogen and nitrogen atoms or between nitrogen atoms are indicated in the figure.

bonds C2′–C2 or C2′–C6 or by imidazole tautomeric exchange (Figure 2).

We decided to begin by an evaluation of the actual structure of the free ligand **1** in THF-d_8 or DMSO-d_6 solution, through the analysis of the ^{1}H and ^{13}C NMR spectra at different temperatures and by comparison with benzimidazole **2**, as shown in Tables 1 and 2. In order to have a reference for the structural analyses, we decided to study the ^{1}H and ^{13}C NMR spectra of the protonated **3–5** (Figure 3) and the dianionic species of **6–9** (Figure 4) of compounds **1** and **2**, respectively. We have also prepared the Co(III) compound **10** derived from ligand **1** (Figure 5), which is a stable and diamagnetic complex, in order to analyze the effect of the metallic coordination to **1**.

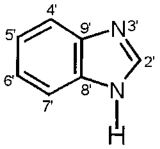
Variable Temperature NMR Study of **1** *and* **2**

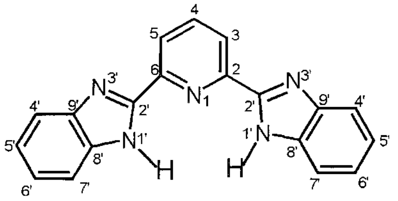
FIGURE 2 Benzimidazole tautomeric equilibrium.

In solution at room temperature, tautomeric equilibrium of benzimidazole **2** makes carbon atoms 8′ and 9′, 7′ and 4′, 5′ and 6′, and protons 4′ and 7′ and 5′ and 6′ equivalent, as depicted in Figure 2. A similar behavior for **1** should be expected; however, examination of its NMR spectra in THF-d_8 or DMSO-d_6 indicates that the imidazolic equilibrium is slower for **1** than for **2**, having as a consequence different chemical shifts for all hydrogen and carbon imidazolic atoms. The spectrum of **1** at 23°C is similar to that recorded at −90°C, showing that the molecule was already anchored at room temperature. An explanation for this behavior could be the presence of a hydrogen bond between the N–H groups and the lone pair of the pyridinic nitrogen atom. The lone pairs at the iminic type N-atoms of imidazole could be interacting with the aromatic hydrogen atoms H-3 and H-5 stabilizing the planar conformer and increasing the rotation energy barrier of C2–C2′ and C6–C2′ bonds.

We have calculated the distances between N-lone pairs and C–H or N–H, between N-lone pairs and between N–H and C–H in order to find stabilizing or destabilizing interactions in the conformers of **1**, Figure 1 [23]. Four stabilizing interactions were found for conformer **I**, two short distances between N–H and N-lone pair (1.92 Å), and two between C–H and N-lone pair (2.21 Å). Whereas, for conformer

TABLE 1 ^{1}H NMR Data, DMSO-d_6





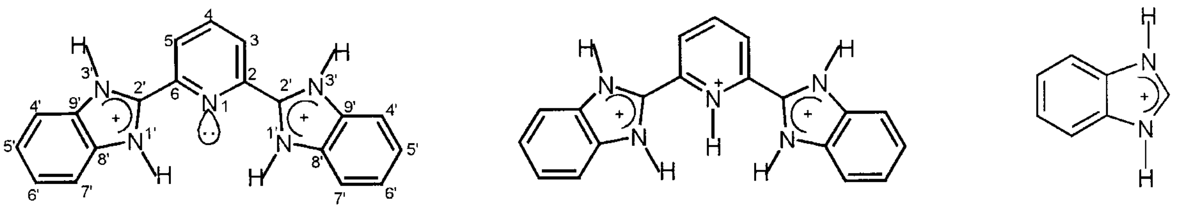
Compound	H4′	H5′	H6′	H7′	H3, H5 or H2′	H-4	NH
1	7.78	7.34	7.26	7.72	8.33	8.13	13.00
1[a]	7.72	7.20	7.20	7.51	8.39	8.00	12.49
1[b]	7.74	7.24	7.63	7.18	8.36	8.03	13.48
2	7.63	7.18	7.18	7.63	8.28	—	12.63
3	7.84	7.48	7.48	7.84	8.57	8.35	8.35
4	8.11	7.71	7.71	8.11	8.72	8.63	11.89
5	7.42	7.13	7.13	7.42	8.84	—	13.70
6	7.56	6.91	6.91	7.56	8.19	7.83	—
7	7.38	6.87	6.87	7.38	8.32	8.01	—
8	7.40	6.75	6.75	7.40	7.71	—	—
9	7.36	6.70	6.70	7.36	7.66	—	—
10	7.27	6.64	6.74	5.69	8.00	8.83	2.94[c], 3.20[c]

[a] THF-d_8 23°C.
[b] THF-d_8 −90°C.
[c] NH or OH

TABLE 2 ^{13}C NMR Data, DMSO-d_6

Compound	C2′	C4′	C5′	C6′	C7′	C8′	C9′	C2, C6	C3, C5	C4
1	151.1	120.3	122.8	124.3	112.3	134.9	144.7	148.3	121.9	139.7
1[a]	150.6	120.0	121.8	123.2	110.9	134.7	145.1	148.5	121.3	138.2
1[b]	150.6	119.7	122.1	123.6	111.6	134.6	144.3	147.9	121.3	138.9
2	142.5	116.3	122.3	122.3	116.3	139.0	139.0	—	—	—
3	149.1	115.9	125.8	125.8	115.9	136.2	136.2	145.8	124.5	140.9
4	147.9	116.6	128.8	128.8	116.6	133.1	133.1	143.6	127.4	142.9
5	143.6	118.3	130.0	130.0	118.3	133.8	133.8	—	—	—
6	161.3	117.4	118.5	118.6	117.3	148.5	148.5	154.6	117.9	137.3
7	159.0	117.0	119.5	119.5	117.0	146.5	146.5	153.7	119.8	138.3
8	153.1	116.4	116.7	116.7	116.4	146.9	146.9	—	—	—
9	153.5	116.8	117.0	117.0	116.8	147.0	147.0	—	—	—
10	165.9	120.3	120.5	122.2	111.4	142.0	147.6	156.4	119.3	143.6

[a] THF-d_8 23°C.
[b] THF-d_8 −90°C.

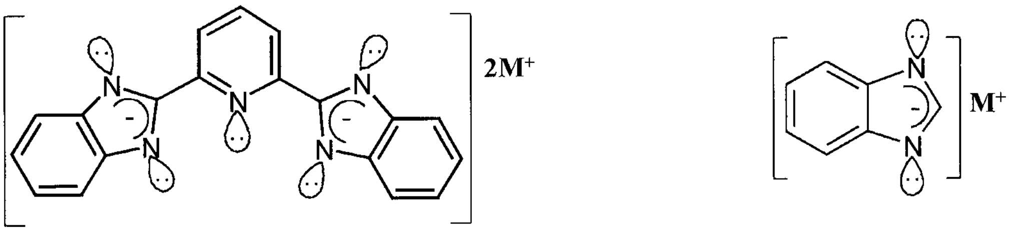


3

4

5

FIGURE 3 Structures of protonated compounds.



6 M+ = Na
7 M+ = Li

8 M+ = Na
9 M+ = Li

FIGURE 4 Structures of the anions derived from 2,6-bis(benzimidazol-2′-yl)pyridine **1** and benzimidazole **2**.

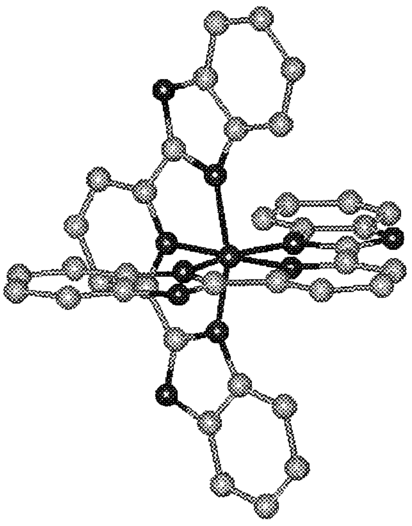


FIGURE 5 MM structure of compound **10;** N–H and C–H bonds are not shown.

II, there are only 2 and none for **III**, conformer **I** must be the more populated. Since the chemical shifts for H-3/H-5 in **1** are similar to those of the deprotonated ligands **6** and **7**, we deduce that in **1**, **6**, and **7** these protons are close to sp^2 nitrogen atoms. The fact that both benzimidazole groups are equivalent [even when observed in ^{1}H and in ^{13}C at -90°C (400 MHz)] indicates that, in conformer **I**, an exchange of the coordination of both N-H to pyridine is present.

In order to evaluate the strength of the hydrogen bonding, we measured the shift of the N-H signal with temperature. The $\Delta\delta/\Delta T$ value found for N-H (-8.61×10^{-3}) is indicative of a rapid exchange of the N-H with the pyridinic nitrogen atom and with the solvent [20].

It has been reported that the ^{13}C chemical shift of C-4 in pyridine allows one to evaluate the nitrogen coordination bond strength [22]. For example, in pyridine itself, C-4 appears at 136.9, while, for its BF_3 adduct, at 143.4. In compound **1**, C-4 gives a signal at 139.7; in DMSO-d_6, comparison with the deprotonated molecule **6** (C-4 at 137.3 in DMSO-d_6) indicates that only a weak bonding to the pyridinic N-atom by the N-H proton is occurring due to the competition with the solvent.

Protonation Reactions

We have added trichloracetic acid to **1** and analyzed the spectrum. Imidazole nitrogen atoms were fully protonated, with a weak protonation of the pyridinic nitrogen atom (compound **3**) also apparent. Therefore we have used a stronger acid such as fuming H_2SO_4 (**4**) and recorded the corresponding NMR spectra in DMSO-d_6, and all the three basic nitrogen atoms were found to be completely protonated. The ^{13}C chemical shift of C-4 at 142.9 clearly indicates protonation at the pyridinic nitrogen atom. The same reaction was performed with **2** to give compound **5**.

Evidence that benzimidazole **2** is protonated or deprotonated results from the symmetry observed in the NMR spectra. Carbon atoms 8′ and 9′, 7′ and 4′, 5′ and 6′, as well as protons 4′ and 7′ and 5′ and 6′, became equivalent [15].

It is known that the δ^{13}C values of the imidazolic ring carbon atoms depend upon their position with respect to the electron pair of the dicoordinate nitrogen atom. For imidazole or benzimidazole, the carbon atom that is adjacent to the lone pair of the dicoordinated nitrogen atom appears 10 ppm to higher frequencies with respect to the carbon atom neighbor to the N-H [14,21]. The protonated benzimidazole **5** presents signals for C-8′ and C-9′ at 133.8 ppm, whereas the deprotonated benzimidazole **8** at 146.9 and **9** at 147.0. Compound **4** shows resonances for C-8′ and C-9′ at 133.1, clear indication that protonation occurred [21]. The effect of the lone pair or of the N–H over the nearest *ipso* carbon atoms can also be observed at the anchored ligand **1** (THF-d_8)

where C-9′ appears at 145.1 ppm, C-8′ at 134.7, C-4′ at 120, and C-7′ at 110.9.

Deprotonation Reactions

Ligand **1** was reacted with metallic sodium in THF to give the solid compound **6** and with LiH in THF to afford a gray powder **7.** Compound **1** lost, in both cases, two N-H protons yielding dianionic species. Similar experiments with sodium and with nBuLi and with benzimidazole itself, **2**, produced the corresponding monoanions **8** and **9**, as recorded in Tables 1 and 2. The ^{13}C chemical shifts for C-8′ and C-9′ in the reaction products show the presence of two lone pairs at each imidazolic group; the spectra show the presence of THF which is coordinating the metal ions. The C-4 at the pyridine ring in **6** and **7** appears at δ 137.3 and 138.3, respectively, denoting no interaction with the metal ion. In order to add information, we have recorded the ^{23}Na NMR spectra for derivatives **6** (δ + 7.5) and **8** (δ + 7.7) and compared these with that of NaOEt in DMSO-d$_6$ (δ + 2.7). A similar behavior was observed for lithium compounds, the ^{7}Li NMR spectra of **7** and **9** afforded signals at +3.0 and +3.7, respectively, whereas the LiOEt in DMSO-d$_6$ appears at +1.9. Addition of pyridine to the solution of LiOEt shifts the Li resonance to +2.3, whereas addition to the NaOEt solution shifts the Na resonance to +3.0. According to our assumption, coordination of **1** and **2** to sodium or lithium atoms would move the metallic resonances to lower frequencies, but our results indicate the opposite, therefore confirming the absence of coordination with the nitrogenated ligands. The anionic structures are interesting for metallic coordination since they contain two lone pairs for benzimidazole **2** and five lone pairs for ligand **1**.

Coordination Behavior

In order to analyze the NMR data when the ligand is bonded to diamagnetic metals such as zinc(II) or cadmium(II), we have prepared the reported compounds [1,3,5] and recorded their spectra under the same conditions. Since the compounds presented broad signals due to their labile metallic coordination and their fast equilibria, we have concluded that they are not very useful systems for NMR studies. We thus decided to coordinate this ligand to cobalt(III) and to determine if it is a better system for studying the NMR effects of coordination because this diamagnetic ion is inert toward ligand substitution, and thus its structure is anchored.

Spectroscopic measurements and elemental analysis inform us that two ligands are bonded to cobalt. We have collected ^{1}H, ^{13}C, HETCOR, and NOESY spectra in order to make unequivocal assignments. The ^{13}C spectrum of **10** shows 10 signals for two magnetically equivalent ligands bonded to Co(III). Carbon atoms C-2 and C-6 and C-3 and C-5 from the pyridine are equivalent; the two-benzimidazole groups are magnetically indistinguishable. The signal at $\delta = 143.6$ for C-4 clearly shows that the pyridinic nitrogen atom is bonded to Co(III), while the δ^{13}C data for C-2′ at 165.9, C-8′ at 142.0, and C-9′ at 147.6 demonstrate the coordination of **1** through the two imidazolic nitrogen atoms. The shift of C-2′, C-8′, and C-9′ to higher frequencies follows the same trend as in the case of the anionic forms of the ligand.

The ^{1}H NMR spectrum of **10** shows 8 signals; the one assigned to H-4 at 8.83 ppm appeared shifted to higher frequency when compared with H-4 in the free ligand, confirming the coordination of the pyridinic N-atom. The resonances assigned to H-6′ (6.74 ppm) and H-7′ (5.69 ppm) are shifted toward lower frequencies due to the proximity of these protons to the benzimidazole ring current of the neighboring ligand, as is shown in the structure calculated by molecular mechanics (Figure 5).

Each molecule of the ligand is monodeprotonated; the remaining two N-H groups are in equilibrium between the four imidazole nitrogen atoms. The formation of the ligand monoanion has been observed previously for Mn(II) [7], and Lu(III) [4]. The counterion for the cobalt(III) coordination compound is HO$^-$. The presence of N–H and O–H groups can be deduced from its ^{1}H NMR spectrum, two broad signals for N–H and O–H appearing in the spectrum at δ 2.94 and 3.20, and which were not assigned. The IR spectrum shows a broad band for ν(N–H) and ν(O–H) vibrations.

The conclusion is that the cobalt(III) compound **10** contains two monodeprotonated ligands strongly bonded to cobalt(III) through the pyridine and the two-imine type nitrogen atoms.

EXPERIMENTAL

Materials and Methods

All new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and by heteronuclear correlation experiments. The anions of benzimidazole and 2,6-bis(2-benzimidazol-2′-yl)pyridine were handled under an N$_2$ atmosphere using carefully dried glassware and dried solvents. $[Co(NH_3)_4CO_3]NO_3$ was synthesized as described in the literature [24]. 2,6-Bis(2-benzimidazol-2′-yl)pyridine and ethanol were analytical grade reagents obtained from Aldrich and used without further purification. A 1.029

N HCl Aldrich standard solution was employed. A FT IR spectrometer (Perkin Elmer 1600) was used for obtaining IR spectra of solid samples in KBr pellets (4000–400 cm^{-1}). The UV-visible spectra (diffuse reflectance) were recorded on a Cary-5E (Varian) spectrometer. Electronic Spectra in the UV-visible range (260–600 nm) were recorded in DMSO solution with a Perkin-Elmer Lambda 12 Spectrophotometer using quartz cells of 1 cm path length. The mass spectra were obtained at 70 eV in a HP 5989 spectrometer. ^{1}H, ^{13}C NMR spectra were recorded on Varian 300 and 400 MHz, Jeol GSX 270 and Eclipse 400, and Bruker 300 MHz spectrometers. ^{23}Na was observed at the frequency of 105.74995692 MHz and ^{7}Li at 155.35011056 MHz at Jeol Eclipse 400. Chemical shifts (δ) are reported in ppm. Solvents were freshly distilled before use according to established procedures. The Microanalysis Laboratory from the University College London performed elemental analyses.

Protonation Reactions of **1** *and* **2**

A mixture of **1** (155 mg, 0.5 mmol) and trichloroacetic acid (415 mg, 2.5 mmol) was dissolved in DMSO-d_6 (**3**), and the ^{1}H and ^{13}C NMR data were recorded, (compound **3**). To **1** (330 mg, 1 mmol) 0.5 mL of 97% H_2SO_4 was added, diluted with DMSO-d_6, and the NMR spectra was recorded (compound **4**). The same procedure was employed for benzimidazole **2** to give compound **5**.

Disodium salt of 2,6-bis(benzimidazol-2′-yl)pyridine **6**

Metallic sodium (148 mg, 6.4 mmol) was added to a solution of **1** (1 g, 3.2 mmol) in 40 mL of dry THF. The solution was refluxed for 6 hours, and the solvent was evaporated afterward to give a green powder **6** (2.74 g, 82.5%). ^{1}H NMR showed that six molecules of THF remained coordinated to the sodium atoms. Decomp. 300°C. ^{23}Na NMR, δ +7.5 (DMSO-d_6).

Dilithium Salt of 2,6-bis(benzimidazol-2′-yl)pyridine **7**

A cooled suspension (0°C) of LiH (53 mg, 6.6 mmol) in 5 mL of dry THF was added to a dry flask containing 1 g (3.2 mmol) of **1** under an inert atmosphere. The solution was allowed to reach room temperature, and gas evolution was observed. Then solvent was evaporated, and a gray powder **7** was obtained (2.38 g, 98%). ^{1}H NMR showed 3 molecules of THF for each lithium atom. Decomp. 380°C. ^{7}Li NMR, δ +3.7 (DMSO-d_6).

Sodium Salt of Benzimidazole **8**

Metallic sodium (195 mg, 8.5 mmol) was added to a solution of benzimidazole (1 g, 8.5 mmol) in dry THF (10 mL) at room temperature. After 1.5 hours the solvent was evaporated to give a white solid **8** (2.96 g, 98%). ^{1}H NMR spectroscopy showed 3 molecules of THF and ^{23}Na NMR, δ +7.7 (DMSO-d_6).

Lithium Salt of Benzimidazole **9**

A solution of benzimidazole (1 g, 8.5 mmol) in 10 mL of dry benzene was cooled to −78°C and 3.4 mL (8.5 mmol) of a solution of *n*-BuLi (2.5 M) in hexane was added. The solution was allowed to reach room temperature and the solution was evaporated to dryness. A gray powder **9** was obtained (1.0 g, 98%), which was dissolved in DMSO-d_6. NMR ^{7}Li, δ +3.0 ppm.

Cobalt Complex of 2,6-bis(benzimidazol-2′-yl)pyridine **10**

A solution of **1** (0.62 g, 2.0 mmol) in ethanol (30 mL) was added with stirring to a slurry of $[Co(NH_3)_4CO_3]NO_3$ (0.249 g, 1 mmol) in ethanol (30 mL), and 2 mmol HCl (2 mL, 1.029 N) were employed to help in dissolving the carbonate complex. The mixture was refluxed for 4 hours. A yellow precipitate was isolated by vacuum filtration (0.509 g, 73%). IR (ν cm^{-1}) 3050, 1605, 1571, 1470, and 785; this spectrum also showed a broad band at 1881 cm^{-1} characteristic of hydrogen bonding. The electronic absorption spectrum presented a shoulder at 17,241 and an intense broad band at 23,529 cm^{-1}. Found: C 65.97%, H 3.52%, N 20.45%; calculated for $C_{38}H_{25}ON_{10}Co$, C 65.52%, H 3.59%, N 20.12%.

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