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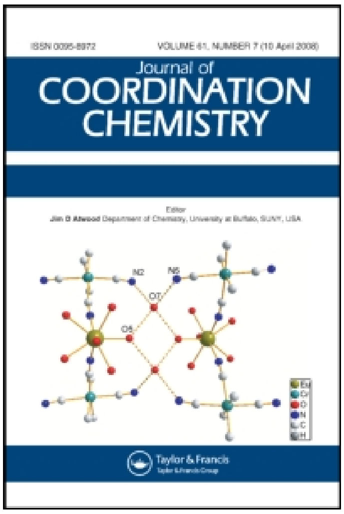

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Synthesis and NMR Characterization of Cobalt(III) Complexes with 1,8-diamino-3,6-dithiaoctane, 2,2-Bipyridine, and 1,10-phenanthroline

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SYNTHESIS AND NMR CHARACTERIZATION OF COBALT(III) COMPLEXES WITH 1,8-DIAMINO-3,6-DITHIAOCTANE, 2,2-BIPYRIDINE, AND 1,10-PHENANTHROLINE

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The complexes [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 (eee, 1,8-diamino-3,6-dithiaoctane) were synthesized and characterized by two-dimensional NMR spectroscopy. The presence of the bidentate aromatic ligands 2,2-bipyridine and 1,10-phenanthroline caused the ^{1}H resonances to be spread into a wider spectral width than previously observed for [Co(eee)$(NO_2)_2$]Cl and [Co(eee)Cl_2]Cl. Separate multiplets were observed for the four protons in the terminal ethylene linkage. It was possible to positively assign each multiplet and to determine the relative spatial orientations of the corresponding protons.

Keywords: Cobalt(III); Tetradentate ligand; NMR spectroscopy

INTRODUCTION

Cobalt(III) complexes with linear tetradentate ligands have been extensively studied over the past three decades [1–30]. Such complexes can potentially form three different geometric isomers, referred to as the *cis*-α, *cis*-β, and *trans* isomers. Sargeson and Searle [1,2] studied cobalt(III) complexes containing triethylenetetramine, which in many ways can be considered to be the prototype tetradentate ligand, and were able to separate and isolate all three geometric isomers. Since this initial work, many triethylenetetramine derivatives were synthesized with the intent of finding a more stereospecific ligand. Some of the modifications include ligands with lengthened carbon chains joining the donor atoms [11–13], ligands with methyl groups attached in various positions [14–18], ligands with SNNS donor sequences, [19,20] and ligands with NSSN donor sequences [21–26]. It was discovered by Worrell and Busch [21,22] that the ligand 1,8-diamino-3,6-dithiaoctance exclusively formed the *cis*-α isomer, a factor which has been attributed to the increased size of the sulfur atoms relative to the nitrogen donors of triethylenetetramine.

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Despite the large number of complexes reported, there have been very few NMR studies of these systems. The ^{1}H spectra of these systems are inherently complex due to a variety of reasons. First is the restricted rotation about the C–C bonds arising from coordination. Depending upon the overall symmetry of the complex, a simple ethylene linkage can contain up to four nonequivalent protons. If the ligand is coordinated in an asymmetric way, every proton could have a unique chemical shift. This problem is exacerbated in a system containing three-carbon linkages joining the donor atoms. A second major obstacle associated with the use of NMR spectroscopy to study these systems is that the chemical shifts are often very similar, causing the spectrum to be crowded into a very narrow spectral width. At the time many complexes were under investigation, the best NMR instruments operated in continuous-wave mode at frequencies of 60 or 90 mHz at best. Fourier transform NMR and the wide array of two-dimensional NMR experiments currently available had yet to come about. As a result, the ^{1}H NMR spectrum was often used as no more than a "fingerprint" to determine the number and type of isomers present. There have been very few attempts to interpret the ^{1}H NMR spectra of these systems.

In previous work, high-field two-dimensional NMR spectroscopy was applied to cobalt(III) complexes [Co(eee)$(NO_2)_2$]Cl [27,28], [Co(eee)Cl_2]Cl [27,28], [Co(epe)$(NO_2)_2$]Cl [27], [Co(epe)Cl_2]Cl [27], [Co(Q)Cl]Cl_2 [27,29] and [Co(QS)Cl]Cl_2 [27] (see Table I for abbreviations). Through the use of two-dimensional NMR [31–38], it was possible to establish connectivities between sets of coupled protons, to determine spatial relationships between protons, and to correlate the ^{13}C resonances with their corresponding ^{1}H resonances. However, even with the use of a high-field instrument there were few cases where individual protons gave rise to separate and distinct multiplets. In the case of [Co(eee)$(NO_2)_2$]Cl [27,28], the presence of a C2 axis simplified the four center methylene ring protons, yielding two sets of two equivalent protons which appeared as a distinct A_2B_2 multiplet. However, there were no other recognizable proton patterns.

It is clear that the identity of the groups occupying the remaining two coordination sites in octahedral complexes having tetradentate ligands can exert considerable influence on the NMR spectrum of the tetradentate ligand. As an example, the NMR spectrum of [Co(eee)$(NO_2)_2$]Cl is much cleaner than for [Co(eee)Cl_2]Cl. In [Co(eee)$(NO_2)_2$]Cl, the A_2B_2 pattern of the center methylene ring protons is not overlapped with other resonances; in [Co(eee)Cl_2]Cl this is not a separate and distinct multiplet. Flat, rigid, aromatic ligands 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen) in the complexes [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 result in a proton spectrum spread into a much wider spectral width than previously observed for [Co(eee)$(NO_2)_2$]Cl and [Co(eee)Cl_2]Cl. This effect was pronounced enough for separate multiplets to be observed for the four protons in the terminal ethylene linkages. With the help of two-dimensional experiments, it was possible to assign each proton resonance.

TABLE I Ligand abbreviations

eee	1,8-diamino-3,6-dithiaoctane	$NH_2CH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$
epe	4-methyl-1,8-diamino-3,6-dithiaoctane	$NH_2CH_2CH_2SCH_2CH(CH_3)SCH_2CH_2NH_2$
Q	7-methyl-4,10-dithia-1,7,13-triazadecane	$NH_2CH_2CH_2SCH_2CH_2N(CH_3)CH_2CH_2SCH_2CH_2NH_2$
QS	1,11-diamino-3,6,9-trithiaundecane	$NH_2CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$
bipy	2,2-bipyridine	$C_{10}H_8N_2$
phen	1,10-phenanthroline	$C_2H_8N_2$

EXPERIMENTAL

All NMR experiments were performed on a Bruker AMX-360 NMR spectrometer. D_2O (99.9%) was obtained from Aldrich chemical. For ^1H experiments, internal DSS was used as a chemical shift standard. For ^{13}C experiments internal 1,4-dioxane was used as the chemical shift standard and assigned a value of 67.40 ppm. All experiments were carried out at approximately 25°C and a concentration of 0.10 M. One-dimensional experiments were acquired using 32 K of computer memory. The reported COSY experiment was acquired over a sweep width of approximately 3.0 ppm with a resolution of 512 × 1024 and zero-filling to a final resolution of 1024 × 1024. The reported NOESY experiment was acquired with the same resolution but over a sweep width of approximately 10.0 ppm; only an expansion of the high-field region of the spectrum is reported. The reported HETCOR was acquired using standard ^{13}C detected experiment with a resolution of 128 × 512.

The compound $[Co(eee)(bipy)]Cl_3$ was synthesized from $[Co(eee)Cl_2]Cl$ and 2,2-bipyridine. $[Co(eee)Cl_2]Cl$ (0.762 g, 0.0022 mol) was mixed with 2,2-bipyridine (0.351 g, 0.0022 mol) in a 50-mL beaker. Approximately 10 mL of absolute ethyl alcohol was added, and the solution was manually stirred with a glass stirring rod. Over a period of approximately 20 min, deionized water was added dropwise, and the solution gradually changed from the blue color of the dichloro complex to the rust-orange color of the bipyridine complex. The solution was filtered through a sintered glass funnel and additional water was added dropwise to the remaining undissolved chloride complex. This was combined with the filtrate and the solution was again stirred. A second filtration was performed and 100 mL of absolute ethyl alcohol was added to the filtrate. A rust-orange precipitate formed and was collected by vacuum filtration, rinsed with a few mL of diethyl ether, and stored in a vacuum dessicator overnight. Analysis by ^{13}C NMR revealed three clean signals arising from the eee ligand at 46.9, 40.7 and 39.8 ppm and five signals arising from the 2,2-bipyridine at 158.1, 155.6, 144.6, 131.4, and 127.4 ppm.

The compound $[Co(eee)(phen)]Cl_3$ was synthesized from $[Co(eee)Cl_2]Cl$ through a procedure analogous to that mentioned above. $[Co(eee)Cl_2]Cl$ (1.0 g, 0.0300 mol) was ground in an agate mortar with a stoichiometric quantity of 1,10-phenanthroline monohydrate (0.060 g, 0.0030 mol). Enough absolute ethanol was added to make a paste, followed by a few drops of deionized water. Over a period of 2 h, the blue color of the dichloro complex gradually changed to the rust-orange color of the phenanthroline complex. The product was transferred to a beaker and absolute ethanol was added to the solution. $[Co(eee)(phen)]Cl_3$ precipitated, was collected by vacuum filtration, washed with absolute ethanol and diethyl ether and stored in a vacuum dessicator overnight. Analysis by C-13 NMR revealed three signals arising from the eee ligand at 39.8, 40.8 and 46.5 ppm and six signals arising from 1,10-phenanthroline at 129.1, 129.5, 133.1, 143.2, 148.1 and 156.2 ppm.

RESULTS AND DISCUSSION

A structural illustration of the compound $[Co(eee)(bipy)]Cl_3$ showing the numbering scheme which will be used in subsequent discussions is shown in Fig. 1. The ^1H spectra for $[Co(eee)(bipy)]Cl_3$ and $[Co(eee)(phen)]Cl_3$ are shown in Fig. 2. The ^1H spectra

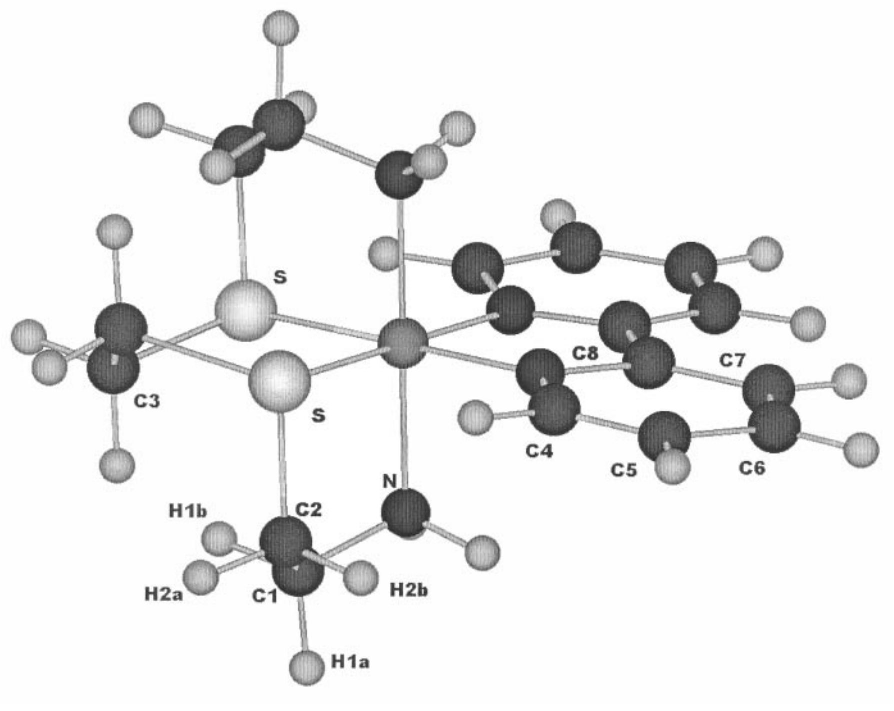

FIGURE 1 Structural illustration of [Co(eee)(bipy)]Cl_3.

for [Co(eee)$(NO_2)_2$]Cl and [Co(eee)$(NO_2)_2$]Cl have been reported [27,28]. Proton assignments for [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 are summarized in Tables II and III, respectively. The basis for the assignments will be made clear in subsequent discussions.

In the previously studied complexes, [Co(eee)Cl_2]Cl and [Co(eee)$(NO_2)_2$]Cl, the four C3 protons give rise to an A_2B_2 multiplet. This pattern is not observed in the present work, suggesting that the C3–C3 dihedral angle and therefore, the magnitude of the coupling constants are different. While a well-defined A_2B_2 pattern for the center methylene protons is lost in [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3, a series of four multiplets between 2.5 and 4.0 ppm appear. The four C1–C2 protons are not interchanged by the C2 symmetry axis and therefore, give rise to separate and distinct signals. Since there are four separate multiplets and four nonequivalent protons, it is logical to assume that each proton has a unique chemical shift and gives rise to a separate multiplet. This initial hypothesis is supported by the two-dimensional NMR experiments. An anomaly is observed in the integration data for the resonance at $\sim$2.9 ppm which proved reproduceable in both complexes. It was initially believed this might be trace solvent. However, additional washings with absolute ethanol and diethyl ether followed by overnight storage in a dessicator failed to remove it. No additional signals of any kind were observed in the ^{13}C NMR spectrum. It is not believed to interfere with the NMR analysis.

The ^{13}C chemical shifts of [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 are tabulated in Table IV. Only three signals are observed, attributable to the tetradentate ligand,

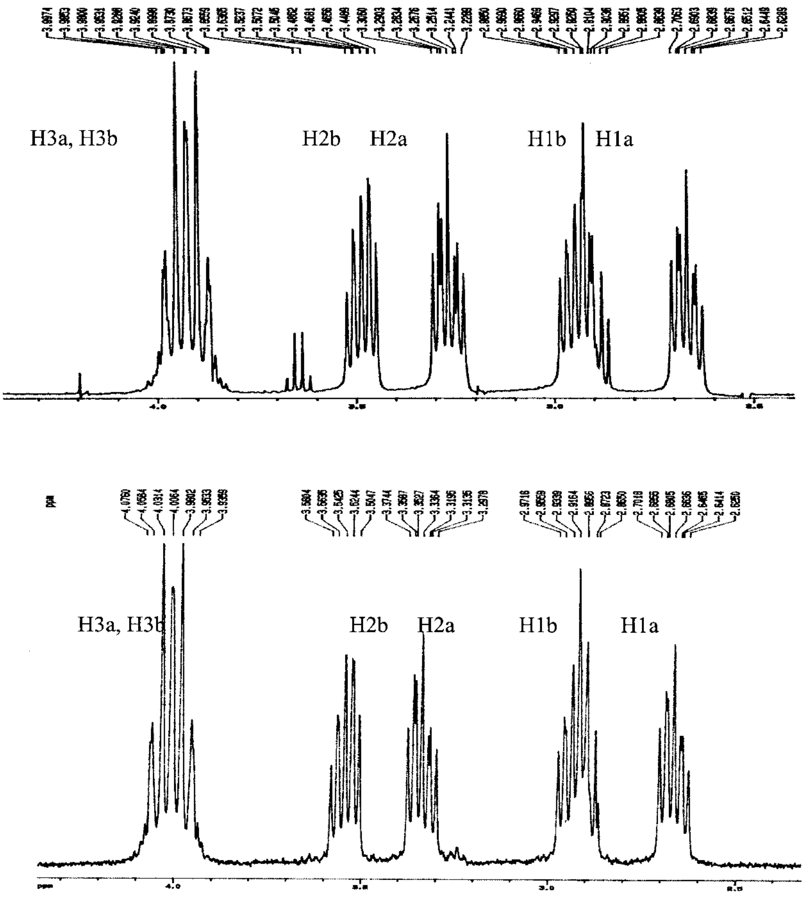

FIGURE 2 Proton NMR spectra of [Co(eee)(bipy)]Cl_3 (top) and [Co(eee)(phen)]Cl_3 (bottom).

TABLE II Summary of ^1H chemical shifts and assignments for [Co(eee)(bipy)]Cl_3

Chemical Shift (ppm)	*Assignment*	*Integration*
2.637–2.699	H1a	1.85
2.905–2.979	H1b	2.88
3.224–3.301	H2a	2.08
3.445–3.503	H2b	1.990
3.868–3.983	H3a, H3b	4.00

indicating retention of a single geometric isomer. While the specific chemical shifts are different than previously observed for [Co(eee)Cl_2]Cl and [Co(eee)$(NO_2)_2$]Cl [27,28] the same general pattern is observed; one signal shifted downfield and two shifted upfield relatively close together. This is to be expected, since one carbon is adjacent to nitrogen whereas the other two are adjacent to sulfur. Previous work with [Co(eee)Cl_2]Cl and [Co(eee)$(NO_2)_2$]Cl showed that the signal shifted furthest downfield is assigned to the

TABLE III Summary of ^1H chemical shifts and assignments for $[Co(eee)(phen)]Cl_3$

Chemical Shift (ppm)	*Assignment*	*Integration*
2.625–2.702	H1a	1.87
2.865–2.972	H1b	2.88
3.298–3.374	H2a	1.77
3.505–3.580	H2b	1.88
3.936–4.076	H3a, H3b	4.00

TABLE IV Summary of ^{13}C chemical shifts for $[Co(eee)(bipy)]Cl_3$ and $[Co(eee)(phen)]Cl_3$

Assignment	$[Co(eee)(bipy)]Cl_3$	$[Co(eee)(phen)]Cl_3$
C1	46.9	46.5
C2	39.8	39.8
C3	40.7	40.8

C1 carbon; the signal at 46.9 ppm is assigned to the C1 carbon on this basis. The other two resonances located at 40.7 and 39.8 ppm are assigned based upon heteronuclear correlation data.

Magnitude COSY

The magnitude COSY spectrum for $[Co(eee)(bipy)]Cl_3$ is shown in Fig. 3. This spectrum shows the four multiplets labeled H1a, H1b, H2a and H2b form a four-spin sytem whereas the multiplet due to H3a and H3b shows no interaction with the other signals. This is to be expected due to the presence of the heteroatoms; the H2 and H3 protons are four bonds apart and therefore, no apparent coupling occurs. The COSY spectrum for $[Co(eee)(phen)]Cl_3$ is virtually identical to that for $[Co(eee)(bipy)]Cl_3$ and is not reported here.

Heteronuclear Correlation

While the previous spectra allow one to deduce that the four labeled H1a, H1b, H2a and H2b all belong to the same spin system, they do not allow any type of distinction between these four protons. This is partially resolved with the heteronuclear correlation spectrum of $[Co(eee)(bipy)]Cl_3$ shown in Fig. 4. The proton muliplets at 2.637–2.699 ppm (H1a) and 2.905–2.979 ppm (H1b) clearly show a correlation to the carbon signal at 46.9 ppm. Since this carbon signal was previously assigned to the C1 carbon, these protons are identified as the H1 protons. Similarly, the proton multiplets at 3.224–2.301 ppm (H2a) and 3.445–3.503 ppm (H2b) correlate to carbon signal at 39.8 ppm. Since these protons are shown to be coupled with the H1 protons in the COSY spectrum, they can be identified as the H2 protons and the carbon resonance at 39.8 ppm is identified as the C2 carbon. Lastly, the proton multiplet at 3.868–3.983 ppm, which must be due to the H3 or center methylene ring protons based upon the lack of coupling with other resonances shown in the COSY spectrum, correlates to the carbon signal at 40.7 ppm. This is therefore, identified as the C3 carbon.

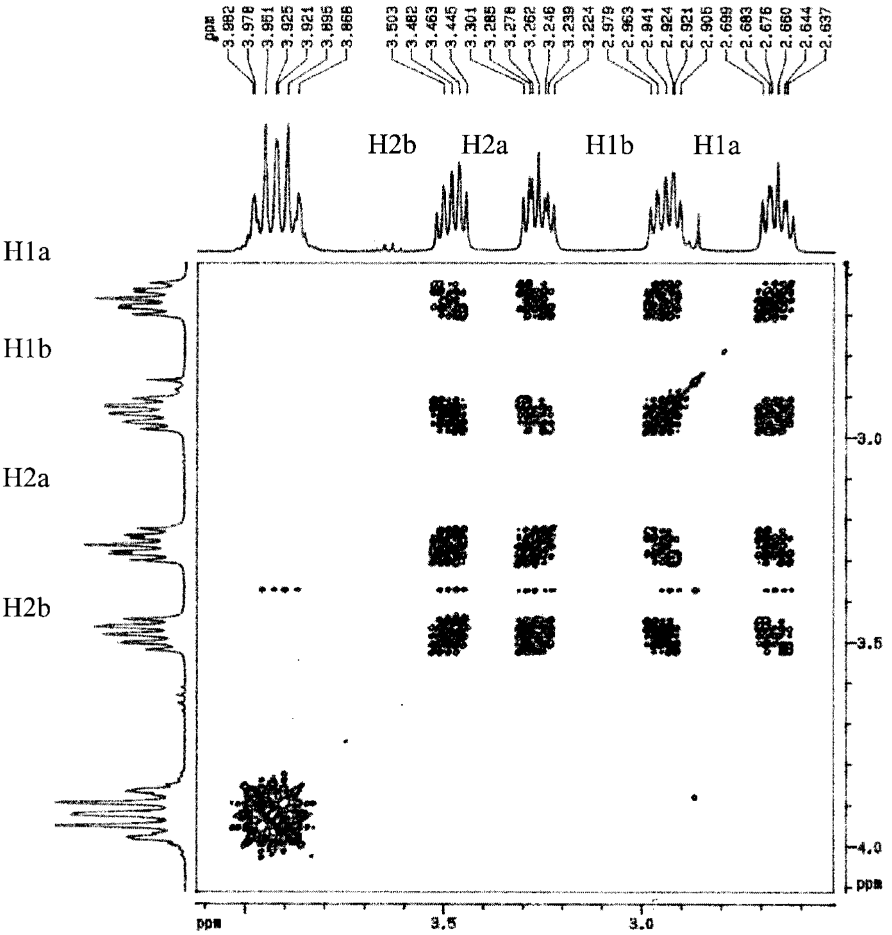

FIGURE 3 Magnitude COSY spectrum of [Co(eee)(bipy)]Cl_3.

NOESY

The proton analysis can be carried one step further by determining the relative orientations of each of the H1 and H2 protons with respect to the H3 protons and the aromatic resonances. Close examination of the illustration shown in Fig. 1 reveals that one of the H1 protons will be spatially oriented towards the H3 protons whereas the other will be spatially oriented towards the aromatic protons. Figure 5 shows the NOESY spectrum of [Co(eee)(bipy)]Cl_3 correlating the aliphatic regions of the spectrum. Examination of this spectrum reveals the presence of cross peaks between the H2a proton and the H3 multiplet, indicating that H2a must be spatially oriented towards the H3 protons. Similarly, a cross peak is detected between the H1b and H3 multiplets. This indicates that the H1b and H2a protons must project towards the same side of the C1–C2 bond, bringing them into a close spatial relationship relative to the H3 protons. Similar arguments can be applied to the H1a and H2b protons, which are spatially oriented in the opposite direction and show cross peaks with the aromatic resonances.

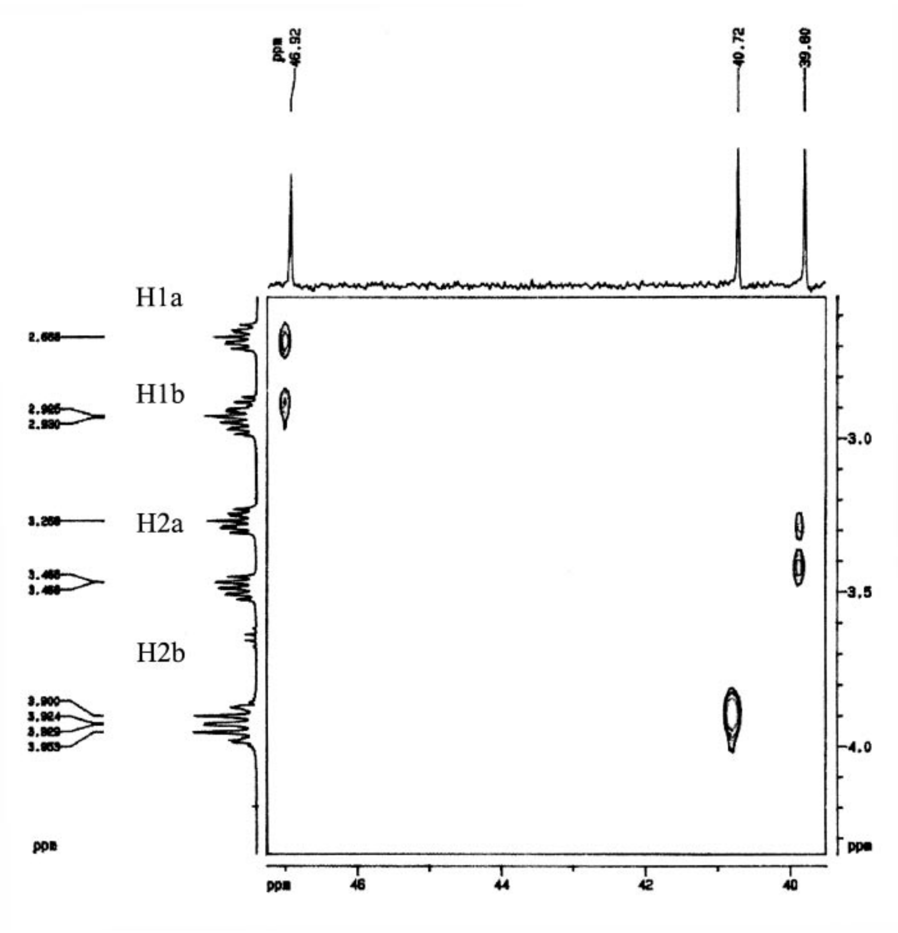

FIGURE 4 Heteronuclear correlation spectrum of $[Co(eee)(bipy)]Cl_3$.

The C1–C2 Dihedral Angle

Upon consulting the H-1 NMR spectra for $[Co(eee)(bipy)]Cl_3$ and $[Co(eee)(phen)]Cl_3$, an astute observer may notice that the "a" multiplets have similar appearances, as do the "b" multiplets. This can be explained from an analysis of the C1–C2 dihedral bond angle. As the C1–C2 angle is increased, the spatial proximity of two protons will be increased while the spatial proximity of the remaining two will be decreased. For the sake of the following argument those protons whose spatial proximity is decreased as the dihedral angle is increased are called the "b" protons and those whose spatial proximity are increased are called the "a" protons. If C1 and C2 form some dihedral angle X, then the angle between H1b and H2b will be $109.5 + X$ and the angle between H1a and H2a will be $109.5 - X$. The "a" protons could just as easily have been defined as those whose spatial proximity are increased as the dihedral angle is increased, in which case the angle between H1a and H2a would become $109.5 + X$ while the angle between H2b and H1b becomes $109.5 - X$. Therefore, regardless of the dihedral angle, the H1a and H2a protons experience the same couplings and therefore, the

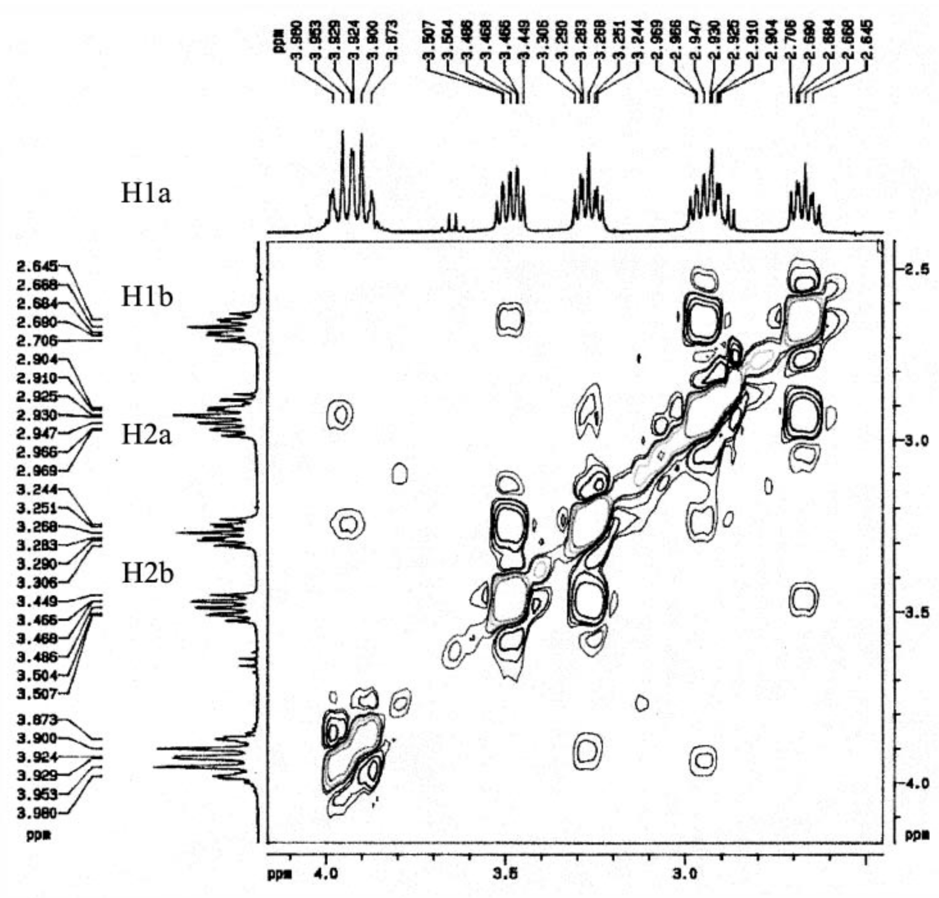

FIGURE 5 NOESY spectrum of [Co(eee)(bipy)]Cl_3.

corresponding multiplets have the same appearance. This argument can be extended to conclude that in a similar fashion the H1b and H2b protons also experience the same couplings and therefore, have the same appearance.

DISCUSSION AND ASSIGNMENT OF AROMATIC SIGNALS

While the focus of this research is the assignment of the ^{1}H resonances associated with the tetradentate ligand, the introduction of aromatic bidentate ligands does introduce a number of additional signals into the spectra. Whereas the ^{1}H spectra of [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 are nearly identical in the aliphatic region, the aromatic regions are obviously different. The aromatic ^{1}H and ^{13}C chemical shifts for [Co(eee)(bipy)]Cl_3 are summarized in Table V. The appearance of the proton spectrum is unchanged relative to 2,2-bipyridine except for changes in the chemical shifts.

Two doublets at 9.28 and 8.74 ppm are observed which can be assigned to the H4 and H7 protons on the basis of multiplicity. The assignment of the signal at 9.28 to

TABLE V Summary of aromatic chemical shifts for [Co(eee)(bipy)]Cl_3

^{1}*H Chemical Shift*	^{1}*H Multiplicity*	^{13}*C Chemical Shift*	*Assignment*
8.05	Triplet	131.4	H5/C5
8.55	Triplet	144.6	H6/C6
8.74	Doublet	127.4	H7/C7
9.28	Doublet	155.6	H4/C4
n/a	n/a	158.1	C8

TABLE VI Summary of ^{1}H chemical shifts for C3–H multiplet centers

Compound	*Chemical shift*
[Co(eee)Cl_2]Cl	3.35
[Co(eee)$(NO_2)_2$]Cl	3.50
[Co(eee)(bipy)]Cl_3	3.90
[Co(eee)(phen)]Cl_3	4.10

H4 is made on the basis of chemical shift. The proton spectrum also contains two triplets at 8.55 and 8.04 ppm which were assigned through the help of a NOESY spectrum. The H4 doublet at 9.28 ppm showed a cross peak with the triplet at 8.05 ppm, allowing this resonance to be assigned to the H5 proton. Similarly, the H7 proton at 8.74 ppm showed a cross peak to the triplet at 8.55 ppm allowing this reasonance to be assigned to H6. The carbon resonances were assigned through the use of a proton–carbon correlation.

Trends in Chemical Shifts

The ligands 2,2-bipyridine and 1,10-phenanthroline introduce clear changes in the ^{1}H spectra of [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 relative to [Co(eee)$(NO_2)_2$]Cl and [Co(eee)Cl_2]Cl. The chief reason for the improvement in the ability to interpret the proton NMR spectra of [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 relative to [Co(eee)$(NO_2)_2$]Cl and [Co(eee)Cl_2]Cl is the spreading of the chemical shifts into a wider spectral width. A comparison of spectra reveals clear trends in the chemical shifts. The A_2B_2 multiplet arising from the center methylene protons is observed to occur at 3.35 ppm for [Co(eee)Cl_2]Cl and at 3.50 ppm for [Co(eee)$(NO_2)_2$]Cl [27,28]. While [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 do not show the same A_2B_2 splitting pattern for the C3 protons, the center of the multiplets are shifted down to 3.9 and 4.1 ppm, respectively. These proton chemical shift data are summarized in Table VI. In contrast, the C1 protons are shifted very little, appearing at approximately 2.9 ppm in [Co(eee)Cl_2]Cl, 2.8 ppm in [Co(eee)$(NO_2)_2$]Cl, and 2.6 ppm in [Co(eee)(phen)]Cl_3. The C_1 shifts are upfield rather than downfield, much smaller in magnitude. Based upon the chemical shift data, the methylene protons in the center ring appear most sensitive to changes in the identity of the monodentate groups. Brubaker and Johnson [13] present a detailed study of ^{13}C chemical shifts for a series of [Co(3,2,3-tet)X_2]X and [Co(2,3,2-tet)X_2]X systems and report a linear relationship between chemical shift differences and ligand field strength.

SUMMARY AND CONCLUSIONS

The presence of 2,2-bipyridine and 1,10-phenanthroline in the complexes [Co(eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3 caused the ^1H chemical shifts of the center chelate ring protons to be shifted downfield, reducing the degree of overlap and allowing separate multiplets to be observed for the four protons in the terminal chelate rings. Through the use of COSY, NOESY, and HETCOR experiments it was possible to assign each of the four protons in the terminal chelate rings and to determine their relative spatial orientations.

It has been suggested that shift of the ^1H signals arising from the center chelate ring could be a result of the increased charge on the complex. For example, the complexes [Co(eee)$(NO_2)_2$]Cl and [Co(eee)Cl_2]Cl contain charged ligands which reduce the overall charge on the complex on to $+1$. On the other hand, the complexes reported here retain a full $+3$ charge. However, current work on a different tetradentate system with NO_2^-, Cl^-, 2,2-bipyridine, ethylenediamine, and 1,2-diaminobenzene supports the conclusion that increased charge is not responsible for differences in spectra reported here.

References

[1] A.M. Sargeson and G.H. Searle (1965). *Inorg. Chem.*, **4**, 45.
[2] A.M. Sargeson and G.H. Searle (1966). *Inorg. Chem.*, **6**, 787.
[3] D.A. Buckingham, P.A. Marzilli and A.M. Sargeson (1967). *Inorganic Chemistry*, **6**, 1032.
[4] G.R. Brubaker, D.P. Schaefer, J.H. Worrell and J.I. Legg (1971). *Coord. Chem. Rev.*, **7**, 161.
[5] Y. Yamamoto and E. Toyota (1979). *Bull. Chemical Soc. of Jpn.*, **9**, 2540.
[6] Yoshihisa Yamamoto, Hiroko Kudo and Eiko Toyoka (1983). *Bull. Chem. Soc. Jpn.*, **56**, 1051.
[7] E. Toyota, Y. Yamamoto and Y. Yamamoto (1983). *Bull. Chem. Soc. Jpn.*, **56**, 2721.
[8] Y. Yamamoto and H. Kudo (1984). *Bull. Chem. Soc. Jpn.*, **57**, 287.
[9] Yoshihia Yamamoto, Eiko Toyota and Shoko Tsukuda (1985). *Bull. Chem. Soc. of Jpn.*, **58**, 1595.
[10] Y. Yamamoto, K. Yoshi and E. Toyota and K. Konno (1989). *Bull. Chem. Soc. of Jpn.*, **62**, 724.
[11] B. Bosnich, R.D. Gillard, E.D. McCkenzie and G.A. Webb (1966). *J. Chem. Soc.* (*A*), 1331.
[12] D. Alexander and H.G. Hamilton Jr. (1969). *Inorg. Chem.*, **8**, 2131.
[13] G.R. Brubaker and D.W. Johnson (1982). *Inorg. Chem.*, **21**, 2223.
[14] R.G. Asperger and C.F. Liu (1965). *Inorg. Chem.*, **4**, 1395.
[15] S. Yoshikawa, T. Sekihara and M. Goto (1966). *Inorg. Chem.*, **6**, 169.
[16] M. Goto, M. Saburi and S. Yoshikawa (1968). *Inorg. Chem.*, **8**, 358.
[17] M. Goto, A. Okubu, T. Sawai and S. Yoshikawa (1970). *Inorg. Chem.*, **9**, 1488.
[18] G.H. Searle, M. Petkovic and F.R. Keene (1974). *Inorg. Chem.*, **13**, 399.
[19] K. Yamanari, N. Takeshita and Y. Shimura. (1984). *Bull. Chem. Soc. Jpn.*, **57**, 1227.
[20] K. Yamanari, N. Takeshita and S. Shimura. (1984). *Bull. Chem. Soc. Jpn.*, **57**, 2852.
[21] J.H. Worrell and D.H. Busch (1969). *Inorg. Chem.*, **8**, 1563.
[22] J.H. Worrell and D.H. Busch (1969). *Inorg. Chem.*, **8**, 1572.
[23] B. Bosnich, W.R. Kneen and A.T. Phillip (1969). *Inorg. Chem.*, **8**, 2567.
[24] J.H. Worrel, T.E. MacDermott and D.H. Busch (1969). *J. Chem. Soc.*, **92**, 3317.
[25] I. Bernal, J. Cetrullo, J.H. Worrell and T. Li (1994). *Polyhedron*, **13**, 663.
[26] I. Bernal, J. Cetrullo, J. Cai, R.A. Geanangel and J.H. Worrell (1995). *J. Chem. Soc. Dalton Trans.*, 100.
[27] M.R. McClure, M.S. Thesis (1994). University of South Florida.
[28] M.R. McClure, K.W. Jung and J.H. Worrell (1998). *Coord. Chem. Rev.*, **174**, 33.
[29] M. McClure and J.H. Worrell (1988). *J. Coord. Chem.*, **43**, 143.
[30] M.R. McClure (1999). Ph.D. Dissertation. University of South Florida.
[31] A. Ault and G.O. Dudek (1976). *NMR: An Introduction to Proton Nuclear Magnetic Resonance Spectroscopy*. Holden-Dag, San Francisco.
[32] R.J. Abraham, J. Fisher and P. Loftus (1988). *Introduction to NMR Spectroscopy*. John Wiley and Sons, New York.
[33] H. Friebolin (1991). Basic One and Two-Dimensional NMR Spectroscopy. VCH Publishers, New York.
[34] A.E. Derome (1987). *Modern NMR Techniques for Chemical Research*. Pergamon Press, New York.
[35] J. Sanders and B. Hunter (1993). *Modern NMR Spectroscopy: A Guide for Chemists*, 2nd Edn. Oxford University Press, New York.

[36] G.E. Martin and A.S. Zektzer (1988). *Two-Dimensional NMR Methods for Establishing Molecular Connectivity: A Chemists' Guide to Experimental Selection, Performance, and Interpretation*. VCH Publishers, New York.
[37] W.R. Croasmun and R.M.K. Carlson (1994). *Two-Dimensional NMR Spectroscopy: Applications for Chemists and Biochemists*. VCH Publishers, New York.
[38] S. Braun, H.O. Kalinowski and S. Berger (1996). *100 and More Basic NMR Experiments*. VCH Publishers, New York.