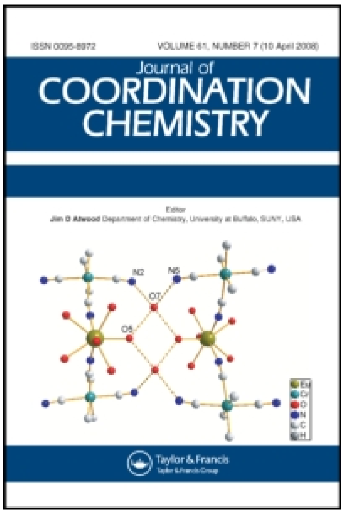

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USING TWO DIMENSIONAL NMR TECHNIQUES TO ASSIGN PROTON AND CARBON SPECTRA FOR COBALT(III) COMPLEXES DERIVED FROM LINEAR QUINQUEDENTATE LIGANDS CONTAINING NITROGEN AND SULFUR DONOR ATOMS

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High resolution NMR spectroscopy was used to study the structure of a cobalt(III) complex derived from the linear quinquedentate ligand, 7-methyl-4,10-dithia-1,7,13-triazatridecane, NH_2-CH_2CH_2-S-CH_2CH_2-N(CH_3)-CH_2CH_2-S-CH_2CH_2-NH_2. The flexibility of this ligand allows it theoretically to form four distinct structural isomers with metal ions. The one dimensional proton spectrum exhibited by [Co(NSNSN)Cl]Cl_2, is complicated and does not provide structural insight. A combined utilization of proton, carbon, DEPT, COSY, NOESY and HETCOR spectra was employed to establish geometric structure type, make individual proton assignments, identify proton-proton connectivities that result from scalar coupling, and distinguish interactions occurring as a result of through-space interactions. Information about the five-membered chelate ring orientations was also obtained. Two groups of signals were shown to correlate with each carbon signal, exhibiting a definite nonequivalence between geminal protons. Geminal protons were found to have coupling constants of 14 Hz. In contrast, the vicinal protons were found to have coupling constants of 5-7 Hz.

Keywords: 2-D NMR, quinquedentate, cobalt(III), carbon spectrum, structure, proton spectrum

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INTRODUCTION

The stereochemistry of cobalt(III) complexes derived from quinquedentate ligands containing nitrogen and sulfur donor atoms has been of interest to us for several decades [1-4]. In the beginning, the application of proton NMR spectroscopy to metal-polydentate chelate structure and stereochemistry had limited success [1,2]. Legg and co-workers [5] first used ^1H NMR to identify isomers of Co(EDDA)XX^-. More recently Yamomoto and others have extensively published cobalt(III) complexes derived from tripodal and linear quadridentate ligands [6-13]. Toscano and co-workers [14,15] also used carbon and proton NMR coupled with X-ray structure data to demonstrate a high stereospecificity for several cobalt(III)-NNSN quadridentate ligand systems.

Aside from the presence of an occasional unique structural feature on the ligand, such as a methyl group or pyridine ring, chelate compounds produce convoluted proton spectral patterns which usually defy interpretation and assignment. The net result is that one-dimensional proton and carbon spectra become NMR fingerprints used to identify or support the purity of specific geometrical or optically active isomers [5-15].

Modern FT NMR technology coupled with high field strengths and two dimensional experimental techniques [16-19] provides an opportunity for metal-chelate spectral interpretation and proton assignments. Towards this end, we report the first two-dimensional NMR study involving a cobalt(III) complex containing a flexible, linear quinquedentate having a NSNSN donor sequence [1,2,4]. Both carbon and proton NMR data are presented for the octahedral complex $[CoQCl]Cl_2$, where Q = 7-methyl-4,10-dithia-1,7,13-triazatridecane, NH_2-CH_2CH_2-S-CH_2CH_2-N(CH_3)-CH_2CH_2-S-CH_2CH_2-NH_2.

EXPERIMENTAL

All NMR data were acquired on a Bruker AMX360 Fourier Transform NMR spectrometer operating at a proton frequency of 360 MHz. Wilmad Glass #507 NMR tubes were used for all samples. A 5 mm inverse detection broad band probe was used to acquire COSY, NOESY and proton data. A standard 5 mm broad-band probe was used for carbon, DEPT and Heteronuclear Correlation experiments. All data were acquired at a temperature of 298K. Instrument parameters are presented below in Table 1.

Deuterium oxide with a deuterium purity of 99.9% was used to dissolve the complex. Internal DSS, 3-(trimethylsilyl)-1-propane sulfonic acid, was used as the chemical shift reference for proton data. Dioxane ($C_4H_8O_2$) was used as the chemical shift reference for carbon and DEPT experiments. The $[Co(Q)Cl]Cl_2$

TABLE I Instrument parameters

Figure	*Bruker Pulse Program*	*number of scans*	*WDW [F1] [F2]*	*TD [F1] [F2]*	*SI [F1] [F2]*	*Complex Conc., M*
2	ZG	8	SINE	32	16	0.05
3	COSY90	8	SINE	512	1024	0.05
SINE	1024	1024				
5	COSYPR	4	SINE	256	512	0.10
SINE	512	512				
6	HXCO	48	QSINE	64	128	0.20
QSINE	512	512				
7	NOESYTP	16	EM	256	512	0.10
EM	512	512				
8	COSYDFT	8	QSINE	512	1024	0.10
P	QSINE	1024	1024			

was prepared and purified using literature methods [1,2]. Complex solution concentrations were 0.05 to 0.2 M.

RESULTS AND DISCUSSION

The various proton sets on $[Co(Q)Cl]Cl_2$ are very similar with respect to their chemical environments. This, and the fact that they are constituents of four different five-membered chelate ring systems which can each exist in a λ or δ ring conformation, produces a complicated proton spectrum. Early attempts to analyze the proton spectrum based on splitting patterns and chemical shifts alone, were unsuccessful. Excluding the methyl group, the proton signals are crowded into a window approximately 0.8 ppm wide. Carbon and DEPT spectra [20] were used to provide information about the symmetry of this metal complex in solution. Only two of the five carbon signals could be assigned on the basis of chemical shift and DEPT phasing. A COSY spectrum [21] provided information about connectivities between the various proton signals, but specific assignments remained elusive. A long-range COSY spectrum revealed interactions between the methyl group and adjacent protons, providing the basis for the first specific assignments in the proton spectrum. Another COSY acquired in acidic solution, reveals the presence of cross peaks with amine protons. This helped to assign additional proton signals. Finally, a heteronuclear correlation [22] was performed which made the remaining assignments possible.

Carbon and Dept Spectra

Complexes with pentadentate ligands are capable of forming four different geometric isomers. Chemical and physical evidence to date establishes the

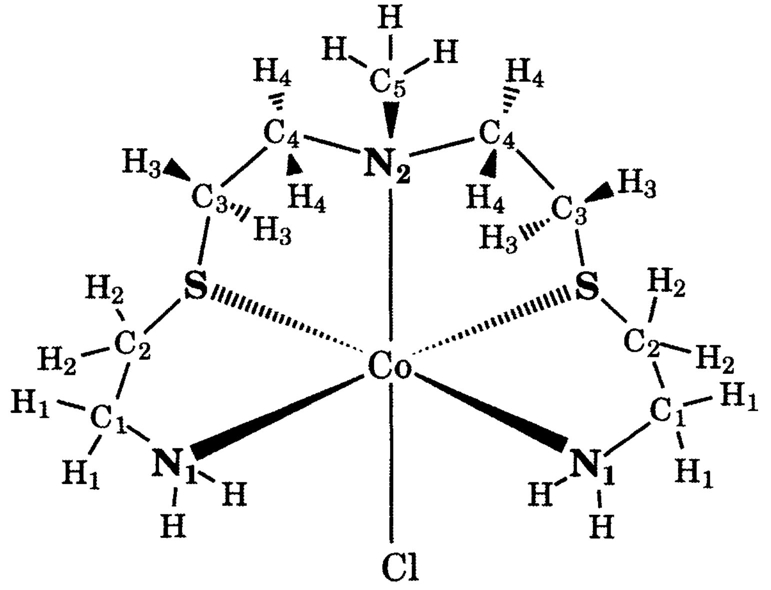

FIGURE 1 The (α,α) Isomer of $[Co(Q)Cl]Cl_2$.

existence and isolation of only the (α,α) isomer. This isomer and the atom numbering system which is used in subsequent sections is shown in Figure 1. Since the (α,α) isomer is the only isomer (of the four possible) to possess a mirror plane, its structure is confirmed by the number of carbon signals. The metal chelate contains nine carbon atoms, and the carbon spectrum exhibits only five signals (32.32, 41.73, 43.36, 49.35, and 66.62 ppm), consistent with the symmetrical (α,α) geometry.

Literature reports place secondary carbons bonded to sulfur (C-S) typically between 25 and 45 ppm and secondary carbons bonded to nitrogen (C-N) between 40 and 60 ppm [6,23]. Similar assignments were made by Massoud and Milburn [24,25] who studied cobalt(III) complexes containing the tripodal ligand tripropylenetriamine. In contrast, chemical shifts for carbons adjacent to a coordinated $-NH_2$ group were reported to occur at approximately 43 ppm [6].

The resonance at 66.62 ppm is shifted considerably downfield from the other carbon signals and is clearly outside the chemical shift range for S-C carbons. If a downfield shift resulting from coordination is considered, then this resonance does fall within expected values for a secondary C-N carbon. However, $[Co(Q)Cl]Cl_2$ contains two C-N carbons, C1 and C4. As will be shown later, additional information allows the carbon signal at 66.62 ppm to be assigned with certainty to C4.

TABLE II Carbon spectrum data for $[Co(Q)Cl]Cl_2$

Chemical Shift (ppm)	*DEPT Phasing*	*Basis for Assignment*	*Assignment*
32.32	negative	COSY/HETCOR	C3
41.73	negative	COSY/HETCOR	C2
43.36	negative	COSY/HETCOR	C1
49.35	positive	DEPT Phasing	C5
66.62	negative	Chemical Shift	C4

A mirror plane divides the molecule such that there are two C1, C2, C3, and C4 carbons. There is a single C5 carbon. The less intense resonance at 49.35 ppm is assigned to the methyl C5 carbon and is consistent with the DEPT spectrum [20] which shows the 49.35 ppm resonance phased differently from the others.

No other carbon signals can be assigned on the basis of chemical shift and DEPT phasing alone. The signal at 32.32 ppm is most likely due to C3 adjacent to sulfur, based on its chemical shift. On the basis of the carbon data alone it is not possible to distinguish between C2 and C3, the carbons adjacent to sulfur. As will be discussed later, these two assignments are made from a combination of COSY and HETCOR [22] spectra. Table 2 summarizes the chemical shifts for carbon resonances and their ultimate assignments.

Proton Spectra

The proton spectrum for $[Co(Q)Cl]Cl_2$ is shown in Figure 2. The chemical shifts and integration values are listed in Table 3. This spectrum is impossible to assign

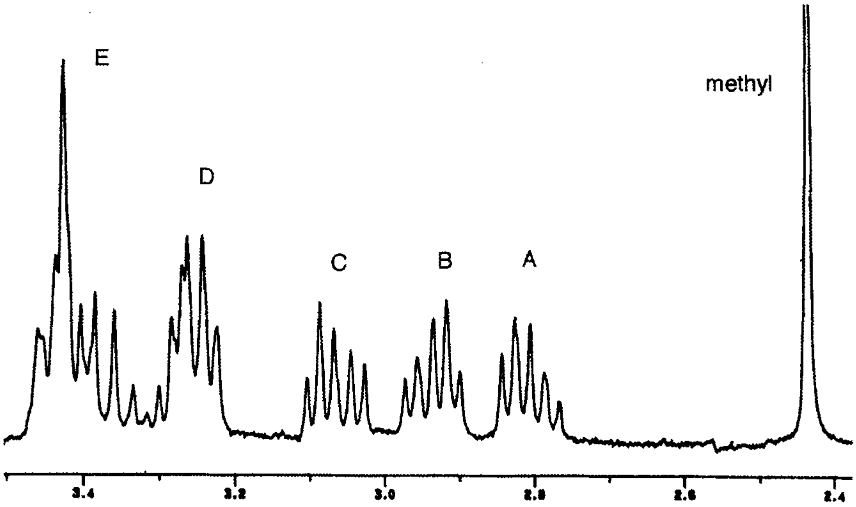

FIGURE 2 Proton Spectrum of $[Co(Q)Cl]Cl_2$.

TABLE III Summary of proton data for $[Co(Q)Cl]Cl_2$

Chemical Shift (ppm)	*Integration*	*Region Label*	*Protons On*
2.43	2.99	methyl group	C5
2.79-2.84	2.03	A	C4
2.90-2.97	1.99	B	C4
3.03-3.10	1.99	C	C3
3.22-3.30	4.00	D	C2 and C3
3.33-3.46	5.88	E	C1 and C2

solely on the basis of chemical shifts and splitting patterns. Since the methyl group is isolated from the nearest protons by more than three bonds, its resulting signal appears as a singlet at 2.43 ppm. It is necessary to examine additional spectral data (HETCOR) before other assignments can be made.

COSY Spectrum

The COSY spectrum of $[Co(Q)Cl]Cl_2$ is shown in Figure 3. Spatially, the methyl group of $[Co(Q)Cl]Cl_2$ is isolated from other protons by four bonds and appears as a singlet, not showing connectivity to other protons. No other signals are readily identifiable on the basis of multiplicity. To further interpret this COSY spectrum it is necessary to visually examine a model of the molecule and identify potential interactions between protons. Since couplings detected by COSY are strongest over three bonds, the protons attached to C1 and C2 are not expected to interact with those attached to C3 and C4. An interaction between a C2 proton and a C3 proton would have to occur over four bonds and should appear very weak in comparison to interactions occurring over three bonds. Such couplings are usually not detected unless the pulse program is specifically configured to detect long-range couplings [16,18]. Based on this scenario, *two* isolated spin systems are expected. One formed by the two protons (four total) attached to C1 and C2, and the other formed by the two protons (four total) attached to C3 and C4. Also, because the ligand is coordinated and rotation about carbon-carbon bonds is restricted, the two protons attached to each carbon become nonequivalent. Each spin system therefore contains *four nonequivalent* protons. Consider carbon C1. The two nonequivalent protons attached to this carbon are designated H1a and H1b. Each of these protons have *three* potential interactions. For example H1a may interact with H2a and H2b over three bonds and with H1b over two bonds. The expected net result is a complex multiplet for each proton.

The proton spectrum in Figure 1 is readily divided into five distinct regions. For the sake of simplicity, letters are used to designate each region. For example "A" is used to denote the multiplet centered at approximately 2.8 ppm, "B" is

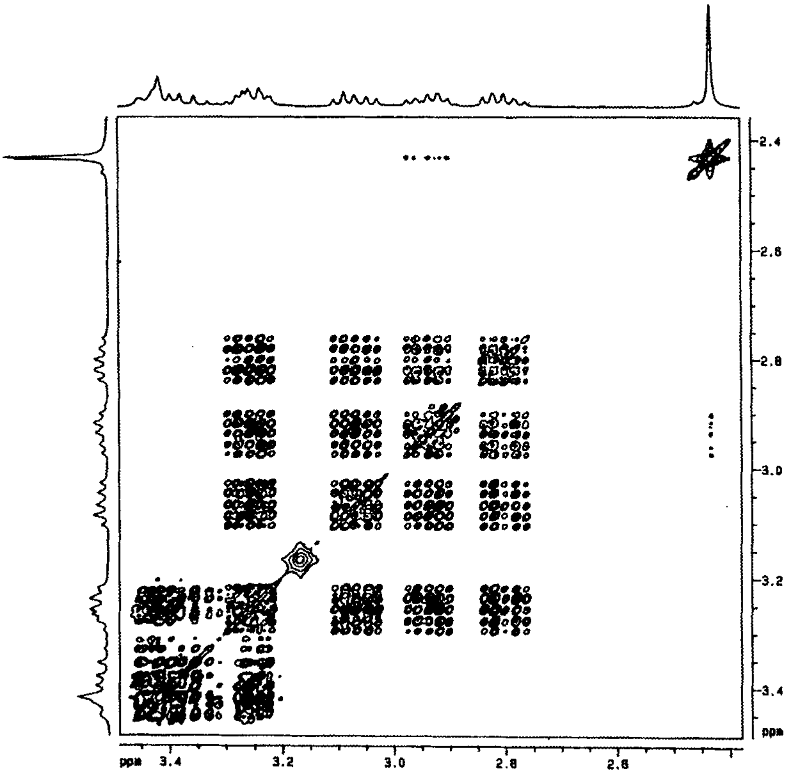

FIGURE 3 Magnitude COSY Spectrum of $[Co(Q)Cl]Cl_2$.

	E	D	C	B	A
A		AD	AC	AB	AA
B		BD	BC	BB	BA
C		CD	CC	CB	CA
D	DE	DD	DC	DB	DA
E	EE	ED			

FIGURE 4 Simplified Representation of the COSY Spectrum.

used to denote the multiplet centered at approximately 2.9 ppm and so forth. These designations are included with the chemical shifts in Table 3.

Using this system of designations, a simplified COSY spectrum can be constructed as shown in Figure 4. Mutual interactions are present between the "A", "B", "C" and "D" regions of the spectrum. Interactions also occur between the "D" and "E" regions of the proton spectrum but not between the "E" protons and the "A", "B", or "C" protons. Finally, the "D" region shows interactions with all of the others.

From these data it can be concluded that the "A", "B", "C" and "D" regions form one spin system, whereas the "E" and "D" regions form a second spin system. Ideally the two spin systems would be totally isolated. However, the "D" region which shows interactions with all of the other regions, must contain overlapping absorptions from both spin systems. This is not surprising since the chemical shifts of CH_2-S and CH_2-N protons are similar.

Now the goal is to assign each region to a specific proton. Four regions of the proton spectrum, "A", "B", "C" and "D" belong to the same spin system with each spin system containing four nonequivalent protons. Region "A" might be assigned to H4a, region "B" to H4b, region "C" to H3a, and region "D" to H3b. This is a logical assignment. However, there is not enough information for specific structural assignments in the proton spectrum. For example, region "A" might correspond to C1, C2, C3 or C4 protons. There is no way to tell without having at least one signal which can be unambiguously assigned.

This dilemma is resolved by considering a Long-Range COSY acquired with additional time delays to enhance long-range couplings. This reveals the presence of long-range coupling between the methyl C5 protons and the area "B" protons. The "B" area resonances are therefore assigned to C4 protons, H4a and/or H4b. It follows that the spin system represented by regions "A", "B", "C" and "D" must be due to the C3 and C4 protons. Additional support for this hypothesis comes from a COSY spectrum exhibiting cross peaks with the four amine protons at 5.84 ppm as shown in Figure 5. Cross peaks are detected with the "E" region of the proton spectrum, confirming that this region can be assigned to the C1 protons. Coordination greatly reduces the rate of terminal -NH_2 proton exchange with D_2O. The amine proton resonance is readily observable with a freshly prepared sample of complex. The broad resonance at 5.2 ppm is due to HOD.

HETCOR Spectrum

The heteronuclear correlation spectrum for $[Co(Q)Cl]Cl_2$ (Figure 6) confirms the previous proton assignments and allows one to make the remaining assignments in both the proton and carbon spectra. Coupling is clearly observed between the C5 methyl proton signals at 2.43 ppm and the C5 carbon signal at 49.35 ppm., confirming these two assignments.

Earlier the carbon signal at 66.62 ppm was assigned to C4 on the basis of its chemical shift. C4's corresponding protons were located using a long-range COSY experiment and assigned to region "B." Heteronuclear couplings are

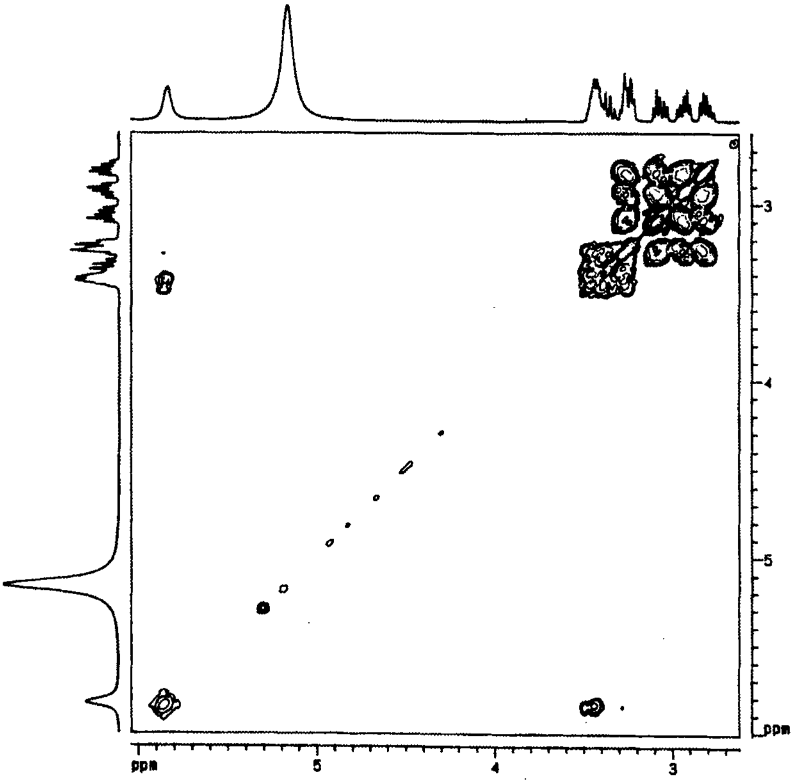

FIGURE 5 Magnitude COSY Showing Cross Peaks With Amine Protons.

clearly observed between C4 and region "B." This corroborates the C4 (and C5) assignment made previously.

Next, consider the new information which can be obtained from the heteronuclear correlation. If two protons attached to the same carbon (such as H4a and H4b) have different chemical shifts as previously hypothesized, then these two proton signals should show connections to the same carbon. The heteronuclear correlation clearly shows that the "A" and "B" regions of the proton spectrum correlate with the same carbon, the C4 signal at 66.62 ppm. Therefore the non-equivalence of two protons attached to the same carbon is clearly established.

Additional Carbon Assignments

At this point, only two of the five carbon resonances are definitively assigned, C4 on the basis of chemical shift data and C5, on the basis of DEPT phasing. In the COSY spectrum, it was shown that regions "A", "B", "C" and "D" interact with

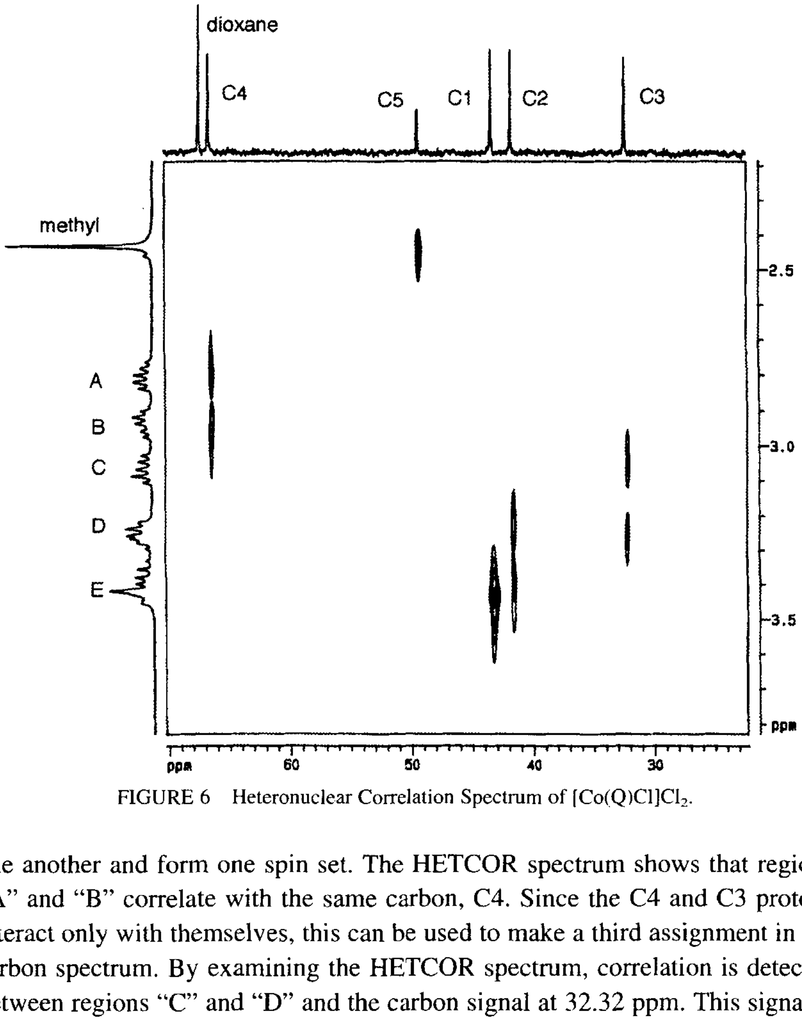

FIGURE 6 Heteronuclear Correlation Spectrum of [Co(Q)Cl]Cl_2.

one another and form one spin set. The HETCOR spectrum shows that regions "A" and "B" correlate with the same carbon, C4. Since the C4 and C3 protons interact only with themselves, this can be used to make a third assignment in the carbon spectrum. By examining the HETCOR spectrum, correlation is detected between regions "C" and "D" and the carbon signal at 32.32 ppm. This signal is therefore assigned to the C3 carbon. This carbon is indeed adjacent to sulfur as originally suggested on the basis of chemical shift data alone. Referring to the HETCOR spectrum, region "E" exhibits a correlation with the C1 carbon signal at 43.36 ppm. Finally, the one remaining carbon signal at 41.73 ppm can be assigned to C2 through a process of elimination (see Table 2).

NOESY SPECTRUM[26]

The preceding discussions divide the proton spectrum into different regions, assign the signals to different spin systems, and correlate the proton and carbon

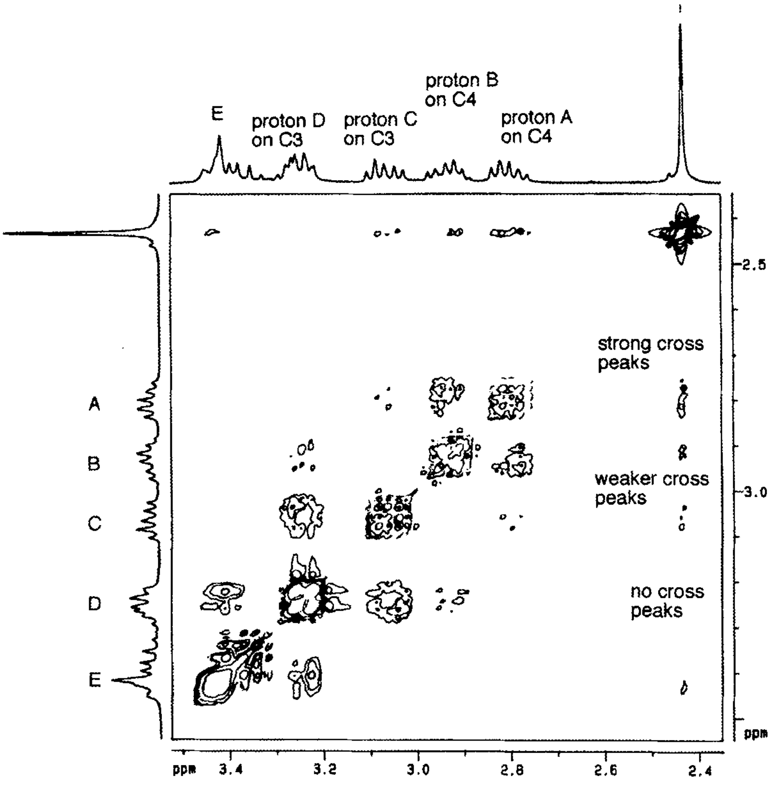

FIGURE 7 NOESY Spectrum of $[Co(Q)Cl]Cl_2$.

signals. However, a certain degree of ambiguity remains in the assignment of the proton signals. For example, the heteronuclear correlation clearly shows the C4 carbon to correlate with two different protons, but it is not possible to distinguish between these two protons. The structure of the molecule is such that the methyl group projects forward, giving the H4a and H4b protons different orientations, one projecting towards the methyl group and the other projecting away from it. The H3a and H3b protons also have different orientations with respect to the methyl group. It should therefore be possible to take the analysis one step further and assign specific resonances to these protons.

This is achieved by considering the NOESY spectrum shown in Figure 7. Consider the cross peaks with the C5 methyl singlet. The strongest interactions occur with the "A" region of the proton spectrum. This region is therefore assigned to the C4 proton which projects towards the methyl group. Cross peaks are also observed with the "C" region of the proton spectrum but not the "D" region, again indicating that one proton projects towards the methyl group while one proton projects away from it.

Geometry can be used to show that, excluding any twisting of the carbon-carbon bonds, the distance between vicinal protons is approximately 1.30 times greater than the distance between geminal protons. Any twisting of the carbon-carbon bond will increase the through space distance between the vicinal protons, whereas the distance between geminal protons remains the same. Because five-membered chelate rings can exist in either a λ or δ ring conformation, twisting of the carbon-carbon bond may occur, decreasing the distance between geminal protons and increasing distances for vicinal protons.

Phase-Sensitive COSY

The previous discussions do not address an interpretation of the pentet splitting patterns observed in the proton spectrum of $[Co(Q)Cl]Cl_2$. The A, B, C, and D envelopes result from an isolated spin system containing four non-equivalent protons. Each proton interacts with three others, one interaction occurring across two bonds and the other two occurring across three bonds. The signal from an individual proton is split into a doublet, then again into a pair of doublets, and once more into a sextet. Each proton resonance pattern appears as a distorted pentet due to overlapping doublet components.

In a *phase sensitive* COSY experiment, the *active coupling*, or the coupling responsible for the formation of a cross peak, will appear in antiphase. Each proton will have three cross peaks connecting with three other protons. However, the phasing of the signals will be different in each of the three cross peaks depending upon which couplings are active and which couplings are passive. By carefully examining the phasing of the cross peaks, it is possible to explain the origin of the pentet structure as well as to distinguish between the three interactions.

Cross peaks between proton A and protons B, C and D are shown in Figure 8. The top cross peak display is the result of the proton A-proton B interaction. The splitting of the signals due to proton A would occur as follows: First, the signal is split into a doublet by a two-bond interaction with proton B. Since this is the active coupling, the resulting doublet components have *opposite phase*. Next, each doublet component is split again by a three-bond interaction. This is a *passive* coupling, and so the phasing remains the same. Finally, the signals are split once more by the second three-bond interaction. This coupling is also passive. Since the magnitude of two-bond couplings is typically larger than for three-bond couplings, the original phasing introduced by the two-bond interaction is maintained. In other words, positive signals appear on one side and

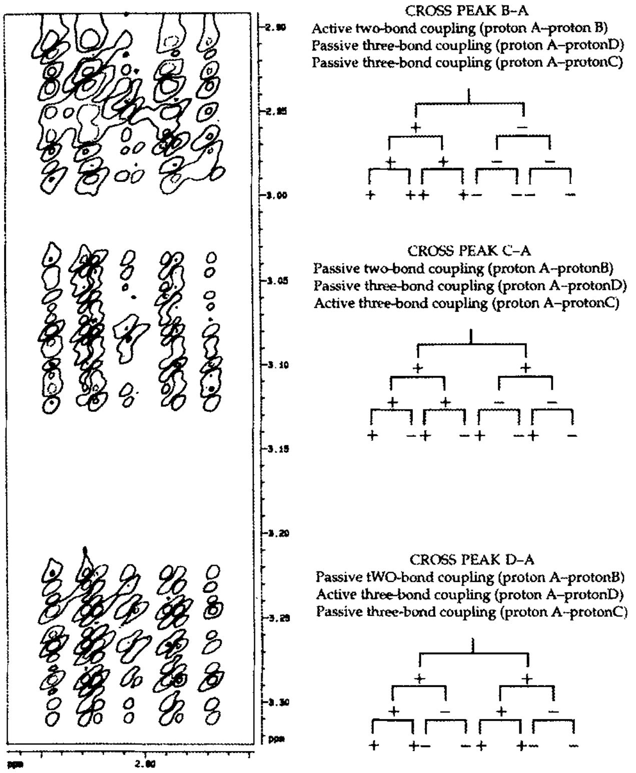

FIGURE 8 Cross Peak Correlations Between Proton A and Protons B, C and D.

negative signals appear on the other. The two-bond coupling is shown to be 14.4 Hz, which is very close to the value we observe for other complexes.

The center cross peak display is the result of the interaction between proton A and proton C. The signal due to proton A is first split by a two-bond interaction with proton B. This time, the two-bond coupling is passive and opposite phasing of the doublet components does not occur. Each doublet component is split by the *active* three-bond coupling, and opposite phasing of the signals is produced. Finally, these signals are again split by the second three-bond coupling, which is *passive*.

The lower cross peak display occurs as a result of proton A and proton D interaction. Here the signal from proton A is split into a doublet by passive coupling with proton B as before. Each doublet is split again by a three-bond interaction, only this time the coupling is passive. The second three-bond interaction, the active coupling in this case, results in the phasing shown in the third (last) tier of the splitting pattern of Figure 8.

CONCLUSIONS

In spite of the NMR proton spectral complexities, the assignment of all the carbon atoms and all but two of the proton resonance patterns for $[Co(Q)Cl]Cl_2$ is possible using two dimensional techniques.

Coordination chemists have traditionally used proton NMR in a restrained way (no 2D NMR studies) to provide a fingerprint for identifying geometric isomers of metal chelates. Actual proton assignments have been limited to small bidentate ligands which usually contain a selectively placed methyl group or another unique structural feature that assists in spectral assignments.

This is the first 2-Dimensional NMR study of a monomeric cobalt(III) complex derived from a flexible, linear quinquedentate ligand. This is a complicated system in comparison to previously studied chelate compounds. The preliminary results allow interpretation and proton assignment for the majority of protons present. More importantly, this study demonstrates the power and value of 2D NMR techniques when applied to inorganic coordination compounds.

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