

High-resolution NMR analysis of cobalt(III) complexes with 1,8-diamino-3,6-dithiaoctane

Mark R. McClure, K.W. Jung, Jay H. Worrell *

Department of Chemistry, The University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620-5250, USA

Received 9 June 1997; accepted 27 September 1997

Contents

Abstract	33
1. Introduction	34
2. Background	34
3. Applications of NMR to the study of cobalt(III) complexes	38
4. Experimental	39
5. Carbon and dept spectral data	40
6. Proton and heteronuclear correlation data	41
7. Cosy spectra	44
8. Related complexes	47
9. Conclusions	48
Acknowledgements	48
References	49

Abstract

This article summarizes NMR data obtained for cobalt(III) complexes derived from linear and tripodal tetradentate or pentadentate ligands containing nitrogen and/or sulfur donor atoms, and not complexes of large Schiff-base macrocycles, porphyrins or corrins. The review is supplemented with recent NMR work on complexes that had their origin in the laboratories of Professor Busch at a time when the use of NMR spectroscopy as an inorganic structural tool was in its infancy. The more recent capabilities and uses of nuclear magnetic resonance spectroscopy for assisting in metal complex structure assignments and isomeric identification are illustrated by the following work.

Cobalt(III) complexes containing the quadridentate ligand 1,8-diamino-3,6-dithiaoctane (eee) were examined by high resolution one and two-dimensional NMR techniques. The spectra acquired using conventional pulse sequences include proton, carbon, DEPT, COSY and heteronuclear correlation. $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ and $[\text{Co}(\text{eee})\text{Cl}_2]\text{Cl}$ both give rise to

* Corresponding author. Tel: +1 813 974 4238; Fax: +1 813 974 3203; e-mail: worrell@chuma.cas.usf.edu

carbon-13 spectra which contain only three signals and ^1H -proton spectra which contain a highly pronounced A_2B_2 pattern. This data is supportive of the *symmetrical cis* geometry. Assignments in the proton spectra were assisted by the use of the COSY experiment. Carbon-13 signals were assigned by heteronuclear chemical shift spectroscopy. The DEPT spectra confirmed all carbon signals arise from methylene carbons. The study highlights the power of ^1H and ^{13}C NMR spectroscopic techniques for the structural characterization of inorganic complexes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: 2-D NMR; quadridentate; cobalt(III); carbon spectrum; structure; proton spectrum

1. Introduction

Over the last decade numerous researchers have studied the stereochemistry of polydentate ligands coordinated to cobalt(III). The tools commonly employed to distinguish different geometrical and optical isomers have traditionally been various types of optical spectroscopy coupled with chemical interconversion reactions. Nuclear magnetic resonance studies met with very limited success. Without a unique structural feature on the ligand, such as a methyl group or pyridine ring, polydentate chelate compounds produce convoluted proton spectral patterns which usually defy interpretation and assignment. The net result has been that one-dimensional proton and carbon spectra were used only as NMR fingerprints to identify or support the purity of a specific geometrical or optically active isomer. Modern FT NMR technology and recent two-dimensional experimental techniques provides an opportunity for metal-chelate nuclear magnetic resonance spectral interpretation and proton assignments.

In the work to follow, we summarize NMR data obtained for cobalt(III) complexes derived from linear and tripodal tetradentate or pentadentate ligands containing nitrogen and/or sulfur donor atoms, and not complexes of large Schiff-base macrocycles, porphyrins or corrins. The review is supplemented with recent NMR work on complexes that had their origin in the laboratories of Professor Busch at a time when the use of NMR spectroscopy as an inorganic structural tool was in its infancy. The study highlights the power of ^1H and ^{13}C NMR spectroscopic techniques for the structural characterization of inorganic complexes by examining two cobalt(III) complexes derived from 1,8-diamine-3,6-dithiaoctane, first studied by Busch and Worrell [1,2] many years ago.

2. Background

Cobalt(III) complexes with the quadridentate ligand 1,8-diamino-3,6-diazaoctane (trien) were first reported by Sargeson and Searle thirty years ago [3,4] with additional studies extended by Buckingham et al. [5]. It was recognized very early on that metal complexes may adopt more than one isomeric geometry, depending on the connectivities between donor atoms of the ligand as it binds to a metal center. The three possible geometric isomers for linear tetradentate ligands are the *symmetri-*

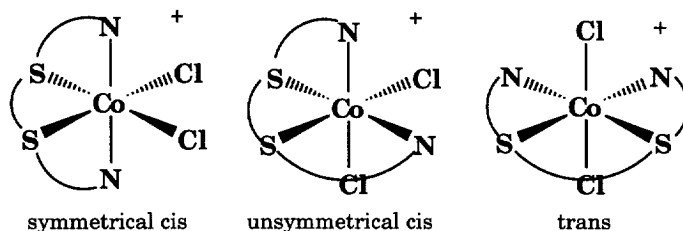


Fig. 1. Three possible geometric isomers for coordinated linear tetradentate ligands.

cal cis isomer, the *trans* isomer and the *unsymmetrical cis* isomer as shown in Fig. 1. Researchers immediately began to investigate ligands similar in structure to trien and to study their influence upon coordination geometry. An extensive list of reported linear tetradentate ligands are presented in Table 1 and are discussed in the following sections. This early synthetic work occasionally included a 60 or 100 MHz proton spectrum for the complexes (see Table 1).

Several approaches have been used to study the effect of ligand design on isomer distributions and geometry. One was to increase the length of the carbon chains ($-\text{CH}_2)_n-$) joining sequential nitrogen donor atoms, such as in the ligands 2,3,2-tet, 3,2,3-tet and 3,3,3-tet, where tet is $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}-(\text{CH}_2)_n-\text{NH}-(\text{CH}_2)_n-\text{NH}_2$. Alexander and Hamilton [6] studied 3,2,3-tet and report the favored formation of the *trans* isomer, presumably because of increased flexibility of the terminal arms. Synthesis of the *symmetrical cis* isomers was possible only when a bidentate ligand was used to occupy the remaining two coordination sites. Similarly, the ligand 2,3,2-tet was also reported to preferentially form the green *trans* isomer [7]. Later, Yamamoto and co-workers [8–10] began to supplement their synthetic and structural studies by using both carbon and proton NMR spectroscopy to identify the stereochemistry of *cis* and *trans* dichlorocobalt(III) complexes derived from 2,2,2-tet, 2,3,2-tet, 3,2,3-tet and 3,3,3-tet.

Another approach was the introduction of symmetrically placed methyl groups on the carbon atoms of the side chains. In such cases stereospecificity depends upon the placement of the methyl groups. Asperger and Liu [11] report that all three geometrical isomers are possible for the ligand 2,9-dimethyl-4,7-diazadecane. Goto et al. report the preferential formation of the *unsymmetrical cis* isomer for the ligand 5,6-dimethyl-4,7-diazadecane [12]. Placement of methyl groups on the 3,8 positions results in the formation of the *trans* isomer [13].

Goto et al. report several linear ligands having methyl groups placed on chain carbon atoms and terminal nitrogen atoms. Among those studied were 2,5,8,11-tetraazadodecane and 2,5,9,12-tetraazatridecane. These two ligands can be viewed as derivatives of 2,2,2-tet and 2,3,2-tet, respectively, containing methyl groups attached to the *terminal* amine donors. Cobalt(III) complexes preferentially form the *trans* isomer [14].

The ligand 4,7-dimethyl-1,4,7,10-tetraazadecane was later studied by Searle et al., being a derivative of 2,2,2-tet with methyl groups positioned at the two *central secondary nitrogen* donors. Apparently, no stereospecificity is observed [15].

Worrell and Busch pioneered the study of ligands with *nitrogen and sulfur* donor

Table 1

Summary of NMR work and ligands studied

Tetradentate ligands bound to Co(III)	NMR work	Ref.
NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂ (2,2,2-tet)	100 MHz proton	[3–5]
NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂ (2,3,2-tet)	none reported	[7]
NH ₂ CH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NH ₂ (3,2,3-tet)	none reported	[6]
NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂ (2,2,2-tet)	60 MHz proton	[8–10]
NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂ (2,3,2-tet)	carbon spectra	
NH ₂ CH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NH ₂ (3,2,3-tet)		
NH ₂ CH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NH ₂ (3,3,3-tet)		
NH ₂ (CH ₃)CHCH ₂ NCH ₂ CH ₂ NCH ₂ CH(CH ₃)NH ₂	60 MHz proton	[11]
NH ₂ CH ₂ CH ₂ NH(CH ₃)CHCH(CH ₃)NHCH ₂ CH ₂ NH ₂	100 MHz proton	[12]
H ₂ NCH ₂ CH(CH ₃)NCH ₂ CH ₂ N(CH ₃)CHCH ₂ NH ₂	none reported	[13]
(CH ₃)NHCH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH ₂ NH(CH ₃)	60 MHz proton	[14]
(CH ₃)NHCH(CH ₃)CH ₂ NHCH ₂ CH ₂ NCH ₂ CH(CH ₃)NH(CH ₃)		
(CH ₃)NHCH(CH ₃)CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH(CH ₃)NH ₂		
(CH ₃)NHCH ₂ CH ₂ NHCH(CH ₃)CH ₂ NHCH ₂ CH ₂ NH(CH ₃)		
(CH ₃)NHCH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NH(CH ₃)		
Tetradentate/pentadentate ligands bound to Co(III)		
NH ₂ CH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ NH ₂	60 MHz proton	[14]
NH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ NH ₂ (eee)	100 MHz proton	[1,2]
NH ₂ CH ₂ CH ₂ SCH(CH ₃)CH ₂ SCH ₂ CH ₂ NH ₂ (epe)	none reported	[16]
NH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ NH ₂ (EEE)	100 MHz proton	[17]
NH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ NH ₂ (ETE)		
NH ₂ CH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ CH ₂ NH ₂ (TET)		
NH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ SCH ₂ CH ₂ NH ₂ (Q)	60 MHz proton	[18–20]
NH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ NH ₂ (QS)	none reported	[21,22]
HSCH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ SH	90 MHz proton	[23,24]
HSCH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ SH		
HSCH ₂ CH ₂ N(CH ₃)CH(CH ₃)CH ₂ CH ₂ N(CH ₃)CH ₂ CH ₂ S	(used to identify isomers)	
HSC(CH ₃) ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ C(CH ₃) ₂ CSH		
(2-py)CH ₂ NH(CO)CH ₂ SCH ₂ CH ₂ NH ₂	300 MHz proton and carbon	[25,26]
NH ₂ CH ₂ (CO)CH ₂ CH ₂ SCH ₂ CH ₂ NH ₂		
N(CH ₂ CH ₂ NH ₂) ₃ (tren)	300 MHz proton and carbon	[27]
N(CH ₂ CH ₂ CH ₂ NH ₂) ₃ (trpn)	90 MHz, carbon	[28,29]
Other ligands bound to Co(III)		
Several pentadentate tripodal ligands containing one or more (2-pyridyl) donors	200 MHz, carbon	[30]
(2-Py)–CH ₂ (NH)CH ₂ CH ₂ (NH)CH ₂ –(2-Py)	200 and 360 MHz proton	[31]
(2-pyridylmethyl)ethylenediamine (uns-penp)	300, 360 MHz proton	[32]
<i>N,N,N',N'</i> -tetrakis(2-pyridylmethyl)-ethylenediamine (tpen)	COSY	
<i>N,N,N',N'</i> -tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn)		
<i>N,N,N'',N'</i> -tetrakis(2-pyridylmethyl)-1,2-propanediamine (tppn)		
(2-pyridyl)CH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ (2-pyridyl)	none reported	[33]
1,4,7,11,14,17-hexathiacycloisocane, 1,4,7-trithiecan-9-ol	proton and carbon	[34]
1,6-bis(2-thienyl)-2,5-dithiahexane	for ligands only	
1,9-bis(2-thienyl)-2,5,8-trithianonane		
1,9-bis(2-pyridyl)-2,5,8-trithianonane		
1,9-bis(2-benzimidazolyl)-2,5,8-trithianonane		
1,9-bis(3,5-dimethyl-1-pyrazolyl)-2,5,8-trithianonane		
1,12-bis(2-pyridyl)-2,5,8,11-tetrathiadodecane		
3,6,9,12,15-pentathiaheptadecane		
Co(II) complexes with: 1,4,7,11 hexathiacycloisocane, 1,4,7-trithiecan-9-ol, 1-oxa-4,8-dithiacyclodecane and 1,11-dioxo-4,8,14,18-tetrathiacycloeicosane	none reported	[35]

atoms. This was a significant innovation, with many nitrogen–sulfur polydentate and cyclic ligands being synthesized and studied in subsequent years. Ligand *eee* was a derivative of 2,2,2-tet but possessing an N–S–S–N donor sequence [1,2]. Surprisingly, this ligand was observed to form only the *symmetrical cis* isomer, illustrated in Fig. 1. Extensive attempts to synthesize other isomers proved futile. The ligand *epe* was later synthesized [16], which is a derivative of *eee* containing a methyl group located on the carbon atom adjacent to sulfur on the center chain. Studies performed on this ligand also revealed the exclusive formation of the *symmetrical cis* isomer. The stereospecificity of these two ligands has been attributed to the C–S–C bond angle requirements of coordinated sulfur atoms relative to nitrogen. The ligands *EEE*, *ETE* (an NSSN analog of 2,3,2-tet) and *TET* (an NSSN analog of 3,2,3-tet) were studied by Bosnich et al. [17]. The exclusive formation of the *symmetrical cis* isomer for *EEE* complexes was again observed. In contrast, dichloro-complexes with the ligand *ETE* are reported to form a green *trans* isomer and a red-violet *unsymmetrical cis* isomer. The *TET* ligand was reported to form a red-violet *unsymmetrical cis* and a blue *symmetrical cis* isomer [17]. By lengthening the carbon chains, the arms of the ligands could then more readily reach the octahedral bonding sites. Later, Worrell and Jackman went on to study the *pentadentate* ligand *Q* having a donor atom sequence N–S–N–S–N. For pentadentate systems, *four different isomers* are theoretically possible. However, complexes were found to form only a single isomer. Again, this is attributed to the specificity introduced by the short, two carbon chains and the larger sulfur donors [18–20]. Similar results are observed for complexes with the ligand *QS* (N–S–S–S–N) [21,22].

In the early 1980s, ligands designed with an S–N–N–S donor sequence were investigated by Yamanari et al. By placing the sulfur atoms at the terminal ends of the ligand negates their isomeric specificity and multiple geometric isomers were produced using these ligands. The complex $[\text{Co}(\text{SNNS})\text{en}]^+$ where SNNS represents the ligand 2,9-dimethyl-4,7-diazadecane-2,9-dithiol is reported to form both a deep violet *unsymmetrical cis* and a dark-green *trans* isomer. Complexes with the S–N–N–S ligand 2,9-dimethyl-4,7-diazadecane-2,9-dithiol form only the *unsymmetrical cis* isomer [23,24]. Still others have synthesized a series of unsymmetrical ligands which contain an N–S–N–N donor sequence [25,26].

Investigations using two non-linear *tripodal* tetradentate ligands were recently reported. Toyota et al. studied the coordination chemistry of the ligand tris(2-aminoethyl)amine (*tren*) [27] and Massoud and Milburn investigated the chelate behavior of 3,3',3''-triaminotripropylamine (*trpn*) [28,29]. These two ligands differ in that the former has nitrogen donors separated by two-carbon links, whereas in the latter they are separated by three-carbon links. Both *tren* and *trpn* form a single geometric isomer with cobalt(III) and were characterized using only carbon-13 NMR.

The addition of a fifth coordination site results in the possibility of three or four different geometric isomers depending on the ligand design. A number of *pentadentate* tripodal ligands have come under investigation. These include 3,4-(2-pyridyl)-3-azabutyl-3-azapentane-1,5-diamine, 3,4-(2-pyridyl)-3-azabut-3-enyl-3-aza-pentane-1,5-diamine and 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane.

The structures of complexes with these ligands have been determined by X-ray crystallographic methods [30].

A number of tetradentate ligands having terminal pyridyl arms have also been studied [31,32]. These do not contain sulfur donors, and all place a single carbon between the pyridine ring and the next heteroatom, [(2-py)-C-N]. A cobalt(II) complex containing the ligand 1,8-bis(2-pyridyl)-3,6-dithiaoctane has also been studied and its X-ray structure determined [33]. This ligand can be viewed as a derivative of eee, the difference being that here the terminal nitrogen donors are located within the two pyridine rings.

Research into sulfur-containing ligands is continuing. In a recent submission to Inorganic Synthesis [34], Lucas describes the synthesis of ten different thiol-containing ligands for which carbon and proton NMR data are given. Although no cobalt(III) work is reported, one paper describes the synthesis of cobalt(II) complexes with four of these ligands [35].

3. Applications of NMR to the study of cobalt(III) complexes

The NMR spectra for coordination compounds are inherently complex. This arises notably because of the restricted rotation about the C–C bond which results from ligand coordination. A simple $-\text{CH}_2-\text{CH}_2-$ linkage can contain up to *four nonequivalent* protons. Due to extensive coupling pathways, signals with multiplet structure will be observed in the ^1H NMR spectra. This and a crowding of signals in a narrow spectral range of 1–2 ppm complicate resonance assignments.

Occasionally, metal–ligand complexes may exhibit an overall symmetry which creates sets of equivalent protons thus simplifying the resulting spectra. An example of this is the A_2B_2 splitting pattern characteristic of symmetrical *cis* complexes containing the ligand eee. This was first noted by Worell and Busch in a 100 MHz proton spectrum of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ [1]. Some of the early studies focused mostly on the signals due to selectively placed methyl side groups. These were used to provide a fingerprint for the complex and imply the existence of a single geometric isomer. For example, consider the ligand 5,6-dimethyltriethylenetetramine studied by Goto et al. [12]. The researchers observed *two* methyl doublets in the NMR spectrum, which helped to assign the *unsymmetrical cis* geometry to the complex. If the complex had adopted the *symmetrical cis* or *trans* isomers, then a single methyl doublet would have been observed due to the complex's symmetry. Despite the limited successes illustrated here, it should be noted that in these cases the complexity of the proton spectra prevented attempts to assign all proton resonances.

Yamanari et al. [24] relied upon carbon NMR to help determine the coordination geometries created by their SNNS ligands. Several factors make carbon NMR ideally suited for the study of these systems. A single unique signal is observed for each carbon atom, thus eliminating the complex splitting patterns often observed for protons in these systems. Since carbon nuclei are typically characterized within a much wider NMR sweep width, overlapping of signals is less likely to be a problem. Furthermore, carbon NMR can be readily used to determine the geometry of such

systems. For example, if the ligand 2,2,2-tet were to adopt a *symmetrical cis* or *trans* isomer, only three carbon signals would be observed. If the *unsymmetrical cis* isomer were adopted, then six separate signals would be observed.

Many of the studies previously performed relied on the use of NMR spectroscopy to assist in isomer identification or structural elucidation. Due to instrument limitations, only limited spectral information was available for these complexes for some time. However, with the advent of high field spectrophotometers and two-dimensional techniques [36–41], to date a wealth of information can be obtained for these complexes.

Recently, several complexes derived from linear tetradentate and pentadentate nitrogen–sulfur ligands were investigated using two-dimensional NMR techniques [42,43]. In the following sections we present high-resolution NMR data for $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ and $[\text{Co}(\text{eee})(\text{Cl}_2)]\text{Cl}$, two of the cobalt complexes originally studied by Worrell and Busch [1,2].

4. Experimental

The complexes were prepared as described in the literature [1,2]. All data were acquired on a Bruker AMX 360 FT NMR spectrometer. Proton and COSY experiments were performed using a 5 mm inverse broadband probe. Carbon, DEPT and HETCOR experiments were acquired with a 5 mm standard broadband probe. Wilmad Glass #407 tubes were used for all measurements. Deuterium oxide (99.9% D) was used as a solvent and solutions were acidified with DCl to a concentration of 0.1M to prevent the aquation of the metal complex. Internal DSS was used as a chemical shift reference for proton work. Internal dioxane was used as the reference for carbon work and assigned a value of 67.40 ppm. All experiments were carried out at 298 K. One-dimensional datasets were acquired using 32 K of computer memory without zero-filling and processed with an exponential window function. COSY spectra of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ and $[\text{Co}(\text{eee})\text{Cl}_2]\text{Cl}$ were acquired with a resolution of 512×1024 , with zero-filling to a final resolution of 1024×1024 . The acquisition and processing parameters are detailed in Table 2.

Table 2
Acquisition and processing parameters

FIGURE	3	4	6	7,8	9
PULPROG	zgh2pr	hxco	cosy90	cosydfp	zgh2pr
NS	4	48	4	8	24
WDW [F1, F2]	em	qsine, qsine	em, em	qsine, qsine	em
TD [F1, F2]	32K	128, 512	512, 1024	512, 1024	32K
SI [F1, F2]	16K	256, 512	1024, 1024	1024, 1024	16K
LB (MHz)	0.10	n/a	0, 0	n/s	0.10
SSB	n/a	4, 4	n/a	4, 4	n/a
SW (ppm)	12.0	1.5, 10	3.0	2.0	16.0
CONC (M)	0.09	0.17	0.09	0.17	0.13

PULPROG refers to the pulse program used to acquire the data. Pulse program descriptions are found in the Bruker UXN MR user's guide, version 91091. *TD* is the amount of computer memory used to store the free induction decay. *SI* refers to the amount of computer memory used in processing the datasets. Without zero-filling $SI = TD/2$. If $SI > TD/2$ then the FID is filled out with $(2 \cdot SI) - TD$ zeroes before transformation. *NS* is the number of scans. *WDW* refers to the window function used to process the free induction decay prior to the Fourier transform. Line broadening (*LB*) is used with the exponential multiplication (em) window function to enhance resolution. The shifted sine bell (SSB) is used with the q sine window function. *SW* is the spectral width used to acquire the data.

5. Carbon and DEPT spectral data

Information concerning the geometrical arrangement of the ligand around the complex can be deduced from the carbon spectra. The carbon spectrum of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ contains three distinct signals at 46.46, 41.27 and 40.14 ppm. All signals are attributed to methylene carbons based upon the phasing of the signals in a DEPT spectrum. The *trans* form contains a mirror plane, and the symmetrical *cis* form contains a C2 axis. Both symmetry operations divide the complex into *three* sets of two equivalent carbons. If $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ were to adopt either of these geometries, then *three* carbon signals would be observed. It is unlikely that the sample contains a mixture of symmetrical *cis* and *trans* isomers since only three carbon resonances are observed and such a mixture would certainly not produce signals at exactly the same chemical shifts. The unsymmetrical *cis* form, in contrast, does not contain any symmetry elements and if $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ were to adopt this geometry, then *six* carbon signals would be observed. We know this compound is not the *trans* geometry from an X-ray structure [44,45].

Several ligand carbon assignments are readily made by comparing their chemical shifts with known carbon types. In the subsequent discussion the atoms will be referred to by their labels in Fig. 2. It is logical to expect C2 and C3 to have similar chemical shifts since they are both adjacent to sulfur, whereas C1 is different, being adjacent to nitrogen. Two singlets for the ^{13}C resonances are observed at 40.15 and 41.27 ppm and are relatively close together. They are due to carbons having very similar chemical environments. These two signals are assigned to C2 and C3, respectively. Since the terminal nitrogen atom is more electronegative than sulfur, the C1 carbon should be more deshielded than the others, the result being its ^{13}C resonance is shifted downfield. Therefore, the singlet signal at 46.46 ppm is assigned to the C1 carbon. As will be shown later, these assignments are also confirmed by correlation with the proton spectra. The chemical shifts are shown in Table 3 for $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$, $[\text{Co}(\text{eee})(\text{Cl})_2]\text{Cl}$ and for *eee*-HCl itself. The chemical shifts are only slightly different for the dichloro- relative to the dinitro- complex.

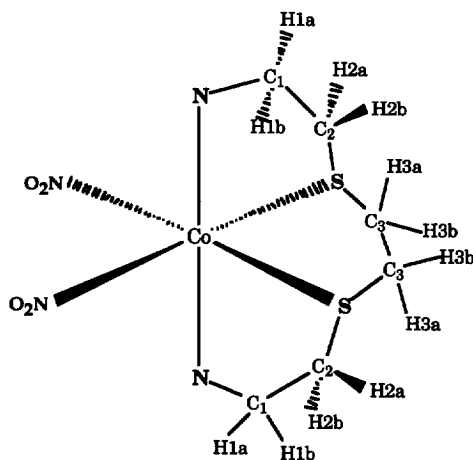


Fig. 2. Perspective view of the symmetrical *cis* isomer of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$.

Table 3
Summary of ^{13}C chemical shifts

Assignment	$[\text{Co}(\text{eee})(\text{NO}_2)]\text{Cl}$	$[\text{Co}(\text{eee})\text{Cl}_2]\text{Cl}$	$\text{eee}-2\text{HCl}$
C1	46.46	47.11	39.36
C2	40.14	40.51	29.05
C3	41.27	42.63	31.37

6. Proton and heteronuclear correlation data

$[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$. The crowded 360 MHz NMR proton spectrum for $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ is shown in Fig. 3. Analysis of the spectrum is best facilitated by first identifying three general proton resonance regions; 2.73–2.90 ppm (two protons), 3.1–3.25 ppm (six protons) and 3.25–3.65 ppm (four protons). To obtain further understanding of each of these regions one must obtain and analyze a two-dimensional heteronuclear correlation spectrum.

The heteronuclear correlation spectrum which reveals connectivities between a carbon atom and its directly bonded protons is shown in Fig. 4 for $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$. The multiplicity of the proton signals resulting in the apparent A_2B_2 doublets located between 3.37 and 3.65 ppm only correlate with the C3 carbon signal at 41.27 ppm, so these proton signals are assigned to the protons attached to the two backbone C3 carbon atoms. Recall that the backbone C3 carbons are adjacent to sulfur, and their ^{13}C signal was originally assigned on the basis of its carbon chemical shift alone.

The proton signals at 2.73–2.90 ppm show cross peaks with the amine protons in the COSY spectrum and here correlate only to the C1 carbon signal at 46.46 ppm. This signal is therefore assigned to the two C1 carbon atoms positioned adjacent to

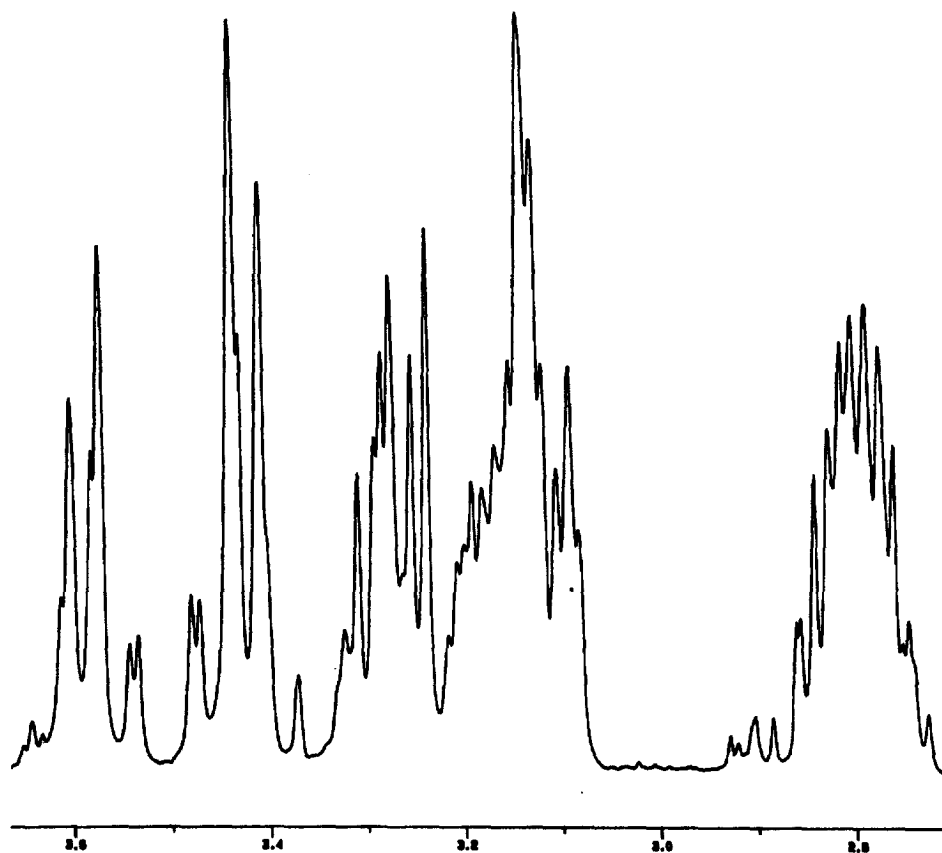


Fig. 3. Proton spectrum of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$.

the terminal nitrogen donor in the coordinated *eee* ligand. Finally, the one remaining carbon resonance at 40.14 ppm is assigned (by a process of elimination) to the two C2 carbon atoms adjacent to sulfur in the terminal arms of the ligand. The complexity of the proton region 3.1–3.25 ppm is, in part, due to coupling of one or more protons on both C1 and C2.

Assignment for the protons on C1 and C2 of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ is in agreement with published chemical shifts for similar complexes. Yamamoto and Toyota [5–7] reported resonances in the region 2.7–2.9 ppm as belonging to carbon protons immediately adjacent to the terminal NH_2 groups for cobalt(III) complexes derived from 2,2,2-tet and 2,3,2-tet. For $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$, signals observed at 2.74–2.90 ppm and assigned to *one* proton (Ha or Hb) on each of the C1 carbons. The remaining signals at 3.08–3.32 ppm are due to the two remaining C1 protons and the four C2 protons. These resonance patterns at 360 MHz do not allow us to assign a specific resonance to each of the four nonequivalent protons in these two spin systems.

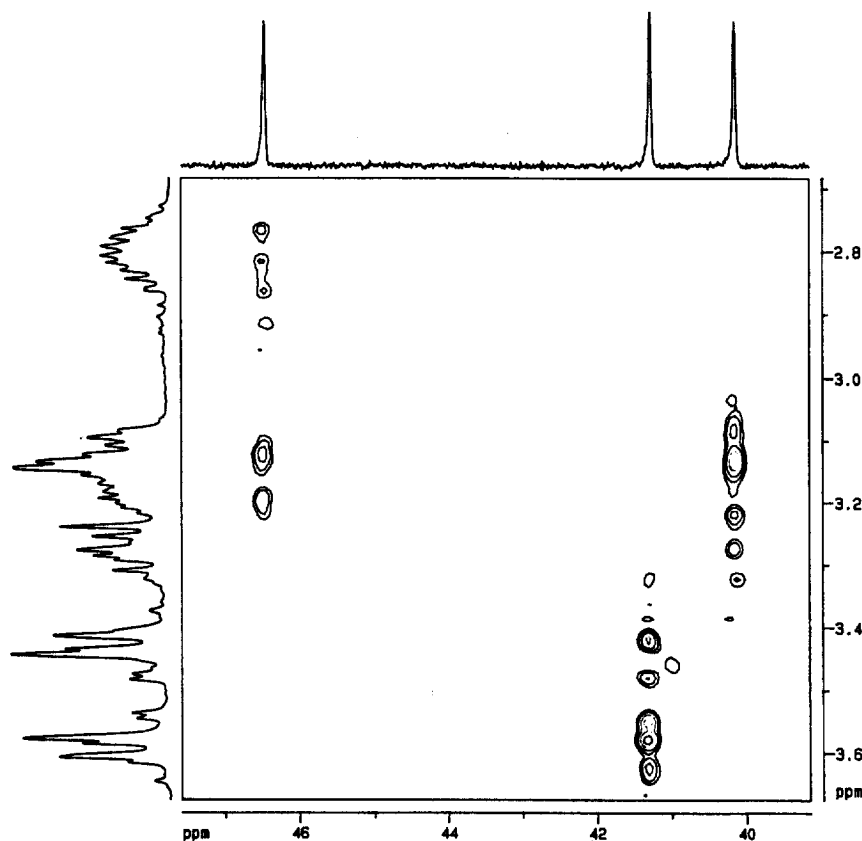


Fig. 4. HETCOR spectrum of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$.

The most discernible feature of the proton spectrum is the potential A_2B_2 pattern found at 3.73–3.65 ppm. The compound's C_2 symmetry divides the C3 protons into *two sets of two equivalent* protons. Each proton is split by both a *two-bond* and a *three-bond* interaction. In addition to the main pairs of doublets, this region also contains several smaller resonances at 3.37, 3.48, 3.54 and 3.65 ppm. These smaller signals must be included if the region from 3.73 to 3.65 ppm is to integrate to the expected four protons. Based on this and other NMR data, the most plausible explanation is that there are two different chelate ring conformations present for the five-membered ring containing the two C3 protons.

Information about the orientation of protons attached to the C3–C3 ring system can be obtained by carefully examining the splitting pattern of the A_2B_2 doublets. Two different coupling constants are clearly measurable in the 3.37–3.45 ppm region. The larger of the two couplings, approximately 10.8 Hz, is assigned to the two-bond interaction H3a–H3b. The smaller of the two, equal to approximately 3.0–3.5 Hz, is assigned to the three-bond interaction H3a–H3a' or H3a–H3b'. Applying the

relationship between a proton's dihedral bond angle and coupling constants, the H3a–C3–C3'–H3a' bond angle is found to be approximately 54–57° (Fig. 5). This is a little more than half of the normal 109.5°. This calculation suggests that the center ring's C3–C3 bond is contorted, resulting in a staggered conformation.

7. COSY spectra

[Co(eee)(NO₂)₂]Cl. A magnitude COSY spectrum is a two-dimensional NMR experiment used to detect connectivities between sets of protons and is shown in Fig. 6 for [Co(eee)(NO₂)₂]Cl. Analysis of this spectrum endorses the following. The four C3 protons form one isolated spin system. Of particular interest are the smaller signals at 3.37, 3.48, 3.54 and 3.65 ppm. Close examination of these signals reveals the presence of cross peaks with the main A₂B₂ resonance. If two ring conformations were present which were not capable of interconverting, then one would expect the smaller signals to show cross peaks only with themselves. This data suggests that the two ring conformations are capable of interconverting at room temperatures. The remaining signals are due to the C1 and C2 protons which form a spin system consisting of four nonequivalent protons. Some overlap of signals occurs, as four distinct signals are not cleanly identified. However, the signals at 2.73–2.90 ppm originally assigned to *one* of the C1 protons do show cross peaks with the resonances found at 3.08–3.20 and 3.20–3.32 ppm. Integration of the entire region at 3.08–3.32 reveals approximately six protons. Thus all eight protons are accounted for. Some weaker couplings are also detected between the A₂B₂ doublet and the signals at 2.20–3.32 ppm. These signals are ascribed to a long-range coupling and confirms that the signals at 3.20–3.32 ppm can be assigned to the C2 protons. When several COSY spectra are obtained to encompass a larger ppm range, then cross peaks are detected between the amine protons and the resonances at 2.73–2.90 ppm and 3.08–3.22 ppm. These two resonances are therefore assigned to the two nonequivalent C1 protons, which have different spatial orientations as a result of coordination.

The A₂B₂ splitting pattern observed for the C3 protons arises as a consequence of the C2 symmetry axis which divides the four C3 protons into two sets of two

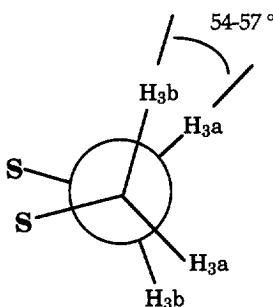


Fig. 5. The C3–C3' dihedral angle between protons on adjacent carbons.

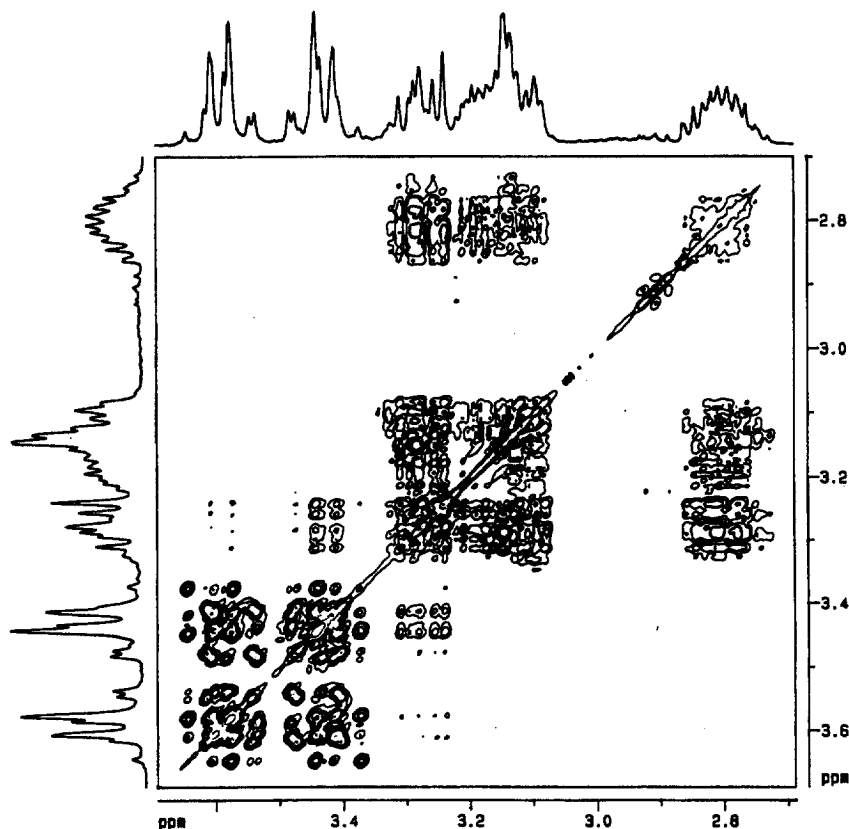


Fig. 6. Magnitude COSY spectrum of $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$.

equivalent protons. Each proton is split by a two-bond geminal coupling (both protons on the same carbon) and by a three-bond vicinal coupling (two protons on adjacent carbons) interaction. However, in examining the proton spectrum, it is not clear which of the two splittings arises as a result of the two-bond coupling and which arises as a result of the three-bond coupling. This is resolved through the use of the phase-sensitive COSY experiment. The advantage of phase-sensitive COSY over magnitude COSY is that phasing information is encoded into the cross peaks. A phase-sensitive COSY spectrum for $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$ is shown in Fig. 7. Overlaid on the spectrum is a retouched map illustrating the phasing of the signals [46].

In the typical phase-sensitive experiment the active coupling, or coupling responsible for the formation of a particular set of cross peaks, is shown in antiphase. The heteronuclear correlation experiment demonstrated that the pairs of doublets at ~ 3.59 ppm and ~ 3.42 ppm are due to *geminally* related protons since both proton signals correlate with a single carbon signal. Therefore by looking at the phasing of the cross peaks between H3a and H3b, whichever of the two couplings arises from the *geminal* interaction will be shown in antiphase. Examining Fig. 7, the phasing

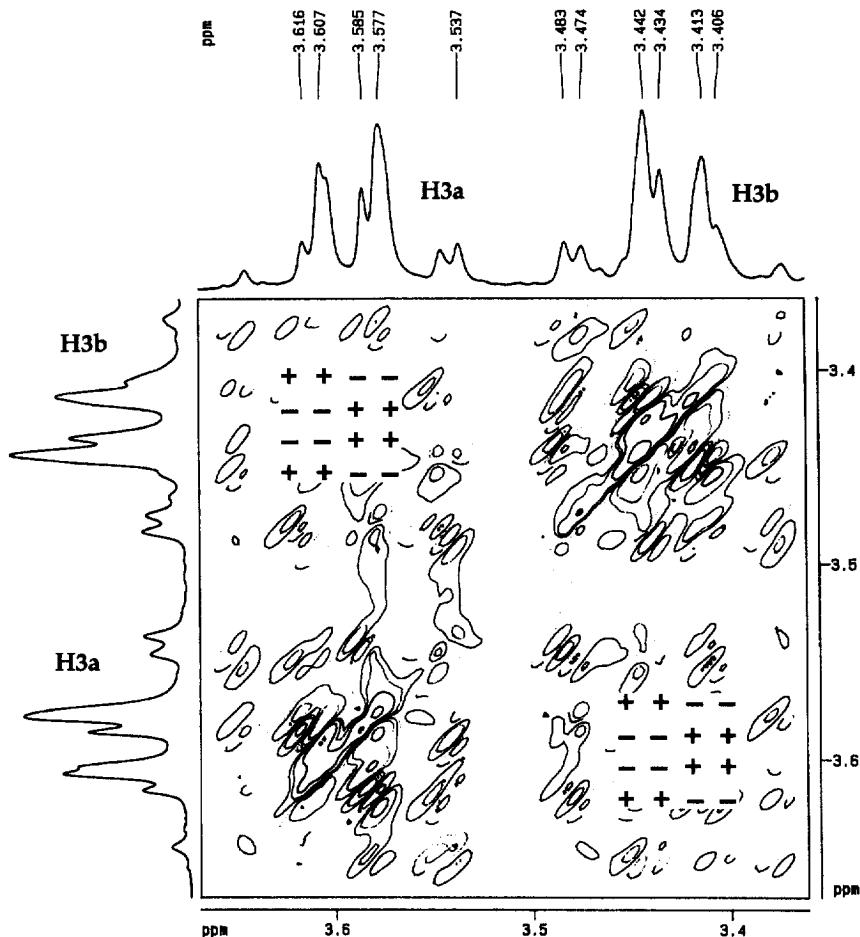


Fig. 7. Phase-sensitive COSY of $[\text{Co}(\text{ene})(\text{NO}_2)_2]\text{Cl}$.

of the signals between protons H3a and H3b is shown to vary with the *larger* of the two couplings [46]. Therefore the *larger* of the two splittings is due to the *geminal* H3a–H3b interaction.

Finally, proton signals observed at 5.18 and 5.84 ppm (not shown in Fig. 3) are assigned to the amine protons based upon their chemical shift as well as their decrease in area with time due to H/D exchange. Although signals due to exchangeable protons are usually observed only in a solution which is ~90% H_2O and ~10% D_2O , we observe that for cobalt complexes, an acidified solution is sufficient to keep the protons from rapidly exchanging with deuterons. The N–H resonances are most pronounced in a fresh solution but slowly diminish even in acidified solutions. (See Table 4).

Table 4
Summary of proton data for $[\text{Co}(\text{eee})(\text{NO}_2)_2]\text{Cl}$

Chemical shift (ppm)	Integration	Assignment
2.73–2.90	2.00	C1–H
3.08–3.20	6.37	C1–H
3.20–3.32	–	C2–H
3.37–3.48	2.07	C3–H
3.54–3.65	2.04	C3–H
5.18	1.47	N–H
5.84	1.81	N–H

8. Related complexes

$[\text{Co}(\text{eee})\text{Cl}_2]\text{Cl}$. The proton spectrum for the dichloro complex is shown in Fig. 8. The same general features are found in it as in the spectrum of the dinitro complex. There are three major resonance regions. The main A_2B_2 pattern is observed, as

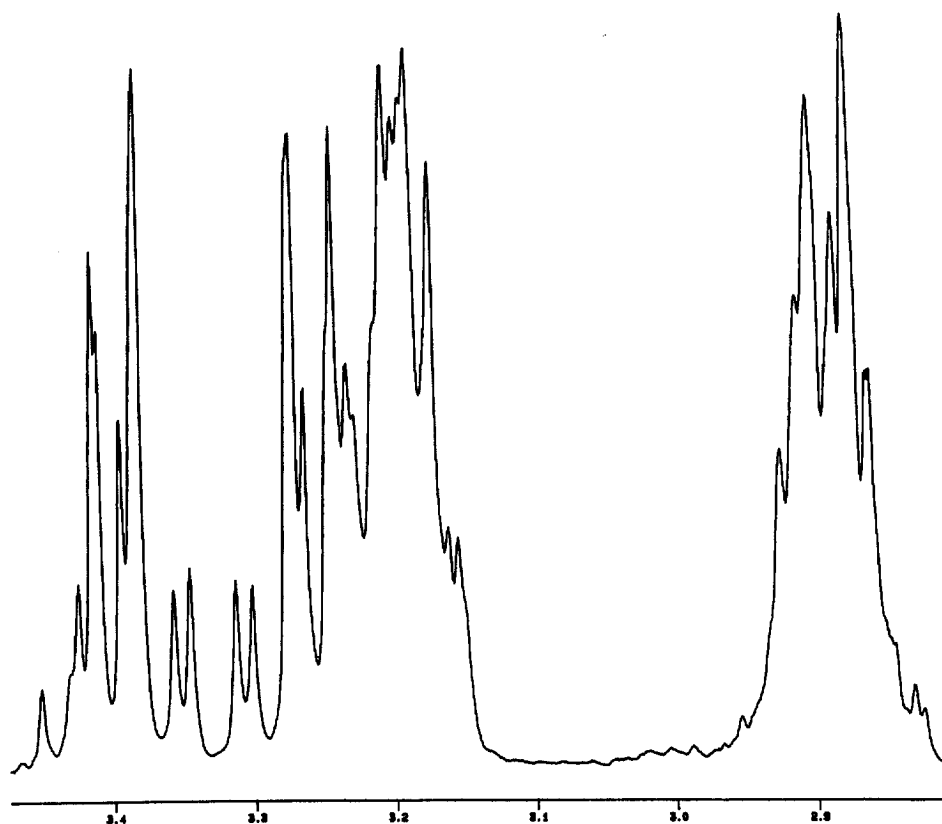


Fig. 8. Proton spectrum of $[\text{Co}(\text{eee})\text{Cl}_2]\text{Cl}$.

well as the smaller signals between the more prominent A_2B_2 doublets. This helps to support the conclusion that these are not an anomaly observed only for the dinitro compound. The region attributed to the C1 protons is generally better resolved than for the dinitro complex but the A_2B_2 doublets are partially overlapped with the C1 proton and C2 proton resonances.

The magnitude COSY spectrum for the dichloro complex exhibits features that are generally similar to the dinitro complex and clearly shows two independent spin systems due to the C1–C2 protons, and the C3 protons. In the dichloro complex, the A_2B_2 doublets are partially overlapped with the C1–C2 protons. This work now prompted us to quickly run a proton spectrum on several derivatives. We note that although the proton spectral patterns for different *symmetrical cis*-diacido-(eee)cobalt(III) complexes are similar in structure, going from the dinitro, to the dichloro, to the diaquo, to a bipyridyl ligand, the diacido groups occupying the other two octahedral sites greatly influence the location and coupling (overlap) of proton signals on C1, C2 and C3. We intend to follow up on these observations in future work.

9. Conclusions

Use of present generation high field nuclear magnetic resonance machines coupled with two-dimensional NMR experimental techniques provides the modern inorganic coordination chemist with tools to examine chelate ring proton interactions and to better confirm or reject isomeric geometries for coordination compounds derived from polydentate ligands. Activities which were impossible using older 100 MHz instruments.

The proton spectrum for $[Co(eee)(NO_2)_2]Cl$ was presented and proton assignments made. General regions of the proton spectrum were assigned to particular protons attached to specific carbon atoms. Additionally, COSY techniques provided a new means of greatly improving the interpretation of which two bond and three bond proton interactions are coupled. It is anticipated that in time as additional two-dimensional NMR studies are reported by chemists, a general model of proton interactions and their respective patterns will emerge which when catalogued, will greatly facilitate characterization of the chelate ring systems of coordination compounds derived from polydentate ligands.

Acknowledgements

We acknowledge instrument instructional assistance and the donation of instrument time from Dr. Jan Robert and Mr. Ronald Federspiel during the data collection stages of this work.

References

- [1] J.H. Worrell, D.H. Busch, *Inorg. Chem.* 8 (1969) 1563–1571.
- [2] J.H. Worrell, D.H. Busch, *Inorg. Chem.* 8 (1969) 1572–1579.
- [3] A.M. Sargeson, G.H. Searle, *Inorg. Chem.* 4 (1965) 45–52.
- [4] A.M. Sargeson, G.H. Searle, *Inorg. Chem.* 5 (1966) 787–796.
- [5] D.A. Buckingham, P.A. Marzilli, A.M. Sargeson, *Inorg. Chem.* 6 (1967) 1032–1041.
- [6] M.D. Alexander, H.G. Hamilton Jr., *Inorg. Chem.* 8 (1969) 2131–2134.
- [7] B. Bosnich, R.D. Gillard, E.D. McKenzie, G.A. Webb, *J. Chem. Soc. A* (1996) 1331.
- [8] Y. Yamamoto, H. Kudo, E. Toyota, *Bull. Chem. Soc. Jpn.* 56 (1983) 1051–1056.
- [9] E. Toyota, Y. Yamamoto, Y. Yamamoto, *Bull. Chem. Soc. Jpn.* 56 (1983) 2721–2726.
- [10] Y. Yamamoto, H. Kudo, *Bull. Chem. Soc. Jpn.* 57 (1984) 287–288.
- [11] R.G. Asperger, C.F. Liu, *Inorg. Chem.* 4 (1965) 1395–1397.
- [12] M. Goto, M. Saburi, S. Yoshikawa, *Inorg. Chem.* 8 (1968) 358–366.
- [13] S. Yoshikawa, T. Sekihara, M. Goto, *Inorg. Chem.* 6 (1966) 169–171.
- [14] M. Goto, A. Okubu, T. Sawai, S. Yoshikawa, *Inorg. Chem.* 9 (1970) 1488–1496.
- [15] G.H. Searle, M. Petkovic, F. Keene, *Inorg. Chem.* 13 (1974) 399.
- [16] J.H. Worrell, T.E. MacDermott, D.H. Busch, *J. Am. Chem. Soc.* 92 (1969) 3317–3325.
- [17] B. Bosnich, W.R. Kneen, A.T. Phillip, *Inorg. Chem.* 8 (1969) 2567.
- [18] T.A. Jackman, J.H. Worrell, *J. Inorg. Nucl. Chem.* 39 (1977) 981–983.
- [19] T.A. Jackman, *J.H. Worrell, Inorg. Chem.* 17 (1978) 3358–3361.
- [20] T.A. Jackman, Ph.D. thesis, University of South Florida, 1976.
- [21] J.H. Worrell, P. Behnken, R.A. Goddard, *J. Coord. Chem.* 9 (1979) 53–58.
- [22] R.A. Goddard, Ph.D. thesis, University of South Florida, 1977.
- [23] K. Yamanari, N. Takeshita, Y. Shimura, *Bull. Chem. Soc. Jpn.* 57 (1984) 1227–1234.
- [24] K. Yamanari, N. Takeshita, Y. Shimura, *Bull. Chem. Soc. Jpn.* 57 (1984) 2852–2858.
- [25] P.J. Toscano, K.A. Belsky, T. Hsesh, T. Nicholson, J. Zubeita, *Polyhedron* 9 (1991) 977–991.
- [26] P.J. Toscano, K.A. Belsky, T. Nicholson, J. Zubieta, *Inorg. Chim. Acta* 206 (1993) 77–82.
- [27] E. Toyota, Y. Yamamoto, Y. Yamamoto, *Bull. Chem. Soc. Jpn.* 61 (1988) 3175–3180.
- [28] S.S. Massoud, R.M. Milburn, *Inorg. Chim. Acta* 154 (1988) 115–119.
- [29] S.S. Massoud, R.M. Milburn, *Polyhedron* 8 (1989) 2389–2394.
- [30] G.A. McLachlan, S.J. Brudenell, G.D. Fallon, R.L. Martin, L. Spicca, E. Tiekink, *J. Chem. Soc., Dalton Trans.* (1995) 439–447.
- [31] R.R. Fenton, R.S. Vagg, P. Jones, P.A. Williams, *Inorg. Chim. Acta* 128 (1987) 219–229.
- [32] J.B. Mandel, C. Maricondi, B.E. Douglas, *Inorg. Chem.* 27 (1988) 2990–2996.
- [33] V. Castineiras, W. Hiller, J. Strahle, J. Sordo, *Acta Cryst. C* 41 (1985) 41–43.
- [34] C.R. Lucas, private communication, work submitted to volume 32 of *Inorganic Synthesis*.
- [35] C.R. Lucas, S. Liu, J.N. Bridson, *Can. J. Chem.* 73 (1995) 1023–1034.
- [36] A. Ault, G.O. Dudek, *NMR: An Introduction to NMR Spectroscopy*, Dover Publications, New York, 1978.
- [37] R.J. Abraham, J. Fisher, P. Loftus, *Introduction to NMR Spectroscopy*, John Wiley and Sons, New York, 1988.
- [38] A.E. Derome, *Modern NMR Techniques for Chemical Research*, Pergamon Press, Oxford, 1987.
- [39] J. Sanders, B. Hunter, *Modern NMR Spectroscopy: A Guide for Chemists*, 2nd ed., Oxford University Press, Oxford, 1993.
- [40] G.E. Martin, A.S. Zektzer, *Two-Dimensional NMR Methods for Establishing Molecular Connectivity: A Chemist's Guide to Experiment Selection, Performance, and Interpretation*, VCH, Weinheim, 1988.
- [41] W.R. Croasmun, R.M.K. Carlson, *Two-Dimensional NMR Spectroscopy: Applications for Chemists and Biochemists*, VCH, Weinheim, 1994.
- [42] M. McClure, M.S. thesis, University of South Florida, 1995.
- [43] M. McClure, J.H. Worrell, *J. Coord. Chem.* 1998 in-press.

- [44] I. Bernal, J. Cetrulio, T. Li, J.H. Worrell, *Polyhedron* 13 (1994) 463–468.
- [45] I. Bernal, J. Cetrulio, J. Cai, R. Geanangle, J.H. Worrell, *J. Chem. Soc., Dalton Trans.* (1995) 99–104.
- [46] To see the phasing, one needs to examine the actual six color instrument output. The manuscript's reduced, computer scanned-in image loses resolution and detail because the colors of the original do not transfer equally into the black and white image.