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Synthesis of N-Substituted (Ethylenediaminetriacetato)(thiocyanato)cobaltate(III) Complexes and Structural Characterization by ^{1}H and ^{13}C NMR Spectroscopy

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Four N-substituted (ethylenediaminetriacetato)(thiocyanato)cobaltate(III) complexes of formula [Co(Red3a)NCS]$^-$, where the N-substituent is hydrogen (ed3a), methyl (med3a), hydroxyethyl (hed3a), and benzyl (bed3a), have been prepared and characterized by ^{1}H and ^{13}C NMR spectroscopy, which provides evidence that the cis-equatorial isomers of all the thiocyanato complexes have been isolated. The ^{1}H NMR spectra yield stereochemical and structural information concerning the electronic environment of individual protons. The AB patterns of the glycinate protons and the ethylenediamine proton peaks are discussed and correlated to one another. The AB coupling constants of the glycinate rings are approximately 16.0, 17.5, and 19.0 Hz for the G, R1, and R2 rings, respectively; this is generally consistent with results observed for similar complexes. The average peak position for the R1 glycinate protons is generally shifted downfield as the size of the N-substituent increases. The ^{1}H NMR spectra of the thiocyanato complexes generally prove to be intermediate between those of the nitro and aqua complexes with respect to average chemical shift and spread of the AB patterns. Furthermore, the ^{1}H NMR spectra of the aqua and nitro N-benzyl ed3a complexes have also been interpreted completely, and these results are consistent with the ^{1}H NMR spectrum of the N-benzyl thiocyanato complex. The ^{13}C NMR spectra of the four thiocyanato complexes show similar chemical shifts for the strain-relieved half of the molecule; the peaks of the two methylene carbons bonded to the substituted nitrogen are shifted downfield in going from R = H to R = Me but are shifted slightly upfield again in going from N-methyl to heavier N-substituents. This trend is consistent with the ^{13}C spectra of other ed3a-type cobalt(III) complexes.

Introduction

Octahedral metal complexes of the trivalent anion of the quinquedentate ligand ethylenediaminetriacetic acid may have three possible geometrical orientations (Figure 1), depending upon the arrangement of the glycinate chelate rings that lie either parallel to (G rings) or perpendicular to (R rings) the plane of the ethylenediamine nitrogens. These G rings are generally thought to be more strained than R rings;[4,5] therefore, omission of a G ring in complexes of quinquedentate ligands is expected to favor the cis-equatorial isomer. Few crystal structures of cobalt(III) edta-type complexes have been reported,[5–8] and the structure[8] of [Co(ed3a)NO$_2$]$^-$ is the only one dealing with cobalt(III) ed3a-type complexes. Therefore, limited solid-state structural information is available. In recent years, however, ^{1}H and ^{13}C NMR spectroscopy has emerged as a powerful tool in the study of the structural characteristics of these complexes in solution.[3,4,9–20] The glycinate methylene protons have been found

to yield AB patterns with coupling constants of approximately 16 Hz for G rings and 18 Hz for R rings.

In this study,[21] we report the syntheses and ^{1}H and ^{13}C NMR spectra of a series of cobalt(III) N-substituted-ed3a thiocyanato complexes where the N-substituent is hydrogen (ed3a), methyl (med3a), hydroxyethyl (hed3a), and benzyl (bed3a). Furthermore, the ^{1}H NMR spectra of the nitro and aqua cobalt(III) bed3a complexes are reported and, although previously described, are more completely interpreted here. Making the correct assignments of the proton peaks is essential in determining the correct assignments of the carbon peaks, since proton-selective-decoupling techniques are utilized in this process. The results reported here are also compared to those for similar complexes.

Experimental Section

Preparation of Ethylenediamine-*N*,*N*,*N'*-triacetic Acid and Its Aqua- and (Thiocyanato)cobaltate(III) Complexes. The ligand was prepared according to modified methods of Maricondi and Maricondi[17] and Blackmer et al.[14] A solution containing of 11.4 g (0.065 mol) of ethylenediamine-*N*,*N'*-diacetic acid, 7.8 g (0.195 mol) of sodium hydroxide, 8.2 g (0.070 mol) of sodium chloroacetate, and 180 mL of water was stirred for 90 min. After the pH of the solution was lowered to 5.0 by the addition of concentrated hydrochloric acid, 18.9 g (0.065 mol) of cobalt(II) nitrate hexahydrate, 5 mL of 30% hydrogen peroxide, and 3 g of activated charcoal were added to the solution. Air was bubbled through the mixture while being stirred for 3 days. The charcoal was then filtered off, and the solution was diluted to a volume of 1 L. This solution was passed through consecutive ion-exchange columns, first through 1000 mL of Dowex 50W-X8 cation-exchange resin (100–200 mesh, Na$^+$ form) and then through 1000 mL of Dowex 1-X8 anion-exchange resin (100–200 mesh, Cl$^-$ form). Excess NaCl was removed by rotary evaporation and filtration, and the resulting purple filtrate was assumed to be neutral [Co(ed3a)H$_2$O]. To this stirred solution were added 20 drops of trifluoroacetic acid and 7.0 g of sodium thiocyanate, which produced an immediate color change from purple to violet. The solution was rotary evaporated to dryness, the residue was dissolved in 200 mL of water, and the resulting solution was passed through a column containing 700 mL of Dowex 1-X8 anion-exchange resin, as noted above. The large violet band that eluted first with 0.10 M NaCl was collected and rotary evaporated to small volume in order to precipitate most of the salt, which was then filtered off. The sodium salt of the thiocyanato complex precipitated upon the addition of methanol to the filtrate, and the complex was recrystallized from warm water. Infrared analysis revealed the presence of a strong peak at 2225 cm^{-1}, indicative of the C–N triple-bond stretch and the presence of coordinated thiocyanate.

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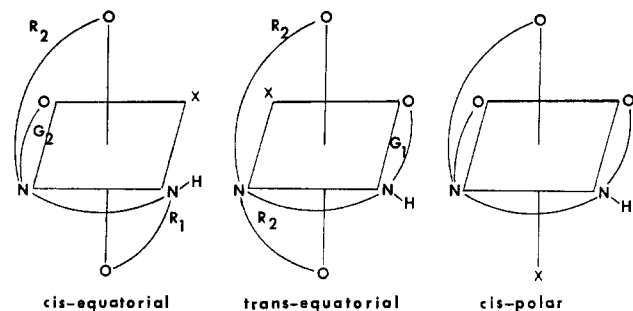(21) Rohly, K. Ph.D. Thesis, University of Pittsburgh, 1985.

Figure 1. The three possible geometrical isomers of octahedral ed3a-type complexes.

Anal. Calcd for $C_9N_3H_{16}O_{8.5}CoNaS$ (Na[Co(ed3a)NCS]·2.5H$_2$O): C, 25.97; H, 3.87; N, 10.10. Found: C, 26.14; H, 3.88; N, 10.13.

Preparation of *N*-Methylethylenediamine-*N*,*N'*,*N'*-triacetic Acid and Its Nitro-, Aqua-, and (Thiocyanato)cobaltate(III) Complexes. The ligand was prepared from *N*-methylethylenediamine and sodium chloroacetate in basic solution according to a modified procedure of Van Saun and Douglas,[22] and the complexes were prepared according to modified procedures of Maricondi and Maricondi.[23] A solution containing of 9.6 g (0.13 mol) of *N*-methylethylenediamine, 16.0 g (0.40 mol) of sodium hydroxide, 46.5 g (0.40 mol) of sodium chloroacetate, and 250 mL of water was stirred for 90 min and then acidified to pH 5 with concentrated hydrochloric acid. To this med3a ligand solution at 50 °C was added 52.5 g (0.13 mol) of sodium cobaltinitrite with stirring. The solution turned red-brown, and NO$_2$ gas was evolved. After continued stirring at 50 °C for 0.5 h, the temperature was raised to 85 °C, and stirring was continued for another 0.5 h. The solution was then allowed to cool to room temperature. After 200 mL of 95% ethanol was added, the solution was cooled in an ice bath for 2 h. The solid was filtered off and recrystallized from water twice; yield 25 g (52%). Twenty grams of this complex was transferred to a round-bottom flask containing 300 mL of water. Three milliliters of trifluoroacetic acid was added to this solution, which was then warmed on a steam bath for 2 h. The solution was rotary evaporated to dryness, and the solid was redissolved in 150 mL of water. Twenty drops of trifluoroacetic acid and 8.7 g (0.107 mol) of sodium thiocyanate were added to the solution, and the flask was placed in a refrigerator for 3 days. The solid was filtered off, washed with ethanol and acetone, and recrystallized from water; yield 13.6 g. Infrared analysis again confirmed the presence of coordinated thiocyanate. Anal. Calcd for $C_{10}N_3H_{17}O_8CoNaS$ (Na[Co(med3a)NCS]·2H$_2$O): C, 28.51; H, 4.07; N, 9.98. Found: C, 28.42; H, 4.12; N, 9.95.

Preparation of the Nitro-, Aqua-, and (Thiocyanato)(*N*-(hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetato)cobaltate(III) Complexes. The compound *N*-(hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid was obtained from Aldrich Chemical Co. The nitro, aqua, and thiocyanato complexes were prepared according to the procedures described above for the preparation of the *N*-methyl ed3a complexes. Infrared analysis confirmed the presence of coordinated thiocyanate. Anal. Calcd for $C_{11}N_3H_{20}O_{9.5}CoNaS$ (Na[Co(hed3a)NCS]·2.5H$_2$O): C, 28.70; H, 4.38; N, 9.13. Found: C, 28.63; H, 4.46; N, 9.16.

Preparation of *N*-Benzylethylenediamine-*N*,*N'*,*N'*-triacetic Acid and Its Nitro-, Aqua-, and (Thiocyanato)cobaltate(III) Complexes. The ligand *N*-benzylethylenediamine-*N*,*N'*,*N'*-triacetic acid and its cobalt(III) nitro, aqua, and thiocyanato complexes were prepared according to the procedures described above for the preparation of the *N*-methyl ed3a complexes. For the novel bed3a thiocyanato complex, infrared analysis again confirmed the presence of coordinated thiocyanate. Anal. Calcd for $C_{16}N_3H_{20}O_{7.5}CoNaS$ (Na[Co(bed3a)NCS]·1.5H$_2$O): C, 39.35; H, 4.13; N, 8.60. Found: C, 39.43; H, 4.30; N, 8.54.

Elemental Analyses. The elemental analyses of the four thiocyanato complexes were carried out by Galbraith Analytical Laboratories, Knoxville, TN. All samples were recrystallized twice and checked for free chloride ion (by dissolving a portion of sample in silver nitrate solution).

Infrared Spectroscopy. All infrared data were obtained with use of a Digilab FTS-10M Fourier-transform infrared spectrophotometer. The samples were prepared and analyzed as potassium bromide salt pellets.

Visible Absorption Spectroscopy. Visible absorption spectra were obtained on a Hewlett-Packard Model 8540A diode-array spectrophotometer. All samples were prepared volumetrically as analytical standards, and molar extinction coefficients were calculated.
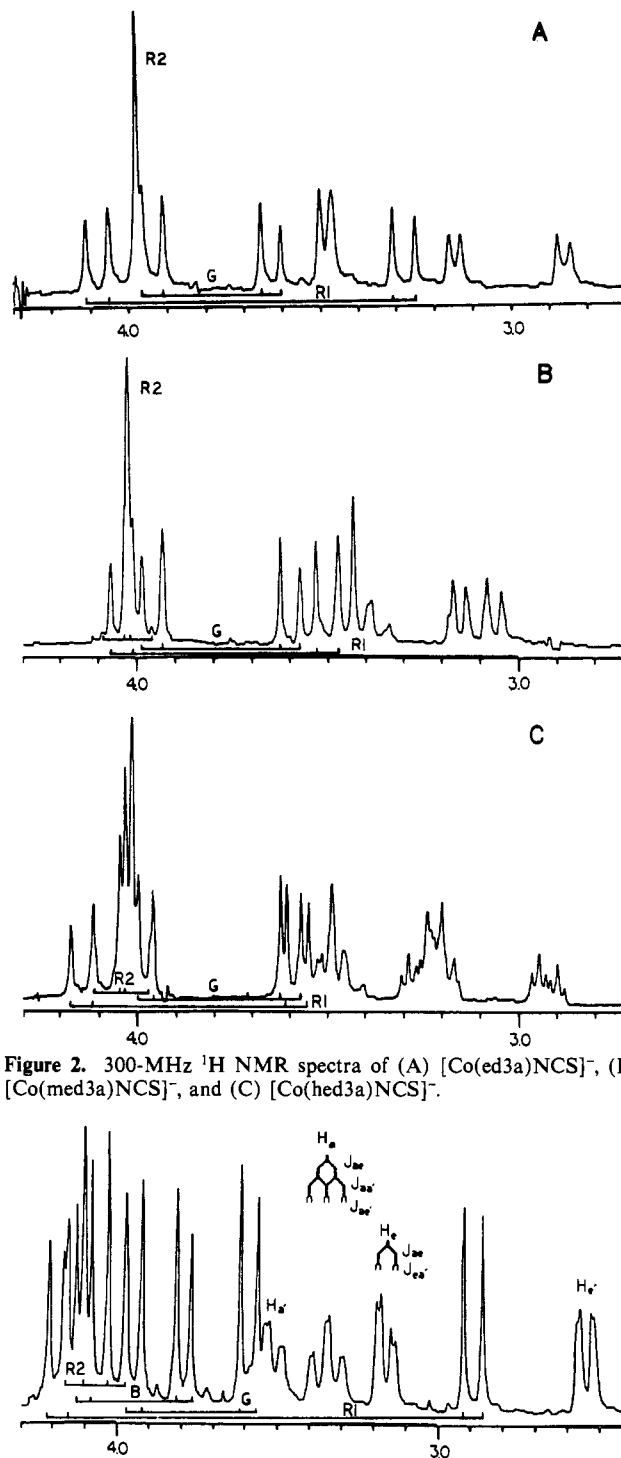
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Figure 2. 300-MHz ^{1}H NMR spectra of (A) [Co(ed3a)NCS]$^-$, (B) [Co(med3a)NCS]$^-$, and (C) [Co(hed3a)NCS]$^-$.

Figure 3. 300-MHz ^{1}H NMR spectrum of [Co(bed3a)NCS]$^-$.

Nuclear Magnetic Resonance Spectroscopy. All NMR spectra were recorded on a Bruker WH300 Fourier-transform nuclear magnetic resonance spectrometer. Deuterium oxide was the solvent of choice for all samples. The 300-MHz superconducting magnet provided much better spectral resolution than the weaker magnets (60–100 MHz) that have previously been used to study the stereochemistry of edta-type transition-metal complexes.

All ^{1}H NMR samples contained sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) as the internal standard. Spin-tickling experiments involved irradiation of the sample at a specific frequency with approximately 0.002 W of power, whereas selective decoupling experiments used irradiation power of about 0.05 W. The resultant spectra could then be used to correlate related peaks unequivocally.

The ^{13}C samples all contained 1,4-dioxane as the internal standard, which was fixed at 66.554 ppm with respect to Me$_4$Si. Broad-band decoupling, or irradiation of the sample at all proton frequencies with approximately 1.0 W of power, was employed to decouple completely the

Table I. Coupling Constants for the Glycinate Methylene AB Patterns of the Cobalt(III) ed3a-Type Thiocyanato Complexes

	R1	R2	G	B
[Co(ed3a)NCS]⁻	17.6	...	15.6	
[Co(med3a)NCS]⁻	17.3	19.5	16.1	
[Co(hed3a)NCS]⁻	17.7	18.7	16.1	
[Co(bed3a)NCS]⁻	17.1	18.9	16.1	13.7

^{13}C spectra. Selective decoupling of the carbon-13 peaks involved irradiating the sample with about 0.3 W at only one proton frequency; this resulted in the collapse of the corresponding methylene carbon peaks to a singlet. The assignment of protons to corresponding carbons was made in this way.

Results and Discussion

^{1}H NMR Results. Figures 2 and 3 illustrate the ^{1}H NMR spectra of the four thiocyanato complexes. The AB patterns of the glycinate ring protons are reasonably well resolved in all cases, and their coupling constants are listed in Table I. The coupling constants are approximately 19.0, 17.5, and 16.0 Hz for the R2, R1, and G rings, respectively. These results are reasonably consistent with the previously calculated coupling constants of 18 Hz for R rings and 16 Hz for G rings.[10] Maximum coupling of glycinate protons is predicted to occur when the internuclear H–H axis is perpendicular to the plane of the π functionality, according to molecular orbital theory.[24] Therefore, the more planar (or less strained) a glycinate chelate ring, the greater the expected coupling constant. On the basis of coupling constants alone, one would predict that the R2 ring should experience the least strain, the G ring should be the most strained, and the R1 ring should be of intermediate strain. Spin-tickling and spin-decoupling experiments, which have been described extensively elsewhere,[15,17,18] verified the peak assignments.

In the spectrum of [Co(ed3a)NCS]⁻ shown in Figure 2A, the ethylenediamine backbone protons appear as doublets centered at 2.86, 3.15, and 3.49 ppm. By comparison with the ^{1}H NMR spectra of the analogous aqua and nitro complexes, the two doublets furthest upfield may tentatively be assigned to the two equatorial protons whereas the doublet at 3.49 ppm probably corresponds to the two axial ethylenediamine protons. Many cobalt(III) ed3a complexes show this same poor resolution of the ethylenediamine proton peaks. On the other hand, the R1 and G glycinate protons appear as sharp AB patterns that are assigned easily. The R2 proton peak, which splits into an AB pattern only slightly if at all since the protons are in nearly identical chemical environments, remains unsplit at 3.97 ppm.

The ^{1}H NMR spectrum of [Co(med3a)NCS]⁻ is shown in Figure 2B. As was the case for the ed3a complex, the ethylenediamine protons are again somewhat ill resolved; however, the doublets centered at 3.07 and 3.16 ppm may represent equatorial protons. The sharp peak at 3.43 ppm, its two broadened peaks upfield, and its two broadened peaks downfield (buried beneath those of the R1 AB pattern) are considered to be due to the axial ethylenediamine protons. The G and R1 glycinate protons again are split into sharp, well-resolved AB patterns. Although the R2 protons exhibit only very slight splitting, the relatively large geminal coupling constant may be determined from the spectrum (J = 19.5 Hz).

The ^{1}H NMR spectrum of [Co(hed3a)NCS]⁻ is shown in Figure 2C. The complex multiplet centered at 2.93 ppm is produced by one of the methylene protons on the carbon of the hydroxyethyl group that is adjacent to the ethylenediamine nitrogen (the α-carbon), and the total area under these peaks corresponds to one proton. A second complex multiplet, centered at about 3.3 ppm and assigned to the other proton on the α-carbon, appears to be covered partially by the rather large ill-resolved contribution from the equatorial ethylenediamine protons. This pattern matches that of the ^{1}H spectrum[15] of [Co(hed3a)NO₂]⁻ in that similar multiplets are seen for the hydroxyethyl protons, except both multiplets are shifted further upfield and are isolated

from other peaks in the case of the nitro complex. The fact that these two multiplets are present at different chemical shifts indicates that the two α-carbon methylene protons of the hydroxyethyl group are in distinctly different environments. Not only does each proton couple with the two methylene protons of the carbon bearing the hydroxy group (the β-carbon) to yield a triplet, but also they couple with each other to split further into a doublet of triplets. The strong peak appearing at 4.01 ppm corresponds to the two protons on the carbon next to the hydroxy group. Their appearance at the same chemical shift indicates that they exist in nearly identical chemical environments. The ^{1}H NMR spectra of the cyano and nitro hydroxyethyl complexes[15,25] show that there is really a triplet present for these protons, and this may explain the increased intensity of the two neighboring AB pattern peaks. Since the α-carbon is held rather rigidly by the locked orientation of the ethylenediamine nitrogen, these protons do not experience free rotation about the single bond as observed for the β-carbon protons. Therefore, greater shielding is expected for the α-carbon protons than for the β-carbon protons, and this is evidenced by the location of their peaks. Although the ^{1}H NMR spectra of cobalt(III) hydroxyethyl complexes have been described previously, to our knowledge this is the first complete assignment of the peaks of the hydroxyethyl methylene protons for cobalt(III) ed3a-type complexes. The R2 glycinate proton peaks, although difficult to distinguish from the hydroxyethyl peaks at about 4.2 ppm, were identified by spin-tickling experiments and by the large observed coupling constant. The G and R1 glycinate protons yield clear AB patterns that are again readily identified and assigned.

The 300-MHz ^{1}H NMR spectrum of [Co(bed3a)NCS]⁻ is by far the most informative of the four presently discussed (Figure 3). The normal R1, R2, and G glycinate ring AB patterns appear in the expected regions and are assigned easily. For this complex, a unique AB pattern emerges that has an AB coupling constant of approximately 14 Hz, and it is assigned to the methylene protons on the benzyl group. The bulky benzene ring apparently restricts the motion of the benzyl group, and this helps to create an environment for the ethylenediamine backbone protons similar to the one created when the unidentate ligand in the sixth coordinating position is strong field, as in the cases of the cyano and nitro complexes. This is evidenced by the sharp resolution seen for the peaks corresponding to the individual ethylenediamine protons. Assignments are made on the basis of decoupling experiments and comparisons with the resolved ethylenediamine proton peaks of [Co(ed3a)CN]⁻.[11] The equatorial and axial protons are split into four and six peaks, respectively, according to the coupling scheme shown in Figure 3. An axial proton is split by its geminal equatorial proton (J_{ae} = 14 Hz), by its vicinal axial proton ($J_{aa'}$ = 14 Hz), and by its vicinal equatorial proton ($J_{ae'}$ = 4 Hz). On the other hand, the equatorial proton is split only by its geminal axial proton (J_{ae} = 14 Hz) and by its vicinal axial proton ($J_{ea'}$ = 4 Hz). The axial and equatorial protons denoted with a prime are on the carbon adjacent to the benzyl-substituted ethylenediamine nitrogen. A Dreiding stereomodel indicates that the dihedral angle between the equatorial protons on the ethylenediamine backbone is very close to 90°, which may explain why the coupling constant is small.[26,27]

The ^{1}H NMR spectra of the *N*-benzyl nitro and aqua cobalt(III) complexes have not yet been interpreted completely, so these complexes were prepared and characterized by ^{1}H NMR. The 300-MHz ^{1}H NMR spectrum of the *N*-benzyl nitro complex is shown in Figure 4A. Bause[15] assigned an AB pattern with a coupling constant of 14 Hz to the R1 ring for [Co(bed3a)NO₂]⁻; however, these peaks actually are part of the AB pattern due to the two benzyl methylene protons. If the downfield range is extended to 4.61 ppm, the R1 AB pattern becomes completely visible. This R1 AB pattern has the largest spread of any co-

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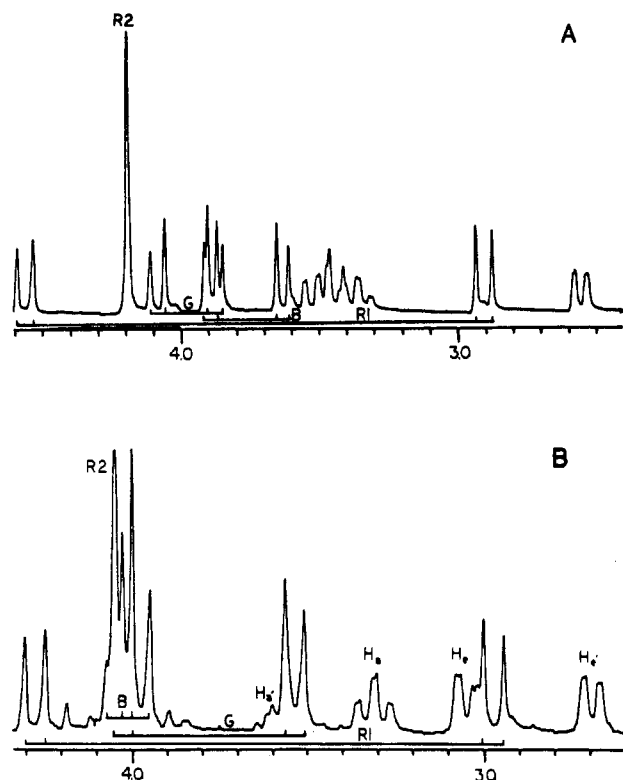
Figure 4. 300-MHz ^{1}H NMR spectra of (A) [Co(bed3a)NO$_2$]$^-$ and (B) [Co(bed3a)H$_2$O].

Table II. Chemical Shifts for the Glycinate Methylene Protons of Cobalt(III) ed3a-Type Complexes Arranged according to Unidentate Ligand[a]

	R1	R2	G
[Co(ed3a)CN]$^-$	3.52 (0.82)	4.13 (0.13)	4.07 (0.05)
[Co(med3a)CN]$^-$	3.64 (0.55)	4.19 (0.17)	4.03 (0.13)
[Co(ed3a)NO$_2$]$^-$	3.62 (1.05)	4.05 (0.00)	3.97 (0.11)
[Co(med3a)NO$_2$]$^-$	3.78 (0.80)	4.09 (0.00)	3.94 (0.19)
[Co(hed3a)NO$_2$]$^-$	3.88 (0.89)	4.12 (0.00)	3.96 (0.22)
[Co(bed3a)NO$_2$]$^-$	3.73 (1.66)	4.19 (0.00)	3.98 (0.21)
[Co(ed3a)NCS]$^-$	3.68 (0.82)	3.97 (0.00)	3.78 (0.32)
[Co(med3a)NCS]$^-$	3.77 (0.54)	4.03 (0.06)	3.78 (0.36)
[Co(hed3a)NCS]$^-$	3.86 (0.56)	4.04 (0.09)	3.88 (0.39)
[Co(bed3a)NCS]$^-$	3.64 (1.30)	4.09 (0.10)	3.79 (0.38)
[Co(ed3a)H$_2$O]	3.66 (0.81)	3.92 (0.00)	3.71 (0.40)
[Co(med3a)H$_2$O]	3.73 (0.49)	3.97 (0.00)	3.72 (0.42)
[Co(hed3a)H$_2$O]	3.81 (0.56)	3.95 (0.00)	3.71 (0.45)
[Co(bed3a)H$_2$O]	3.63 (1.31)	4.05 (0.00)	3.76 (0.44)

[a] The numbers in parentheses indicate the spreads between the average chemical shifts of the AB patterns. The data for the aqua and nitro complexes were taken from ref 10, and the data for the cyano complexes were taken from ref 11.

balt(III) ed3a-type complex known. This is probably due to the π-electronic effect of the nitro group, which is directed toward the R1 ring, in addition to the effect of the nearby benzyl group previously described. The R2 glycinate methylene proton peak remains unsplit, indicating the high equivalency of the two protons on this methylene carbon. This is in contrast to the moderate splitting of the R2 proton peaks observed for the analogous *N*-benzyl thiocyanato complex. However, none of the nitro complexes studied thus far shows the R2 ring to be split. This may be attributed to the effect of the nitro group on the trans ethylenediamine nitrogen that anchors the G and R2 rings. Crystallographic data[28] indicate significantly longer Co–N(trans) bond distances for the nitro complexes compared to those of the aqua and thiocyanato complexes (N(trans) being the nitrogen opposite the sixth coordinating ligand in the Co(III) octahedron). This smaller Co–N distance should result in a slightly less strained environment for the R2 and G rings of the thiocyanato and aqua complexes, resulting in a decrease in the spreads of their AB patterns (more equivalent environments of the glycinate protons), and this is observed to be the case. The AB patterns for the G and R1 glycinate protons are assigned easily by their coupling constants and by spin-tickling experiments.

The 300-MHz ^{1}H NMR spectrum of the *N*-benzyl aqua complex is shown in Figure 4B. The results seen for this complex are similar to those observed for the *N*-benzyl thiocyanato complex, but some noticeable differences are observed: (1) the R2 ring protons of the aqua complex are collapsed into one large peak, and (2) although the average chemical shifts of the benzyl AB pattern are about the same, the spread seen for the thiocyanato complex (0.35) is significantly greater than the shift of the aqua complex (0.06). The second observation may be best explained in terms of the orientation of the benzyl group toward the unidentate ligand. The benzyl group may have freedom to rotate in the aqua complex since the size of the water molecule is relatively small compared to that of the long thiocyanate entity, and the water may rotate about the Co–O bond to alleviate steric interactions. The spread of the AB pattern of the benzyl protons

in the *N*-benzyl nitro complex (0.26) supports this assumption. As was the case for the thiocyanato complex, the ethylenediamine backbone protons are reasonably well resolved and may be readily identified. These protons remain at about the same average chemical shifts as those observed for the thiocyanato complex. The H$_{e'}$ proton peaks occur between 2.5 and 2.7 ppm for all three benzyl complexes, appearing further upfield than the same proton peaks of ed3a complexes with other N-substituents. Therefore, this proton apparently experiences approximately the same degree of shielding for the benzyl complexes, this shielding being significantly greater than that observed for other N-substituents because of the proximity of the benzyl group.

The available ^{1}H NMR results for all of the cobalt(III) ed3a-type complexes studied to date are listed in Table II. The spectra of the four thiocyanato complexes and the nitro and aqua *N*-benzyl-substituted complexes are also included in this listing. The data reported for the other complexes are literature values.[4,12] The table is arranged according to decreasing ligand field strength of the unidentate ligand in the sixth coordinating position in going down the chart. Although many of the chloro and bromo complexes of N-substituted ed3a cobalt(III) have been prepared, their ^{1}H NMR spectra have not yet been reported. Furthermore, the *N*-hydroxyethyl and *N*-benzyl derivatives of the cyano complex have not yet been reported, so Table II is not complete.

When the average chemical shifts within an N-substituted series for a specific unidentate ligand are examined, several trends immediately become apparent. For the R1 methylene protons, for example, the average chemical shift generally moves further downfield with increasing molecular weight of the N-substituent except for the *N*-benzyl complexes. The bulky benzyl group apparently shields the methylene proton facing it much more than the other proton, causing the spread of the corresponding AB pattern to be significantly greater than the spreads seen for the R^1 AB patterns of the other complexes in the series. This, in turn, leads to average chemical shift values seen further upfield for the R1 protons of the *N*-benzyl complexes rather than being in accordance with the general trend of greater downfield shift with increasing weight of the N-substituent.

Furthermore, the average chemical shifts of the R2 glycinate ring AB patterns are generally shifted downfield with increasing weight of the N-substituent. Although this shifting is rather slight, it may be attributed to steric compression of the ethylenediamine backbone by the increased bulkiness and weight of the N-substituent. The AB pattern of the R2 methylene protons is generally collapsed into one large peak except in a few cases. With the exception of the case in which R = H, the thiocyanato complexes exhibit splitting of the R2 peak into a typical AB pattern. This splitting increases with increased molecular weight of the R group and is an indication of the increased nonequivalence of the two

(28) Rohly, K. E.; Douglas, B.; Maricondi, C., manuscript in preparation.

Table III. Chemical Shifts for the Glycinate Methylene Protons of Cobalt(III) ed3a-Type Complexes Arranged according to Quinquedentate Ligand[a]

	R2	R1	G
[Co(ed3a)CN]⁻	3.52 (0.82)	4.13 (0.13)	4.07 (0.05)
[Co(ed3a)NO₂]⁻	3.62 (1.05)	4.05 (0.00)	3.97 (0.11)
[Co(ed3a)NCS]⁻	3.68 (0.82)	3.97 (0.00)	3.78 (0.32)
[Co(ed3a)H₂O]	3.66 (0.81)	3.92 (0.00)	3.71 (0.40)
[Co(med3a)CN]⁻	3.64 (0.55)	4.19 (0.17)	4.03 (0.13)
[Co(med3a)NO₂]⁻	3.78 (0.80)	4.09 (0.00)	3.94 (0.19)
[Co(med3a)NCS]⁻	3.77 (0.54)	4.03 (0.06)	3.78 (0.36)
[Co(med3a)H₂O]	3.73 (0.49)	3.97 (0.00)	3.72 (0.42)
[Co(hed3a)NO₂]⁻	3.88 (0.89)	4.12 (0.00)	3.96 (0.22)
[Co(hed3a)NCS]⁻	3.86 (0.56)	4.04 (0.09)	3.80 (0.39)
[Co(hed3a)H₂O]	3.81 (0.56)	3.95 (0.00)	3.71 (0.45)
[Co(bed3a)NO₂]⁻	3.73 (1.66)	4.19 (0.00)	3.98 (0.21)
[Co(bed3a)NCS]⁻	3.64 (1.30)	4.09 (0.10)	3.79 (0.38)
[Co(bed3a)H₂O]	3.63 (1.31)	4.05 (0.00)	3.76 (0.44)

[a] The numbers in parentheses indicate the spreads between the average chemical shifts of the AB patterns. The data for the aqua and nitro complexes were taken from ref 10, and the data for the cyano complexes were taken from ref 11.

Table IV. Visible Absorption Spectral Data of Cis-Equatorial ed3a-Type Complexes

complex	λ, nm	ε, cm⁻¹ M⁻¹	λ, nm	ε, cm⁻¹ M⁻¹
[Co(ed3a)H₂O]	545	230	378	175
[Co(med3a)H₂O]	552	165	386	139
[Co(hed3a)H₂O]	553	248	386	208
[Co(ed3a)NCS]⁻	534	282	368	470
[Co(med3a)NCS]⁻	542	351	365	703
[Co(hed3a)NCS]⁻	546	313	350	931
[Co(bed3a)NCS]⁻	548	388	366	579
[Co(ed3a)NO₂]⁻	585 sh	90	490[a]	193
[Co(med3a)NO₂]⁻	585 sh	90	493[a]	182
[Co(hed3a)NO₂]⁻	585 sh	110	495[a]	232
[Co(bed3a)NO₂]⁻	595 sh		495[a]	240

[a] Higher energy component of the "first" band. The second ligand field band is obscured for the nitro complexes.

methylene protons on this glycinate ring.

The G ring methylene protons yield AB patterns that are typically at the same average chemical shift for a specific unidentate ligand. In addition, the average spreads are about the same within a series, although there is usually a very slight increase in spread in going from R = H to R = CH₃.

Table III is arranged so that differences among the individual unidentate ligands are emphasized. The average chemical shifts for the R1 ring methylene protons do not seem to follow any regular pattern that holds for all series of complexes. The nitro complexes generally show the largest spreads of the R1 AB patterns. This may be attributed to the through-space shielding effect of the nitro group upon the R1 proton nearest it, making the two methylene protons significantly nonequivalent. The X-ray single-crystal structure[11] of [Co(ed3a)NO₂]⁻ shows the nitro group angled in such a way that one oxygen of the nitro group is in reasonably close proximity to the R1 methylene proton that faces it. Although this is a representation of the complex in the solid state, the consistently large spreads of this AB pattern indicate that a very similar orientation probably exists in solution.

The average chemical shifts of the R2 rings move gradually upfield as the ligand field strength of the unidentate decreases. Since this same effect is also observed for the G ring, one may assume that the ligand field strength of the sixth coordinating ligand affects the trans ethylenediamine nitrogen to which the R2 and G rings are bound. These effects seem to be substantiated by differences in bond lengths and ring angle sums obtained by X-ray crystallography.[28]

In general, the proton chemical shifts observed for the cobalt(III) ed3a complexes described show remarkably similar trends. The peak assignments yield stereochemical and structural

Table V. ¹³C NMR Peaks of the N-Substituted ed3a Thiocyanato Complexes

			methylene		
compd	carboxylate	NCS	N2	N1	other
[Co(ed3a)NCS]⁻	183.77	139.74	65.67	57.03	
	182.92		64.51	55.36	
	181.77		61.16		
[Co(med3a)NCS]⁻	182.51	139.45	65.97	66.98	49.73
	181.90		64.39	65.78	
	181.60		60.06		
[Co(hed3a)NCS]⁻	182.90	139.67	65.90	64.74	56.01
	182.67		64.33	63.81	
	182.58		61.36	63.26	
[Co(bed3a)NCS]⁻	182.64	139.99	65.94	63.97	131.78
	182.06		64.45	62.93	129.67
	181.66		61.09	65.94	128.98
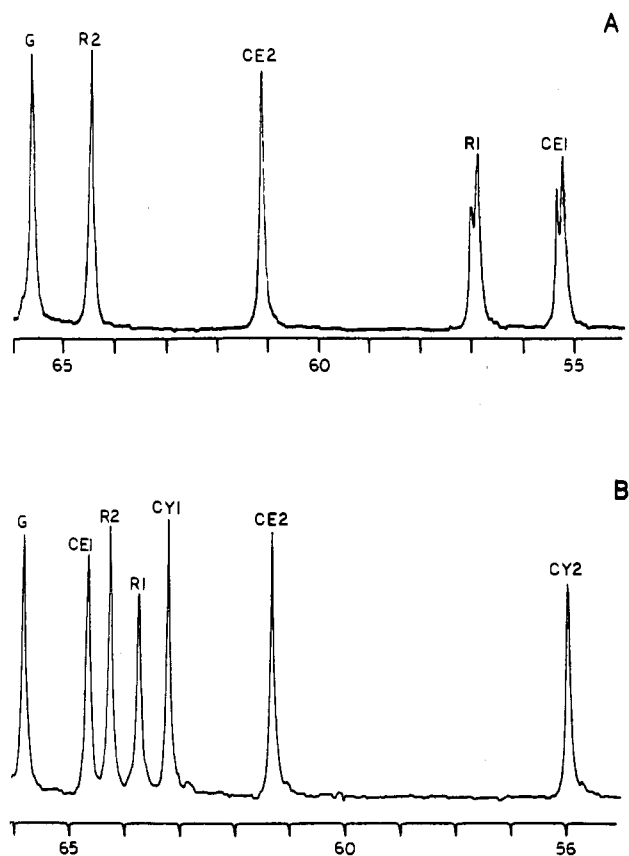
Figure 5. 300-MHz ¹³C NMR spectra of the methylene protons of (A) [Co(ed3a)NCS]⁻ and (B) [Co(hed3a)NCS]⁻.

information concerning the electronic environment of individual protons and the strain that various chelate rings experience. The proton NMR spectra of the thiocyanato complexes generally prove to be intermediate between those of the nitro and aqua complexes with respect to average chemical shift and spread of the AB patterns, but they are more similar to those of the aqua complexes. This is same as the order of their ligand field strengths H₂O ≈ NCS⁻ < NO₂. The UV–visible data support these conclusions in that the spectra of the thiocyanato complexes are clearly more similar to those of the corresponding aqua complexes than to those of the analogous nitro complexes (Table IV).

¹³C NMR Results. ¹³C NMR has only recently been utilized as a tool in the structural characterization of transition-metal complexes. Chang[9,15,16] has been particularly instrumental in applying ¹³C chemical shifts in the structure and stereochemistry of various cobalt(III) polyamino polycarboxylates. Although peak assignments may generally be made with reasonable confidence by selective decoupling and acid-catalyzed deuteration experiments, correlations between series of complexes have been primarily
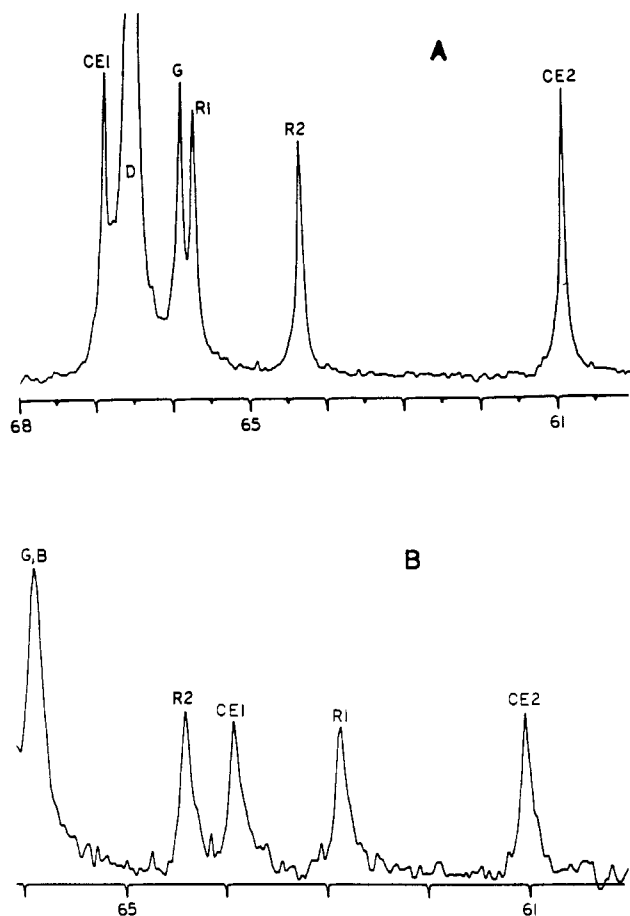
Figure 6. 300-MHz ^{13}C NMR spectra of the methylene protons of (A) [Co(med3a)NCS]$^-$ and (B) [Co(bed3a)NCS]$^-$.
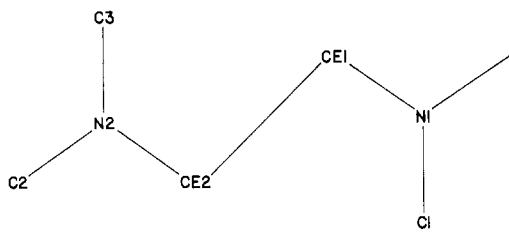

Figure 7. Representation of the cis-equatorial geometry of the ethylenediamine backbone and the arrangement of carbons about the ethylenediamine nitrogens.

Figure 8. Diagram of the glycinate and ethylenediamine methylene ^{13}C peaks of the thiocyanato complexes.

Table VI. Methylene ^{13}C Chemical Shifts of N-Substituted ed3a Thiocyanato Cobalt(III) Complexes Arranged according to Unidentate Ligand[a]

compd	G	R2	CE2	CE1	R1
[Co(ed3a)CN]$^-$	64.5	62.6	59.1	56.4	57.3
[Co(med3a)CN]$^-$	64.7	62.6	59.8	67.3	66.8
[Co(ed3a)NO$_2$]$^-$	66.48	65.18	61.12	56.1	57.2
[Co(med3a)NO$_2$]$^-$	66.96	65.29	60.89	67.5	67.3
[Co(hed3a)NO$_2$]$^-$	66.83	65.26	61.24	65.26	64.38
[Co(bed3a)NO$_2$]$^-$	64.33	62.86	61.58	62.86	61.88
[Co(ed3a)NCS]$^-$	65.67	64.51	61.16	55.36	57.03
[Co(med3a)NCS]$^-$	65.97	64.39	60.96	66.98	65.78
[Co(hed3a)NCS]$^-$	65.90	64.33	61.36	64.74	63.81
[Co(bed3a)NCS]$^-$	65.94	64.45	61.09	63.97	62.93
[Co(ed3a)H$_2$O]	67.32	66.53	62.71	56.6	57.1
[Co(med3a)H$_2$O]	67.61	67.12	62.02	66.2	66.2
[Co(hed3a)H$_2$O]	67.61	64.87	62.22	63.59	63.00
[Co(bed3a)H$_2$O]	66.33	65.26	62.32	62.91	60.95

[a] The data for the nitro and aqua complexes are cited from ref 15; the data for the cyano complexes are cited from ref 11.

empirical since few crystal structures are known.

The 300-MHz ^{13}C NMR spectra of the four thiocyanato complexes have been obtained, and the peaks are listed in Table V. All spectra are referenced to 1,4-dioxane, which was used as the internal standard in all cases and whose single resonance was fixed at 66.554 ppm relative to Me$_4$Si. The carboxylate carbon peaks appear at the expected chemical shifts in all cases; however, little structural information may be obtained from these resonances. In addition, the thiocyanate carbon is observed for each complex, but this peak is generally broad and structurally uninformative.

The spectra of the methylene carbons for the four thiocyanato complexes are shown in Figures 5 and 6. The two split upfield peaks seen for the unsubstituted complex (R = H; Figure 5A) correspond to the methylene carbons adjacent to the N1 ethylenediamine nitrogen whose hydrogen undergoes deuterium exchange with the D$_2$O solvent over a period of weeks in neutral solution.

On the other hand, the methylene carbon peaks provide much information as to the stereochemistry of the carbon atoms, since the ^{13}C chemical shift is highly dependent upon the steric and electronic environment. Peak assignments were made on the basis
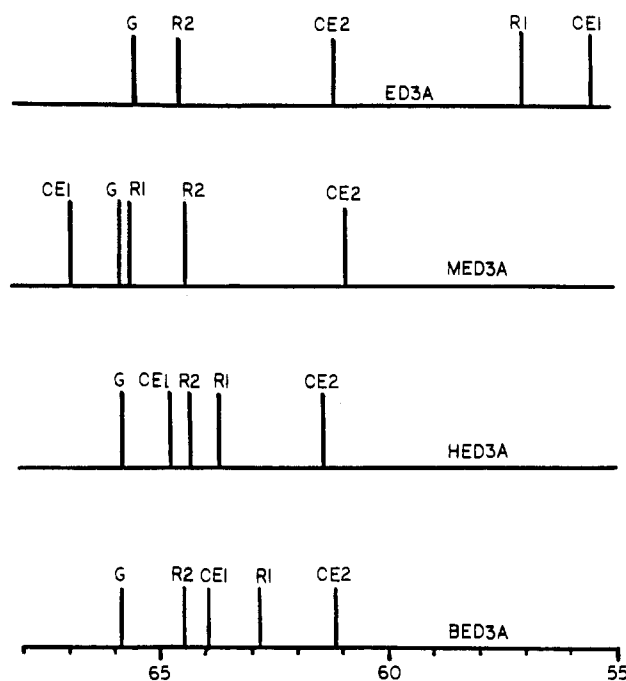
of selective decoupling of the corresponding proton resonances. The peaks in Table V listed under the heading N2 represent the methylene carbons adjacent to the ethylenediamine nitrogen bound to two glycinate rings whereas the peaks under the heading N1 represent the methylene carbons about the ethylenediamine nitrogen with only one glycinate ring attached. The order of the methylene protons listed going down the table for N2 is G (C2), R2 (C3), and CE2 according to the notation shown in Figure 7. The order of the methylene protons listed going down the table for N1 is CE1, R1 (C1), and the substituent group methylene carbon. The methyl carbon peak, the β-hydroxyethyl carbon peak, and the peaks due to the benzene ring are listed in the "other" category.

If a plane is drawn through the cobalt and the R1 and R2 ring coordinating oxygens so that it bisects the ethylenediamine backbone, the resultant halves of the molecule are expected to show different ^{13}C chemical shifts as the substituent group on N1 changes. For example, in the strain-relieved half of the molecule, the R2, G, and CE2 methylene carbon resonances should be only slightly affected as the N-substituent changes, since the chemical environments of these carbons remain about the same. On the other hand, the R1 and CE1 methylene resonances will be changed

significantly in going from the hydrogen-substituted complex to the methyl-substituted complex because of the hydrogen inductive through-bond electronic effect. Changes in the R1 and CE2 resonances should be more subtle as the substituent is changed from methyl to hydroxyethyl to benzyl since steric interactions are expected play a more prominent role.

These trends are well evidenced by the stick diagram of the methylene carbon peaks shown in Figure 8. The three methylene carbons about N2 exhibit approximately the same chemical shifts for all four complexes. The R1 and CE1 carbons are shifted dramatically downfield in going from the *N*-hydrogen to the *N*-methyl complex. These two peaks gradually shift slightly upfield as the N-substituent size is increased.

The trends observed here are completely analogous to those observed for the other series of N-substituted ed3a complexes of cobalt(III) with nitro, aqua, and cyano groups in the sixth coordinating position, as may be observed in Table VI.

Organometallic S,S Ligands with π-Donor Properties. Structure and Magnetism of [{(C₅H₅)Ni[P(S)(OCH₃)₂]₂}₂Ni], a Complex with Tetrahedral NiS₄ Coordination

Wolfgang Kläui,*[1a] Karin Schmidt,[1a] Anja Bockmann,[1a] David J. Brauer,*[1b] Jochen Wilke,[1b] Heiko Lueken,*[1a] and Ulrich Elsenhans[1c]

The sodium salts of the organometallic anions L⁻ = [(C₅H₅)Ni{P(S)R₂}₂]⁻, R = OCH₃, CH₃, react as S,S-chelate ligands with transition-metal ions M$_{aq}^{2+}$ = Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Hg²⁺ to give tetrahedral ML₂ complexes. Reactions of L⁻ with [PdCl₂(C₆H₅CN)₂], CH₃HgCl, and Bi(NO₃)₃·5H₂O yield planar PdL₂, CH₃HgL, and [BiL₂]NO₃, respectively. No ML₃ complexes could be synthesized. Crystals of [{(C₅H₅)Ni[P(S)(OCH₃)₂]₂}₂Ni] belong to the monoclinic space group C2/c with a = 19.108 (2) Å, b = 8.8044 (8) Å, c = 18.663 (1) Å, β = 102.683 (6)°, and Z = 4. Refinement converged with a conventional R value of 0.031 for 3878 reflections with F ≥ 4σ(F). The trinuclear structure possesses two terminal (C₅H₅)Ni fragments. Each of these enters two Ni–P bonds averaging 2.1363 (4) Å. The central Ni atom, which is located on a crystallographic twofold axis, bonds to a distorted tetrahedral array of four S atoms. The two crystallographically independent Ni–S distances are significantly different, and the S–Ni–S bond angles vary from 97.74 (2) to 138.25 (3)°. The magnetism μ$_{eff}$ of FeL₂ (4.7 μ$_B$ (μ$_B$ = Bohr magneton)), CoL₂ (4.3 μ$_B$), and NiL₂ (2.9 μ$_B$), R = OCH₃, has been determined in methylene chloride solution. The temperature-dependent magnetic moment of NiL₂, R = OCH₃, in the solid state (μ$_{eff}$(3.8 K) ≈ 1.9 μ$_B$, μ$_{eff}$(298 K) ≈ 3.3 μ$_B$) can roughly be interpreted in terms of a tetrahedral NiS₄ model. It is postulated that the ligands L⁻ are good π-donors and that it is this property which favors the tetrahedral over planar NiS₄ coordination.

Introduction

Ligands with sulfur donor atoms are unique in the sense that they cannot be assigned a characteristic position in the spectrochemical series I < Cl < O < N < C.[2] Jørgensen has shown that the ligand field strength of sulfur donors covers a remarkable range beginning at that of chloride, traversing that of oxygen ligands and ending at that of alkylamines.[3] In terms of ligand field theory this means that the relative σ-donor and π-acceptor vs. π-donor properties are particularly variable. As a consequence of this the coordination chemistry of sulfur ligands is remarkably many-sided.[4] We have recently described the synthesis of a new type of S,S-chelate ligand 3a,b.[5,6] The zinc complexes 2a,b were prepared via eq 1 and 2, and the sodium salts 3a,b of these organometallic S,S-chelate ligands were obtained from 2a,b via eq 3.

Now we have studied the coordination chemistry of these novel ligands in order to characterize their steric and electronic prop-

(1)

(2)

R = OCH₃(a), CH₃(b)

(3)
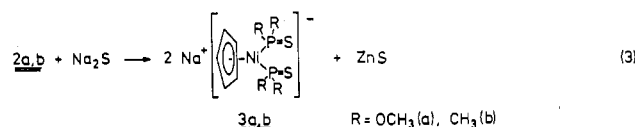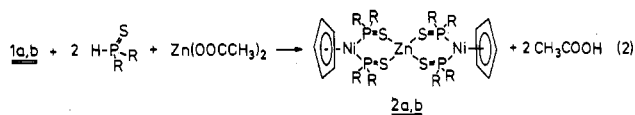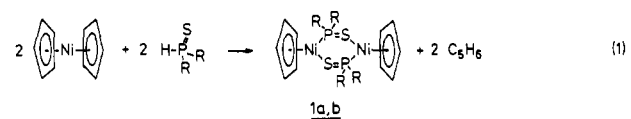
erties. We expected that the coordination chemistry of the S,S-chelates 3 would resemble that of dithioacetylacetonate (SacSac) since the O,O-chelate ligands [(C₅H₅)Ni{P(O)R₂}₂]⁻, which are homologous to 3, have been reported to possess a coordination chemistry which is similar to that of acetylacetonate.[7] The preparation and properties of metal complexes of the S,S-chelates 3, which are reported below, demonstrate that their electronic properties differ drastically from those of SacSac compounds.

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