A. G. Sykes were greatly appreciated.

Registry No. $\mathrm{Co(NH_3)_5OH_2^{3+}}$, 14403-82-8; $\mathrm{Co(NH_3)_5OH^{2+}}$, 16632-75-0; $\mathrm{Co(NH_3)_5MoO_4^{+}}$, 60464-07-5; $\mathrm{HMoO_4^{-}}$, 14259-84-8.

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Nuclear Magnetic Resonance Investigation of Cobalt(II) Aminocarboxylates: Evidence for Pentadentate Coordination by EDTA

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Received June 9, 1976 AIC60428G

The nuclear magnetic resonance temperature dependence of the complexes $\mathrm{Co^{II}[EDTA]^{2-}}$, $\mathrm{Co^{II}[1,2\text{-}PDTA]^{2-}}$, $\mathrm{Co^{II}[EDDA]}$, $\mathrm{Co^{II}[(EDTA)(CN)]^{3-}}$, $\mathrm{Co^{II}[ED3A]^{-}}$, $\mathrm{Co^{II}[CyDTA]^{2-}}$, $\mathrm{Co^{II}[1,3\text{-}PDTA]^{2-}}$, $\mathrm{Co^{II}[(EDTA)(OH)]^{3-}}$, $\mathrm{Co^{II}[IDA]}$, and $\mathrm{Co^{II}(IDA)_2^{2-}}$ are reported. Racemization is rapid for $\mathrm{Co^{II}[EDTA]^{2-}}$, $\mathrm{Co^{II}[(EDTA)(CN)]^{3-}}$, $\mathrm{Co^{II}[(EDTA)(OH)]^{3-}}$, and $\mathrm{Co^{II}[1,3\text{-}PDTA]^{2-}}$ at 34 °C; racemization of $\mathrm{Co^{II}[ED3A]^{-}}$ is intermediate at 34 °C and rapid by 50 °C. $\mathrm{Co^{II}[EDTA]^{2-}}$, $\mathrm{Co^{II}[1,2\text{-}PDTA]^{2-}}$, and $\mathrm{Co^{II}[1,3\text{-}PDTA]^{2-}}$ exist in solution predominantly as pentacoordinate species. The spectrum of $\mathrm{Co^{II}[EDTA]^{2-}}$ is essentially pD independent in the pD range 2.7–11.6; pD dependence above pD 12 results from the formation of a mixed hydroxy complex. Deuteration of $\mathrm{Co^{II}[CyDTA]^{2-}}$ is stereospecific; both in-plane and out-of-plane acetate arms experience first-order base-catalyzed deuteration. First-order rate constants for deuteration of $\mathrm{Co^{II}[CyDTA]}$ are reported. Cis $\rightleftharpoons$ trans equilibration is rapid in $\mathrm{Co^{II}(IDA)_2^{2-}}$ at room temperature. The reaction $\mathrm{Co^{II}(IDA) + Co^{II}(IDA)_2 \rightleftharpoons Co^{II}(IDA)_2 + Co^{II}(IDA)}$ is rapid at elevated temperature with retention of IDA configuration. An $\mathrm{S_N2}$ type mechanism is proposed for this reaction. The following abbreviations are used: $\mathrm{EDTA^{4-}}$, $\mathrm{(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2}$; $\mathrm{1,2\text{-}PDTA^{4-}}$, $\mathrm{(^-O_2CCH_2)_2NCH(CH_3)CH_2N(CH_2CO_2^-)_2}$; $\mathrm{EDDA^{2-}}$, $\mathrm{(^-O_2CCH_2)NHCH_2CH_2NH(CH_2CO_2^-)}$; $\mathrm{ED3A^{3-}}$, $\mathrm{(^-O_2CCH_2)NHCH_2CH_2N(CH_2CO_2^-)_2}$; $\mathrm{CyDTA^{4-}}$, *trans*-1,2-$\mathrm{(^-O_2CCH_2)_2N(}$*c*-Hx$\mathrm{)N(CH_2CO_2^-)_2}$; $\mathrm{1,3\text{-}PDTA^{4-}}$, $\mathrm{(^-O_2CCH_2)_2NCH_2CH_2CH_2N(CH_2CO_2^-)_2}$; $\mathrm{IDA^{2-}}$, $\mathrm{(^-O_2CCH_2)_2NH}$.

Introduction

The solution structure of bivalent and trivalent transition metal complexes of EDTA and related ligands has long been investigated. The results of these investigations are conflicting and no one has succeeded to date in unambiguously determining the number of coordination sites actually utilized by EDTA type ligands to coordinate labile metal ions. The early works of Schwarzenbach[1] concluded that transition metal–EDTA complexes assume a pentacoordinate structure with a molecule of H_2O, OH^-, or some other unidentate ligand occupying the sixth position. Jorgensen,[2] on the basis of electronic spectroscopy data, also assigned pentacoordination to such complexes. Higginson[3] compared acid dissociation constants of various metal–EDTA complexes and concluded that for most bivalent transition metal–EDTA complexes only five of the possible six sites available are utilized by the EDTA chelate. More recently, Higginson spectrophotometrically determined stability constants for mixed-complex formation of EDTA and various unidentate ligands and concluded that aqueous solutions of metal complexes containing EDTA and other related ligands, PDTA and CyDTA, exist as hexacoordinate species approximately 70% of the time [76% for Co(II)].[4] Charles[5] concluded from the viscosities of aqueous solutions containing bivalent metal–EDTA complexes that, with the exception of Pb, a hexacoordinated structure is favored. Later, on the basis of large differences found between the Jones–Dale viscosity coefficients for $\mathrm{Co^{II}EDTA}$ and $\mathrm{Co^{III}EDTA}$, Yasuda[6] proposed that $\mathrm{Co^{II}EDTA}$ is present as a pentadentate complex or possibly as a mixture of the penta- and hexacoordinated species. The x-ray studies of Hoard[7,8] have clearly shown that an uncoordinated acetate exists in solid $\mathrm{Co^{II}EDTA}$ but did not allow for the assignment of a coordination number to the solution structure of this complex. The spectrophotometric studies of EDTA complexes mixed with OH^- and NH_3 led Bhat[9] to assume hexacoordination for $\mathrm{Co^{II}EDTA}$ and $\mathrm{Cu^{II}EDTA}$ and pentacoordination for $\mathrm{Ni^{II}EDTA}$. Burnett[10] interpreted the free energy and enthalpy changes which accompanied the protonation of divalent metal–EDTA complexes as a hexacoordinate geometry existing in the original species. Margerum and Rosen[11] utilized kinetic behavior of $\mathrm{Ni^{II}EDTA}$ to assign pentacoordination while Wilkins and Yelin[12] interpreted their kinetic scheme to indicate at least 80% hexacoordination for $\mathrm{Co^{II}EDTA}$. Later, Wilkins and Yelin[13] rapidly oxidized the labile $\mathrm{Co^{II}EDTA}$ and examined the resultant inert $\mathrm{Co^{III}EDTA}$ complexes; the results of these experiments were in agreement with their previous conclusions. ^{13}C and ^{17}O NMR spectroscopy led Matwiyoff[14] to conclude hexacoordination for $\mathrm{Ni^{II}EDTA}$ in a pH range of 4–10 and, at pH <4, an equilibrium between hexa- and pentacoordination. In his work Matwiyoff stated that if $\mathrm{Co^{II}EDTA}$ is hexacoordinate, it is stereochemically nonrigid.

It has been well established[15] for Ni(II) complexes of EDTA and related ligands that the conformationally different protons of the ethylene backbone and acetate arms experience large chemical shifts resulting from the delocalization of the unpaired d electrons toward the ligand. It has also been determined[15-17] that the strong dependence of the contact shift on the dihedral angle results in equatorial protons appearing at much lower fields than their axial counterparts. This Fermi contact shift has also been shown[15] to occur in Co(II) complexes. Unlike Ni(II) however, Co(II) also gives rise to a pseudo contact shift.[18,19]

In a previous publication[20] it was shown that rapid axial $\rightleftharpoons$ equatorial interchange occurs in $\mathrm{Ni^{II}EDTA}$ at 78 °C. It was argued that rapid Δ to Λ equilibrium was responsible for the interchanging of axial and equatorial protons thus resulting in the coalesence of all resonance signals into two time-average signals corresponding to backbone and acetate protons. It is known[22] that neither Ni–N bond rupture followed by N inversion nor rapid δ to λ equilibration of ethylene "backbone" would result in the observed temperature dependence of the contact shift spectrum. In this study it was concluded on the basis of NMR temperature dependencies that $\mathrm{Ni^{II}EDTA}$ exists in solution predominantly as a pentacoordinate species and that the uncoordinated acetate arm is an important factor in the rapid $\Delta \rightleftharpoons \Lambda$ conversion of this complex. These results agreed with the ^{17}O study of Grant et al.,[23] who concluded that $\mathrm{NiEDTA^{2-}}$ exists predominantly in the form with one uncoordinated acetate.

In this work evidence is presented for pentacoordination and rapid racemization of $\mathrm{Co^{II}EDTA}$ at room temperature. These studies suggest that racemization is accelerated by an uncoordinated acetate. Deuteration studies of $\mathrm{Co^{II}CyDTA}$ indicate that the rate of acetate deuteration is stereospecific and that in-plane acetate protons do exchange in this case contrary to what is observed in the corresponding Ni(II) complexes.[28]

Experimental Section

All ligands were commercial products except for 1,3-PDTA and ED3A. ED3A was prepared by the method of Blackmer et al.[24] The ligand was separated from the EDDA and EDTA produced in the reaction by forming the Co(III) complexes and passing successively through cation- and anion-exchange columns in the K^+ and Cl^- forms, respectively; the band corresponding to $\mathrm{Co^{III}EDDA^+}$ was retained on the cation-exchange column and $\mathrm{Co^{III}EDTA^-}$ was retained on the anion-exchange column while the $\mathrm{Co^{III}ED3A}$ was not retained by either column. This complex was subsequently reduced to the cobalt(II) complex in approximately 20 min with zinc amalgam in neutral solution. The Zn^{2+} was not removed as the resonance resulting from the diamagnetic $\mathrm{Zn(ED3A)^-}$ was easily identified. 1,3-PDTA was graciously donated by Dr. J. Sarneski; EDTA, 1,2-PDTA, CyDTA, and IDA were recrystallized once from H_2O. A 2 M Co^{2+} solution was prepared by dissolving $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ in deuterium oxide (99.8%). This solution was standardized by potentiometric titration with standard potassium ferricyanide according to standard procedures.[25] Complexes were formed under nitrogen atmosphere by adding an equimolar amount of 2 M Co^{2+} to the neutralized ligand in D_2O. The pD was determined with a Corning 110 pH meter equipped with a microelectrode. The pD was varied, when necessary, by addition of 2 N NaOD and 2 N DCl. The usual approximation of pD = pH + 0.4[26] was used to determine the pD's. No high-temperature correction was made.[27]

The contact shift measurements were made on a Hitachi R 20 B nuclear magnetic resonance spectrometer equipped with a Hewlett-Packard Model 230B rf amplifier as previously reported.[20] The temperature was varied by means of the Hitachi Model R202VT temperature controller which was calibrated with ethylene glycol at high temperature and methyl alcohol at low temperature. The deuteration study was accomplished by observing the decrease in acetate signal and treating the data as previously outlined by Erickson et al.[28] First-order rate constants were calculated from the half-life via $k = 0.693/t_{1/2}$.

Discussion

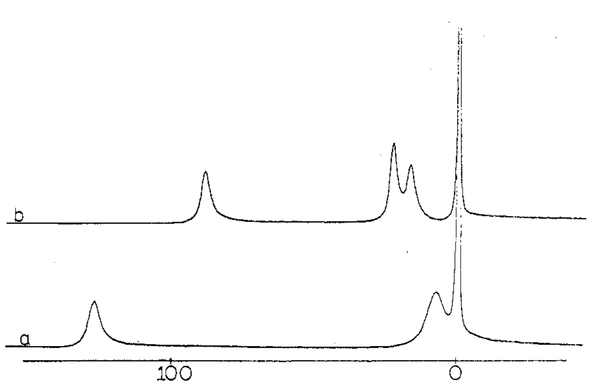

Figure 1. Contact shift temperature dependence of $\mathrm{Co^{II}(EDTA)}$ at pD 6.3 (shift scale ppm from H_2O): (a) 34 °C; (b) 105 °C.

Examination of Figure 1a shows that at 34 °C the contact shift spectrum of $\mathrm{Co^{II}EDTA}$ consists of two peaks with relative intensity of approximately 1:2. Accurate integration of the higher field (larger) signal was not possible due to overlap with the water resonance at zero. At 105 °C (Figure 1b) the resonance at −7 ppm is seen to actually consist of two equal-intensity peaks. Thus, the apparent two-peak spectrum at 34 °C is, in fact, a three-peak spectrum with the two most upfield peaks overlapping. Upon deuteration of the acetate protons of $\mathrm{Co^{II}EDTA}$, the downfield peak and one of the two (unresolved) upfield peaks disappear. The disappearance of the low-field signal and the decrease in intensity of the high-field signal further imply that at 34 °C the contact shift spectrum of $\mathrm{Co^{II}EDTA^{2-}}$ is composed of three approximately equal-intensity peaks with the two most upfield resonances unresolved. After deuteration of the acetates, only one peak remains in the −7-ppm region. At 105 °C only one peak is observed at the same position as the more upfield of the pair of upfield peaks in Figure 1b. Therefore, one of the two peaks observed in this region for the protonated compound at 105 °C (Figure 1b) must have been exchanged for deuterium (i.e., one of these resonances is due to acetate protons). Development of two signals in the −7-ppm region was observed at high temperature in the spectrum of $\mathrm{Co^{II}EDTA}$ at all pD's in the range $2.7 < \mathrm{pD} < 11.6$. In view of the data presented it is clear that three chemically distinct resonances are present in the room-temperature contact shift spectrum of $\mathrm{Co^{II}EDTA}$. Two of these signals correspond to acetate protons (−128 and −7 ppm) and one corresponds to ethylenediamine protons (−7 ppm); at 34 °C the similar shifts of acetate and "backbone" resonances give the appearance of a single peak.

In order to explain the $\mathrm{Co^{II}EDTA}$ spectrum it is necessary to consider the contact shift spectrum of the corresponding nickel(II) complex which has been well studied.[28,29] When the rate of any intramolecular process that interchanges proton conformation is slow on the NMR time scale, four signals are observed in the contact shift spectrum of $\mathrm{Ni^{II}EDTA}$.[20,28] Rapid $\Delta \rightleftharpoons \Lambda$ conversion of $\mathrm{Ni^{II}EDTA}$ at 78 °C, however, results in the averaging of axial and equatorial ethylenediamine protons and also the averaging of axial in-plane with equatorial out-of-plane acetate protons and axial out-of-plane with equatorial in-plane acetate protons yielding a single unresolved peak for all of these resonances.[20] Thus, at high temperature, the four-peak spectrum coaleses to a single peak (actually the single peak consists of three unresolved signals consisting of one peak due to all the ethylenediamine protons, one peak due to the averaged in-plane axial and out-of-plane equatorial acetates, and one peak due to the averaged in-plane equatorial and out-of-plane axial acetates).

Clearly, observation of only one resonance for ethylenediamine protons at room temperature in $\mathrm{Co^{II}EDTA}$ implies either chemical equivalence (i.e., a planar nonpuckered ring) or rapid interconversion of axial and equatorial protons of a puckered ring. The existence of such a nonpuckered five-membered ring cannot be discounted at this point; however, considerable evidence has been accumulated which indicates that such a planar ring is energetically unfavored.[24,29,30] These

Table I. Spectral Assignments

Complex	Shift[a]	Assignment[b]
EDTA	−128	2 OP A OAc + 2 IP E OAc
	−7	2 OP E OAc + 2 IP A OAc + 4 en
1,2-PDTA	−148	2 OP A OAc
	−121	2 IP E OAc
	−90	1 E en
	−71	1 OP E OAc
	−42	1 OP E OAc
	+13	3 CH_3
	+52	2 IP A OAc
	+89	2 A en
$(IDA)_{1.5}$	−88	$Co(IDA)_2$
	−76	Co(IDA)
	−10	$Co(IDA)_2$
	−5	Co(IDA)
ED3A	−125	Same as EDTA
	−7	Same as EDTA
1,3-PDTA	−110	2 OP A OAc + 2 IP E OAc
	−55	4 en
	−33	2 OP E OAc + 2 IP A OAc
	+101	β CH_2
EDDA	−148	2 A OAc
	−67	2 E OAc
	−60	2 E en
	−18	2 A en
EDTA(CN)	−64	4 OAc
	−55	4 en
	−41	4 OAc
EDTA(OH)	−65	4 OAc
	−57	4 en
	−48	4 OAc
CyDTA	−143	2 OP A OAc
	−100	2 IP E OAc
	−20	2 IP A OAc
	−8	2 OP E OAc
	−6	2 RP
	+1	Uncoord ligand
	+7	2 RP
	+14	2 RP
	+19	2 RP
	+56	2 RP

[a] Ppm from water. [b] The following shorthand is used in the assignments: IP, in-plane; OP, out-of-plane; A, axial; E, equatorial; OAc, acetate; en, ethylenediamine; RP, ring proton.

previous studies, along with further evidence presented below, indicate that a rapid averaging of axial and equatorial protons of the ethylenediamine protons is responsible for the single resonance observed.

The consequences of nitrogen inversion and $\Delta \rightleftharpoons \Lambda$ conversion have been previously considered in detail.[28] Conformational averaging of "backbone" protons eliminates the possibility of only nitrogen inversion acting as an intramolecular averaging process because, in such a process, the ethylenediamine protons retain their conformational identity. $\Delta \rightleftharpoons \Lambda$ conversion, however, results in racemization of the complex. If only Fermi contact shifts were operative, rapid $\Delta \rightleftharpoons \Lambda$ conversion would lead to observation of either one acetate peak (as seen in Ni^{II}EDTA) or two closely spaced acetate peaks and one ethylenediamine proton peak. The presence of pseudo contact shifts in the cobalt(II) complexes, however, provides a mechanism to rationalize the appearance of two very different acetate signals under conditions of rapid $\Delta \rightleftharpoons \Lambda$ conversion. For example, if out-of-plane axial acetate protons have a shift of δ_1, out-of-plane equatorial acetate protons δ_2, in-plane axial acetates δ_3, and in-plane equatorial acetates δ_4, rapid $\Delta \rightleftharpoons \Lambda$ conversion results in the appearance of peaks at $(\delta_1 + \delta_4)/2$ and $(\delta_2 + \delta_3)/2$.[28] If only Fermi contact shifts are present, these two peaks are very nearly identical (e.g., Ni^{II}EDTA), but the presence of large pseudo contact shifts can remove this degeneracy by making $\delta_1 \neq \delta_3$ and $\delta_2 \neq \delta_4$.

To demonstrate that such a room-temperature racemization does in fact occur it is necessary to examine a case where such a process is not possible or a case in which a preferred conformation leads to incomplete averaging. Under these conditions separate resonances for axial and equatorial ethylenediamine protons would be observed as well as resonances for out-of-plane equatorial, out-of-plane axial, in-plane equatorial, and in-plane-axial acetate protons (i.e., a six-line spectrum is expected). Attempts to demonstrate the rapid racemization of Co^{II}EDTA by slowing the rate to observable time scales at low temperature were, however, unsuccessful. Spectra were obtained in deuteriomethanol to −30 °C, but excessive broadening made it impossible to tell if the racemization was slowed significantly.

It is possible, however, to introduce a conformational preference by incorporation of an alkyl group into the ethylenediamine portion of the ligand.[21] The strong pseudoequatorial preference of the methyl group in Co^{II}[1,2-PDTA] offers an excellent model for viewing such a desired conformation. Because of this conformational preference, averaging is incomplete even though $\Delta \rightleftharpoons \Lambda$ conversion may be fast.[28] Such differentiation of geometrically and conformationally unique acetate protons would facilitate the interpretation of the spectrum of Co^{II}EDTA because the chemical shift values obtained for this complex should be close to the "frozen" values desired for the Co^{II}EDTA species.

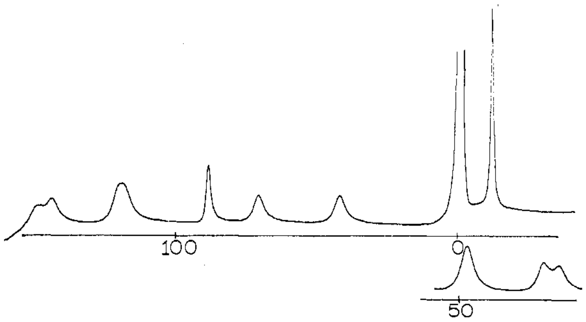

Figure 2. Contact shift spectrum of Co^{II}(1,2-PDTA) at pD 8.0 and 34 °C (shift scale ppm from H_2O).

Examination of Figure 2 shows that the room-temperature contact shift spectrum of Co^{II}[1,2-PDTA] consists of 12 peaks. Under the conditions employed in Figure 3 only 10 resolved peaks are observed. The peaks at −121 and +52 ppm can be resolved into two peaks at different pH's[19] and at high temperature. The observation of 12 peaks instead of the six predicted above arises because of the asymmetry introduced by the methyl substituent. Identification of the acetate resonances is easily accomplished by deuteration. Upon deuteration, signals at −148, −121, −71, −42, and +52 ppm disappear indicating that these resonances correspond to acetate protons. Respective intensities of signals at +89, +13, and −90 ppm indicate their assignment as axial ethylenes, methyl, and equatorial ethylene, respectively. It is assumed that the methyl occupies an equatorial environment and, thus, only one equatorial ethylenediamine proton is observed. The assignments of the spectra reported here are summarized in Table I. The effect of the methyl substituent on ethylene-

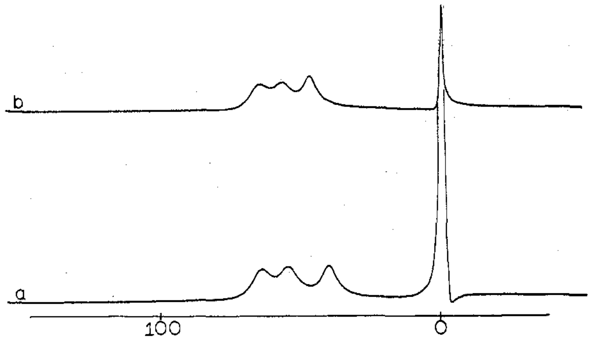

Figure 3. Contact shift spectra of (a) $Co^{II}[(EDTA)(CN)]^{3-}$ and (b) $Co^{II}[(EDTA)(OH)]^{3-}$ at 34 °C and pD ~12 (shift scale ppm from H_2O).

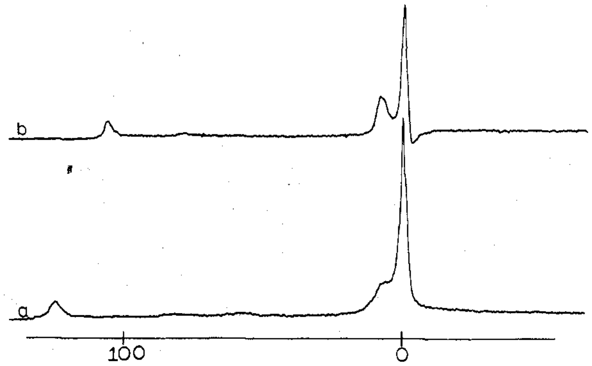

Figure 4. Contact shift temperature dependence of Co^{II}(ED3A) at pD 8.5 (shift scale ppm from H_2O): (a) 34 °C; (b) 105 °C.

diamine protons is clearly seen in the contact shift spectrum by the presence of two signals for axial ethylene protons. A similar effect on the protons of the in-plane and out-of-plane acetate arms adjacent to the methyl group can be expected and in fact is observed; in-plane and out-of-plane acetate protons opposite the methyl experience essentially no effect from the methyl substituent because of their distances from the group, while acetates on the same side as the methyl are significantly altered. Such an effect further differentiates between acetate protons that are either adjacent to or opposite the methyl.

Considering chemical shift values of δ_1 for out-of-plane axial, δ_2 for out-of-plane equatorial, δ_3 for in-plane axial, and δ_4 for in-plane equatorial acetates, rapid $\Delta \rightleftharpoons \Lambda$ conversion results in resonance at $(\delta_1 + \delta_4)/2$ and $(\delta_2 + \delta_3)/2$ corresponding to the averaged positions of these protons. The structural similarity between Co^{II}EDTA and Co^{II}[1,2-PDTA] suggests that the bond lengths and dihedral angles in these complexes should be similar. Thus, the PDTA resonance positions should represent, to a close approximation, the "frozen" positions of the EDTA complex. Considering $\Delta \rightleftharpoons \Lambda$ conversion as the operative mechanism for the observed molecular racemization of Co^{II}EDTA at 34 °C, the values obtained by averaging the shifts of the in-plane equatorial with out-of-plane axial protons, $(\delta_1 + \delta_4)/2$, and the in-plane axial with out-of-plane equatorial protons, $(\delta_2 + \delta_3)/2$, of Co^{II}[1,2-PDTA] should parallel those seen in Co^{II}EDTA. When these average values are determined, $-(148 + 121)/2 = -134$ ppm and $(-56 + 52)/2 = -2$ ppm, it is seen that they do in fact agree reasonably well with the observed chemical shift values of acetate resonances taken from the contact shift spectrum of Co^{II}EDTA, −128 ppm for $(\delta_1 + \delta_4)/2$ and −7 ppm for $(\delta_2 + \delta_3)/2$; the averaged value of −2 ppm for the ethylenediamine protons of Co^{II}[1,2-PDTA] also agrees well with the observed value of −7 ppm for those respective protons in Co^{II}EDTA. These data further support the agrument that Co^{II}EDTA undergoes rapid racemization at 34 °C via rapid $\Delta \rightleftharpoons \Lambda$ conversion.

In a previous publication,[20] the failure to observe rapid axial $\rightleftharpoons$ equatorial interconversion for Ni^{II}EDDA and Ni^{II}MED3A up to 105 °C was interpreted to imply that an uncoordinated acetate is an important factor in the rapid $\Delta \rightleftharpoons \Lambda$ conversion of Ni^{II}EDTA at 34 °C.[20] Considering the effect of an uncoordinated acetate on the rate of racemization of $Ni^{II}EDTA(H_2O)^{2-}$, the rapid racemization of Co^{II}EDTA at room temperature raises the question of whether predominant pentacoordination also exists in Co^{II}EDTA.

Figure 3 shows the contact shift spectrum of Co^{II}(EDTA)(CN). Deuteration of this complex allows assignment of resonances at −64 and −41 ppm as acetate signals and that at −55 ppm as ethylenediamine protons. The appearance of only three resonances for this clearly pentacoordinated species indicates that rapid racemization will occur when a ligand arm is uncoordinated. In spite of the strong coordination of cyanide, racemization is rapid in this complex which has an uncoordinated carboxylate. This similar racemization behavior is consistent with the EDTA complex also having an uncoordinated acetate. It is not surprising that the values of the shifts change drastically because the electron distribution within the mixed cyanide complex is certainly different from that in the aquo complex. The important feature is that, since only three peaks are observed once again, the $\Delta \rightleftharpoons \Lambda$ racemization process is still rapid even though the complex now contains a coordinated cyanide. Since the EDTA ligand certainly utilizes only five of the possible six donor groups in Co^{II}(EDTA)(CN), the resemblance of these spectra seems to indicate that only five of the possible six sites are utilized by EDTA in Co^{II}EDTA. If Co^{II}EDTA was predominantly hexacoordinate, addition of the cyanide anion would be accompanied by displacement of a cobalt–acetate bond and significant changes in the contact shift spectrum would be expected. This displacement would almost certainly result in the production of additional peaks since the symmetry of the complex would be destroyed. The shift differences in the spectra of these two complexes are explainable due to the presence of the negatively charged cyanide. The temperature dependency of the spectrum of Co^{II}(EDTA)(CN) is essentially identical with that of $Co^{II}(EDTA)(H_2O)$. It should be noted that the previous unresolved resonances at −7 ppm in Co^{II}EDTA separate into two distinct resonances after incorporation of the cyanide anion.

Furthermore, at high pH, a spectrum very similar to that obtained for $Co(EDTA)(CN)^{3-}$ is obtained (see Figure 3). This is believed to occur by formation of the hydroxy complex above pD 11.6 via the reaction

$$Co(EDTA)(H_2O)^{2-} + OH^- \rightarrow Co(EDTA)(OH)^{3-} + H_2O$$

The electrostatic effect of the coordinated negative hydroxy group has an effect on the NMR spectrum very similar to the effect of a negative cyanide group but does not appear to change the structure or rate of racemization. Since the colors of the two solutions of Figure 3 are different, it is apparent that they arise from different species.

Further strong evidence for pentacoordination in Co^{II}EDTA is found in the contact shift spectrum of Co^{II}ED3A (Figure 4). Two widely separated resonances are observed with relative intensities of low- and high-field signals of about 1:2. Comparison of the essentially identical contact shift spectra of Co^{II}ED3A and Co^{II}EDTA suggests a very strong resemblance in their solution structures and dynamics. The room-temperature spectra of both complexes consist of two signals; the higher field signal in Co^{II}EDTA, however, consists of two unresolved resonances. The shift differences between the downfield and upfield signals is 121 ppm for Co^{II}EDTA and 118 ppm for Co^{II}ED3A. Deuteration of Co^{II}ED3A

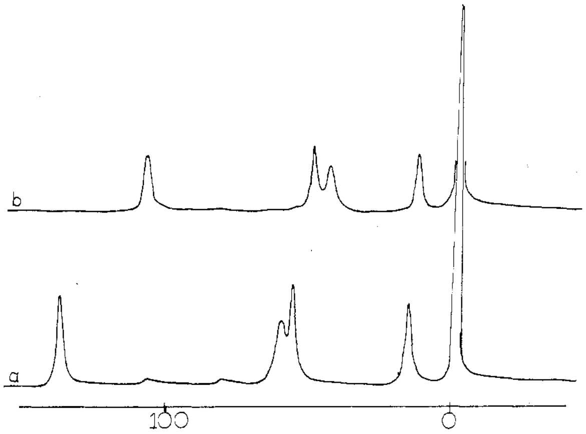

Figure 5. Contact shift temperature dependence of Co^{II}(EDDA) at pD 6.3 (shift scale ppm from H_2O): (a) 34 °C; (b) 105 °C.

resulted in the same behavior as reported for the EDTA complex. With only pentacoordination possible for Co^{II}ED3A it can be concluded that the EDTA complex exists predominantly as a pentacoordinate species also. The possibility of rapid pentacoordinate $\rightleftharpoons$ hexacoordinate equilibration occurring in Co^{II}EDTA cannot be completely disregarded from this study; however, the strong similarity of the spectral data for obviously pentacoordinate Co(ED3A)$^-$ and Co(EDTA)$^{2-}$ strongly suggests that any such equilibration would favor the pentacoordinate form by a large amount.

Previously it was proposed that the presence of an uncoordinated acetate arm in the corresponding Ni(II) complexes greatly increases the rate of intramolecular racemization.[20] Ni^{II}EDDA and Ni^{II}MED3A were found not to undergo appreciable intramolecular rearrangement up to −105 °C. Examination of the contact shift spectrum of Co^{II}EDDA (Figure 5) shows that axial and equatorial protons of both ethylenediamine and acetate protons are well resolved up to 105 °C, implying a slow rate of any intramolecular averaging processes. This spectrum is consistent with the assumed stereochemically rigid transcoordination of EDDA. Some averaging process appears to be occurring at higher pD's;[31] however, it is easily argued that Co^{II}EDDA should racemize at least as rapidly as Co^{II}EDTA if the averaging process does not involve an uncoordinated acetate arm. In fact, it could be argued that Co^{II}EDDA should racemize even more rapidly than Co^{II}EDTA because of the smaller number of bonds which must be stretched for this process to occur. Addition of an acetate to EDDA (ED3A) results in the coalesence of both acetate and backbone protons. Careful examination of Figure 4, however, shows that the resonance at ∼−2 ppm is relatively broad at room temperature but becomes sharper at high temperatures. This suggests a kinetic process (which is presumed to be the racemization reaction) whose time scale is comparable to the chemical shift difference of the protons. This same reaction is, however, rapid in Co(EDTA) (i.e., no kinetic broadening is observed) leading to the conclusion that the rate of racemization of this series is Co(EDDA) < Co(ED3A)$^-$ < Co(EDTA)$^{2-}$. This increase in rate of racemization is consistent with the increasing probability of the complex containing an uncoordinated acetate and indicates that Co(ED3A)$^-$ may contain some tetracoordinated form.

The spectrum of Co^{II}(1,3-PDTA) is shown in Figure 6. Deuteration results in assignment of resonances at −110 and −33 ppm as acetate signals with the remaining signals at −55 and +101 ppm corresponding to protons of trimethylenediamine "backbone". The incorporation of a methylene group into the ethylenediamine backbone makes possible the presence of two isomeric forms: skew and chair.[32,33] Presence and slow interconversions of these two isomers would result in resonances for axial and equatorial protons on each carbon (i.e., four signals would be observed). However, if any process occurred which rapidly equilibrated these isomers, two signals for the backbone protons would then be observed (average of protons on carbons 1 and 3 and average of protons on carbon 2). The methylene signals in the contact shift spectrum of Co^{II}(1,3-PDTA) indicate that such an equilibration does occur. In view of the previously presented data concerning the intramolecular racemization of the Co(II) complexes mentioned in this investigation, Figure 6 is interpreted to indicate that $\Delta \rightleftharpoons \Lambda$ conversion of Co^{II}1,3-PDTA occurs rapidly at 34 °C. As previously argued, the presence of a pseudo contact shift removes the degeneracy of acetate protons under the conditions of rapid $\Delta \rightleftharpoons \Lambda$ equilibration.

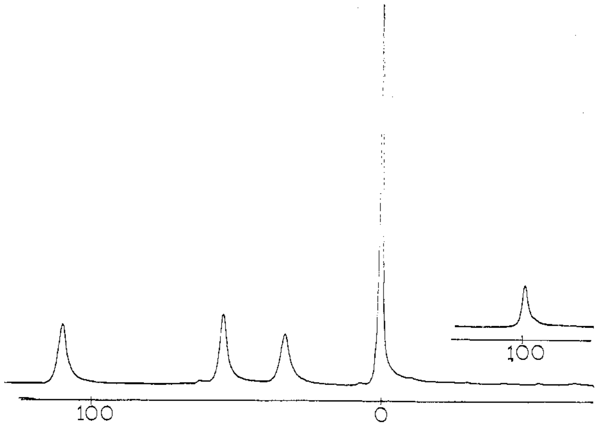

Figure 6. Contact shift spectrum of Co^{II}(1,3-PDTA) at pD 6.0 (shift scale ppm from H_2O).

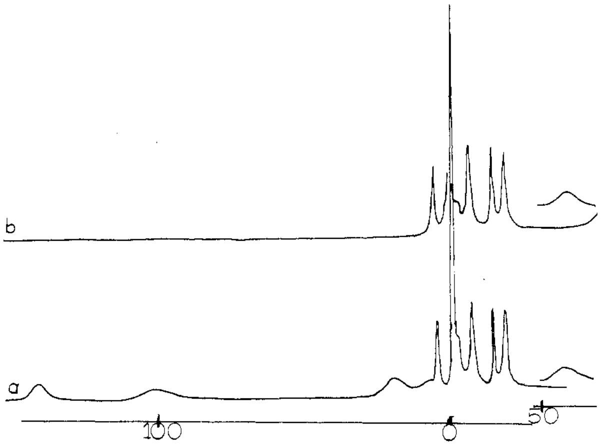

Figure 7. Contact shift spectra of Co^{II}(CyDTA) at 34 °C (a) before and (b) after deuteration (shift scale ppm from H_2O).

This differentiation of in-plane and out-of-plane axial as well as in-plane and out-of-plane equatorial acetates can be observed when examining the contact shift spectrum of Co^{II}CyDTA, Figure 7. The assignments of the four acetate signals are listed in Table I. It has been established for Ni(II) complexes that in-plane acetate protons undergo deuteration at an extremely slow rate.[28] The cyclohexane "backbone" of the CyDTA ligand makes this complex stereochemically rigid, incapable of any intramolecular rearrangement other than that which would occur with rupture of the N–Co bond followed by nitrogen inversion. Therefore, the cyclohexane "backbone" of the Co^{II}CyDTA complex prevents acetate arms from experiencing (on the NMR time scale) any process which would allow an in-plane arm to equilibrate to an out-of-plane position. Thus in-plane acetates are fixed in their position and are incapable of reorientating to an out-of-plane geometry. In Figure 7b, it is observed that all acetate protons of Co^{II}CyDTA

Table II. Rate of Deuteration of CoCyDTA Acetates

Peak position	First-order rate const (71 °C), s^{-1}	Assignment
−143	6.5×10^{-3}	Out-of-plane axial
−100	8.2×10^{-4}	In-plane equatorial
−20	2.5×10^{-3}	In-plane axial
−8	6.0×10^{-3}	Out-of-plane equatorial

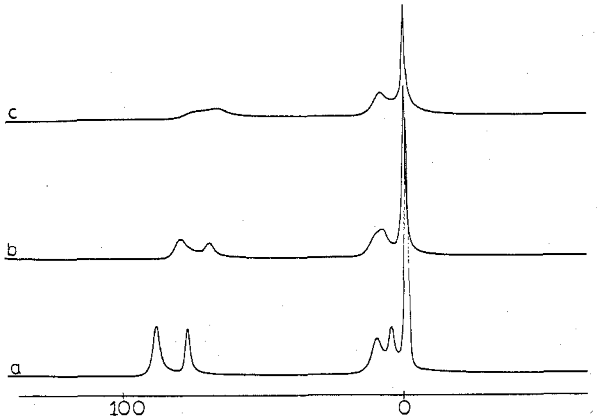

Figure 8. Contact shift temperature dependence of $Co^{II}(IDA)$ with $[IDA]/[Co] = 1.5/1$ at pD 6.2 (shift scale ppm from H_2O): (a) 34 °C; (b) 80 °C; (c) 105 °C.

exchange with deuterium. This is contrary to what is observed in the corresponding Ni^{II}CyDTA. Rate constants for the exchange reaction were determined by a method previously outlined by Erickson et al. and are reported in Table II. Out-of-plane and axial acetates are assumed to deuterate at the fastest rates and the spectral assignments are made on this basis. These assignments are consistent with the 1,2-PDTA assignments made on the basis of the proposed racemization mechanism.

The last piece of evidence which supports the contention that an uncoordinated acetate is an important factor in determining the rate of intramolecular rearrangement is seen in Figure 8. This figure shows the behavior of a solution in which the mole ratio of IDA to Co(II) is 1.5:1. Peaks assignable to mono and bis complexes are observed, but the cis and trans isomers of the bis complex are not observed. This indicates that cis ⇌ trans isomerization is rapid in the bis complex. Rapid cis ⇌ trans isomerization has also been observed in $Ni(IDA)_2^{2-}$. Despite the rapid cis ⇌ trans isomerization, the axial and equatorial protons are not averaged indicating that the individual ring conformations are not averaged (i.e., the complex is not racemized). In this case there is no uncoordinated acetate and, hence, the racemization is slow on the NMR time scale.

The most surprising feature of the data presented in Figure 8 is the coalescence of peaks due to mono and bis complexes at high temperature. This equilibration occurs without racemization of the complex. In other words, even though a bond-breaking mechanism must be operative in the mono ⇌ bis reaction, the conformations of the chelate rings are retained. This indicates an S_N2 type mechanism in which the new bond is at least partially formed before the old bond is completely broken.

These results, therefore, indicate that the estimate that $Co(EDTA)(H_2O)^{2-}$ oxidizes 5–12 times slower than $Co(EDTA)^{2-}$ [13] may be incorrect. This estimate was used in order to estimate the amount of pentadentate form which could exist when essentially 100% of hexadentate cobalt(III) species is obtained upon oxidation. It would appear that the oxidation of the pentadentate isomer is much slower than that of the hexadentate form, hence, yielding the previous results.

Acknowledgment. This work was supported by the National Institutes of Health under Grant GM20645. We thank Drs. C. N. Reilley and J. E. Sarneski of the University of North Carolina for some 1,3-PDTA.

Registry No. $Co^{II}[EDTA]^{2-}$, 14931-83-0; $Co^{II}[1,2\text{-}PDTA]^{2-}$, 26425-15-0; $Co^{II}[IDA(H_2O)_3]$, 34387-45-6; $Co^{II}[IDA]_2^{2-}$, 23314-45-6; $Co^{II}[ED3A]^{-}$, 60645-76-3; $Co^{II}[1,3\text{-}PDTA]^{2-}$, 16904-03-3; $Co^{II}[EDDA]$, 29977-10-4; $Co^{II}[EDTA(CN)]^{3-}$, 60645-77-4; $Co^{II}[EDTA(OH)]^{3-}$, 15091-47-1; $Co^{II}[CyDTA]^{2-}$, 28161-91-3.

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