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Proton Magnetic Resonance Studies of Pentadentate Cobalt(III) Aminocarboxylates. Structures and Reactions of Nitro- and Aquo-Substituted Complexes

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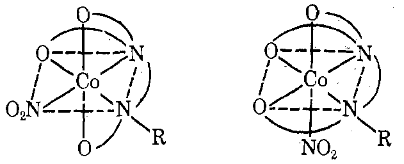
A series of six-coordinate cobalt(III) complexes having the general formula Co(Y)X, where X is NO_2^- or H_2O, have been prepared and studied by 100-MHz pmr spectroscopy. The pentadentate aminocarboxylate ligands, Y, include ethylenediaminetetraacetic acid (EDTA), ethylenediaminetriacetic acid (ED3A), *N*-methylethylenediaminetriacetic acid (MEDTA), *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA), and a new ligand 1,2-diamino-2-methylpropanetriacetic acid (DMP3A). All evidence points to the existance of only one geometrical isomer, where the monodentate ligand, X, occupies an in-plane or equatorial site, contrary to recent literature favoring out-of-plane or polar substitution. Synthetic routes are summarized for interconversion of the nitro, aquo, chloro, and bromo complexes of a given sample of any pentadentate cobalt(III) aminocarboxylate.

Introduction

Whenever hexadentate ethylenediaminetetraacetate (EDTA) complexes of six-coordinate transition metal ions undergo substitution by monodentate ligands, a question arises as to the position occupied by the substituent ligand. If the substituent displaces a glycinate arm lying in the plane formed by the metal and two nitrogen atoms, the *equatorial* isomer is formed, whereas if the substituent displaces a glycinate arm not lying in this plane, the *polar* isomer is formed. It is known[1] that the in-plane glycinate arms in the Co(EDTA)$^-$ complex are more strained than the out-of-plane glycinate arms; thus monodentate ligand substitution might be expected to favor the equatorial isomer. However, the numerous studies[2-19] carried out on pentadentate aminocarboxylate complexes have produced conflicting reports on this point.



equatorial polar

$\widehat{N\ N} = NCH_2CH_2N$
$\widehat{N\ O} = NCH_2CO_2^-$
$R = CH_2CO_2^-$

Most recently[17,19] the *polar* isomer has been proposed as the structure of nitro-substituted pentadentate aminocarboxylate complexes of cobalt(III), based on pmr studies. In the present work, we show that pmr evidence actually favors the *equatorial* isomer for eleven different complexes involving six different pentadentate aminocarboxylate ligands. The spectral assignments are supported by "tickling" experiments, stereospecific acid- and base-catalyzed deuterations, magnitudes of glycinate geminal coupling constants, magnitudes of H–N–C–H coupling constants, and chemical shift correlations.

A new easily prepared diaminetriacetate ligand 1,2-diamino-2-methylpropanetriacetic acid (DMP3A) is reported. Synthetic routes are presented which utilize the aquo complex as a synthetic intermediate in the interconversions of nitro-, chloro-, and bromo-substituted pentadentate cobalt(III) aminocarboxylates.

Experimental Section

Chemicals.—Commercial chemicals of the highest available purities were used without further treatment. EDTA was obtained from J. T. Baker Chemical Co. and HEDTA was obtained from Geigy Chemical Co. D_2SO_4 (99.5% minimum isotopic purity, 98% in D_2O) and D_2O (99.8% minimum isotopic purity) were obtained from Diaprep, Inc.

Preparation of Ligands ED3A, MEDTA, and DMP3A.—Ethylenediaminetriacetic acid (ED3A) was prepared by Blackmer's method,[18] and *N*-methylethylenediaminetriacetic acid (MEDTA), by the method of Van Saun and Douglas.[16]

1,2-Diamino-2-methylpropanetriacetic acid (DMP3A) was prepared in a manner similar to the preparation of ED3A and MEDTA. To 0.3 mol (28.2 g) of monochloroacetic acid, dissolved in 25 ml of cold water, maintained at 10° in an ice bath, was added a cold solution of sodium hydroxide (0.3 mol, 12.0 g) in water (33 ml). The NaOH solution was added dropwise with constant stirring to keep the temperature of the reacting solution below 15°. One-tenth mole (9.9 ml, 8.8 g) of 1,2-diamino-2-methylpropane was added, followed by an additional quantity of sodium hydroxide solution (0.3 mol, 12.0 g). The resulting solution was allowed to stand at room temperature for 6 days, acidified to pH 6 with concentrated hydrochloric acid, and diluted to 250 ml. No attempt was made to isolate the free acid DMP3A. Instead, it was separated from other possible reaction products in complexed form with cobalt(III).

Preparation of Complexes.—The cobalt(III) complexes of the series Co(ED3A)X$^-$,[18] Co(MEDTA)X$^-$,[16] Co(HEDTA)X$^-$,[4] and Co(EDTA)X^{2-},[2] where X$^-$ = NO_2^-, Cl$^-$, or Br$^-$, were prepared by the literature methods and were found to be analytically pure.

Potassium nitro(1,2-diamino-2-methylpropanetriacetato)cobal-

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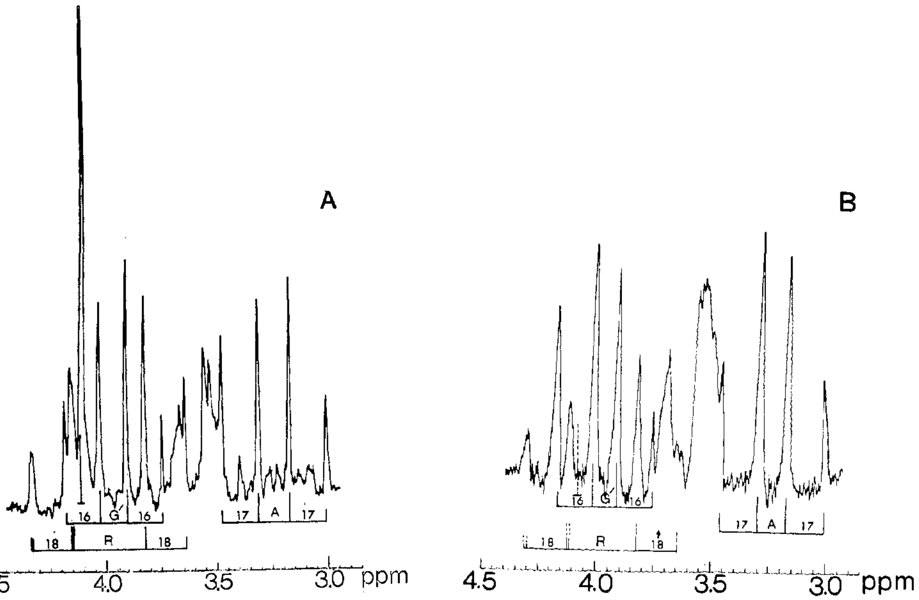

Figure 1.—(A) Observed 100-MHz pmr spectrum of Co(EDTA)NO_2^{2-} in neutral D_2O solution. (B) Observed 100-MHz pmr spectrum of Co(EDTA)NO_2^{2-} in basic D_2O solution, pD 10.5.

tate(III) hydrate was prepared in a manner similar to that employed by Dwyer and Garvan[7] in their preparation of the nitro complex of cobalt(III) with EDTA functioning as a pentadentate ligand. A 75-ml aliquot (3.0×10^{-2} mol) of the previously prepared DMP3A solution was added to solid sodium cobaltinitrite (12.1 g, 3.0×10^{-2} mol) and the mixture was warmed with vigorous stirring, to 50°. After 0.5 hr the temperature was increased to 85° and stirring was continued for 10 min. The deep red solution was then cooled, diluted to 4 l., and allowed to pass through 700 ml of a Dowex 1-X8 anion-exchange resin column (100–200 mesh, Cl^- form) at a drop rate of ~10 drops/min. The brick red band retained by the resin was eluted with 2.5×10^{-2} *M* KCl at a 10-drop/min rate. The red band separated on elution into two distant bands, an intense brick red lower band and an orange upper band. The two bands were collected separately, reduced in volume on a rotary evaporator at room temperature, and treated with absolute methanol. Crystallization occurred for the brick red product upon refrigeration.

The orange band, presumably a dinitrodiacetic acid complex, was collected, but no crystalline product was isolated. The brick red compound was recrystallized from aqueous methanol, washed with ethanol and then acetone, and dried under vacuum at room temperature. The first eluted band, the DMP3A–NO_2 complex, gave brick red crystals. Total yield based on sodium cobaltinitrite was ~40%. *Anal.* Calcd for K[Co(DMP3A)NO_2]·H_2O: C, 28.58; H, 3.84; N, 10.00. Found: C, 28.56; H, 3.76; N, 10.05.

Interconversion of Complexes.—The nitro and bromo cobalt(III) complexes of the pentadentate ligands were converted to their corresponding chloro complexes by (a) dissolving the complex in a small amount of water, adding concentrated hydrochloric acid, and evaporating the solution to dryness on a steam bath,[5] (b) adding silver acetate to a solution of the bromo complex, removing the precipitated silver bromide, and evaporating to dryness with the addition of concentrated hydrochloric acid,[16] and (c) electrolytic reduction[20] of the cobalt(III) complexes, in aqueous solution, to the cobalt(II) form followed by reoxidation of the cobalt(II) species to cobalt(III) with chlorine gas.[3]

The nitro and chloro complexes were converted to the bromo complex by reducing the complexes electrolytically[20] and reoxidizing to cobalt(III) with bromine.[3]

The chloro and bromo species were easily converted to the aquo species in aqueous solution by the addition of mercury(II) nitrate[7] or silver acetate.[16] The chloro, bromo, and nitro complexes were also converted to the aqueous complexes by dissolving the complexes in water and lowering the pH to 0.5–1.0 with HCl. The solution was then heated to 90° for ~10 min to complete the conversion to the aquo species. Pmr spectra of each of the three types of complexes, treated in this manner and dissolved in D_2O, were identical with those of the corresponding aquo complexes (*e.g.*, Figures 2C and 3B).

The aquo complexes can be reconverted to the nitro, chloro, or bromo species, respectively, by (a) treating with $NaNO_2$,[18] (b) addition of HCl and evaporation to dryness,[18] and (c) electrolytic reduction of the aquo complex to the cobalt(II) species and subsequent reoxidation to cobalt(III) with bromine.[4]

All of the complexes prepared through the interconversion techniques were isolated by the ion-exchange procedures outlined earlier.[18]

Acid- and Base-Catalyzed Deuterations.—Acid-catalyzed deuterations were carried out at a pD value of 0.9 obtained by the addition of D_2SO_4. Base-catalyzed deuterations were carried out at a pD of 10.5 obtained by the addition of Na_2CO_3.

Proton Magnetic Resonance Spectra.—All spectra were recorded at 100 MHz using a Varian HA-100 nmr spectrometer having an ambient probe temperature of 36 ± 1°. Acid-catalyzed deuterations, however, were carried out in sealed tubes at 90°. Base-catalyzed deuterations were maintained at ~22° except for the period of time required to obtain pmr spectra.

Results

Figure 1A shows the 100-MHz pmr spectrum of Co(EDTA)NO_2^{2-}, I (B = H, A, = $CH_2CO_2^-$), in D_2O solution. The three designated AB patterns and the large singlet are assigned to the eight glycinate protons, and the remaining lines are assigned to the four ethylenic protons.

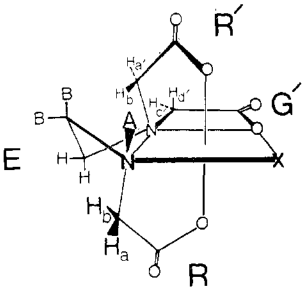

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TABLE I

CHEMICAL SHIFTS FOR GLYCINATE PROTONS OF COBALT(III) AMINOCARBOXYLATES

	J = −18.0 Hz, R rings (out-of-plane)				J = −16.0 Hz, G rings, (in-pane)		
	R		R′		G′		
	H_a	H_b	$H_a{}'$	$H_b{}'$	$H_c{}'$	$H_d{}'$	Other resonances
$Co(EDTA)NO_2{}^{2-}$	4.22	3.75	4.11[f]		4.08	3.86	3.36 3.13[d]
	3.98[f]				3.97[f]		3.24[f]
$Co(ED3A)NO_2{}^-$	4.15	3.10[a]	4.05[f]		4.08	3.87	
	3.62[f]				3.97[f]		
$Co(MEDTA)NO_2{}^-$	4.18	3.38	4.09[f]		4.04	3.85	2.24[e]
	3.78[f]				3.94[f]		
$Co(DMP3A)NO_2{}^-$	3.63	3.27	4.02	4.31	4.14	3.89	1.43[e]
	3.45[f]		4.16[f]		4.01[f]		1.37[e]
$Co(HEDTA)NO_2{}^-$	4.33	3.44	4.12[f]		4.07	3.85	
	3.88[f]				3.96[f]		
$Co(DPTA)NO_2$[b]	4.27	3.42	4.15[f]		4.11	3.90	
	3.84[f]				4.00[f]		
$Co(EDTA)^-$[c]			3.81	3.94	3.89	3.57	
			3.88[f]		3.73[f]		
$Co(ED3A)H_2O$	4.07	3.26	3.92[f]		3.91	3.51	
	3.66[f]				3.71[f]		
$Co(MEDTA)H_2O$	3.98	3.49	3.97[f]		3.93	3.51	2.40[e]
	3.73[f]				3.72[f]		
$Co(DMP3A)H_2O$	3.73	3.32	3.91	4.07	3.95	3.54	1.47[e]
	3.52[f]		3.99[f]		3.74[f]		1.41[e]
$Co(HEDTA)H_2O$	4.09	3.53	3.95[f]		3.94	3.49	
	3.81[f]				3.71[f]		

[a] Corrected value.[18] [b] Reference 17. [c] Reference 20. [d] Free acetate AB pattern. [e] Methyl resonances. [f] Average chemical shifts.

The grouping of lines as AB patterns was proved by "tickling"[20] (*vide infra*), and the results are in close agreement with the identification of AB patterns in the 60-MHz spectrum of this compound reported previously.[19] Based on chemical shifts and coupling constants, the AB pattern at highest field is assigned to the free or "dangling" glycinate arm (A), in agreement with previous authors.[19] We also agree with the previous assignments regarding the singlet and the closely spaced AB pattern centered at 3.97 ppm (J = −16 Hz) being due to out-of-plane (R′) and in-plane (G′) glycinate protons, respectively (see Table I).

However, the widely spaced AB pattern centered at 3.98 ppm (J = −18 Hz) was previously assigned to an in-plane glycinate arm because it was not observed to undergo loss of intensity due to base-catalyzed deuteration, unlike the singlet which readily lost intensity in basic solution. The assignment of this AB pattern is the key to the question of polar *vs.* equatorial isomer. We disagree with the previous authors' results[19] and have shown that at least partial diminution of the low-field member of the widely spaced AB pattern (and redistribution of the high-field member into a new peak at 3.75 ppm, though partly obscured by backbone resonances) can be effected under correctly chosen conditions for base catalysis (Figure 1B). It is common for different out-of-plane glycinate protons to undergo different deuteration rates.[14,20] The tendency of $Co(EDTA)NO_2{}^{2-}$ to undergo decomposition in strong base at room temperature, yielding broad pmr lines, was offset by using a moderate pD (10.5), keeping the temperature low (22°), and waiting for approximately 30 hr.

Acid-catalyzed deuteration of any nitrocobalt(III) aminocarboxylate, as we shall show, is preceded by displacement of the nitro group by water. In the case of $Co(EDTA)NO_2{}^{2-}$, the water molecule is displaced rapidly by the free glycinate arm, and $Co(EDTA)^-$ is formed. However, the identities of the various proton resonances remain clear during aquation, and the results for acid-catalyzed deuteration of the aquo complexes help to support our claim of exclusively *equatorial* isomers for both nitro and aquo complexes.

In addition to the deuteration results, the magnitudes of the glycinate geminal proton spin-coupling constants are a useful diagnostic.[20] For in-plane, out-of-plane, and free glycinate protons in cobalt(III) aminocarboxylate complexes, we expect geminal coupling constants of approximately −16.0, −18.0, and −16.7 Hz, respectively (all ± 0.5 Hz). There are no known exceptions to this rule. Thus the magnitude of the geminal coupling constants also suggests the existence of the *equatorial* isomer of $Co(EDTA)NO_2{}^{2-}$.

It is interesting to note that in $Co(EDTA)NO_2{}^{2-}$ and in several other nitro-substituted pentadentate cobalt(III) aminocarboxylate compounds, an observable long-range spin coupling exists between H_a in the R glycinate ring and any N–C–H protons on substituent A (I). This long-range coupling, which is comparable in magnitude to the line width (∼0.5 Hz), appears as a broadening of the H_a resonance. When the ligand has no N–C–H proton on substituent A (*e.g.*, N-deuterated ED3A), the broadening disappears, proving that H_a is coupled to protons on substituent A rather than to ethylenediamine backbone protons. Upon aquation, this coupling seems to disappear—a fact which can be explained by the overall increase in all line widths.

ED3A is a structural modification of EDTA in which one of the glycinate arms has been replaced by a proton. Figure 2A shows the 100-MHz pmr spectrum of $Co(ED3A)NO_2{}^-$ in neutral D_2O solution. It is analogous to the EDTA complex, $Co(EDTA)NO_2{}^{2-}$, consisting of three coordinated acetate AB patterns (one being highly collapsed) arising from the three chelated glycinate rings (see Table I). There also exists a complex ABCD pattern from the backbone ethylenic protons. This highly complex pattern frequently causes uncertainty in spectral assignments of AB patterns and

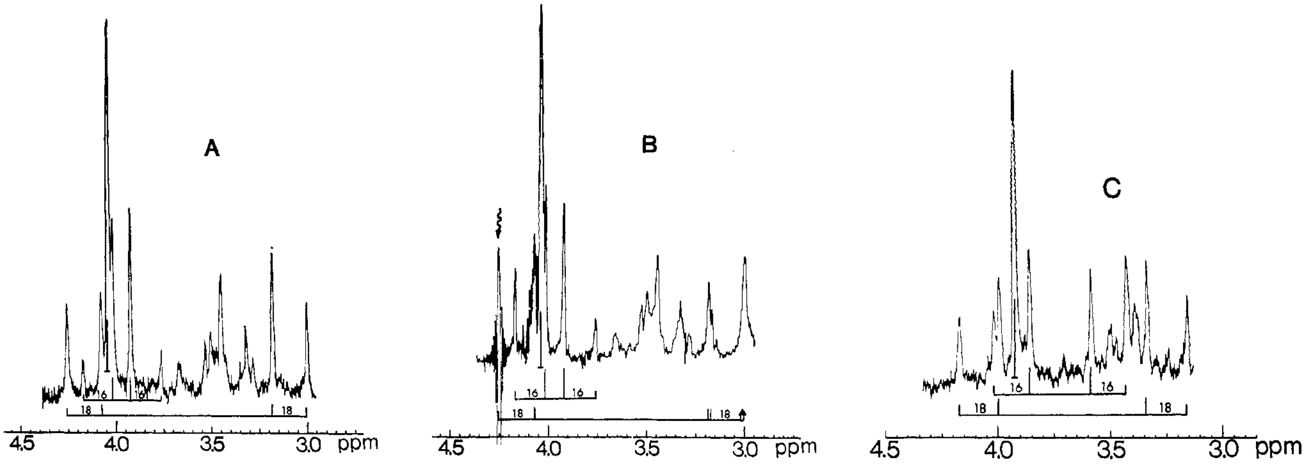

Figure 2.—(A) Observed 100-MHz pmr spectrum of the acetate portion of $Co(ED3A)NO_2^-$ in neutral D_2O solution. (B) "Tickled" pmr spectrum of $Co(ED3A)NO_2^-$ in neutral D_2O solution. (C) Observed 100-MHz pmr spectrum of $Co(ED3A)OH_2$ in acidic D_2O solution.

makes integral area measurements extremely difficult. Special techniques which aid in the unraveling of complex spectra of this type have been outlined earlier.[20] Figure 2B illustrates the use of one such technique ("tickling") to assign individual resonances belonging to a particular AB pattern. By applying an irradiating field to a particular transition frequency occurring on the low-field side of an AB pattern (indicated by the wavy line, Figure 2B) splitting of the corresponding high-field portion of that AB pattern occurs. One of the lines of the high-field pair is split into a sharp doublet with a corresponding loss of intensity. The remaining line is split into a broad doublet accompanied by an increase in total intensity. These changes in intensity are attributed to the general nuclear Overhauser effect.[21] The beat pattern located at the applied frequency is caused by interference of the irradiating and observing magnetic fields. Systematic "tickling" of each peak of the pmr spectrum resulted in direct proof of the correctness of the spectral assignments indicated in Figure 2A (see I, A = H, B = H). The "tickling" technique was applied to all of the compounds studied in this investigation to establish the data listed in Table I.

Base-catalyzed deuteration studies of $Co(ED3A)NO_2^-$ resulted in the deuteration of two glycinate rings as was observed for $Co(EDTA)NO_2^{2-}$. The first peak to deuterate was the out-of-plane acetate singlet (collapsed AB patterns corresponding to R′ in I) occurring at 4.05 ppm. At much longer deuteration times the second out-of-plane (R ring) AB pattern ($J = -18$ Hz) began to diminish in intensity, accompanied by the emergence of a new peak at 3.10 ppm, the calculated chemical shift of the high-field portion of the AB pattern. The in-plane pattern, G′, $J = -16$ Hz, remained unaffected, as was the case with $Co(EDTA)NO_2^{2-}$.

Also, in accordance with $Co(EDTA)NO_2^{2-}$, the base-catalyzed deuteration of $Co(ED3A)NO_2^-$ was difficult to control and the spectrum contained some broadening. For these reasons the nitro complex, $Co(ED3A)NO_2^-$, was converted to the "aquo" species, $Co(ED3A)OH_2$ (see Experimental Section), and acid-catalyzed deuteration studies were conducted. Although more time consuming, acid catalysis is more easily controlled, imparts less line broadening of spectral lines, and minimizes decomposition. Figure 2C shows the pmr spectrum obtained for the aquo complex in acid solution with its spectral assignments as confirmed by "tickling." The aquo complex exhibits the same general features as either the ED3A- or the EDTA-NO_2 complexes—containing one highly collapsed AB singlet and two AB patterns with coupling constants of −16 Hz (in-plane) and −18 Hz (out-of-plane), respectively. It is unlikely that ligand rearrangement takes place in the conversion from the nitro complex to the aquo species since (1) the nitro complex can be regenerated from the aquo complex to give a spectrum identical with Figure 1A, (2) the coupling constants of the in-plane ($J = -16$ Hz) and out-of-plane ($J = -18$ Hz) AB patterns correlate perfectly for the two species (nitro and aquo), and (3) the widely spaced AB pattern ($J = -18$ Hz) undergoes acid-catalyzed deuteration, following the disappearance of the acetate singlet, in a similar fashion to the base-catalyzed deuteration of the nitro complex. Upon acid-catalyzed deuteration of the aquo complex of $Co^{III}ED3A$, the widely spaced AB pattern ($J = -18$ Hz) diminishes in intensity with the appearance of a new peak at 3.26 ppm (the calculated chemical shift of the high-field portion of the out-of-plane pattern).

There are, however, shifts in the location of the acetate resonances as a result of exchanging a water molecule for the NO_2^- group in the Co(III) coordination sphere. To determine the exact nature of these shifts another pentadentate Co(III) complex was studied, namely, $Co(MEDTA)NO_2^-$.

This compound was chosen first because of its similarity to the EDTA and ED3A complexes and second because of the presence of the methyl group attached to one of the nitrogen atoms of the ligand. This methyl group provides a pmr resonance which offers a convenient means of monitoring the aquation reaction (conversion from the nitro species to aquo complex). The change in location of this resonance also gives an indication of the magnitude of chemical shifts that can be expected for ligand-bound protons as a result of the electron withdrawal and anisotropic effects of the NO_2^- substituent when chelated to the Co(III) ion.

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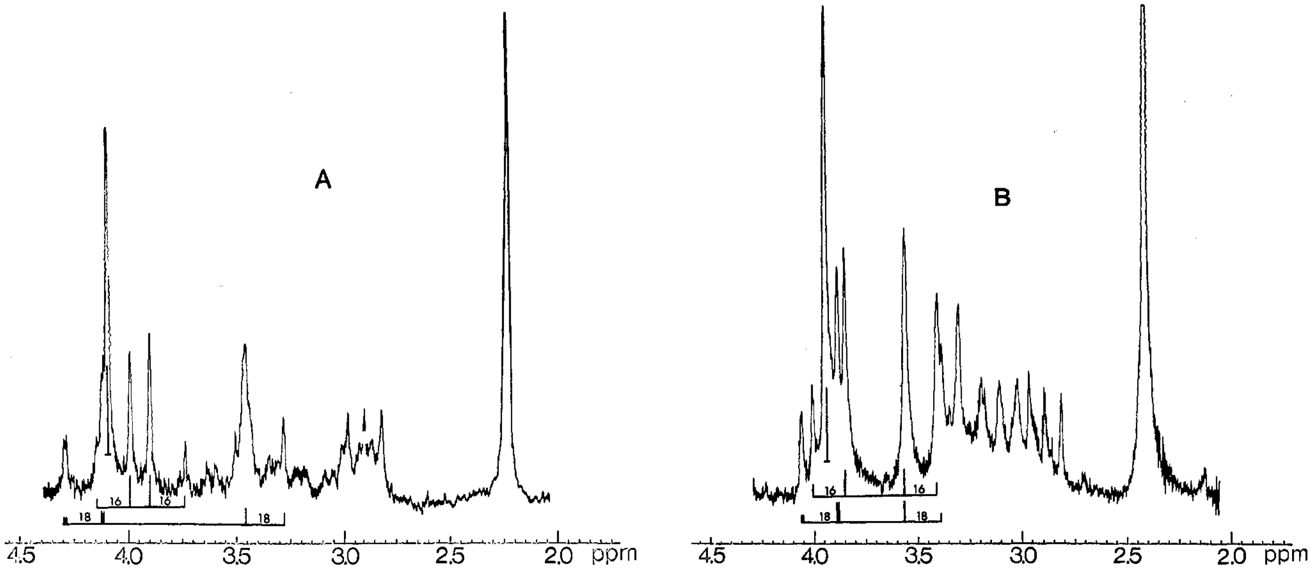

Figure 3.—(A) Observed 100-MHz pmr spectrum of Co(MEDTA)NO_2^- in neutral D_2O solution. (B) Observed 100-MHz pmr spectrum of Co(MEDTA)OH_2 in D_2O solution, pD 0.9.

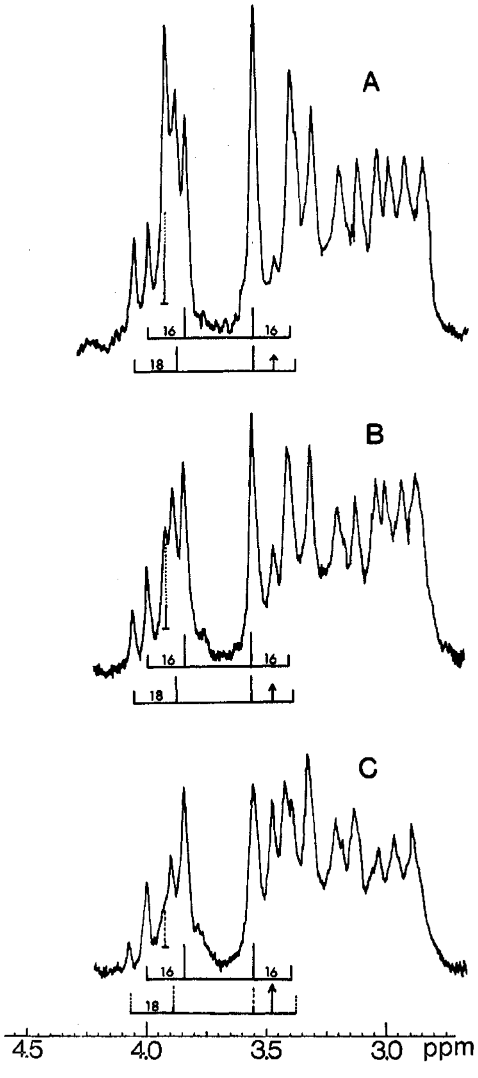

Figure 4.—(A) Pmr spectrum of Co(MEDTA)OH_2 after acid-catalyzed deuteration (pD 0.9) for 2 hr at 90°. (B) Pmr spectrum of Co(MEDTA)OH_2 after acid-catalyzed deuteration (pD 0.9) for 7 hr at 90°. (C) Pmr spectrum of Co(MEDTA)OH_2 after acid-catalyzed deuteration (pD 0.9) for 10.5 hr at 90°.

Figure 3A shows the pmr spectrum of Co(MEDTA)NO_2^- with "tickling" confirmed assignments. In I, A is now CH_3 and B = H. The single methyl resonance occurring at 2.24 ppm indicates the presence of only one geometrical isomer. The acetate portion of the spectrum is nearly identical with that of the nitro complexes of EDTA and ED3A (Figures 1 and 2A). The triplet-like resonances occurring between 2.8 and 3.0 ppm are due to, and characteristic of, the presence of DSS. Long-range coupling ($J \lesssim 1$ Hz) to the low-field portion of the widely spaced out-of-plane AB pattern is again readily evident. This phenomenon is observed in all of the pentadentate complexes which have an uncoordinated alkyl substituent (MEDTA, HEDTA, EDTA). Conversion of the MEDTA nitro complex to the aquo species, Co(MEDTA)OH_2, results in the pmr spectrum indicated in Figure 3B. Upon aquation, the methyl resonance is noticeably shifted downfield and now appears at 2.40 ppm. In a fashion perfectly analogous to the ED3A–H_2O species, the acetate portion of the MEDTA–H_2O complex undergoes chemical shift changes while the coupling constants ($J = -18$ Hz for out-of-plane and $J = -16$ Hz for in-plane glycinate rings) remain unchanged (Table I). Acid-catalyzed deuterium-exchange studies of this complex, shown in Figures 4A, B, and C, directly support the out-of-plane glycinate ring assignment of the base-catalyzed exchange studies discussed earlier. Figure 4A represents the pmr spectrum of Co(MEDTA)OH_2 after acid-catalyzed deuteration (90°, pD 0.9) for 2 hr. The acetate singlet, R′ in I, has decreased in intensity by approximately 50%. The more widely spaced out-of-plane AB pattern, R ($J = -18$ Hz), has only just begun to decrease in intensity with a hint of a new peak growing in on the high-field portion at 3.49 ppm (indicated by the vertical arrow). Spectrum 4B was obtained after an additional 5 hr of heating at 90°. Deuteration of the acetate singlet, R′, is now nearly complete and a significant amount of the second out-of-plane acetate ring, R, has undergone deuterium exchange as evidenced by the increased intensity of the peak emerging at 3.49 ppm.

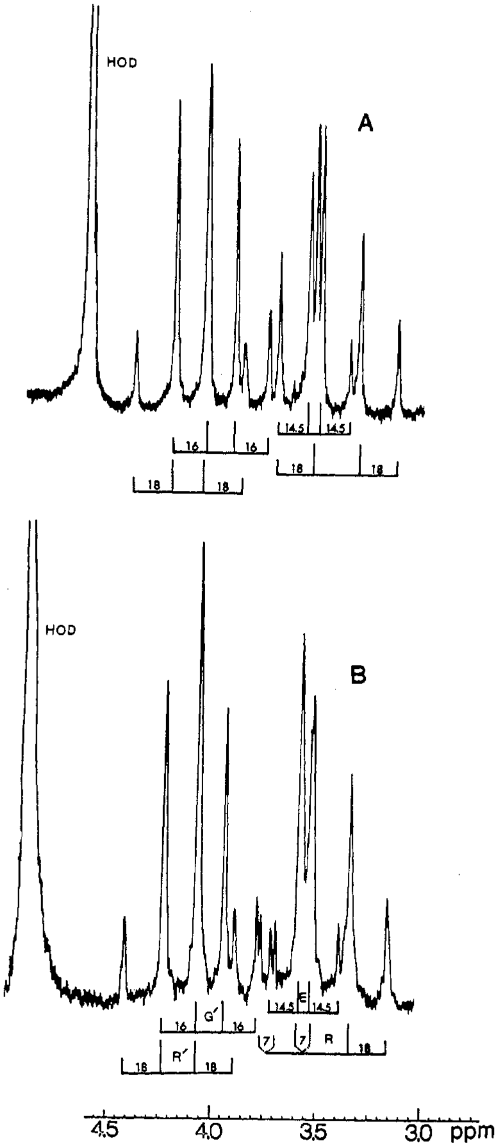

Figure 5.—(A) Observed 100-MHz pmr spectrum of the acetate portion of $Co(DMP3A)NO_2^-$ in neutral D_2O solution. (B) Observed 100-MHz pmr spectrum of the acetate portion of $Co(DMP3A)NO_2^-$ in acidic D_2O solution.

After 10.5 hr of acid-catalyzed deuteration at 90° spectrum 4C was obtained. The acetate singlet has now completely disappeared and only a small amount of the remaining out-of-plane AB pattern persists. The new peak at 3.49 ppm is now quite intense, but it, too, upon longer deuteration times, gradually diminishes to zero intensity. The remaining AB pattern ($J = -16$ Hz) is unchanged, apart from slight line broadening, and confirms its in-plane assignment.

The pmr spectrum of the nitro complex of Co(III) containing the newly synthesized DMP3A ligand might be expected to contain unique acetate chemical shifts as a result of steric compressions caused by the bulky methyl substituents attached to one of the carbon atoms of the ethylenediamine backbone (labeled B in I, A = H). Steric effects of this type are also found in the pmr spectrum of Co^{III}PDTA.[20] The presence of a similarily placed methyl group in PDTA causes splitting of otherwise highly collapsed AB patterns (as in $Co^{III}EDTA^-$) as well as gross changes in deuteration rates of the individual out-of-plane glycinate protons. Additional strains in the DMP3A complex and, subsequently, distortions in the pmr spectrum may arise from the inability of either of the backbone methyl groups completely to acquire the energetically preferred equatorial position.

Such is indeed the case with $Co(DMP3A)NO_2^-$ as indicated in Figure 5A. The two AB patterns having geminal coupling constants of -18 Hz are each assigned to an out-of-plane glycinate ring. These two patterns exhibit steric crowding effects of the methyl groups to a much greater degree than does the AB pattern with $J = -16$ Hz assigned to the remaining in-plane (G′) acetate group. The R′ ring is most noticeably affected, being split into a widely spaced AB pattern (see Table I). The AB pattern labeled E with $J = -14.5$ Hz and average chemical shift 3.56 ppm is attributed to the two geminal ethylenic protons of the ethylenediamine backbone. The two methyl resonances (not shown in Figure 5) occur at 1.43 and 1.37 ppm. They are of equal intensity and are separated by 6 Hz. Figure 5B shows the pmr spectrum of the nitro complex of Co^{III}DMP3A dissolved in cold acidic solution immediately after mixing. The positions and relative intensities of the two methyl peaks are unchanged from those of the pmr spectrum in neutral solution indicating that no appreciable decomposition of the nitro complex had occurred. All other resonances remain unchanged with the exception of the low-field portion of one of the out-of-plane ($J = -18$ Hz) acetate AB patterns, which is noticeably split (7 Hz). No noticeable splitting for the high-field portion of this pattern occurred (indicating a coupling constant of less than 1 Hz). The splitting of the low-field portion of the AB pattern is explained in terms of vicinal coupling between the amine proton of the ligand (A in I) and the acetate proton (H_a) of the R glycinate ring. In acid solution deuterium exchange of the N–H proton is slow and spin–spin coupling to the glycinate protons of the chelated R ring can occur. The existence of the N–H proton is confirmed by a broad resonance line occurring at 5.9 ppm (not shown in Figure 5).

Molecular models predict the splitting pattern observed when a dihedral angle measurement is made ($HNCH_a \approx 35°$ and $HNCH_b \approx 90°$) and the Karplus[22] equations are applied for the acetate ring chelated to the out-of-plane position. Models which have the glycinate group coordinated to the in-plane position predict large H–N–C–H splittings for both portions of the AB pattern ($HNCH_a \approx 15°$ and $HNCH_b \approx 125°$). Since no coupling to the high-field portion of the AB pattern was observed and since the low-field portion of the pattern was split by the same degree as was reported earlier for similar compounds,[18,23,24] the AB pattern in question can be definitely ascribed to an out-of-plane glycinate ring. This is substantiated by its geminal coupling constant of -18 Hz. This particular AB pattern may also, therefore, be assigned to the R ring (I) since it must be bound to the same nitrogen as the amine proton so that the aforementioned H–N–C–H splitting can occur. Further, since the AB pattern arising from the E ring (I) is not complicated by similar

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[22] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[23] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

[24] J. L. Sudmeier and G. Occupati, *ibid.*, **7**, 2524 (1968).

amine proton coupling, the ethylenic protons must be well removed from the N–H proton. The methyl groups must necessarily than be attached to the carbon atom neighboring the amine nitrogen. Thus the ligand coordination sites and the total geometrical configuration of the Co(DMP3A)NO_2^- complex are completely established.

The techniques of assigning ligand-bonding positions described above, for the complexes of EDTA, ED3A, MEDTA, and DMP3A, were also applied to the cobalt(III) complexes of the remaining pentadentate ligand of the series, HEDTA. The results of these experiments correlated perfectly with those of the previously discussed compounds. The data for the cobalt(III) complex compounds of this ligand are tabulated together with the data for all of the compounds of the corresponding pentadentate ligands in Table I.

Discussion

An inspection of Table I clearly indicates the similarities inherent in the pmr spectra of the nitro complexes of the pentadentate ligands studied as well as the corresponding aquo complexes. Perhaps the most obvious distinction that can be made with regard to the glycinate AB splitting patterns, irrespective of complex (nitro or aquo), is that of the geminal coupling constants. For all of the complexes studied no variance from the rules[20] regarding geminal coupling constants ($J = -18$ Hz for out-of plane, R, chelated glycinate ring protons and $J = -16$ Hz for in-plane, G, chelated glycinate ring protons) was observed.

Classification of the in-plane (G ring) and out-of-plane (R ring) protons by their geminal coupling constants (-16 and -18 Hz, respectively) constitutes the same classification that is obtained solely on the basis of the AB patterns that undergo deuteration. The two out-of-plane (R) rings can be further divided into two groups, R and R′, based on (1) ease of deuteration (R′ undergoing deuterium exchange more readily than R), (2) the magnitude of separation of H_a and H_b chemical shifts, and (3) residual factors such as N–H coupling, long-range coupling to alkyl substituents, and positioning of average chemical shifts (designated in Table I).

Striking similarities in chemical shifts are immediately obvious when classifications of the aforementioned type are made. The pronounced consistency arising from the chemical shifts of the individual chelate rings throughout the series of nitro and/or aquo complexes under investigation lends additional credence to the formalism of classification employed here. The proton H_c' assigned to the in-plane (G′) glycinate ring, I, varies in chemical shift only to the extent of 0.10 ppm for the nitro complexes and 0.06 ppm for the aquo species. The proton chemical shift for H_d' of the G′ ring varies only 0.05 ppm for the nitro complexes and 0.08 ppm for the corresponding aquo species. The average chemical shifts of the nitro and aquo complexes vary by 0.07 and 0.03 ppm, respectively. The average chemical shifts of the out-of-plane (R′) ring demonstrate a similar consistency varying by 0.11 ppm for both the nitro and aquo complexes of the pentadentate ligands.

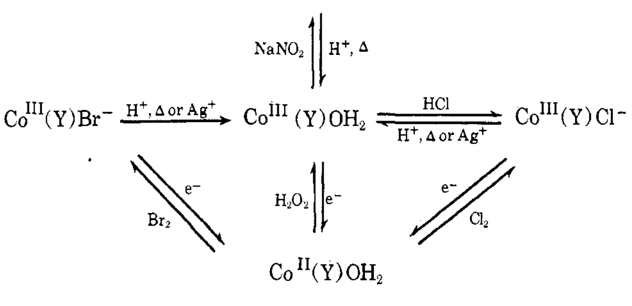
The chemical shifts for protons H_a and H_b of the remaining out-of-plane ring, R, are subject to considerable variance since they are more directly influenced by steric effects of alkyl substituents and their C–N bond anisotropies as well as electronegativity effects of the monodentate ligand. The average chemical shifts of these AB patterns are still moderately consistent, however, occurring at 3.71 ± 0.27 ppm for the nitro species and 3.66 ± 0.14 ppm for the aquo complex.

It is of additional interest to note that the nitro and aquo complexes of corresponding ligands vary in average chemical shift by proportionate amounts. The difference in average chemical shift of the R rings of corresponding ligands in going from the nitro to the aquo species equals 0.07 ± 0.03 ppm. The corresponding changes for the R′ and G′ rings are 0.17 ± 0.05 and 0.24 ± 0.03 ppm, respectively. Thus, the average chemical shift change of an AB pattern for a given pentadentate cobalt(III) complex in going from the nitro form to the aquo species is perfectly predictable and precise to 0.05 ppm. This change in chemical shift is a direct consequence of the loss of NO_2^- from the coordination sphere of the metal ion in exchange for a water molecule. This is shown more clearly in the spectra of the compounds whose pentadentate ligands possess methyl groups (*i.e.*, MEDTA and DMP3A). For the MEDTA complex ($A = CH_3$ and $B = H$ in I) the methyl group is in quite close proximity to the highly electronegative NO_2^- group and its resonance, appearing at 2.24 ppm, is shifted downfield by 0.16 ppm upon aquation of the complex. In the DMP3A complex ($A = H$ and $B = CH_3$ in I) the methyl groups are farther removed from the NO_2^- group so they resonate at higher field strengths (1.43 and 1.37 ppm) and undergo a smaller shift (0.06 ppm) on aquation of the complex.

All of the trends discussed in this work are consistent with the formation of only one geometrical isomer of the cobalt(III) complexes discussed, namely, the *equatorial* isomer with NO_2^- or H_2O in the *in-plane* position of the cobalt(III) coordination sphere.

A similar complex, Co(DTPA)NO_2^-, where DTPA = diethylenetriaminepentaacetic acid which also functions as a pentadentate ligand, was previously postulated[17] to be of the *polar* isomeric form. A reinterpretation of these data is included in Table I and is consistent with our classification techniques for *equatorial* models in every respect, including the geminal coupling constants. We feel that the slower rate of base-catalyzed deuterium exchange in these nitro complexes is not sufficient evidence to discount the formation of an *equatorial* isomer of this complex. In fact, the nitro complex of cobalt(III) DTPA so completely cor-

SCHEME I



responds to all of the trends characteristic of similar equatorial complexes (listed in Table I) that we submit Co(DTPA)NO$_2^-$ is indeed an *equatorial* isomer.

Aquo Complex Intermediates.—In this work, the aquo complexes of the pentadentate aminocarboxylate ligands have been identified by pmr. The importance of these aquo species as synthetic intermediates has not been adequately stressed in previous literature. A number of these interconversion reactions are shown in Scheme I. The details describing these interconversions are outlined in the Experimental Section.

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Polarography of the Planar Dithioacetylacetone Complexes of Cobalt(II), Nickel(II), Palladium(II), and Platinum(II) and Other Related Complexes of the Same Ligand in Acetone[1]

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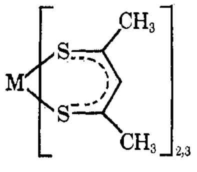
The dc polarographic behavior of the planar dithioacetylacetonates M(SacSac)$_2$ with M(II) = Co, Ni, Pd, and Pt, the octahedral complexes M(SacSac)$_3$ with M(III) = Co and Ir, and the ruthenium nitrosyl complex Ru(NO)(SacSac)$_2$Cl, using acetone as solvent and tetraethylammonium perchlorate as the supporting electrolyte, is described. It has been established that, in general, the transition metal dithioacetylacetonates have a well-defined capacity to accept one or more electrons in a reversible stepwise manner, the number varying systematically with the d-electron configuration and stereochemistry of the central metal ion. The magnitude of the reduction potentials and their reversible nature suggest that the isolation of metal dithioacetylacetonates in unusually low formal oxidation states should be possible.

Introduction

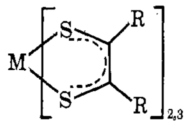
In a recent paper we described the polarographic behavior of the Fe(III), Ru(III), and Os(III) low-spin octahedral d_ϵ^5 complexes of dithioacetylacetone in acetone.[2] The polarography of these systems was well-defined. Each of these complexes was found to undergo a ready reversible one-electron reduction which can be regarded as effectively completing the occupancy of the d_ϵ subshell. In contrast, the low-spin d_ϵ^6 complex Rh(SacSac)$_3$ (where SacSac$^-$ is the dithioacetylacetone ligand S$_2$C$_5$H$_7^-$), in which the stabilized metal subshell is fully occupied, could only be reduced irreversibly at much more negative potentials.

The polarographic behavior of these M(SacSac)$_3$ complexes (I) is completely consistent with their known chemical and spectroscopic properties and provides useful information on the chemistry of dithioacetylacetone complexes. The results of this work suggested that further polarographic studies on other dithioacetylacetone complexes should be fruitful.



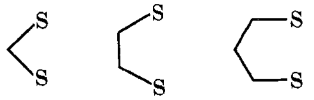
I

The recent discovery[3] of ready stepwise reductions of the neutral metal "dithienes" M(S$_2$C$_2$R$_2$)$_x$ (II) and the isolation of series of "dithiolene" complexes, [M(S$_2$C$_2$R$_2$)$_3$]$^{0,1-,2-,3-}$ and [M(S$_2$C$_2$R$_2$)$_2$]$^{0,1-,2-}$ provides a further incentive for extending our previous studies of the octahedral d^5 and d^6 complexes to the corresponding d^7 and d^8 planar complexes (I).



II

McCleverty has suggested that since the planar dithioacetylacetonates have resonance-stabilized delocalized ground states, they might show similar reversible redox properties[3] to the dithiolenes which have nonclassical ground states. However, according to Schrauzer, there is a fundamental difference between the π-electronic structures of "even" and "odd" unsaturated organosulfur ligands[4] and he predicted that the remarkable electron affinity of the dithienes should not be shared either by the dithioacetylacetonates or by complexes of 1,1-dithio ligands such as dithiocarboxylates and dithiocarbamates.



odd even odd

Extensive studies by Fackler[5] and Gray and coworkers[6] have confirmed that metal(II) bis(dithiocarba-

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[1] This work is also described in a thesis presented by G. A. Heath to the University of Melbourne, in partial fulfillment of the requirements for the Ph.D. degree, Oct 1970.

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[5] J. P. Fackler and D. Coucouvanis, *Chem. Commun.*, 556 (1965); *J. Amer. Chem. Soc.*, **88**, 3913 (1966).

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