Electronic Spectra of Chelates.—The cobalt(III) complexes give intensely purple solutions in alcohol, chloroform, and benzene. Some spectral data in benzene are shown in Figure 1 and Table II. Low-spin d^6 ions in an octahedral crystal field show two spin-allowed transitions which may get split in fields of lower symmetry.[28] In no case could crystal field bands be confidently located for the tris chelates of arylazo-oximes. Intense allowed transitions in the visible region probably mask them completely.

Acknowledgment.—Thanks are due Mr. A. H. Siddiqui of this department for the microanalyses.

[28] A. Chakravorty, K. C. Kalia, and T. S. Kannan, *Inorg. Chem.*, **5**, 1623 (1966); E. Larsen and S. F. Mason, *J. Chem. Soc., A*, 313 (1966).

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Proton Nuclear Magnetic Resonance Studies of the Ethylenediaminetetraacetic Acid Complexes of Rhodium(III)

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The proton nmr spectra of several complexes of ethylenediaminetetraacetic acid (EDTA) with rhodium(III) have been studied in aqueous solutions from pH 0 to 10. For the monoaquo and monochloro EDTA complexes the spectra indicate that EDTA acts as a pentadentate ligand at low pH values (~1), with one uncoordinated carboxylate group. At higher pH values (~4–8) the spectra for the monoaquo complex indicate that ionization of the unbound carboxylic acid proton is accompanied by coordination to form the sexadentate complex. The spectra of the dichloro and dibromo EDTA complexes confirm that EDTA functions as a tetradentate ligand and indicate that the complexes have the *trans* configuration (with respect to the carboxylate oxygen atoms).

The structures of metal–ethylenediaminetetraacetic acid (EDTA)[1] complexes in aqueous solutions have been studied extensively by a variety of physicochemical techniques.[2] These studies have established that EDTA can occupy five or six positions in the coordination sphere of a metal ion (coordination number of 6). However, in many cases the number of donor atoms bound to the metal ion in a given complex has not been established definitely, although it is of considerable interest.[2] The work of Hoard and his colleagues[3] has established the X-ray crystal structures of several of the complexes in the solid phase, but extrapolation to the solution phase is questionable.

Rhodium(III) has been shown to form complexes with EDTA and some of these have been isolated.[4–8] The monoaquo complex[5–7] ($Rh(HEDTA)(OH_2)$) and its ammonium,[5] potassium,[5] and sodium[6,7] salts have been prepared, resolved, and studied by chemical and X-ray analyses and by infrared, spectrophotometric, polarographic, and potentiometric techniques.[5–9] These studies have led to the conclusion that EDTA functions as a pentadentate ligand. The acid and sodium salts of the monohalo complexes $Rh(HEDTA)X^-$ (X = Cl, Br, I) have been isolated and studied by similar methods;[6–8] the data indicate that the complexes contain pentadentate EDTA. The acid,[5] potassium,[5] and sodium[8] salts of the dichloro and dibromo complexes ($Rh(H_2EDTA)Cl_2{}^-$ and $Rh(H_2EDTA)Br_2{}^-$) have been isolated, resolved, and studied by the same methods. On the basis of these measurements EDTA has been shown to be tetradentate; however, conclusions have not been made about the stereochemistry of the complexes (four geometrical isomers are possible, as indicated in Figure 4C). Gillard and Wilkinson[9] have studied the infrared spectra of several of the complexes in D_2O solutions and have concluded that the structures are the same in both the solid and solution phases. No Rh(III)–EDTA complex in which EDTA acts as a sexadentate ligand appears to have been prepared, and, to date, no evidence has been presented which demonstrates that a sexadentate Rh(III)–EDTA complex is formed in solution. The present work is believed to include the first evidence for the formation of this species in solution in a limited pH range.

The current investigation has been undertaken to study the proton nmr spectra of several Rh(III)–EDTA complexes as a function of pH (pH 0–10) and to determine the structures and stereochemistry of the complexes in aqueous solution. Such studies of Rh(III)–EDTA complexes have not been reported previously and are of interest for comparison with the data obtained by other methods.[5–9] Proton nmr spectroscopy

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[1] EDTA denotes the tetraanion $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2{}^{4-}$, HEDTA the trianion $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)(CH_2COOH)^{3-}$, and H_2EDTA the dianion $(HOOCCH_2)(OOCCH_2)NCH_2CH_2N(CH_2COOH)(CH_2COO)^{2-}$.

[2] F. L. Garvan, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 7.

[3] J. L. Hoard, G. S. Smith, and M. Lind, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 296, and references given therein. See also ref 2.

[4] W. MacNevin, H. D. McBride, and E. A. Hakkila, *Chem. Ind.* (London), **4**, 101 (1958).

[5] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **82**, 4823 (1960).

[6] K. Sugiura and K. Yamasaki, *Naturwissenschaften*, **48**, 552 (1961).

[7] K. Sugiura and K. Yamasaki, *Nippon Kagaku Zasshi*, **88**, 948 (1967).

[8] N. A. Ezerskaya and V. N. Filimonova, *Russ. J. Inorg. Chem.*, **8**, 424 (1963).

[9] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 4271 (1963).

has proved to be an extremely useful technique for studying the structural and bonding characteristics of metal complexes in solution and has been used recently to study several metal–EDTA complexes.[10–14] The geometry of rhodium(III) has been established to be octahedral and the metal–ligand bonding in Rh(III)–EDTA complexes is expected to be nonlabile (long-lived). The nmr spectra therefore are expected to exhibit multiplet splitting patterns for the ligand protons which can provide insight into the structures and stereochemistries of the complexes. The infrared and absorption spectra of the complexes also have been measured to confirm the results of previous studies.[5–9]

Experimental Section

Preparation of the Complexes. Materials.—$Rh(NO_3)_3 \cdot 2H_2O$ and $Na_3RhCl_6 \cdot 12H_2O$ were obtained from Alfa Inorganics, Inc., and the acid form and disodium salt of EDTA were obtained from J. T. Baker Chemical Co.

(1) **Rh(HEDTA)(OH$_2$).**—The complex was prepared by the method of Dwyer and Garvan.[5] *Anal.* Calcd for Rh(HEDTA)-(OH$_2$): C, 29.28; H, 3.69; N, 6.83. Found: C, 29.17; H, 4.39, N, 6.78.

(2) **Na[Rh(HEDTA)Cl] and H[Rh(HEDTA)Cl].**—The sodium salt of the complex was prepared by the procedure of Ezerskaya and Filimonova.[8] The acid salt complex was obtained by passing a solution of the sodium salt complex through a Dowex 50W-X12 cation-exchange resin (H^+ form) and evaporating the solution on a steam bath to a small volume. On cooling the solution, the complex which precipitated was collected, recrystallized from hot water, and dried *in vacuo*. *Anal.* Calcd for Na[Rh(HEDTA)Cl]·2H$_2$O: C, 24.69; H, 3.52; N, 5.76; Cl, 7.29. Found: C, 24.57; H, 3.51; N, 5.74, Cl, 7.24. Calcd for H[Rh(HEDTA)Cl]·2H$_2$O: C, 25.84; H, 3.91; N, 6.03; Cl, 7.63. Found: C, 25.61; H, 3.89; N, 5.95; Cl, 8.07.

(3) **H[Rh(H$_2$EDTA)Cl$_2$] and H[Rh(H$_2$EDTA)Br$_2$].**—These complexes were prepared by the method of Dwyer and Garvan.[5] *Anal.* Calcd for H[Rh(H$_2$EDTA]Cl$_2$]·H$_2$O: C, 24.86; H, 3.55; N, 5.80; Cl, 14.68. Found: C, 24.56; H, 3.76; N, 5.69; Cl, 14.34. Calcd for H[Rh(H$_2$EDTA)Br$_2$]·H$_2$O: C, 21.00; H, 3.00; N, 4.90; Br, 27.94. Found: C, 21.53; H, 3.24; N, 4.92; Br, 27.62.

Elemental analyses were carried out by Elek Microchemical Laboratories, Torrance, Calif. All of the complexes are sufficiently soluble in D_2O to permit nmr studies.

Instrumentation.—The proton nmr spectra of the complexes in D_2O solutions were recorded either with a Varian Model HA-100 or A-60 proton nmr spectrometer operating at 35 ± 1°, the temperature within the probe. Measurements were made with 4-mm i.d. Varian precision-bore tubes, using *t*-butyl alcohol as an internal reference. All of the resonances occurred on the low-field side of the *t*-butyl alcohol and the chemical shifts are referred to TMS* (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt) as zero; the *t*-butyl alcohol resonance occurs at 1.233 ppm on the low-field side of TMS*.

Concentrations from 0.1 to 0.5 *F* were used to obtain good signal to noise ratios. The chemical shifts were found to be essentially independent of concentration provided the solution pH remained constant. The pH values of the solutions were measured (at 25°) with a Leeds and Northrup line-operated pH meter, equipped with miniature electrodes. Solution pH was varied by the addition of anhydrous sodium carbonate and nitric acid. The reported pH values are uncorrected because the D_2O solutions often contained significant amounts of H_2O. Assuming pure D_2O, the reported values should be corrected by +0.4 pH unit to give the true pD values.[15] In all cases the spectra were recorded within a few minutes of the dissolution of the complexes. The error in the chemical shifts is ±0.01 ppm and in the coupling constants ±0.1 cps.

The infrared spectra of D_2O solutions of the complexes were measured using BaF_2 cells with a Perkin-Elmer Model 621 double-beam grating instrument; for the solid complexes the Nujol mull technique was used. The absorption spectra of the complexes were recorded with a Cary Model 14 spectrophotometer using 5×10^{-3} *F* aqueous solutions in 1-cm cells.

Results

Proton Nmr Spectra.—Typical spectra of the complexes are illustrated in Figures 1–3, and Figure 4 indicates the possible geometrical isomers for the complexes. The spectral parameters for the complexes are summarized in Table I.

The spectrum of the Rh(HEDTA)(OH$_2$) complex (Figure 1A) appears to consist of two acetate singlets at 4.22 and 4.12 ppm and two acetate AB patterns, plus several ethylenic resonances at higher field. The assignment of the AB patterns is uncertain because the two lowest field resonances are obscured by one of the singlets (at 4.22 ppm); a possible assignment is indicated in Figure 1A. Although some of the ethylenic resonances (a complex ABCD pattern) may be superimposed on the acetate proton resonances causing inaccuracies in intensity (area) measurements, each acetate singlet and each AB pattern probably represent equal numbers of protons.

When the pH of a solution of the monoaquo complex is increased, the acetate proton resonances (two singlets and two AB patterns) appear to decrease in intensity while new resonances appear and become more intense. Several of the original resonances and the new resonances appear to be superimposed. The spectrum continues to change until approximately pH 4. The ethylenic ABCD pattern appears to alter considerably in the range from pH 1 to 4. From pH 4 to 8 the spectrum shows little change (Figure 1B); it appears to contain four intense acetate resonances (at 4.03, 4.01, 3.95, and 3.87 ppm) and several weaker resonances in the same region. These resonances appear to constitute two equally intense AB patterns (as indicated in Figure 1B), plus some additional weak resonances. The ethylenic resonance pattern is at lower field than at pH 0.5 and partially overlaps with the acetate resonances. The assignment of the AB patterns shown in Figure 1B is tentative; other assignments are possible although the spectrum does appear to consist mainly of two equally intense acetate AB patterns and an ethylenic resonance pattern. Above pH 8 the resonances broaden somewhat and alter their intensities; also, additional resonances are visible, making assignments difficult.

The spectrum of the Na[Rh(HEDTA)Cl] complex (Figure 2A) contains one clearly visible acetate AB pattern centered at 4.18 ppm which has a relatively large chemical shift difference between the two protons ($\delta_A - \delta_B = 0.65$ ppm), a second acetate AB pattern centered

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(10) S. I. Chan, R. J. Kula, and D. T. Sawyer, *J. Am. Chem. Soc.*, **86**, 377 (1964).

(11) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *ibid.*, **85**, 2930 (1963).

(12) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

(13) Y. O. Aochi and D. T. Sawyer, *Inorg. Chem.*, **5**, 2085 (1966).

(14) L. V. Haynes and D. T. Sawyer, *ibid.*, **6**, 2146 (1967).

(15) K. Mikkelson and S. O. Nielson, *J. Chem. Phys.*, **64**, 632 (1960).

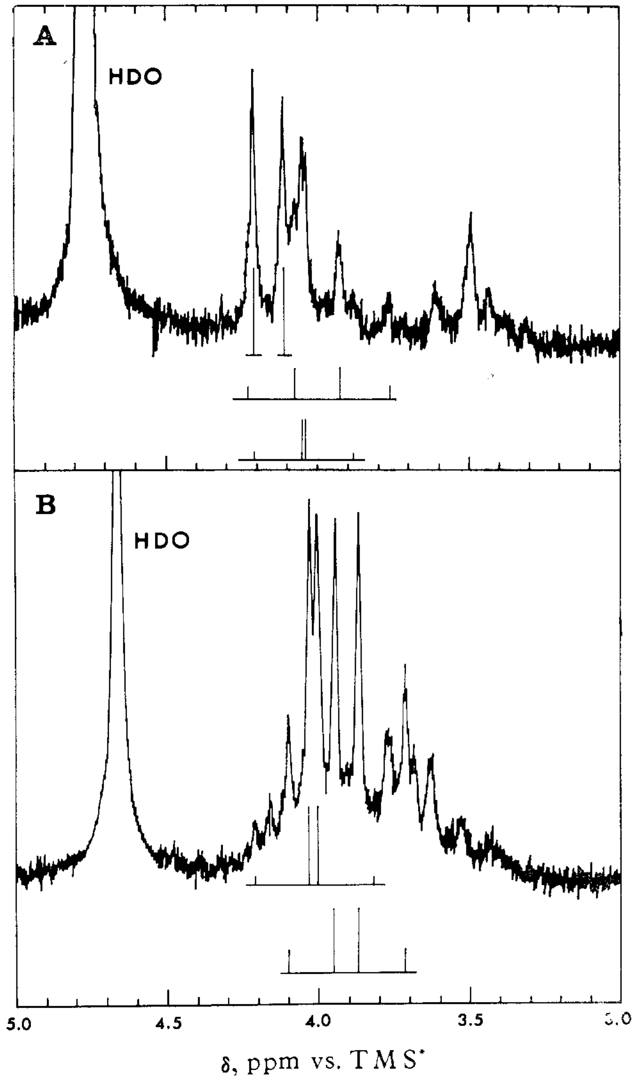

Figure 1.—The 100-Mc proton nmr spectrum of Rh(HEDTA)-(OH_2) at (A) pH 0.5 and (B) pH 6. Tentative assignments are indicated for the acetate protons.

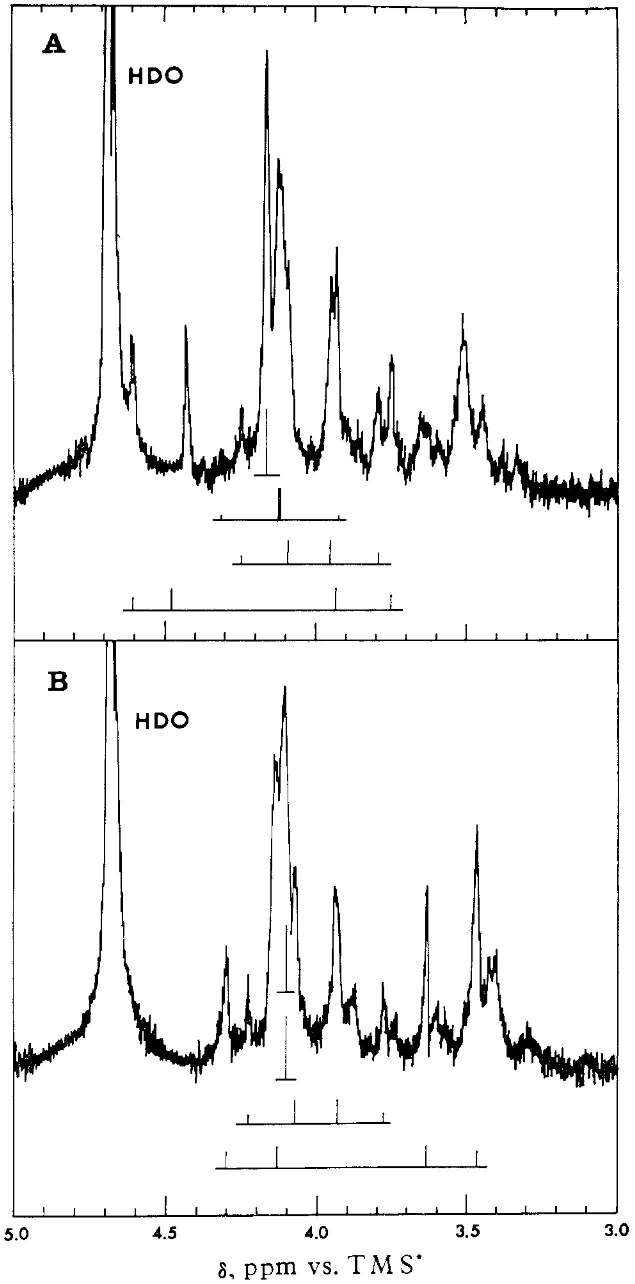

Figure 2.—The 100-Mc proton nmr spectrum of Na[Rh-(HEDTA)Cl] at (A) pH 2 and (B) pH 6.5. Tentative assignments are indicated for the acetate protons.

at 4.02 ppm ($\delta_A - \delta_B = 0.25$ ppm), and two intense resonances at 4.16 and 4.12 ppm; these latter two resonances probably represent acetate CH_2 groups. (They also could represent two superimposed acetate AB patterns with small $\delta_A - \delta_B$ values, whose weak outer satellites are obscured by the other acetate resonances.) The acetate resonances therefore appear to consist of two AB patterns and two singlets (or four AB patterns) of equal intensities. The higher field ethylenic resonance appears to be a complex ABCD pattern whose lower field part overlaps with the higher field acetate resonances. (The spectrum of the acid salt complex is almost identical with that of the sodium salt complex.) When the pH of the solution is increased from pH 2 to 5 the AB pattern with $\delta_A - \delta_B = 0.65$ ppm shifts upfield by 0.29 ppm; the other acetate resonances appear to be affected little by the pH increase although the ethylenic resonance pattern changes somewhat. At pH 6.5 (Figure 2B) two AB patterns are observed plus a large, broad singlet at 4.10 ppm which probably represents the other two singlets (or AB patterns) which have coalesced. Further increases in pH have little effect on the spectrum.

The spectra of the $H[Rh(H_2EDTA)X_2]$ complexes (X = Cl or Br) contain two equally intense acetate AB patterns and an ethylenic resonance at higher field consisting of an intense, broad, central peak with two symmetrically placed satellites (Figure 3A for the dichloro complex). The ethylenic resonances presumably represent symmetrical A_2B_2 patterns. In each case the higher field acetate proton (designated the B proton) of the AB pattern with the smaller chemical shift difference ($\delta_A - \delta_B$ value) appears to be split into a doublet, with a coupling constant close to 1 cps. When the pH values of solutions of the complexes are increased in each case, the AB pattern with the larger $\delta_A - \delta_B$

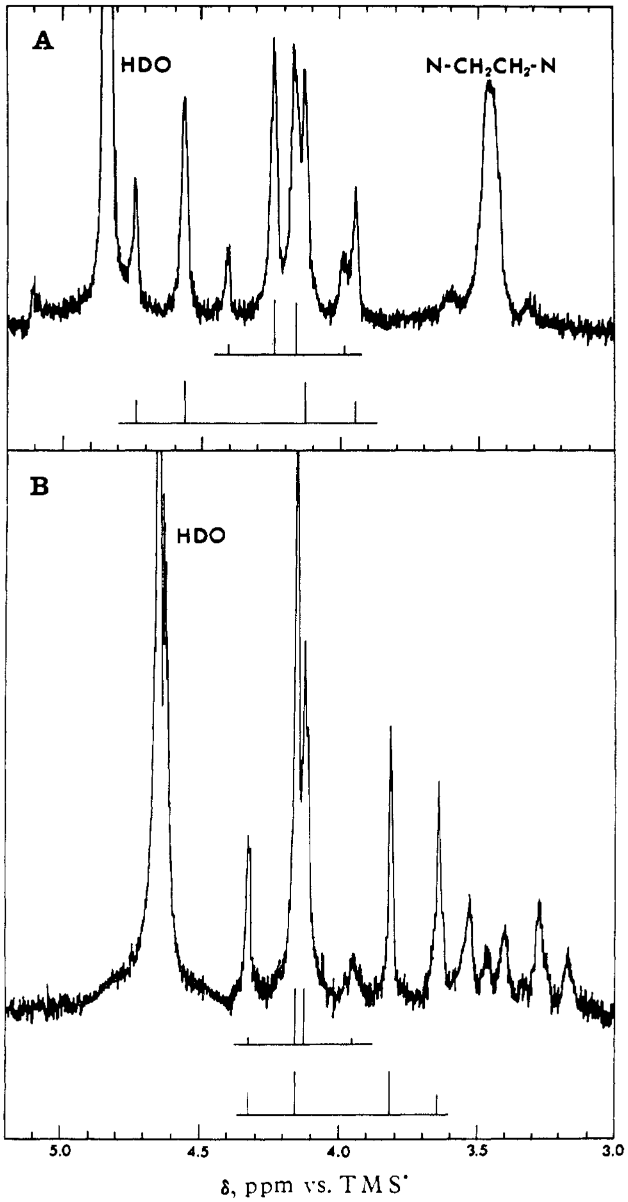

Figure 3.—The 100-Mc proton nmr spectrum of $H[Rh(H_2EDTA)Cl_2]$ at (A) pH 0.5 and (B) pH 6. Assignments for the acetate AB protons are indicated.

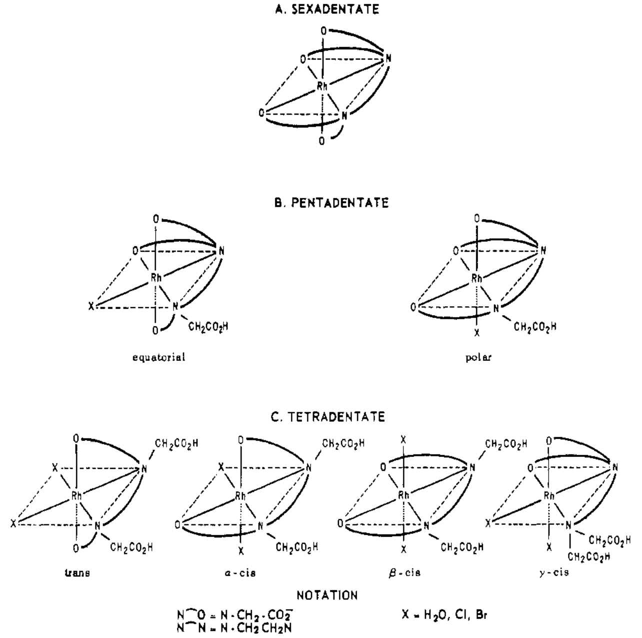

Figure 4.—The possible geometrical isomers for the Rh(III)–EDTA complexes: (A) sexadentate; (B) pentadentate; (C) tetradentate.

value shifts upfield considerably. Thus, in the range from pH 0.5 to 5 the B protons shift upfield approximately 0.3 ppm and the A protons shift approximately 0.4 ppm. Simultaneously, the ethylenic A_2B_2 resonance appears to collapse into a symmetrical multiplet containing several sharp resonances, the center of which shifts upfield slightly. The other AB patterns (the ones with the smaller $\delta_A - \delta_B$ values) are relatively unaffected by the pH increase (Figure 3B for the dichloro complex). From pH 5 to 9 the spectra show no further changes.

Infrared Spectra.—The asymmetrical carboxylate stretching frequency has been established as a good criterion for distinguishing between protonated carboxylate groups (1700–1750 cm.$^{-1}$) and carboxylate groups coordinated to transition metal ions (1600–1700 cm^{-1}) in EDTA complexes.[16] The results that are obtained at these frequencies in the present work for both the solid and solution spectra agree well with those reported in previous studies.[5,9] Thus, the data indicate that the complexes contain both coordinated and protonated carboxylate groups in probable ratios of 3:1 for $Rh(HEDTA)(OH_2)$ and $Rh(HEDTA)Cl^-$ and 1:1 for $Rh(H_2EDTA)X_2^-$ (X = Cl or Br). As an extension of the previous work, the infrared spectra of these complexes in aqueous solution have been studied as a function of pH. When the pH of a solution of $Rh(HEDTA)(OH_2)$ is increased, the band at 1727 cm^{-1} (protonated carboxylate group) decreases in intensity and finally disappears at pH 5. From pH 5 to 8 only one symmetrical band at 1639 cm^{-1} is visible. Similar observations are obtained with the other complexes. A separate band at ~1600 cm^{-1} is not observed for any of the complexes. Such a band would be indicative of uncoordinated, ionized carboxylate groups and has been observed for similar cobalt(III) complexes.[17] For the tetradentate complexes the broad band near 1600 cm^{-1} presumably represents both the coordinated and the free ionized carboxylate groups. The broad band at 1639 cm^{-1} for $Rh(HEDTA)(OH_2)$ is at a frequency that does not establish whether uncoordinated, ionized carboxylate groups are present in the complexes at higher pH values.

Absorption Spectra.—The absorption spectra of the complexes have been studied previously.[5–8] The results obtained in the present work are identical with those of the earlier authors. In addition, the spectra have been measured at different pH values. From pH 1 to 7 the spectra exhibit little change, although the spectrum of $Rh(HEDTA)(OH_2)$ shows a small shift of

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(16) D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **75**, 4574 (1953); **78**, 716 (1956).

(17) Reference 2, p 317.

TABLE I

CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] FOR THE RHODIUM(III)–EDTA COMPLEXES

Complex	pH	AB acetate protons δ_A	δ_B	$\delta_A - \delta_B$	δ_{CH_2}	No. of protons	$\delta_{CH_2CH_2}$[d]	J_{AB}
$Rh(HEDTA)(OH_2)$[c]	0.5	4.15	3.89	0.26		2		*ca.* 16.5
		4.08	4.01	0.07		2		*ca.* 16.5
					4.22	2		
					4.12	2		
$Rh(EDTA)^-$[c]	5.0	4.07	3.97	0.10		4	3.71	18.4
		4.00	3.83	0.17		4		15.6
$Co(EDTA)^-$[e]		3.97	3.84	0.13		4		18.5
		3.91	3.58	0.33		4		16.0
$Na[Rh(HEDTA)Cl]\cdot 2H_2O$	2.0	4.50	3.85	0.65		2		17.9[f]
		4.14	3.89	0.25		2		15.6
					4.16	2		
					4.12	2		
	6.5	4.21	3.56	0.65		2		16.9[f]
		4.13	3.88	0.25		2		15.6
					4.10	4		
$H[Rh(H_2EDTA)Cl_2]\cdot H_2O$	0.5	4.63	4.03	0.60		4	3.45	17.9[f]
		4.28	4.10	0.18		4		16.9
	6.0	4.23	3.75	0.48		4	3.41	17.0[f]
		4.20	4.09	0.11		4		17.0
$H[Rh(H_2EDTA)Br_2]\cdot H_2O$	0.5	4.84	4.03	0.81		4	3.45	17.9[f]
		4.37	4.13	0.24		4		16.8
	6.0	4.44	3.74	0.70		4	3.41	16.9[f]
		4.31	4.13	0.18		4		16.9

[a] In ppm on the low-field side of TMS* (TMS* = zero). [b] In cps. [c] Tentative assignment. [d] Center of ethylenic A_2B_2 pattern. [e] From R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1236 (1965). [f] Uncoordinated acetate AB protons.

the first band to higher energy, accompanied by a small decrease in intensity.

Discussion and Conclusions

The proton nmr spectrum of the $Rh(HEDTA)(OH_2)$ complex indicates the presence of four different types of acetate CH_2 protons. In addition, stereomodels of the complex establish that four different types of acetate CH_2 protons are present in both the equatorial and the axial isomers (Figure 4B). Thus, an nmr spectrum containing four different acetate AB patterns and an ethylenic ABCD pattern is expected for either isomer; the observed spectrum is consistent with the presence of a pentadentate EDTA ligand and supports the conclusions of earlier workers.[5-9] The observation of two acetate CH_2 singlets instead of the two expected AB patterns probably results from the accidental degeneracy of the two protons in each group. Which of the two possible isomers is present cannot be deduced from the spectrum (both could be present if there was a rapid equilibrium between them). However, the X-ray studies of Hoard and his colleagues[3] on similar monoaquo pentadentate EDTA complexes have established that the equatorial isomer is favored, presumably because it is less strained than the axial form. Therefore, the complex present in solution probably is the equatorial isomer. Terrill and Reilley[18] have studied the protonation of the sexadentate complex $Co(EDTA)^-$ to give the pentadentate $Co(HEDTA)(OH_2)$ complex in acidic D_2O and their results indicate that the water molecule in the latter occupies a polar site.

The nmr spectral changes that are observed with increasing pH for the $Rh(HEDTA)(OH_2)$ complex are consistent with at least a part of the possible hydrolysis equilibria

$$\begin{tikzcd}
\underset{\text{I}}{Rh(HEDTA)(OH_2)} \arrow[rr, shift left, ""] \arrow[dr, shift left] & & \underset{\text{II}}{Rh(EDTA)(OH_2)^-} \arrow[ll, shift left] \arrow[dr, shift left] \arrow[dl, shift left] & \\
& \underset{\text{III}}{Rh(EDTA)^-} \arrow[ul, shift left] \arrow[ur, shift left] \arrow[rr, shift left] & & \underset{\text{IV}}{Rh(EDTA)(OH)^{2-}} \arrow[ll, shift left] \arrow[ul, shift left]
\end{tikzcd}$$

Thus, increasing the pH would be expected to cause ionization of the uncoordinated carboxylic acid of complex I to give complex II. This would be indicated by an upfield shift of 0.3–0.4 ppm for the uncoordinated acetate protons. Such an upfield shift is characteristic for uncoordinated acetate protons during the ionization of their carboxylic acids in these types of complexes[19] and is observed for the $Rh(HEDTA)Cl^-$ and $Rh(H_2EDTA)X_2^-$ complexes. However, this shift is not observed for any of the acetate resonances (singlets or AB patterns) of the $Rh(HEDTA)(OH_2)$ complex from pH 0 to 5 which indicates that uncoordinated, ionized carboxylate groups are not present in this pH range. The gradual disappearance of the original resonances and the appearance and growth of new resonances imply that a new species is formed in solution as the unbound carboxylic acid ionizes. The spectrum at pH 5 is consistent with the presence of a sexadentate complex (complex III); the additional weak resonances probably represent a small amount of the pentadentate complex. The spectrum of the analogous sexadentate Co(III)–EDTA complex has been discussed by Day and Reilley;[12] it consists of two equally intense acetate AB patterns and a symmetrical A_2B_2 ethylenic resonance. The spectrum of the Rh(III) complex at pH 5 is quite similar, containing two equally intense AB

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(18) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).

(19) B. B. Smith and D. T. Sawyer, *ibid.*, **7**, 922 (1968).

patterns and an ethylenic resonance. The coupling constants for the two AB patterns are similar in both cases (Table I). Thus, on the basis of similarity of the spectrum to that of the sexadentate Co(III)–EDTA complex and the apparent absence of uncoordinated, ionized carboxylate groups, the major species present in solution at pH 5 is concluded to be a sexadentate Rh(III)–EDTA complex (complex III). The proton nmr spectrum at 60 Mc supports this conclusion by also having two acetate patterns of equal intensity. Garvan[2] has indicated that solutions of the monoaquo pentadentate Al(III)– and Cr(III)–EDTA complexes contain considerable amounts of the corresponding sexadentate complexes at some intermediate range of pH.

The spectral changes which occur at pH >8 probably are associated with the dissociation of one of the coordinated carboxylate groups and incorporation of hydroxide ion into the coordination sphere to give complex IV (which may be polymeric). Previous workers,[5,7] on the basis of potentiometric studies, have suggested that the reaction scheme I → II → IV occurs with increasing pH and have determined pK values for the ionization of the two protons in the two steps (p$K_1 \approx$ 2, p$K_2 \approx$ 9–10). However, the formation of the sexadentate complex III, which then reacts with hydroxide ion to give complex IV, also is consistent with the potentiometric measurements. The infrared solution spectra and the absorption spectra are not helpful in providing additional evidence for the presence of the sexadentate complex.

The proton nmr spectrum of the Rh(HEDTA)Cl$^-$ complex clearly contains four different types of acetate CH$_2$ protons. The AB pattern with the large $\delta_A - \delta_B$ value, which shifts upfield considerably as the pH is increased from pH 1 to 5, is assigned to the CH$_2$ protons of the unbound acetate group. The other AB pattern and singlets represent the three CH$_2$ groups in the three coordinated acetate groups. Day and Reilley[20] have studied the proton nmr spectra of the analogous Co(III) complexes, Co(HEDTA)X$^-$ (X = Cl or Br), and have observed one AB pattern with a large $\delta_A - \delta_B$ value and three closely similar AB patterns. They have assigned the former pattern to the unbound acetate CH$_2$ protons because of its difference from the other three patterns and its larger broadening by paramagnetic ions. Thus, the assignment in the present Rh(III) complex, which is made on the basis of pH shifts, agrees with their assignments for the Co(III) complexes. The spectra for the Rh(HEDTA)Cl$^-$ complex from pH 1 to 9 are consistent with the presence of the pentadentate EDTA complex, and there is no evidence for the formation of any other species. As in the case of the monoaquo pentadentate complex, this complex probably is present as the equatorial isomer.

The spectra of the dichloro and dibromo complexes establish that they contain two different types of acetate protons. The upfield shifts that are observed with increasing pH for one of the two AB patterns (large $\delta_A - \delta_B$ value) in each of the complexes indicate that these acetate CH$_2$ protons are uncoordinated; this implies that EDTA functions as a tetradentate ligand, in agreement with the earlier studies.[5,8] The complexes have four possible geometrical isomers (Figure 4C). In addition, several optical forms are possible for these geometrical isomers. Consideration of stereomodels indicates that of the four geometrical isomers only the *trans* and *β-cis* forms are consistent with the nmr spectra (more than two acetate AB patterns would be expected for the other two isomers). The models also indicate that the *β-cis* configuration has considerable strain. In a recent study of the complexes formed by Co(III) with ethylenediaminediacetic acid (EDDA) and some N-substituted analogs Legg and Cooke[21] have isolated the *trans* and *α-cis* complexes but the *β-cis* isomer was not obtained. The strain present in the *β-cis* configuration probably prevents the formation of this isomer. The simplicity of the nmr spectra of the present complexes indicates that only one of the possible geometrical isomers is present; from the work of Legg and Cooke[21] and model studies this probably has the *trans* configuration. The spectra do not distinguish between the possible optical isomers.

The collapse of the ethylenic A$_2$B$_2$ resonance to a sharp multiplet pattern, which occurs when the pH is increased from pH 0.5 to 5, may have several explanations. One interpretation is that the spectra indicate a decrease in the rate of racemization of the complex with increasing pH. Thus, at low pH values the rate is sufficiently rapid to average partially the environments of the A$_2$B$_2$ ethylenic protons and a broad resonance with two satellites is observed; at higher pH values the process is slowed sufficiently such that one conformation (*gauche*) of the ethylenic ring is favored and the resonance consists of a symmetrical A$_2$B$_2$ splitting pattern. Busch, Im, and Cooke[22] have studied the racemization of the sexadentate Co(EDTA)$^-$ complex and have observed that it is base catalyzed. The present spectra, if so interpreted, indicate the opposite behavior, *i.e.*, an acid-catalyzed racemization. How the ionization of the unbound carboxylic acids can affect the rate of racemization of the complex is difficult to rationalize. A more likely explanation is that ionization of the unbound carboxylic acids alters the chemical shifts and coupling constants of the ethylenic protons because of the change in the inductive and long-range shielding effects of the groups, thus altering the appearance of the resonance pattern.

Comparison of the chemical shift positions in the present complexes with those in the analogous and similar Co(III) complexes indicates that the environments of the two protons in each AB pattern in the Rh(III) complexes are more similar than those in the Co(III) complexes. This also has been noted for a series of Co(III) and Rh(III) complexes with similar ligands.[19] The resonances in the Rh(III) complexes generally occur at

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[20] R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1236 (1965).

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

[22] D. W. Cooke, Y. A. Im, and D. H. Busch, *ibid.*, **1**, 13 (1962).

lower field than those of the corresponding Co(III) complexes, which agrees with earlier work.[19]

The AB proton coupling constants (15.6–18.4 cps) for all of the complexes are similar to those obtained in other metal–EDTA complexes.[10–14,19] The decrease in the coupling constant of the unbound acetate CH_2 group from approximately 18 to 17 cps during the ionization of the carboxylic acids appears to be characteristic. The additional small coupling (~1 cps) observed for the B protons in the acetate chelate rings of the tetradentate complexes may arise from coupling with the rhodium nucleus ($I = {}^1/_2$).

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Ammonia Exchange of Nickel–Ammine Complex in Aqueous Ammonia Measured by Proton Magnetic Resonance[1,2]

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The exchange rate of $Ni(NH_3)_6^{2+}$ in aqueous ammonia is determined by proton magnetic resonance. The relaxation time T_2 is obtained from the line width of the water resonance, and T_1 is measured by the saturation recovery method. At −17°, the exchange is fairly slow and the $Ni(NH_3)_6^{2+}$ resonance occurs at high field about 9500 Hz from the solvent resonance, with a full width of about 2600 Hz. The hyperfine coupling constant is negative and large: $A/h = -1.70 \times 10^6$ Hz. The exchange rate (sec^{-1}) of the NH_3 molecules is $\log (1/\tau) = 13.53 - (2610/T)$. If NaOH is added to the solution, complexes such as $Ni(NH_3)_5OH^+$ are formed, and the NH_3 is more labile: $\log (1/\tau) = 13.79 - (2610/T)$ in 0.103 *M* NaOH and $13.97 - (2610/T)$ in 0.326 *M* NaOH. The exchange rates are the same as the rates obtained by ^{14}N nmr, demonstrating that individual protons exchange at a much slower rate.

Introduction

Water-exchange rates in aqueous solutions of transition metal ions have been determined by ^{17}O nuclear magnetic resonance.[3] Hunt, *et al.*,[4,5] determined the ammonia-exchange rate of a solution containing $Ni(NH_3)_6^{2+}$ in aqueous ammonia by ^{14}N resonance. In the present investigation, the proton-exchange rate of this complex is determined by proton nmr. By comparison of the ^{14}N and ^{1}H results, the importance of the exchange of individual protons follows. The exchange rate in anhydrous ammonia has also been measured by ^{14}N resonance.[5] Swift and Lo[6] obtained a different result by proton resonance, but this work has been criticized by Rice and Wayland,[7] who confirm Hunt's[5] results.

Basic Equations

The protons of ammonia and water in the bulk of the solution exchange rapidly, and only a single peak is observed. Several processes[8] contribute to the relaxation rate, $1/T_1$, of these protons

$$\frac{1}{T_1} = \frac{1}{T_{1A}} + \frac{P}{T_{1M} + \tau} + \frac{P}{T_{1C}} \qquad (1)$$

The contribution $1/T_{1A}$ represents the relaxation rate in the absence of paramagnetic ions. T_{1M} is the relaxation time of the ammonia protons in the first coordination sphere of the Ni, and τ is their lifetime. P is the mole fraction of these protons. Thus, in the present case

$$P = 18[\mathrm{Ni(NH_3)_6}^{2+}]/\{3[\mathrm{NH_3}] + 2[\mathrm{H_2O}]\} \qquad (2)$$

The third term of eq 1 represents the dipole relaxation of NH_3 and H_2O protons surrounding a complex nickel ion. The protons in the second and higher coordination shells relax by interaction with the magnetic dipole of the unpaired, "magnetic" electrons of the nickel complex.

For slow exchange, $|\tau\Delta\omega| \gg 1$, and the spectrum consists of two resonances, separated by a chemical shift $\gamma\Delta H = \gamma(H_M - H_A) = -\Delta\omega = -(\omega_M - \omega_A)$. The weak resonance γH_M at high field is due to $Ni(NH_3)_6^{2+}$.

The chemical shifts are measured with respect to an internal standard R. The resonance separation $\gamma\Delta H$ can be obtained by measuring the chemical shift $\delta\omega$ relative to R as a function of the nickel concentration

$$\delta\omega - \delta\omega_A = P(\delta\omega_M - \delta\omega_A) = P\Delta\omega \qquad (3)$$

The electron–proton coupling constant, A/h, follows from the resonance separation by [3,9]

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[1] Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; Abstract No. H99.

[2] The effect of hydroxide ions was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; Abstract No. L75.

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