lated by Hill[20] which places less emphasis on the H···H interactions than that of Mason and Kreevoy.[19] Using this expression in the present circumstances for the complex configurations where all interactions are minimized we obtained practically zero energy difference between the *meso* and active forms for the nonbonded H···H interactions but calculated 1 kcal/mole in favor of the active form from all nonbonded interactions. This calculation agrees substantially with the observed free energy difference whereas that derived from Mason and Kreevoy's expression would be substantially greater. It remains to be seen which potential function gives the most reliable result for those instances where the equilibrium position can be measured.

Acknowledgment.—The authors thank Professor S. F. Mason and Dr. C. J. Hawkins for the CD spectra, C. E. Schäffer for improving the discussion of circular dichroism, the Microanalytical Section of The John Curtin School of Medical Research for the C, H, and N analyses, and Mr. S. Brown for the pmr spectra.

[20] T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

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Proton Nuclear Magnetic Resonance Studies of Nitrilotriacetic Acid, N-Methyliminodiacetic Acid, and Iminodiacetic Acid Complexes of Cobalt(III) and Rhodium(III) in Aqueous Solutions

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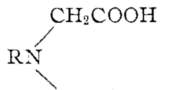
Several 1:1 and 1:2 (metal ion:ligand) complexes of Co(III) and Rh(III) with nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA) have been prepared and their proton nmr spectra studied in aqueous solutions (D_2O) as a function of pH. The spectra exhibit characteristic multiplet splitting patterns for the ligand acetate protons, indicating that both the metal–nitrogen and the metal–carboxylate bondings are relatively nonlabile (long-lived). The metal ions form both 1:1 and 1:2 complexes with NTA, in which the latter functions as a tetradentate and tridentate ligand, respectively. In addition, Rh(III) forms 1:2 complexes with MIDA and IDA; both ligands form *trans*-facial isomers while IDA also has a *cis* isomer. With the exception of the 1:1 Co(III)–NTA complex, this represents the first reported synthesis and isolation of the complexes. The infrared and visible absorption spectra of the complexes have been measured further to characterize their structures.

Numerous studies (mainly employing pH titrimetric, electrochemical, and spectrophotometric methods) of the metal complexes formed by nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA)



NTA, R = CH_2COOH
MIDA, R = CH_3
IDA, R = H

have been reported and the stability constants for many of the complexes have been determined.[1] Schwarzenbach and co-workers have established that NTA functions as a tetradentate ligand while both MIDA and IDA act as tridentate ligands.[2,3]

Recently, several proton nmr studies of both diamagnetic[4–9] and paramagnetic[10,11] metal–NTA, –MIDA, and –IDA complexes have been discussed. These studies and those reported for the closely related diamagnetic metal–ethylenediaminetetraacetic acid (EDTA) complexes[4,12–14] have indicated that with certain metal ions an AB splitting pattern is observed for the ligand acetate protons. Cooke has prepared and characterized the 1:2 Co(III)–MIDA and –IDA complexes and has studied their aqueous nmr spectra;[7] AB patterns are observed for the acetate protons in all of the complexes.

The present paper reports the preparation of several Co(III)- and Rh(III)-NTA, -MIDA, and -IDA complexes and summarizes the results of a detailed study of their proton nmr spectra in aqueous solutions (D_2O). The octahedral geometry of both metal ions is well established and both are expected to form complexes

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[1] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, and references cited therein.

[2] G. Schwarzenbach, E. Kampitsch, and R. Sterms, *Helv. Chim. Acta*, **28**, 828, 1133 (1945).

[3] G. Schwarzenbach and W. Beidermann, *ibid.*, **31**, 331 (1948).

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

[5] R. J. Kula, *Anal. Chem.*, **38**, 1382 (1966).

[6] R. J. Kula, *ibid.*, **39**, 1171 (1967).

[7] D. W. Cooke, *Inorg. Chem.*, **5**, 1411 (1966).

[8] L. V. Haynes and D. T. Sawyer, *ibid.*, **6**, 2146 (1967). The complexes are diamagnetic dimers.

[10] R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

[11] B. B. Smith, Ph.D. Thesis, University of London, 1966.

[12] R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963).

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

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

with nonlabile bonding. Their nmr spectra are of interest because they can provide information about the structures (and stereochemistry) and certain bonding features of the complexes. For the NTA complexes, the observation of AB splitting patterns is especially interesting because it confirms the presence of both nonlabile metal–nitrogen and metal–carboxylate bonding; these are the first reported cases of AB splitting patterns for metal–NTA complexes. Preliminary work in this laboratory on more labile metal–NTA complexes and work elsewhere[4,8,9,11] has indicated that metal–NTA complexes exhibit simple one-line nmr spectra even when the corresponding MIDA, IDA, and EDTA complexes exhibit AB splitting patterns. The Rh(III)–MIDA and –IDA complexes are of interest in view of their similarity to the NTA complexes; they represent a series analogous to the previously prepared Co(III) complexes.[7] Proton nmr studies of Co(III)–NTA complexes have not been reported previously; however, several 1:1 complexes have been prepared and studied by infrared and visible spectrophotometry.[15]

Experimental Section

Reagent grade $CoCl_2 \cdot 6H_2O$ and $Rh(NO_3)_3 \cdot 2H_2O$ were obtained from Baker and Adamson and Alfa Inorganics, respectively. The acid forms of NTA, MIDA, and IDA were obtained from Matheson Coleman and Bell, from Aldrich Chemical Co., Inc., and from Geigy Chemical Corp., respectively. All were reagent grade and were used without further purification.

Cobalt(III) Complexes.[16] (1) **1:1 Co(III)–NTA Complex.**—The complexes **α-K[Co(NTA)(OH)(OH$_2$)]·2H$_2$O** and **β-K[Co(NTA)(OH)(OH$_2$)]·3H$_2$O** were prepared by the method of Mori and co-workers.[15] The C, H, and N analyses were satisfactory. The blue α isomer is sparingly soluble in water while the red-violet β form is very soluble.

(2) *trans*-**Facial 1:2 Co(III)–NTA Complexes.**—The complex $K_3[Co(NTA)_2] \cdot 4H_2O$ was prepared by a similar method to that given by Tsuchida and co-workers for the 1:2 IDA complexes.[17] $CoCl_2 \cdot 6H_2O$ (2 g) was added to a solution of NTA (4 g) and potassium hydroxide (3.5 g) in water (25 ml). The mixture was cooled in an ice bath and 30% hydrogen peroxide (5 ml) was added dropwise. After stirring well, the solution was left to evaporate in an air stream. A small quantity of the blue α 1:1 complex gradually separated and was removed. The concentrated filtrate was kept overnight in a refrigerator and the red-violet product which separated was collected, recrystallized from a small quantity of water, and air dried.

Anal. Calcd for $K_3[Co(NTA)_2] \cdot 4H_2O$: C, 23.08; H, 3.23; N, 4.49. Found: C, 23.16; H, 3.58; N, 4.52. The product is very soluble in water giving a red-violet solution.

The acid salt, $H[Co(NTAH)_2] \cdot 2H_2O$, was prepared by acidifying a solution of the tripotassium salt and collecting the pink product which separated from the cooled solution. It was recrystallized from a small quantity of hot water and air dried.

Anal. Calcd for $H[Co(NTAH)_2] \cdot 2H_2O$: C, 30.39; H, 4.04; N, 5.91; Co, 12.43. Found: C, 30.12; H, 4.25; N, 5.83; Co, 12.27. The pink product is sufficiently soluble in cold water to permit nmr studies and is very soluble in hot water.

The monopotassium salt $K[Co(NTAH)_2] \cdot 2H_2O$ also was obtained from the reaction mixture for the 1:1 complexes. After the isolation of the 1:1 complexes,[15] the filtrate was acidified with 6 *F* hydrochloric acid (pH ∼1) and the solution was heated on a steam bath for about 30 min. On cooling the pink product separated. It was recrystallized from hot water and air dried.

Anal. Calcd for $K[Co(NTAH)]_2 \cdot 2H_2O$: C, 28.13; H, 3.54; N, 5.74. Found: C, 28.59; H, 3.54; N, 5.51.

Acidification of a solution of the monopotassium salt and cooling produced the acid salt.

Rhodium(III) Complexes. (1) **1:1 Rh(III)–NTA Complex.**—Although a 1:1 NTA complex was not prepared in a pure state, on heating an equimolar solution of $Rh(NO_3)_3$ and NTA on a steam bath for several hours a brown residue was obtained containing an apparent mixture of 1:1 and 1:2 complexes. When an excess of NTA was used only the 1:2 complex was obtained. When excess Rh(III) was used, a mixture of the 1:1 complex and another species (probably a dimer or polymer) was obtained. Attempts to separate the mixture using solubility and ion-exchange techniques were unsuccessful. The 1:1 complex is believed to be present because of the similarity of its spectrum to that of the 1:1 Co(III)–NTA complex.

(2) **1:2 Rh(III)–NTA, –MIDA, and –IDA Complexes.**—The *trans*-facial 1:2 Rh(III)–NTA, –MIDA, and –IDA complexes and the *cis* 1:2 Rh(III)–IDA complex were prepared by a modification of the method of Dwyer and Garvan for the preparation of the 1:1 Rh(III)–EDTA complex.[18] Freshly precipitated rhodium hydroxide (made by adding KOH to a hot solution of $Rh(NO_3)_3$ at pH 7) was suspended in water in a Pyrex tube and a large excess of the ligand was added. The tube was then sealed and heated at 120–130° for several hours. After cooling, the tube was opened carefully and a small quantity of metallic rhodium was removed. The individual complexes were then isolated from the filtrates.

(a) *trans*-**Facial 1:2 H[Rh(NTAH)$_2$]·2H$_2$O.**—The filtrate was passed through a Dowex 50W-X12 cation-exchange resin (H^+ form) to remove the excess NTA and then concentrated on a steam bath. On cooling in ice–water pale yellow crystals separated and were collected, recrystallized from hot water, and air dried. Further concentration of the filtrate yielded more of the product.

Anal. Calcd for $H[Rh(NTAH)_2] \cdot 2H_2O$: C, 27.81; H, 3.70; N, 5.41. Found: C, 27.83; H, 3.80; N, 5.77.

(b) *trans*-**Facial 1:2 H[Rh(MIDA)$_2$]·2H$_2$O.**—After removal of the excess MIDA and concentration to a small bulk, ethanol was added to the cooled filtrate. The pale yellow crystals which separated were collected and recrystallized by dissolving in water and adding ethanol to the cooled solution; they were air dried.

Anal. Calcd for $H[Rh(MIDA)_2] \cdot 2H_2O$: C, 27.91; H, 4.45; N, 6.51. Found: C, 27.88; H, 4.62; N, 6.05.

(c) *trans*-**Facial 1:2 H[Rh(IDA)$_2$]·3H$_2$O.**—The excess IDA was removed and the filtrate was concentrated slightly on a steam bath. On cooling in ice-water, white crystals separated and were collected and recrystallized from hot water. This substance proved to be a decomposition product of IDA. Concentration of the filtrate and cooling precipitated a pale yellow solid which was a mixture of the required complex and the decomposition product. Further concentration and cooling gave pale yellow crystals of the *trans* isomer, which was recrystallized from hot water and air dried.

Anal. Calcd for $H[Rh(IDA)_2] \cdot 3H_2O$: C, 22.88; H, 4.08; N, 6.67. Found: C, 22.99; H, 4.34; N, 6.43.

(d) *cis* **1:2 H[Rh(IDA)$_2$]·2H$_2$O.**—The above filtrate was concentrated to a very small bulk and cooled in ice–water; then ethanol was gradually added. The initial yellow precipitate obtained was a mixture of the *cis* and *trans* isomers.

Further addition of a large volume of ethanol then precipitated the bright yellow crystals of the *cis* isomer. It was recrystallized by dissolving in a small quantity of water and adding a large amount of ethanol to the cooled solution. The mixture of *cis* and *trans* isomers also was separated by ion-exchange techniques.[7]

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[15] M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, *Bull. Chem. Soc. Japan*, **31**, 940 (1958).

[16] NTA denotes the trianion $N(CH_2COO)_3^{3-}$ and NTAH the dianion $(HOOCCH_2)N(CH_2COO)_2^{2-}$. MIDA and IDA denote the dianions $CH_3N(CH_2COO)_2^{2-}$ and $HN(CH_2COO)_2^{2-}$, respectively.

[17] J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **35**, 567 (1962).

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

Anal. Calcd for $H[Rh(IDA)_2]\cdot 2H_2O$: C, 23.90; H, 3.76; N, 6.97. Found: C, 23.80; H, 4.13; N, 6.97.

The three pale yellow *trans*-facial complexes are soluble in water while the bright yellow *cis* complex is very soluble.

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

Concentrations in the range 0.1–0.5 *F* for the complexes were used to obtain suitable signal to noise ratios. The chemical shifts for the complexes were essentially independent of concentration provided the solution pH was kept constant. Solution pH was measured using a Leeds and Northrup line-operated pH meter, equipped with miniature electrodes. Because of the use of D_2O as a solvent, the observed pH values should be corrected by +0.40 pH unit to give the true pD value (assuming pure D_2O).[19] This correction was not made because the solvents usually contained appreciable amounts of H_2O. The pH was varied by the addition of anhydrous sodium carbonate and nitric acid. In all cases the spectra were recorded within a few minutes of the initial mixing. The error in the chemical shifts is ±0.01 ppm and in the coupling constants ±0.1 cps.

The infrared spectra for several of the complexes were recorded on a Perkin-Elmer Model 621 double-beam grating instrument using the KBr-disk technique. Visible absorption spectra of the complexes were recorded with a Cary Model 14 spectrophotometer at room temperature (25 ± 1°) using 10^{-2} *F* aqueous solutions in 1-cm cells.

Results

The possible geometrical isomers for the 1:1 Co(III)–NTA complexes and the 1:2 complexes are illustrated in Figure 1. The 1:2 Co(III)–MIDA and –IDA complexes previously have been prepared and characterized.[7] In the present work the analogous Rh(III) complexes have been synthesized as well as the 1:2 NTA complexes of Rh(III) and Co(III). The distribution of *cis*- and *trans*-facial isomers for the 1:2 Rh(III)–IDA complex apparently agrees with that found for the Co(III) complexes (*i.e.*, considerably more of the *trans* isomer than the *cis* is obtained). Also, the much greater solubility of the *cis* isomer is common to both Co(III) and Rh(III).

Efforts to obtain the *trans*-meridional isomer for the 1:2 complexes have not been successful, probably because of the C–N–C angle strain in this configuration as indicated by stereo models. Space-filling models also indicate considerable steric interaction between the N–R groups in the *cis*-facial isomer when R is CH_3 or CH_2COOH. This probably accounts for the failure to obtain any of this isomer in the NTA and MIDA preparations. Isomerization is not observed for the *cis* and *trans* IDA complexes at room temperature.

Attempts to isolate the 1:1 Co(III)– and Rh(III)–MIDA and –IDA complexes have not been made although these undoubtedly exist in solution under favorable conditions of concentration and pH.

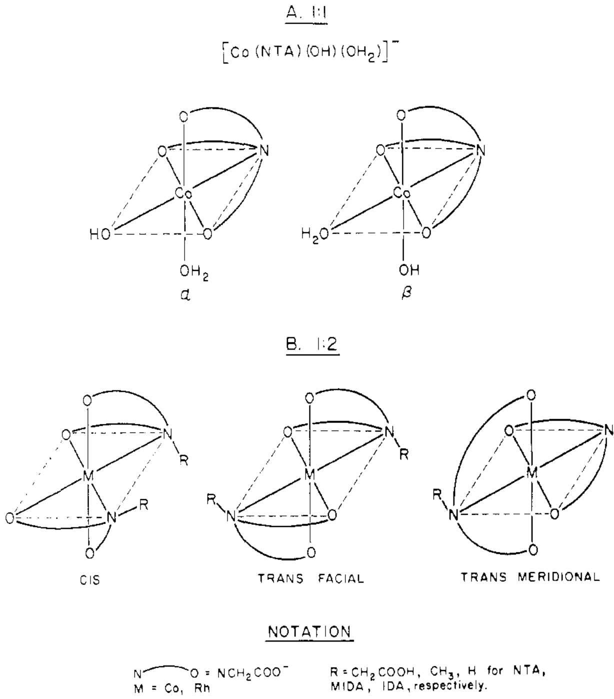

Figure 1.—The possible geometrical isomers for (A) the 1:1 Co(III)–NTA complexes and (B) the 1:2 complexes.

Proton Nmr Spectra.—The proton nmr spectra of the complexes are shown in Figures 2–7, and the spectral parameters for all of the complexes are summarized in Table I. All of the C–H resonances are relatively sharp while those of the N–H protons (Figures 6 and 7) are fairly broad. The spectra of the 1:1 NTA complexes consist of one simple AB pattern and a singlet, with relative intensities of 2:1. When the pH values of solutions of the α and β 1:1 Co(III)–NTA complexes are lowered, the AB pattern of the β complex and the singlets shifts downfield (Figure 2), while the AB pattern of the α complex shifts upfield; at pH 0.5 the spectra of both complexes are identical (Table I). The spectrum of the 1:1 Rh(III)–NTA complex is relatively insensitive to pH variation.

The spectra of the 1:2 Co(III)- and Rh(III)–NTA complexes (Figures 3 and 4) consist of one AB pattern and a singlet (relative intensities, 2:1). When the pH values of the solutions are increased from pH 1 to 6, the singlets shift upfield 0.27 and 0.29 ppm, respectively. In addition, the AB pattern in the spectrum of the Rh(III) complex collapses to a sharp singlet and shifts upfield slightly (Figure 4B); the AB pattern in the spectrum of the Co(III) complex is little affected by the pH variation. Increases in pH above 6 cause no further spectral changes. (The spectra of the mono- and tripotassium salts of 1:2 Co(III)–NTA complexes are identical with those of the acid salt complexes at pH 2 and 6, respectively.) The spectrum of the 1:2 Rh(III)–MIDA complex (Figure 5), which contains one AB pattern and a singlet (relative intensities, 2:1), is unaffected by pH variation in the range pH 0–10.

The spectra of the *trans*-facial and *cis* 1:2 Rh(III)–IDA complexes (Figures 6 and 7) contain one and two

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[19] K. Mikkelsen and S. O. Nielsen, *J. Phys. Chem.*, **64**, 632 (1960).

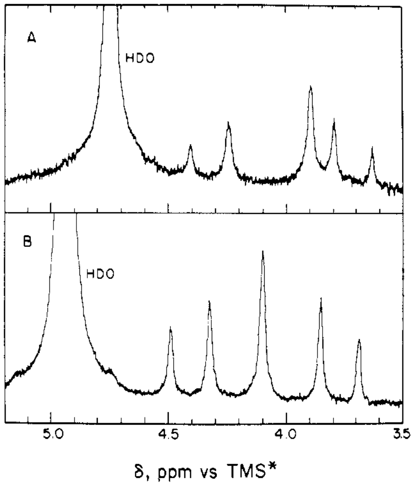

Figure 2.—100-Mc proton nmr spectra of β-K[Co(NTA)(OH)-(OH_2)] at (A) pH 6.0 and (B) pH 0.5.

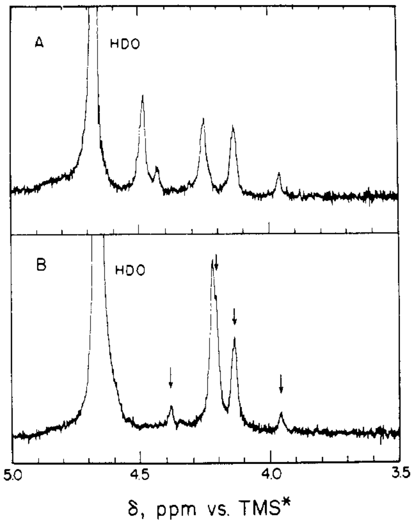

Figure 3.—100-Mc proton nmr spectra of H[Co(NTAH)$_2$] at (A) pH 1.0 and (B) pH 6.0.

(equally intense) AB patterns, respectively, on the high-field side of the HDO resonance and a broad N–H resonance on the low-field side (relative intensities, 4:1). The AB protons are coupled differently to the N–H protons to produce the extra splitting observed. Similar CH_2–NH proton coupling has been reported for the analogous Co(III) complexes[7] and the 1:1 Mo(VI) complex.[6] The N–H protons slowly exchange with the solvent deuterium, and when exchange is complete, after several months at room temperature for the *trans* complex and approximately 8 days at room temperature for the *cis* complex, the spectra simplify to one AB pattern and two AB patterns for the *trans*-facial and *cis* complexes, respectively (Figures 6B and 7B). Increasing the pH values of solutions of the complexes produces more rapid exchange, as expected, but the same spectra are always obtained. When the exchange is incomplete, the spectra are composites of Figures 6A and 6B and Figures 7A and 7B. Isomerization is not observed for the complexes at room temperature.

Infrared Spectra.—To provide additional evidence

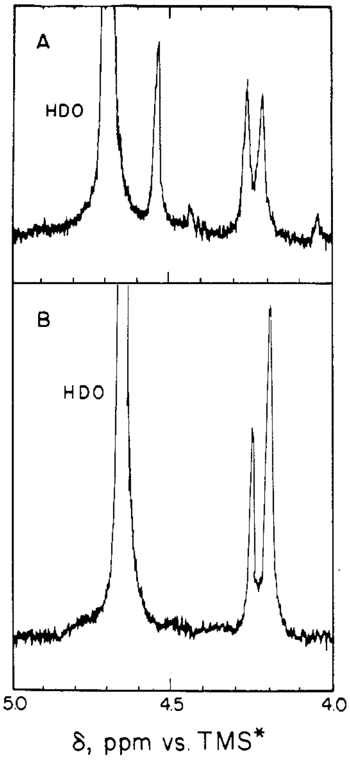

Figure 4.—100-Mc proton nmr spectra of H[Rh(NTAH)$_2$] at (A) pH 0.7 and (B) pH 7.0.

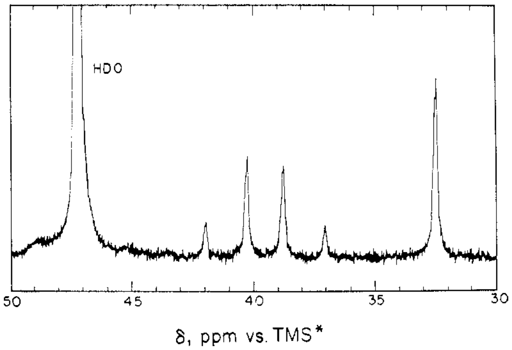

Figure 5.—100-Mc proton nmr spectrum of H[Rh(MIDA)$_2$].

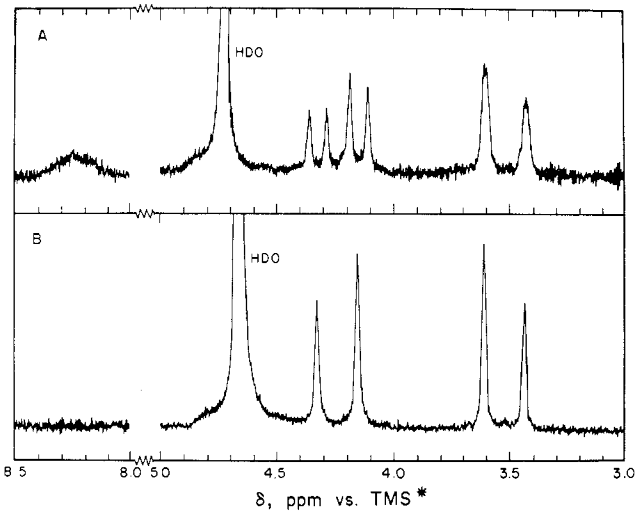

Figure 6.—100-Mc proton nmr spectra of *trans*-H[Rh(IDA)$_2$] (A) before NH exchange and (B) after NH exchange.

TABLE I

CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] FOR COBALT(III) AND RHODIUM(III) COMPLEXES WITH NTA, MIDA, AND IDA

Complex	pH	Acetate protons δ_A	δ_B	$\delta_A - \delta_B$	δ_R[h]	J_{AB}	J_{NH-H_A}	J_{NH-H_B}
α-K[Co(NTA)(OH)(OH_2)]·$2H_2O$	6.0	4.60	3.89	0.71	3.97	16.1		
β-K[Co(NTA)(OH)(OH_2)]·$3H_2O$	6.0	4.34	3.75	0.59	3.91	16.1		
Co(NTA)$(OH_2)_2$[c]	0.5	4.41	3.79	0.62	4.11	16.5		
Rh(NTA)$(OH_2)_2$[c, d]	1.0	4.46	4.11	0.35	4.23	16.3		
trans-H[Co$(NTAH)_2$]·$2H_2O$	1.0	4.34	4.11	0.23	4.51	17.6		
	6.0	4.28	4.11	0.17	4.24	17.5		
trans-H[Rh$(NTAH)_2$]·$2H_2O$	0.7	4.30	4.16	0.14	4.55	17.3		
	7.0	4.19			4.26			
trans-H[Rh$(MIDA)_2$]·$2H_2O$	0.8	4.09	3.82	0.27	3.25	17.1		
trans-H[Rh$(IDA)_2$]·$3H_2O$	1.0[e]	4.25	3.55	0.70	8.25	17.4	7.6	*Ca.* 1.5
	1.0[f]	4.23	3.54	0.69		17.5		
cis-H[Rh$(IDA)_2$]·$2H_2O$	0.5[e,g]				7.72	16.8	6.2	*Ca.* 1.0
						17.9	8.0	*Ca.* 1.0
	0.5[f]	3.98	3.43	0.55		16.8		
		4.28	3.44	0.84		17.9		

[a] In ppm on the low-field side of TMS* (TMS*, zero). [b] In cps. [c] Not isolated. [d] Tentative assignment. [e] Before N–H exchange. [f] After N–H exchange. [g] Spectrum not analyzed completely because of unresolved overlapping B-proton resonances. [h] Chemical shifts for R group: CH_2, CH_3, and H, respectively.

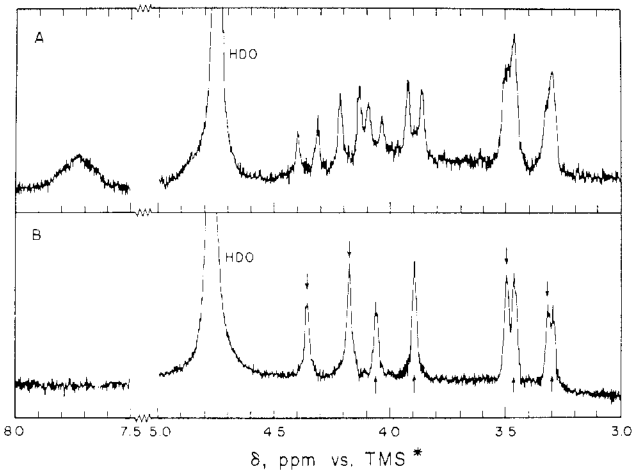

Figure 7.—100-Mc proton nmr spectra of *cis*-H[Rh$(IDA)_2$] (A) before N–H exchange and (B) after N–H exchange.

in support of the nmr data, the infrared spectra of the solid complexes have been measured. The asymmetrical carboxylate stretching frequency has been established as a reliable criterion for distinguishing between protonated carboxylate groups (1700–1750 cm^{-1}) and carboxylate groups which are coordinated to transition metal ions (1600–1650 cm^{-1}) in these types of metal–aminopolycarboxylic acid complexes.[20] Table II gives the assignments for the asymmetrical carboxylate stretching frequency for all of the complexes isolated. Except for the monopotassium and acid salt forms of the 1:2 metal–NTA complexes, all contain only coordinated carboxylate groups. Splitting also is observed in some cases. The monopotassium and acid salt forms of the 1:2 NTA complexes have both coordinated and protonated carboxylate peaks, whose intensities indicate twice as many coordinated carboxylate groups as uncoordinated.

Visible Absorption Spectra.—The absorption spectra of the 1:1 Co(III)–NTA complexes have been measured previously by Mori and co-workers;[15] the results obtained in the present work are identical with theirs and therefore are not included. The spectra of the Rh(III) 1:2 complexes in the visible and near-ultraviolet regions are shown in Figure 8; Table III summarizes the results for all of the 1:2 complexes. For *cis* and *trans* isomers of [Ma_4b_2] type, crystal field theory predicts that the first band splitting should be twice as great in *trans* isomers as in *cis* isomers.[21,22] Generally, for inert Rh(III) complexes of tetragonal symmetry the splitting with *cis* isomers only broadens the band, while with the *trans* isomers the splitting is observed.[23] Also, the theory predicts that the spectrum of the *cis* isomer should be more intense than that of the *trans* isomer;[21] this has been observed for Rh(III) complexes.[23] Figure 8 indicates that the first band of the *trans* complexes is split while that of the *cis* complex is only broadened. Also, the spectrum of the *cis* complex is more intense than those of the *trans* isomers.

TABLE II

INFRARED ASYMMETRICAL CARBOXYLATE STRETCHING FREQUENCIES FOR THE COMPLEXES[a]

Complex	COOM	COOH
α-K[Co(NTA)(OH)(OH_2)]·$2H_2O$	1674 s	
	1636 sh	
	1615 s	
β-K[Co(NTA)(OH)(OH_2)]·$3H_2O$	1634 s	
trans-K_3[Co$(NTA)_2$]·$4H_2O$	1620 s	
	1600 sh	
trans-K[Co$(NTAH)_2$]·$2H_2O$	1617 s	1739 m
trans-H[Co$(NTAH)_2$]·$2H_2O$	1623 s	1731 m
trans-H[Rh$(NTAH)_2$]·$2H_2O$	1615 s	1723 m
trans-H[Rh$(MIDA)_2$]·$2H_2O$	1627 s	
trans-H[Rh$(IDA)_2$]·$3H_2O$	1622 s	
cis-H[Rh$(IDA)_2$]·$2H_2O$	1624 s	
	1584 sh	

[a] Frequencies are given in wave numbers, cm^{-1}. Abbreviations: s, strong; m, medium; sh, shoulder.

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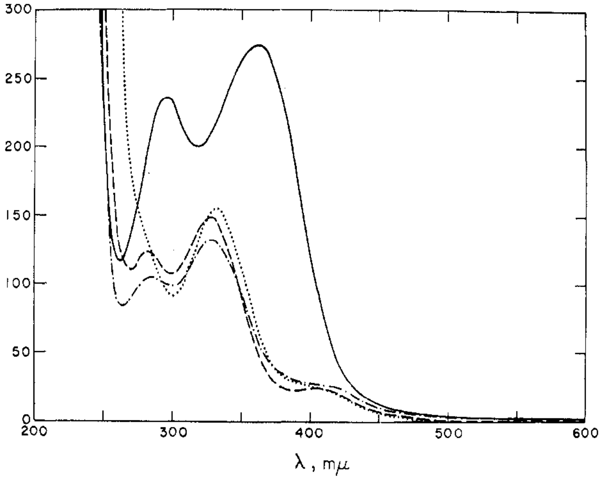

Figure 8.—Absorption spectra of *trans*-H[Rh(NTAH)$_2$] (· · · ·), *trans*-H[Rh(MIDA)$_2$] (– – – –), *trans*-H[Rh(IDA)$_2$] (- · - - ·), and *cis*-H[Rh(IDA)$_2$] (———).

TABLE III

VISIBLE ABSORPTION SPECTRA OF THE 1:2 COMPLEXES[a]

Complex	Band I$_a$	ε	Band I$_b$	ε	Band II	ε
trans-H[Co(NTAH)$_2$]·2H$_2$O	~600[b]	sh (17.5)[b]	516	62.5	~360[b]	sh[c]
trans-H[Rh(NTAH)$_2$]·2H$_2$O	~400[b]	sh (26.5)[b]	332.5	154	~280[b]	sh[c]
trans-H[Rh(MIDA)$_2$]·2H$_2$O	404	25	328	149	282	124
trans-H[Rh(IDA)$_2$]·3H$_2$O	~400[b]	sh (28)[b]	328	132.5	284	104.5
cis-H[Rh(IDA)$_2$]·2H$_2$O	362	274			295	237

[a] Spectral bands given in millimicrons (mμ). [b] Values for shoulders are estimated. [c] Obscured by intense ultraviolet band.

Discussion and Conclusions

1:1 Complexes.—In the proton nmr spectra of the 1:1 complexes the AB patterns are assigned to the nonequivalent coupled acetate protons in the two *trans* (with respect to the carboxylate oxygen atoms) chelate rings and the singlets are assigned to the acetate CH$_2$ groups in the third ring. Stereo models indicate that the two acetate protons in this ring are in identical environments. The α and β forms of the 1:1 Co(III)–NTA complex would be expected to interconvert rapidly in solution at pH 6 because of proton exchange and are expected to give the same spectrum. The observation of different spectra for the α and β complexes at pH 6 suggests that one of them is present as another species. A possible explanation is that one of the complexes is an oxo- or hydroxo-bridged dimer and the other one is the monoaquo species (Figure 1A). The shifts observed when the solutions are made more acidic are probably consistent with the protonation of the coordinated hydroxyl group to form the diaquo complex in one case and the rupture of the oxo or hydroxo bridges giving the diaquo complex in the other case. The spectrum at pH 0.5 is attributed to the presence of the diaquo complex, in which the NTA functions as a tetradentate ligand. If this explanation is correct, the α complex probably is the dimeric form because its lower field AB proton positions (compared with those of the β complex) would result from deshielding associated with the magnetic anisotropy of the metal–oxo or –hydroxo region. Although the pure 1:1 Rh(III)–NTA complex has not been isolated, the similarity of its spectrum to those of the 1:1 Co(III) complexes and its insensitivity to pH variation imply that Rh(III) forms a diaquo 1:1 complex with NTA, in which the latter acts as a tetradentate ligand.

1:2 Complexes.—Recently, Cooke has discussed the nmr spectra expected for the three possible geometrical isomers (Figure 1B) of the 1:2 Co(III)–MIDA and –IDA complexes.[7] In the *trans*-facial isomer the plane of symmetry through the N–Co–N atoms places each acetate CH$_2$ group in an identical environment, which results in only one AB pattern. In both the *cis*- and *trans*-meridional isomers the two CH$_2$ groups in each coordinated ligand molecule are in slightly different environments, and two different (equally intense) AB patterns are expected. Thus, the number of acetate AB patterns observed in the spectrum provides a criterion for distinguishing between the *cis*- and *trans*-facial isomers. The presence of only one AB pattern in the spectra of the present complexes except for one form of the Rh(III)–IDA complex therefore is consistent with the *trans*-facial configuration; the observation of two equally intense AB patterns for one form of the Rh(III)–IDA complex also is consistent with the *cis* configuration. The absorption spectral data provide further support to the nmr assignments; thus, the band intensities and the first band splitting show that one form of the Rh(III)–IDA complex has the *cis* configuration while the other complexes have the *trans* configuration.

The AB patterns in all of the spectra are assigned to the nonequivalent coupled acetate protons in the chelate rings. The singlets observed in the spectra of the NTA complexes are assigned to the free (uncoordinated) acetate groups. That one acetate group in each NTA molecule is free is shown by the upfield shift of the singlet as the pH of the solution is increased (Figures 3 and 4); from pH 1 to 6 the shifts of 0.27 and 0.29 ppm for the Co(III) and Rh(III) complexes, respectively, are characteristic for an acetate CH$_2$ group during the ionization of its carboxylic acid.[24] The presence of one free (protonated) acetate group in each NTA molecule also is indicated by the infrared spectra of the complexes (Table II).

Several explanations are possible for the observed collapse of the AB pattern in the spectrum of the 1:2 Rh(III)–NTA complex when the pH of the solution is increased. (a) The ionization of the carboxylic acids of the uncoordinated acetate groups could change the conformation of the complex enough to place the two acetate protons in each ring in identical environ-

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[24] D. T. Sawyer and B. B. Smith, unpublished work.

ments; they are only in slightly different environments in the protonated complex as shown by the $\delta_A - \delta_B$ value of 0.14 ppm. Although such a collapse is not observed for the analogous Co(III) complex, the $\delta_A - \delta_B$ value decreases from 0.23 to 0.17 ppm when the pH is increased from 1 to 6, indicating that the two protons become more similar. (b) When the carboxylic acid groups ionize, the shielding of the acetate AB protons is expected to be altered because of the change in the magnetic anisotropy and inductive effect of the groups; this could place the two protons in more similar environments. (c) The acetate AB protons could be accidently degenerate. (d) The rhodium(III)-carboxylate bonding could become more labile with increasing pH. However, the latter explanation is considered less likely because an averaging of the three acetate CH_2 groups in each NTA molecule would be expected if increased bond lability occurred, which would result in a coalescence into one line. Averaging of the uncoordinated and coordinated acetate protons is not observed.

The observation of more rapid exchange for the *cis* N-H protons compared with that for the *trans* N-H protons also has been noted for the analogous Co(III)-IDA complexes.[7] In fact, the exchange rates of the Co(III) and Rh(III) complexes appear to be quite similar. The slower exchange of the *trans* isomer may, as Cooke has pointed out,[7] be partly due to its lower solubility. Slower exchange for *trans*-amine protons than for *cis* has been reported previously.[25,26]

The over-all trends in the chemical shifts of the acetate AB protons of the 1:2 Rh(III)-MIDA and -IDA complexes appear to be similar to those found in the corresponding Co(III) complexes[7] and can be explained qualitatively in the same way in terms of the carbon-nitrogen and metal-carboxylate bond anisotropies. The substitution of a CH_2COOH group for a CH_3 group in the NTA complexes deshields both of the acetate protons compared with the MIDA complexes. This is a consequence of the inductive effect and magnetic anisotropy of the acetate group.

The coupling between the AB protons for the 1:1 and 1:2 complexes lies in the range 16.1-17.9 cps and is similar to the couplings found for other metal-aminopolycarboxylic acid complexes.[4-9,12-14] The vicinal coupling between protons attached to carbon atoms has been shown to depend on the dihedral angle between the protons, varying from about 8 cps at an angle of 0°, through a minimum close to 0 at 90°, to a maximum of 9 cps at 180°.[27] The coupling through a tetrahedrally bound nitrogen atom has been found to be similar to that through a carbon atom.[6,7,28] Stereo models show that the $H-N-C-H_A$ (H_A is the lower field of the two AB protons) dihedral angle is approximately 0° and the $H-N-C-H_B$ angle is approximately 110° for both IDA complexes,[29] which would be expected to give couplings of about 8 and 1 cps, respectively. The observed values of 7.6 and 1.5 cps for the *trans*-facial complex and those of 8.0 and 6.2 cps (for the two different A protons) and about 1 cps (for the two different B protons) for the two AB groups in the *cis* complex are therefore close to the theoretical values.

The observation of the AB patterns for all of the complexes confirms that both the metal-nitrogen and metal-carboxylate bonds are nonlabile, as expected. Stereo models indicate that the 1:1 complexes are highly strained owing to the *trans* arrangement of two of the acetate rings. This might be expected to weaken the metal-carboxylate bonding, leading to increased bond lability and an averaging of all of the acetate protons, as suggested previously to explain the observation of simple one-line spectra for 1:1 metal-NTA complexes.[11] However, the presence of the AB patterns firmly establishes the inert nature of the metal-carboxylate bonding. Splitting patterns have not been observed for the 1:2 NTA complexes with Ni(II),[11] Co(II),[11] and Tl(III)[9] (only a single broad line is observed), although an AB pattern is observed for the corresponding MIDA and IDA complexes. For these generally more labile systems the metal-carboxylate bonding in the NTA complexes probably is more labile than it is in the MIDA and IDA complexes.[30]

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[29] The conformational flexibility of the chelate rings allows a variation of about 25° in these values; thus $H-N-C-H_A$ can range from about 0 to 25° and $H-N-C-H_B$ from about 110 to 85°.

[30] The presence of the third, uncoordinated acetate group on each NTA ligand could promote metal-carboxylate bond lability because of the competition between the three acetate groups for the two metal coordination sites. This driving force is absent in the MIDA and IDA complexes.