

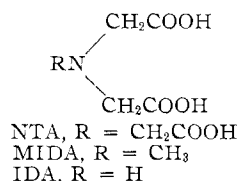
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502**Proton Nuclear Magnetic Resonance Studies of Nitrilotriacetic Acid, N-Methyliminodiacetic Acid, and Iminodiacetic Acid Complexes of Palladium(II)**

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Received February 21, 1968

Several 1:1 and 1:2 (metal ion:ligand) complexes of nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA) with palladium(II) have been synthesized and isolated, and their proton nmr spectra have been studied in aqueous solutions ( $D_2O$ ) as a function of pH and temperature. In the 1:1 complexes MIDA and IDA function as tridentate ligands forming two *trans* (with respect to the two carboxylate oxygen atoms) acetate chelate rings, with the fourth site of the square-planar Pd(II) occupied by a solvent molecule. Their spectra exhibit relatively sharp AB splitting patterns for the ligand acetate protons, which establishes that metal-ligand bonding is nonlabile. In the presence of added ammonia the spectra indicate the formation of several mixed ammine-MIDA and -IDA complexes. The 1:1 NTA complex appears to be a dimer or a polymer in which the ligand acts as a bridge between adjacent metal ions. The 1:2 complexes appear to have the *trans* (with respect to the nitrogen atoms) configuration, with each ligand forming one acetate ring. Infrared spectra of the complexes have been measured to characterize their structures further.

Nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA) form



stable metal complexes in solution which have been studied extensively in terms of their formation constants.<sup>1</sup> NTA forms complexes containing three chelate rings while both MIDA and IDA form complexes with two rings.<sup>2</sup>

Recently, several proton nmr studies of diamagnetic<sup>3-10</sup> and paramagnetic<sup>11,12</sup> metal-NTA, -MIDA, and -IDA complexes in aqueous solutions have been reported. These, and those reported for related complexes,<sup>13-16</sup> have proved useful in elucidating the structural and bonding features of the complexes. The previous work has established that AB splitting patterns are observed for the ligand acetate protons with certain metal ions. Thus, the spectra of the Co(III)<sup>5,8</sup> and Rh(III)<sup>8</sup> complexes with NTA, MIDA, and IDA,

in which the metal-ligand bonding is characteristically nonlabile, exhibit such AB patterns. The spectra of other complexes, in which the metal-ligand bonding is more labile,<sup>3,4,7,10-12</sup> can exhibit AB patterns for the acetate protons in the MIDA and IDA cases, although they are not observed in the corresponding NTA complexes.

In the present paper the synthesis and isolation of several new Pd(II)-NTA, -MIDA, and -IDA complexes and the results of a detailed study of their proton nmr spectra in aqueous solutions ( $D_2O$ ) as a function of pH and temperature are summarized. Pd(II) characteristically forms four-coordinate, square-planar complexes, in which the metal-ligand bonding is expected to be nonlabile. The spectra, which provide insight to the structures of the complexes and their metal-ligand bond dynamics, represent the first proton nmr studies of square-planar metal-NTA, -MIDA, and -IDA complexes. The system is of interest in terms of metal-ligand bond lability because it probably represents an intermediate case between the inert Co(III) and Rh(III) systems and more labile systems.

Two proton nmr studies of Pd(II) and Pt(II) complexes with ethylenediaminetetraacetic acid (EDTA)<sup>15</sup> and amino acids<sup>16</sup> have been discussed recently; their spectra exhibit AB patterns for the acetate protons.

The infrared spectra of the complexes have been measured to obtain further evidence in support of the proposed structures.

**Experimental Section**

**Preparation of the Complexes.**<sup>17</sup> **Materials.**—Pd( $\text{NO}_3$ )<sub>2</sub> was obtained from Alfa Inorganics, Inc. The acid forms of NTA, MIDA, and IDA were obtained from Matheson Coleman and Bell, Aldrich Chemical Co., Inc., and Geigy Chemical Corp., respectively.

The 1:1 complexes were prepared by heating a 50-ml aqueous solution containing 0.002 mol of the ligand and a small excess

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(17) NTA, MIDA, and IDA denote the anions  $\text{N}(\text{CH}_2\text{COO})_3^{3-}$ ,  $\text{CH}_3\text{N}(\text{CH}_2\text{COO})_2^{2-}$ , and  $\text{HN}(\text{CH}_2\text{COO})_2^{2-}$ , respectively; NTAH<sub>2</sub>, MIDA<sub>H</sub>, and IDAH denote the anions  $(\text{HOOCCH}_2)_2\text{N}(\text{CH}_2\text{COO})^-$ ,  $(\text{HOOCCH}_2)\text{N}(\text{CH}_2\text{COO})^-$ , and  $(\text{HOOCCH}_2)\text{NH}(\text{CH}_2\text{COO})^-$ , respectively.

TABLE I  
 CHEMICAL SHIFT<sup>a</sup> AND COUPLING CONSTANT<sup>b</sup> DATA FOR THE COMPLEXES

| Complex                                                   | pH  | Temp,<br>°C | AB acetate protons |            |                       | $\delta_{CH_3}$              | $\delta_{CH_3}$ | $J_{AB}$ |
|-----------------------------------------------------------|-----|-------------|--------------------|------------|-----------------------|------------------------------|-----------------|----------|
|                                                           |     |             | $\delta_A$         | $\delta_B$ | $\delta_A - \delta_B$ |                              |                 |          |
| Pd(MIDA)(OH) <sub>2</sub> ·H <sub>2</sub> O               | 2.0 | 35          | 4.31               | 3.35       | 0.96                  |                              | 2.86            | 16.1     |
| Pd(MIDA)(NH <sub>3</sub> ) <sup>c</sup>                   | 4.0 | 35          | 4.25               | 3.42       | 0.83                  |                              | 2.83            | 16.1     |
| Pd(IDA)(OH) <sub>2</sub> ·H <sub>2</sub> O                | 1.5 | 35          | 3.93               | 3.42       | 0.51                  |                              |                 | 16.0     |
| Pd(IDA)(NH <sub>3</sub> ) <sup>c</sup>                    | 3.0 | 35          | 3.71               | 3.18       | 0.53                  |                              |                 | 16.1     |
| H <sub>n</sub> [Pd(NTA)] <sub>n</sub> ·3nH <sub>2</sub> O | 2.0 | 35          |                    |            |                       | 4.05<br>3.89 sh <sup>e</sup> |                 |          |
| Pd(MIDAH) <sub>2</sub> <sup>d</sup>                       | 2.0 | 0           |                    |            |                       |                              | 2.89            |          |
| Pd(IDAH) <sub>2</sub>                                     | 4.0 | 0           | 3.64               | 3.46       | 0.18                  | 3.27                         |                 | Ca. 16.5 |
|                                                           | 4.0 | 80          | 3.50               | 3.36       | 0.14                  | 3.40                         |                 | Ca. 16.5 |
| Pd(NTAH <sub>2</sub> ) <sub>2</sub>                       | 3.5 | 35          |                    |            |                       | 4.01<br>3.78                 |                 |          |
|                                                           | 3.5 | 80          |                    |            |                       | 3.86                         |                 |          |
|                                                           | 7.0 | 35          |                    |            |                       | 3.73                         |                 |          |

<sup>a</sup> In ppm on the low-field side of TMS\* (TMS\* = zero). <sup>b</sup> In cps. <sup>c</sup> Not isolated. <sup>d</sup> Spectrum not analyzed because of superimposed B proton resonances; acetate lines at 4.18, 4.01, 3.71, 3.55, 3.39, 3.36, 3.23, and 3.20 ppm, and both  $J_{AB} = ca. 16.5$  cps. <sup>e</sup> sh, shoulder.

of palladium nitrate (0.0022 mol) on a steam bath for approximately 30 min. The solutions were filtered and the filtrates concentrated to small volumes (~5 ml). On cooling the NTA and IDA filtrates in an ice-water mixture, orange-brown crystals were deposited; addition of acetone to the filtrates yielded more of the products. The MIDA complex was precipitated by adding acetone to its concentrated filtrate. The complexes were recrystallized from water by the same procedure and vacuum dried to give orange-brown crystals.

The 1:2 complexes were prepared by adding an aqueous solution of palladium nitrate (0.001 mol in 10 ml) to an aqueous solution containing a twofold excess of the ligand (0.002 mol in 40 ml) and warming briefly on the steam bath. The hot solutions were filtered and, on cooling the filtrates, pale yellow NTA and IDA complexes were deposited. They were washed thoroughly with hot water and dried *in vacuo*. The MIDA filtrate was concentrated to a smaller volume (~10 ml) and cooled in an ice-water mixture; the yellow crystals which separated were collected, recrystallized from hot water, and vacuum dried.

*Anal.* Calcd for Pd(MIDA)(OH)<sub>2</sub>·H<sub>2</sub>O: C, 20.89; H, 3.86; N, 4.87. Found: C, 20.33; H, 3.83; N, 5.05. Calcd for Pd(IDA)(OH)<sub>2</sub>·H<sub>2</sub>O: C, 17.56; H, 3.32; N, 5.12. Found: C, 17.25; H, 3.07; N, 5.28. Calcd for H<sub>n</sub>[Pd(NTA)]<sub>n</sub>·3nH<sub>2</sub>O: C, 20.61; H, 3.75; N, 4.01. Found: C, 20.26; H, 3.17; N, 4.58. Calcd for Pd(MIDAH)<sub>2</sub>: C, 30.13; H, 4.05; N, 7.03. Found: C, 30.43; H, 4.20; N, 6.94. Calcd for Pd(IDAH)<sub>2</sub>: C, 25.93; H, 3.27; N, 7.56. Found: C, 25.75; H, 3.53; N, 7.55. Calcd for Pd(NTAH<sub>2</sub>)<sub>2</sub>: C, 29.62; H, 3.31; N, 5.76. Found: C, 29.51; H, 3.51; N, 5.64.

The 1:1 MIDA and NTA and the 1:2 MIDA complexes are soluble in water, while the 1:1 IDA complex is only sparingly soluble, and the 1:2 NTA and IDA complexes are practically insoluble.

**Instrumentation.**—The proton nmr spectra of the complexes in D<sub>2</sub>O solutions were recorded either with a Varian Model A-60 or a Varian Model HA-100 proton nmr spectrometer operating at 35 ± 1°, the temperature within the probe. The spectrometers were equipped with Varian variable-temperature units for the temperature studies. The details of sample preparation, solution pH, and the nmr measurements were the same as described in an earlier paper.<sup>8</sup>

Because of the insolubility of the 1:2 NTA and IDA complexes small amounts of base were added to cause their dissolution before the spectra were measured. The chemical shifts are referred to TMS\* (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt) as zero.

The infrared spectra were measured with a Perkin-Elmer Model 621 double-beam grating instrument, using the KBr-disk technique.

## Results

**Proton Nmr Spectra. 1:1 Complexes.**—The spectral parameters for all of the complexes are summarized in Table I. A representative spectrum of the MIDA complex is illustrated by Figure 1A, which consists of one acetate AB pattern centered at 3.83 ppm and a methyl singlet at 2.86 ppm (relative intensities, 4:3). The spectrum of the IDA complex consists of one AB pattern centered at 3.68 ppm; no N-H resonance or H-N-C-H coupling is observed, presumably because of rapid N-H proton exchange.

When ammonia is gradually added to a solution of the MIDA complex, the spectral changes shown in Figure 1B-D are observed. As the pH increases the original AB pattern and methyl resonance diminish and a new AB pattern and a methyl singlet appear and become more intense; at pH 4 the spectrum consists almost entirely of the new resonances. Further increases in pH cause these resonances to diminish and finally disappear and three further resonances to appear: two relatively sharp methyl singlets (2.78 and 2.83 ppm) and a broad, unresolved acetate band (3.33 ppm). Their appearance is accompanied by the appearance and growth of the free MIDA resonances. At higher pH's (>7) the free MIDA resonances become intense and gradually replace the other three. In addition, the solution changes gradually from orange-yellow at pH 2 to colorless at pH 10. Comparable AB pattern spectral changes are observed when ammonia is added gradually to a solution of the IDA complex.

Similar spectral changes occur when the pH values for solutions of both complexes are increased by adding sodium carbonate, although the B proton resonances in the MIDA case appear to be little affected and all of the resonances are considerably broader than in the ammonia case. Also, a fine brown precipitate is formed in the solutions and redissolves at higher pH (>6).

The A proton resonances in all of the AB patterns are broader than those of the B protons; a similar broaden-

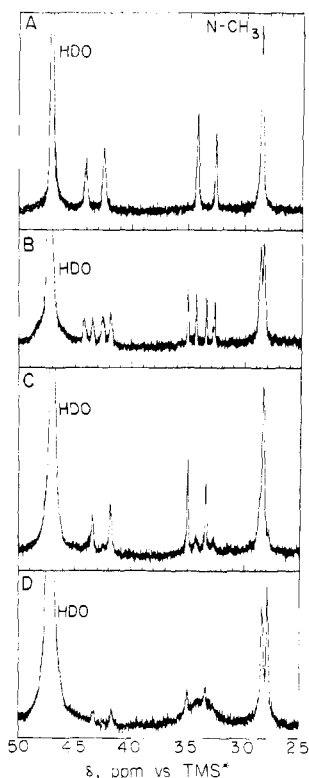


Figure 1.—The 100-Mc proton nmr spectra of the 1:1 MIDA complex: (A) at pH 2; (B) ammonia added, pH 3; (C) ammonia added, pH 4; (D) ammonia added, pH 6.5.

ing has been noted previously for the Ni(II) and Co(II) complexes.<sup>12</sup>

The spectrum of the NTA complex consists of a broad resonance at 4.05 ppm, with a shoulder visible at 3.89 ppm; these represent all of the acetate protons in the complex. At higher temperatures (80°) the resonance becomes narrower while at lower temperatures (0°) it becomes slightly broader. When the pH of the solution (at 35°) is increased, the resonance sharpens and shifts upfield slightly; above pH 7 it separates into two resonances, one of which shifts upfield approximately 0.2 ppm as the pH is increased to pH 10. The addition of ammonia to a solution of the complex causes the broad resonance to sharpen and separate into three fairly sharp lines at higher pH; simultaneously, a free NTA resonance appears and becomes more intense while the other three lines diminish and finally disappear.

**1:2 Complexes.**—The spectrum of the MIDA complex at 35° consists of a relatively sharp methyl singlet at 2.89 ppm, a broad, asymmetrical, partially resolved acetate band at 3.43 ppm, and a weak, broad acetate resonance at 3.95 ppm; the intensity ratio of the combined broad acetate resonances to that of the methyl singlet is approximately 4:3. The spectrum at 0° (Figure 2) exhibits fairly sharp splitting patterns for the acetate protons. At higher temperatures (80°) the acetate resonances merge into one broad, unresolved, symmetrical band whose chemical shift position (3.58 ppm) appears to be a weighted average of the two lines

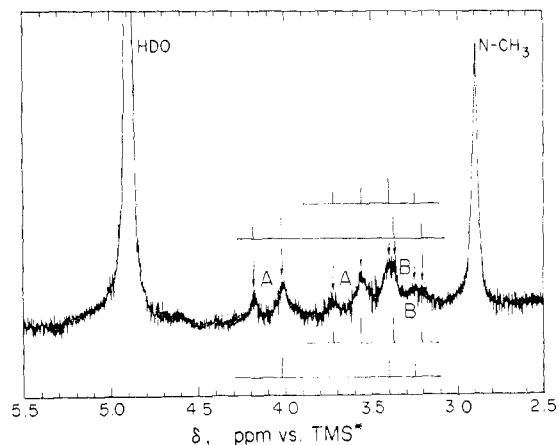


Figure 2.—The 100-Mc proton nmr spectrum of the 1:2 MIDA complex at 0° (pH 2). The two possible combinations of the AB patterns are indicated above and below the spectrum.

at 35°. The methyl resonance appears to be unaffected by the temperature increase.

When the pH of a solution of the complex at 35° is increased, the broad acetate resonances coalesce at approximately pH 6 into two sharper, overlapping lines (3.25 and 3.40 ppm); further increase in pH causes no additional spectral changes. Similar changes occur when ammonia is added to the solution and, in addition, the free MIDA resonance appears and gradually replaces those of the complex; above pH 5 two sharp methyl resonances appear.

The spectrum of the IDA complex at 35° consists of several broad superimposed resonances (Figure 3B). However, at 0–10° it is resolved into an AB pattern centered at 3.55 ppm and a singlet at 3.27 ppm of approximately equal intensities, plus several other weak resonances (Figure 3A). Of these weak resonances at least one AB pattern is visible and additional lines may be obscured by the intense resonances of the major AB pattern and singlet. The spectrum at 75° (Figure 3C) appears to consist mainly of a superimposed AB pattern and a singlet, with the resonances considerably sharper than those at 35°. Also, the AB pattern appears to have shifted upfield, and the singlet downfield, relative to the positions at 0°. Addition of base (sodium carbonate or ammonia) to a solution of the complex at 35° causes a gradual sharpening of the broad band as the pH increases from 4 to 10; also, when ammonia is used, the free IDA resonance appears and gradually replaces those of the complex.

The spectrum of the NTA complex as a function of temperature is illustrated in Figure 4. At 35° two resonances are visible, a broad one at 4.01 ppm plus a relatively sharp one at 3.78 ppm, with approximate relative intensities of 2:1. At 0–10° the sharper line becomes sharper and the broad line broadens. As the temperature is increased, the two lines broaden, coalesce, and then sharpen again (Figure 4B and C). At 80° the spectrum consists of one relatively sharp line, whose chemical shift position is a weighted average of the positions of the two lines at 35°. When the pH of a solution at 35° is increased, the lower field reso-

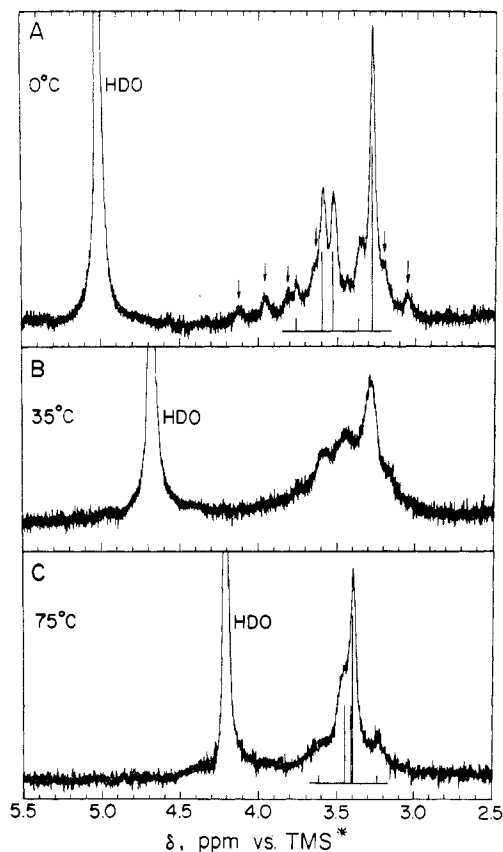


Figure 3.—Temperature dependence of the 100-Mc proton nmr spectrum of the 1:2 IDA complex at pH 4: (A) 0°, where the arrows indicate the resonances of a small amount of a second isomer; (B) 35°; (C) 75°.

nance broadens and merges with the high-field resonance; also, the latter shifts upfield slightly as the pH increases from 3.5 to 6. At pH 6 only one line is observed. The final chemical shift position of the resonance is at a higher field (3.73 ppm) than that in the temperature study (3.86 ppm) because an upfield shift is produced during the ionization of the free carboxylic acid protons as the pH increases from 3.5 to 6. Addition of ammonia to the solution results in closely similar spectral changes, accompanied by the appearance and growth of the free NTA resonance.

**Infrared Spectra.**—The infrared spectra of the complexes have been measured to provide additional evidence in support of the proposed structures. Previous studies have established that the asymmetrical carboxylate stretching frequency is a reliable criterion for distinguishing between carboxylate groups coordinated to transition metal ions (1600–1700  $\text{cm}^{-1}$ ) and protonated carboxylate groups (1700–1750  $\text{cm}^{-1}$ ) in these types of complexes.<sup>18</sup> Values of the asymmetrical carboxylate frequencies are given in Table II for all of the complexes isolated. On the basis of these data all of the 1:1 complexes contain only coordinated carboxylate groups. In the 1:2 complexes both types of carboxylate groups are present; for the MIDA and IDA cases the peak intensities are consistent with equal

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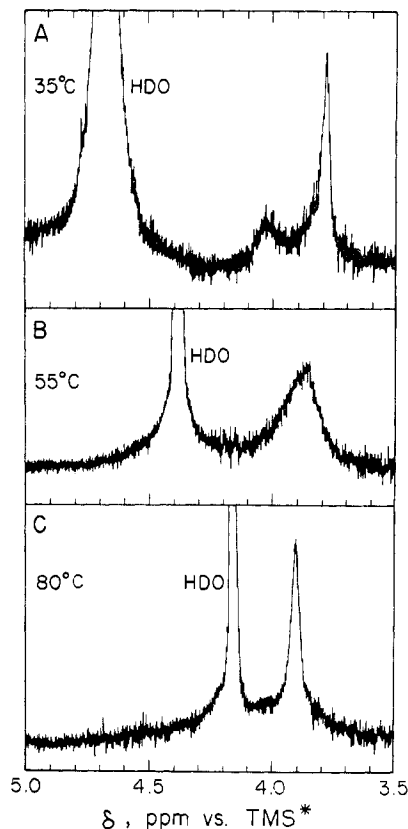


Figure 4.—Temperature dependence of the 100-Mc proton nmr spectrum of the 1:2 NTA complex at pH 3.5: (A) 35°; (B) 55°; (C) 80°.

TABLE II  
INFRARED ASYMMETRICAL CARBOXYLATE STRETCHING  
FREQUENCIES FOR THE COMPLEXES<sup>a</sup>

| Complex                                                   | COOPd           | COOH   |
|-----------------------------------------------------------|-----------------|--------|
| Pd(MIDA)(OH <sub>2</sub> )·H <sub>2</sub> O               | 1605 s          |        |
| Pd(IDA)(OH <sub>2</sub> )·H <sub>2</sub> O                | 1618 s          |        |
| H <sub>n</sub> [Pd(NTA)] <sub>n</sub> ·3nH <sub>2</sub> O | 1622 s          |        |
| Pd(MIDAH) <sub>2</sub>                                    | 1604 s          | 1730 w |
| Pd(IDAH) <sub>2</sub>                                     | 1581 s, 1615 sh | 1726 m |
| Pd(NTAH <sub>2</sub> ) <sub>2</sub>                       | 1580 s, 1629 s  | 1733 s |

<sup>a</sup> Frequencies are given in wave numbers,  $\text{cm}^{-1}$ . Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

numbers of the two types while in the NTA case more protonated than coordinated carboxylate groups are indicated.

### Discussion and Conclusions

**1:1 Complexes.**—In the spectra of the MIDA and IDA complexes the AB patterns are assigned to the two nonequivalent acetate protons in each of the *trans* chelate rings (Figure 5A). Stereo models indicate that there is a plane of symmetry through the N–Pd–OH<sub>2</sub> atoms and that the AB protons in the two rings are in identical environments; also, the *trans* arrangement of the rings involves considerable angle strain. The presence of the relatively sharp AB patterns supports the proposed structures of Figure 5A; it implies also that both the palladium(II)–nitrogen and the palladium(II)–carboxylate bonding are nonlabile.

The spectral changes which accompany the addition

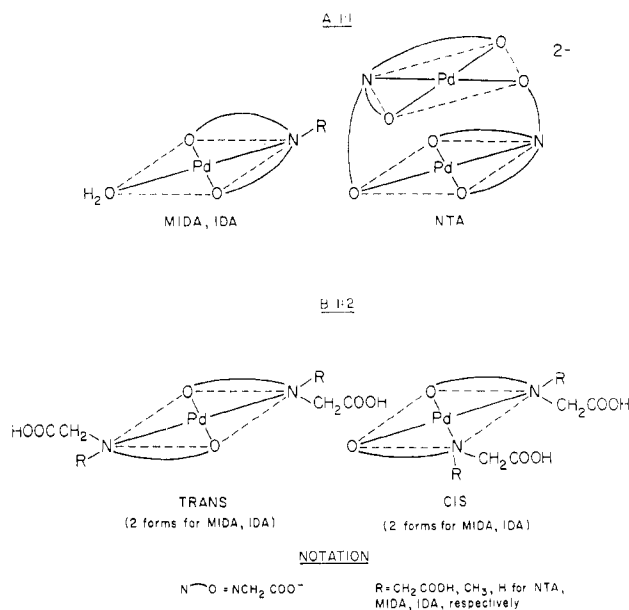
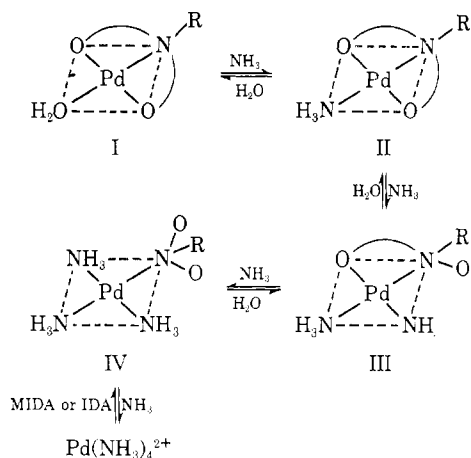


Figure 5.—(A) The geometrical arrangement of the 1:1 MIDA and IDA complexes and a possible structure of the NTA complex; (B) the possible geometrical isomers of the 1:2 complexes.

of ammonia to solutions of the complexes are most plausibly explained by the reaction scheme



where N-O represents NCH<sub>2</sub>COO<sup>-</sup>.

In the spectra the initial formation of the new AB pattern (and methyl singlet in the MIDA case) as ammonia is added to the solutions is attributed to the formation of the monoammine complex II. As the pH increases further, complex III is formed and this gives rise to the broad, unresolved resonance (and one of the methyl singlets in the MIDA case) in both cases. At higher pH values complex IV and the tetraammine, Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, are formed. The above scheme does not include all of the possible species present in the solutions; aquo, hydroxo, and polymeric species may be present also. The observation of the sharp resonances attributed to complex II indicates that the metal-ligand bonding in this complex is nonlabile. The broad resonance in each case may be due to more labile metal-carboxylate bonding in complex III, although intermolecular ligand exchange with other species is possible.

The most probable explanation for the spectral changes observed with increasing pH on addition of sodium carbonate to the solutions is the formation of hydroxo and/or polymeric species; however, the nature of these cannot be determined from the spectra, although similar species to those in the scheme for ammonia may be formed. The solutions of both complexes are fairly acidic (a 0.1 *F* solution has a pH of approximately 2); this implies ready ionization of one of the protons of the coordinated water molecule to form hydroxo and/or polymeric species.

In a recent study of the octahedral *cis* and *trans* 1:2 Co(III)-MIDA and -IDA complexes, Cooke has explained the trends in the chemical shifts of the AB protons in terms of the shielding effects associated with the magnetic anisotropies of the bonds.<sup>5</sup> The shifts for the analogous Rh(III) complexes<sup>8</sup> are in agreement with this explanation. Thus, in the *trans facial* and *trans meridional* isomers, on the basis of shielding effects associated with C-N bond anisotropies, the lower field proton is assigned as the one which is aligned along the C-N bond axis associated with the other CH<sub>2</sub> group; in Figure 6 this is designated as the B proton. The higher field proton is assigned as the one in the region perpendicular to the C-N bond axis (designated the A proton in Figure 6). When the N-H proton is replaced by a methyl group, the effect of introducing an additional anisotropic C-N bond causes the lower field proton to shift upfield and the higher field proton to shift downfield by a somewhat smaller amount. Also, in the mixed *trans meridional* complexes of Co(III) with MIDA, IDA, and diethylenetriamine (dien) the environments of the A and B protons are quite similar.<sup>6</sup>

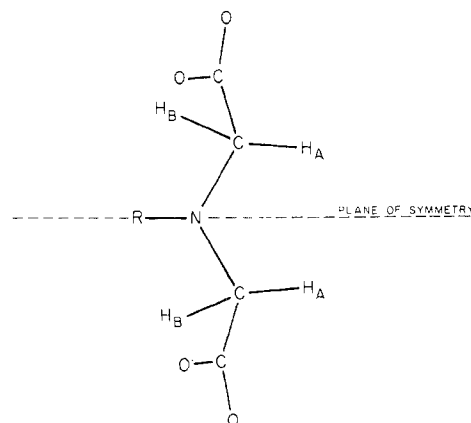


Figure 6.—Representation of the 1:1 MIDA and IDA complexes (pictured looking down the N-Pd bond). The diagram is not drawn to scale.

In the present square-planar complexes the environments of the AB protons in the IDA complex are considerably different ( $\delta_A - \delta_B = 0.51$  ppm); when a methyl group is substituted for the N-H proton, this difference is increased ( $\delta_A - \delta_B = 0.96$  ppm) because the A proton is deshielded considerably (0.38 ppm) and the B proton is shielded slightly (0.07 ppm). The assignment of the A and B protons in these complexes is the opposite of

that given for the similar octahedral ones.<sup>5,8</sup> Thus, in Figure 6  $H_A$  is deshielded and  $H_B$  is shielded; when R is changed from H to  $CH_3$  the introduction of an additional anisotropic bond should deshield  $H_A$  and shield  $H_B$ , in agreement with the observations. The trends in the shifts of the monoamine complexes appear to be similar to those discussed for the monoquo complexes. However, the  $H_B$  proton is less shielded in the MIDA complex than in the IDA complex, in contrast to the monoquo case.

The nmr spectra and the infrared spectrum of the 1:1 NTA complex indicate that all of the acetate groups are coordinated to Pd(II) ions. The most likely explanation (although the product may be a mixture of several isomers or polymers) is that the complex is a dimer or polymer in which the third acetate of NTA is unable to bond to the same Pd(II) and acts as a bridge between the adjacent metal ions. Molecular models indicate that a likely structure is one in which the NTA forms two *trans* acetate rings with one Pd(II) ion (as is found for the MIDA and IDA complexes), with the third acetate group coordinated to an adjacent Pd(II) ion to form a cyclic dimer (Figure 5A). The temperature dependence of the line width and the absence of AB splitting patterns indicate that the palladium(II)-carboxylate bonding probably is labile, allowing an averaging of the environments of the acetate protons.

**1:2 Complexes.**—For the 1:2 complexes *cis* and *trans* configurations are possible as illustrated by Figure 5B. In addition, for the MIDA and IDA complexes both configurations have two possible geometrical forms, one in which the R groups are on the same side of the coordination plane and the other in which they are on opposite sides of the plane. From a consideration of molecular models the *trans* configurations appear to be preferred because the *cis* isomers have considerable steric interaction between the R and free acetate groups when R is  $CH_3$  or  $CH_2COOH$ . In the IDA case the steric interaction is much less severe and some of the *cis* isomer may be formed; the nmr spectra show the presence of a small amount of another species. If this is the *cis* isomer it agrees with the earlier studies of the 1:2 Co(III)<sup>-5</sup> and Rh(III)-IDA<sup>8</sup> complexes, in which both *cis* and *trans* isomers are formed with the latter in preponderance. Alternatively, the second IDA species may be the other form of the *trans* complex. Models indicate that of the two possible *trans* forms the one with the R groups on opposite sides of the coordination plane is favored for steric reasons.

In the nmr spectrum of the MIDA complex (Figure 2) the sharp splitting patterns observed for the acetate protons are tentatively assigned as two equally intense AB patterns, corresponding to the ring and free acetate groups. A complete analysis of the spectrum has not been made because of the superimposition of the resonances of the higher field protons of each AB pair (the B protons). The two possible line assignments are indicated in Figure 2. The intensities of the resonances and the presence of one methyl resonance indi-

cates that the complex is present in one form only; this is concluded to be the *trans* isomer with the methyl groups on opposite sides of the coordination plane. For this configuration models indicate that both types of acetate protons (ring and free) are nonequivalent and should give equally intense AB patterns. Although rotation of the free acetate groups about the C-N bonds is possible, the environments of the two protons do not become identical because of the asymmetry of the nitrogen atoms. The chemical shift between the protons of one of the AB patterns ( $\delta_A - \delta_B$ ) is considerably larger than that for the other pattern; this larger difference probably occurs with the ring acetate protons. Hence, the lower field A proton and one of the two superimposed B protons (Figure 2) tentatively are assigned to the ring protons, and the other A and B protons to the free acetate groups.

In the spectrum of the IDA complex at 0–10° (Figure 3A) the AB pattern and the singlet are assigned tentatively to the ring and free acetate protons, respectively, in the more favored form of the *trans* isomer. The additional weak resonances (indicated by arrows in Figure 3A) probably result from the presence of a small amount (<10%) of another isomer. This minor complex could be the less favored form of the *trans* isomer or one of the forms of the *cis* isomer. No definite conclusions can be made about the nature of this species from the spectra.

The trends in the chemical shifts of the acetate protons in the *trans* IDA and MIDA complexes at 0° are similar to those discussed for the 1:1 complexes. The AB protons in the rings of the IDA complex are in more similar environments than those of the MIDA complex. As in the 1:1 cases, the shift positions can be explained in terms of the shielding associated with the magnetic anisotropy of the C-N bonds and the Pd-O-C plane. In addition, for the 1:2 complexes there is greater freedom of movement within the rings and this motion should average the environments of the two ring protons somewhat. The observation of a singlet for the free acetate protons in the IDA complex is not surprising in view of the quite similar environments of the two ring protons.

In the spectrum of the 1:2 NTA complex at 35° (Figure 4A) the broader lower field resonance is assigned to the ring acetate protons and the high-field resonance to the free acetate protons in the *trans* complex. AB splitting patterns are not expected because models indicate that the two ring protons can easily interchange their positions and thus are in the same averaged environment; the free acetate protons are in identical averaged environments. The broadness of the lower field resonance probably results from conformational motion of the rings and also possibly from some palladium(II)-carboxylate exchange. The coalescence of the resonances which occurs with increasing temperature probably arises from an increase in the palladium(II)-carboxylate bond lability; if this exchange becomes sufficiently rapid, a complete averaging of the environments of the ring and free

acetate protons is expected and this is observed at higher temperatures (80°).

The spectral changes which occur when the pH values of solutions of all of the 1:2 complexes are increased may indicate an increase in the palladium(II)-carboxylate bond labilities (particularly in the NTA case). When ammonia is used as base, mixed ammine-MIDA, -IDA, and -NTA species probably are formed.

The temperature studies of the 1:2 complexes indicate the presence of nonlabile metal-ligand bonding at low temperatures and labile palladium(II)-carboxylate bonding at elevated temperatures. The separate,

sharp free ligand resonances observed when the ligands are added to solutions of the complexes implies also that intermolecular ligand exchange is slow; this presumably is a consequence of the relatively inert palladium(II)-nitrogen bonding. The present work is believed to represent the first good evidence for the presence of both labile and nonlabile bonding present simultaneously in this type of complex.

**Acknowledgment.**—This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-34, Project No. 45.

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## Studies on the Acetatopentaquo-chromium(III) Ion<sup>1</sup>

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Received February 23 1968

The kinetics of the acid-assisted, chromium(II)-catalyzed and vanadium(II)-catalyzed aquations of the acetatopentaquo-chromium(III) ion were investigated, as well as the rate of isotope exchange between this ion and chromium(II). The analysis of the kinetic data for the acid-catalyzed aquation suggests that substantial protonation of the coordinated acetate takes place. At 25°,  $\mu = 4.00$ , the protonation constant is  $0.25 \pm 0.10 F^{-1}$  ( $\Delta H \approx 1$  kcal/mol). The specific rate constant (25°,  $\mu = 4.00$ ) for the aquation of the protonated acetatopentaquo-chromium(III) ion is  $(95 \pm 5) \times 10^{-6} \text{ sec}^{-1}$  ( $\Delta H^\ddagger = 18.6 \pm 1.0$  kcal/mol), and the specific rate constant for the unprotonated ion is  $(0.74 \pm 0.02) \times 10^{-6} \text{ sec}^{-1}$  ( $\Delta H^\ddagger$  varies from 13 to 33 kcal/mol as the temperature varies from 25 to 55°). Chromium(II)-catalyzed aquation occurs predominantly by a path inverse in ( $H^+$ ). With the acid dissociation constant of the acetatopentaquo-chromium(III) ion at 25° and  $\mu = 1.00$  measured as  $(2.9 \pm 0.7) \times 10^{-5} F$  ( $\Delta H = 5.5 \pm 1.5$  kcal/mol), the specific rate constant corresponding to the activated complex of composition  $Cr^{2+} \cdot Cr(OH)OAc^+$  is  $0.85 \pm 0.20 M^{-1} \text{ sec}^{-1}$  ( $\Delta H^\ddagger = 16 \pm 3$  kcal/mol), and that for  $Cr^{2+} \cdot CrOAc^{2+}$  is  $(1.56 \pm 0.08) \times 10^{-3} M^{-1} \text{ sec}^{-1}$  ( $\Delta H^\ddagger = 26.7 \pm 1.5$  kcal/mol). The  $Cr^{2+}$ - $CrOAc^{2+}$  isotope-exchange reaction is inverse first order in acid, implying that the electron transfer proceeds *via* a double bridge; at 25°,  $\mu = 1.00$ ,  $k_{ex} = (5.8 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}$  ( $\Delta H^\ddagger = 18.9 \pm 0.9$  kcal/mol). The vanadium(II)-catalyzed aquation is a complex reaction, being inhibited by acetic acid, chromium(II), and vanadium(III). At high concentrations of vanadium(II) ( $\geq 0.07 F$ ) the rate law is  $-d(CrOAc^{2+})/dt = (V^{2+})(CrOAc^{2+})(k_0 + A'/(H^+))$  with  $k_0 = 0.163 \pm 0.009 M^{-1} \text{ sec}^{-1}$  and  $A' = (6.7 \pm 1.4) \times 10^{-3} \text{ sec}^{-1}$ , at 25°,  $\mu = 1.00$ .

### Introduction

Extensive studies of the inner-sphere electron-transfer reactions  $(NH_3)_5Co^{III}X^{n+} + Cr^{2+} + 5H^+ \rightarrow Cr^{III}X^{n+} + Co^{2+} + 5NH_4^+$ , where X is a carboxylate ion, have led to an interest in the chemistry of chromium(III) carboxylates as the primary products of these reactions. Butler and Taube<sup>2</sup> observed that the initial chromium(III) product of the chromium(II) reduction of the glycolatopentaamminecobalt(III) complex was metastable, decaying to a final product which was assumed to be the glycolatopentaquo-chromium(III) ion. This behavior was taken as evidence for chromium being chelated by glycolate in the activated complex. Huchital and Taube<sup>3</sup> studied the rate of ring closure of the monodentate malonatopentaquo-chromium(III) complex in order to clarify the chemistry of the reduction by chromium(II) of the acid malonatopentaam-

minecobalt(III) ion<sup>4</sup> and the corresponding half-ester complex.<sup>5</sup> Since these two studies were carried only far enough to answer immediate questions, it was felt that a thorough and detailed study of one carboxylato-chromium(III) ion would be a significant contribution to the understanding of inner-sphere reaction mechanisms as well as to the chemistry of chromium complexes in general.

### Experimental Section

**Materials.**—All common laboratory chemicals were of reagent grade. Water was distilled three times (first distillation from alkaline permanganate) in Pyrex equipment. Lithium chloride, bromide, and perchlorate were crystallized at least two times before being used in kinetic runs. Hexaaquo-chromium(III) perchlorate was prepared by the reduction of chromium trioxide with formic acid in the presence of excess perchloric acid,<sup>6</sup> followed by crystallization from dilute perchloric acid and then from water. Vanadyl sulfate was converted to vanadyl perchlorate

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