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Proton Nuclear Magnetic Resonance Studies of Some Nitrilotriacetic Acid, N-Methyliminodiacetic Acid, and Iminodiacetic Acid Complexes of Platinum(II)

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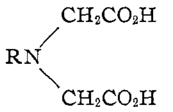
Several 1:1 and 1:2 (metal ion:ligand) complexes of nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA) with platinum(II) have been isolated, and their proton nmr spectra have been studied in D_2O solutions as functions of pH and temperature. The spectra exhibit characteristic AB splitting patterns for the ligand acetate protons, indicating that the metal–ligand bonding is nonlabile (long-lived). In the 1:1 complexes MIDA and IDA are tridentate with a chloride ion occupying the remaining site of the square-planar Pt(II). The ^{195}Pt–^{1}H coupling constants provide insight to the conformation of these complexes. The NTA complex appears to be a polymer in which the ligand bridges adjacent Pt(II) ions. The 1:2 NTA and IDA complexes are assigned the *trans* configuration, with each ligand forming one acetate ring. The 1:2 MIDA complex is not soluble and probably is a polymer. The infrared spectra of the complexes have been measured to characterize their structures further.

Several recent proton nmr studies of diamagnetic[1–10] and paramagnetic[11,12] metal complexes of nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA) have proved useful in elucidating the structural and bonding features of the complexes. These earlier studies and similar studies reported for related complexes (particularly those of ethylenediaminetetraacetic acid (EDTA))[13–20] have established that AB splitting patterns are observed for the ligand acetate protons with certain metal ions. For example, the spectra of the cobalt(III)[4,8] and rhodium(III)[8] complexes with NTA, MIDA, and IDA, in which the metal–ligand bonding (both the metal–nitrogen and metal–oxygen) is characteristically nonlabile (long-lived), exhibit such AB patterns. The spectra of other MIDA and IDA (and EDTA) complexes[1,2,5,6,9–12] which have more labile metal–ligand bonding can exhibit AB patterns, although they are not observed with the corresponding NTA complexes. These NTA complexes may have labile metal–oxygen bonding.[8,12] The spectra of NTA, MIDA, and IDA complexes which have labile metal–ligand bonding do not exhibit AB patterns.[7,21]



NTA, R = CH_2CO_2H
MIDA, R = CH_3
IDA, R = H

The present paper reports the preparation of some 1:1 and 1:2 Pt(II)–NTA, –MIDA, and –IDA complexes and a study of their proton nmr spectra in D_2O solutions as functions of pH (0–10) and temperature (0–100°). The spectra provide information about the structures and stereochemistries of the complexes, as well as an insight into their metal–ligand bond dynamics. The platinum(II) complexes are of interest for comparison with the previously discussed palladium(II) system,[9] in which the spectra indicate increased metal–oxygen bond lability for the 1:2 complexes at higher temperatures. For the Pt(II) complexes the metal–ligand bonding is expected to be nonlabile, and this is confirmed by the present work. Also, use has been made of the additional spectral feature of ^{195}Pt–^{1}H spin coupling (^{195}Pt, $I = {}^{1}/_{2}$; abundance, 33%) to aid in making assignments and to provide information about the preferred conformations of the 1:1 MIDA and IDA complexes. This work represents the first reported synthesis and study of Pt(II)–NTA, –MIDA, and –IDA complexes. In addition to those of the Pd(II) system,[9] proton nmr studies of square-planar Pt(II)[20] and Pd(II)[15] complexes with EDTA and several amino acids have been reported.

The infrared spectra of the solid complexes have been measured (in the 2000–1500-cm^{-1} region) to provide additional information about their structures.

Experimental Section

Preparation of the Complexes.[22] **Materials.**—K_2PtCl_4 and the acid forms of NTA, MIDA, and IDA were obtained commercially.

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[21] B. B. Smith and D. T. Sawyer, unpublished observations.

[22] NTA, MIDA, and IDA denote the anions $N(CH_2CO_2)_3^{3-}$ CH_3N-$(CH_2CO_2)_2^{2-}$, and $HN(CH_2CO_2)_2^{2-}$, respectively; $NTAH_2$ and IDAH denote the anions $(HO_2CCH_2)_2N(CH_2CO_2)^-$ and $(HO_2CCH_2)NH(CH_2CO_2)^-$, respectively.

TABLE I

CHEMICAL SHIFT[a] AND COUPLING CONSTANT[b] DATA FOR THE COMPLEXES OF Pt(II) WITH NTA, MIDA, AND IDA

		Acetate AB protons			δ_{CH_2}				J_{Pt-CH_2}
Complex	pH	δ_A	δ_B	$\delta_A - \delta_B$	or δ_{CH_3}	J_{AB}	J_{Pt-H_A}	J_{Pt-H_B}	or J_{Pt-CH_3}
$H[Pt(MIDA)Cl] \cdot 2HCl$	0.5	4.53	4.08	0.45	3.17	17.1	5.5	33.5	27.1
$K[Pt(IDA)Cl] \cdot 2HCl$	1.0	4.50	3.76	0.74	...	17.5	5.5	35.5	...
1:1 Pt–NTA[c,d]	1.0	4.58	4.44	0.14	4.69	16.5	13.0	37.0	10.5
$H_{2n}[Pt(MIDA)_2]_n$[e]									
$Pt(IDAH)_2$	5.0	3.78	3.42	0.36	...	16.8	43.0[d]	22.0[d]	...
		3.56	3.39	0.17	...	16.7	22.0[d]	18.0[d]	...
$Pt(NTAH_2)_2$[f]	9.0	3.87	3.78	0.09	4.02	15.9	28.0[d]	18.5[d]	26.5[d]

[a] In ppm on the low-field side of TMS* (TMS* = zero). [b] In cps. [c] At 70°. [d] Possible assignment. [e] Insoluble from pH 0 to 10. [f] At 60°.

1:1 Complexes.—The MIDA and IDA complexes were prepared by heating aqueous solutions (100 ml) containing K_2PtCl_4 (0.002 mol) and the appropriate ligand (0.004 mol) on a steam bath for approximately 5 hr. The solutions were than evaporated to small volumes (5–10 ml), filtered, and cooled in ice water. The yellow crystals which separated were collected, recrystallized from small quantities of hot water, washed with small amounts of ice-cold water, and dried *in vacuo* (yields, 50–70%). The MIDA product contained some free ligand (observed in its nmr spectrum) which proved difficult to remove by repeated recrystallization. This was removed by passing a solution of the complex through a Dowex 50W-X4 cation-exchange resin (H^+ form); the solution was then evaporated to dryness in an air stream and finally dried *in vacuo*. Further amounts of the acid-salt complexes were obtained by evaporating the mother liquors to smaller volumes (2–3 ml), collecting the solids which separated, and removing the free ligand impurities with the cation exchanger. *Anal.* Calcd for $H[Pt(MIDA)Cl] \cdot 2HCl$: C, 13.36; H, 2.24; Cl, 23.66. Found: C, 13.26; H, 2.57; Cl, 23.12. Calcd for $K[Pt(IDA)Cl] \cdot 2HCl$: C, 10.15; H, 1.49; Cl, 22.45. Found: C, 10.58; H, 1.42; Cl, 21.78. The complexes are soluble in water giving fairly acidic solutions, indicating that they crystallize as hydrochlorides.

The NTA complex was prepared in a similar way using an equimolar solution of K_2PtCl_4 and the ligand. Elemental analyses for three separate preparations of the complex were not reproducible (C, 10–12%; H, 1.5–2.2%; Cl, 21–26%), although their nmr and infrared spectra were identical. The product probably is a dimer or a polymer hydrochloride; it is soluble in water giving an acidic solution.

1:2 Complexes.—The complexes were prepared by heating aqueous solutions (200 ml) containing K_2PtCl_4 (0.002 mol) and the appropriate ligand (0.008 mol) for several hours (>5) on a steam bath. The volumes of the solutions were maintained approximately constant during the heating by addition of water. The solutions gradually changed from orange to yellow to colorless as the white products separated; they were collected, washed thoroughly with hot water, and vacuum dried (yields, 50–60%). *Anal.* Calcd for $Pt(NTAH_2)_2$: C, 25.05; H, 2.80; Cl, 0.00. Found: C, 25.37; H, 3.16; Cl, 0.26. Calcd for $H_{2n}[Pt(MIDA)_2]_n$: C, 24.64; H, 3.31; Cl, 0.00. Found: C, 24.91; H, 3.07; Cl, 0.89. Calcd for $Pt(IDAH)_2$: C, 20.92; H, 2.63; Cl; 0.00. Found: C, 20.91; H, 2.75; Cl, 0.21. The complexes are practically insoluble in water. However, the NTA and IDA complexes are soluble in the presence of base, permitting nmr studies.

Elemental analyses were carried out by Elek Microanalytical Laboratories, Torrance, Calif.

Instrumentation.—The proton nmr spectra of the complexes in D_2O solutions were measured with a Varian Model HA-100 spectrometer operating at 33°. Some measurements also were carried out using a Varian Model A-60 instrument. Both instruments were equipped with Varian variable-temperature units for the temperature studies. The procedure for sample preparation, measurement of solution pH, and measurement of the spectra was the same as described in an earlier paper.[8] The chemical shifts, which all lie on the low-field side of the reference (internal, *t*-butyl alcohol), are referred to TMS* (3-trimethylsilyl-1-propanesulfonic acid, sodium salt) as zero. Chemical shifts and coupling constants were obtained directly from the precalibrated chart paper. Small amounts of base were added to the 1:2 NTA and IDA complexes to cause dissolution before the spectra were measured. The infrared spectra were recorded on 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 studied are given in Table I. The spectrum of the MIDA complex is shown in Figure 1A; it consists of one acetate AB pattern centered at 4.31 ppm and a methyl singlet at 3.17 ppm. In addition, each resonance has a pair of weak, symmetrically placed satellites due to the $^{195}Pt-^{1}H$ coupling; the assignments for these eight extra resonances (the AB part of an ABX-type splitting pattern) are indicated on the figure. A similar spectrum is obtained for the IDA complex (Figure 1B), except for the absence of the methyl resonance. No N–H resonance or H–N–C–H coupling is observed because of rapid N–H proton exchange. Variation of temperature in the range 0–100° has little effect on the spectra.

When the pH of a solution of the MIDA complex is increased (by addition of potassium carbonate), the resonances diminish in intensity at approximately pH 5 and finally disappear by pH 7–8; simultaneously, many new resonances appear and become more intense. The interpretation of the spectrum is difficult, although the new resonances appear to consist of several superimposed methyl singlets and acetate AB patterns, plus the corresponding ^{195}Pt satellites. Exact assignments are difficult to make; however, at pH 7 at least three distinct methyl singlets appear to be present and these may represent the methyl groups in three different species. Similar AB pattern spectral changes are observed when the pH of a solution of the IDA complex is increased. Also, the solutions of both complexes change from yellow to brown as their pH values are increased from 5 to 10.

The resonances in the spectrum of the NTA complex at 33° are largely obscured by the intense HDO resonance. At higher and lower temperatures the HDO resonance shifts upfield and downfield, respectively,

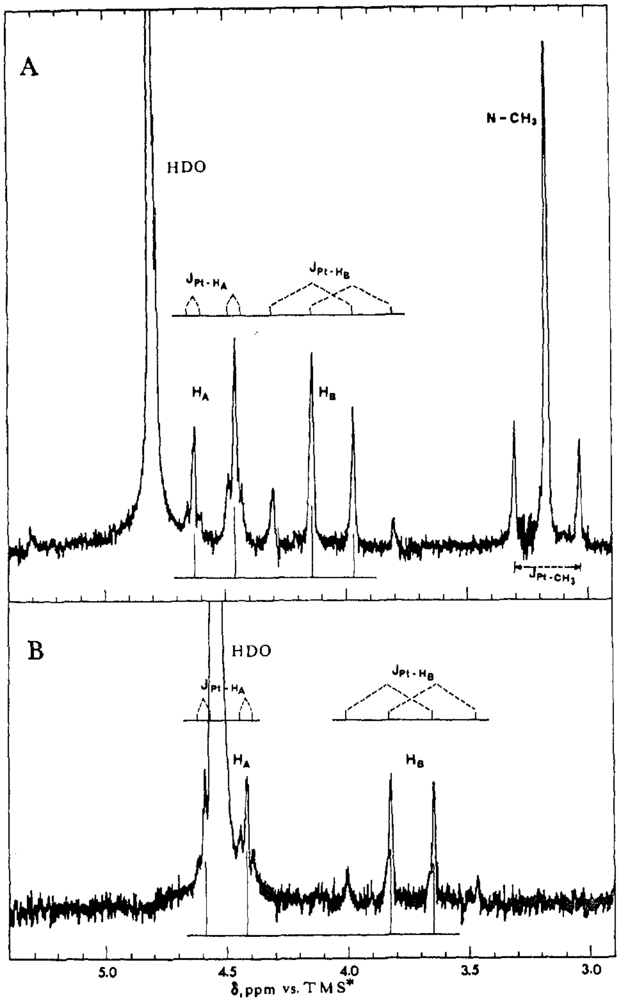

Figure 1.—The 100-Mc proton nmr spectra of (A) the 1:1 MIDA complex at pH 0.5 (20°) and (B) the 1:1 IDA complex at pH 1 (45°).

and all of the resonances become visible. The spectrum at 70° (Figure 2) consists of several sharp resonances; an exact assignment is difficult to make because of the superimposition of some of the resonances. One possible interpretation is that the spectrum consists of an AB pattern centered at 4.51 ppm and a singlet at 4.69 ppm (relative areas, 2:1), plus the corresponding ^{195}Pt satellites. However, other weak resonances appear to be present and these may represent another species.

When the pH of a solution of the complex is increased to 2, the intense resonances diminish while some of the weaker resonances grow in intensity; at higher pH values the original resonances disappear completely and the new resonances become intense. The new spectrum contains one AB pattern and several other superimposed resonances, again making assignments difficult.

1:2 Complexes.—The insolubility of the MIDA complex from pH 0 to 10 did not permit nmr studies. However, at pH >12 the complex dissolved slowly on prolonged heating at approximately 90° with the appearance of a small amount of black precipitate,

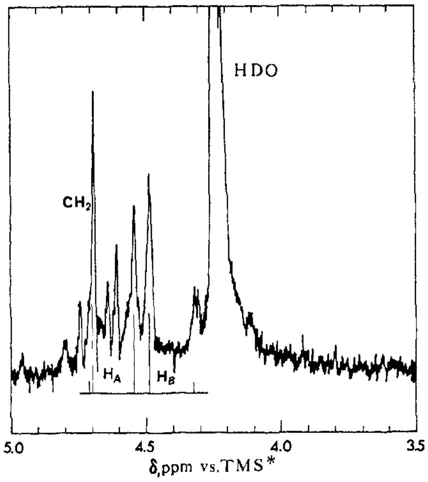

Figure 2.—The 100-Mc proton nmr spectrum of the 1:1 NTA complex at 70° (pH 1).

indicating that at least partial decomposition had occurred. The spectrum of this solution showed two resonances.

The spectrum of the IDA complex at pH 5 (Figure 3A) consists of two equally intense AB patterns centered at 3.60 and 3.48 ppm, together with some weaker resonances. These latter resonances (which are indistinct) probably are ^{195}Pt satellites, although they may represent a small amount of another species. At higher temperatures the resonances show slight shifts (0.01–0.02 ppm) and become a little sharper.

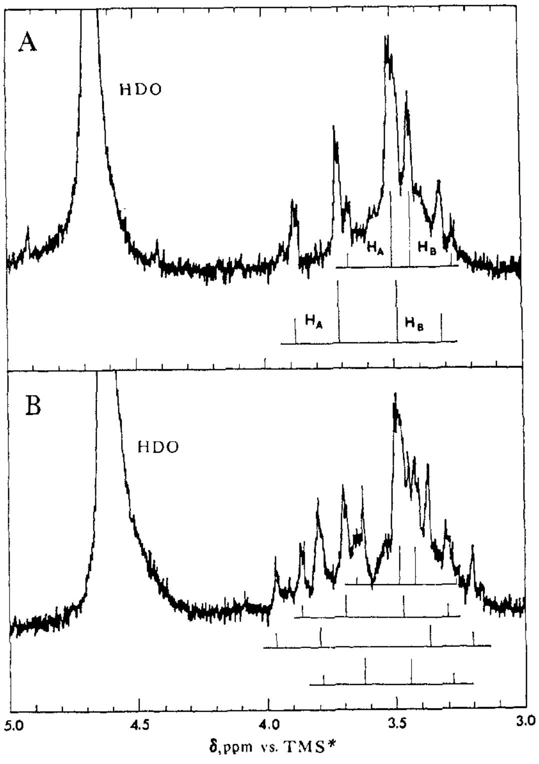

Figure 3.—The 100-Mc proton nmr spectra of the 1:2 IDA complex at (A) pH 5 and (B) pH 6 after the solution is heated at 80° for 1 hr.

The spectrum at 33° is unchanged when the pH of the solution is increased to 9. When a solution at pH 6 is heated to approximately 80°, the resonances appear to diminish in intensity and broaden while new resonances appear and become more intense. The spectrum of this heated solution (Figure 3B at 33°) appears to contain four AB patterns of approximately equal intensities. Further heating of the solution causes no further spectral changes, although the resonances are much broader at higher temperatures. On increasing the pH of this solution to 9, the resonances (at 33°) broaden considerably. Heating this solution of pH 9 to about 75° causes the broad resonance to diminish in intensity and finally disappear completely after approximately 1 hr. This presumably is the result of complete exchange of the C–H protons with deuterium.

The spectrum of the NTA complex (Figure 4) exhibits an AB pattern centered at 3.83 ppm and a singlet at 4.02 ppm (relative areas, 2:1), plus some other weak resonances. With increasing temperature the resonances become sharper. The weak resonances probably are ^{195}Pt satellites, although they are indistinct. A possible assignment for these is indicated in the figure. The spectrum is independent of pH in the range from pH 4 to 10.

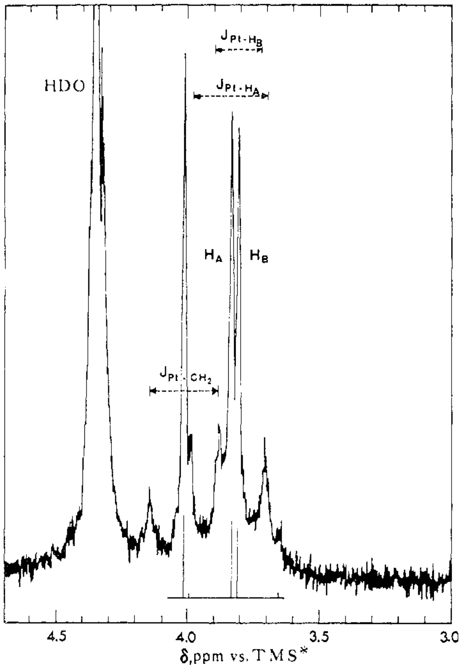

Figure 4.—The 100-Mc proton nmr spectrum of the 1:2 NTA complex at 60° (pH 9).

Infrared Spectra.—Earlier studies have established that the asymmetrical carboxylate stretching frequency is a reliable criterion for distinguishing between coordinated (1600–1700 cm^{-1}) and protonated (1700–1750 cm^{-1}) carboxylate groups in these types of complexes.[23] The values of these frequencies for all of the complexes isolated are summarized in Table II. On the basis of these data all of the complexes except the 1:2 IDA and NTA complexes contain only coordinated carboxylates; the 1:2 IDA and NTA complexes contain both types. The intensities of the frequencies of the latter two complexes are consistent with the presence of one and two protonated carboxylates per ligand, respectively. Thus, these infrared results are consistent with the structures proposed for the complexes.

Table II

Infrared Asymmetrical Carboxylate Stretching Frequencies for the Complexes[a]

Complex	COOPt	COOH
$H[Pt(MIDA)Cl]\cdot 2HCl$	1678 s	
$K[Pt(IDA)Cl]\cdot 2HCl$	1686 s	
	1673 sh	
1:1 Pt-NTA	1667 s	
$H_{2n}[Pt(MIDA)_2]_n$	1702 s	
	1715 sh	
	1643 sh	
$Pt(IDAH)_2$	1596 s	1730 m
$Pt(NTAH_2)_2$	1592 s	1718 s
	1630 sh	1731 sh

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

Discussion and Conclusions

1 : 1 Complexes.—The possible geometrical arrangements for all of the complexes are shown in Figure 5. The AB patterns in the spectra of the MIDA and IDA complexes are assigned to the two nonequivalent acetate protons in the two *trans* (with respect to the carboxylate oxygen atoms) chelate rings (Figure 5A). Stereomodels indicate that the AB protons in the two rings are in identical environments and the observed spectrum therefore supports the proposed structure. The spectra also establish that both the metal–nitrogen and the metal–oxygen bonding are nonlabile.

The spectral changes which occur when the pH values of the solutions are increased from pH 5 to 10 probably are caused by the formation of aquo, hydroxo, and/or polymeric complexes. From the complexity of the spectra several species apparently coexist in this pH range. Also, the solution color changes which occur above pH 7 indicate the formation of other species. No definite conclusions about the nature of the species formed can be made from the spectra.

In a recent study of the octahedral *cis* and *trans* 1:2 Co(III)–MIDA and –IDA complexes Cooke[4] 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 C–N bonds. The shifts for the analogous Rh(III) complexes agree with this explanation.[8] In the square-planar monoaquo and monoammine 1:1 Pd(II)–MIDA and –IDA complexes[9] an assignment of the A and B protons opposite to that in the octahedral complexes has been made on the basis of the shielding effects associated with the C–N bond anisotropies. In the present monochloro Pt(II)–MIDA and –IDA complexes an assign-

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[23] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 205.

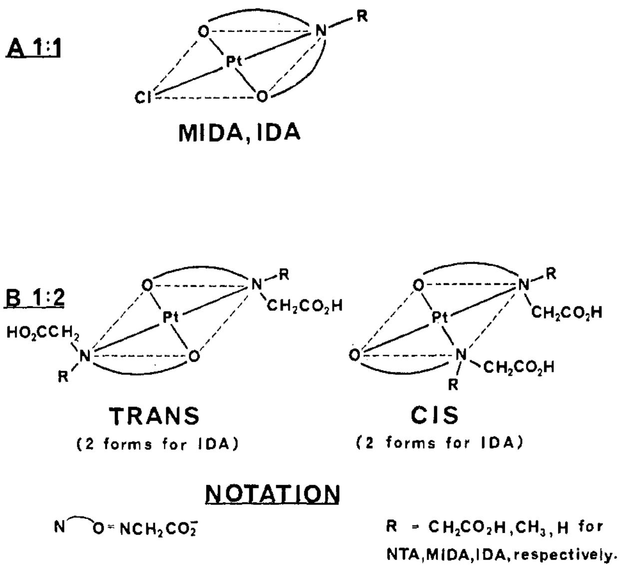

Figure 5.—(A) The geometrical arrangement of the 1:1 MIDA and IDA complexes. (B) The possible geometrical isomers for the 1:2 IDA and NTA complexes.

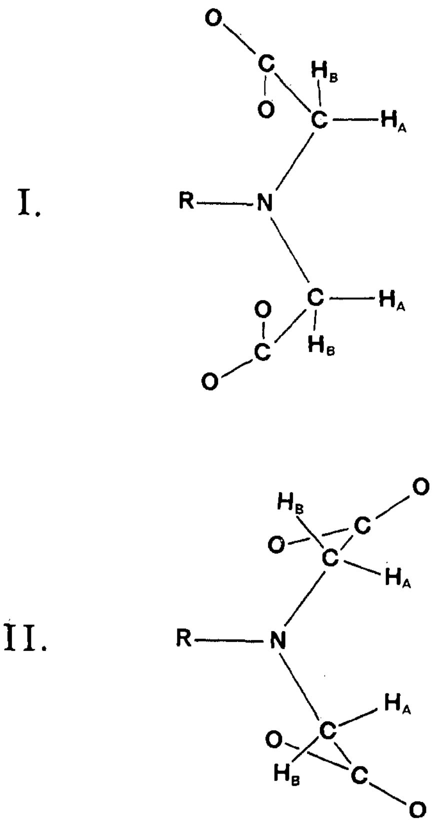

Figure 6.—Representation of the two extreme conformational forms of the 1:1 MIDA and IDA complexes (pictured looking along the N–Pt bond). The diagram is not drawn to scale.

ment of the A and B protons using C–N bond anisotropies does not appear valid because of the similar chemical shift values for the lower field protons (Table I). However, a plausible assignment can be made on the basis of the different coupling of the two ring protons to the ^{195}Pt nucleus. ($J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ is 5.5 cps for the lower field protons in both cases and 33.5 cps and 35.5 cps for the higher field protons in the MIDA and IDA complexes, respectively.) Karplus[24] has shown that the vicinal coupling between protons attached to carbon atoms depends on the dihedral angle (ϕ) between the protons, varying from about 8 cps at an angle of 0°, through a minimum close to 0 cps at 90°, to a maximum of 9 cps at 180°. This dihedral angle dependence has been found to hold for protons coupled to other nuclei (^{19}F, ^{31}P, ^{195}Pt).[25] Thus, by assuming a Karplus type of dependence of the ^{195}Pt–^{1}H coupling on ϕ, assignments of the A and B protons are possible. From a consideration of stereomodels ϕ values for the extreme conformational forms (I and II in Figure 6) of the complexes can be estimated. In form I $\phi_A \approx 80°$ and $\phi_B \approx 155°$, and in form II $\phi_A \approx \phi_B \approx 120°$. The large difference in the values of the ^{195}Pt–^{1}H couplings indicates a type I conformation; the lower field proton is assigned as A and the higher field proton as B in Figure 6. This assignment of the AB protons is the same as that in the similar 1:1 Pd(II) complexes.[9] Further support for this proposed assignment in the MIDA case is provided by molecular models, which indicate substantial steric interference between the methyl protons and the B protons in conformation II; this interference is absent in conformation I. Smaller ^{195}Pt–^{1}H couplings for the lower field protons than for the higher field protons have also been observed in the 1:1 Pt(II)–amino acid complexes.[20]

The environments of the AB protons in the present complexes are considerably different ($\delta_A - \delta_B = 0.45$ and 0.74 ppm for the MIDA and IDA complexes, respectively) which also is true for the 1:1 Pd(II) complexes.[9] However, $\delta_A - \delta_B$ is larger for the MIDA complex than for the IDA complex in the latter case. The chemical shifts in the Pt(II) complexes are at lower fields than those in the Pd(II) complexes; this may be a consequence of the presence of the chloride ion in the former case.

The infrared spectrum of the NTA complex indicates that all of the carboxylate groups are coordinated to the metal ion. This implies that the complex is a polymer in which the ligand bridges adjacent Pt(II) ions. Also, the spectral changes observed with increasing pH and the analysis results indicate that the complex contains Pt–Cl bonds. The exact nature of the complex is difficult to determine from the nmr spectra. However, the presence of sharp splitting patterns at all temperatures establishes that the Pt(II)–oxygen and the Pt(II)–nitrogen bondings are nonlabile, in contrast to the 1:1 and 1:2 Pd(II)–NTA complexes which probably have fairly labile Pd(II)–oxygen bonding at higher temperatures.

1 : 2 Complexes.—The MIDA complex probably is a polymer in view of its infrared spectrum which indicates

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

[25] Reference 20 and references cited therein.

the presence of only coordinated carboxylate groups and its insolubility from pH 0 to 10.

For the IDA and NTA complexes *cis* and *trans* configurations are possible; also, for the IDA complex each configuration has two possible geometrical forms, with the free acetate groups either on the same side or on opposite sides of the coordination plane. Molecular model studies indicate that the *trans* configurations are favored because of steric interaction between the R and free acetate groups, particularly when R is CH_2CO_2H. In the IDA complex the interaction between H and CH_2CO_2H is less, and some of the *cis* isomer may be formed. The models also indicate that of the two geometrical forms the one with the free acetate groups on opposite sides of the coordination plane is favored sterically.

In the nmr spectrum of the IDA complex (Figure 3A) the two acetate AB patterns are assigned to the ring and free acetate protons in the more favored form of the *trans* isomer. The other weak resonances probably are the ^{195}Pt satellites, although a small amount of another isomer may be present; if so, this could be the less favored form of the *trans* isomer or one of the *cis* forms. The AB pattern with the larger $\delta_A - \delta_B$ value may represent the free acetate groups. Previous studies on similar complexes have indicated that the $\delta_A - \delta_B$ values are somewhat larger for free acetate groups than for ring acetate groups in the same complexes.[16,19] The spectrum of the analogous Pd(II) complex exhibits a singlet and an AB pattern for the two types of acetate protons.[9]

The spectral changes which occur when a solution of the complex at pH 6 is heated may have several explanations. (a) An additional isomer may be formed; *i.e.*, isomerization occurs; this could be one of the *cis* forms or the less favored *trans* form. (b) One of the coordinated carboxylate groups may dissociate from the Pt(II) to form a species containing three free acetate groups. The apparent equal intensities of the four visible AB patterns (Figure 3B) favors this latter explanation because models indicate that four AB patterns would be expected for this complex. The severe broadening of the resonances at higher temperatures and as the pH of this solution is increased to 9 may be caused by increased Pt(II)–oxygen bond lability in a complex of type b, although isomerization processes also are possible. The complete disappearance of the resonances at higher temperatures (pH 9) indicates that all of the C–H protons are replaced by deuterium. Exchange of this type has been observed previously in basic solutions of similar complexes.[26]

In the nmr spectrum of the NTA complex (Figure 4) the singlet is assigned to the ring protons and the AB pattern to the free acetate protons in the *trans* isomer. Stereomodels indicate that the two protons in the puckered five-membered ring can interchange their positions by a ring-flipping process, and if this is rapid enough, they are in the same averaged environment; this is consistent with the observation of a singlet. The models also show that the free acetate protons do not completely average their environments, although free rotation about the C–N bond is possible to give an AB pattern with a small $\delta_A - \delta_B$ value. In the spectrum of the corresponding Pd(II) complex the averaging of these free acetate protons is complete.[9] The slight narrowing of the resonances at higher temperatures is the result of a lower solution viscosity rather than of any dramatic changes in the metal–ligand bond dynamics.

The spectra of the IDA and NTA complexes do not indicate the presence of labile Pt(II)–oxygen bonding under the conditions studied (with the possible exception of an IDA species which may be formed by heating a solution of pH 6), in marked contrast to the effects observed with the analogous Pd(II) complexes.[9] This is in agreement with the known rates of substitution reactions of Pt(II) and Pd(II) complexes.[27]

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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