CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Proton Nuclear Magnetic Resonance Studies of Some Ethylenediaminetetraacetic Acid and Ethylenediaminediacetic Acid Complexes of Palladium(II)

BY B. B. SMITH AND DONALD T. SAWYER

Received October 10, 1968

Several complexes of ethylenediaminetetraacetic acid (EDTA) and ethylenediaminediacetic acid (EDDA) with palladium(II) have been prepared and proton nmr spectra of their aqueous (D_2O) solutions have been studied as a function of pH and temperature. In most cases the spectra exhibit AB splitting patterns for the ligand acetate protons. For the $Pd(H_4EDTA)Cl_2$ and $Pd(H_2EDDA)Cl_2$ complexes[1] the spectra indicate that a mixture of bidentate and tridentate species is present in solution. The spectra of the tetradentate $Pd(H_2EDTA)$ complex exhibit AB patterns for the two different types of acetate protons (free and uncomplexed). The tetradentate Pd(EDDA) complex is not sufficiently soluble in D_2O to permit nmr studies. The infrared spectra of the complexes in both solution and solid phases also have been measured; they indicate that the bidentate complexes contain some tridentate species.

Several recent proton nmr studies of metal–ethylenediaminetetraacetic acid (EDTA) complexes have provided useful information about the structural and bonding features of the complexes.[2–8] These earlier studies have established that AB patterns are usually observed for the ligand acetate protons in the complexes if the metal–nitrogen atom bond lifetimes are sufficiently long. For relatively short bond lifetimes AB patterns are not observed.

This paper summarizes the results of a proton nmr study of the square-planar bidentate dichloro and tetradentate Pd(II)–EDTA and Pd(II)–EDDA complexes in aqueous solutions (D_2O) as a function of pH (pH 1–10) and temperature (0–100°). The spectra are interesting because they provide information about the structures of the complexes present in solution and an insight into their metal–ligand bond dynamics. Proton nmr studies of Pd(II)–EDTA complexes have been discussed as a part of an earlier paper.[5] However, the earlier work differed in the important respect that the individual complexes were not first isolated and subsequently studied; solutions were prepared by mixing $PdCl_2$ and EDTA. Because of some ambiguities in the earlier work the complexes have been synthesized and isolated prior to studying their nmr spectra. Differences in the spectra reported earlier and those reported here have been found. In addition, the Pd(II)–EDDA complexes have been isolated and studied for comparison with the EDTA system; Pd(II)–EDDA complexes have not been reported previously.

The Pd(II)–EDTA complexes were first prepared by Busch and Bailar,[9] who assigned them bidentate and tetradentate structures on the basis of analysis, titration, and infrared spectral studies. The structure of the bidentate complex has recently been confirmed by X-ray analysis.[10] Liu[11] has prepared the Pt(II)–EDDA complexes analogous to the Pd(II)–EDDA ones isolated in the present work.

Erickson and his colleagues have recently discussed the proton nmr spectra of the Pt(II)–EDTA complexes[12] and have observed separate resonances for bidentate, tridentate, and tetradentate species in solution. Previous nmr studies of EDDA complexes appear to be limited to those of Legg and Cooke,[13] who isolated *cis*- and *trans*-Co(III)–EDDA complexes with ethylenediamine and ammonia.

Experimental Section

Preparation of the Complexes. Materials.—$PdCl_2$, $Pd(NO_3)_2$, $(NH_4)_2PdCl_4$, H_4EDTA, Na_2H_2EDTA, and H_2EDDA were obtained commercially and were used as supplied for the syntheses of the complexes.

$Pd(H_4EDTA)Cl_2$ and $Pd(H_2EDDA)Cl_2$.—These complexes were prepared by the methods of Busch and Bailar[9] and Liu[11] for the corresponding Pt(II) complexes. The products were washed with water and dried *in vacuo* (yields, 70%). The EDDA compound separates as yellow, water-soluble crystals. *Anal.* Calcd for $Pd(C_{10}H_{16}N_2O_8Cl_2)\cdot 5H_2O$: C, 21.40; H, 4.64; Cl, 12.68. Found: C, 21.58; H, 4.87; Cl, 12.97. Calcd for $Pd(C_6H_{12}N_2O_4Cl_2)$: C, 20.39; H, 3.42; Cl, 20.06. Found: C, 20.59; H, 4.03; Cl, 15.59. The low chlorine value for the EDDA compound indicates that some tridentate species, Pd(HEDDA)Cl, probably is present; this is supported by the infrared spectrum. The analysis results were consistent for several different preparations of the complexes.

Pd(EDDA).—This complex was prepared from the bidentate complex by the procedure given by Liu[11] for the corresponding Pt(II) complex. A bright yellow crystalline solid was obtained which was washed thoroughly with water and dried *in vacuo* (yield, 90%). *Anal.* Calcd for $Pd(C_6H_{10}N_2O_4)\cdot 3H_2O$: C, 21.54; H, 4.82; Cl, 0.00. Found: C, 21.61; H, 4.57; Cl, 0.00. The compound is practically insoluble in water.

$Pd(H_2EDTA)$.—This complex was prepared by heating an

---

[1] H_4EDTA and H_2EDDA denote the fully protonated forms of the ligand; H_3EDTA and HEDDA denote the monoanions and H_2EDTA and EDDA denote the dianions of the ligands.

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

[3] S. I. Chan, R. J. Kula, and D. T. Sawyer, *ibid.*, **86**, 377 (1964).

[4] R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964); **37**, 1236 (1965).

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

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

[7] D. E. Leyden and J. F. Whidby, *Anal. Chim. Acta*, **42**, 271 (1968).

[8] B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **7**, 2020 (1968).

[9] D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **78**, 716 (1956).

[10] D. J. Robinson and C. H. L. Kennard, *Chem. Commun.*, 1236 (1967).

[11] C. F. Liu, *Inorg. Chem.*, **3**, 680 (1964).

[12] L. E. Erickson, J. C. McDonald, J. K. Howie, and R. P. Clow, *J. Am. Chem. Soc.*, **90**, 6371 (1968). We thank these authors for a copy of their manuscript before publication.

[13] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

aqueous solution (50 ml) containing $Pd(NO_3)_2$ (0.01 mol) and Na_2H_2EDTA (0.01 mol) on a steam bath for approximately 20 min. The solution was filtered, evaporated to a smaller volume (20 ml), and cooled in ice. The yellow crystals which separated were collected, recrystallized from hot water, and dried *in vacuo* (yield, 80%). *Anal.* Calcd for $Pd(C_{10}H_{14}N_2O_8)\cdot 5H_2O$: C, 24.68; H, 4.97; Cl, 0.00. Found: C, 24.67; H, 4.83; Cl, 0.00.

Instrumentation.—The proton nmr spectra of the complexes in D_2O solutions were recorded with a Varian Model HA-100 spectrometer (normal probe temperature, 33°), equipped with a Varian variable-temperature unit. Some measurements also were made using a Varian Model A-60 instrument. The details of sample preparation, measurement of solution pH, and measurement of the spectra were the same as described in an earlier paper.[8] The resonances, which all lie on the low-field side of the reference (internal, *t*-butyl alcohol), are referred to TMS* (3-(trimethyl silyl)-1-propanesulfonic acid, sodium salt) as zero. The chemical shifts and coupling constants were obtained directly from the precalibrated chart paper. A Varian Model C-1024 computer of average transients was used in an unsuccessful attempt to obtain spectra of the tetradentate Pd(II)–EDDA complex. The infrared spectra were recorded with a Perkin-Elmer Model 621 double-beam grating instrument, using the KBr-disk technique for the solids and BaF_2 cells for D_2O solutions.

Results

Infrared Spectra.—The asymmetric carboxylate stretching frequency has been established as a reliable criterion for distinguishing between carboxylate groups bound to transition metal ions and protonated carboxylates in these types of complexes;[14] thus, a band at 1600–1700 cm^{-1} is indicative of coordinated carboxylates, and a band at 1700–1750 cm^{-1}, of protonated carboxylates. The absorption frequencies for the four prepared complexes in the solid phase and in D_2O solutions are summarized in Table I; the spectra in the range 2000–1500 cm^{-1} appear to be qualitatively similar for both phases. From these data both $Pd(H_4EDTA)Cl_2$ and $Pd(H_2EDDA)Cl_2$ appear to contain coordinated carboxylates in both phases. The intensities of the COOPd and COOH bands are comparable in both cases. However, the ratio of coordinated to protonated carboxylates cannot be determined from the intensities of the bands; the molar absorptivities for the coordinated carboxylates probably are considerably higher than those of the protonated carboxylates.[14] The presence of both types of bands in the $Pd(H_2EDTA)$ complex (solid and solution) and the absence of COOH bands in the Pd(EDDA) complex (solid) are consistent with tetradentate structures.

Proton Nmr Spectra.—The nmr data for all of the complexes are summarized in Table II.

$Pd(H_4EDTA)Cl_2$.—The spectrum of the complex at 33° (Figure 1A, pH 1) consists of an acetate AB pattern centered at 4.31 ppm (the lowest field resonance is obscured by the intense HDO resonance) and an ethylene resonance at 3.36 ppm (designated BI in the figure), plus two much broader resonances at 3.48 and 4.17 ppm (acetate and ethylene, respectively; designated TRI in the figure.) Below 33° the broad resonances become broader and the sharp ones broaden slightly. At temperatures above 33° the ethylenic resonances appear to coalesce to a singlet and the acetate resonances broaden and coalesce to give a broad asymmetrical resonance pattern underneath the HDO resonance (Figure 1B, 80°). This latter resonance ap-

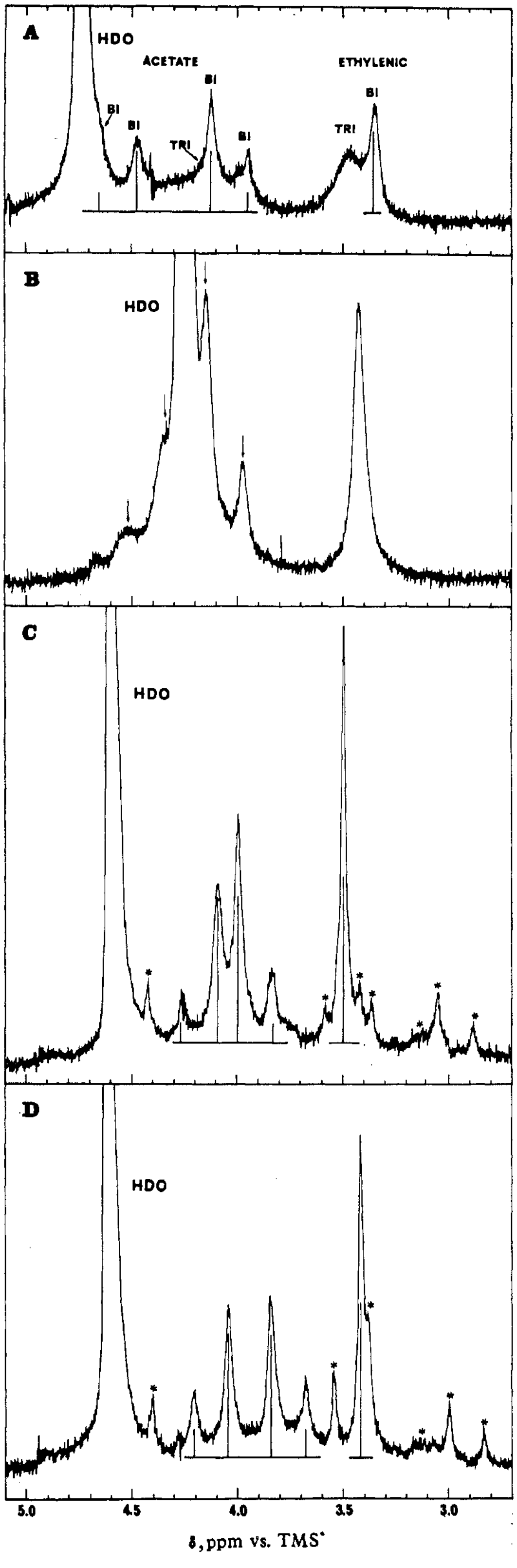

Figure 1.—The 100-Mc proton nmr spectra of $Pd(H_4EDTA)Cl_2$ at (A) pH 1 (33°); (B) pH 1 (80°); (C) pH 3.5 (33°); (D) pH 10 (33°). Tentative assignments are indicated. The asterisks indicate the tetradentate complex.

---

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

Table I

Infrared Asymmetrical Carboxylate Stretching Frequencies for the Complexes[a]

Complex	Solid		D_2O soln	
	COOPd	COOH	COOPd	COOH
$Pd(H_4EDTA)Cl_2$	1623 s	1724 vs	1632 s	1714 vs
$Pd(H_2EDDA)Cl_2$	1622 s	1723 s	1618 s	1710 s
$Pd(H_2EDTA)$	1676 vs 1634 vs	1729 s	1631 vs	1711 s
Pd(EDDA)	1605 vs		b	

[a] Frequencies are given in wave numbers, cm^{-1}. Abbreviations: vs, very strong; s, strong. [b] Practically insoluble.

pears to be an asymmetrical AB pattern (*i.e.*, the two lowest field resonances are considerably broader than the two higher field ones).

Table II

Chemical Shift[a] and Coupling Constant[b] Data for the Pd(II) Complexes with EDTA and EDDA

Complex	pH	Temp, °C	Acetate AB protons				No. of protons	$\delta_{CH_2CH_2}$[c]	J_{AB}
			δ_A	δ_B	$\delta_A - \delta_B$	δ_{CH_2}			
$Pd(H_4EDTA)Cl_2$	1.0	33	4.55	4.07	0.48	...	8	3.36	17.5
	10.0	33	3.78	4.11	0.33	...	8	3.42	16.0
$Pd(H_3EDTA)Cl$	1.0	33	...	...	...	4.17	8	3.48	...
$Pd(H_2EDDA)Cl_2$[d]	1.5	80	3.72	3.58	0.14	...	4	2.89	17.0
			...	...	...	3.81	4	2.93	...
Pd(HEDDA)Cl	4.5	80	3.62	3.35	0.27	...	4	2.85	16.5
			3.82	3.50	0.32	...	4	2.95	16.5
$Pd(H_2EDTA)$	1.8	33	4.57	3.42	1.15	...	4	3.48	16.0[e]
			3.58	3.17	0.41	...	4	...	17.5[f]
Pd(EDDA)[g]	4.0	80	...	...	...	...	...	2.84	...

[a] In ppm on the low-field side of TMS* (TMS* = zero). [b] In cps. [c] Center of ethylenic pattern. [d] Possible assignment. [e] Coordinated acetate groups. [f] Protonated acetate groups. [g] Practically insoluble in D_2O.

Acidification of a solution of the complex at 33° (*i.e.*, pH <1) causes the two broad TRI resonances to diminish and finally disappear completely; below pH 0 the BI resonances become weaker and free EDTA resonances appear and become more intense. When the pH of a solution of the complex (at 33°) is increased (*i.e.*, pH >1), the BI resonances become weaker and finally disappear while the TRI resonances become more intense and sharper; at pH 2 the spectrum contains a symmetrical ethylenic resonance and a broad asymmetrical acetate resonance (relative areas, 1:1). When the temperature of the pH 2 solution is increased, the ethylenic singlet becomes sharper and the acetate resonances appear to sharpen into an asymmetrical AB pattern. Increasing the pH to 3 (33°) causes a further sharpening of all of the resonances (Figure 1C). In addition, other sharp, weak resonances (indicated by asterisks in Figure 1C) become visible. At temperatures above 33° the ethylenic resonance again sharpens and the acetate resonances become a fairly sharp, more symmetrical AB pattern. Further increase in pH to 6 causes the resonances to become still sharper (at 33°); at higher temperatures (pH 6) the AB pattern collapses into a sharp singlet (at approximately 70°). Also, the increase in pH from 1 to 6 (at 33°) causes the acetate resonance (midpoint) to shift upfield by 0.18 ppm and the ethylenic singlet to shift downfield slightly (0.02 ppm). Further increase in pH from 6 to 10 (Figure 1D, 33°) causes the acetate AB pattern chemical shift difference $\delta_A - \delta_B$ between the two protons to increase because the upper field proton shifts upfield considerably; the ethylenic resonance shifts upfield by 0.08 ppm. Above 33° $\delta_A - \delta_B$ decreases and the resonances sharpen. Below 33° the spectra have the same acetate and ethylenic resonances from pH 2 to 10, although they are broadened considerably. The additional weak, sharp resonances (*) which appear at approximately pH 3 shift with increasing pH but are little affected by changes of temperature.

$Pd(H_2EDDA)Cl_2$.—The spectrum of this complex at 33° (Figure 2A, pH 1.5) consists of a broad ethylenic resonance at 2.87 ppm and two broad acetate resonances at 3.59 and 3.85 ppm (ethylenic:acetate relative areas 1:1). At higher temperatures all of the resonances sharpen considerably; at 80° (Figure 2B) the acetate resonances appear to consist of a singlet and an unsymmetrical AB pattern, and the ethylenic resonance consists of two superimposed singlets. At lower temperatures the resonances broaden further, although the one at 3.59 ppm appears to sharpen.

Addition of acid to a solution of the complex at 33° (*i.e.*, pH <1) causes the ethylenic resonance to collapse into an unsymmetrical multiplet pattern, while the acetate AB pattern becomes weaker and shifts downfield slightly (~0.08 ppm); its $\delta_A - \delta_B$ value becomes smaller until it is a singlet. The acetate singlet appears to grow stronger and splits into an AB pattern with a small $\delta_A - \delta_B$ value. Below pH 0 free EDDA resonances also appear.

When the pH of a solution of the complex at 33° is increased, the acetate resonances alter their intensities and shift upfield, while the ethylenic resonances broaden. At higher temperatures (80° at pH 4.5, Figure 2C) the resonances sharpen considerably, and the spectrum contains two ethylenic singlets and apparently two superimposed acetate AB patterns of unequal intensities. At lower temperatures the ethylenic resonance is a broad multiplet and the acetate resonances consist of several superimposed sharp and broad resonances. At pH 7 (33°) all of the resonances are broad; at higher temperatures the solution becomes darker, finally giving a black precipitate due to the decomposition of the species present; at lower temperatures the resonances become sharper than at 33°.

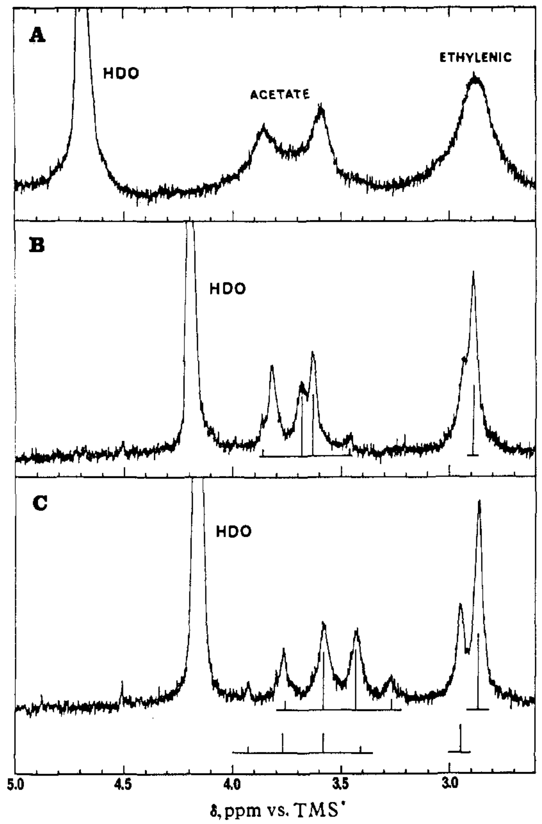

Figure 2.—The 100-Mc proton nmr spectra of $Pd(H_2EDDA)Cl_2$ at (A) pH 1.5 (33°); (B) pH 1.5 (80°); (C) pH 4.5 (80°). Tentative assignments are indicated.

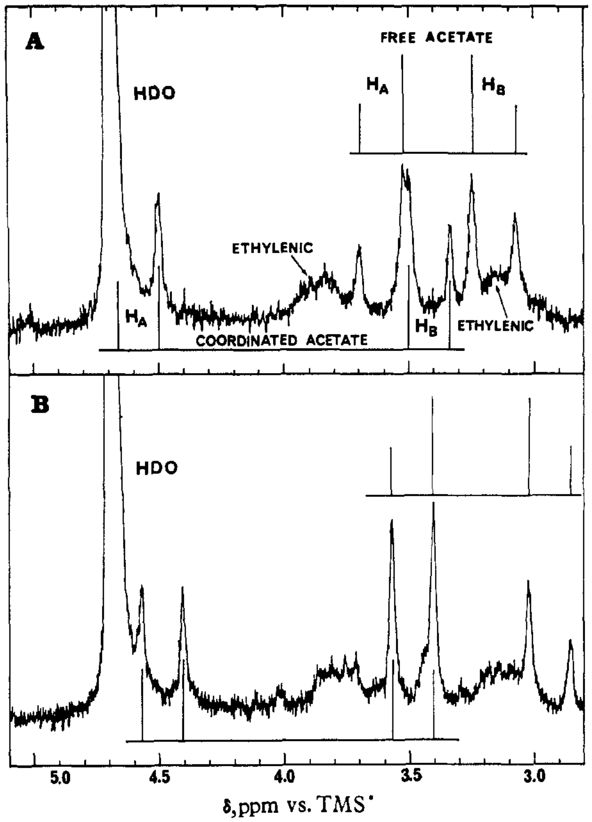

Figure 3.—The 100-Mc proton nmr spectra (33°) of $Pd(H_2EDTA)$ at (A) pH 1.8; (B) pH 10.

Above pH 7 (33°) both the acetate and the ethylenic resonances sharpen, although at pH 10 the ethylenic resonances broaden again. The low-temperature spectra (pH 7–10) show broader superimposed resonances.

$Pd(H_2EDTA)$ and $Pd(EDDA)$.—The spectrum of the EDTA complex at 33° (Figure 3A, pH 1.8) consists of two sharp acetate AB patterns centered at 3.38 and 4.00 ppm (indicated in the figure) and some other broad resonances; these latter resonances appear to be symmetrical about a point at 3.48 ppm and constitute an ethylenic A_2B_2 resonance pattern. When the pH of the solution is increased to 6, six of the acetate resonances shift upfield (designated free H_A and H_B and coordinated H_A in Figure 3) while the remaining two shift downfield slightly (coordinated H_B); the ethylenic A_2B_2 resonance shows a small upfield shift. At the same time two new weak resonances at 3.63 and 3.87 ppm appear. At temperatures above 33° these new resonances become more intense. When the pH of the solution (33°) is increased from pH 6 to 10, the new resonances diminish and become very weak; the other resonances are unaffected by the pH change (Figure 3B). Below 33° all of the resonances broaden slightly in the range pH 1–10.

The EDDA complex apparently is not sufficiently soluble in D_2O or in the presence of base (to pH 10) to allow nmr studies; attempts to obtain a good-quality spectrum using the C-1024 computer were unsuccessful. At 80° a weak ethylenic resonance at 2.84 ppm is clearly visible and other weaker resonances appear to be present. Whether these resonances represent the true tetradentate complex is not certain. The complex dissolves in the presence of acid to give a yellow solution whose spectrum exhibits two ethylenic and two acetate resonances, plus those of free EDDA.

Discussion and Conclusions

The geometrical arrangements for the bidentate, tridentate, and tetradentate complexes are illustrated in Figure 4. For the tetradentate complexes two optical forms (*meso* and racemic) are possible for both complexes because of the asymmetry of the nitrogen atoms. In the bidentate and tridentate cases two forms are possible for the EDDA complexes but only one form is possible for the EDTA complexes.

$Pd(H_4EDTA)Cl_2$ and $Pd(H_2EDDA)Cl_2$.—In the nmr spectrum of $Pd(H_4EDTA)Cl_2$ (Figure 1A) the sharp AB pattern (designated BI) is assigned to the protons in the four free acetate groups of the bidentate complex. Although free rotation about the C–N bonds is possible, the two acetate protons in each of the four groups evidently do not average their environments. The other two broad resonances in the spectrum (designated TRI) are assigned to the ethylenic and acetate resonances of the tridentate complex. An equilibrium of the type

$$\underset{\text{BI}}{Pd(H_4EDTA)Cl_2} \underset{H^+}{\overset{OH^-}{\rightleftarrows}} \underset{\text{TRI}}{Pd(H_3EDTA)Cl} + H^+ + Cl^-$$

probably exists in solution. The disappearance of the broad resonances in acidic solutions and of the sharp

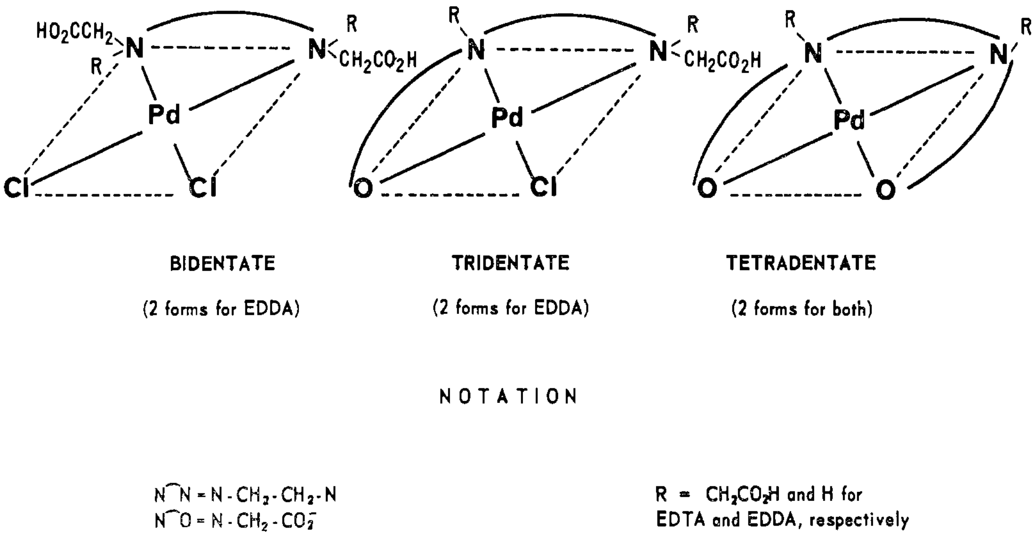

Figure 4.—The geometrical arrangements of the complexes.

resonances at higher pH values supports this conclusion, as does the observation of a strong COOPd band at 1632 cm^{-1} in the solution infrared spectrum. The broadness of the resonances of the tridentate complex probably results from labile palladium(II)–oxygen bonding; model studies indicate that four different acetate AB patterns and an ethylenic ABCD pattern are expected for the complex. Four distinct acetate resonances are observed for the analogous Pt(II) complex.[12] At higher temperatures the bidentate and tridentate complexes appear to average their proton environments; this could result from a rapid equilibrium between the species. In addition high temperatures may favor the bidentate species.

The infrared spectrum of the solid Pd(H$_4$EDTA)Cl$_2$ complex indicates the presence of palladium(II)–carboxylate bonds. Busch and Bailer[9] observed protonated carboxylate bands at 1707 and 1730 cm^{-1} but no coordinated carboxylate band. In the present work a medium-strong band at 1623 cm^{-1} is always present for several different preparations of the complex, which indicates the presence of some tridentate species; in contrast the analytical data indicate a pure bidentate complex.

The nmr spectral changes which occur when the pH of a solution of the complex is increased from 1 to 6 are difficult to explain. The spectra appear to be too simple (one ethylenic singlet and one acetate AB pattern), especially at higher temperatures, to be attributed entirely to the presence of the tridentate species. However, a rapid BI $\rightleftarrows$ TRI equilibrium would simplify the spectra. The sharp, weak resonances which appear at pH 3 and persist at higher pH values appear to be due to the formation of a small amount of the tetradentate complex (the resonances are identical with the spectra of the tetradentate complex). At pH 3 a mixture of the bidentate, tridentate, and tetradentate complexes probably is present. The observation of a sharp symmetrical acetate AB pattern and a sharp ethylenic singlet at higher temperatures (pH 3–6) may indicate that the major species present is bidentate, although a tridentate species would be expected to be favored at higher pH. (How the tridentate complex could give such a simple spectrum is difficult to visualize.) Similarly, the simple spectrum observed from pH 6 to 10 indicates the presence of a bidentate species; however, the AB pattern spectral changes and the shift of the ethylenic resonance which occur in this pH range may indicate replacement of the coordinated chloride ions by hydroxyl groups. The spectral changes with pH and temperature that are observed here for the complex appear to differ from those reported earlier.[5]

The high-temperature spectrum of the EDDA complex (80°, Figure 2B) appears to contain an unequal mixture of two species because of the observation of two different acetate and ethylenic resonances. As in the EDTA case, the spectrum may represent a mixture of bidentate and tridentate species (both species have two possible optical isomers); this is indicated by the presence of a strong COOPd band at 1618 cm^{-1} in the solution infrared spectrum. Unlike the EDTA case, addition of acid or base to the solution of the complex does not cause one of the species to disappear, although in more acidic media the appearance and intensities of the resonances change with the acetate singlet becoming more intense and the acetate AB pattern becoming less intense. The observation of two acetate AB patterns and two ethylenic singlets at temperatures above 33° from pH 2 to 7 (Figure 2C) again indicates that two species are present in this range. If the two species present are bidentate and tridentate, the spectrum of the latter would be expected to be more complex than a simple acetate AB pattern and an ethylenic singlet. An alternative explanation, consistent with the spectra, is that the two species are the two optical isomers (*meso* and racemic) of the bidentate complex. Separate resonances have been observed for the *meso* and racemic isomers in the bidentate complexes of N,N′-dimethylethylenediamine and EDDA with Pt(II).[12,15] However, this explanation is not consistent with the presence of the strong COOPd band in the infrared spectrum.

The nmr spectral changes which occur above pH 7

(15) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **90**, 2293 (1968).

may indicate the formation of new species by replacement of the chloride ions. The broadness of the acetate resonances at 33° from pH 1 to 7 may be due to labile palladium(II)–oxygen bonds in a tridentate species, although other exchange processes also are possible (*e.g.*, ring "flipping," *meso* ⇄ racemic conversion, monomer ⇄ dimer).

Tetradentate Complexes.—In the spectrum of the EDTA complex (Figure 3A) the acetate AB patterns are assigned to the two different types of acetate protons (coordinated and protonated), and the broad symmetrical resonance pattern is assigned to the ethylenic protons. Two forms (racemic and *meso*) of the complex are possible and the spectrum can be interpreted in two ways. (a) Only one of the isomers is present; this could be either the racemic or *meso* form in which the palladium(II)–oxygen bonding is nonlabile. Model studies indicate that the racemic form is the less strained of the two isomers and would be expected to be favored. Busch and Bailar[9] have reported that they were only able to isolate the racemic form. (b) Both isomers may be present and interconverting rapidly (*i.e.*, *meso* ⇄ racemic) so that the observed spectrum is an average of the spectra for the two forms. An interconversion of this type would require labile palladium(II)–oxygen bonding. Racemic and *meso* isomers and their interconversion recently have been observed in the nmr spectra of bidentate complexes of N,N′-dimethylethylenediamine with Pt(II).[15] However, in these cases the interconversion does not require breaking of Pd–O bonds. For the present complex the spectra do not distinguish between the two possible explanations. However, if (b) applies, broadening of the acetate resonances at low temperatures and an averaging of the ethylenic resonances might be expected; these are not observed.

The large upfield shift of the highest field acetate proton when the pH of the solution is increased from 1 to 6 indicates that it is one of the protonated acetate protons; thus, the AB pattern centered at 4.00 ppm is assigned to the free protonated acetate protons and the AB pattern centered at 3.38 ppm is assigned to the coordinated acetate protons. The two additional resonances which appear in the intermediate pH range and disappear at higher pH values probably represent the formation of some tridentate species. The spectra appear to differ from the one reported earlier for the tetradentate complex.[5] The infrared spectrum of the complex supports the conclusions from the nmr measurements.

The insolubility of the EDDA complex does not allow nmr studies. However, its infrared spectrum and the analytical data strongly indicate that it has the proposed tetradentate structure. Its insolubility agrees with that found by Liu[11] for the corresponding Pt(II) complex. The spectrum obtained when the compound is dissolved in acidic media may represent a mixture of tridentate and bidentate complexes.

In summary, the nmr and infrared spectra of the prepared $Pd(H_4EDTA)Cl_2$ and $Pd(H_2EDDA)Cl_2$ complexes indicate that their solutions contain some tridentate species. For the EDTA complex the nmr spectra indicate that bidentate, tridentate, tetradentate, and hydroxy species probably are present at higher pH. For the EDDA complex *meso* and racemic forms may be present and are indicated by the severely broadened resonances below 33°. The nmr spectra of the $Pd(H_2EDTA)$ complex confirm that it has a tetradentate structure and are consistent with the presence of (a) either a *meso* or a racemic form or (b) a rapid *meso* ⇄ racemic equilibrium. Pd(EDDA) appears to have a tetradentate structure but it is not soluble enough for nmr studies.

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