Volume 5
Number 12
December 1, 1966

Inorganic Chemistry

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Proton Nuclear Magnetic Resonance Studies of Ethylenediaminetetraacetic Acid Complexes of Zirconium(IV), Hafnium(IV), and Palladium(II)[1a]

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Received April 28, 1966

The proton nuclear magnetic resonance spectra for the ethylenediaminetetraacetic acid complexes of zirconium(IV), hafnium(IV), and palladium(II) have been studied in aqueous solution. The spectra for these complexes exhibit characteristic multiplet splittings that are indicative of nonlabile bonding between the metal ion and the donor groups of the ligand. The hafnium(IV) and zirconium(IV) EDTA complexes exist as simple 1:1 complexes at low pH, but form hydrolytic species above pH 3.5. The nmr data establish that EDTA is capable of acting as either a bidentate or tetradentate ligand in the case of the palladium(II) complex. Assignment of the resonances due to coordinated and nonbonded acetate groups has been accomplished by comparison of the spectra for the two types of coordination. At high pH incorporation of hydroxyl ion into the coordination sphere of palladium(II) causes EDTA to become a bidentate donor.

Proton nmr studies have proven useful for elucidating the protonation sites of ethylenediaminetetraacetic acid (EDTA)[2] and related ligands,[3,4] for determining the nature of the metal–ligand equilibria for EDTA complexes,[2] and for investigating the metal–ligand lability and structures of EDTA and related complexes.[5-7] For those EDTA complexes where the metal–ligand bonding is relatively nonlabile an AB splitting pattern has been observed for the methylenic protons of the ligand. The nonequivalency of these protons has been attributed to inert metal–nitrogen bonding by Day and Reilley[6] and to both inert metal–nitrogen and metal–carboxylate bonding in the case of molybdenum(VI)–EDTA.[5]

Because the EDTA complexes of zirconium(IV), hafnium(IV), and palladium(II) can be expected to have relatively inert bonding, the nature of their proton nmr spectra is of interest, especially in terms of AB splitting patterns. Both zirconium(IV) and hafnium(IV) represent more complicated metal–EDTA systems than have previously been studied, and their high oxidation states and strong affinity for oxygen provide differences which affect the electronic environment of the ligand protons.

The palladium(II)–EDTA complex provides an interesting system for correlating the proton nmr spectra with the coordination structure. Because palladium(II) forms four-coordinate, square-planar bonding, analysis of the nmr spectra for its EDTA complexes provides a means for interpreting more complicated EDTA systems such as molybdenum(VI)[5] and cobalt(III).[6]

A final reason for studying these three additional metal–EDTA systems has been to complete a general nmr study of diamagnetic metal–EDTA complexes. The present discussion summarizes the results of a detailed nmr study of the EDTA complexes of zirconium(IV), hafnium(IV), and palladium(II) as a function of mole ratio of metal to ligand and as a function of solution pH. Certain generalizations have proven possible regarding the relation between the nmr spectra and the structure and lability of EDTA complexes.

Experimental Section

Equipment.—The 60-Mc proton nuclear magnetic resonance spectra were recorded on a Varian Model A-60 high-resolution spectrometer. Temperature of the probe was controlled to 38 ± 1°. The 100-Mc spectra of the palladium(II)- and hafnium(IV)–EDTA complexes were recorded on a Varian Model HA-100 spectrometer at Varian Associates, Palo Alto, Calif. *t*-Butyl alcohol (TBA) was used as an internal standard for all chemical shift measurements. The resonance for this material is 1.233 ppm downfield from 3-(trimethyl silyl)-1-propanesulfonic acid, sodium salt (TMS*), and the reported resonances can be converted to this reference by adding the difference. The TBA refer-

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(1) (a) Presented before the Western Regional Meeting of the American Chemical Society, Los Angeles, Calif. (b) Taken in part from a thesis submitted by Y. O. Aochi for the degree, Master of Science, to the faculty of the University of California, Riverside, Calif., Aug 1965.

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

(3) R. J. Kula and D. T. Sawyer, *Inorg. Chem.*, **3**, 458 (1964).

(4) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).

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

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

(7) R. J. Day and C. N. Reilley, *ibid.*, **37**, 1326 (1965).

ence has the advantage of a constant chemical shift, independent of solution pH and composition, which is close to the chemical shifts for the protons being studied. This permitted smaller and more sensitive sweep widths than would have been possible by using TMS*. The TBA was added to each solution in comparable concentration to the complex being studied before adjusting the pH. Both the 60- and 100-Mc spectra were scanned at a rate of 1 cps.

The pH of the sample solutions was measured by means of a Leeds and Northrup line-operated pH meter. Miniature pH electrodes were used to enable measurement of small volumes of solution.

Reagents.—Ethylenediaminetetraacetic acid (J. T. Baker Chemical Co.) was used for all solution preparation; this material had an assay of 100.0% and was used without purification. Adjustment of solution pH was accomplished with potassium hydroxide, ammonium hydroxide, or nitric acid. The zirconium(IV) and hafnium(IV) solutions were prepared from zirconium sulfate and hafnium oxychloride, respectively; these materials were obtained from Alfa Inorganics, Inc. Solutions of palladium(II) were prepared from reagent grade palladium chloride obtained from Englehard Industries, Inc. As a check on possible impurities in this material, solutions of palladium(II) also were prepared from Johnson-Matthey Specpure ammonium chloropalladite. Deuterium oxide (Volk Inc., assay 99.77%) was used as a solvent for all solutions to minimize distortion of the complex resonances near the HDO resonance. Attempts to reduce the size of the HDO resonance by recrystallization of EDTA in deuterium oxide resulted in little improvement. Considering the use of D_2O, a more valid measure of the acidity of the sample solutions could be obtained by use of the equation given by Mikkelson and Nielson[8]

$$\text{pD} = \text{meter reading} + 0.40$$

However, because the concentration of H_2O varied from solution to solution and because of the change in temperature for the sample solution, the actual meter readings were used without correction.

Solutions of zirconium(IV)-EDTA and hafnium(IV)-EDTA were prepared by stirring the metal salt and EDTA in acidified deuterium oxide and slowly adding concentrated ammonium hydroxide until the solid material dissolved. The difficulty of dissolving the hafnium(IV) complex was overcome by using a slight excess of EDTA beyond the stoichiometric amount. The maximum concentration obtainable for the zirconium(IV) complex was approximately 0.3 *F*. With the hafnium(IV) complex, concentrations as high as 0.5 *F* were possible through the use of an excess of EDTA. Solutions of palladium(II) were prepared by the addition of a stoichiometric amount of palladium chloride to a solution of EDTA in deuterium oxide. The mixture was heated and stirred until the solid dissolved giving a dark red solution. For these conditions the resulting complex has two of the four donor sites filled by chloride ions with the other two being satisfied by the two nitrogens of the EDTA ligand. The final concentration of the complex was 0.5 *F*.

The palladium(II)-EDTA complex with four-coordinate bonding by the EDTA was prepared in solution by the procedure outlined by Busch and Bailar.[9] This consisted of adding an amount of silver nitrate equivalent to the chloride content of the palladium-EDTA complex solution. After addition the solution was stirred until the precipitated silver chloride had coagulated and then filtered through a fine porosity fritted glass filter.

Results and Discussion

Zirconium(IV)- and Hafnium(IV)-EDTA Complexes.—The nmr spectra for the 1:1 solutions of zirconium(IV)-EDTA and hafnium(IV)-EDTA as a function of solution are qualitatively similar. Both systems exhibit extensive changes over a relatively small pH range.

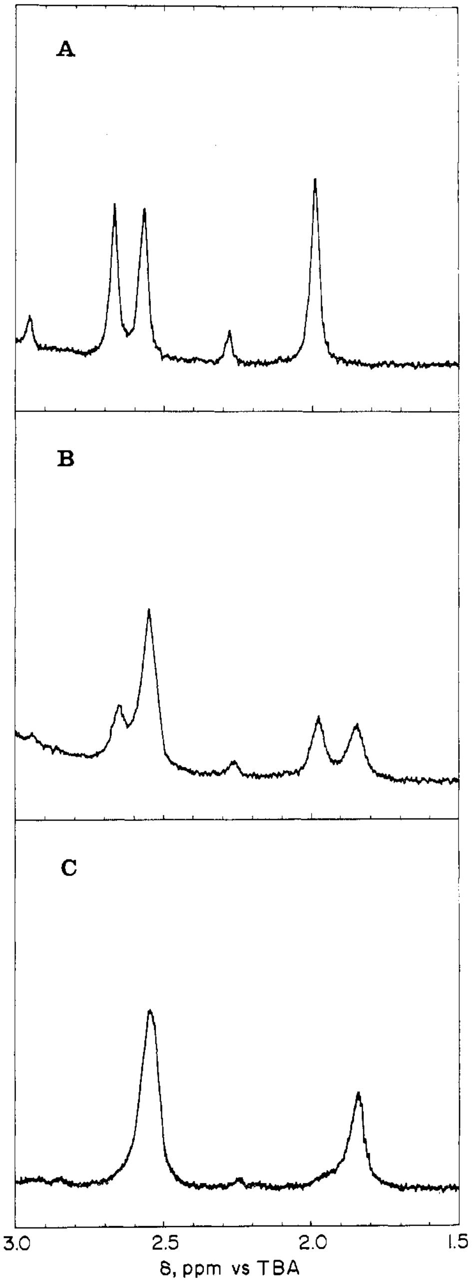

Figure 1.—Proton nmr spectra for zirconium(IV)-EDTA: curve A, pH 3.5; curve B, pH 4.5; curve C, pH 5.5; concentration of 1:1 metal complex, 0.5 *F*.

The spectrum at pH 3.5 for zirconium-EDTA is shown in Figure 1A and indicates a simple AB quartet centered at 2.61 ppm with a single ethylenic resonance upfield at 1.99 ppm. The quartet is similar to the quartets observed for the molybdenum(VI)- and cobalt(III)-EDTA complexes[5,6] that have been attributed to the nonequivalency of the two protons for each of the four methylene groups of the EDTA ligand. Coupling constants for such quartets are evaluated by measuring the distance between an outer satellite and the adjacent major branch of the quartet. The chemical shift difference, $\delta_A - \delta_B$, can be calculated by taking the geometric difference between the distance from the first to the third peaks of the quartet and the coupling

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

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

constant.[10] For the quartet in Figure 1A the coupling constant is 17.1 cps and the chemical shift difference is 0.257 ppm. As the pH is increased above pH 3.5 the central peaks of the quartet become unsymmetrical and at the same time another resonance appears approximately 0.12 ppm upfield from the original ethylenic resonance. This variation at higher pH values is illustrated by Figure 1B and 1C. At pH 5.0 the original quartet and ethylenic resonance are no longer present. The spectrum now consists of a multiplet with a broad central peak at 2.55 ppm and a single resonance upfield at 1.87 ppm for the ethylenic resonance. The smaller peaks of the multiplet are separated from the central peak by approximately 18 cps, which is slightly larger than the coupling constant for the original quartet. The low-intensity peaks of the multiplet no longer are observed when the solution has been adjusted to pH 8, and another set of resonances arising from uncomplexed EDTA appears above pH 9.

The necessity of adding excess EDTA to obtain adequate concentrations of the hafnium(IV)–EDTA complex has resulted in somewhat complicated spectra. Because the resonances for the methylenic protons of uncomplexed EDTA coincide with one of the peaks of the methylenic quartet for the complex, the calculation of values for the chemical shift difference is difficult. Hence, this quantity has been calculated by using the coupling constant to obtain a measure of the separation for the central peaks of the quartet; this approach gives a constant value of 0.277 ppm for the chemical shift difference. Over the pH range for which the quartet can be observed this value does not change and is essentially the same as that observed for the zirconium complex (the quartet collapses above pH 4).

As the pH of the solution containing the hafnium complex is increased the same pattern of asymmetry that is observed for the zirconium system is observed. However, in the case of the hafnium complex the low-intensity resonances which are symmetrical about the broad resonance at 2.55 ppm are more pronounced and persist even above pH 9. When solutions containing two EDTA ligands per hafnium(IV) are prepared the same general spectrum as observed for the 1:1 solution is observed with two additional resonances appearing for uncomplexed EDTA. With the 1:2 solution the quartet collapses at a lower pH because of the increased lability of the chelate brought about by the excess ligand. The uncomplexed EDTA resonances remain separated from the resonances for the coordinated EDTA over the entire pH range studied.

To facilitate the interpretation of the 60-Mc spectra of hafnium–EDTA and zirconium–EDTA, 100-Mc spectra of the hafnium complex have been recorded. Figure 2 illustrates both the 60- and the 100-Mc spectra at pH 6.8; resonances for uncomplexed EDTA are indicated by arrows in the figures. Only a single ethylenic resonance and a multiplet with a broad central peak are observed for the complex in the 60-Mc spectrum. For the 100-Mc spectrum the broad central peak of the multiplet is split into two peaks giving a quartet with J equal to 17.1 cps and $\delta_A - \delta_B$ equal to 0.128 ppm. Using this value of $\delta_A - \delta_B$ the separation of the central peaks of the quartet at 60 Mc is calculated to be approximately 1.7 cps. Considering the broadness of the resonances observed for these complexes in aqueous solution, the lack of resolution for the splitting at 60 Mc is reasonable.

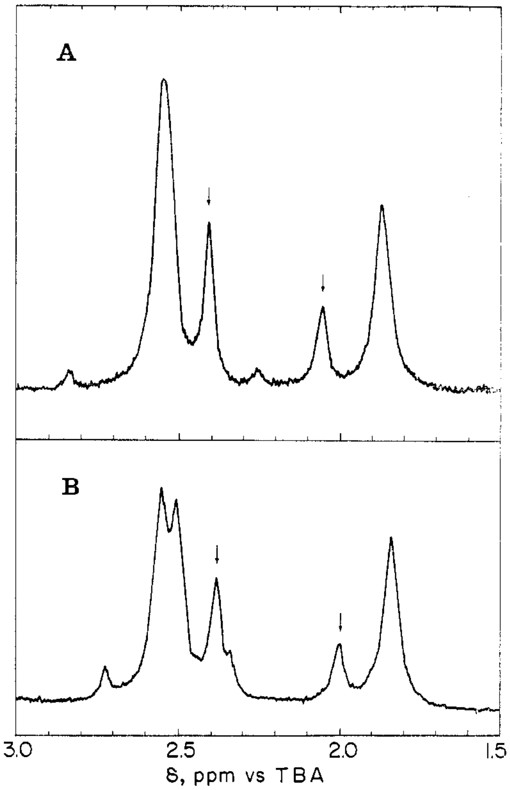

Figure 2.—Proton nmr spectra for hafnium(IV)–EDTA at pH 6.8 for a 0.5 F solution: curve A, 60 Mc; curve B, 100 Mc.

At pH 4.3 the two ethylenic resonances for the hafnium(IV)–EDTA system are of approximately the same area, but the quartet is somewhat asymmetric (Figure 3). The uncomplexed EDTA has a methylenic resonance which is actually hidden beneath the resonance indicated by the arrow at low field in both the 60- and 100-Mc spectra. The 100-Mc spectrum at this pH contains five fairly intense plus four less intense resonances. The two resonances at 2.72 and 2.34 ppm have identical chemical shifts as the resonances which constitute the outer satellites of the quartet at pH 6.8. Apparently a second quartet is superimposed on the high pH quartet and consists of the resonances at 2.81, 2.64, 2.55, and 2.39 ppm. This second quartet must be the methylenic portion of the spectrum which corresponds to the ethylenic resonance at 1.95 ppm. The value of $\delta_A - \delta_B$ is calculated to be 0.198 ppm from the 100-Mc spectrum; this agrees with the value of 0.203 ppm calculated from the 60-Mc spectrum. The coupling constant for this quartet also has a value of 17.1 cps.

The relative areas of the two ethylenic resonances in the 60- and 100-Mc spectra as a function of pH indi-

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[10] J. A. Pople, W. C. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 119.

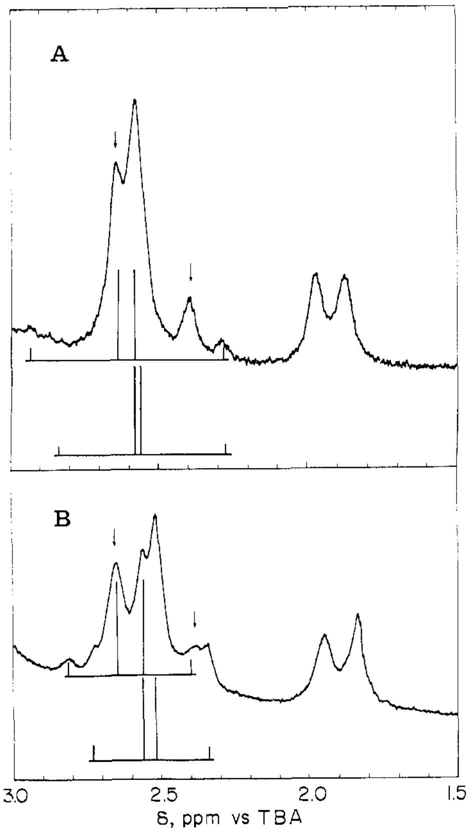

Figure 3.—Proton nmr spectra for hafnium(IV)–EDTA complex at pH 4.3 for a 0.5 F solution: curve A, 60 Mc; curve B, 100 Mc.

cate that they arise from two different types of ethylenic protons, with the protons for each type equivalent. The peak assignments have been substantiated by integration of the areas for spectra recorded in the range from pH 3.5 to 5.0. A ratio of 2:1 for each quartet relative to its corresponding single ethylenic resonance has been established at each pH.

Because the ions of zirconium and hafnium are known to exhibit extremely similar behavior in all their chemistry, properties of their EDTA complexes in solution should be closely related. Interpretation of their proton nmr spectra is facilitated by considering their spectra together; most of the conclusions are applicable to both metal ions.

The nmr spectrum for zirconium(IV)–EDTA at pH 3.5 (Figure 1A) is similar to the spectra for the EDTA complexes of cadmium(II),[6] molybdenum(VI),[5] and yttrium(III).[11] Reilley and co-workers[6,12] first proposed that the observed quartet results from spin–spin interaction of the two nonequivalent methylenic protons of each acetate group. The prerequisite for the appearance of such a quartet is nonlabile bonding of the nitrogen groups to the metal ion such that the nitrogen becomes an asymmetric center. The situation is then similar to that of the substituted ethanes of the type WF_2CCXYZ, in which preferred orientations about the carbon–carbon bond cause nonequivalence of the *gem* fluorine atoms. This phenomenon, observed first by Nair and Roberts,[13] has been discussed from a theoretical standpoint by Pople[14] for conditions of rapid and of slow rotation.

The spectra above pH 6 for hafnium–EDTA and zirconium–EDTA, illustrated by Figure 2, indicate that only one species is present within the nmr time scale because only one ethylenic resonance is observed The 100-Mc spectrum establishes that the methylenic portion is a quartet arising from the small chemical shift difference between the methylenic protons.

At intermediate pH values (between 3.5 and 6), a gradual transition from the low pH form to the high pH form of the complex occurs; the nmr spectra show a superimposition of the two quartets, as well as two separate ethylenic resonances. Resolution of some of the resonances which are superimposed in the 60-Mc spectrum is accomplished by recording the 100-Mc spectrum (Figure 3). Because the chemical shifts for the complex and the chemical shift differences for the methylenic protons, $\delta_A - \delta_B$, do not change with pH for either quartet, assignments for the resonances have been made easier. If one quartet is present below pH 3.5 and another quartet is present above pH 6, spectra for solutions between these two pH values should reasonably be expected to include two quartets even if all the resonances cannot be resolved in the 100-Mc spectrum.

Consideration of the different types of bonding that might give rise to the observed spectra permits some reasonable speculation concerning the structure for the complexes. The chemical shift differences for the two quartets for hafnium(IV), 0.277 and 0.128 ppm, are not greatly different from the values of 0.356 and 0.17 ppm which Day and Reilley[6] have reported for the two quartets observed for octahedral cobalt(III)–EDTA. They assigned the two quartets to in-plane and out-of-plane acetate groups. Thus, the EDTA complexes of zirconium(IV) and hafnium(IV) could be assumed to be octahedral. Two factors, however, are inconsistent with this proposal. The variation of the spectra between pH 3.5 and 5.0 implies that if the two quartets were assigned to in-plane and out-of-plane acetate groups, respectively, then only in-plane coordination occurs at low pH and only out-of-plane coordination occurs above pH 5. Such a phenomenon is difficult to justify on the basis of known chelate chemistry.

Also, coordination with hafnium(IV) and zirconium(IV) is not likely to be octahedral because the probable coordination number is eight. Thus, the complexes for these ions should be either square antiprismatic or dodecahedral. Intorre and Martell[15] have proposed that zirconium(IV)–EDTA may be square antiprismatic with EDTA filling six coordination positions and water molecules filling the other two. Hoard, Willstadter, and Silverton,[16] however, have carried out an X-ray crystallographic analysis of bisnitrilotriacetato-

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[11] R. J. Kula, Ph.D. Dissertation, Department of Chemistry, University of California, Riverside, Calif., 1964.

[12] J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1707 (1964).

[13] P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

[14] J. A. Pople, *Mol. Phys.*, **1**, 3 (1958).

[15] B. J. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 358 (1960).

[16] J. L. Hoard, E. Willstadter, and J. V. Silverton, *ibid.*, **82**, 1610 (1960).

zirconate(IV) ion and unequivocally assigned the coordination type as dodecahedral. On the basis of the similarity of the structure and chelation sites of nitrilotriacetate and EDTA, the conclusion that the EDTA complexes of zirconium(IV) and hafnium(IV) are dodecahedral is reasonable.

The positions of the atoms of EDTA in a dodecahedral configuration are identical with the framework described for the seven-coordinate[17] $[Fe(OH_2)EDTA]^-$ ion. Hoard[18] has stated that this configuration is obtained by expansion of the central metal atom until swelling of the arms of the chelate leaves two more coordination positions to be filled. From the symmetry elements of the polyhedron, all four acetate groups could undergo similar shielding or deshielding as a consequence of diamagnetic anisotropy of the other bonds in the molecule. Thus any one type of zirconium– or hafnium–EDTA complex would be expected to exhibit only a single quartet due to the methylenic protons.

Correlations are possible between the results of Intorre and Martell[15] and the results discussed here. They observe an inflection in the potentiometric titration curve of a 1:1 solution of zirconium(IV)–EDTA between pH 3 and 4, which they take to indicate the formation of the simple chelate. A buffer region at about pH 3.5 indicates that an additional mole of base adds to the complex and possibly results in some polymerization. At about pH 9 precipitation of the hydrous oxide occurs. The nmr data indicate that below pH 3.5 only the simple chelate is present giving rise to a single quartet and a single ethylenic line. Above this pH base is added to the complex resulting in a species which is in equilibrium with the simple chelate. When the pH is increased beyond pH 5, hydrolysis and polymerization is almost complete. Although precipitation is not observed for solutions above pH 9, uncomplexed EDTA resonances appear under these conditions and indicate that complete hydrolysis of the EDTA complexes of zirconium and hafnium has occurred.

The rather small value for the chemical shift difference for the two methylenic protons also may be explained on the basis that hydroxide ions are being incorporated into the coordination sphere of the metal ion. The presence of hydroxide ion would be expected to decrease the effective charge of the atom, to weaken the bonding between the chelating agent and the metal, and to increase the lability of the chelate.

The final point of interest concerns the absence of any observable A_2B_2 splitting of the ethylenic resonance for the hafnium– and zirconium–EDTA complexes. Such splitting has been reported for the cobalt(III)–EDTA complexes[6] and for some cobalt(III) complexes with ethylenediamine-N,N′-diacetic acid.[19] Such nonequivalence would be expected when both the nitrogen-to-metal bonds and the acetate-to-metal bonds are long lived. Because zirconium(IV) and hafnium(IV) are known to have high affinity for oxygen and because of the very large stability constant for zirconium(IV)–EDTA,[20] $\log K = 29$, nonlabile bonding appears as a reasonable situation. Hoard,[18] however, has pointed out that the metal–nitrogen bonds in the bisnitrilotriacetate complex of zirconium(IV) are extraordinarily long. If the bonding situation is similar with EDTA, then perhaps such weak coordination of the nitrogens would allow rapid interconversion of the ethylenic protons, thereby eliminating any nonequivalence among them.

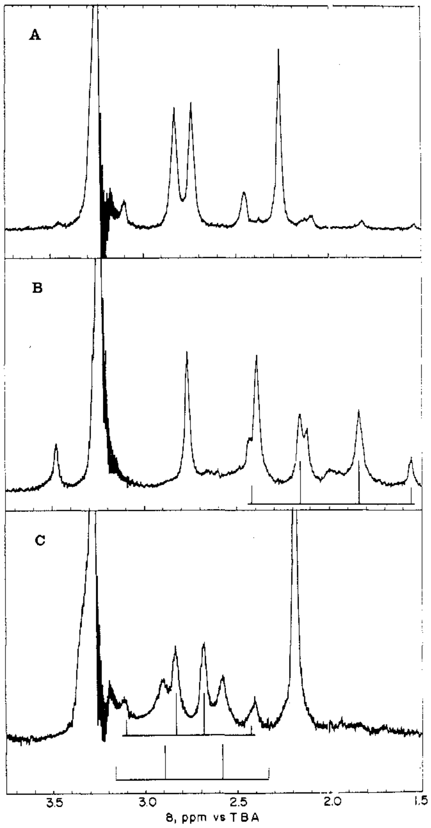

Figure 4.—Proton nmr spectra for palladium(II)–EDTA: curve A, typical spectrum for the bidentate complex between pH 3.0 and 10.5; curve B, spectrum for the tetradentate complex at pH 5.0; curve C, spectrum for the bidentate complex at pH 11.6. Metal chelate concentration, 0.5 *F*.

Palladium(II)–EDTA; Bidentate Complex.—A 1:1 solution of palladium(II)–EDTA which has been prepared from palladium chloride gives the nmr spectrum shown in Figure 4A from pH 3 to 10.5. Below pH 3.0, considerable broadening of the resonance lines occurs and above pH 11 the spectra are complicated by additional resonances. The spectrum consists of a quartet adjacent to the HDO resonance centered at 2.78 ppm and a single ethylenic resonance at 2.28 ppm. Several low-intensity resonances are present on both the high-field and low-field sides of the ethylenic resonance as well as one additional minor resonance on the low-field side of the HDO resonance. None of these minor resonances is symmetrical about the ethylenic

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[17] J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

[18] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

[19] J. L. Legg and D. W. Cooke, *ibid.*, **4**, 1576 (1965).

[20] B. J. Intorre and A. E. Martell, *ibid.*, **3**, 81 (1964).

resonance and their chemical shifts do not change with pH even when the ethylenic resonance does.

Chemical shifts for both the acetate and ethylenic protons change only very slightly between pH 3.5 and 10.5. However, between pH 10.5 and 12.5 the ethylenic resonance shifts approximately 0.083 ppm upfield. Above pH 10.5 two additional resonances appear in the region of the quartet, and as the pH is increased the low-intensity resonances near the ethylenic peak begin to diminish and essentially disappear above pH 11. The new resonances at 2.90 and 2.58 ppm increase in magnitude as the area of the quartet decreases while the ethylenic resonance remains constant in size (Figure 4C). Considering this spectrum and the integrated areas for the resonances, the quartet and the two additional resonances together constitute the methylenic portion of the spectrum; the ethylenic resonance is a single line at 2.20 ppm. Above pH 13, the original quartet no longer is observed. The effect of solution pH on the chemical shift difference for the quartet of the bidentate palladium(II)–EDTA complex is shown in Figure 5. There is relatively little change with pH up to about pH 9.5, after which there is a rapid increase in the difference with increasing pH. The coupling constant for this quartet remains constant at 16.7 cps for all conditions of pH.

The 100-Mc spectrum for the bidentate palladium(II)–EDTA complex also has been recorded; the quartet has a coupling constant of 16.8 cps and a chemical shift difference of 0.278 ppm, in reasonable agreement with the 60-Mc data, 16.7 cps and 0.255 ppm, respectively. A more significant observation with the high-frequency spectrum is that the relative positions of the low-intensity resonances upfield from the ethylenic resonances are separated by 16 cps, which is the same as their separation in the 60-Mc spectrum. If the two high-field minor resonances as well as the resonances at 2.15 and 2.44 ppm constitute a quartet, then their chemical shift difference is equal to 0.510 ppm.

The experiments of Busch and Bailar[9] on EDTA complexes of platinum(II) and palladium(II) and those by Liu[21] on ethylenediamine-N,N′-diacetic acid complexes of platinum(II) have established definitely that EDTA acts as a bidentate ligand when chloride is available to fill two of the coordination positions on the metal ion. Thus the spectrum shown in Figure 4A can reasonably be concluded to represent the bidentate form of dichloropalladium(II)–EDTA. Apparently the nitrogens are bonded sufficiently strongly to cause nonequivalence of the methylenic protons due to preferred rotational conformation. The fact that this spectrum remains essentially constant over the pH range from 3.0 to 11 is in accord with the observations of MacNevin and Kriege,[22] who reported the presence of the 1:1 complex over approximately the same pH range. A plot of the wavelength of the maximum absorbance as a function of pH reported by these authors is similar to a plot of the chemical shift difference *vs.* pH as shown in Figure 5. Thus chemical shift difference appears to be comparable to the wavelength of the absorption maximum as an indicator of structural and compositional changes.

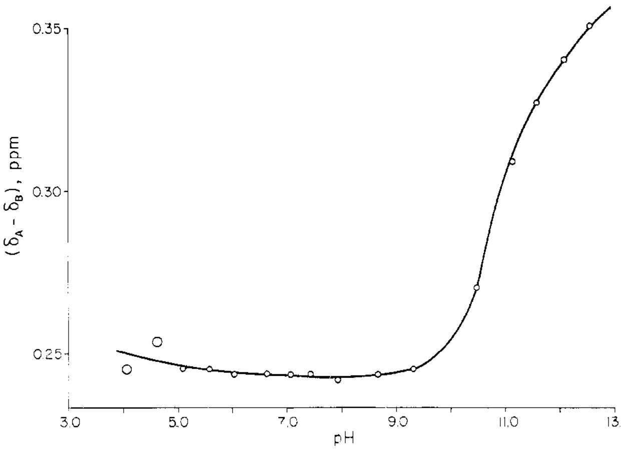

Figure 5. Chemical shift difference for the methylenic protons of the bidentate palladium(II)–EDTA complex as a function of solution pH. Concentration of the 1:1 metal complex, 0.5 *F*.

Tetradentate Complex.—By removing the chloride ion from a palladium(II)–EDTA solution the two sites occupied by the chloride ions on the metal ion are made available for coordination by the carboxylate groups of the ligand. The spectrum for such a chloride-free solution at pH 5.0 is shown in Figure 4B. By comparison with the spectrum for the bidentate complex, the resonance at 2.77 ppm is concluded to result from the collapse of the quartet. This probably results because of coincidental field symmetry for these protons. The chemical shift for the ethylenic resonance is at 2.38 ppm, which is slightly downfield from that for the bidentate complex. The most striking feature of the spectrum is the set of resonances upfield from the ethylenic resonance. On the basis of the values of their chemical shifts, these resonances appear to be the same anomalous resonances which are observed in the spectrum of the bidentate complex as minor lines. Four resonances at 2.44, 2.15, 1.85, and 1.55 ppm appear to constitute a quartet with a coupling constant of 16.7 cps and a chemical shift difference equal to 0.510 ppm. Integration of the areas for the resonances supports the conclusion that these peaks are due to the methylenic protons. The other resonances at 2.12 and 3.50 ppm are difficult to assign; they increase and decrease in magnitude in harmony with the quartet.

The five resonances at 2.44, 2.15, 2.12, 1.85, and 1.55 ppm are almost identical with the F^{19} spectra reported by Phillips[23] for $CF_2BrCBr(CN)(CH_3)$ at −110° and for CF_2BrCBr_2CN at −98°. Both of these spectra have been interpreted as representing slow rotation about the carbon–carbon bond. Thus, the quartet together with the fifth resonance near its center (Figure 4B) may be due to different rotational configurations. The observation of resonances for different rotational configurations has not been previously reported for EDTA complexes. That this type of spectrum may occur for

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

[22] W. M. MacNevin and O. H. Kriege, *J. Am. Chem. Soc.*, **77**, 6149 (1955).

[23] W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

palladium(II)–EDTA is surprising in view of the much higher temperature and also the relative "freedom" of the acetate groups in the tetradentate complex.

Assignment of the single methylenic resonance in Figure 4B to the nonbonded acetate groups and the high-field quartet to the coordinated acetate groups is based primarily on the values of the chemical shifts. Because the quartet adjacent to the HDO resonance is assigned to nonbonded acetate groups in the case of the bidentate complex and because coordination would not be expected to cause mere collapse of the quartet without simultaneously altering the chemical shift, the single methylenic resonance is assigned to the nonbonded acetate groups in the tetradentate complex. The high-field set of resonances must then arise from the coordinated acetate groups. The value of the chemical shift difference, 0.510 ppm, supports this conclusion because it is close to the value of 0.356 ppm which Day and Reilley[6] tentatively attributed to the in-plane bonding of the acetate groups for cobalt(III)–EDTA. The region of the spectrum in which this quartet occurs for the cobalt(III) complex also is fairly high upfield and close to the ethylenic resonance. The appearance of five resonances instead of a simple quartet must somehow be associated with the size of the palladium(II) ion, the size-to-charge ratio, and the lability of the chelate. These factors also probably contribute to the abnormally high upfield chemical shift for this methylenic multiplet. The presence of these resonances in the spectrum for the bidentate complex (Figure 4A) indicates that a small percentage of the tetradentate complex is formed even in the presence of chloride ion.

As the pH of the chloride-free chelate solution is increased the multiplet decreases in magnitude while the single methylenic resonance increases; the ethylenic resonance remains constant in area as a singlet. The latter resonance apparently is a degenerate A_2B_2 pattern. At about pH 10.5 the single methylenic resonance splits into a quartet with the same chemical shift and the same coupling constant as that found for the bidentate complex under similar conditions of pH. There is no change in the chemical shift for the ethylenic resonance up to pH 9.5. However, when the single methylenic resonance splits there is immediate upfield shift of the ethylenic resonance by 0.083 ppm to the position that is identical with that of the bidentate complex. As the pH of the solution is increased above pH 9.5 the ethylenic resonance continues to shift upfield.

Above pH 10.5 the spectra for the bidentate and tetradentate complexes are essentially the same. However, in the case of the tetradentate complex the chemical shift difference is smaller and increases from 0.165 ppm at pH 10.6 to 0.248 ppm at pH 12.3. Also the additional resonances around the central peaks of the quartet, which appear at about pH 10.5 for the bidentate complex, do not appear until pH 11.5 for the tetradentate complex.

The similarity of the spectra for the bidentate and tetradentate complexes above pH 10.5 indicates that at this solution acidity the coordination for both systems becomes essentially identical. Two situations could bring about this similarity in the spectra. The existence of unprotonated carboxylate groups in the bidentate complex might cause displacement of the two chloride ions to give the tetradentate structure. A more plausible possibility is that the increased hydroxyl ion concentration causes displacement of the coordinated carboxylated groups in the tetradentate complex to a structure similar to the bidentate complex. That the latter is the cause is further supported by the slight but definite shift of the ethylenic resonance to higher fields and the broadening of all the resonances at this pH. Incorporation of hydroxyl ions into the inner coordination sphere of the palladium ion would be expected to decrease the effective charge of the metal ion which the chelate interacts with and thereby would decrease the amount of deshielding which the ethylenic protons experience. Incorporation of hydroxyl ions would also be expected to increase the lability of the chelate and thereby produce broadening of all the resonances.

By the time the additional resonances appear in the vicinity of the quartet all of the resonances are so broad that determination of whether these are part of another quartet is difficult. However, integration establishes that these peaks together with the quartet constitute the methylenic portion of the spectrum associated with a single ethylenic resonance. Thus, the extra resonances are concluded to be part of another quartet due to a second form of the complex in equilibrium with the first. These two forms may involve coordination by one and two hydroxyl ions, respectively. Because the second quartet appears only at high pH values and is the only one existing above pH 13, this quartet is assigned to the form with two hydroxyl ions. Further evidence for this assignment is the slightly high-field chemical shift of the center of the quartet. Displacement of the ligand by hydroxyl ions would reasonably be expected to occur at a higher pH for the tetradentate complex than for the bidentate complex because the hydroxyl ions must overcome the stabilizing effect of the chelate ring to displace the carboxylate groups.

On the basis that the upfield quartet in Figure 4B is due to the in-plane methylenic groups for the bonded carboxylate groups of the tetradentate complex, the upfield quartet observed for the cobalt(III)–EDTA complex can reasonably be concluded to be due to the in-plane acetate groups. Thus the present data support the tentative conclusion of Day and Reilley.[6]

A number of metal–EDTA complexes have been investigated by proton nmr during the past few years. For several of these complexes AB quartets are observed because of the nonequivalency of the methylenic protons due to nonlabile bonding between the metal ion and the nitrogen donor groups of the ligand. Table I summarizes the chemical shifts, the coupling constants, and the chemical shift differences for the AB quartets for the EDTA chelate systems studied until