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Nuclear Magnetic Resonance Studies of Diamagnetic Metal–Aminopolycarboxylate Complexes

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Proton resonance spectra of EDTA, MEDTA, and HEDTA complexes of diamagnetic ions including alkali, alkaline earth, and rare earth metals are described. Quartet splittings of the methylenic protons of the acetate groups, indicative of long-lived metal–nitrogen bonds, are found for each ligand in the complexes of the cations of higher charge density. The ligand proton chemical shifts are shown to correlate with the effective charge density of the metal ion. Evidence is presented that this correlation is reflective of ordering in the solvation shell rather than a result of direct metal–ligand electrostatic or inductive effects.

Introduction

Proton resonance spectra for the complexes in aqueous solution of ethylenediaminetetraacetate, EDTA, *N*-hydroxyethylethylenediaminetriacetate, HEDTA, and *N*-methylethylenediaminetriacetate, MEDTA, with a number of diamagnetic metal ions including alkali, alkaline earth, and trivalent lanthanide ions have been obtained to learn more about the bonding and structural characteristics of these complexes. Day and Reilley[1,2] interpreted the spectra of EDTA complexes of alkaline earth and transition metals in terms of the labilities of the metal–oxygen and metal–nitrogen bonds. Kostromina et al.[3] extended these studies to the HEDTA and EDTA complexes of the diamagnetic lanthanide cations. Sawyer and co-workers[4] investigated the pH dependence of the exchange rates for the alkali, alkaline earth, and some transition metal complexes of EDTA. Ryhl[5] studied the kinetics of ligand exchange of LaEDTA⁻ and LuEDTA⁻ using line shape analysis. In addition to these studies of diamagnetic ions there have been a number of investigations of paramagnetic lanthanide complexes emphasizing their use as shift reagents for organic systems.[6,7] Both the theory and the practical aspects of paramagnetic shift reagents are sufficiently complex that a fuller understanding might result from a more complete interpretation of the somewhat simpler spectra of the diamagnetic lanthanide complexes.

The structures of EDTA, MEDTA, and HEDTA are shown in Figures 1, 3, and 6, respectively. EDTA is normally a hexadentate ligand although there are examples of pentachelation.[8,9] Neibohr[10] has observed an unbonded acetate group in the spectrum of EuEDTA⁻ at low temperatures in 3 M LiCl. Elgavish and Reuben proposed that in a LiCl

medium, the hexachelated LnEDTA⁻ complexes are shifted to pentachelation;[6b] thus the low-temperature "pentadentate" species was probably EuLiEDTA. MEDTA, with a methyl group replacing one acetate of the EDTA structure, can only be five-coordinate. HEDTA, in which an ethanolic group has replaced an acetate of the EDTA structure, can fill either five- or six-coordination positions. Powell and Burkholder[11] explain the elution trends of LnHEDTA complexes from cation-exchange resins by assuming that HEDTA is pentadentate with the heavier lanthanide ions (i. e., Tb–Lu) and hexadentate with the lighter members of the series (i. e., La–Tb). From infrared and dehydration studies Moeller and Horwitz[12] inferred five coordination positions for HEDTA in lanthanide complexes. In a thermodynamic study Gritmon proposed that the trends for ΔH_{101} and ΔS_{101} with lanthanide atomic number suggested that the β-hydroxyethyl group of HEDTA interacts with the cation via an intermediate water molecule.[13] Thus the majority of opinions favor pentadentation for HEDTA with lanthanides but the evidence is rather indirect.

Experimental Section

Reagents and Solutions. Alkaline earth metal stock solutions of 0.25 M were prepared by dissolving either the chloride or nitrate salt in D₂O. Lanthanides of purity >99.99% were obtained from the American Potash and Chemical Corp. Stock solutions were prepared by dissolving a stoichiometric amount of the appropriate rare earth oxide in concentrated HClO₄. The concentration of metal ion in the stock solution was determined by titration with Baker "reagent" grade EDTA using xylenol orange as an indicator in an acetate (pH 5) buffer. The lanthanide perchlorates in D₂O were taken to dryness several times to eliminate H₂O. The sodium deuterioxide used for most pH adjustments was obtained from Diaprep Inc. as a 40% solution in D₂O.
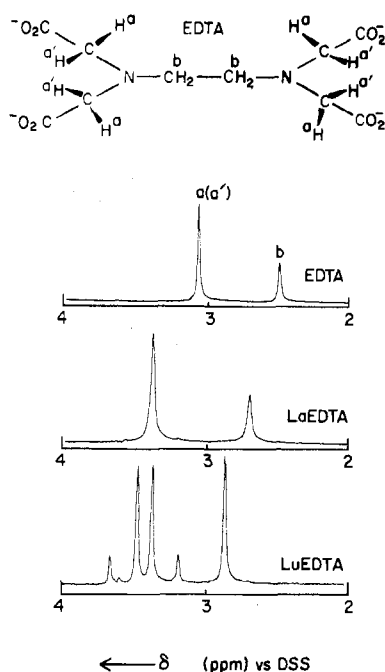
Figure 1. Proton resonance spectra (90 MHz) and assignments for EDTA complexes. The quartet pattern for acetate protons was observed only for yttrium, lutetium, and indium complexes.

The other alkali metal deuterioxides, except CsOD, were prepared by dissolving the hydroxides in D_2O. CsOD was prepared by passing a solution of CsCl through a Dowex 2-X8 anion-exchange column in the deuterioxide form.

EDTA and HEDTA were obtained commercially as the sodium salts (Na_4EDTA and Na_3HEDTA) and used without further purification. MEDTA was synthesized by Dr. J. E. Powell and co-workers[14] and supplied to us in acid form. All ligand stock solutions in D_2O were prepared to be 0.1 M.

NMR samples of 1:1 ligand-to-metal ratio in D_2O were prepared by mixing an aliquot of the metal solution with an appropriate amount of ligand solution. The alkaline earth solutions were adjusted to a pH range of 8.5–10 with NaOD while the lanthanide solutions were adjusted to a pH between 7 and 8. The final concentrations of the lanthanide complexes were limited by the solubility but were in the range of 0.01–0.1 M except for the MEDTA complexes which exceeded 0.1 M. The solubility of all of the alkaline earth complexes appeared to decrease with increasing cation atomic number for all of the ligands studied. The solubility of the lanthanide EDTA complexes appeared to increase across the cation series while the reverse trend was found for the HEDTA complexes. The low solubility of some systems resulted in relatively low signal-to-noise ratios which limited the information obtainable from those spectra.

Proton magnetic resonance measurements were made using the pulsed Fourier transform mode with a deuterium lock on both the Bruker 90-MHz and Bruker 270-MHz spectrometers in the Florida State University NMR Laboratory. All spectra were obtained at 30 °C and were measured relative to an internal standard, sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS).

Results and Discussion

The proton magnetic resonance spectrum of a solution of the sodium salt of EDTA (Figure 1) contains two singlets of intensities 1:2. This implies that the four ethylenic protons on the backbone of the EDTA anion are equivalent as are the eight protons on the four acetate groups. The spectra of sodium salts serve as the reference for changes related to stronger complexing and are labeled as free ligand spectra in the figures even though a study of [23]Na resonance has shown that sodium forms weak chelates with EDTA and HEDTA.[15]

Day and Reilley[1,2] described the spectral patterns for EDTA complexes for four limiting cases of bond labilities. The simplest spectrum, consisting of two singlets, is expected if both
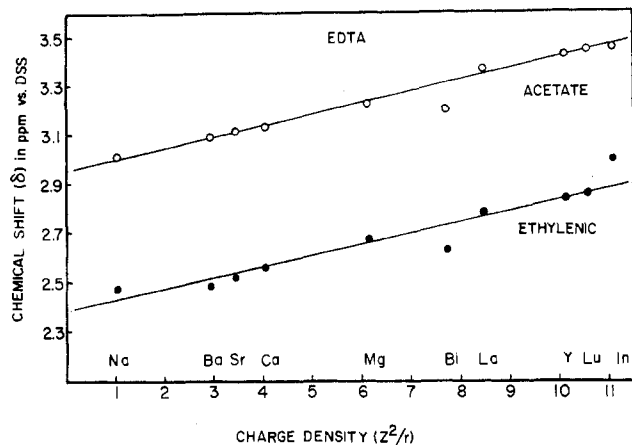

Figure 2. Chemical shift variation with effective charge density for EDTA complexes.

the metal–oxygen and the metal–nitrogen bond lifetimes are very short. A short metal–oxygen lifetime with long metal–nitrogen lifetime, which precludes inversion through the nitrogen, results in equivalent A–B quartet patterns for each of the four acetate proton pairs while the ethylene protons would exhibit a singlet since they are equivalent. The most complicated spectrum appears with long lifetimes for both the metal–nitrogen and the metal–oxygen bonds as this gives rise to multiplet patterns for both the acetate and the ethylenic protons. The final limiting case with a long metal–oxygen and a short metal–nitrogen bond lifetime is not distinguishable from the third case unless inversion occurs at the nitrogen which is unlikely. Our complexes can be expected to fit one or more of the first three cases.

The spectra observed for EDTA complexes of bismuth, lanthanum, and the alkaline earths have the two-singlet pattern indicating short lifetimes for both the metal–oxygen and metal–nitrogen bonds (Figure 1). LuEDTA⁻, InEDTA⁻, and YEDTA⁻ have an A–B quartet pattern for the acetate protons and a singlet for the ethylenic protons, which implies long metal–nitrogen and short metal–oxygen bond lifetimes. The chemical shifts of both acetate and ethylenic protons are metal ion dependent.

If the bonding in all of these complexes is predominantly ionic, we expect a relationship between the chemical shifts of the ligand atoms and the electrostatic interaction with the metal ion, the latter depending on the cation charge and the metal–ligand separation. Specific data on these distances are not available but as a first approximation we can use cation radii to compare the interactions for similar complex structures. For cations of different charge, Z^2/r (where Z is the charge and r is the cationic radius) has been shown to correlate with log β_{101} (β is the stability constant) in such a way as to allow interpretation that Z^2/r represents a measure of the effective charge density of the cations.[16] As the effective cation charge density detected at the ligand site increases, the proton would tend to be deshielded and a shift of the resonance toward lower fields (larger chemical shifts) would be expected. The slope of such a correlation reflects the way in which a particular type of proton samples its electrostatic environment. In Figure 2 we see that the relative chemical shifts for both the acetate and the ethylenic protons of EDTA move toward lower field as the value of Z^2/r of the metal ion increases. This correlation is seen to be remarkably linear for both acetate and ethylenic protons of EDTA complexes of sodium, four alkaline earth ions, lanthanum, lutetium, and indium which span a range from 1 to 11.4 in the charge density parameter. The acetate and ethylenic protons also display the same slope suggesting that the two types of proton sample the environment in a
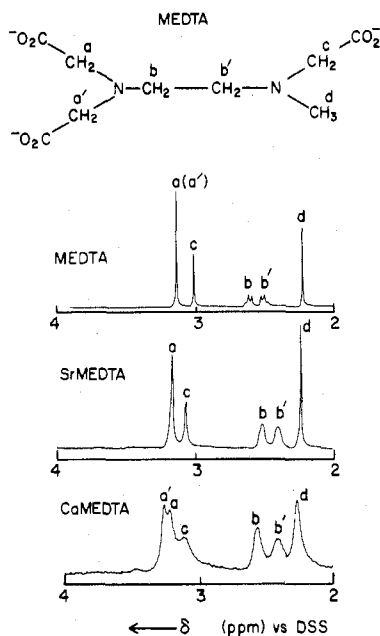
Figure 3. Proton resonance spectra (90 MHz) and assignments for MEDTA complexes.

Figure 4. Proton resonance spectra (270 MHz) of diamagnetic lanthanide–MEDTA complexes.

Figure 5. Chemical shift–effective charge density correlations for MEDTA. The dashed lines represent the EDTA correlations from Figure 2.

similar way. The shifts for the bismuth(III) complex (and the ethylenic protons of the indium complex) show a significant deviation from the effective charge density correlation.

Since the metal–ligand bonding is primarily ionic, it is not unreasonable to expect that the activation barrier for bond breakage and, thus, the rates of bond formation and rupture should show a correlation with the charge density of the metal ion. The alkali and alkaline earth ions of relatively low charge density have spectra with two singlets (Figure 1) consistent with rapid bond breaking of both M–N and M–O bonds. For the In, Lu, and Y ions of higher charge density, the A–B multiplet pattern for the acetate protons indicates that at least the nitrogen inversion is slow for these complexes. The lanthanum complex with an intermediate charge density has an intermediate spectrum of two broad singlets with different line widths.

The spectrum of MEDTA in Figure 3 is more complicated than that of EDTA. The two acetate resonances are assigned on the basis of intensities. The low field line (a, a') arises from the four protons of the two acetate groups attached to the same nitrogen and the upfield resonance (c) arises from two protons of the lone acetate group on the opposite side of the molecule. The ethylenic protons are not equivalent in this ligand but are coupled to give two triplets (b, b') with $J = 7$ Hz. The methyl group protons appear as a singlet (d).

For the MEDTA complexes (Figures 3 and 4), the SrMEDTA$^-$ and BaMEDTA$^-$ spectra resemble that of NaMEDTA^{2-} with two acetate peaks. The MgMEDTA$^-$ and CaMEDTA$^-$ spectra are similar with three separate singlet peaks for the acetate protons. The diamagnetic lanthanide complexes of MEDTA (Figure 4) also exhibit different resonances for each of the three acetate groups. These spectra are more complex due to the presence of A–B quartets. In each case one A–B quartet could be separated unambiguously with intensity arguments since $J_{AB} \gg \delta_{AB}$ (A–B pattern 1 in Figure 4). Determination of the remaining coupled A–B patterns was accomplished by double-resonance experiments. The spectra for the YMEDTA and LuMEDTA complexes showed three different acetate groups, each split into A–B quartets. In the LaMEDTA spectrum, however, only two A–B quartets were observed with the third acetate appearing as a broad singlet.
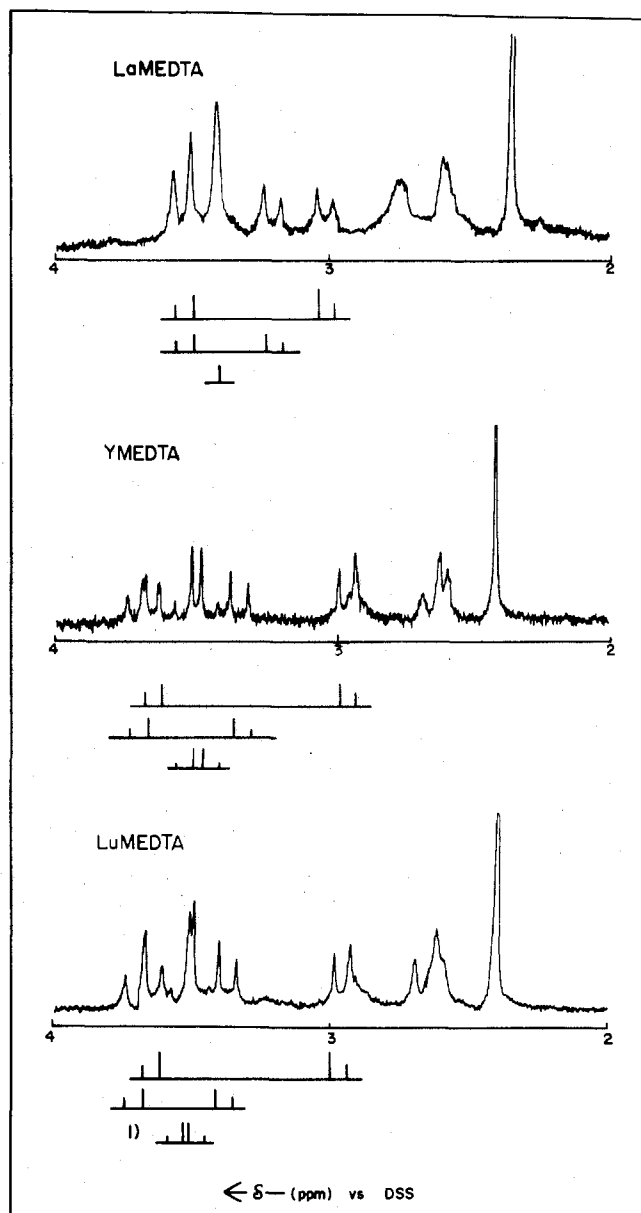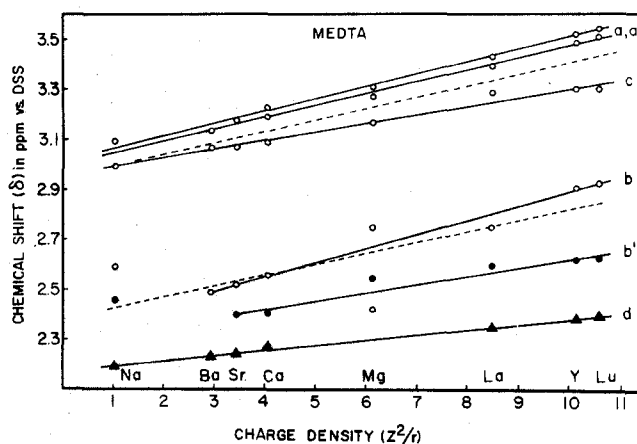
A plot of chemical shift vs. charge density for each type of proton in the metal–MEDTA complexes in Figure 5 reveals
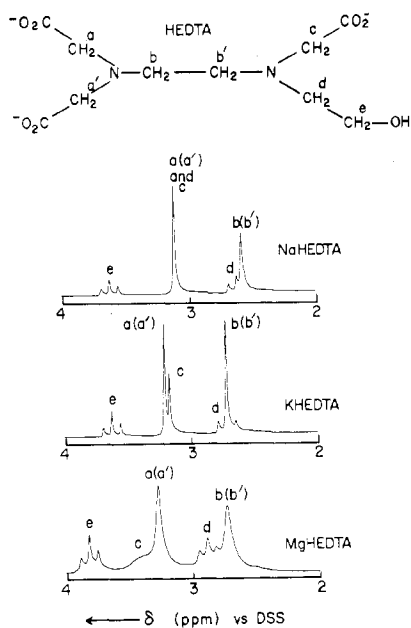
Figure 6. Proton resonance spectra (90 MHz) and assignments for HEDTA complexes.

linear relationships similar to those for EDTA (which are indicated by dashed lines for comparison). If the assumption is made that the chemical shift difference between the two nonequivalent acetate groups on the same nitrogen atom is small, the two lines designated as a, a' on the plot can be assigned to the pair of such acetate groups. The assignment of c to the "lone" acetate is not unreasonable in view of the fact that what must be the lone acetate resonance in the BaMEDTA⁻ and SrMEDTA⁻ spectra (from intensity) is found at higher field. The similarity of the a, a' slope to that of the EDTA acetate is also supportive of the assignment while the smaller slope of the c line is indicative of a different acetate environment. The ethylenic resonances b and b' have slopes similar to that of the ethylenic resonances in EDTA while the methyl protons d have a linear but lesser dependence on the charge density. Resolution of the a, a' acetate resonances was not achieved for $Z^2/r < 4$ reflecting the lability of the complexes of lower charge density. As with EDTA, the complexes of higher charge density show A–B quartets for the acetate protons indicating that both nitrogens have long-lived bonds to the metal. For MEDTA, each of the lanthanide complexes has one very narrow A–B quartet which in the case of LaMEDTA appears as a broad singlet. However, the assignment of this line to the a, a' set requires that this singlet be an unresolved quartet and neither nitrogen is exchanging rapidly. The largest A–B quartet splitting in the lanthanide complexes corresponds to the lone acetate of the ligand. Such a large splitting would result if the nonpolar methyl group is displaced from the high charge density region near the metal ion by more polar solvent groups thereby forcing the single acetate group into a configuration with dissimilar proton positions.

The spectrum of the sodium salt of HEDTA and the assignments are shown in Figure 6. The four ethylenic protons labeled b and b' are not necessarily equivalent, although only the lanthanum complex had a b–b' splitting in this study. The d and e protons are spin coupled and appear as a pair of triplets. The e protons adjacent to the hydroxyl group are assigned to the triplet at low field due to the deshielding effect of the oxygen. While the NaHEDTA²⁻ spectrum has all three acetate groups equivalent with a single resonance line, Sudmeier and Reilley[17] observed two acetate resonances with relative areas of 2:1 for KHEDTA²⁻ solution. The lithium and
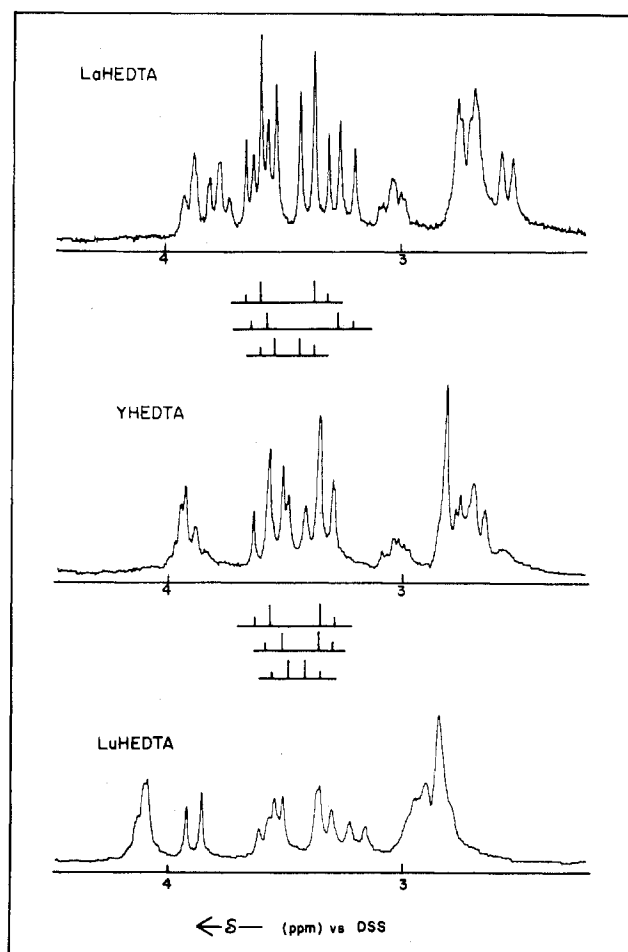

Figure 7. Proton resonance spectra (270 MHz) for diamagnetic lanthanide–HEDTA complexes. Assignments of the three quartets of LuEDTA are not shown because two different ones are possible as shown in Figure 8.

cesium forms of HEDTA, adjusted to a pH of 12 to prevent protonation, also showed only two acetate resonances. These observations correspond to those of an earlier study[4] of the variation of the chemical shift with pH for solutions of different alkali metal–EDTA complexes which showed that the frequencies for both the acetate and ethylenic protons, at a constant pH, varied for the different alkali metal ions.

The spectra of the HEDTA complexes of barium, calcium, and magnesium show the same general pattern as that of the K–HEDTA spectra except that the relative positions of the two acetate peaks are reversed. The Sr–HEDTA spectrum has only a single acetate resonance as in the Na–HEDTA spectrum. The only alkaline earth–HEDTA complex to exhibit all three peaks of the triplet due to the d protons was that of magnesium (Figure 6).

The spectra of the lanthanide complexes with HEDTA are much more complicated than the corresponding alkaline earth spectra because the acetate resonances are split into three overlapping A–B quartet patterns and the multiplet resonances for the d and e protons become more complex. The spectra of LaHEDTA, YHEDTA, and LuHEDTA are shown in Figure 7. For the lutetium and yttrium complexes, the b and b' ethylenic protons are equivalent, giving rise to a singlet, whereas for LaHEDTA, the ethylenic protons are no longer equivalent and splitting of the singlet results.

The correlation of chemical shift with charge density for the HEDTA complexes in Figure 8 is more complicated than for EDTA or MEDTA. The acetate and ethylenic resonances show similar shifts to those in EDTA as we see from their fit
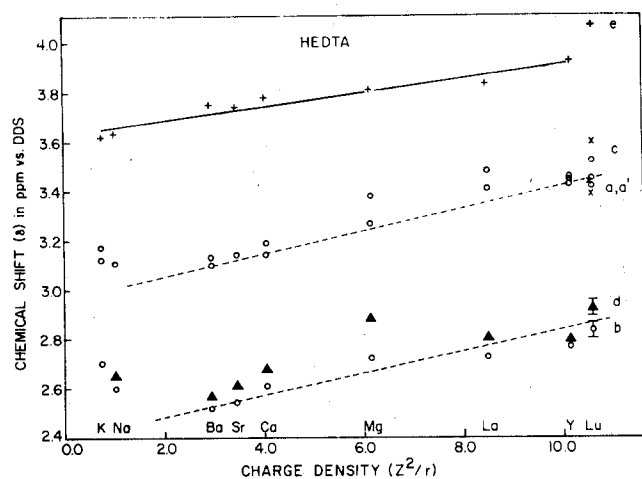
Figure 8. Correlation of proton chemical shifts with effective charge density for HEDTA complexes. The dashed line represents the similar correlation for EDTA from Figure 2, for comparison. Two assignments of the acetate quartets (one designated by × and the other by O) are shown for LuHEDTA both of which feature one very low-field resonance.

Table I. Chemical Shift Distance Comparison for the Acetate Protons of CoEDTA⁻

	Proton	δ,[b] ppm	r(M–H),[c] Å
R ring[a]	H_a	3.81	3.48
Out-of-plane glycinate	H_b	3.94	3.53
G ring	H_c	3.89	3.06
In-plane glycinate	H_d	3.57	3.68

[a] The nomenclature, labeling, and shift assignments are given in ref 19. [b] Chemical shift vs. DSS. [c] Distances are calculated from the positions of the heavier atoms[18] and the reasonable assumption that the NCC plane bisects the HCH angle and that the deviation from the tetrahedral angle is of equal magnitude but of opposite sign for NCC and HCH. The metal–hydrogen distance is quite insensitive to the choice of HCH angle.

to the dashed (EDTA) lines. The e protons adjacent to the alcohol group show the smoothest correlation with charge density and display a slope similar to the b′ ethylenic protons of MEDTA. The lutetium complex has the e resonance shifted far downfield suggesting that the alcohol has a different involvement in coordination in LuHEDTA than it does in the other complexes.

The general results are that all the types of protons in the diamagnetic complexes of EDTA, MEDTA, and HEDTA show a linear correlation with the effective charge density of the metal ion (Z^2/r). Separate resonances for each of the three acetates of MEDTA and HEDTA are resolved only for larger values of the charge density parameter and A–B quartet splittings indicative of long-lived metal nitrogen bonds are resolved only for the largest values of Z^2/r. The proton shifts do not appear to be sensitive to the net charge on the complex as M^+, M^{2+}, and M^{3+} complexes with both L^{3-} and L^{4-} ligands exhibit the same charge density correlations.

Three mechanisms appear plausible for the sensing of metal charge density by the ligand protons: (1) a direct (through-space) electrostatic interaction, (2) an inductive (through-bond) interaction, and (3) an interaction with the structured solvation shell outside the ligand. This third mechanism represents an alternative pathway by which polarization can be transferred to the ligand protons. The amount of dipole ordering in the solvation shell beyond the coordinated ligand depends on the charge density of the metal ion [and to some extent on the electrostatic insulation (dielectric effect) of the intervening ligand]. All of the ligand protons protrude into the ordered solvation shell and are subjected to dipole–induced dipole effects from the second shell with consequent deshielding. The first of these mechanisms can be tested by comparing the chemical shifts of specific protons with their distance from the metal in a complex of well-defined geometry. The EDTA complex of cobalt(III) fits this latter criterion and the data in Table I[18,19] illustrate that the chemical shift is not even monotonically related to metal–proton distances. The second mechanism involving inductive effects does not appear to be in accord with the general sensitivity of ligand protons to metal charge density because such effects usually decrease rapidly with the number of bonds. Specifically, the acetate protons and the ethylenic protons of the EDTA complexes are subject to quite different inductive pathways from the metal ion, but the chemical shift sensitivity to charge density is identical for the two types of proton. Thus,

neither of the first two mechanisms accounts for the sensing of the metal charge density by the ligand protons.

The third mechanism involving ligand proton interaction with the ordered solvation shell about the complex is less readily tested but it does appear to fit most of the observations. The general sensitivity of all ligand protons is explained because even unbound groups such as the methyl group in MEDTA are in contact with the solvation shell. Sensing of the charge density via interaction with the enveloping hydration shell makes the smooth correlations observed more understandable because both temporal and spatial averaging of the ligand–solvent interactions moderate the criterion of similar ligand configurations from complex to complex. Two aspects of the ligand control the resultant chemical shift variations (slopes) in this model. The dielectric shielding of the metal ion from the solvation shell by the interposed ligand and the specific ligand proton–solvent interaction both contribute to the sensitivity of the shift to the cation charge density. For example, the acetate and ethylenic protons of EDTA and the diacetate end of MEDTA have similar slopes but the protons on the methyl end of MEDTA have smaller slopes. Thus, the major features of the charge density correlations are in accord with control of the ligand proton chemical shift by the solvation shell.

There are several attractive prospects for utilization of a probe of the solvation sphere around complexes. Studies of order–disorder effects in the solvent, selective solvation in mixed solvents, and the effect of ion pairing on the solvation layer are among the most obvious possibilities.

Registry No. Na₄EDTA, 64-02-8; BaEDTA²⁻, 19267-06-2; SrEDTA²⁻, 17652-37-8; CaEDTA²⁻, 19267-05-1; MgEDTA²⁻, 14852-71-2; BiEDTA⁻, 17250-73-6; LaEDTA⁻, 21647-53-0; YEDTA⁻, 11063-50-6; LuEDTA⁻, 14947-77-4; InEDTA⁻, 14947-73-0; Na₃MEDTA, 62029-49-6; BaMEDTA⁻, 62059-27-2; SrMEDTA⁻, 62059-23-8; CaMEDTA⁻, 62059-22-7; MgMEDTA⁻, 62059-21-6; LaMEDTA, 62059-20-5; YMEDTA, 62059-19-2; LuMEDTA, 62059-18-1; K₃HEDTA, 62029-50-9; Na₃HEDTA, 139-89-9; BaHEDTA⁻, 62059-26-1; SrHEDTA⁻, 62059-25-0; CaHEDTA⁻, 12247-60-8; MgHEDTA⁻, 62059-24-9; LaHEDTA, 39018-94-5; YHEDTA, 39018-95-6; LuHEDTA, 15955-60-9; CoEDTA⁻, 15136-66-0.

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Study of the Aqueous Equilibrium System Involving *meso*-Tetrapyridylporphine, Alkali Metal Ions, and Hydrogen Ions

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Hydrogen ion and alkali metal ion complexes of *meso*-tetrapyridylporphine (PH_2) were examined spectrophotometrically in aqueous media. Our data can be interpreted quantitatively and self-consistently if we assume the existence of an equilibrium scheme involving the free base PH_2, the monocation PH_3, the dication PH_4, and two metal–porphyrin complexes PH_2M and PH_3M. Equilibrium constants for the system were obtained in the range 15–55 °C. The metal complexes PH_2M and PH_3M appear to be spectrophotometrically identical with PH_3 and PH_4, respectively, and it seems probable that there is a definite relationship between the core charge of the porphyrin molecule and the spectral character of the porphyrin moiety.

Introduction

For many years there has been considerable interest in the possible existence of the sitting-atop complex (SAT) precursor to metalloporphyrin formation suggested originally by Fleischer and Wang[1] to explain their observations on metal ion incorporation by protoporphyrin dimethyl ester in acetone. Fleischer, Choi, Hambright, and Stone[2] found that many metal ions apparently form 1:1 SAT complexes in aqueous *meso*-tetrapyridiniumporphine (TpyP) solutions. Recently Baker, Hambright, and Wagner[3] reported acid–base and kinetic studies of *meso*-tetra-4-methylpyridylporphine (TMpyP) in which they found that the values of pK_1' and pK_2' defined in the equations

$$PH_3 = PH_2 + H^+, \quad K_1'$$
$$PH_4 = PH_3 + H^+, \quad K_2'$$
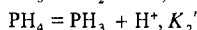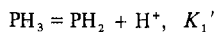
appeared to increase with increasing ionic strength. [Note: we are using the symbols PH_3 and PH_4 to represent the monocation and the dication, respectively. The charges are omitted.] Thus as $NaNO_3$ or NaCl was added, the concentration of the diprotonated porphyrin cation, PH_4, appeared to increase. On the basis of their results Baker et al. concluded that there is no evidence for the existence of SAT complexes in aqueous solutions containing TpyP or TMpyP.

The SAT complex does get strong support from the study by Mackay and Letts[4] of the interaction of Cu(II) ion, *meso*-tetraphenylporphine (TPP), and triphenylphosphine in a benzene-in-water microemulsion in which they observed the stabilization of a copper–porphyrin complex in the interphase region of the system.

We have decided to reexamine the possibility that *meso*-tetrapyridylporphine (TpyP) may form stable, long-lived metallo complexes. In the first phase of this work, which is reported here, we have studied the spectra of TpyP in aqueous solutions as a function of temperature (15–55 °C), pH (1–2), and concentration of $LiNO_3$, $NaNO_3$, and KNO_3 (0.1–3 M); the concentration of TpyP was always roughly 8×10^{-5} M. In the pH range of our studies all pyridyl residues of TpyP

Table I. Extinction Coefficients ($\bar{x} \times 10^{-3}$) for the Porphyrinic Species in Solution[a]

Species	Band I (6380 Å)	Band II (5850 Å)	Band III (5530 Å)	Band IV (5170 Å)
PH_2	2.1	5.7	5.5	18.8
PH_3	~0.0	5.6	8.0	~0.0
PH_4	16.0	13.9	3.3	1.4

[a] The extinction coefficients, ϵ_i, are listed for the three porphyrinic species at the four wavelengths at which free-base TpyP (or PH_2) exhibits maxima.

are protonated. Alkali metal ions do not incorporate to form true metalloporphyrins under the conditions of our experiments.

Experimental Section

The visible absorbance of aqueous solutions of TpyP was monitored with the Cary 14 spectrophotometer as a function of temperature, pH, and concentration of added electrolytes, $LiNO_3$, $NaNO_3$, and KNO_3. All solutions were prepared volumetrically from doubly distilled water. The temperature was controlled to ±0.05 °C. The pH was varied by using various concentrations of HNO_3. The nitric acid and metal nitrates were reagent grade and were used without further purification. The TpyP was prepared by the method of Longo, Finarelli, and Kim.[5]

Results

For convenience we shall refer to solutions containing HNO_3 as acidified or acidic solutions and to solutions containing both HNO_3 and a metal salt as metal solutions.

Visible spectra of the free-base porphyrin (PH_2) and diprotonated cation porphyrin (PH_4) are respectively four and two banded. The bands of PH_2 are numbered from the long-wavelength end of the spectra. See Table I. The complete spectrum of the monocation (PH_3) was not determined quantitatively but it is definitely three banded.

Band IV absorbance always increases with increasing temperature of pH and decreases with increasing metal salt concentration; band I behaves in an opposite manner. At a pH >1.45 a sharp cross point develops in the isotherms at