

This is also in line with the color change during complexation. The sodium salt is colorless while the complex is bright yellow, which is typical of nitro compounds where the  $\text{NO}_2$  group cannot resonate with a ring. The complex contains appreciable covalent character as shown in the Mössbauer study and the partially localized  $\pi$ -cloud between the nitrogen atoms as shown in Fig 1 will not allow resonance of the nitro group; thus a color change is observed.

The  $1431\text{-cm.}^{-1}$  band in the nitro complex and at  $1438\text{-cm.}^{-1}$  in the sodium salt is a combination band of the  $660\text{-cm.}^{-1}$  nitro group deformation band<sup>27</sup> and the  $840\text{-cm.}^{-1}$  C- $\text{NO}_2$  stretching band.<sup>27</sup>

The  $1408\text{-cm.}^{-1}$  band in the sodium salt of the nitro-tetrazole is shifted to the  $1449\text{-cm.}^{-1}$  region and is the band associated with the partially localized N=N bond.<sup>28</sup>

The trifluoromethyltetrazole system shows a shift from  $1410\text{-cm.}^{-1}$  in the salt to  $1420\text{-cm.}^{-1}$  in the complex with a slight change in intensity. This too can be attributed to the N=N bond.

The peak near  $1508\text{-cm.}^{-1}$  in the trifluoromethyltetrazole salt and complex is the C- $\text{CF}_3$  stretching frequency while the peak near  $757\text{-cm.}^{-1}$  is the C- $\text{CF}_3$  deformation frequency.<sup>29</sup> The peak at  $1038\text{-cm.}^{-1}$  seems to be a combination peak involving the C- $\text{CF}_3$ . The area from 8 to  $9\ \mu$  has previously been assigned<sup>30</sup> to the  $\text{CF}_3$  group and shows the typical broad diffuse bands.

The stretching frequency of the C=N delocalized part of the ring appears in all free salts at about  $1635\text{-cm.}^{-1}$ ; it disappears in all the complexes where a partially localized N=N bond is formed giving an *endo*-C-N single bond.<sup>31</sup>

In the sodium salt of the nitro and chloro complexes where the electrons from the group substituted in the 5-position can be delocalized into the ring system, we find a doublet occurring in the  $9$  to  $10\ \mu$  region which has

(27) A. Weissberger, Editor, "Techniques of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 540.

(28) R. J. W. Le Febvre and R. L. Werner, *Australian J. Chem.*, **10**, 262 (1957).

(29) L. J. Bellamy, ref. 26a, p. 332.

(30) L. J. Bellamy, ref. 26a, p. 330.

(31) L. J. Bellamy, ref. 26a, p. 272.

been previously assigned<sup>32</sup> to the skeletal vibrations of the tetrazole ring. In the complexes where delocalization has been decreased, only a single appears. In the trifluoromethyl compound where no delocalization of the substituent group can occur, only a singlet appears in the sodium salt. However, in the complex, a doublet appears. The peak in the region  $1055\text{--}1065\text{-cm.}^{-1}$  of the three complexes is intensified. This band can then be tentatively assigned to the ring skeletal N=N bond vibration. The second peak of this doublet is at  $1038\text{-cm.}^{-1}$  and has been assigned previously to a C- $\text{CF}_3$  combination peak.

Even though these complexes are formed in very strongly acidic media, no protonation of the free electron pairs on any of the nitrogen atoms seems to occur as shown by the absence of C-H and N-H stretching bands.

Finally, the peaks in the water region of the spectrum are very unusual. These peaks are usually quite broad; in the spectra of the dihydrates of these complexes, however, they are narrow and quite sharp. This seems to indicate that the waters of hydration in these compounds are quite unusual. It is possible that the two molecules of water of hydration are bound to the complex through the hydrogens in a manner that restricts their vibrational ability; this should narrow and sharpen their infrared absorption bands.

The X-ray powder diffractograms have been obtained, but no correlations have as yet been made. Further work is now in progress on these and similar compounds.

**Acknowledgments.**—The authors gratefully acknowledge the assistance of J. O. Terry for the infrared spectra and D. N. E. Buchanan for the Mössbauer measurements. They also thank Dr. R. A. Henry and Dr. W. McEwan of the U. S. Naval Ordnance Test Station, China Lake, Calif., and Dr. Carl H. Brubaker of Michigan State University for many stimulating discussions. This research has been supported in part by the Research Council of Rutgers, The State University, the U. S. Atomic Energy Commission, the Office of Naval Research, and Bell Telephone Laboratories, Murray Hill, N. J.

(32) E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 2594 (1951).

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## Nuclear Magnetic Resonance Studies of Metal-Ethylenediaminetetraacetic Acid Complexes<sup>1</sup>

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RECEIVED MARCH 30, 1963

The proton n.m.r. spectra for the ethylenediaminetetraacetic acid complexes of Li(I), Na(I), K(I), Cs(I), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Pb(II), Hg(II), and Al(III) have been measured in aqueous solutions as a function of solution pH. Chemical shift data for the methylenic and ethylenic protons indicate that the nitrogen sites of the ligand rather than the carboxylate groups are protonated as the pH is lowered in solutions of the Li, Na, K, Cs, Sr, and Ba complexes. Similar evidence, however, is lacking over the accessible pH range for the chelates of Mg, Pb, Zn, Hg, and Al. The relative ease of protonation for the various metal chelates has been used to establish the extent of coordination of the metal ions with the ligand nitrogen sites. Additional evidence for the relative stabilities of the various chelates is provided by pH studies for solutions with a metal-to-ligand ratio of 1:3. A strong metal ion and pH dependence is observed for the exchange rates of the metal ions between ligands. The exact nature of the bonding of the four carboxylate groups in the metal chelate is not completely evident, but the simplicity of the spectra seems to indicate that the metal-oxygen bonds are relatively labile.

Because of the extensive applications of ethylenediaminetetraacetic acid (EDTA) and its metal-chelate analogs in chemistry, many papers have appeared con-

cerning their properties and structures. A number of these papers have been summarized in the monographs on metal chelate chemistry.<sup>2,3</sup> Several structures

(1) Presented before the Division of Inorganic Chemistry, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) (a) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952; (b) S.

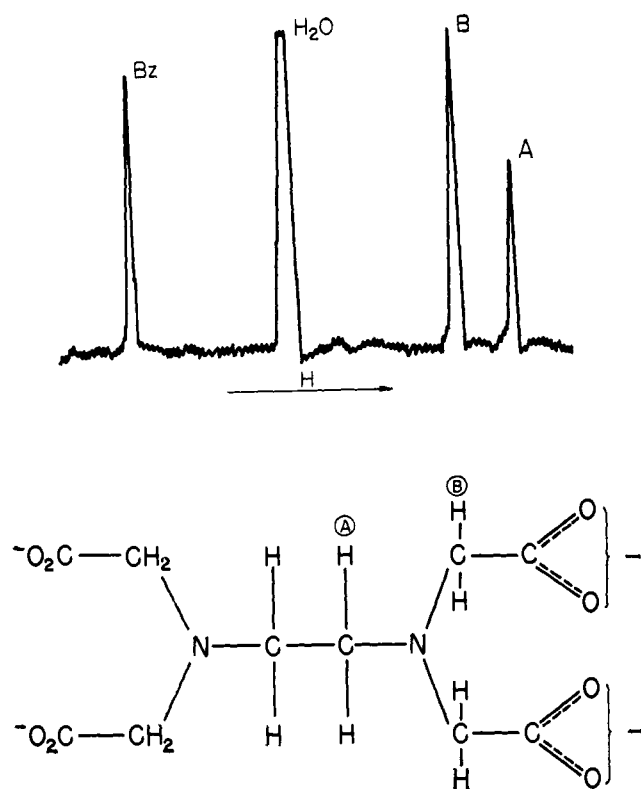


Fig. 1.—(Top) Proton n.m.r. spectrum for  $(\text{CH}_3)_4\text{N}^+$  EDTA at high pH. The  $(\text{CH}_3)_4\text{N}^+$  resonance has been deleted.  $(\text{CH}_3)_4\text{NOH}$  was used to adjust the pH;  $\delta_A = 3.77$  p.p.m.,  $\delta_B = 3.26$  p.p.m. from benzene. (Bottom).—Structure of the EDTA tetraanion showing the A and B labeling for the ethylenic and methylenic protons.

have been proposed by numerous investigators for these chelate systems, but in general the evidence for any particular case has been far from conclusive. Using X-ray crystallography, Hoard and co-workers have established the structures of the EDTA complexes of cobalt(III),<sup>4</sup> nickel(II),<sup>5</sup> iron(III),<sup>6</sup> and manganese(II).<sup>7</sup> While these X-ray studies have provided considerable insight into the problem, a danger exists in extrapolating these results to aqueous solutions.

Spectrophotometric<sup>8,9</sup> and electrochemical<sup>10</sup> methods have contributed a great deal toward understanding aqueous metal-EDTA chelate systems, particularly with regard to the species present and the equilibria associated with them. Recently, a series of infrared studies has been undertaken in aqueous solution to elucidate the nature of the bonding for EDTA complexes.<sup>11-13</sup>

Chapman<sup>14</sup> has studied the infrared spectra of various iminocarboxylic acids and also recorded their n.m.r. spectra. To date, however, no n.m.r. studies have

Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959.

(3) J. C. Bailar, Jr., "The Chemistry of the Co-ordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956.

(4) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

(5) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

(6) J. L. Hoard, M. Lind, and J. V. Silverton, *ibid.*, **83**, 2770 (1961).

(7) J. L. Hoard, B. Pedersen, S. Richards, and J. V. Silverton, *ibid.*, **83**, 3533 (1961).

(8) V. L. Hughes and A. E. Martell, *J. Phys. Chem.*, **57**, 694 (1953).

(9) A. E. Martell and R. C. Plumb, *ibid.*, **56**, 993 (1952).

(10) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

(11) D. T. Sawyer and J. E. Tackett, *J. Am. Chem. Soc.*, **85**, 314 (1963).

(12) D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 2390.

(13) K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, **85**, 309 (1963).

(14) D. Chapman, D. R. Lloyd, and R. H. Prince, *Proc. Chem. Soc.*, 336 (1962).

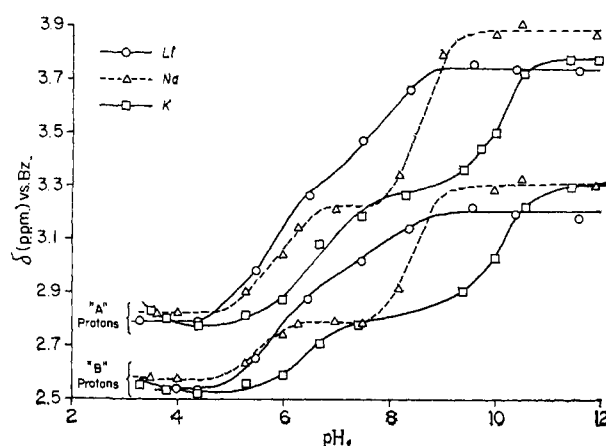


Fig. 2.—Chemical shift vs. pH curves for solutions of the alkali metal-EDTA chelates. The respective alkali hydroxides were used to adjust the pH.

been reported on metal-EDTA chelate systems. An n.m.r. investigation of these chelates seemed appropriate since the method is well adapted to solution studies and has proved to be a powerful tool in studying bonding and structures of organic molecules.<sup>15</sup>

Although the protons of the EDTA tetraanion are not directly bonded to the metal ions in the chelate, they are located sufficiently close to potential coordination sites that the electronic environment in the vicinity of these coordination sites may readily be monitored. Chemical shift data can provide useful clues concerning changes in the bonding due to coordination and the rate of exchange of cations between ligands may shed additional light on the stability of the complex. In this paper, the effects of different metal species and acidities on the proton resonances of the EDTA tetraanion are presented and discussed.

### Experimental

The proton n.m.r. spectra were recorded with a Varian DP-60 high-resolution spectrometer, equipped with a 56.4 Mc. oscillator. Concentric tubes, with benzene as an external reference, were used for all samples. Chemical shifts were measured using a variable-range audiooscillator and a frequency counter in the standard way. The pH of the solutions was measured with a Leeds and Northrup line-operated pH meter equipped with a high-range glass electrode. The meter was standardized with National Bureau of Standards buffers.

The sample solutions were prepared determinately from ethylenediaminetetraacetic acid (Fisher Scientific Co.) with an assay of 99.9% and from the hydroxides and/or nitrates of the metal ions. The pH of the metal EDTA solutions was initially brought to some high value with concentrated base (KOH unless otherwise noted), and samples were taken as the pH was lowered with nitric acid. No significant advantages in resolution were obtained by deaerating the solutions, or by using deuterium oxide as the solvent. In order to obtain reasonable intensities, it was necessary to prepare samples with EDTA concentrations of approximately 0.2 to 0.5 *F*. All samples were run at room temperature. The metals which could be studied were limited to those which are diamagnetic because of the extreme relaxation effects on proton resonances by paramagnetic species in solution. The chemical shifts are reported in p.p.m. from benzene. Bulk susceptibility corrections were not made.

### Results

**N.m.r. Spectrum.**—The spectrum depicted in Fig. 1 is for tetramethylammonium EDTA at a pH of about 12. For simplicity, the methyl resonance for  $\text{N}(\text{CH}_3)_4^+$  is not shown. There is reason to believe that the species under study is that of the tetraanion, since  $\text{N}(\text{CH}_3)_4^+$  is not expected to be an effective coordinating agent.

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

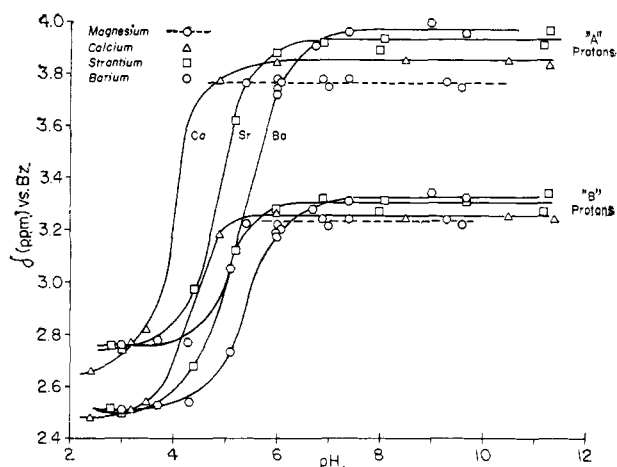


Fig. 3.—Chemical shift vs. pH curves for solutions of the alkaline earth-EDTA chelates (metal:EDTA = 1:1).

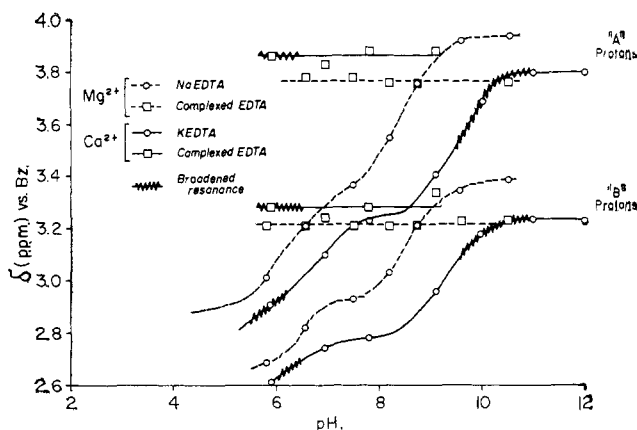


Fig. 4.—Chemical shift vs. pH curves for Mg EDTA and Ca EDTA solutions in which metal:EDTA = 1:3. Lines of constant chemical shift are due to the complexed EDTA and curves with breaks represent the excess or free EDTA.

Two nonequivalent sets of protons are present in the tetraanion of EDTA ( $Y^{4-}$ ), the ethylenic and methylenic protons. Two distinct resonances are thus expected in the proton n.m.r. spectrum. Because the methylenic protons are twice as abundant as the ethylenic protons, there can be no ambiguity in their assignment. The ethylenic and methylenic protons are denoted henceforth by A and B, respectively. The spectrum in Fig. 1 indicates that the B protons resonate at a lower field than the A protons.

**The Alkali Metals.**—The n.m.r. spectra for alkali metal-EDTA solutions all show the type of resonance pattern illustrated in Fig. 1. Some variations in the  $\delta$ -values exist for different metal ions, but these are small compared to the much larger changes observed when the pH is lowered. As can be seen in Fig. 2, both the A and B resonances shift to lower fields as the pH is lowered. Furthermore, two distinct breaks appear in the  $\delta$  vs. pH curves for both the A and the B protons.

The dependence of the breaks on the concentration of the metal ion has been established by making measurements at various metal ion concentrations. A solution of sodium EDTA with a metal-to-ligand ratio of 1:3, for example, gives breaks which are shifted to higher pH's compared to solutions in which  $Na^+$  is in excess (tetramethylammonium hydroxide is used to adjust the pH). Rapid exchange of the  $Na^+$  between ligands is indicated since only one set of reso-

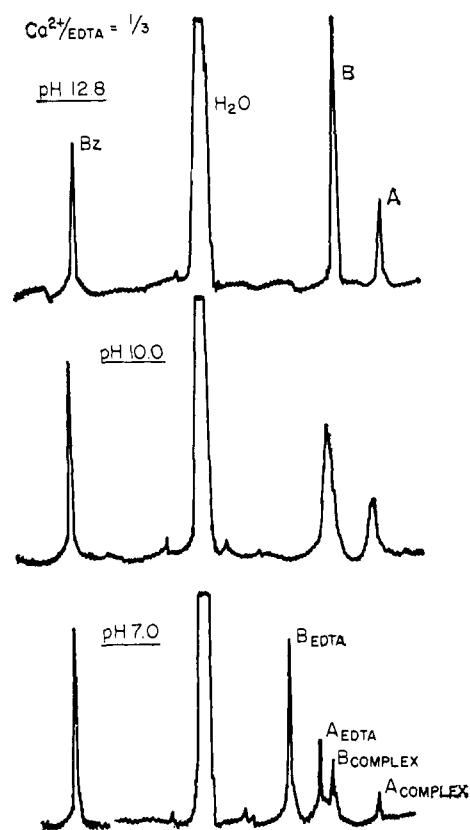


Fig. 5.—Spectra for a Ca:EDTA = 1:3 solution at various pH values, illustrating exchange broadening.

nances is observed. The other alkali metal ions show a similar behavior.

**The Alkaline Earth Metals.**—Chemical shift data as a function of pH for solutions containing alkaline earth ions and EDTA in a 1:1 mole ratio are shown in Fig. 3. At high pH values, where the metal chelate is expected to be most stable, the variation of the  $\delta$ -values from one metal to another is again of the same order of magnitude as that for the alkali metals. The overall change in  $\delta$ 's from high to low pH's is approximately the same as the sum of the two breaks for the alkali metal ions. Again, the total change is greater for the A protons than for the B protons.  $\delta_A$  and  $\delta_B$  for both the alkali metals and the alkaline earths approach the same limiting values below pH 4. As in the case of the alkali metals, the position of the breaks is dependent upon the metal ion.

The pH dependence of the chemical shift is, however, somewhat different from that found for the alkali metals. The plots show only one break rather than the two demonstrated for the alkali metals. Magnesium EDTA does not give a break at all over its accessible pH range.

The resonances for the Ca, Sr, and Ba chelates all show a broadening effect at intermediate pH regions which indicates that a slow exchange process ( $\sim 100$  c.p.s.) is taking place. A satisfactory method of studying this process is to study solutions with a metal-to-ligand ratio of 1:3. The pH of these solutions can be varied by using  $HNO_3$  and a relatively noncomplexing metal hydroxide such as KOH.

Such studies can be expected to exhibit different n.m.r. spectra depending upon the stability of the metal chelate under investigation. Thus, two distinct sets of A and B resonances are found for magnesium over the pH range studied (10.5 to 5). Calcium exhibits one or two sets, depending upon pH. One set of

sharp resonances is observed above pH 11.5 which becomes broadened between 11.5 and 9.5. From pH 9.5 to 6, two sets of sharp resonances appear, and below pH 6 precipitation occurs causing the signals again to be broad. The results of these studies are shown in Fig. 4 and 5. For strontium and barium, only one set of A and B resonances appears but line broadening occurs between pH 10 and 5 for strontium, and between pH 9 and 4.5 for barium with the lines being quite sharp above and below these pH values.

When two sets of resonances are observed, the chemical shifts of both the A and B protons for one set remain constant, while the other set varies with pH, in a manner depending on which alkali metal hydroxide is used to vary the pH. The former set can be assigned to the "complexed ligand" and the latter to the "free ligand."

**Other Metals.**—The chemical shifts for the A and B protons in a Pb-EDTA solution with a metal-to-ligand ratio of 1:1 are pH-independent over the pH range from 12 to 3. A solution with a 1:2 Pb-to-EDTA ratio gives two sets of resonances.

The n.m.r. data for zinc EDTA are similar to those for the lead chelate. Thus, a solution with a 1:1 metal-to-ligand ratio gives constant chemical shifts from pH 12 to 3. Changing the metal-to-ligand ratio to 1:3 yields two sets of resonances over this pH range, with pH independent  $\delta$ -values for the set having the smaller resonances. However, in the vicinity of pH 14, only one set of broadened resonance lines is observed. The  $\delta$ -values of this broadened set are intermediate between those for the two sets observed at pH 12.

The mercury-EDTA system with a metal-to-ligand ratio of 1:3 has been studied over the pH range from 13.5 to 3.5. From the highest pH to approximately pH 9, only one set of broadened resonance lines occurs. From pH 9 to 4, two sets of resonances appear. These are sharp in the center of this region and broadened at the extreme. Again one set of chemical shifts is not pH dependent. Below pH 3.5 precipitation occurs and only an extremely broad resonance is observed.

The aluminum-EDTA system with a metal-to-ligand ratio of 1:3 is essentially analogous to the mercury system. However, only one set of resonances is observed over the pH range from 14 to 6.5. From pH 6.5 to 4, two sets of resonances appear, the resonances for the chelate having chemical shifts to much lower fields ( $\sim 0.5$  p.p.m. relative to Mg-EDTA). Below pH 4, precipitation occurs.

Because the existence of a  $\text{Mo}_2\text{EDTA}$  species has been reported,<sup>16</sup> solutions with a 2:1 molybdenum(VI)-to-EDTA ratio have been investigated. The n.m.r. spectra at high pH show the normal set of resonances, but as the pH is lowered these two lines diminish in size and five resonances appear at lower fields. Work is still in progress on this system and the results will be reported in a later communication.

The chemical shifts for the various metal-EDTA chelates and the protonated forms of EDTA are summarized in Table I.

### Discussion of Results

**General.**—The positions of both the A and B resonances for EDTA and its metal chelates are expected to be shifted according to changes in the electronic environment about these protons (Fig. 1). Such changes can be brought about through changes in the bonding at the coordination sites owing to the presence of more effective coordinating cations in the solutions.

(16) R. L. Pecsok and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5496 (1956).

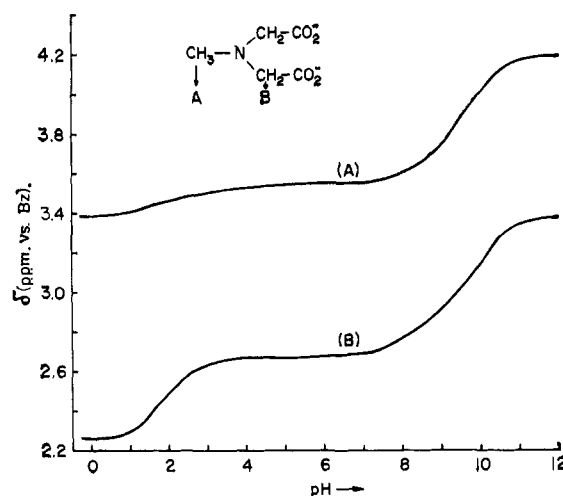


Fig. 6.—Chemical shift vs. pH curve for a 0.5 *F* solution of methyliminodiacetic acid.

The effect, of course, depends upon the site of coordination as well as the degree of coordination. Thus, if coordination occurs solely at the carboxylate groups, only the B protons would be affected. If coordination occurs at the nitrogen sites the A and B protons would be expected to be affected to approximately the same extent. To illustrate, we may consider the protonation of certain model compounds. An example of a compound involving "pure nitrogen interaction" is trimethylamine for which a strong pH dependence has been noted for the chemical shift of the methyl protons.<sup>17</sup> A simple compound capable of both "nitrogen"

TABLE I

SUMMARY OF THE CHEMICAL SHIFTS OF THE METHYLENIC AND ETHYLENIC PROTONS IN DIFFERENT METAL-EDTA CHELATES<sup>a</sup>

Metal ion	$\delta_A$ , p.p.m. <sup>b</sup>	$\delta_B$ , p.p.m. <sup>b</sup>	$\delta_A - \delta_B$ , p.p.m. <sup>c</sup>
$(\text{CH}_3)_3\text{N}^+, \text{Y}^{4-}$	3.77	3.26	0.51
$\text{HY}^{3-}$	3.30	2.91	.39
$\text{H}_2\text{Y}^{2-}$	2.86	2.61	.25
Li	3.74	3.20	.54
Na	3.88	3.31	.57
K	3.78	3.30	.48
Cs	3.56	3.07	.49
Mg	3.76	3.23	.53
Ca	3.85	3.25	.60
Sr	3.93	3.30	.63
Ba	3.97	3.32	.65
Hg	3.60	3.08	.52
Al	3.24	2.68	.56
Pb	3.25	2.67	.58
Zn	3.57	3.06	.51

<sup>a</sup> For the alkali metals and for the Sr and Ba chelates the chemical shifts are taken at high pH's where  $\delta_A$  and  $\delta_B$  are constant. For the other metal chelates they are taken at pH's where distinct resonances occur for the complexed ligand. <sup>b</sup> Not corrected for bulk susceptibilities. <sup>c</sup> Independent of bulk susceptibility corrections.

and "carboxylate" interactions is methyliminodiacetic acid. We have studied the chemical shift of the  $\text{CH}_3$  protons and the  $\text{CH}_2$  protons as a  $f(\text{pH})$ . The results are given in Fig. 6. The first break in a KOH solution corresponds to protonation of the nitrogen as both the A and B resonances are shifted downfield. As the pH is reduced further any protonation must occur at

(17) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 641 (1957).

the carboxylate groups. As noted, this results in a downfield chemical shift of only the methylenic protons adjacent to the carboxylate groups.

Other factors also influence the A and B proton resonances. In aqueous solutions, the metal ions may exchange between ligands and the rate of exchange may be a function of the metal ion. This time-dependent process can have a rather dramatic effect on the width and the shape of each of the resonance peaks provided the time scale is in the proper range. Thus, in the limit of no or slow exchange (<1 c.p.s.), distinct resonances are observed for the complexed ligand and for the free ligand if the ligand is in excess (Fig. 4). For intermediate situations, these resonances gradually broaden and finally collapse into *one* broad resonance. In the limit of rapid exchange (>100 c.p.s.), each resonance in the spectrum is an average resonance over both species. These exchange rates, of course, depend upon the mechanism of exchange, which may involve either a displacement or a dissociation process. For either process, however, some correlation of the exchange rates with the stability of the chelates is not unexpected.

**Protonation of EDTA.**—Figure 7 indicates the predominant EDTA species present in solution at various pH's based on the measured  $pK_a$ 's of EDTA,<sup>18</sup> which

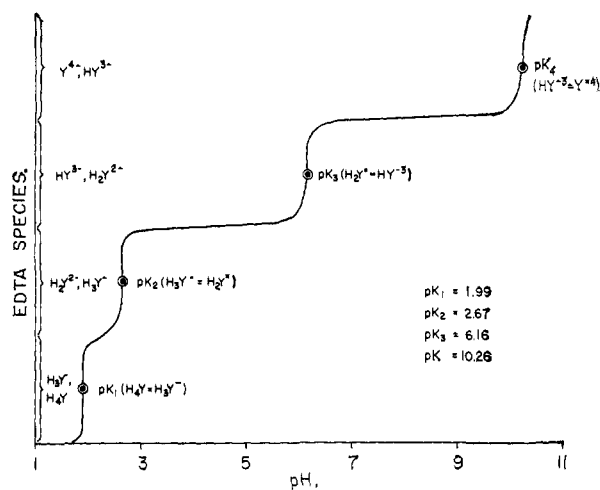


Fig. 7.—Protonated EDTA species present in solution as a function of pH.

are 1.99, 2.67, 6.16, and 10.26. From these  $pK_a$ 's the first two protons are expected to add to the tetra-anion of EDTA in a pH range of 11 to 4 if the coordination between the metal ion and the ligand is weak. The positions of the breaks depicted in Fig. 2 fall nicely within this pH range. These two breaks accordingly are interpreted to correspond to two successive protonations of the EDTA tetra-anion. Below pH 4, two more protons are presumably added in a relatively narrow pH range. Unfortunately,  $H_4Y$  quickly precipitates from solution, thus preventing further n.m.r. studies.

If the first proton is added to one of the carboxylate groups,  $\delta_B$  may vary and  $\delta_A$  should remain nearly constant. However, as Fig. 2 indicates, the change in  $\delta_A$  with the addition of the first proton is about the same as the corresponding change in  $\delta_B$ . In fact  $\Delta\delta_A > \Delta\delta_B$ . Some electrical disturbance quite near both A and B protons is thus prevailing, suggesting protonation at one of the nitrogen sites. Evidence for rapid exchange of this proton is provided by the absence of additional resonance peaks in the spectrum.

(18) J. Bjerrum, G. Schwarzenbach, and L. Sillén, "Stability Constants, Part I," The Chemical Society, London, 1957, p. 76.

The over-all effect of the addition of two protons on the chemical shifts is approximately to double the effect of the first protonation. The second breaks thus suggest that the second proton also adds to the nitrogen atoms.

Several proposals have previously been put forward regarding the nature of the EDTA species. In one theory, the protons in  $HY^{3-}$  and  $H_2Y^{2-}$  are thought to be attached to the nitrogens and the other protons in  $H_3Y^-$  and  $H_4Y$  are thought to be added to the carboxylate groups.<sup>19</sup> An alternate postulate has all of the four protons attached to the four carboxylate groups in the  $H_4Y$  species.<sup>20</sup> We feel that the n.m.r. data are consistent with the former interpretation. Although the effect of the third and fourth proton cannot be seen by n.m.r. studies because of our fairly high concentrations and subsequent precipitation of  $H_4EDTA$ , it seems clear that the first two protons have coordinated with the nitrogen atoms.

The shift of the resonance to lower fields as the pH is lowered is understandable. Owing to the much greater charge-to-radius ratio of the proton compared to the metal ions, the replacement of a metal ion by a proton is expected to increase the electrostatic perturbation on the A and B protons.

**Alkali Metals.**—The pH's at which the breaks occur for various metal chelates indicate their relative stabilities toward protonation: the greater the interaction of the metal with nitrogen, the lower the pH at which the breaks occur. Figure 2 indicates that the relative stabilities of the alkali metal–nitrogen bonds go in the order:  $Li^+ > Na^+ > K^+ \approx Cs^+$ . It is also noteworthy that this is the order of known stabilities of the alkali metal–EDTA chelates. A consideration of the mid-points of the first pH breaks, the metal ion concentration, and the  $pK$  value of the  $HY^{3-}$ – $Y^{4-}$  equilibrium (10.3) allows a calculation of the formation constant of the metal chelate. For example, the value found for Li–EDTA is  $10^{2.5}$ , which agrees well with the literature value<sup>18</sup> of  $10^{2.79}$ .

The chemical shift curves for  $K^+$  and  $Cs^+$  show an almost identical pH dependence as a  $(CH_3)_4N^+$ –EDTA solution. Consequently, these ions must have very little tendency to coordinate with the nitrogen atoms of EDTA, as expected from charge-to-radius considerations. The position of the  $\delta$ -breaks in these solutions is therefore governed solely by the  $H_2Y^{2-}$ – $HY^{3-}$ – $Y^{4-}$  equilibria.

The chemical shifts for the ethylenic and methylenic protons in the doubly-protonated species,  $H_2Y^{2-}$ , are given by the limiting  $\delta_A$  and  $\delta_B$  in the vicinity of pH 4 (Fig. 2). These  $\delta_A$  and  $\delta_B$  values (2.86 and 2.61, respectively) also are observed for any metal chelates capable of protonation in the pH range of interest. The plateau after the first break in the vicinity of pH 7 represents the chemical shift for the monoprotonated species. If the monoprotonated species in alkali–EDTA mixtures is  $HY^{3-}$ , overlapping breaks at the low pH end should be observed for all the alkali metal ions. The fact that different breaks are observed for Li, Na, and K tends to imply that metal–nitrogen interaction is still present at these pH's for Li and Na. The monoprotonated species is most likely MHEDTA.

**Alkaline Earth Ions.**—The n.m.r. data for the alkaline earth EDTA chelates (Fig. 3) have been interpreted in an analogous manner to that for the alkali metals, *i.e.*, the alkaline earth metals are coordinated in varying degrees with the nitrogen atoms. Thus, proton attachment to the nitrogen atoms by displace-

(19) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

(20) D. Chapman, *J. Chem. Soc.*, 1766 (1955).

ment of the metal ion is hindered until a fairly low pH is reached. When this occurs, and the complex dissociates,  $\delta_A$  and  $\delta_B$  shift to lower values. Since only one break occurs and since the limiting  $\delta$ -values at low pH approach the values associated with the  $H_2Y^{2-}$  species, both protons must add in a very narrow pH range, displacing the metal ion from EDTA. The positions of the breaks are governed by the relative stabilities of the metal chelates, the pH of the midpoint of the break being lower the greater the stability of the chelate. A calculation similar to that used for the alkali metals, but considering the addition of two protons, gives an order of magnitude estimate of the formation constants and is shown in Table II. The discrepancies between the calculated formation constants and the values found in the literature may be our failure to take into account such species as  $BaHY$  and  $SrHY$  whose existence is known,<sup>18</sup> but whose presence cannot be detected by our n.m.r. techniques.

TABLE II

ALKALINE EARTH-EDTA FORMATION CONSTANTS FROM N.M.R. CHEMICAL SHIFT DATA

Metal ion	N.m.r. pH breaks	pK	
		Calcd.	Lit. <sup>18</sup>
Mg	No break	...	8.7
Ca	4.0	9.4	10.6
Sr	4.9	7.6	8.6
Ba	5.5	6.2	7.8

The data of Fig. 4 and 5 confirm the conclusions drawn from the 1:1 metal-to-EDTA studies (Fig. 3). That is, that magnesium ion forms a tightly bound coordinate linkage to the nitrogen atoms and does not exchange between ligands. Calcium ion also appears to coordinate readily to nitrogen at intermediate pH values, but to exchange rapidly at high pH's, and at low pH's the protons become effective in displacing the metal ion from nitrogen. With strontium and barium the exchange between ligands seems to be rapid at high pH's and of the order of 10 cycles/sec. at intermediate pH's.

Two explanations for the exchange phenomena observed for the alkaline earth chelates appear plausible at this time: (1) With the exception of magnesium, the alkaline earth EDTA chelates are probably coordinated loosely enough that at high pH's where there are not sufficient protons available to compete with the metal ions for the nitrogen sites, the metal ions can exchange rapidly between the EDTA species ( $Y^{4-}$ ). However, at intermediate pH values (less than 10) the "free" EDTA species is  $HY^{3-}$ . (Evidence for this species is provided by the alkali metal studies.) At this point the exchange of the metal ions between ligands is expected to be slowed down (since "free" EDTA is no longer as available). The more stable the metal chelate, the higher the threshold pH at which broadening begins to appear; thus: Ca, pH 11; Sr, pH 10; Ba, pH 9. As the pH is lowered, the exchange gradually slows down to the extent that, in the case of Ca, two sets of peaks appear (Fig. 5). At still lower pH's the proton becomes a much more effective coordinating agent than the metal ions and displaces the metal ion from nitrogen. Here, line widths are determined by exchange of  $H^+$ 's between ligands and a single sharp set of resonances corresponding to those for  $H_2Y^{2-}$  appears.

(2) The coordination of metal hydroxy species to the ligand constitutes another possible explanation for the exchange phenomena. When  $OH^-$  is complexed to the metal ion, the effective charge of the ion becomes

one unit less, and the tendency for electrostatic interaction with nitrogen is decreased. Also, the  $OH^-$  can block a coordination site of the metal and limit the number of EDTA sites which can coordinate to the metal. Therefore, a weaker chelate is formed enabling the metal( $OH$ )<sup>+</sup> species to exchange rapidly between ligands. At intermediate pH values the  $OH^-$  is neutralized and the doubly-charged cation can then form a stronger metal-nitrogen bond. While stable metal-hydroxy species are not expected to be important with the alkaline earth ions at these pH's, there is strong evidence for this latter mechanism in the EDTA chelates of mercury(II), aluminum(III), and zinc(II).

**Other Metal Ions.**—The ions of lead, zinc, mercury, and aluminum are known to coordinate quite strongly to EDTA,<sup>18</sup> and the n.m.r. data are in general accord with this fact. The pH-independent  $\delta_A$  and  $\delta_B$  values for lead EDTA must mean that the ion is strongly coordinated to the nitrogen atoms to the extent that displacement by  $H^+$  is hindered. This phenomenon is noteworthy in that no ammonia complexes of lead are known. Apparently coordination to the carboxylate groups permits the metal ion to remain in solution by preventing any hydroxide precipitation so that metal-nitrogen coordination is possible. The slow exchange phenomenon which is observed for zinc EDTA has been discussed for the alkaline earth chelates and may be explained by either of the mechanisms advanced there. Here, however, the existence of a  $Zn(OH)Y^{3-}$  species is suspected, which would enhance the exchange. Polarographic work is currently being carried out to establish the possibility of such a species at high pH's.

The single set of broadened resonances at high pH for mercury EDTA is again indicative of slow exchange of some metal species between ligands. The polarographic work of Matyska and Kössler<sup>21</sup> has shown the existence of a  $Hg(OH)Y^{3-}$  species having a formation constant of  $10^{5.1}$  according to the reaction  $HgY^{2-} + OH^- = Hg(OH)Y^{3-}$ . Thus, it is not unreasonable that the broadened peaks arise from exchange of  $Hg(OH)^+$  between EDTA ligands. In fact, these broadened peaks should resolve into two sharper sets of resonances when  $HgY^{2-}$  is present in appreciable amounts. A simple calculation demonstrates that this should occur at about pH 9, in agreement with the experimental data. Because aluminum ion forms hydroxy complexes readily, it is probable that a similar exchange mechanism is involved with  $Al(OH)_2Y^{3-}$  and  $Al(OH)Y^{2-}$  species at high pH's. From pH 6.5 to 4, the species is probably  $AlY^-$ . The large chemical shifts to low fields are indicative of a larger degree of charge distortion than for the ions of the alkali metals and alkaline earths. Thus, the central ion must possess a high charge-to-radius ratio.

## Conclusions

In general, the n.m.r. chemical shift data for the metal-EDTA chelates are in qualitative agreement with known stability constants.<sup>18</sup> Thus, from the n.m.r. measurements the stabilities of the chelates are indicated to be in the order:  $Ca > Sr > Ba > Li > Na > K \approx Cs$ . The exact position of Mg in this series cannot be determined because precipitation prevents measurement of chemical shifts below pH 5.5. Nevertheless, the data indicate that Mg-EDTA is at least as stable as Sr-EDTA. Although classical measurements<sup>18</sup> place Mg between Ca and Sr in terms of stability constants, the n.m.r. exchange studies establish that Mg exchanges more slowly between ligands

(21) B. Matyska and I. Kössler, *Collection Czech. Chem. Commun.*, **16**, 221 (1951).

than does Ca. This might indicate that the coordinate bonding for Mg-EDTA is more stable than for Ca-EDTA. The EDTA chelates of Pb, Al, Zn, and Hg, on the basis of the n.m.r. data, all are more stable than the alkaline earth chelates.

The mono- and diprotonated species of EDTA are concluded to be protonated on the nitrogen atoms. Although attempts to observe these protons have been unsuccessful, the n.m.r. chemical shift data (Fig. 2) appear convincing. Thus, the n.m.r. studies confirmed the results obtained by classical methods<sup>19</sup> and by recent infrared measurements.<sup>11</sup> It is inconceivable that the metal ions are coordinated only to the nitrogen atoms from the consideration of the high stability constants of the chelates. Thus, at least some, if not all, of the carboxylate groups are expected to be involved in chelation. If, however, the metal-oxygen bonds were firmly fixed, then any less than four carboxylates coordinated to metal ions would appear as additional resonances in the spectra. Since no such additional peaks were found, it seems reasonable to conclude that the carboxylate groups are rapidly (faster than the metal ions exchange between ligands) coordinating and dissociating from the metal ions, the exchange displaying only a single, averaged B resonance. Molecular

models of a metal EDTA chelate show that each set of methylenic protons would not be equivalent if the chelate is rigidly hexadentate and this would lead to additional splitting of the B resonances. Thus, even if the chelates approach hexadentate coordination there is a rapid coupling and decoupling of the metal-carboxylate groups, resulting in a single, averaged resonance for the methylenic protons.

It might be expected that variations in the  $\delta_A - \delta_B$  values would reflect variations in the extent of carboxylate coordination (a larger  $\delta_A - \delta_B$  value indicating a larger degree of metal-carboxylate interaction). However the situation is fairly complex, involving such other factors as the radius of the metal ion, the charge of the metal ion, and the extent of the metal-nitrogen interaction. As a result, no distinct correlation could be found between the  $\delta_A - \delta_B$  values and the metal-carboxylate coordination.

**Acknowledgments.**—We wish to thank the United States Atomic Energy Commission for support of this work (Contract No. AT(11-1)-34, Project No. 45) and the National Science Foundation for a predoctoral fellowship to R. J. K. We are also indebted to Professors Ronald Archer and Theodore Kuwana for stimulating discussions and helpful criticisms.