Raman Spectra of Ethylenediaminetetraacetic Acid and Its Metal Complexes[1]

K. Krishnan and Robert A. Plane

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received November 13, 1967*

Abstract: Raman spectra were measured of aqueous solutions of EDTA and its complexes with Be^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Bi^{3+}, and Pb^{2+}. For the free ligand, spectra are reported at pH 4.5 and 11 in H_2O and at pH 4.5 in D_2O. Of special interest is the Raman band near 920 cm^{-1} which is diagnostic of protonation of the ligand. In H_2O, protonation appears to involve the acetate groups, in addition to the nitrogen atom, as if an internal H-bonded structure is formed. However, in D_2O the spectrum changes significantly, indicating strong solvent involvement. For the metal complexes, Raman lines characteristic of metal–nitrogen stretching frequencies are observed in the 400–500-cm^{-1} region with intensities indicating significant covalent bonding for all the metal ions studied except Mg^{2+} and Ca^{2+}. The frequency of the metal–nitrogen stretching bands decreases with increasing radius of the metal ion, independent of the stability of the complex. In no case are there any Raman lines characteristic of covalent bonding of the acetate groups which apparently is mainly electrostatic. For the complexes of Cu^{2+} and Hg^{2+} the spectra show changes at both low and high pH consistent with a single protonation of the ligand in acid solution and coordination of an OH^- in basic solution. For the Cu^{2+} complex at pH 12, a line at 430 cm^{-1} is observed which can be assigned to Cu–OH stretching.

Ethylenediaminetetraacetate (EDTA or A^{4-}) forms very strong complexes with a variety of metals.[2] Sawyer and his coworkers have recorded the infrared spectra of a large number of metal–EDTA complexes in the solid state[3–5] and also in aqueous solution.[6,7] Nuclear magnetic resonance studies have also been carried out for aqueous solutions of EDTA and its metal complexes by Sawyer and coworkers.[8] As far as we are aware, no Raman spectral studies have been made on either EDTA or its metal complexes. Raman spectra of such complicated molecules cannot be analyzed completely in order to give, directly, structural information. However, from spectral changes with concentration, inferences can be drawn as to the formulation of the solute species present. The situation is thus reminiscent of solution studies done with visible and ultraviolet spectrophotometry and the results of the Raman study should be just as significant. The Raman method can be used to obtain complete vibrational spectra and unlike infrared studies it is not limited to the carbonyl stretching region.

Experimental Section

EDTA, as the disodium salt of reagent grade, was supplied by Fisher Scientific Co. The various metal salts used were also of reagent grade. Nitrate salts were used for Pb(II) and Bi(III) and chloride salts for all the other metal ions. For recording the Raman spectra of the metal complexes, concentrated solutions were prepared which contained equimolar ratios of the disodium EDTA salt and the various metal salts. The concentration of the metal ions varied from 0.25 to 0.75 *M*. Raman spectra of the solutions were recorded at various pH values. The pH of the solutions were varied by adding either the corresponding acid or sodium hydroxide. For most of the metal complex solutions, except that of Cu(II), it was not possible to get solutions having pH values below 3.0, because precipitation occurred in this pH range. For Cu(II), however, it was possible to prepare solutions having pH values between 2.0 and 3.0, from which precipitation did not occur for the time necessary to run the Raman spectra. The Raman spectra were recorded using a Cary Model 81 Raman spectrophotometer.

Results

The Raman spectra of disodium EDTA were recorded at pH of 4.5, 8.8, and 11.0 in aqueous solution. A Raman spectrum of the salt in heavy water was recorded at a measured pH of 4.5. There were some changes in the Raman spectra of the aqueous solutions as the pH was changed. The most prominent changes were in the 900-cm^{-1} region. Figure 1 illustrates the Raman spectra of aqueous solutions of disodium EDTA between 850 and 1000 cm^{-1} at pH 4.5, 8.8, and 11.0. As can be seen the broad band at pH 4.5, which actually seems to consist of two lines at 912 and 930 cm^{-1}, sharpens up and increases in height as the pH is increased. The frequencies of the Raman lines of the disodium EDTA at pH 4.5 and 11.0 are given in Table I. The solution in D_2O at pH 4.5 (meter reading) has only a comparatively sharp line at 925 cm^{-1}. At low pH the Raman spectrum of the H_2O solution contains a broad band of medium intensity at 1220 cm^{-1}. At higher pH a new line appears at 1265 cm^{-1} with a shoulder at 1280 cm^{-1}.

Raman spectra were recorded for the metal complex solutions of Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Be^{2+}, Ca^{2+}, and Bi^{3+}, at various pH values. The main feature of the spectra of the above solutions, except for those of Ca^{2+} and Mg^{2+}, is the appearance of a strong polarized Raman line between 500 and 400 cm^{-1}. For Ca^{2+} and Mg^{2+} the new lines are of but medium intensity. In all the above spectra, at the same pH (about 4.5) where the aqueous solution of the disodium EDTA salt gave two Raman lines in the 900-cm^{-1} region, only a sharp intense band was observed. Another feature of the spectra of the complexes was the slight decrease in intensity of the Raman line at 1400 cm^{-1}.

---

[1] Supported by the Office of Saline Water, U. S. Department of the Interior.

[2] "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

[3] D. T. Sawyer and P. J. Paulsen, *J. Am. Chem. Soc.*, **80**, 1597 (1958).

[4] D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).

[5] D. T. Sawyer and J. M. McKinnie, *ibid.*, **82**, 4191 (1960).

[6] D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 314 (1963).

[7] D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 2390 (1963).

[8] R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *ibid.*, **85**, 2930 (1963).

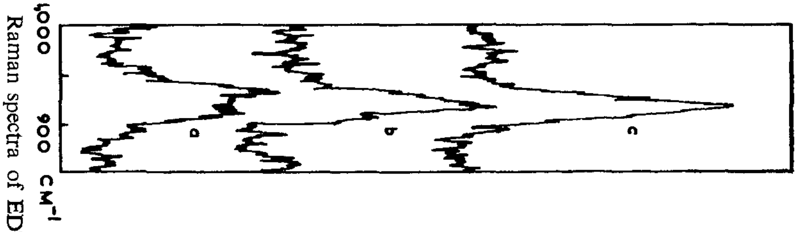

Figure 1. Raman spectra of EDTA solutions: (a) pH 4.5, (b) pH 8.8, (c) pH 11.0.

Figure 2. Raman spectra of Cu(II)–EDTA solutions: (a) pH 2.5, (b) pH 7.0, (c) pH 12.0.

Table I. Raman Spectra of EDTA and Its Metal Complexes (in Neutral Aqueous Solution)[a]

pH 4.5	pH 11	D_2O[b]	Cu^{2+}	Hg^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Mn^{2+}	Be^{2+}	Bi^{3+}	Ca^{2+}	Mg^{2+}
			235 w, sh									
			280 w, sh	280 w, sh	310 vw, b		275 m, sh			300 m, sh		
355 m	350 m, b	340 m, b	390 m, b	355 m	385 m	365 m, b	355 s	365 m	365 m	370 s	375 m	350 vw, sh
	400 m, b											
430 m, b	450 m, b	430 m, b	430 w, sh		425 w, sh				430 m		420 m	
			470 s	425 vs	460 s	435 s	424 vs	445 s	490 s	442 vs	445 m	450 m, b
480 w, sh	480 w, sh	475 w, sh	525 s	500 m	485 w, sh	490 m, b	495 m	490 vw, b		500 s	485 w, sh	490 vw, sh
585 w, b	595 w, b	600 vw	595 w, b	590 w, b	590 w, b	610 vw	600 w, b		600 vw	600 vw	600 vw	590 vw, b
715 w, b	710 w, b		720 w, b	710 w	720 w, b			740 w, b			725 w, b	725 w, b
800 w, b	800 w, b			815 w	810 w	820 w, b	820 w			825 w	810 vw	820 vw
850 w, b	845 w, b			855 vw	860 w	850 w	855 vw	865 m		855 w	855 w	865 w
912 s, b	918 vs	925 vs	920 vs	920 s	915 s	918 s	915 s	920 vs	925 s	925 m	918 vs	918 vs
930 s, b									940 m, sh			
945 m, sh	975 w, b	950 w, sh	970 m	970 m	970 w	965 m	965 m	970 m	980 m	970 w	968 m	975 w
1004 w	1020 w	1000 w, b	1015 w	1005 vw	1010 vw			1028 w			1000 vw	1015 vw
1075 w, b	1085 w	1050 w, b		1085 w	1070 vw		1093 m				1060 ?	
1125 w	1140 m, b	1100 w	1120 m, vb	1118 w	1120 m	1130 m	1120 m	1125 m	1115 m	1100 m	1125 m	1125 m
1220 m, b	1200 w	1200 m, b	1175 vw	1175 w	1180 w	1185 m	1180 m	1180 m	1160 w	1175 m	1185 m	1175 m
	1265 m		1265 m, b	1255 m, b	1255 m, b	1265 m, b	1255 m, b	1260 m, b	1260 m, b	1260 m, b	1250 m, b	1250 m, b
	1280 vw, sh		1280 w, sh	1280 w, sh	1280 w, sh	1290 w, sh	1290 w, sh				1280 w, sh	1280 w, sh
1325 s	1335 s	1320 m	1325 m	1335 s	1330 m	1338 m	1335 s	1335 s	1330 m	1330 s	1330 s	1335 m
1400 vs	1406 vs	1400 vs	1400 vs	1400 vs	1402 vs	1408 vs	1402 vs	1408 vs	1400 vs	1400 vs	1405 vs	1400 vs
1435 m, sh	1435 m, sh	1440 s, sh	1440 s	1440 s	1445 s	1445 s	1440 s	1445 s	1455 s, b	1440 s	1435 s, sh	1445 s, sh
1454 m, sh	1450 m, sh	1454 m, sh	1465 m	1455 s, sh	1468 s	1462 s	1455 m, sh	1465 s		1450 m, sh	1454 m, sh	1460 m, sh
1625 m, b	1600 m, b	1625 m, b	1605 m, b	1605 m, b	1600 m, b	1610 m, b	1605 m, b	1605 m, b	1610 m, b	1630 ?	1600 m, b	1600 m, b

[a] s = sharp; m = medium; w = weak; v = very; b = broad; sh = shoulder. [b] Nominal pH 4.5.

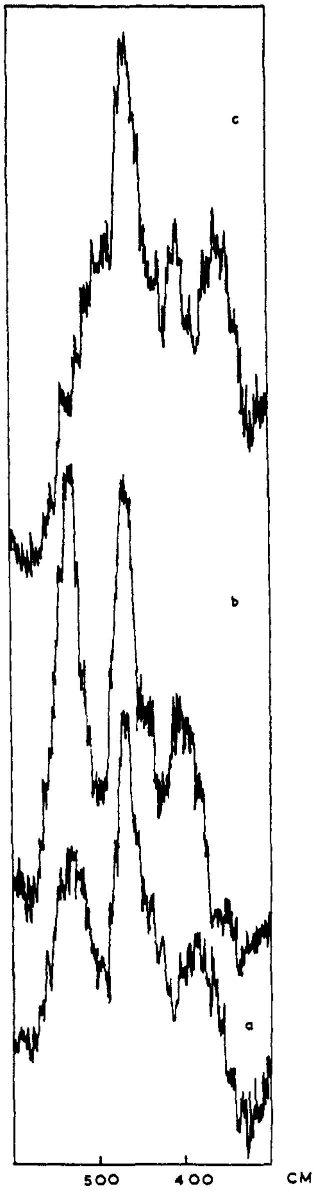

Figure 3. Raman spectra of Cu(II)–EDTA solutions: (a) pH 2.5, (b) pH 7.0, (c) pH 12.0.

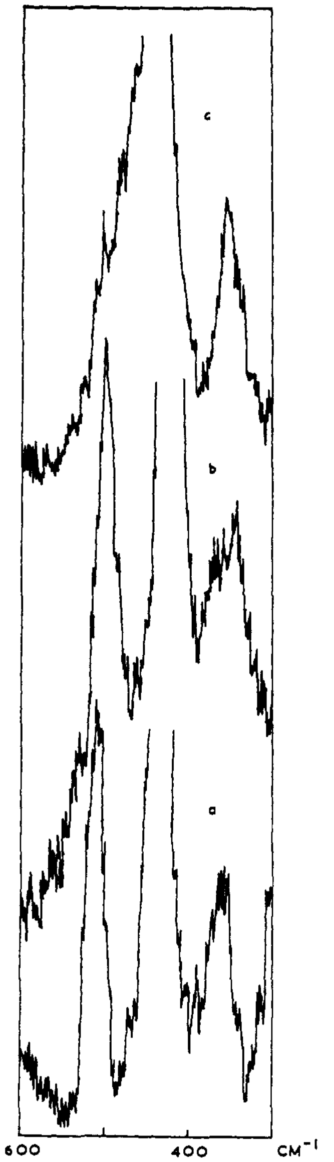

Figure 4. Raman spectra of Hg(II)–EDTA solutions: (a) pH 2.9, (b) pH 5.0, (c) pH 12.0.

The Raman spectra of the metal–EDTA complexes of Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+} remained practically unaltered in the pH range 3.0–11.0. For Mn^{2+} and Be^{2+}, it was not possible to prepare concentrated solutions at pH values above 5.0 and the spectra did not change in the pH range 3–5.

The spectrum of the Cu^{2+} complex of EDTA showed some striking changes with the change in pH of the solution. At a pH of 2.5, the Raman spectrum in the 900-cm^{-1} region consists of a band of medium intensity at 920 cm^{-1} with a broad shoulder at 890 cm^{-1}. As the pH is increased, the 890-cm^{-1} shoulder disappears and there is only one strong line at 918 cm^{-1}. This is illustrated in Figure 2. In the region below 600 cm^{-1}, at pH 2.5, there is a strong Raman line at 470 cm^{-1}, accompanied by a broad band of medium intensity at 525 cm^{-1}. As the pH is increased, the band at 525 cm^{-1} becomes stronger and at pH of 7.0 is almost as strong as the 470-cm^{-1} Raman line. As the pH of the solution is still further increased, the Raman line at 525 cm^{-1} begins to lose intensity, and at pH 11.0 this line is barely visible as a shoulder. The Raman line at 470 cm^{-1} seems to remain practically unaffected over the entire pH range. These features are illustrated in Figure 3.

The mercury–EDTA complex (Figure 4) at pH 2.9 has a very strong Raman line at 425 cm^{-1} and a strong line at 500 cm^{-1}. As the pH of the solution is increased, this line remains unaffected until a pH of 7.0 is reached. As the pH is further increased, the Raman line at 500 cm^{-1} begins to decrease in intensity, and at a pH of about 11.0 the line at 500 cm^{-1} has almost disappeared. The line at 425 cm^{-1} becomes broader as the pH is increased above 7.0, and at a pH of 11, where the line at 500 cm^{-1} has practically disappeared, this line is very broad and seems to have shifted to 440 cm^{-1}. Changes in the mercury–EDTA complex spectra are very similar to those occurring in the Cu–EDTA spectra, shown in Figure 3, except for the fact that we were not able to record the Hg–EDTA spectrum at a low enough pH to show the splitting of the 900-cm^{-1} band, and for the decrease in intensity of the 500-cm^{-1} Raman line.

For comparison purposes, the Raman frequencies of EDTA complexes of Cu, Hg, Zn, Cd, Pb, Mn, Be, Bi, Ca, and Mg in neutral aqueous solution are listed in Table I.

Discussion

Spectra of EDTA Solutions. At pH values above 11.0, EDTA exists as its tetraanion, A^{4-}, in solution. As the pH is lowered, protonation occurs, and around a pH of 9.0 the predominant species should be the ion HA^{3-}. As the pH is lowered further the diprotonated form H_2A^{2-} becomes the predominant species in the pH range 4.0–5.5. Below a pH of 4.0 the tri- and tetraprotonated forms should exist, but these species are insoluble, and precipitation occurs.[6]

The structure of the protonated forms of EDTA has been the subject of much controversy. Various structures have been proposed for the structure of the diprotonated ion H_2A^{2-}. Schwarzenbach and Ackermann,[9] Carini and Martell,[10] Olson and Margerum,[11] Sawyer and Tackett,[6] and Nakamoto, Morimoto, and Martell[12] favor a structure for the H_2A^{2-} ion in which the nitrogen atoms, and not the carboxyl groups, are protonated. Chapman[13] originally proposed that the carboxylate groups were protonated, from an infrared study of the solid disodium dihydrogen EDTA. Recently, however, from his infrared and nmr studies of aqueous solutions of EDTA,[14] he has proposed that the nitrogen atoms are protonated in H_2A^{2-}, each proton forming a bifurcated (internal) hydrogen bond to the adjacent carboxylate oxygens. Charles[15] from his visocity measurements has proposed that the hydrogen atoms in H_2A^{2-} form internal hydrogen bridges between the nitrogen and one of the two adjacent carboxylate oxygen atoms. More recently Novak, *et al.*,[16,17] have recorded the ir spectra of the various salts of EDTA and their deuterated analogs in the solid state and have concluded that in H_2A^{2-} the nitrogen atoms are protonated.

No detailed vibrational analysis of the EDTA molecule is reported in the literature, nor is it very fruitful to attempt one in view of the complexity of the molecule. Previous investigators, however, have assigned the carbonyl frequencies in the 1400–1700-cm^{-1} region. The C–N stretching frequency has been identified with the infrared absorption around 1100 cm^{-1}. In the Raman spectrum of EDTA at a pH of 11, where the predominant species is expected to be A^{4-}, there is a strong line at 918 cm^{-1}. There is good reason to believe that this line is due primarily to the C–C stretching frequency of the acetate group. In acetic acid the C–C stretching frequency is at 886 cm^{-1},[18] in the acetate ion at 926 cm^{-1},[19] and in the glycine zwitterion at 893 cm^{-1}.[20]

If we assume as above that the assignment of the 918-cm^{-1} line to the acetate part of the EDTA molecule is correct, the splitting of the Raman line, as the pH is lowered, would indicate that as protonation of the A^{4-} ion occurs, acetate C–C bonds are becoming nonequivalent. At pH 4.5 where these are now two broad peaks at 912 and 930 cm^{-1} of equal height could mean that there is an equal number of two distinct C–C bonds. It is also interesting to note from Figure 1 that the heights of the peaks at pH 4.5 are approximately half the height of the peak at pH 11. An obvious way of explaining the above changes would be to postulate the protonation of the two carboxyl groups, which would give rise to an equal number of two distinct C–C bonds in the H_2A^{2-} ions, but such a conclusion is precluded by the nmr work on aqueous solutions of EDTA.[8,14] Furthermore, in heavy water solutions of EDTA, only one C=O infrared stretching frequency is observed[6,12,14] at 1620 cm^{-1} for H_2A^{2-}, indicating the presence of only one type of carboxylate group in the ion. Thus, apparently the nitrogen atoms are protonated. In our Raman spectrum of the D_2O solution, there is only a single, sharp line at 925 cm^{-1} which would indicate only one type of acetate C–C bonds in D_2O solution. But the fact that this result differs from the H_2O solution shows that the structure of H_2A^{2-} is dependent on the solvent. In H_2O solutions, an internal H bond between the N–H and one of the adjacent acetate groups would account for the existence of structurally different acetate groups. The fact that the two become equivalent in D_2O could indicate that this internal hydrogen bond is bifurcated as proposed by Chapman,[14] or completely broken as proposed by Sawyer.[6] Because hydrogen bonding of the acetates to the solvent may also be involved, decision between the plausibility of the two explanations is difficult, and both are consistent with all spectral data.

Shimanouchi, *et al.*,[21] have found that the $-CH_2COOH$ group has a characteristic frequency near 1200 cm^{-1}, and they have assigned it to the CH_2 wagging motion, to which some contributions are made from C–O and C–C stretching vibrations. In the Raman spectrum of EDTA at pH 4.5 (the H_2A^{2-} ions), there is a broad band at 1220 cm^{-1} in the aqueous solution and at 1200 cm^{-1} in heavy water solution. In the spectrum of the aqueous solution at pH 11, this band seems to have shifted up to 1265 cm^{-1}. This change again seems to indicate some changes taking place around the acetate group. Because of the complications due to the water band around 1650 cm^{-1} and a mercury line near 1670 cm^{-1}, we could not make any definite measurements in the carboxylate antisymmetric stretching region.

Raman Spectra of the Complexes. Shevchenko[22] has summarized the results of the study of the infrared spectra of solid metal–EDTA complexes. He concludes that all the metal ions studied here, except Be^{2+} and Pb^{2+} which he has not considered, form ionic bonds to the carboxylate groups. Such bonds are not expected to give rise to strong metal–oxygen Raman lines. All the metal–EDTA solutions investigated here except

---

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

(10) F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 4810 (1953).

(11) D. C. Olson and D. W. Margerum, *ibid.*, **82**, 5602 (1960).

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

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

(14) D. Chapman, D. R. Lloyd, and R. H. Prince, *ibid.*, 3645 (1963).

(15) R. G. Charles, *J. Am. Chem. Soc.*, **78**, 3946 (1956).

(16) A. Novak, M. Cotrait, J. Joussot-Dubien, and J. Lascombe, *Inorg. Chem.*, **4**, 767 (1965).

(17) A. Novak, M. Cotrait, J. Joussot-Dubien, and J. Lascombe, *Bull. Soc. Chim. France*, 1440 (1965).

(18) M. Haurie and A. Novak, *J. Chim. Phys.*, **62**, 137 (1965).

(19) K. Ito and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

(20) S. Suzuki, T. Shimanouchi, and M. Tsuboi, *Spectrochim. Acta*, **19**, 1195 (1963).

(21) T. Shimanouchi, M. Tsuboi, T. Takenishi, and N. Iwata, *ibid.*, **16**, 1328 (1960).

(22) L. L. Shevchenko, *Usp. Khim.*, **32**, 457 (1963).

for Ca^{2+} and Mg^{2+} give rise to a strong, polarized Raman line between 400 and 500 cm^{-1}. These are assigned as metal–nitrogen stretching frequencies. The great intensities of these lines show that the metal–nitrogen bonds are quite covalent, a conclusion which has been anticipated by previous investigators. By contrast the weaker *ca.* 450-cm^{-1} lines for the Mg^{2+} and Ca^{2+} complexes mean that covalent coordination to nitrogen is significantly less for these cases. Another feature of the observed metal–nitrogen frequencies is that, regardless of the formation constant of the complex, they show a fairly general decrease with increasing ionic radius of the metal. Such a trend has been observed also for the C–N stretching vibrations in the infrared spectra of the metal complexes in the solid state.[4]

In the same pH range where the EDTA solution yields the two broad Raman lines in the 900-cm^{-1} region, the complexes show only a very strong, sharp line. This indicates, consistent with our assignment of this line to a C–C stretching frequency, the equivalence of the four carboxylate groups and thus is a criterion for the metal–oxygen coordination. The appearance of the single sharp line in the 900-cm^{-1} region coupled with the presence of the metal–nitrogen stretching frequency would indicate hexacoordination of the metal ion by the EDTA. The various features observed in the spectra of the metal complexes are discussed below in detail.

Spectra of Mg^{2+} and Ca^{2+} Complexes. Sawyer has concluded from his infrared and nmr studies on aqueous solutions of alkaline earth metal–EDTA complexes[7,8] that the nitrogen atoms are protonated at low pH, and that as the pH is increased some metal nitrogen coordination is possible, and at very high pH they give rise to spectra which are identical with those of the A^{4-} ion. The bonding between the metal and the oxygen atoms must be primarily ionic. He also indicates that at lower pH dissociation of the complex may occur.

The Raman spectrum of Ca–EDTA at a pH of about 3.8 shows a broad line at 918 cm^{-1}. The rest of the spectrum is virtually identical with that of the H_2A^{2-} ion. As the pH is increased, the 918-cm^{-1} line sharpens and becomes stronger. The spectra of Mg–EDTA recorded at pH 4.0 and 6.0 are identical, with a sharp strong Raman line at 920 cm^{-1}. The spectra of the two metal–EDTA solutions do not contain any strong lines in the low-frequency region. At a pH of 6, the two solutions contain polarized Raman lines of medium intensities at 445 cm^{-1} for Ca^{2+} and 450 cm^{-1} for Mg^{2+}. It is possible that these lines may arise from metal–nitrogen or metal–oxygen vibrations; however, this assignment is far from certain. The 445-cm^{-1} line in Ca–EDTA does not seem to be present in the spectrum of the solution at pH 3.8. If this line is indeed due to metal–nitrogen stretching, this fact would tend to support the conclusions of Sawyer, *et al.*,[7,8] that coordination to nitrogen may occur in the intermediate pH range.

Raman Spectra of the Complexes of Zn^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+}. The spectra of the complexes of these four metals are unchanged in the pH range 4.0–11.0, indicating that the structure of these complexes do not change through this pH range. The spectra exhibit a single line in the 900-cm^{-1} region, which is very strong in the Zn^{2+} and Cd^{2+} complexes and of strong or medium intensity in the Pb^{2+} and Bi^{3+} complexes. The last observation is difficult to explain. Possibly, because of strong ionic bonding between the oxygen atoms and the metal ions, the C–C bonds acquire considerable polar character, with the subsequent decrease of intensity of the C–C Raman line. The single Raman line shows that all the carboxylate groups are bound to the metal in the pH range noted above. This was also the conclusion reached by Sawyer. Since all these solutions exhibit a very strong metal–nitrogen stretching frequency, one can conclude that these metals are all six-coordinate in solution. Langer[23] indicates that Pb is four-coordinate in the solid state. However, in solution, our results would indicate six-coordination. Sawyer, *et al.*,[9] indicate the possibility that at very high pH zinc forms some hydroxy complex with EDTA. We were, however, not able to record a spectrum of the solution at any pH greater than 11.

Spectra of Mn^{2+} and Be^{2+} Complexes. For neither of these complexes was it possible to prepare solutions at pH above 5.0. Also, the solutions were highly fluorescent. The spectra for the two complexes recorded at pH 3 and 5 seem to be identical. They contain a strong Raman line below 500 cm^{-1} which can be assigned to metal–nitrogen vibrations. The Mn–EDTA complex contains only one strong, sharp Raman line at 920 cm^{-1}. For the Be–EDTA complex, even at a pH of 5.0, the peak at 925 cm^{-1} seems to be very broad. Possibly the Be^{2+} ion does not coordinate to all the four carboxylate groups. Hoard, *et al.*,[24] have determined the crystal structure of a Mn–EDTA complex and find that the Mn atom is seven-coordinate, with the formula $Mn(H_2O)A^{2-}$. The Raman spectra provide no way of concluding whether the water molecule is bound to the Mn^{2+} ion or not.

Spectra of Cu^{2+} Complex. At a pH of 2.5, the Cu–EDTA spectrum shows a Raman line at 920 cm^{-1}, with a broad shoulder at 890 cm^{-1}. There is a strong, polarized Raman line at 470 cm^{-1} which can be assigned to Cu–N stretching vibration. The two lines in the 900-cm^{-1} region indicate two different types of C–C bonds in the complex. Since the Cu–EDTA complex is known to be protonated at low pH and since the presence of a metal–nitrogen line indicates that protonation is not at nitrogen, it seems that the carboxylate group is protonated. As the pH is increased, the 920-cm^{-1} Raman line gains in intensity at the expense of the weaker 890-cm^{-1} line, and above a pH of about 4.5 there is only one sharp line at 920 cm^{-1}. Also in this pH range, the weaker 525-cm^{-1} Raman lines begins to gain intensity (see Figure 3). These spectral changes must reflect structural changes. The single C–C stretching frequency indicates that all the carboxylate groups are at least electrostatically coordinated to the metal, and the line characteristic of this situation is the one at 920 cm^{-1}. Hence, at lower pH the lower frequency, 895 cm^{-1}, which is also of lower intensity, must be characteristic of the CH_2COOH free arm of the complex. Since this line is weaker than the one at 922 cm^{-1}, it is probable that there is only one free arm. The coordination sphere might also include a water molecule. Such a structure for the copper–EDTA complex has been

---

[23] H. G. Langer, *J. Inorg. Nucl. Chem.*, **26**, 767 (1964).

[24] S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

established by Hoard, *et al.*,[25] by X-ray methods. More recently Kusakina and Yakimets[26] have found that HCeA·$2H_2O$ which is prepared from an equimolar mixture of $CeCl_3$ and Na_2H_2A at pH 1.5, has an ir spectrum in which one of the carboxylate arms of the ligand is protonated, very similar to what is proposed here.

When the pH is increased, the proton from the free arm is removed, and it coordinates to the metal to change the spectrum as observed. Bhat and Krishnamurthy[27] have reached the same conclusion, from a spectrophotometric study of Cu–EDTA complexes. They have also found that at much higher pH (11 or more), copper forms a hydroxy complex with EDTA. As can be seen from Figure 3, the Raman spectrum changes again on increasing the pH above 7. These changes apparently accompany the coordination of the hydroxide ion. It is noteworthy that the 470-cm^{-1} band is essentially unchanged in either frequency or intensity, indicating that OH^- coordination does not occur at the expense of N coordination. However, the 525-cm^{-1} line, characteristic of the normal complex of Cu and other metal ions, disappears at high pH as it also does at low pH. If indeed there is a competition at low pH between H_2O and a carboxylate arm for coordination of Cu, then there may be a similar competition with OH^- at high pH. In both cases the 525-cm^{-1} line is absent. That the OH^- should not compete with a N atom seems likely from other work.[28] Finally, it should be noted that a new band (430 cm^{-1}) appears at high pH. The frequency is very nearly that (440 cm^{-1}) found for the stretching mode of H_2O molecules bound to Cu^{2+},[29] and may be direct confirmation of the OH^- coordination.

Evaporation of the Cu–EDTA solutions at pH 2.5 and at pH 7.0 yielded two different solids. When the infrared spectra of these solids were taken, it was found that the solid from the solution at pH 2.5 showed two carbonyl stretching frequencies, one around 1700 cm^{-1} and another near 1600 cm^{-1}, indicating the presence of both COOH and COO^- groups. The infrared spectrum of the solid from the solution of pH 7 showed only one line at 1600 cm^{-1}, showing it contained only the COO^- groups. These results lend definite support to our previous conclusions concerning changes at low pH.

Spectra of Hg^{2+} Complex. The Raman spectrum of mercury–EDTA solution at pH 3.0 shows a slightly broadened Raman line at 920 cm^{-1}, and a very strong Hg–N stretching line at 425 cm^{-1}. The 920-cm^{-1} Raman line seems to sharpen up as the pH is increased and the rest of the spectrum remains unaltered until a pH of 7.0 is reached. Further increase of pH broadens and shifts the M–N stretching line toward higher frequencies and, as mentioned before, the 500-cm^{-1} line begins to disappear. Matyska and Kössler[30] have shown the existence of the species $Hg(OH)A^{3-}$ at higher pH, and this is supported by the nmr work of Sawyer, *et al.* Hence the changes observed in the Raman spectrum can be explained in a manner analogous to that of the Cu–EDTA complex at higher pH's. Previous studies[2] have indicated hydroxy–metal–EDTA complexes for only Hg and Cu of the metals which were studied here at high pH. (Unfortunately Zn^{2+} could not be so studied.) It seems significant that these are the only two which show changes of Raman spectra consistent with coordination of OH^-.

---

(25) G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959).

(26) N. P. Kusakina and E. M. Yakimets, *Zh. Neorg. Khim.*, **10**, 1013 (1965).

(27) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963).

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

(29) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 768 (1964).

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