A Raman Spectroscopic Study of the Mono- and Di-protonated Ethylenediaminetetra-acetate Ions

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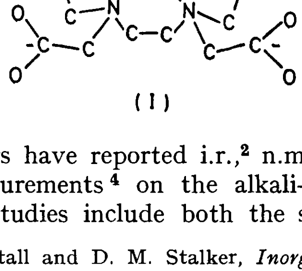
Raman spectra of aqueous solutions of Na^+ and ethylenediaminetetra-acetate (edta) at pH 4.5—13 have been obtained together with those of a number of related solid complexes of edta. Analysis of the data suggests that the $Hedta^{3-}$ ion adopts a configuration, at pH 7.5 in water, in which both nitrogens are equally protonated and hydrogen bonds are formed to two carboxylate groups. The configuration of the H_2edta^{2-} ion is probably similar, but involves hydrogen bonds to four carboxylate groups.

In a previous communication[1] we reported the changes in Raman spectra indicative of protonation of a carboxylate group of ethylenediaminetetra-acetate (edta) complexes of nickel(II) and copper(II) in acid solutions. In this paper we report Raman spectroscopic evidence which indicates that initial protonation occurs symmetrically (I) at the two nitrogens for aqueous solutions of Na^+ and $edta^{4-}$



(I)

Many papers have reported i.r.,[2] n.m.r.,[3] and other physical measurements[4] on the alkali-metal salts of edta; these studies include both the solid state and aqueous solutions which find such extensive use in analytical chemistry. Later reports agree, and *X*-ray diffraction results confirm,[5] that the two protons of the H_2edta^{2-} ion in the solid state are bonded to nitrogen. The *X*-ray data show that these protons are also very extensively hydrogen-bonded to carboxylate oxygens; indeed the structures of the dipotassium and dirubidium salts differ markedly, apparently being stabilized by different hydrogen-bond configurations. For aqueous solutions the data reported are less conclusive: in particular, studies of i.r. spectra in D_2O have been interpreted as favouring initial protonation of a single nitrogen in alkali-metal edta solutions; in contrast the n.m.r. data suggest that both nitrogen atoms are involved in the initial protonation. Because of the differing time scales[6] for the two techniques the observations are not mutually exclusive: labile proton exchange may cause n.m.r. to see a single protonated species while i.r. detects the separate species. It is significant, however, that Fujiwara and Reilley[4] interpreted the n.m.r. spectrum of the monoprotonated cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate ($Hcdta^{3-}$) ion as pointing to symmetrical

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[1] R. H. Nuttall and D. M. Stalker, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 639.

[2] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, 1963, **85**, 309; D. T. Sawyer and J. E. Tackett, *ibid.*, p. 314.

[3] R. J. Kula, D. T. Sawyer, S. I. Chann, and C. M. Finley, *J. Amer. Chem. Soc.*, 1963, **85**, 2930; D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, 1963, 3645; J. L. Sudmeier and C. N. Reilley, *Analyt. Chem.*, 1964, **36**, 1698.

[4] Y. Fujiwara and C. N. Reilley, *Analyt. Chem.*, 1968, **40**, 890; refs. 1—10 therein identify previous important papers on the protonation of edta.

[5] M. Cotrait, *Acta Cryst.*, 1970, **B26**, 1152.

[6] I. R. Beattie, *Chem. Soc. Rev.*, 1975, **4**, 107.

protonation between nitrogens, involving in addition the formation of hydrogen bonds to two carboxylate oxygens. Whether this same conformation is important for $Hedta^{3-}$ in aqueous solution cannot be determined by n.m.r. spectroscopy because of proton equivalences and an increased number of available conformations.

Raman spectroscopy has the time-scale advantage of i.r. methods,[6] and in contrast to the latter can also be used to study the system in water rather than D_2O. This latter advantage is significant since previous Raman data [7] show differences in spectra between the two media, which cannot be fully interpreted on the basis of isotopic shifts. Krishnan and Plane [7] reported the Raman spectra of Na^+–edta in water at pH 4.5 and 11; their study was restricted to the 200—1 600 cm^{-1} region of the spectrum and no interpretation of the data in terms of conformation was offered. We have therefore obtained the Raman spectra of Na^+–edta species in aqueous solution at pH 4.5—13 at intervals of 0.5 pH units. Our data include the ν(C–H) region, which shows significant sensitivity to nitrogen protonation in glycine [8] and ethylenediamine,[9] and can usefully be compared with the Raman-active ν(C–H) frequencies of the solid mono-, di-, and tri-sodium and -potassium salts of edta which we have also obtained.

EXPERIMENTAL

The compounds H_4edta, Na_4[edta]·$2H_2O$, and Na_2-[H_2edta]·$2H_2O$ were obtained commercially; all the other complexes were prepared by literature methods and analysed for carbon, hydrogen, and nitrogen.

Raman spectra of solids and solutions were obtained on a Spex Ramalog spectrophotometer using the 488-nm line of an argon laser. The spectra were obtained from the powdered solids or from aqueous solutions in capillary tubes; the scattered radiation was collected at 90° to the incident beam. Data were collected for aqueous solutions of Na^+–edta at intervals of 0.5 pH units over the range pH 4.5—13. In the interest of brevity, we only report the ν(C–H) and ν(C–C) vibrational frequencies for solutions in which significant changes of spectra were observed. Similarly we restrict the tables of data for the solid complexes to the regions discussed. The data are presented more fully elsewhere.[10]

RESULTS AND DISCUSSION

The Raman spectra of aqueous solutions of Na^+–edta at pH 4.5—13 correspond to the addition of two protons to $edta^{4-}$. The wide separation of the p*K* values [11] suggests that at intermediate pH the mono- and diprotonated species will predominate. N.m.r. data [3] indicate, however, that interaction between Na^+ and edta lowers the pH range at which the first proton is added so that at pH >10 $edta^{4-}$ predominates, $Hedta^{3-}$ is at a maximum at pH 7—8, and H_2edta^{2-} attains maximum concentration at pH 4.5. Solution i.r. spectra [2] similarly indicate that $Dedta^{3-}$ attains maximum concentration in D_2O at pH 8.1, and is absent at pH <5.

The observed Raman spectra of aqueous solutions are in good agreement with the above data since the major changes in spectroscopic features correspond to the process of protonation over the intervening pH ranges. The most obvious changes in the Raman spectra occur in the ν(C–H) region at *ca.* 3 000 cm^{-1} and in the acetate ν(C–C) region at *ca.* 920 cm^{-1}.[12] These bands are also strong features of the spectra. In contrast to the i.r. studies, ν(C=O) frequencies provide no information since the asymmetric stretch coincides with a water band between 1 600 and 1 700 cm^{-1}, and the symmetric stretch although observable does not shift appreciably with protonation. Slight changes also occur in the ν(C–N) region of the spectra. Inspection of the change in the ν(C–H) region shows that, over the monoprotonation range, two strong polarized bands completely below 3 000 cm^{-1} are replaced by one new strong polarized band at $<3\,000$ cm^{-1} and a second band of lower intensity at $>3\,000$ cm^{-1}; during diprotonation, slight additional changes occur in this region. In contrast, ν(C–C) does not shift during monoprotonation, but splits into two components in the course of diprotonation as was first reported by Krishnan and Plane.[7]

The emergence of separate and increasingly intense new ν(C–H) frequencies in the course of monoprotonation indicates that Raman spectroscopy detects a distinct monoprotonated species. In contrast, examination of the Raman spectra of both the sodium and potassium salts of edta shows that in the tetrametal salts there is a group of bands entirely below 3 000 cm^{-1}, while in the dimetal salts a new group of bands includes components at $>3\,000$ cm^{-1}. For the trimetal salts both sets of bands are present. Comparisons of the spectra of equivalent sodium and potassium salts show major differences elsewhere in the spectra, which are very complex. *X*-Ray diffraction has shown that the *N*-protonated H_2edta^{2-} ion is also present in $[Mg(OH_2)_6]$-$[H_2edta]$;[13] the Raman spectrum of this complex also has ν(C–H) bands at $>3\,000$ cm^{-1}. In contrast, the solution Raman spectra of transition-metal complexes of edta have ν(C–H) bands at $<3\,000$ cm^{-1},[10] and no bands appear at $>3\,000$ cm^{-1} in the spectra of strongly acid solutions of copper(II) and nickel(II) complexes of edta which contain carboxyl groups.[1,10] Apparently, neither carboxylate protonation nor metal complex formation causes similar shifts to those observed on acidification of solutions of Na^+ and edta.

The Raman spectrum of glycine in water provides a useful model for the spectroscopic changes we have observed;[8] thus, for $HN_2CH_2CO_2^-$, ν(C–H) bands are observed at 2 940 cm^{-1}, but for $\overset{+}{N}H_3CH_2CO_2^-$ at 3 013

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[7] K. Krishnan and R. A. Plane, *J. Amer. Chem. Soc.*, 1968, **90**, 3195.

[8] M. Takeda, R. E. S. Iavazo, D. Garfinkel, I. H. Scheinberg, and J. T. Edsall, *J. Amer. Chem. Soc.*, 1958, **80**, 3813.

[9] S. A. Ghazanhafar, J. T. Edsall, and D. V. Myers, *J. Amer. Chem. Soc.*, 1964, **86**, 559.

[10] D. M. Stalker, Ph.D. Thesis, University of Strathclyde, 1976.

[11] J. Bjerrum, G. Schwarzenbach, and L. Sillén, 'Stability Constants of Metal-Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1957, No. 17, p. 76.

[12] A. A. McConnell and R. H. Nuttall, *Inorg. Chim. Acta*, 1976, **19**, 253.

[13] M. O'D. Julian, V. W. Day, and J. L. Hoard, *Inorg. Chem.*, 1973, **12**, 1754.

and 2 971 cm^{-1}; addition of a second proton to the carboxylate group causes a major shift in ν(C=O) but no accompanying change in ν(C–H). In general, the vibrations of CH_2 groups α to carboxylate groups are little influenced by carboxylate protonation, but for groups in proximity to nitrogen are shifted to higher frequency on *N*-protonation;[8,9] the shift in ν(C–H) on diprotonation of ethylenediamine is also to increased frequency, and the *N*-protonation of ethanolamine and β-alanine suggests that CH_2 groups α and β to protonated nitrogen have different ν(C–H) frequencies.[8] For this group of compounds the ν(C–H) bands are a very strong feature of the Raman spectrum.

The shifts which we observe on initial protonation of Na^+–edta in aqueous solutions correspond to the sum of those observed for glycine and ethylenediamine. Thus the two strong bands observed for solutions at pH 13 correspond to the values reported for ν(C–H) of ethylenediamine. That at 2 960 cm^{-1} is also probably coincident with ν(C–H) of the acetate arms. On the basis of the reported shifts of the model compounds, these two bands would remain coincident within the band envelope centred at 2 990 cm^{-1} at pH 8. The additional weaker band at 3 025 cm^{-1} probably corresponds to that at 3 013 cm^{-1} reported for $\overset{+}{N}H_3CH_2CO_2^-$; since it is depolarized, it may be the asymmetric ν(C–H). The shifts in the values of ν(C–H) observed for the solid sodium and potassium salts of edta may be similarly correlated with nitrogen protonation. This spectral region is very complex for the tripotassium salt and the evident relation of the frequencies of the bands observed to those of both the tetra- and di-potassium salts is consistent with localized protonation at one nitrogen such as might occur in the solid state; an alternative is the presence of both non- and di-protonated ions in equal numbers. The spectrum of the trisodium salt has far fewer medium and strong bands in the ν(C–H) region, possibly indicating a less complex structure; an increase in vibrational frequency to intermediate values is nevertheless evident. The ν(C–H) bands of the salts containing the H_2edta^{2-}

TABLE 1

ν(C–H) and ν(C–C) bands (cm^{-1}) in the Raman spectra of aqueous solutions of Na^+ and edta

pH	ν(C–H)					ν(C–C)	
13.08			2 966vs		2 864s		922vs
9.50			2 966vs		2 859s		919vs
8.99		2 984s	2 964m (sh)	2 884vw	2 858m		921vs
8.47	3 040w	2 990vs		2 886vw			922vs
7.97	3 028w	2 987vs		2 890vw			921vs
7.51	3 035m	2 988vs					921vs
6.52	3 032m	2 986vs				935 (sh)	916s
5.92	3 029m	2 986vs				935s	913s
5.05	3 026m	2 984vs				935s	911s

Polarization data were obtained at pH 13.08, 7.97, and 5.05. At pH 13.08 the bands at 2 966 and 2 864 cm^{-1} were polarized, and a residual spectrum with bands at 2 974w, 2 860m, 2 902w, 2 868w, and 2 854w cm^{-1} was observed. At pH 7.97 and 5.05 the bands at 2 987 and 2 984 cm^{-1} were polarized, and no additional bands were observed in the residual spectrum in the ν(C–H) region. At all three pH values the ν(C–C) bands were polarized. The spectra at high and low pH were closely similar to those reported by Krishnan and Plane [7] throughout the 400—1 600 cm^{-1} region.

TABLE 2

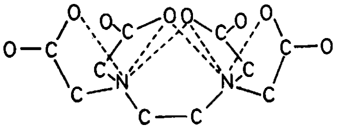
ν(C–H) bands (cm^{-1}) in the Raman spectra of solid edta salts

$K_4[edta]\cdot 3H_2O$	$K_3[Hedta]\cdot 2H_2O$	$K_2[H_2edta]\cdot 2H_2O$
	3 023m	3 025m
	3 007m	3 013s
2 990vw	2 992m	2 985vs
2 970m	2 973vs	2 971m (sh)
2947s	2 948m	2 963m
	2 937m	
	2 916w	2 906vw
	2 850s	
2 812s, br	2 833s	
2 740w		

$Na_4[edta]\cdot 2H_2O$	$Na_3[Hedta]\cdot 3H_2O$	$Na_2[H_2edta]\cdot 2H_2O$	$[Mg(OH_2)_6][H_2edta]$
		3 036m	3 061vw
	3 020vw	3 028w	
		3 017s	3 015s
	2 997w	3 001s	
		2 992s	
2 972m	2 978m	2 974vs	2 976vs
2 943m	2 950s		2 962s
2 928vs		2 924w	2 920w
2 907w			
2 892w	2 890m (sh)	2 897vw	2 900w
2 865w	2 850vs		
2 849m	2 820w		
2 812m			
2 740vw			

ion share a similar range of frequencies, with all the medium and strong bands between 2 960 and 3 040 cm^{-1}, a very much narrower span than that observed for the tetra-anion.

It is apparent that the shifts observed on monoprotonation in solution are little different in magnitude from those observed for diprotonation in the solid state; in addition there is no evidence for localized protonation at one nitrogen. Since the solution spectra at pH 9 demonstrate the presence of both Hedta^{3-} and edta^{4-} ions in equilibrium, achievement of an equal degree of protonation at two nitrogens at lower pH by an exchange process involving deprotonation is excluded. The *X*-ray structure [5] of $K_2[H_2edta]$ is clearly relevant for it demonstrates that the H_2edta^{2-} ion can assume a folded configuration akin to that postulated for Hcdta^{3-}. A similar structure for the monoprotonated ion in solution would allow the first proton to occupy a symmetrical position with respect to the nitrogen atoms, and as pictured by Fujiwara and Reilley would initially involve hydrogen bonds to two carboxylates (I). Addition of a second proton could then take place with the formation of hydrogen bonds to the two remaining carboxylates as in $K_2[H_2edta]$. In this configuration (II) there are two different types of hydrogen-bonded carboxylate ring, and the splitting observed for ν(C–C) in the course of diprotonation would then arise because of the differing degrees of strain involved in these rings. The slight changes in intensity in the ν(C–H) region during the course of diprotonation may be associated with the changing configuration of the carboxylate arms. However, in the course of the addition of a second proton no additional shifts in the ν(C–H) frequency are induced and it is necessary to postulate that the formation of additional bridging bonds to carboxylate groups provides a means for delocalizing charge.



(II)

(redrawn from ref. 5)

It is interesting to note that a combined *X*-ray diffraction and Raman study of the complex $Cs[H(NO_3)_2]$ provides evidence for the presence of a proton in a four-co-ordinate environment bridging the two nitrate moieties.[14] The observation lends some support to the structure we postulate for Hedta^{3-}. Our spectroscopic observations for solutions of Na^+ and edta cannot differentiate between an Hedta^{3-} ion with coplanar nitrogen and oxygen atoms and the non-planar alternative. Either arrangement would be readily converted into that we propose for H_2edta^{2-} which has a similar conformation to that observed for six-co-ordinate edta complexes. These structures are in accord with the n.m.r. data, and correspond to the ratios of free and hydrogen-bonded carboxylate groups detected by i.r. spectroscopy during protonation.[2] The differences in the ν(C–C) region for H_2edta^{2-} and D_2edta^{2-} species may be explained by assuming that deuterium bonding is weaker than hydrogen bonding and the carboxylate groups remain equivalent by an exchange process. Anomalies in this region are a feature of deuteriation studies of nitrogen-containing compounds,[8,9] which cannot be purely the result of isotopic mass, and which are observed in circumstances where hydrogen bonding is present.

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[14] J. M. Williams, N. Dowling, R. Gunde, D. Hadzi, and B. Orel, *J. Amer. Chem. Soc.*, 1976, **98**, 1581. We thank a referee for drawing this paper to our attention.